Roadmap on Printable Electronic Materials for Next-Generation Sensors

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Roadmap on Printable Electronic Materials for Next-Generation Sensors

Vincenzo Pecunia[1,57,58], Luisa Petti[2,57,58], Joseph B. Andrews[3,4,57,58], R. Ollearo[5,6], G.H. Gelinck[5,6], Bahareh Nasrollahi[1], Javith Mohammed Jailani[1], Ning Li[7], Jong H. Kim[8], Tse Nga Ng[9], Hanru Feng[10], Zhizhou Chen[10], Yupeng Guo[11], Liang Shen[10], Emmanuel Lhuillier[12], Lidia Kuo[13], Vinod K. Sangwan[13], Mark C. Hersam[13], Beatrice Fraboni[14], Laura Basiricò[14], Andrea Ciavatti[14], Haodi Wu[15], Guangda Niu[16], Jiang Tang [15,16], Ge Yang[17], Doup Kim[17], Derek Dremann[18], Oana D. Jurchescu[18], Dmytro Bederak[19], Artem G. Shulga[19], Pedro Costa[20], Nikola Perinka[21], Senentxu Lanceros-Mendez[20,21,22], Alex Chortos[23], Saurabh Khuje[24], Jian Yu[25], Shenqiang Ren[24], Antonello Mascia[26], Mattia Concas[26], Piero Cosseddu[26], Robert J Young[27], Tomoyuki Yokota[28], Takeo Somoya[28], Sung Jae Jeon[29], Naixin Zhaon[29], Yuning Li[29], Darpan Shukla[30], Shuang Wu[30], Yong Zhu[30], Kuniharu Takei[31], Yubin Huang[32], Jean Spiece[32], Pascal Gehring[32], Krishna Persaud[33], Eduard Llobet[34], Soufiane Krik[2], Sahira Vasquez[2], Martina Aurora Costa Angeli[2], Paolo Lugli[2], Barbara Fabbri[35], Elena Spagnoli[35], Arianna Rossi[35], Luigi G. Occhipinti[36], Chenyu Tang[36], Wentian Yi[36], Dafydd Ravenscroft[36], Tharun R. Kandukuri[36], Zain Ul Abideen[37], Zahra Azimi[38], Antonio Tricoli[37,39], Almudena Rivadeneyra[40], Sara Rojas[41], Andrea Gaiardo[42], Matteo Valt[42], Vardan Galstyan[43], Dario Zappa[43], Elisabetta Comini[43], Vincent Noël[44], Giorgio Mattana[44], Benoît Piro[44], Elliot Strand[45], Eloise Bihar[45], Gregory L. Whiting[45], Bajramshahe Shkodra[2], Mattia Petrelli[2], Giulia Moro[46], Ada Raucci[46], Antonella Miglione[46], Stefano Cinti[46], Alexander J. Casson[47], Zixin Wang[47], David Bird[47], John C. Batchelor[47], Le Xing[47], Liam S. J. Johnson[47], Aula A. Alwattar[48], Adrica Kyndiah[49], Fabrizio Antonio Viola[49,50], Mario Caironi[49], Faris M. Albarghouthi[51], Brittany N. Smith[51], Aaron D. Franklin[51,52], Arnab Pal[53], Kaustav Banerjee[53], Zachary T. Johnson[54], Jonathan C. Claussen[54], Akshay Moudgil[55,56], Wei Lin Leong[55].

[1] School of Sustainable Energy Engineering, Simon Fraser University, Surrey V3T 0N1, BC, Canada
[2] Faculty of Engineering, Free University of Bozen-Bolzano, Italy
[3] Department of Mechanical Engineering, University of Wisconsin – Madison, Madison, WI, 53716, United States of America
[4] Department of Electrical and Computer Engineering, University of Wisconsin – Madison, Madison, WI, 53716, United States of America
[5] Eindhoven University of Technology, Eindhoven, The Netherlands
[6] TNO/Holst Centre, Eindhoven, The Netherlands
[7] School of Electronic and Optical Engineering, Nanjing University of Science and Technology, People's Republic of China
[8] Department of Molecular Science and Technology, Ajou University, Republic of Korea
[9] Department of Electrical and Computer Engineering, University of California San Diego, United States of America
[10] State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, International Center of Future Science, Jilin University, Changchun, People's Republic of China
[11] College of Chemistry, Jilin University, Changchun, People's Republic of China
[12] Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France
[13] Department of Materials Science and Engineering, Northwestern University, Evanston, IL, 60208, United States of America
[14] Department of Physics and Astronomy, University of Bologna, Viale C. Berti Pichat 6/2, 40127, Bologna, Italy
[15] Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, Hubei Province, People's Republic of China
[16] Optics Valley Laboratory, Wuhan 430074, Hubei Province, People's Republic of China

[17] Department of Nuclear Engineering, North Carolina State University, 2500 Stinson Drive, Raleigh, NC, 27607-7909, United States of America
[18] Department of Physics and Center for Functional Materials, Wake Forest University, Winston Salem, NC 27109, United States of America
[19] QDI systems B.V, L.J. Zielstraweg 1, 9713 GX, Groningen, The Netherlands
[20] Physics Centre of Minho and Porto Universities (CF-UM-UP) and 2Laboratory of Physics for Materials and Emergent Technologies, LapMET, University of Minho 4710-053 Braga, Portugal
[21] BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain
[22] IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain
[23] Purdue University, West Lafayette, IN, 47907, United States of America
[24] Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, 20742, United States of America
[25] DEVCOM Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States of America
[26] Department of Electrical and Electronic Engineering, University of Cagliari, Piazza d'Armi, 09123 Cagliari, Italy
[27] National Graphene Institute and the Department of Materials, University of Manchester, Manchester M13 9PL, United Kingdom
[28] Department of Electric and Electronic Engineering, The University of Tokyo, Tokyo, Japan
[29] Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN) University of Waterloo, 200 University Ave West, Waterloo, Ontario N2L 3G1, Canada
[30] Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC, 27695, United States of America
[31] Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan
[32] Institute of Condensed Matter and Nanosciences, Université catholique de Louvain (UCLouvain), 1348 Louvain-la-Neuve, Belgium
[33] Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom
[34] Dept. of Electronic Engineering, Universitat Rovira i Virgili, Avda. Països Catalans, 26, 43007 Tarragona, Catalonia, Spain
[35] Department of Information Engineering, University of Brescia & UdR INSTM of Brescia, via Branze 38, Brescia Italy
[36] Cambridge Graphene Centre, Department of Engineering, University of Cambridge, 9 J J Thomson Avenue Cambridge CB3 0FA, United Kingdom
[37]Nanotechnology Research Laboratory, Research School of Chemistry, College of Science, Australian National University, Canberra, ACT, 2601, Australia
[38] Research School of Physics, Australian National University, Canberra, ACT, 2601, Australia
[39] Nanotechnology Research Laboratory, Faculty of Engineering, University of Sydney, Sydney, NSW, 2006, Australia
[40] Dept. Electronics and Computer Technology, University of Granada, Spain
[41] Dept. Inorganic Chemistry, University of Granada, Spain
[42] MNF—Micro Nano Facility, Sensors and Devices Center, Bruno Kessler Foundation, Via Sommarive 18, 38123 Trento, Italy
[43] Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy
[44] Université Paris Cité, ITODYS, CNRS, F-75006 Paris, France
[45] University of Colorado Boulder, College of Engineering and Applied Science, 4001 Discovery Drive, Boulder, CO, 80303, United States of America
[46] Department of Pharmacy, University of Naples "Federico II", Via Domenico Montesano 49, 80131 Naples, Italy

[47] Department of Electrical and Electronic Engineering, School of Engineering, University of Manchester, Manchester, M13 9PL, United Kingdom
[48] Department of Chemistry, School of Natural Sciences, University of Manchester, Manchester, M13 9PL, United Kingdom
[49] Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Rubattino 81, 20134 Milano, Italy
[50] Università degli Studi di Cagliari, Dipartimento di Ingegneria Elettrica ed Elettronica, Via Marengo 3, 09123 Cagliari, Italy
[51] Department of Electrical & Computer Engineering, Duke University, Durham, North Carolina, 27708, United States of America
[52] Department of Chemistry, Duke University, Durham, North Carolina, 27708, United States of America
[53] Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA 93106, United States of America
[54] Iowa State University, Ames IA 50011, United States of America
[55] School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
[56] Department of Electrical Engineering, Indian Institute of Technology Jodhpur, Karwar 342030, Jodhpur, India

[57] Guest editors of the roadmap.
[58] Authors to whom any correspondence should be addressed.

Guest Editor emails
vincenzo_pecunia@sfu.ca, luisa.petti@unibz.it, joseph.andrews@wisc.edu

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Abstract
The dissemination of sensors is key to realizing a sustainable, 'intelligent' world, where everyday objects and environments are equipped with sensing capabilities to advance the sustainability and quality of our lives—e.g., via smart homes, smart cities, smart healthcare, smart logistics, Industry 4.0, and precision agriculture. The realization of the full potential of these applications critically depends on the availability of easy-to-make, low-cost sensor technologies. Sensors based on printable electronic materials offer the ideal platform: they can be fabricated through simple methods (e.g., printing and coating) and are compatible with high-throughput roll-to-roll processing. Moreover, printable electronic materials often allow the fabrication of sensors on flexible/stretchable/biodegradable substrates, thereby enabling the deployment of sensors in unconventional settings. Fulfilling the promise of printable electronic materials for sensing will require materials and device innovations to enhance their ability to transduce external stimuli—light, ionizing radiation, pressure, strain, force, temperature, gas, vapours, humidity, and other chemical and biological analytes. This Roadmap brings together the viewpoints of experts in various printable sensing materials—and devices thereof—to provide insights into the status and outlook of the field. Alongside recent materials and device innovations, the roadmap discusses the key outstanding challenges pertaining to each printable sensing technology. Finally, the Roadmap points to promising directions to overcome these challenges and thus enable ubiquitous sensing for a sustainable, 'intelligent' world.

Section 1 – Introduction to printable electronic materials for next-generation sensors

Vincenzo Pecunia[1], Luisa Petti[2] and Joseph B. Andrews[3,4]

[1] School of Sustainable Energy Engineering, Simon Fraser University, Surrey V3T 0N1, BC, Canada
[2] Faculty of Engineering, Free University of Bozen-Bolzano, Italy
[3] Department of Mechanical Engineering, University of Wisconsin–Madison, Madison, WI, United States of America
[4] Department of Electrical and Computer Engineering, University of Wisconsin – Madison, Madison, WI, 53716, United States of America

Universal access to fundamental necessities such as food, medical care, and clean air, water, and energy remains a pressing priority in achieving sustainable development [1]. Sensors have emerged as a crucial technology to address these challenges [2]. Through sensors, we can obtain data from the physical world to optimize our use of resources, reduce waste, and improve our health and environment (Fig. 1a). For instance, sensors can enhance food production by providing farmers with more accurate control over their crops; reduce food waste through smart packaging that accurately monitors food spoilage; and improve access to clean water and air by monitoring water resources and air quality. Moreover, sensors can enable manufacturing with higher yield and reduced waste; and deliver accurate health data for tailored healthcare.

To fully realize the potential of sensors for sustainable development, it is essential to disseminate them widely and provide them with data processing and connectivity—e.g., via the Internet of Things. In fact, it has been predicted that 45 trillion sensors are necessary to enable sustainable development by the mid-2030s [2]. To make this possible, sensors should be easy to fabricate, low-cost, and seamlessly integrate into daily objects and environments, making them affordable for everyone and easily adaptable to different applications.

Printable electronic materials offer a unique opportunity to realize a trillion-sensor universe [3], [4]. This class of materials—including organic semiconductors, carbon nanotubes, metal oxides, two-dimensional materials, halide perovskites, and colloidal quantum dots—can be engineered to respond to a wide range of stimuli for a broad spectrum of applications (Fig. 1a). Since they can be formulated into inks, these materials enable sensor fabrication using low-cost and high-throughput methods such as printing and coating (Fig. 1b,c). These methods are characterized by low energy and material consumption, allowing sensor fabrication with a favourable environmental sustainability profile [5]. Certain classes of emerging printable electronic materials also allow the fabrication of biodegradable sensors, thus offering additional advantages from a sustainability standpoint. Moreover, the sensing capabilities of printable electronic materials can be adjusted by modifying ink compositions and deposition parameters, enabling the customization of sensors for different applications. Printable electronic materials are also typically compatible with sensor fabrication on flexible/stretchable substrates (Fig. 1c), resulting in sensors that are compact and lightweight, hence widely deployable. Importantly, all these features contrast with conventional sensor technologies (e.g., silicon-based sensors), which have complex and costly manufacturing, substantial carbon footprints, limited customizability, and rigid form factors.

Alongside the wide range of benefits discussed above, printable sensors provide considerable market opportunities. The printed sensor market has a worldwide footprint, with growth demonstrated in North America, Europe, and Asia [7]. It was valued at 9.7 billion USD in 2022 and is projected to grow to 15.3 billion USD by 2030, with an annual growth rate of 5.9 % [7].

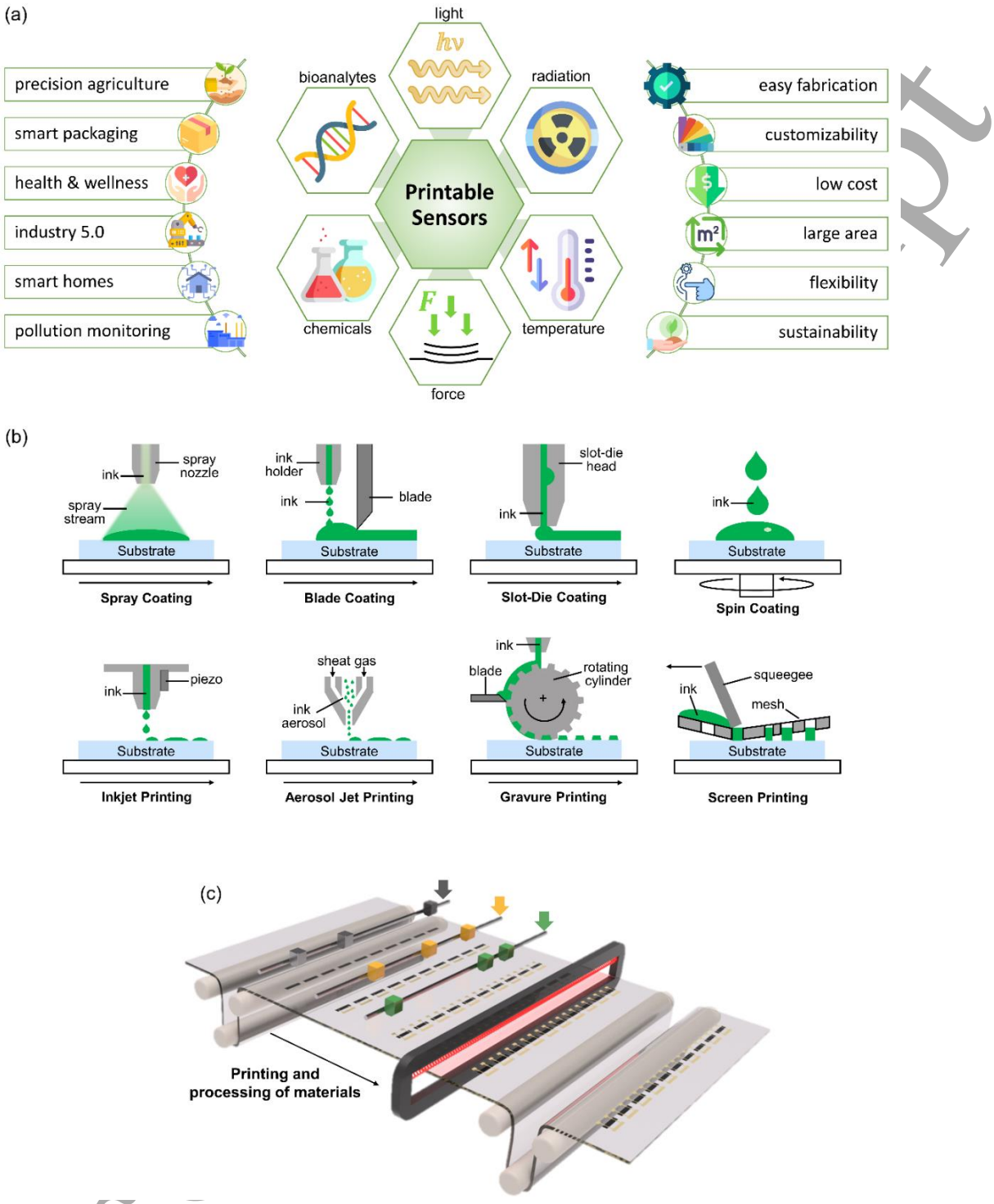

Figure 1 (a) Sensors based on printable electronic materials: (left) examples of applications areas, (centre) types of stimuli that they can sense, and (right) key advantages. (b) Representative methods that can be used to deposit printable electronic materials for sensor fabrication. The sketches representing inkjet printing and spin coating are reproduced with permission from [6], with permission of IOP Publishing Limited through PLSclear (© IOP Publishing Ltd 2020). (c) Roll-to-roll manufacturing of flexible sensors comprising various printable electronic materials, which are deposited sequentially as the flexible substrate is seamlessly moved through the production line. Reproduced with permission from [5]. The following icons in (a) are from www.flaticon.com: 'sprout', 'box', 'healthcare', 'conveyor', 'smart home', 'Dna', 'chemistry', 'radiation', 'temperature', 'easy installation', 'low price', and 'responsibility' (by Freepik); 'factory' (by Chattapat); 'area' (by Sonnycandra); 'color selection' (by Smashicons); and 'elasticity' (by Iconjam).

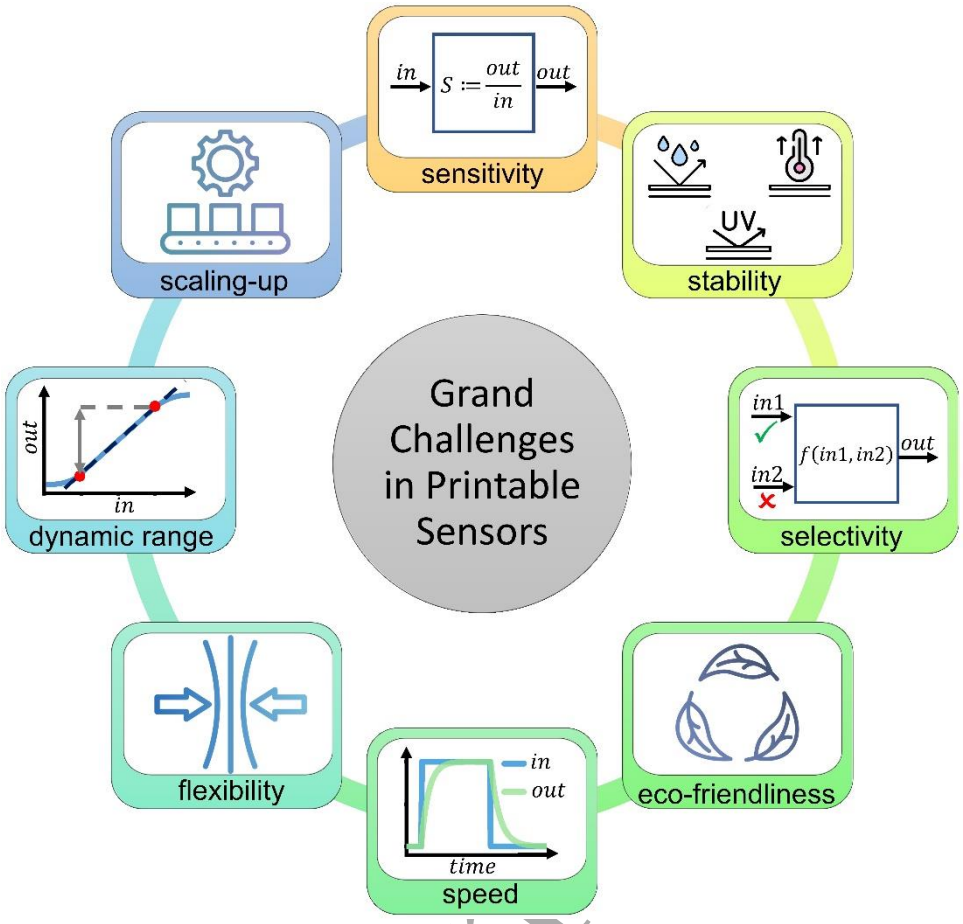

Figure 2 Grand challenges in printable electronics materials for next-generation sensors. This Roadmap extensively discusses these challenges in the context of a wide range of printable sensor technologies. The following icons are from www.flaticon.com: 'resilient' (by Irfansusanto20); 'heat' and 'bio' (by Freepik); 'water resistant' (by Good Ware); 'manufacture' (by afif fudin).

In recent years, considerable progress has been made in printable sensor technologies, as exemplified by the advances in wearable devices for human health monitoring. Nowadays, screen-printed wearable smart sensors are being developed by several companies and research centres, such as BTI Butler Technologies Inc, Quad Industries, Holst Center, and VTT. While these sensors are expected to reach the market in two to three years, research is already moving towards more performing solutions, including epidermal [8] and sweat biosensors [9].

Printable sensor technologies are also becoming increasingly important in other emerging fields, especially in precision agriculture. This field urgently calls for low-cost, sustainable, self-powered, and biocompatible/degradable sensors for soil monitoring (e.g., for the detection of soil microbial activity and moisture) [10]. Although research on printable degradable soil sensors is still in its infancy, various political actions against climate change (e.g., the UN Sustainable Development Goals) promise rapid growth for this technology, with a trend that could potentially follow the one observed with wearable sensors.

Advancing research in printable electronic materials is crucial to unlocking the full potential of printable sensors, as these materials are at the core of such sensors. Despite covering a diverse range of materials, devices, and applications, printable sensor research shares several common overarching goals and challenges, as illustrated in Fig. 2 and discussed in the following.

Sensitivity. To ensure sensor functionality, printable electronic materials are required to enable high sensitivity *S* to the stimulus being sensed (*S* = output signal / stimulus magnitude; see Fig. 2).

Consequently, a grand challenge faced by most printable sensor technologies is to develop new printable electronic materials and create innovative device architectures and fabrication methods to achieve sensitivity levels that rival or surpass conventional sensor technologies.

Selectivity. A grand challenge facing various types of printable sensors (e.g., spectrally selective light sensors and chemical sensors/biosensors, including gas sensors) is to develop robust approaches to achieving selectivity in their responses—i.e., the ability for a sensor to discriminate between the target stimuli/analytes (*in1*; see Fig. 2) and interfering stimuli/analytes (*in2*; see Fig. 2). The sensor should display low or zero cross-sensitivity—i.e., it should not be sensitive to the interfering stimuli/analytes.

Detection Limit and Dynamic Range. Sensors must be also optimized for detection limit, while maintaining an appropriate dynamic range. The detection limit (also called limit of detection) is the smallest change in the stimulus being sensed that elicits a response from the sensor that is statistically different from the response in the absence of the stimulus [11], [12]. As electronic noise plays a fundamental role in determining the detection limit, a grand challenge in printable sensors research is to identify, understand, and minimise their noise sources. On the other hand, the dynamic range is the range of stimulus levels that can be quantitatively measured by the sensor, spanning from the detection limit to the stimulus level at which the sensor response saturates (Fig. 2). At times, however, optimizing a sensor for a lower detection limit can result in a narrower dynamic range. Therefore, achieving the best balance between detection limit and dynamic range for the intended application is an important challenge to be tackled for many printable sensor technologies.

Speed of Response. Although most target applications of printable sensors involve slowly varying signals with frequencies up to around 1 kHz, some high-end applications (e.g., light sensing for optical communications) require exceptionally fast response times. Consequently, identifying and overcoming speed bottlenecks related to materials properties, processing conditions, and device architectures is a significant challenge for printable electronic materials used in sensing.

Eco-Friendliness. To fully leverage the favourable environmental sustainability profile of printable sensors, an important research priority is to improve the sustainability of their printing processes and bill of materials. This firstly concerns identifying eco-friendly solvents and materials for printing [13], as well as reducing the process temperatures [13]. Moreover, enabling the recycling and reuse of materials employed in printable sensors could drastically improve their cradle-to-grave life cycle sustainability [14].

Flexibility/Stretchability. A major challenge in developing printable sensors that require flexibility/stretchability is accounting for mechanical parameters during the design phase. Specifically, the goal is to achieve a response that is not affected by bending/stretching. In turn, this requires a detailed understanding of the mechanical properties of sensor materials (from substrate to encapsulation) and a thorough design of the sensor geometry.

Stability. Most printable sensor technologies have been developed in academic laboratories, typically aiming for proof-of-principle demonstrations. As a result, data regarding their operational stability is scarce at present. Additionally, due to the emerging nature of many target applications, standards for stability characterization relevant to such applications are often lacking. Addressing these challenges is a key priority in the field. Specifically, it is important to assess the degradation mechanisms of these materials under the stressors relevant to specific applications, as well as to develop suitable accelerated aging tests. Another key challenge is to enhance the device stability through materials, processing, and device engineering techniques.

Manufacturability and Scalability. As their development has been primarily carried out in academic laboratories, a significant challenge in printable electronic materials and sensors thereof is to ensure that their fabrication can be scaled up for mass production, which requires high device reproducibility and uniformity over large areas. To this end, it essential to prioritize printable electronic materials and

sensors thereof that are robust against the inherent variability of printing and coating methods, which is greater than that of conventional semiconductor device manufacturing methods.

While building on existing accomplishments in printable sensors research, this Roadmap aims to look forward. To this end, the Roadmap discusses the aptitude of an extensive range of innovative printable materials for all prominent sensing applications: the detection of light (Chapter 2), ionizing radiation (Chapter 3), and mechanical stimuli (Chapter 4), temperature sensing (Chapter 5), the detection of gases and vapours (Chapter 6), sensing non-biological analytes in solid or liquid media (Chapter 7), and sensing biological analytes and electrophysiological activity (Chapter 8). Each section, written by experts in the field, highlights current and future challenges faced by a particular class of printable materials for a specific sensing application, providing insights into how upcoming advances could meaningfully address these challenges. Therefore, the Roadmap aims to help researchers identify important outstanding research questions and areas where their expertise could benefit varied communities. Through its forward-looking insights, the Roadmap ultimately aims to expedite the realization of the potential of printable sensors as building blocks for an eco-friendly trillion-sensor universe and a more sustainable future.

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Section 2.1 – Introduction to printable photodetectors

R. Ollearo[1,2] and G.H. Gelinck[1,2]

[1] Eindhoven University of Technology, Eindhoven, The Netherlands
[2] TNO/Holst Centre, Eindhoven, The Netherlands

Digitization

Photodetectors and cameras that capture and convert optical information into electrical signals play a crucial role in our society. It suffices to say that every year 1.8 trillion photos are taken worldwide, corresponding to 57246 cameras operating on average each second. Silicon (CMOS) image sensors dominate this market, which expanded and grew with a frenetic pace to > $20 billion pro annum. As a result of multi-decade optimization, silicon technology and inorganics such as InGaAs by extension, excels in device performance, reproducibility, reliability and durability. With the advent of the internet of things (IoT) era, however, new applications emerge in which light sensing is integrated in everyday objects and this calls for novel photoactive materials and processes. Emerging application examples include transparent imagers for smart glass applications[1], in-display biometric imagers[2–4] and photonic patches that can measure vital signs[5,6]. These applications typically require large-area and/or flexible substrates. Such substrates are incompatible with Si CMOS but are readily combined with low-temperature and printable semiconductors.

Printable photodetectors

Over the last 20 years, printable thin film photodetectors have emerged. Printable semiconductor materials include organics, perovskites, inorganic quantum dots, and metal oxides. Characterized by different chemical and structural composition, each of these material classes can be engineered to target a specific spectral range (within certain limits). Organic semiconductors, i.e., materials consisting prevalently of carbon and hydrogen atoms organized in conjugated segments, can either be small molecules or long polymeric chains, and be functionalized with a virtually unlimited number of molecular structures. This provides a spectral photodetection window extending from the ultraviolet (UV) to the near-infrared (NIR) range. Metal halide perovskites are instead hybrid compounds characterized by a typical ABX_3 unit-cell, consisting of an organic or inorganic cation (A), a metallic cation (B) and a halide anion (X). By engineering the halide composition, as well as by varying the crystal dimensionality using bulky cations, bandgaps ranging from 400 nm to 1100 nm can be achieved, enabling photosensitivity up to the NIR. Quantum dots, also known as inorganic nanocrystals, are semiconducting particles characterized by finite electron energies and bandgaps, which can be tuned by controlling QDs size and shape. Depending on the underlying material, QDs can be synthesized with wavelength cut-offs from the UV (in case of ZnSe), to visible light (in case of CdS and CdSe), to NIR wavelengths (up to »2000 nm, in case of PbS and HgTe). Metal oxides such as ZnO and its binary and tertiary oxides (InZnO, InGaZnO) typically are wide band gap semiconductors and have been employed as transparent electronics, mostly in a transistor-type structure. Metal oxides are also frequently used as charge selective electrode in a diode structure.

Emerging Applications

Lens-less imaging. Supported by the underlying thin-film technology and manufacturing methods of OLED displays these printable photodetector materials can be processed in the form of thin films from solution at relatively low temperatures on large-area substrates. Thus, they lend themselves particularly well for large-area lens-less imaging applications. The lack of bulky optics implies that the imagers remain ultrathin (< 1mm). Medical X-ray detectors, color scanner and biometric finger- and palmprint scanners have been prototyped using organic, perovskite as well as QD materials (Fig. 1b-j). Incorporating printable photodetectors onto glass and plastic can make surfaces smart and interactive, for an enhanced user interface experience (Fig. 1c).

Stacked photodetectors. The high light absorption coefficients of 10^5 cm^{-1} of these semiconductor materials translate into films capable to efficiently harvest light within ca. 100 nm thickness, not only reducing the amount of material used but also reducing parallax[7]. Interestingly, multiple thin-films of printable photodetectors can be stacked on top of each other, e.g., for improved RGB CMOS camera's[8] or spectrally selective narrow-band sensing[9].

NIR sensitive detectors. By extending the light sensitivity to the near-infrared (NIR) region, printable thin film photodetectors have great potential in next-generation biomedical imaging and monitoring, such as for example pulse oximetry[10], skin cancer diagnosis[11] and brain imaging[12], in biometric applications such as vein recognition[13], and various industrial inspection applications[14] (mobile and fast spectroscopic analysis[15], proximity sensors, 3D light detection and ranging (LIDAR[16]), self-powered optical wireless communication/Li-Fi technology) (Fig. 1e-l).

Flexible and stretchable photodetectors. Medical and biometric imagers are made on glass or on silicon substrates. As a result, X-ray imaging still relies on flat image sensors that may suffer from vignetting, i.e., a decrease in image quality approaching the edge of the detectors. Printing and wet processing on unconventional substrates, such as glass or flexible plastic substrates, allows instead to easily adapt to soft and curved objects, i.e., with less rigid form factors. As a result, curved and hemispherical imagers based on organic photodetectors and flexible scintillators on a plastic foil eliminates the need of corrective and bulky lenses and enable compact 3D CT systems[17].

Outlook and Challenges

Efforts in contact engineering, materials design, and processing optimization have resulted in state-of-the-art photodetection performance over the last decade, rapidly closing the gap between printable photodetectors and inorganics technology. With a variety of technological advantages, printable photodetectors can have significant impact in the imaging and sensing market.

In the rapidly escalating field of biometrics, i.e., technologies that measure distinct and unique characteristics of the human body, large-area, flexible and easy-to-integrate scanners for fingerprint, veins and iris recognition can acquire more information and with higher accuracy. For instance, printable photodetector arrays on flexible substrates would enable nail-to-nail fingerprint acquisition, wrapped-around scanners onto door handles[18], and, when semitransparent, glasses with iris scanning sensors integrated in lenses. By fabricating printable photodetectors onto soft and stretchable substrates, the next generation of functionalized skin-like wearable devices can be realized. Such body conformal systems would involve a skin-like base that can flex and stretch, a local power supply, and a wireless communicating systems for continuous read-out of medical data. Compared with traditional monitoring devices, these wearables would ensure a less intrusive experience to the user and enable a constant tracking of heartbeat, respiration, blood oxygenation, glucose, stress levels etc. Printable photodetectors are also emerging in robotic skin that replicate and amplifies the sensing capabilities of human skin, as well as artificial retina and human eye-like hemispherical sensors (Fig. 1h)

Yet, several challenges remain. The ultimate performance of any photodetector is reached when the specific detectivity, i.e., figure of merit describing the capability to detect ultrasmall light signals, is at its maximum. Such upper limit is called BLIP (background-limited infrared photodetection) detectivity, and is calculated assuming a unit external quantum efficiency (EQE = 1) and a bulk thermal generated dark current. BLIP detectivity typically decreases for increasing wavelengths. Most of the reported photodetectors based on printable semiconductors have shown impressive detectivities, but still far from BLIP limit. This is mostly due to the relatively high values of dark current and noise, especially when NIR sensitive, which must be minimized. Identifying, understanding and addressing the underlying causes, such as leakage current, trap and defect states, represent a primary research direction[19,20]. From a material perspective, this translates, for instance, into optimizing processing techniques and developing additives and materials with less impurities[21].

Another future research path will be on the development of recipes that uses less hazardous solvents, preferably water-based or "environmentally benign" options. Here, we point out that lead-free semiconductors have a strong advantage over the lead (or tin-based) perovskites and QDs. Development of lead-free perovskite and QD materials with equal (or better) performance therefore presents a potentially highly rewarding materials challenge[22].

Improving materials stability in air and ambient represents another area for future action, as the elimination of a high-performing thin-film moisture barrier will reduce fabrication costs and enhance mechanical flexibility and stretchability. This holds for both the semiconductor and the electrode materials. In the specific case of bulk heterojunction organic photodetectors, the obtained morphology should remain stable at elevated temperature. Finally, the ligand exchange and typical multi-layer deposition of (PbS) quantum dots are slow processes that require careful alternative approaches.

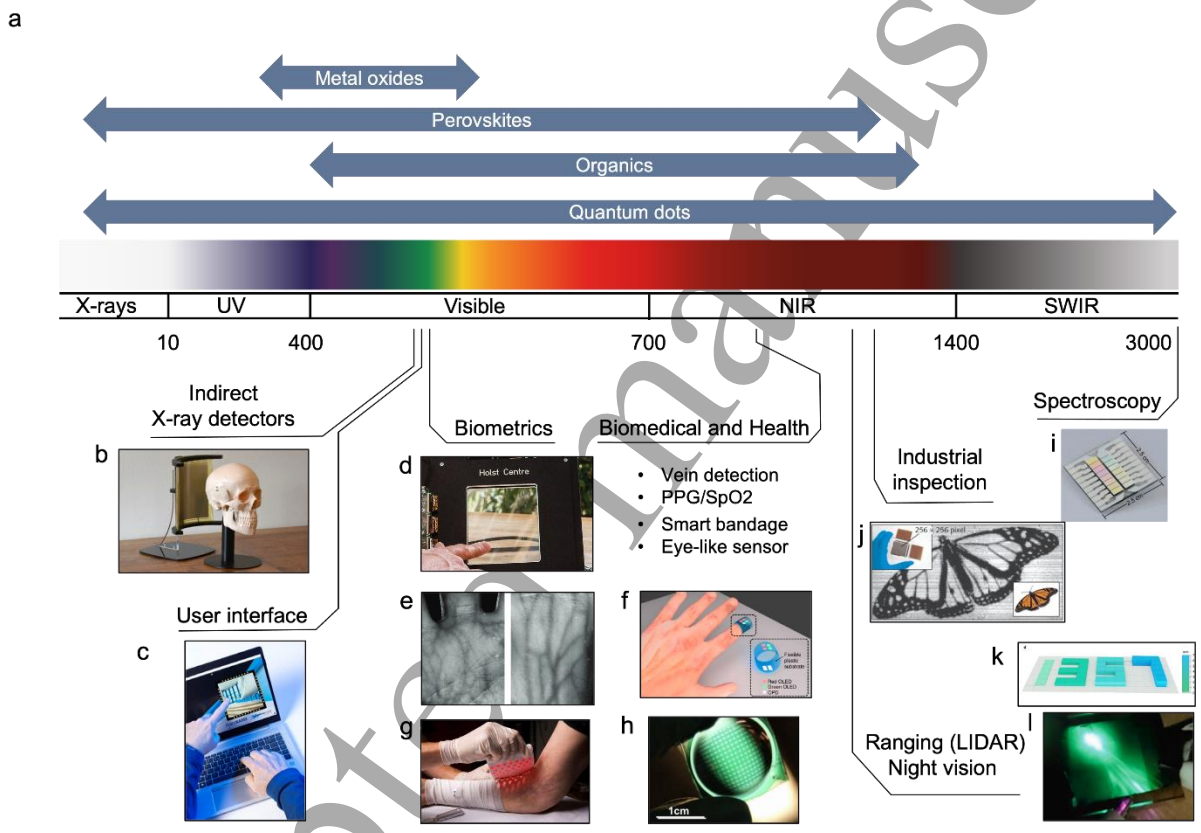

Figure 1 Printable photodetectors and applications. a. Typical printable semiconductor materials for photodetection, comprising metal oxides, perovskites, organics and quantum dots. Depending on their chemical composition, these materials can offer spectral ranges from the X-ray spectral region to the short wavelength infrared (SWIR). b, Curved large-area X-ray imager[17]. c, Visually transparent NIR-sensitive organic photodiodes-based arrays placed in front of a laptop display for gesture recognitionapplications[1], d, Transparent fingerprint scanner[2]. e, Raw images of palm veins obtained with near-infrared organic vein detection imager[13]. f, Pulse oximetry sensor composed of two OLED arrays and two OPDs[10]. g, Smart bandage (Image credit: Holst Centre)[5]. h, Hemispherical organic photodetector focal plane array that mimic the size, function, and architecture of the human eye[24]. i, Senorics spectral sensor based on organic photodetectors (Senorics GmbH, Germany)[25]. j, Infrared shadow cast at 1,310 nm of a slide showing a monarch butterfly obtained with a PbS–QD-sensitized organic NIR imager[14]. k, 3D visualization of sub-millimetre depth variation using perovskite-based light detection and ranging photodetector[16]. l, NIR-to-green night vision enabled by all-organic optical up-conversion device made of OLEDs and organic photodiodes[26].

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Section 2.2 – Printable spectrally selective organic photodetectors

Bahareh Nasrollahi, Javith Mohammed Jailani and Vincenzo Pecunia

School of Sustainable Energy Engineering, Simon Fraser University, Surrey V3T 0N1, BC, Canada

Status

Printable organic semiconductors are carbon-based molecules and polymers with alternating single and double bonds and good solubility in common organic solvents [1], [2]. Their composition, structure, and conformation can be easily tailored to vary their optoelectronic properties over a wide range (Fig. 1a, b) [1]. Such tailorability makes them ideal for photodetectors—referred to as *narrowband* or *spectrally selective*—that can selectively sense light over a narrow wavelength range ($\Delta\lambda \cong$ 15–150 nm to date) within the ultraviolet, visible, and near-infrared regions of the electromagnetic spectrum (wavelength $\lambda \cong$ 300–1700 nm to date) without using external optical filters (Fig. 1a). Generally, this is not possible with conventional semiconductors, which absorb light over a broad spectral range. As a result, narrowband organic photodetectors have simpler and easier-to-make device architectures, which is attractive from both cost and sustainability perspectives [3]. Moreover, their mechanical flexibility allows them to conform to various shapes [4], which could enable their widespread deployment for the Internet of Things, computer vision, wearables, and health and wellness monitoring.

The most widely pursued approach to spectrally selective printable organic photodetectors is termed narrowband absorption (NBA), as it relies on organic semiconductors that absorb light within a narrow wavelength range (Fig. 1b, c) [3]. This approach delivers spectral responses hardwired in the semiconductors used, as the responsivity spectra of the resultant photodetectors closely follow the absorbance spectra of the organic photoactive layers [5], [6].

Alternative schemes to narrowband organic photodetection rely on either *internal filtering* or *microcavity resonance*, at the price, however, of greater complexity in terms of device design and fabrication [7]. Internally filtered approaches require a component of the photoactive layer to suppress the photoresponse outside the target spectral range through loss mechanisms such as optical filtering, carrier recombination, and/or exciton annihilation—as in *charge collection narrowing*, *charge injection narrowing*, and *exciton dissociation narrowing* (Fig. 1d) [8], [9], [10]. Alternatively, reflective electrodes can be used to create an optical resonance within the device stack, thus enhancing the photoresponse within a narrow wavelength range (microcavity resonance; Fig. 1e) [11]. Both internally filtered and microcavity-based devices rely on broadband absorbers, hence their narrowband response is not hardwired in the materials used (Fig. 1d, e). The required loss mechanisms in internally filtered devices may be highly sensitive to the interplay between charge transport/trapping and optical absorption—as in charge collection narrowing and charge injection narrowing—leading to considerable changes in the spectral response by changing thickness or bias voltage [9]. Exciton dissociation narrowing requires the formation of a hierarchical architecture within the organic photoactive layer, which involves its crosslinking and additional processing steps [12]. Finally, the spectral response of microcavity-based photodetectors is highly sensitive to the angle of incidence and the thickness of the photoactive layer [3].

Current and Future Challenges

Sensitivity. A key challenge for printable organic narrowband photodetectors is to boost their sensitivity (Fig. 2). For instance, printable NBA photodetectors have typically achieved external quantum efficiencies below 40% in the visible range, with lower values in the near-infrared region [3]. Internally filtered and microcavity-based devices also suffer from moderate to low external quantum efficiencies—especially in the near-infrared region—due to their inherent loss mechanisms [17].

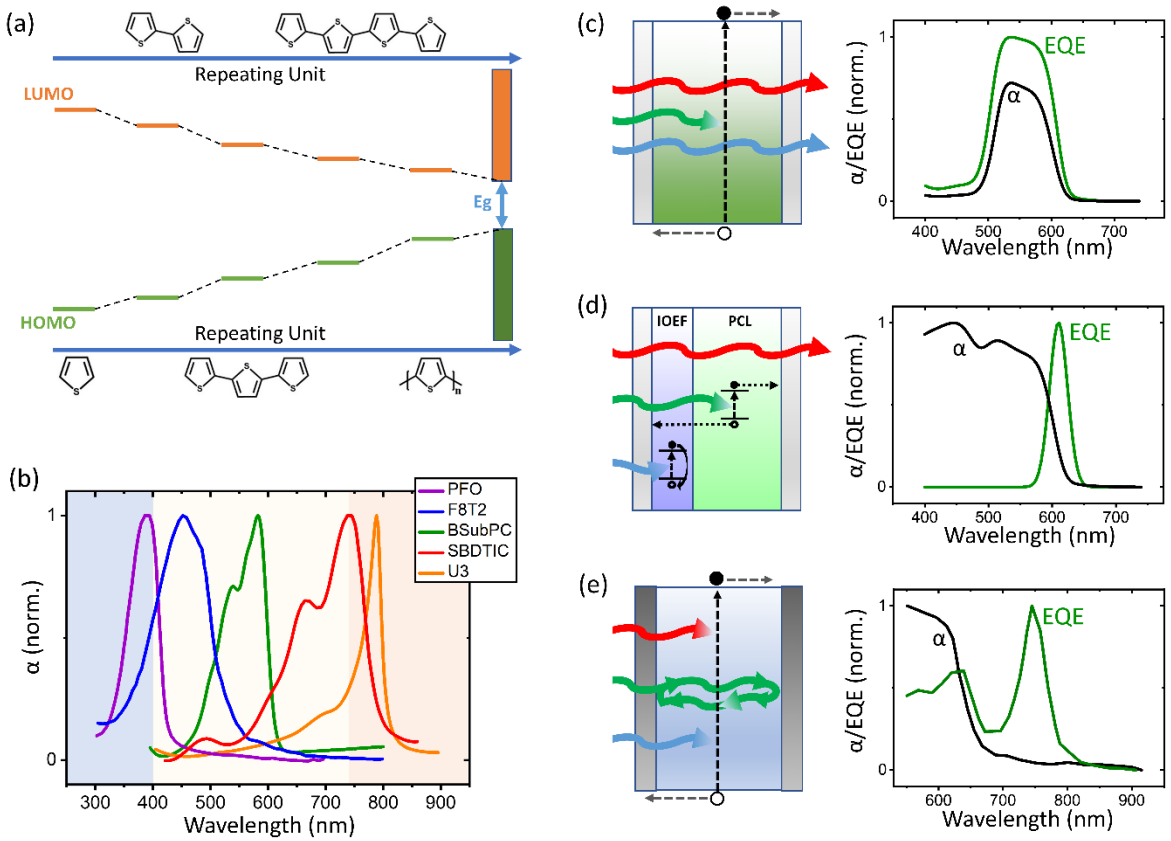

Figure 1. (a) Conjugation length tuning of the optical gap of organic semiconductors. (b) Spectrally selective absorbance of thin films of representative printable organic semiconductors [6], [13], [14], [15], [16]. (c)-(e) Main classes of printable spectrally selective organic photodetectors: (c) narrowband-absorption, (d) internally filtered, and (e) microcavity-based designs. The diagrams on the left represent the general device architectures, while the plots on the right display the normalised spectral characteristics. EQE: external quantum efficiency; α: absorption coefficient; IOEF: internal optoelectronic filter; PCL: photoconversion layer. (c)-(e) were reproduced from [7] with permission of IOP Publishing Limited through PLSclear (© IOP Publishing Ltd 2020).

Speed of Response. Most printable organic narrowband photodetectors have response speeds in the kilohertz-to-megahertz range [4], which are suitable for common applications such as colour sensing and imaging. However, applications such as high-data-rate visible light communications require operational frequencies of several hundred megahertz, which are challenging to achieve (Fig. 2).

Spectral Selectivity. The required full width at half maximum for the responsivity ($FWHM_R$; Fig. 2) generally depends on the target application: ≅ 100 nm for colour imaging and a few nanometres for spectrometry. While printable NBA photodetectors can meet the requirements for colour imaging, an important challenge is to cover the visible range with multiple NBA photodetectors having $FWHM_R$ ≅ 60 nm, as needed for illuminant-independent colour recognition [3]. Additionally, while internally filtered approaches have delivered $FWHM_R$ ≅ 15-50 nm, they are yet to achieve $FWHM_R$ ≤ 10 nm, as needed for high-end spectrometry. Moreover, microcavity-based devices developed to date exhibit a strong out-of-band response (Fig. 1e), which requires optical filtering to suppress, countering the objective of easy-to-fabricate photodetectors.

Spectral Range. The development of printable organic narrowband photodetectors with peak responsivity wavelengths ($\lambda_{p,R}$; Fig. 2) in the near-infrared range is another significant challenge. This challenge is especially pronounced for NBA photodetectors due to the current scarcity of organic semiconductors with narrowband absorption in this range. While internally filtered photodetectors have generally enabled peak wavelengths deeper into the near-infrared range, the limited availability

of organic semiconductors with an optical gap in the vicinity or below 1.0 eV has hindered progress with these approaches.

Specific Detectivity and Noise. State-of-the-art narrowband organic photodetectors typically exhibit specific detectivity (D*) values of 10^{12}–10^{13} Jones for $\lambda_{p,R}$ values in the visible range, with lower values observed in the near-infrared region [3]. However, their ultimate D* potential is considerably higher (Fig. 2). However, a significant challenge remains in obtaining a quantitative understanding of the materials and device parameters giving rise to noise in printable narrowband organic photodetectors [11], which could ultimately allow their engineering towards higher D*.

Manufacturability and Upscaling. The mass production of printable organic narrowband photodetectors faces significant challenges due to the use of devices and fabrication techniques that may have limited resilience to process parameter variations (as inherently found in printing-based manufacturing lines) or that rely on harmful halogenated solvents. In microcavity-based photodetectors, which depend on external filtering for adequate spectral rejection, reducing fabrication complexity by using a minimal number of materials and layers remains a challenge. Moreover, the strong dependence of their spectral response on the thicknesses of the various layers makes this approach particularly prone to non-uniformities due to process parameter variations. Furthermore, the fabrication of microcavity-based photodetectors necessitates the deposition of ultrathin conductive films, with thicknesses down to a few nanometers, as integral components of their electrode assemblies on both sides of the photoactive layer [8]. Achieving this reliably and at high throughput poses a significant technological challenge, particularly in combination with flexible substrates, owing to the tendency for cluster formation at such minimal thicknesses [18]. On the other hand, internally filtered approaches require photoactive layers with thickness in the region of 1 µm or larger, which raises concerns about material consumption and upscaling. The NBA approach is the most robust from a manufacturability perspective, as the resultant narrowband response is hardwired in the photoactive materials used. Indeed, this approach has enabled the first demonstration of solution-based stacking of photodetectors for multicolour sensing [19]. However, upscaling to device stacks consisting of multiple photodetectors, as required for multispectral sensing and imaging (Fig. 2), poses significant technological challenges. This is due to the complexity of identifying printable photoactive materials, interlayers, and electrodes that can be processed from orthogonal solvents, at compatible temperatures, and resulting in smooth films, while also minimizing the optical transmission losses at the electrodes [20].

Stability. While essential for real-world applications, device stability has been rarely characterised in printable organic narrowband photodetectors, which constitutes an important remaining challenge.

Advances in Science and Technology to Meet Challenges

Dedicated synthetic efforts are vital to improve the sensitivity, specific detectivity, and spectral selectivity of printable organic narrowband photodetectors, as well as to extend their spectral range deeper into the near-infrared region (Fig. 2). While the field has largely relied on organic semiconductors drawn from organic photovoltaics, tailored optoelectronic properties are essential for narrowband photodetection. In the NBA case, systematically developing narrowband absorbers with varying conjugation lengths could create palettes of printable organic semiconductors for multicolour/multispectral sensing over a wide spectral region (Fig. 2). Particularly promising target compounds involve molecules with minimal structural alternation upon photoexcitation (cyanine limit) or with spectral narrowing due to aggregation effects [7], [17]. Moreover, the synthesis of new non-fullerene acceptors with optical gaps in the visible and near-infrared regions will be crucial for advancing all types of narrowband organic photodetectors towards multicolour sensing and spectroscopic applications.

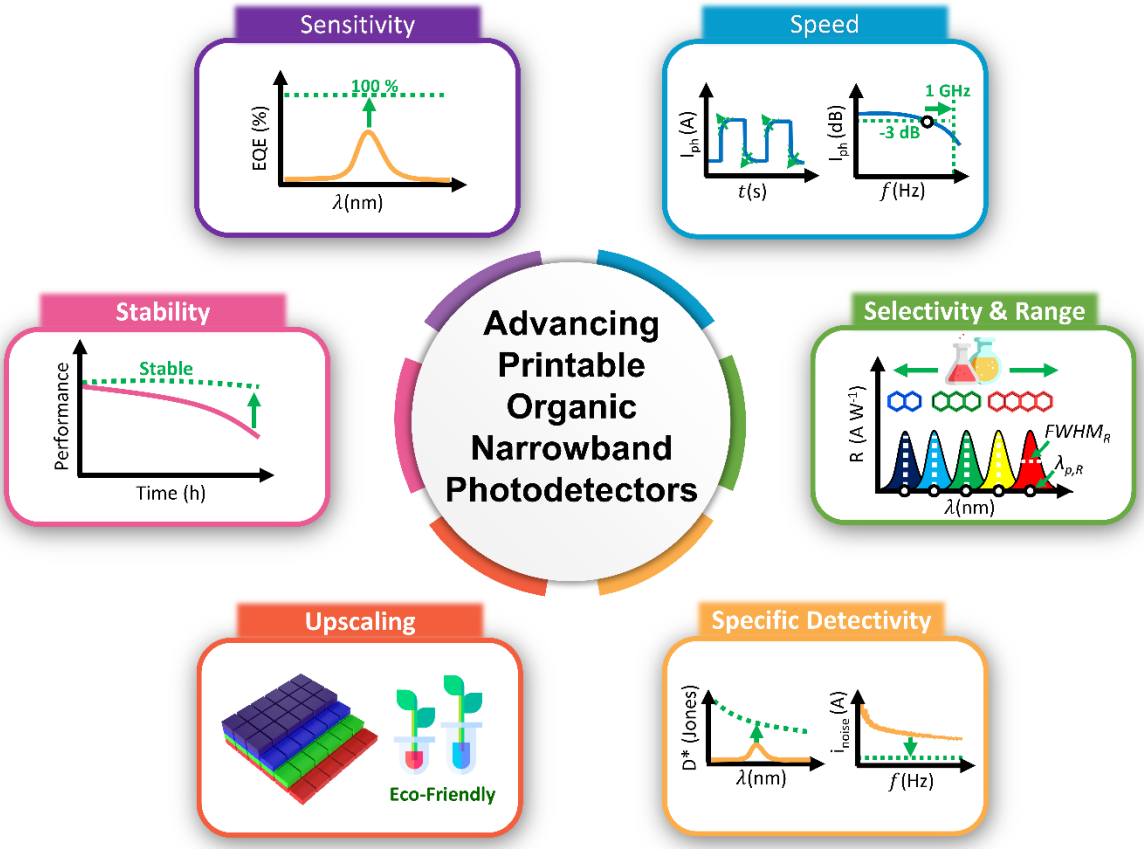

Figure 2. Challenges and goals for printable spectrally selective organic photodetectors to reach technological maturity. The imager stack shown in the upscaling box is reused from [19] with permission. © 2022 Wiley-VCH GmbH. The 'chemistry' and 'test tube' icons in the 'Selectivity & Range' and 'Upscaling' boxes were made by Freepik from www.flaticon.com.

A comprehensive understanding of the origin of dark current is necessary to improve the specific detectivity of organic narrowband photodetectors. Priority research directions include experimentally assessing their trap states, correlating them to first-principle calculations, identifying their origin, and designing passivation protocols.

To enhance the speed of narrowband organic photodetectors towards the gigahertz range, it is essential to gain a quantitative understanding of their transient photoresponse by developing more sophisticated models. Key features to be included are the detailed nanostructure of the photoactive layers, trapping effects in their bulk and at their interfaces, and the dependence of carrier transport on charge density, traps, and electric field.

Given the variety and emerging nature of the target applications of organic narrowband photodetectors, it will be essential for the community to design and reach consensus on accelerated aging tests to evaluate their stability. This will provide a platform to identify degradation pathways specific to the operational requirements of narrowband organic photodetectors, as well as to enhance their stability by design.

To enhance the manufacturability of printable organic narrowband photodetectors, priority should be given to developing device configurations with minimal sensitivity to process parameter variations and a minimal number of layers and materials [21], as well as to processing strategies that rely on eco-friendly solvents (Fig. 2).

Concluding Remarks

Due to their unique optoelectronic properties and manufacturability, printable organic narrowband photodetectors have considerable potential for spectrally selective light sensing beyond the limits of conventional technologies at a fraction of the cost. Realising this potential requires dedicated efforts to synthesise novel compounds with tailored optoelectronic properties, gain comprehensive mechanistic insight, and develop strategies to improve dark current, transient photoresponse, and device stability.

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Section 2.3 – Printable near/shortwave infrared organic photodetectors

Ning Li[1], Jong H. Kim[2] and Tse Nga Ng[3]

[1]School of Electronic and Optical Engineering, Nanjing University of Science and Technology,
[2]Department of Molecular Science and Technology, Ajou University,
[3]Department of Electrical and Computer Engineering, University of California San Diego

Status

The detection of near-infrared (NIR, 0.8-1 μm) and shortwave infrared (SWIR, 1-3 μm) light are essential for a variety of applications including night vision, medical diagnosis, automated navigation, internet of things, etc. Traditional inorganic semiconductors such as silicon (Si, λ_{abs}: 0.3-1.1 μm), germanium (Ge, λ_{abs}: 0.4-1.8 μm), and indium gallium arsenide (InGaAs, λ_{abs}: 0.8-2 μm) are mature technologies for NIR and SWIR detection. However, the brittle and rigid nature of these materials limits their use in large-area, flexible, and wearable applications. Hence, this decade has seen dramatic progress in stretchable, bendable organic photodetector technology [1]. Organic semiconductors offer advantages such as large-area coverage by solution processing [2], [3], high absorption and broadband spectra, biocompatibility, conformal form factor [4], and facile monolithic integration with silicon readout chips and up-conversion structures [5] for high-resolution, compact system designs.

The development of organic infrared detectors has benefited from the knowledge gained from organic photovoltaic research, in which materials have been extended to absorb in the NIR to better match the terrestrial solar spectrum. However, the desired characteristics of photodetectors are different from solar cells, as a detector requires high signal to noise while a solar cell targets high power output and noise issues are often neglected. Unlike solar cells which are mostly sandwich diodes, photodetectors have employed various designs from diodes to transistor structures, to enhance performance through photomultiplication [6] or to extend functionalities such as hyperspectral analyses by printing color-selective pixels side by side on the same plane [7], [8].

One of the most important metrics for photodetectors is the specific detectivity (*D**), which is defined as $D^* = A^{0.5}R/S_n$, with *A* being the detector active area, *R* being the responsivity, i.e., the photocurrent output divided by the incident illumination power, and S_n being the total noise. The *D** is the signal-to-noise ratio, a useful factor to compare different detectors. Figure 1 illustrates the reported *D** of NIR-SWIR organic detectors with examples of chemical structures. The organic NIR detectors have been shown to outperform silicon. Yet for SWIR wavelengths, the performance of organic photodetectors lags behind conventional inorganic counterparts, because the inherent narrow bandgaps exacerbate noise and recombination problems. While organic semiconductors are strong IR absorbers and may transduce in the midwave to longwave IR up to 14 μm [9], [10], more systematic studies are needed to understand the electronic transduction processes including charge generation and transport mechanisms.

Current and Future Challenges

The current key challenges involve materials and device engineering aspects. The progress in material synthesis and modular structure modifications have demonstrated organic semiconductors with SWIR absorption. However, the peak absorption tends to remain in wavelengths shorter than 1.2 μm, and additional research is required to red-shift the absorption characteristics of highly conjugated semiconductors. With regards to device engineering, the high dark current noise due to the narrow bandgap and energetic disorder [11] is an obstacle to improve the detection limit. Schottky-Read-Hall recombination [12], [13] and carrier tunneling [14], [15] introduce noise under an applied bias and diminish the specific detectivity of organic photodetectors. Meanwhile, low responsivity also stems from carrier recombination based on the energy gap law [16] and the strong exciton binding energy of organic materials because of their low dielectric constants [2]. It should be noted that there were errors in some publications where the detectivity values were exaggerated, in which they invoked the

shot-noise assumption and under-estimated the true noise level by orders of magnitude as pointed out by Reference [17].

Other challenges in realizing organic IR detectors include the need for IR transparent electrode materials in order to integrate with readout circuits. Conventional indium tin oxide (ITO) electrodes are SWIR absorbing and would lower the external quantum efficiency of organic photodetectors. With the developments in electrode technologies using high-conductivity PEDOT:PSS, graphene, silver nanowires, and carbon nanotubes, the ITO problem is solvable but requires more efforts to make the new electrode alternatives more conductive, stable, and transparent. The environmental stability of organic materials is another challenge because oxygen and humidity would affect the long-term stability. Nonetheless, this challenge is tractable, because encapsulation technologies are already mature as evident in the commercialization of organic light-emitting displays. Besides environmental factors, the inherent electronic stability of an organic system requires further study to reveal degradation mechanisms. For example, the analysis of the density of states is suitable for identifying the energy levels of traps and their changes over time, to understand the origins of performance degradation and subsequently mitigate the defect states.

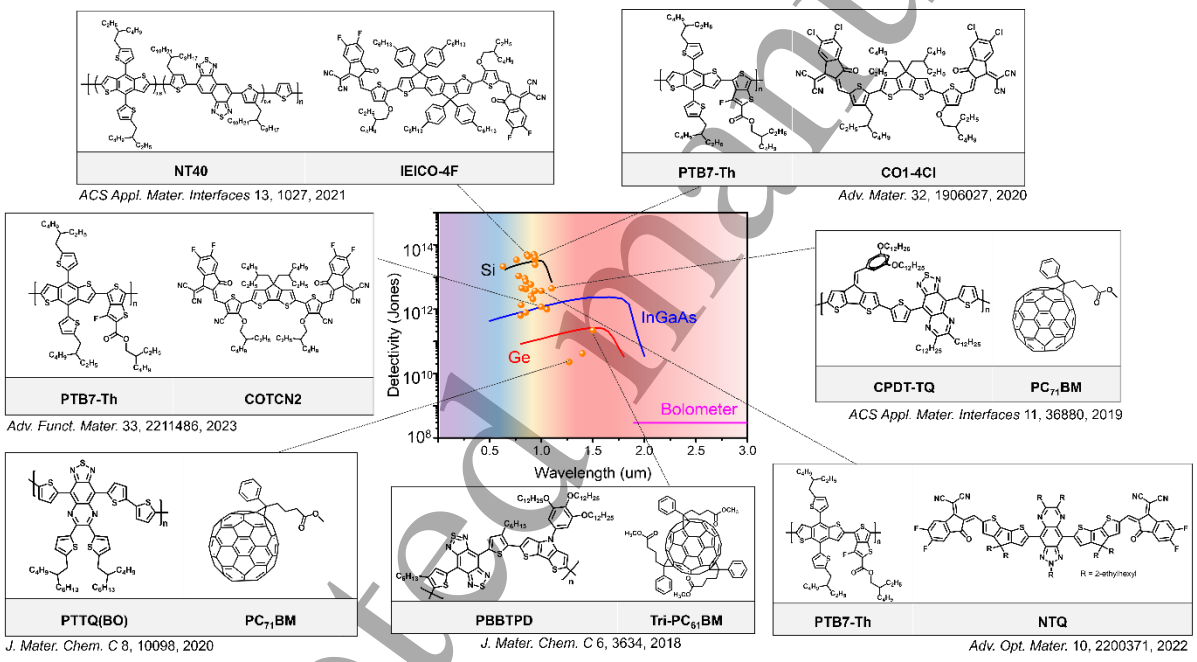

Figure 1 Detectivity, or signal-to-noise ratio, of organic NIR/SWIR detectors, along with the corresponding molecular structures.

Advances in Science and Technology to Meet Challenges

To address the aforementioned challenges, our research community is rapidly amassing foundational knowledge to relate molecular designs to optoelectronic properties. Synthesis of organic IR materials with superior properties are underway using new designs of donor-acceptor polymers, conjugated small molecules, as well as the exploration of interfacial materials to improve electrode contacts. Materials design for low bandgap (E_g < 1.0 eV) involves the substitution of strong electron-withdrawing moieties in donor polymers. The engineering of non-fullerene acceptor molecules has demonstrated efficient manipulation of energy levels. Furthermore, interfacial materials for alleviating energy barriers between active layer and electrodes have been widely developed, which enhances charge extraction and photocurrent. The chemical structures, molecular ordering, and disorder level of organic IR materials are being correlated to the thin-film morphology, charge generation, transport, and recombination properties, to lower the noise level and enhance the photoresponse in the devices.

Besides the material aspect, novel device designs and processing concepts are being investigated to modify interfaces for balancing photomultiplication gain and noise, and strategies based on doping or employing ternary blends are shown to affect mid-gap and sub-gap states near the band edges and suppress noise. The recent advances illustrate that there is room for organic IR detectors to improve by tailoring the optoelectronic properties and to scale up by leveraging the ease of fabrication from digital printing to large-scale roll-to-roll patterning.

In terms of future applications, the flexibility and biocompatibility of organic materials render them suitable to be used in human-computer interfaces such as wearable electronics. New system architectures with neuromorphic computing and machine-learning algorithms can help to enhance the target identification capability of an organic imager despite noisy signals [18]. Advances in scaling up organic device fabrication can make infrared detectors more affordable and ubiquitously deployable like today's cell phone cameras. The promise of room-temperature operation with organic photodetectors will allow size, weight, and power reduction in the next generation of IR systems, with significant impacts on medical diagnostics, machine vision, and optical communications [19], [20] as shown in Figure 2.

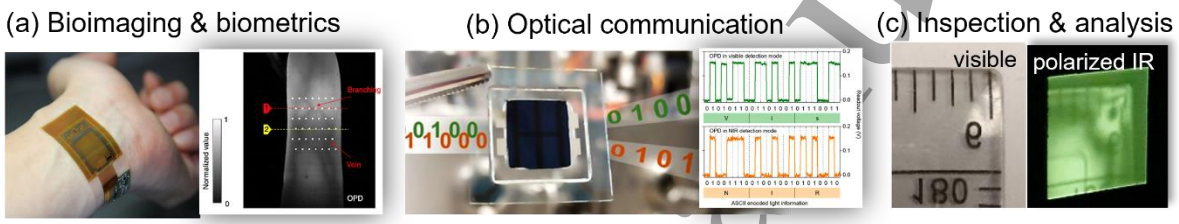

Figure 2 Potential applications of organic IR detectors. (a) Reproduced with permission of Ref. [4]. (b) Reproduced with permission of Ref. [19]. (c) Reproduced with permission of Ref. [6].

Concluding Remarks

With continuing efforts to increase performance, organic NIR/SWIR detectors are catching up to traditional infrared technologies while providing more flexibility in material choices, device designs, and innovations in functionalities. The printable organic IR detectors would potentially lower costs of infrared systems, as today's inorganic devices are prohibitively expensive at ten thousand US dollars per wafer, mostly due to complex processing steps. While the material chemistry and device physics of organic IR semiconductors present new challenges compared to detectors operating in visible wavelengths, great progress is being made to gain more in-depth and complete understandings of the relationships between molecular structures and properties, the mechanisms in charge photogeneration and recombination, aiming at clarifying key criteria for high performance and novel functions in organic IR systems.

Acknowledgements

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Section 2.4 – Lead-halide perovskite photodetectors

Hanru Feng[1], Zhizhou Chen[1], Yupeng Guo[2], Liang Shen[1]

[1]State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, International Center of Future Science, Jilin University, Changchun, People's Republic of China
[2]College of Chemistry, Jilin University, Changchun, People's Republic of China

Status

With the advancement of photoelectric technologies, lead-halide perovskites show great potential and possess desirable characteristics such as solution-processability, high carrier mobilities, long diffusion lengths, tuneable bandgaps, and high defect tolerance. These characteristics enable lead-halide perovskites to provide attractive solutions to challenges faced by conventional photodetector technologies. For instance, Liu et al. demonstrated that avalanche photoelectric diodes based on silicon exhibit notable improvement in the detection of high-energy ultraviolet photons when a $CsPbBr_3$ perovskite quantum dot film is integrated via a drop-casting method. The film downshifts ultraviolet photons to lower-energy visible light photons, as silicon's response to the former is unsatisfactory. The minimum wavelength of the enhanced avalanche photoelectric diode is extended from 350 to 250 nm and the photocurrent increases by 100% for photons with wavelengths under 365 nm. [1]

New types of photodetectors are being developed to adapt to the increasingly complex and specialized tasks in fields such as medicine, self-driving cars, and the exploration of extreme environments. Among them, progress made in the field of bionic lead-halide perovskite detectors and bendable lead-halide perovskite sensors demonstrates extraordinary versatility and has attracted the attention of researchers and the general public alike. A perovskite nanowire array mimicking the human retina fabricated via a vapour-phase method by Gu et al. displayed most of the desirable characteristics of the human eye, such as its extraordinarily wide field of view (155°), sensitivity, and minimal aberration. Notably, the density of perovskite nanowires in the array surpasses that of photoreceptors in the human retina at around 10 million per square centimetre. This suggests that the perovskite nanowire array may even outperform its natural equivalent in terms of resolution (the resolution of the human eye is about 1 arcmin per line pair at the fovea).[2]

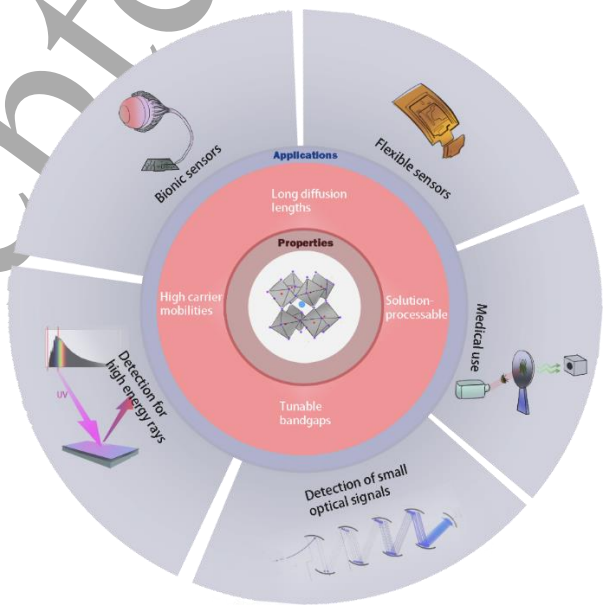

Figure 1 Some potential applications of LHP photodetectors and properties of lead-halide perovskites.

Research by Van Breemen et al. on bendable perovskite photodetectors is also of great interest. They fabricated a bendable photodetector based on an organic halide perovskite, which surpasses its counterparts built on glass substrates. These flexible detectors are advantageous as they are less cumbersome and can be applied in medical settings, such as X-ray detectors that can adapt in shape to accommodate the patient.[3] This innovative approach holds promise for lead-halide-perovskite sensors, as the flexibility inherent in such designs allows for a more precise fit to the specific contours of interest. This not only indirectly enhances their efficiency but also enables the development of more advanced and sophisticated photodetectors.

Current and Future Challenges

Though lead-halide perovskites possess outstanding characteristics, there are areas that warrant improvement, including environmental friendliness, stability, response speed, and spectral width. To minimize the adverse impact of lead on human health and the environment, it is imperative to reduce lead concentration in lead-halide perovskites as much as practically possible. However, this subject is covered by other researchers on this Roadmap (Section 2.5), hence it will not be discussed here. The sensitivity of lead-halide perovskites to moisture, heat, and oxygen makes related photoelectric devices highly susceptible to degradation over time, limiting their performance in environments where exposure to such conditions is unavoidable. Additionally, if lead concentration cannot be eliminated from perovskite sensors, the risk of lead content leakage will rise with their instability. This is especially a concern in fields such as medicine and bionics, where human contact is inevitable. Therefore, increasing the stability of lead-halide perovskites is of great importance.

The response time and spectral width of lead-halide-perovskite photodetectors still have potential for improvement, especially in terms of response speed for photodetectors based on solution-processed lead-halide perovskites. Because it is challenging to create leakage-free compact films from solutions, lateral structures are more likely to arise in photodetectors made of inorganic semiconductor nanoparticles. This could drastically impair response speed. Response time is additionally hampered by the existence of charge traps, which are introduced in solution-processed semiconductors to produce a photoconductive gain.[4] Although lead-halide perovskites are frequently applied to photodetection in the ultraviolet-visible region with a decent response to light in the region 300-800 nm, their lack of response in the near-infrared region (780-2526 nm) necessitates further investigation to extend the spectrum. Methods such as the combination of perovskites with organic semiconductors or other infrared-absorbing materials are a worthwhile subject of investigation.[5] Therefore, optimizing the spectral response range is an area where the performance of lead-halide perovskites has yet to be fully realized.

Advances in Science and Technology to Meet Challenges

To improve the stability of lead-halide perovskites, efforts are focused on suppressing charge-carrier recombination. However, doing so without chemical treatment remains an open challenge. Research by K. J. Lee et al. reveals that the recombination rate in lead-halide perovskites can be significantly decreased (up to six times) by using three-dimensional lead-halide perovskite polycrystalline thin films on hyperbolic metamaterials. This study also demonstrates the importance of dipole interaction in reducing decay rates and increasing photoresponsivity. Further theoretical and practical studies on the transition dipole properties of lead-halide perovskites may open avenues for physically regulating the recombination process. [6]

To achieve ultra-fast and broad-band response in lead-halide-perovskite photodetectors, the use of organic-inorganic halide perovskites over lead-halide perovskites could prove a solution. Research from our lab demonstrates that the high mobility and ultra-low trap density of a perovskite absorber layer achieved through charge-trap passivation enable effective and rapid charge-carrier extraction, resulting in a sub-nanosecond response speed. [4] The incorporation of organic components into lead-halide perovskites, as observed in the $MAPbI_3$ and PDPPTDTPT/PCBM composite detector reported by our group, expands the response range to the near-infrared region. This composite detector exhibits

a wavelength extension to 950 nm with a 5 ns ultrafast response time, surpassing the limitations of MAPbI3, which is restricted to wavelengths below 820 nm and does not cover the near-infrared range. Therefore, we believe that incorporating organic components into lead-halide perovskites could be a viable strategy for further improving the properties of lead-halide-perovskite photodetectors. [7]

Concluding Remarks

The field of lead-halide-perovskite photodetectors is increasingly dynamic and promising. The development of new photodetectors with exceptional capabilities is made possible by the properties of lead-halide perovskites. Such photodetectors hold potential for specialized applications with high efficiency thanks to the design advantages that lead-halide perovskites have over conventional absorbers. However, some fundamental guidelines should be followed when creating new lead-halide-perovskite photodetectors. First, these photodetectors should have high sensitivity, quick response times, and a wide spectral response to fully leverage the advantages of these materials. In addition, considerations during the fabrication and integration of devices should include addressing issues such as manufacturing costs, downsizing, and achieving high integration density. Customization for specific applications is crucial, and the devices should ideally be flexible, wearable, and biocompatible. We believe that the effectiveness of such photodetectors could lead to significant advancements in related industries.

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Section 2.5 – Printable lead-free perovskites and derivatives for photodetection

Vincenzo Pecunia

School of Sustainable Energy Engineering, Simon Fraser University, Surrey V3T 0N1, BC, Canada

Status

Lead-free perovskites and derivatives—hereafter referred to as *lead-free perovskites* for brevity—constitute a diverse family of synthetic materials. They exhibit either a perovskite structure with a general formula ABX_3, or derivative structures featuring corner-sharing or edge-sharing metal-halide BX_6 octahedra (A^+: monovalent cation; B^{2+}: bivalent metal cation; X^-: halide anion; see figure 1) [1]. Lead-free perovskites have attracted considerable interest due to their potential to replicate the favourable optoelectronic properties of lead-halide perovskites without toxic lead [2]. Their appeal for photodetection is firstly due to their diverse spectral properties in the ultraviolet, visible, and near-infrared regions (figure 1), which can be readily tuned by compositional engineering [3], [4]. Moreover, the application of lead-free perovskites in photodetectors has garnered interest due to their printability, which could enable low-cost, high-throughput device fabrication. The printability of lead-free perovskites is harnessed by synthesising these materials through the self-assembly of their component ions from solutions of relevant salts in common organic solvents. An additional attractive feature of lead-free-perovskite photodetectors is their ability to operate in self-powered mode (i.e., with zero applied voltage), which is highly sought-after for place-and-forget sensors for the Internet of Things [5].

The adoption of tin as the metal cation in lead-free perovskites has been primarily explored to realise ABX_3 absorbers (A^+: monovalent cation; B^{2+} = Sn^{2+}; X^-: halide anion). These absorbers adopt a perovskite structure featuring corner-sharing SnX_6 octahedra (figure 1). The bandgaps of these materials can be readily tuned by varying the halide anions X^-, resulting in optical gaps approximately of 1.2–1.3 eV for $ASnI_3$, 1.8–2.1 eV for $ASnBr_3$, and 2.9–3.5 eV for $ASnCl_3$ [4]. The resulting devices have achieved the highest external quantum efficiencies—above 80 %—for all lead-free perovskites while operating without photoconductive gain [6]. However, these performance levels are typically achieved under controlled atmospheres, as tin-based perovskites suffer from significant instability in ambient conditions due to the oxidation of Sn^{2+} to Sn^{4+} [7].

Alternative strategies for lead-free-perovskite photodetectors use bismuth- and antimony-based compounds. The stability of both Bi^{3+} and Sb^{3+} leads to highly stable absorbers [1], which adopt perovskite derivative structures due to their 3+ charge. Many such compounds have a general formula $A_3B_2X_9$ (A^+: monovalent cation; B^{3+}: Bi^{3+} or Sb^{3+}; X^-: halide anion), which can adopt a zero-dimensional structure with isolated B_2X_9 bi-octahedra (figure 1) [1]. Alternatively, $A_3B_2X_9$ absorbers can adopt a two-dimensional structure, featuring planes of staggered, corner-sharing BX_6 octahedra (figure 1) [1]. Because of the reduced self-trapped-exciton effects and enhanced carrier transport and lifetimes of two-dimensional $A_3B_2X_9$ absorbers compared to the zero-dimensional counterparts [8], the resulting photodetectors have achieved significantly higher external quantum efficiencies (up to 62–65 % without photoconductive gain for two-dimensional $Rb_3Sb_2I_9$ and $Cs_3Sb_2I_{9-x}Cl_x$ [9], [10]).

Another subset of Bi- and Sb-based perovskites that have attracted interest for photodetection includes silver/copper pnictohalides with a general formula $A_xB_yX_{x+3y}$ (A^+: Cu^+/Ag^+; B^{3+}: Bi^{3+}/Sb^{3+}; X^-: I^-/Br^-) [11] (figure 1). Thanks to their three-dimensional structures, these materials have achieved the highest external quantum efficiencies (up to ≈ 80 %) among all Sb- and Bi-based lead-free perovskites [12], spanning the visible spectral range and thus offering an attractive solution for near-infrared-blind visible-light photodetectors [13].

Bi- and Sb-based lead-free perovskites may also come as $A_2BB'X_6$ double perovskites (A^+: monovalent cation; B^+: monovalent metal cation; B'^{3+}: trivalent metal cation; X^-: halide anion), which exhibit a three-dimensional structure with alternating, corner-sharing BX_6 and $B'X_6$ octahedra (figure 1). Absorbers of this class have delivered favourable photodetector performance in the near-ultraviolet and blue spectral regions with high stability [14].

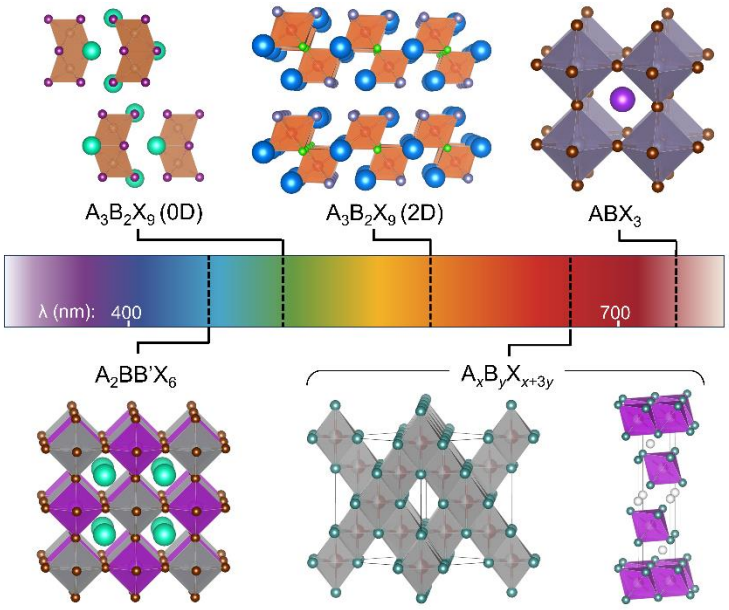

Figure 1 Representative lead-free perovskites for photodetection: general formulas, structures, and maximum cutoff wavelengths. 0D: zero-dimensional; 2D: two-dimensional.

Current and Future Challenges

Materials development and device engineering. To rationally optimise the photodetector performance of lead-free perovskites, a major challenge is to comprehensively establish their structure-processing-property relationships relevant to photodetectors. This is particularly critical due to the wide range of compositions—only partly discovered to date—and processing methods. Additionally, the selection of charge-transport layers to complete the photodetector device stack has narrowly drawn from perovskite photovoltaics research to date, which may not be conducive to optimal charge extraction.

Sensitivity vs Stability. A common challenge faced by lead-free-perovskite photodetectors pertains to achieving both high stability and high external quantum efficiency. For instance, tin-based-perovskite photodetectors typically exhibit superior external quantum efficiencies but considerably degrade in ambient atmosphere. Despite notable progress in addressing the instability of tin-based perovskites, a comprehensive solution to this challenge has yet to be achieved [15]. Conversely, photodetectors using bismuth- and antimony-based absorbers typically exhibit higher stability but lower external quantum efficiencies compared to tin-based counterparts. While photoconductive gain can be implemented to circumvent this sensitivity challenge, this often results in a sluggish response and nonlinear behaviour, limiting the practicality of the resultant devices.

Speed of response. To date, lead-free-perovskite photodetectors have typically exhibited response times in the millisecond range, even when operating without photoconductive gain [3]. This sluggish response restricts their potential applications and is at odds with the transit times predicted based on the reported carrier mobilities [16]. Therefore, a critical challenge involves comprehensively understanding the device and material parameters that influence response speed, aiming to reduce response times to microseconds or less.

Linear dynamic range. A linear relationship between photocurrent and incident optical power in photodetectors is highly sought after for photometric purposes. However, with only a few exceptions [8], [13], many lead-free-perovskite photodetectors developed to date exhibit a sublinear response [17], [18]. Therefore, a key challenge is to identify and overcome the microscopic causes of this sublinear behaviour in order to achieve a linear dynamic range competitive with incumbent photodetectors technologies.

Manufacturability and upscaling. Lead-free-perovskite photodetectors thus far have been developed only in academic laboratories using small device areas. Therefore, to commercialise this technology, an important challenge is to uniformly deposit lead-free perovskites, alongside all other layers in the device stack, over large areas with high throughput [19].

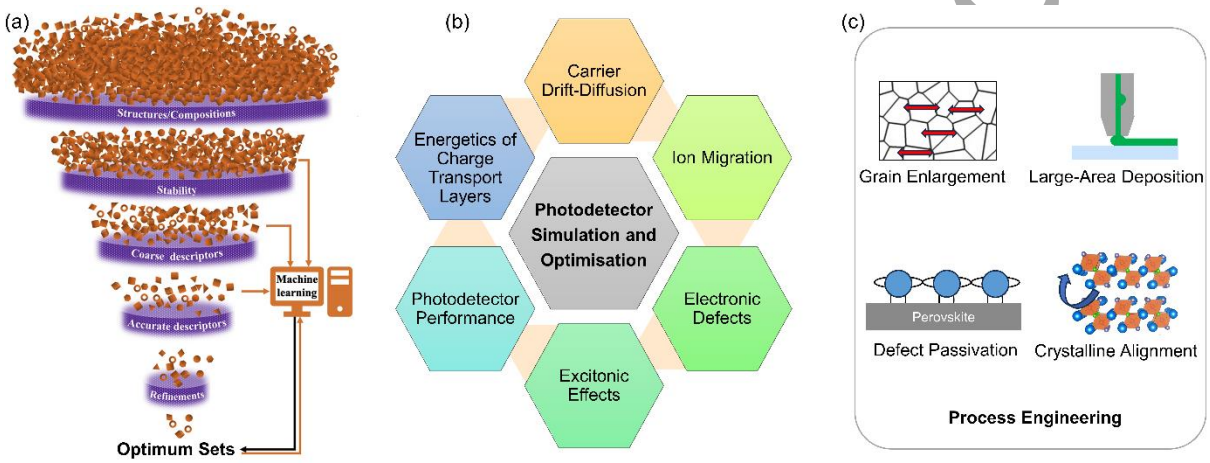

Figure 2 Roadmap for advancing lead-free-perovskite photodetectors: (a) computational materials screening; (b) materials/device characterisation, simulation, and optimisation; (c) process engineering. (a) is reproduced with permission from [20]. Copyright 2020 WILEY-VCH Verlag GmbH KGaA & Co.

Advances in Science and Technology to Meet Challenges

Computational materials screening. The lead-free perovskites investigated for photodetection thus far have predominantly been borrowed from photovoltaics research. However, to fully unlock their potential in photodetection, a systematic investigation involving high-throughput materials screening must be pursued to identify materials tailored to specific spectral ranges and photodetector performance metrics (figure 2(a)). The application of machine learning could play a pivotal role by enabling simulations and predictions of material properties and device performance. This effort should go hand in hand with the systematic screening of charge transport layers to enhance charge collection efficiency and reduce photocurrent noise.

Investigation of structure-processing-properties relations for photodetection. To enhance the speed of response, linearity, external quantum efficiency, and stability of lead-free-perovskite photodetectors, a comprehensive understanding of charge transport, charge-trapping, exciton self-trapping, ion migration, and their interplay with processing conditions is imperative [8], [16] (figure 2(b)). Experimental characterisation should be complemented by device simulations under relevant operational conditions. A systematic investigation of the noise behaviour of lead-free-perovskite photodetectors should also be pursued to assess the detection limits of the resultant photodetectors, given the limited experimental characterisation and mechanistic understanding of this key performance aspect to date.

Process engineering. To enhance photoconversion efficiency and stability, it is imperative to develop experimental protocols capable of increasing grain size in polycrystalline films of lead-free perovskites films beyond the 1 µm threshold (figure 2(c)). Additionally, efforts should focus on achieving the preferred alignment of crystalline planes to enhance charge extraction in photodetectors, as well as

additive engineering for defect passivation (figure 2(c)). Furthermore, a departure from conventional spin-coating methods is recommended to ensure the scalability of the technology (figure 2(c)). Techniques like slot-die coating, spray coating, and inkjet printing, which allow for deposition over larger areas, should be prioritized for fabricating lead-free-perovskite photodetectors with high throughput. Importantly, adopting eco-friendly solvents for the preparation of lead-free-perovskite inks is crucial to ensure the sustainable and straightforward industrial application of these materials.

Concluding Remarks

Lead-free perovskites have emerged as promising candidates for light sensors across the ultraviolet, visible, and near-infrared spectrum, as these absorbers eliminate the use of toxic lead present in their lead-based counterparts. While tin-based embodiments are challenged by their instability, the encouraging stability displayed by bismuth- and antimony-based absorbers holds great potential. Realising this promise requires concerted efforts in material development and device engineering. Equally important is delving into the intricacies of structure-processing-properties relationships specific to photodetection. Alongside these pursuits, engineering processing methods to enhance film quality and deposition scalability is crucial for the advancement of these materials and devices towards commercialisation.

Acknowledgements

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Section 2.6 – Printable infrared quantum-dot photodetectors

Emmanuel Lhuillier

Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

Status

Nanocrystals are semiconductor nanoparticles, see Figure 1a. Thanks to quantum confinement the band gap energy can be easily tuned as opposed to alloying strategy used to tune the band gap of bulk semiconductors. The smaller the particle the bluer will be the spectrum. Such nanocrystals are grown using chemical processes (Figure 1a) leading to the formation of an inorganic core surrounded by organic ligands, whose role is to stabilize the particle within the solution and to electronically passivate the surface.

Interest for such particles was first driven by their bright luminescence which led to applications such as biolabeling, single photon source and most importantly their use as blue light down converters for display. It was only around 2000, that applications involving charge transport in nanocrystal array were because it was crucial to first identify a strategy to increase the particle coupling. At that time, nanocrystals started to raise interest for solar cells. Thanks to their tunable band gap, the size of the particle can be optimized so that their band gap matches the Queisser-Shockley criteria. Despite clear progress in the material performances, the silicon remains a strong challenger in terms of cost and integration. Thus, when it comes to the use of nanocrystal for light sensing, the benefits are obtained at wavelengths that silicon cannot address and at wavelengths longer than its band gap (1.1 µm). This spectral ranges also corresponds to wavelengths that organic electronic cannot address due to a strong exciton vibration coupling. As a result, most of the effort relative to light detection using nanocrystals have been focused on infrared wavelengths. Among the advantages of nanocrystals, one

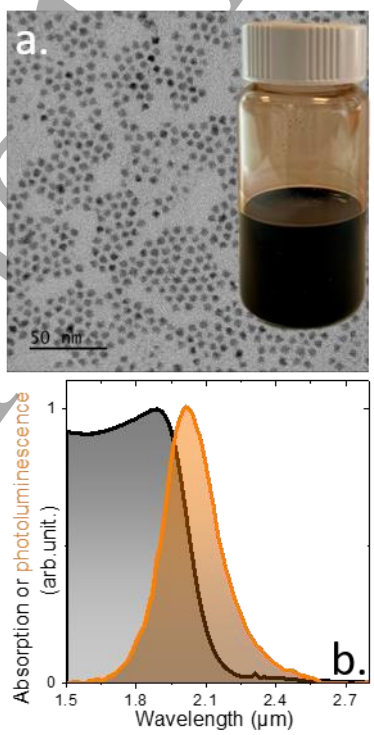

Figure 1 a. Transmission electron microscopy image of infrared nanocrystals. The inset is an image of a vial containing a colloidal solution of infrared absorbing nanocrystals. b. Absorption and photoluminescence spectra of short-wave infrared active HgTe nanocrystals

can cite (i) a reduced fabrication cost, (ii) a broad spectral tunability from visible to THz without constraint coming from being lattice matched, (iii) processability through wet chemical processes (e.g., inkjet and spin coating) which ease the coupling to the read-out integrated circuit and consequently favour the pixel size reduction.

Since one key benefit of nanocrystals over conventional semiconductors is the cost, the main targeted spectral range to date is the short wavelength infrared (from below silicon band gap to 2.5 µm). There the band gap remains large compared to thermal energy at room temperature and operation with limited cooling remains possible.

Current and Future Challenges

Though the concept of infrared sensing using nanocrystals array[1]–[3] has been established almost 20 years ago, the path from material to technology has been quite long. Certainly one of the first challenges to tackle have been hopping conduction. In an array of colloidal particles, the weak interparticle electronic coupling is associated with low mobility values (10^{-6} $cm^2.V^{-1}s^{-1}$ before ligand exchange) and thus short diffusion length. As a result, it was believed that this would be incompatible with high quantum efficiency or may limit the device time response. Ligand exchange procedure that preserves the surface passivation have been developed to bring the mobility in the 10^{-2}-1 $cm^2.V^{-1}s^{-1}$ range. Furthermore, fast sensing down to few ns time response has been reported. This has enabled an increase of photoresponse[4] (i.e. capacity to convert light into an electrical signal) and has brought focus to another bottleneck that is noise. In a nanocrystal array, noise is mostly limited by 1/f noise[5], whose magnitude is also driven by interparticle electronic coupling. This has made the development of photodiode crucial to operate the device under reduced bias and thus under reduced dark current. However, diode design is quite complex since the electronic structure of this colloidal material is far less known than the one of III-V material. Indeed, in addition to bulk electronic structure, quantum confinement and effects relative to surface chemistry must be considered. Thus, rational designs of diode stacks necessitate systematic studies of the band alignment in nanoparticle thin film using methods such as X-ray photoemission[6], [7] or electrochemistry[8].

A major step to demonstrate the potential of this technology beyond the academic level have been the switch from single pixel device to image sensor, see figure 2. To do so, the nanocrystal film is used to functionalize a read-out integrated circuit. Various demonstrations, either using PbS[9], [10] or HgTe[11], [12] nanocrystals, have been obtained, with focus on operation from 950 to 2000 nm. Traditional short-wave infrared read-out integrated circuits have been used with VGA format and 15 µm pixel pitch. The most promising result relates to wafer level processing with pixel size close to the diffraction limit[9]. A size that even recent progress relative to copper-based hybridization is far from reaching[13]. Active imaging applications such as industrial vision (material sorting, detection of damages on food, moisture detection) are particularly targeted because they impose less constraints on the magnitude of the dark current and the quantum efficiency value than astronomy or defense. Fast detection to achieve time of flight measurement is also targeted for LIDAR applications.

Advances in Science and Technology to Meet Challenges

Though a clear increase in mobility values has been obtained the diffusion length remains shorter than the absorption depth and as a result the obtained devices are poorly absorbing. This is why recent efforts focus on the introduction of photonic structure which role is to focus the light over a distance compatible with the diffusion length. This concept is well known from the field of infrared sensing, since for example diffraction gratings have already been used in the 90's to light sensitize quantum wells that selection rule makes blind under normal incidence. However, the transfer of the concept to nanocrystal requires some severe technological update. Indeed, nanocrystals tend to be less robust that conventional semiconductors and present degraded optoelectronic performances after exposure to lithography (baking or exposure to solvent). Thus, fabrication process in which the nanocrystal deposition is coming as one of the final steps have to be favoured. Multiples geometries of light resonator[14] have been tested including plasmonic[15] grating, guided mode resonator[16], and

Fabry Perot cavity. At present, devices absorbing 70 % of the incident light are routinely achieved. An interesting direction to pursue to generate more localized modes and reduce the electrically active volume (that drives the amount of dark current) will be the use of deposition methods that are compatible with spatially selective deposition. Some efforts using inkjet[17] and nanoprinting[18] have already been obtained but will now have to be integrated on chip and repeated over a million pixels. Such localized depositions are also relevant for the fabrication of multicolor sensor[19].

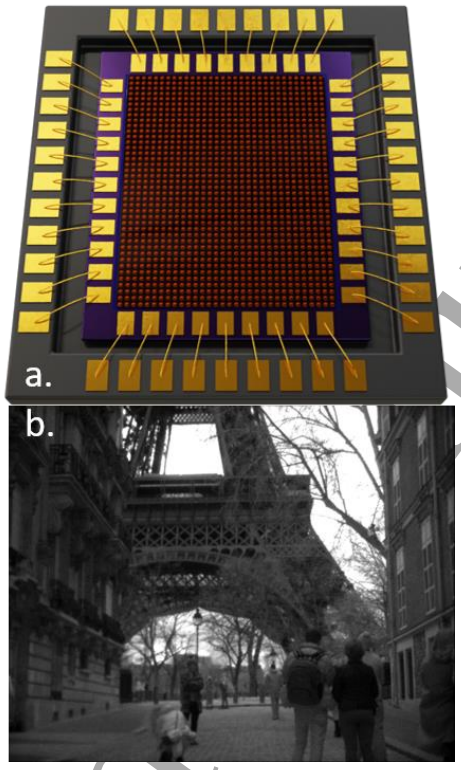

Figure 2 a. Schematic of a ROIC functionalized by a nanocrystal film to sensitize it in the infrared. b. image of the Eiffel tower taken with a HgTe nanocrystal-based infrared camera with 2 µm cut-off wavelength. Reprinted with permission from [20]. Copyright 2023 American Chemical Society.

Certainly, efforts in developing the material also must be continued. PbS and HgTe are the two prevailing materials when it comes to infrared sensing using nanocrystals. However; PbS is prone to oxidation, while HgTe tends to sinter if exposed to elevated temperature. Furthermore; and though the suppression of substrate and low temperature processability reduce the amount of heavy metal and energy consumption compared to traditional semiconductor growth, some efforts are still required to develop greener infrared active colloidal materials. To date III-V (InAs) and silver chalcogenides are the most promising alternative platforms but they lag far behind in terms of integration.

Concluding Remarks

Thanks to their inorganic core, colloidal nanocrystals have become the most advanced platform as an alternative to epitaxially grown semiconductors for infrared optoelectronics. Beyond the growth cost disruption that they bring, they also ease coupling to small pixel size imager. The use of spray and printing methods is very promising to achieve wafer level processing of nanocrystal technology that may shrink by another order of magnitude the device cost.

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Section 2.7 – Photodetectors based on 2D materials

Lidia Kuo, Vinod K. Sangwan and Mark C. Hersam

Department of Materials Science and Engineering, Northwestern University, Evanston, IL, 60208, United States of America

Status

Since the isolation of graphene from graphite, two-dimensional (2D) van der Waals materials have attracted intense research interest due to their atomically thin structure and resulting superlative optoelectronic properties that are particularly well-suited for photodetector applications. Compared to bulk inorganic semiconductors, 2D materials offer a wide range of bandgap tunability and room-temperature excitonic physics that enable tailored spectral response. Moreover, 2D materials can be exfoliated from bulk layered materials via solution processing, resulting in optoelectronically active inks for fully printed and mechanically flexible photodetectors.

The performance of photodetectors based on 2D materials is determined by their thickness-dependent bandgaps, free carrier mobilities, electrostatic field effects, and optical absorbance properties [1]. For example, transition metal dichalcogenides, such as MoS_2, undergo qualitative changes in bandstructure from indirect to direct bandgap when bulk crystals are exfoliated down to atomically thin limit. High-aspect-ratio monolayer nanosheets are desirable for photodetectors due to their increased optical absorbance, strong electrostatic gating, and high mechanical flexibility. The most common solution-based exfoliation method for 2D materials is liquid-phase exfoliation, where thin nanosheets are isolated from bulk layered crystals via ultrasonic energy in the presence of a compatible solvent and/or stabilizing additives, which is then followed by size-selecting centrifugation [2]. Methods based on liquid-phase exfoliation also provide a straightforward pathway to formulating inks for all-printed 2D material photodetectors.

Printable 2D material inks can be formulated for a wide range of printing methods by changing the solid loading of the ink and correspondingly the ink viscosity. Percolating film 2D material photodetectors have been fabricated by inkjet printing [3]–[10], electrohydrodynamic printing [11]–[13], and aerosol-jet printing (Figure 1a) [14], [15] on rigid and flexible substrates including silicon wafers, polyimide, and paper. Printed 2D material photodetectors typically rely on photo-generated excitons being dissociated into free electrons and holes, which are then collected by externally applied electric fields between two electrodes in a vertical or lateral geometry (Figure 1). In fully printed 2D material photodetectors, printed graphene electrodes are frequently employed [5], [6], [8], [10], [14]. Performance metrics such as photoresponsivity, speed, and detectivity are maximized through the refinement of liquid-phase exfoliation methods in addition to optimization of doping, minimization of extrinsic losses, and development of channel geometries that promote efficient photon capture and charge extraction. The earliest demonstrations of printed 2D material photodetectors focused on inkjet-printed, visible-light MoS_2 photodetectors [6], [7], which showed photoresponsivities on the order of 1 mA/W with response times in the range of 10-100 ms. Although early work encountered trade-offs between photoresponsivity and response time, recent improvements in flake crystallinity, printed percolating film morphology, and minimized surface residues have enabled photoresponsivities up to 10^3 A/W with 1 ms response times [9], [14]. Additionally, recent efforts have focused on 2D materials beyond transition metal dichalcogenides, such as inkjet-printed black-phosphorus-based photodetectors that are responsive at near-infrared (NIR) wavelengths [3].

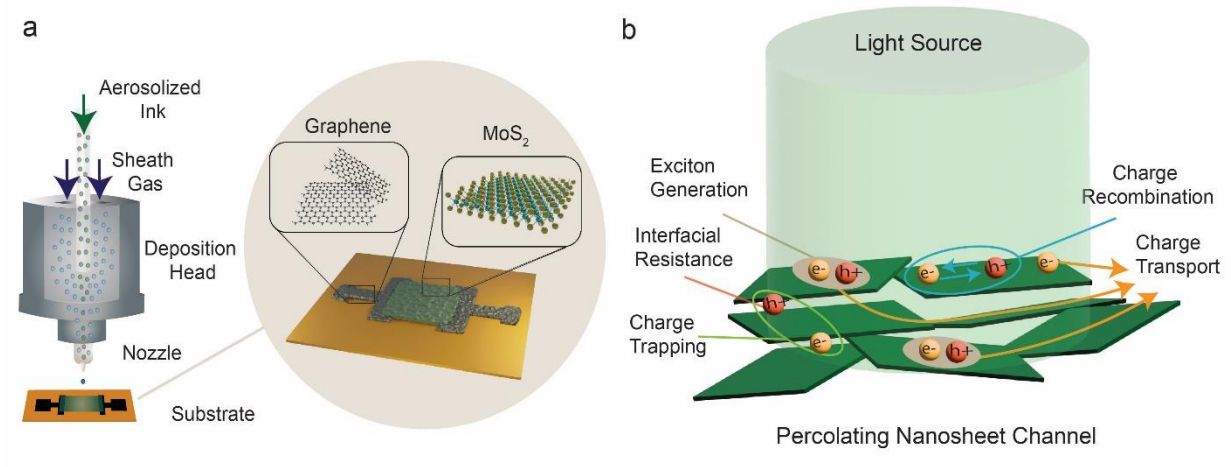

Figure 1 (a) Schematic of an aerosol-jet printed MoS_2 photodetector with printed graphene electrodes, reproduced with permission from reference [14]. Copyright Wiley-VCH, 2022. (b) Schematic depicting a percolating nanosheet channel and various mechanisms that control photodetector performance metrics.

Current and Future Challenges

Concurrently optimizing percolating charge transport and optical absorption in printed 2D material percolating films is a significant challenge for 2D printed photodetectors, influencing performance metrics such as photoresponsivity, speed, and detectivity. In disordered, printed films, variable-range hopping across van der Waals gaps between overlapping nanosheets limits the overall charge transport through the percolating nanosheet network [1]. Additionally, both defects within individual flakes and interfacial residues can act as charge traps and recombination sites that compromise photoresponse [13]. While non-conductive residues can hinder charge transport, conducting residues can quench exciton formation and dissociation processes. Furthermore, the electrode-channel interface not only determines contact resistance but can also generate photocurrent due to the built-in field at metal-semiconductor Schottky junctions [16]. In the case of printed graphene electrodes, a high degree of percolation between graphene and photoactive flakes at the contact-channel interface can improve photodetector performance. Therefore, the morphologies of both the contacts and the channel need to be optimized by tailoring printing methods, solvent choice, ink rheology, deposition parameters, and/or curing conditions.

Another challenge is achieving a high monolayer fraction in solution-processed 2D material inks, which strongly influences optical absorbance and spectral response. Traditional liquid-phase exfoliation methods primarily yield few-layer nanosheets, resulting in relatively poor photoresponsivity compared to monolayer nanosheets, particularly for transition metal dichalcogenides where monolayers are required to achieve a direct bandgap. While size-selection methods such as multi-step liquid cascade centrifugation have been developed to carefully isolate thin nanosheets, these centrifugation methods are arduous and typically insufficient for achieving high monolayer concentrations [17].

Beyond transition metal dichalcogenides, printed photodetectors from alternative 2D semiconductors such as black phosphorus, InSe, and tellurene are of interest due to their promising optoelectronic properties. For example, black phosphorus and tellurene exhibit NIR response at telecommunications-relevant wavelengths, and InSe exhibits a direct bandgap at few-layer thicknesses that enables high optical absorption. However, these alternative 2D semiconductors are chemically unstable in ambient conditions, which requires printing in inert atmospheres and/or passivation schemes that arrest chemical degradation pathways. Thus far, black phosphorus is the most heavily investigated 2D semiconductor beyond transition metal dichalcogenides, but challenges with ambient reactivity have thus far resulted in relatively low photoresponsivities (~10 mA/W) and slow response times (> 1 sec) at NIR wavelengths [3]. Since other NIR-sensitive 2D material photodetectors have shown similar

metrics (Figure 2) [10], additional research effort is still required to achieve high-performance printed 2D NIR photodetectors. In all cases, it would be of high interest to not only achieve isolated photodetectors but also large-area arrays that are directly integrated with readout integrated circuits to achieve video-rate high-resolution cameras at both visible and NIR wavelengths. In this regard, direct printing of 2D material photodetectors could present significant practical advantages over traditional inorganic semiconductors that currently require expensive wafer-bonding methods for integration with a read-out integrated circuit.

Advances in Science and Technology to Meet Challenges

In recent years, the morphology of printed 2D percolating networks has been improved by tailoring ink formulations, printing conditions, and post-deposition processing parameters. A particularly promising approach is the utilization of inks with laterally large but thin nanosheets to decrease the percolation threshold. Towards this end, electrochemical intercalation prior to liquid-phase exfoliation has emerged as a promising approach, where the inter-layer spacing is expanded in van der Waals crystals via the electrochemical insertion of intercalant species, thus lowering the energy threshold to exfoliate into thin flakes with large lateral dimensions. In addition, highly uniform, percolating network morphologies have been achieved by tailoring solvent drying [3], [9]. Another example of a post-processing scheme for improving morphology is calendaring, in which porous films are mechanically pressed to decrease film roughness and inter-flake resistance [18]. Photonic annealing has also been shown to be an effective curing method following printing, which not only removes undesirable residues at relatively low temperatures but also improves intermixing between nanosheets at the electrode-channel interface to lower contact resistance [8], [14]. Further improvements can be anticipated in the future by synergistically combining these best practices to optimize overall photodetector performance. Due to the large processing phase space, high-throughput experimental screening coupled with machine-learning-guided optimization is likely to accelerate progress.

Recently, megasonic exfoliation, in which secondary thinning enriches the monolayer fraction of the ink, has been demonstrated for aerosol-jet printed MoS_2 [14]. Megasonic exfoliation occurs at megahertz sonication frequencies, compared to the kilohertz frequencies of conventional ultrasonic liquid-phase exfoliation processing, resulting in more uniform, localized cavitation during solution processing. This more controlled cavitation promotes efficient exfoliation with reduced flake fracture, ultimately yielding high-aspect-ratio monolayer flakes and dramatically enhanced photoresponsivities that outperform previous reports by up to 4 orders of magnitude. Extending the megasonic exfoliation methodology to other 2D materials beyond MoS_2 remains an open challenge with the potential to enable printed 2D photodetectors with spectral responses over additional wavelength ranges.

For ambient-reactive 2D semiconductors, opportunities remain for the development of solution-based passivation strategies that would result in printable inks that do not require cumbersome inert environment processing. Although post-deposition polymer encapsulation imparts some ambient stability [3], it does not avoid air exposure during ink handling and printing. In addition, encapsulation layers have the potential to absorb or scatter incident light, thereby reducing overall photoresponse. Therefore, direct chemical passivation during solution-based exfoliation is of high interest to broaden the range of 2D semiconductors for printed photodetectors. Alternatively, the identification of additional photoactive and ambient-stable 2D materials would allow the wavelength range of printed 2D photodetectors to be expanded. For example, recent work has shown that solution-processed and ambient-stable $RuCl_3$ exhibits a strong photoresponse at NIR wavelengths [19]. Diversification of the portfolio of printable 2D semiconductors also presents opportunities for realizing solution-processed 2D heterostructures, such as printed p-n heterojunctions, which could present additional exciton dissociation and charge extraction pathways than single-component percolating networks [20]. In this manner, printed 2D photodetectors could be extended to more advanced device architectures, including avalanche photodiodes and single-photon detectors, which represent the state-of-the-art for conventional inorganic semiconductors but have not yet been realized with printable 2D inks.

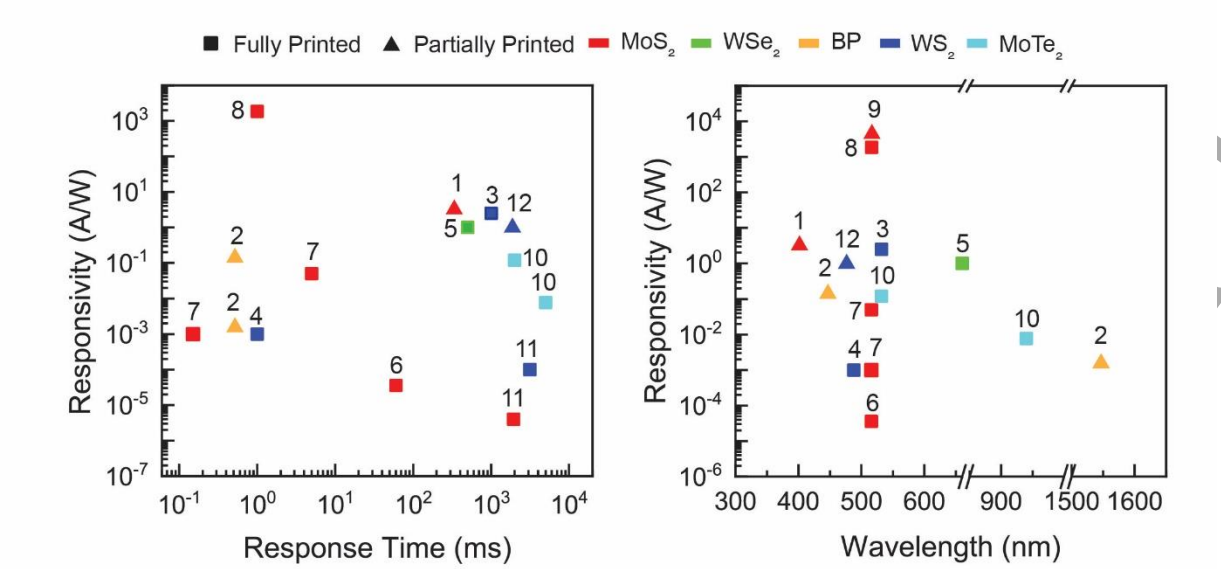

Figure 2 Comparison plots of response time versus responsivity (left) and responsivity versus wavelength (right) for printed 2D photodetectors. Reports that did not provide a response time or wavelength were excluded from the respective plots. Labels correspond to the following references → 1: [11], 2: [3], 3: [4], 4: [5], 5: [15], 6: [7], 7: [8], 8: [14], 9: [9], 10: [10], 11: [12], 12:[13].

Concluding Remarks

Printed 2D material photodetectors hold significant promise for combining the optoelectronic performance of bulk inorganic semiconductors with the high throughput and mechanical flexibility of roll-to-roll additive manufacturing. To realize the full potential of printed 2D material photodetectors, optoelectronically active inks need to be derived using liquid-phase exfoliation followed by optimized printing and post-deposition processing methods. In this context, transition metal dichalcogenides have been the most heavily investigated van der Waals materials to date, although recent work has begun exploring alternative 2D semiconducting inks to cover the entire electromagnetic spectrum from the visible to NIR wavelengths. However, these 2D semiconductors, which go beyond transition metal dichalcogenides, present challenges in high-aspect-ratio exfoliation to the monolayer limit in addition to complications resulting from their higher propensities for chemical degradation in ambient conditions. Chemical passivation coupled with the identification of alternative photoactive and ambient-stable 2D semiconductors provide pathways for not only diversifying the range of single-component 2D photodetectors but also enabling the exploration of more advanced architectures such as p-n heterojunctions and avalanche diodes. In this manner, printed 2D material photodetectors have significant headroom for even higher performance in future work.

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Section 3.1 – Introduction to printable ionizing radiation detectors

Beatrice Fraboni, Laura Basiricò and Andrea Ciavatti

Department of Physics and Astronomy, University of Bologna, Viale C. Berti Pichat 6/2, 40127, Bologna, Italy

During the past decade the employment of ionizing radiation has spread in different fields of human society, from medical treatments and diagnostics to civil security in public places and industrial testing. Such application areas require novel properties and functionalities of ionizing radiation detectors (e.g. large detection area, conformable structures and lower operation power) and innovative technologies for their fabrication. Currently available ionizing radiation detectors are mostly based on inorganic semiconducting materials such as silicon, germanium, cadmium telluride, cadmium zinc telluride.

Despite their outstanding detection performance, the sustainable growth of large-size, high-quality inorganic semiconducting crystals is still an unsolved challenge, as well as their processing into large-area pixelated detector matrices, possibly onto flexible, curved substrates.

Printable active materials offer the possibility to implement ionizing radiation detectors able to cover large areas in the form of pixelated detector panels, fabricated with limited costs and offering lightweight and low power operation. Thanks to the low temperatures associated to printing processes, it is possible to use non-conventional substrates allowing to envision detector panels able to conform to 3D structured surfaces, thus also prospecting innovative scenarios for their application. Figure 1 shows examples of applications for such large-area and bendable panels, such as cargo security inspection systems and radioactive threat prevention, if placed on the walls of public buildings or of spacecrafts to monitor the radiation received from solar particle events or galactic cosmic rays.

Ionizing radiation, i.e. high energy photons (X- and gamma-rays) and charged particles (protons, ions, electrons, alpha particles), can be detected by two different classes of functional materials, both printable: scintillators and semiconductors, working following an indirect and direct detection process, respectively (Figure 2). In scintillators and semiconductors, the impinging radiation interacts with the material by a primary ionization process that results in the production of electron-hole pairs

Figure 1 Scenarios envisaging innovative printable ionizing radiation detectors.

(excitons) as a secondary interaction process. In the case of scintillators, the excitons' energy is first transferred to the luminescent centers present in the material, and then radiatively released as UV-visible light (the emission spectrum depends on the scintillator material). Thus, in the indirect detection mode, the incoming ionizing radiation is transduced into an electrical output signal in a two-steps process: in the first step the scintillator transforms the radiation into visible photons and in the second step a coupled photodiode or a photomultiplier converts them into an electrical signal. In the direct detection process, the excitons resulting from the interaction with the impinging radiation are dissociated by an electric field and generate charges carriers that are directly collected by the device's electrodes as an electrical output signal.

Generally speaking, the direct approach reduces the response time and increases the signal-to-noise ratio thanks to the simpler one-step process with respect to the indirect detection one.

Printable materials can be employed as scintillators and/or UV/vis photodetectors in indirect detectors as well as semiconducting active layers in solid-state direct detectors. Although relatively large single crystals of ionizing radiation sensitive materials can be printed[1,2], printable materials offer the unique opportunity to produce large-area flexible detectors, thus, in the following we will focus on the peculiar properties and processes relevant for printed film-based devices.

In order to fully understand the perspectives and challenges for printable materials as ionizing radiation detectors, the main requirements and fundamental figures of merit will be discussed in the following.

Sensitivity, defined as the total charge collected, per unit exposure of incident radiation and per unit irradiated area, can be considered as one of the benchmark metrics. It describes the ability of a detectors to respond to a specific amount of radiation, that summarizes the overall detection process: from radiation absorption to charge pair creation, transport, and collection. Therefore, sensitivity is directly dependent on three other fundamental metrics: (i) the attenuation fraction, also known as *quantum efficiency* η_0 ($\eta_0 = 1 - e^{-\mu_0 t}$), where μ_0 is the linear attenuation coefficient and t the thickness of the active layer); (ii) the *charge pair generation efficiency*, i.e. the number of the electron-hole pairs created by each absorbed photon, defined as the average absorbed energy divided by the electron-hole pair creation energy *W±*, typical of a specific material; (iii) the *charge collection efficiency*, that depends on the mobility-lifetime ($\mu\tau$) product, on the external electric field, and on the geometry and architecture of the detector. Due to such triple dependence, sensitivity values can vary over several orders of magnitude, typically from 10 up to 10^6 µC Gy^{-1} cm^{-2}.[3–5]

Dark current, the current flowing into the device during working conditions and in the absence of any impinging radiation, is another fundamental parameter for UV-Vis photodetectors or direct detectors. A good sensor has low current, in the range of nA or lower, and can be achieved by high-resistivity

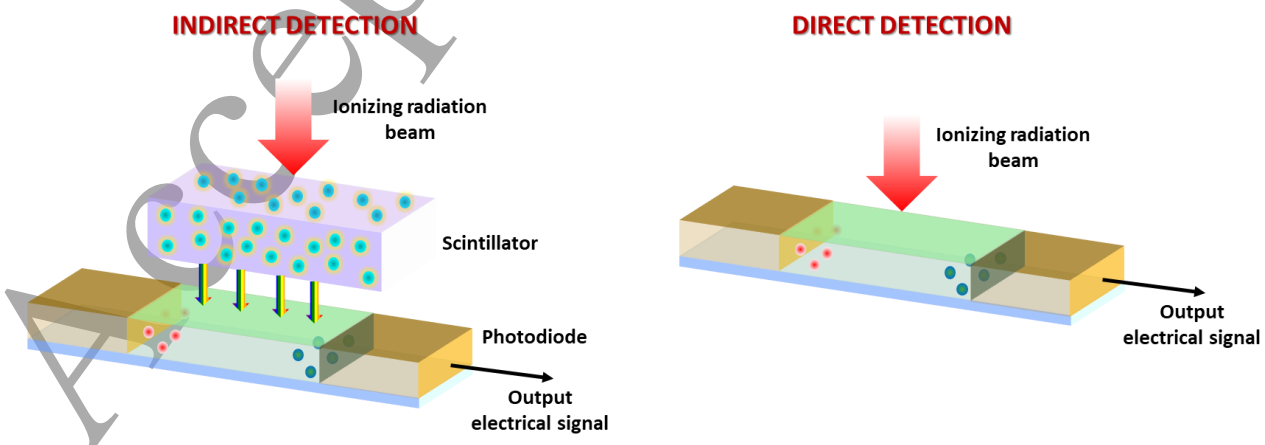

Figure 2 Schematics of the indirect (left) vs. direct (right) radiation detection processes.

photoconductor materials, or by the insertion of charge-blocking layers. The minimum detectable dose, or *limit of detection (LoD)*, is the lowest amount of radiation measurable by the radiation detector. In sensors, it is commonly accepted the definition of LoD as corresponding dose/flux that gives an output signal with signal-to-noise ratio equal to 3.[3,4] By the definition, it is clear that both sensitivity and dark current concur in the LoD value. In order to achieve high-sensitivity and good efficiency, large detector volumes are thus in principle required to maximize the probability of interaction of the impinging radiation in the detector volume. This is particularly relevant for printed thin-film detectors, where an appropriate choice and use of 2D and 3D printing technologies can make the difference in the resulting detectors' performance.

As a matter of fact, the thickness of a printed scintillation layer can be easily increased up to few millimeters by the employment of 3D printing techniques (e.g. material-extrusion method), and the thickness of the active layer of a direct detector achievable without affecting the charge transport by means of 2D printing techniques (inkjet, bar coating, screen printing) can be varied over a quite wide range [10 nm-10 µm].[6–8]

Besides the interaction volume, it is the high atomic number (Z) that assures efficient radiation–atomic interactions, since the cross-section for photoelectric absorption in a material of atomic number Z varies as Z^n, where $4 < n < 5$. Printable materials offer the relevant advantage of the easiness of tailoring the chemical composition of the functional ink by inserting high-Z elements or nanocomposites (e.g. perovskite quantum dots, bismuth- or lead-based nanoparticles) to enhance the absorption of the high energy radiation. Printable semiconductor inks for organic electronic devices are generally based on an intrinsically low-Z matrix (mostly composed of H, C ad O atoms). If such organic printed thin films are employed as detection layers without further blending, their interaction with ionizing radiation results similar to that of human body tissues, i.e. they are considered *tissue equivalent materials*. This is a highly needed and sought after property in medical dosimetry, especially in radiotherapy applications, where the accurate measurement of the actual radiation dose impinging or released onto the patient's body is a crucial requirement to assure radioprotection and to customize therapeutical plans.

Printed semiconducting films typically exhibits micro-nano crystalline morphology usually associated with high trap state density in the bulk, at the surface and at interfaces with electrodes or dielectrics, generally leading to lower mobility values and lower lifetime of the charge carriers with respect to the single crystal counterparts. Achieving good transport properties, i.e. high $\mu\tau$ (i.e. $10^{-5}/10^{-6}$ cm^2 V^{-1} for amorphous selenium/cadmium zinc telluride, as benchmark for large-area detectors)[4], and high collection efficiency for excess charge carriers (electron-hole pairs) generated by the interaction with the radiation, is the most impacting intrinsic limitation of printed thin film based detectors. A poor control of these transport parameters would lead to high dark currents and lower material resistivity (typically $>10^9$ Ω cm is required for efficient radiation detectors), affecting the limit of detection of the device, due to a lower signal-to-noise ratio.

Trap-related effects may also affect the detector response time. The output signal rise-time achievable by printed detectors under irradiation with ionizing radiation, is hardly lower than few microseconds, due to the large charge recombination times. The great benefit of printing techniques is the possibility to efficiently act on the film morphology and crystallization to control trap states that eventually intervene in the detection process. Following this strategy, it is possible to exploit processes such as the photoconductive gain, which dominates the detection of printed detectors based on organic semiconductors, to boost the sensitivity up to extremely high values, such as 10^5-10^6 µC Gy^{-1} cm^{-2}.[9,10]

Concerning printed plastic scintillators, the possibility of printing layers with a thickness in the range [0.1-1] mm allows them to absorb a larger amount of energy from the impinging radiation with respect to thin-film-based direct detectors, maintaining a bendability that grants a superior mechanical and optical coupling with flexible or curved photodetectors (thus implementing a bendable fully printed

indirect detector). Furthermore, the ease of tunability of printable polymeric inks enables the functionalization with a large variety of luminescent nanoparticles or quantum dots (e.g. CdSe:ZnS-, ZnCdSe-, GOS:Tb-based) that can optimize and maximize the optical matching to the coupled photodetector. The issues that may require specific attention for printed scintillators are their light yield, possibly limited by low transparency and the anisotropy of the scintillation output signal.[10,11]

Given all the above considerations, and the exceptional results that the scientific community has provided over just a few years, the greatest challenge for printed ionizing radiation detectors is now to exploit all their unique and extremely valuable properties in applications that are presently not accessible to detectors fabricated with not-printable inorganic materials. A tremendous wealth of science, technology and innovation is ready to surge thanks to the use of printable electronic materials as ionizing radiation detectors.

The following contributions present an insightful roadmap on the most promising printable material platforms for ionizing radiation. Undoubtedly lead halide perovskites (section 3.2) and organic semiconductors (section 3.4), as well as nanocomposites, e.g. quantum dots (section 3.5), have been the most investigated and performing material among them. Further, with the aim to overcome the toxicity of water-soluble Pb compounds, i.e. lead halides, in perovskites, significant efforts are ongoing to develop lead-free counterparts for ionizing radiation detection as testified by section 3.3.

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Section 3.2 – Printable lead-halide-perovskite radiation detectors

Haodi Wu[1], Guangda Niu[1,2], Jiang Tang[1,2]

[1] Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, Hubei Province, People's Republic of China.
[2] Optics Valley Laboratory, Wuhan 430074, Hubei Province, People's Republic of China.

Status

In recent years, lead-halide perovskites gain wide attention in radiation detection due to their exceptional properties [1], such as high X-ray absorption coefficient, low defect density, and high mobility-lifetime ($\mu\tau$) product. These characteristics enable high X-ray detection sensitivity and low detection limit. Furthermore, unlike traditional radiation detection materials such as CdTe and α-Se, lead-halide perovskites offer the advantage of low-temperature solution processing [2]. This permits its direct preparation of large-area film by using printing techniques like doctor-blading and spray coating (Figure 1). Consequently, lead-halide perovskites can be easily integrated with thin-film transistor or complementary metal oxide semiconductor (CMOS) readout arrays, facilitating the fabrication of high sensitivity, high spatial resolution, and low detection limit X-ray flat panel detector (FPD).

In 2017, Yong Churl Kim *et al.* [3] prepared $MAPbI_3$ thick film on a thin-film-transistor array using the doctor-blading technique, which resulted in the first perovskite-based X-ray FPD. This detector achieved a sensitivity of 3,800 μC Gy^{-1} cm^{-2}, which is 190 times that of a traditional α-Se detector. In 2021, Jiuk Jang *et al.* [4] introduced guanidinium into A-site and formed $GA_{0.1}MA_{0.9}PbI_3$, yielding a more stable perovskite composition. Due to solvent evaporation during the annealing process, numerous pores formed inside the thick film, affecting carrier transport and decreasing the film density. In 2022, Menglin Xia *et al.* [5] addressed the issue of film densification by incorporating a polymerizable binder into $MAPbI_3$ and employing soft-pressing. The $\mu\tau$ product of the device increased by an order of magnitude (from 5.3×10^{-5} cm^2 V^{-1} to 6.8×10^{-4} cm^2 V^{-1}), and the sensitivity reached 17432 μC Gy^{-1} cm^{-2}, indicating the improved carrier transport after densification treatment.

Compared to the doctor-blading technique, spray coating and inkjet printing are more advantageous for fabricating dense thick film with columnar crystals [6]. Henning Mescher *et al.* [7] prepared lead-halide-perovskite films using an inkjet-printing method, achieving a flexible film with vertically aligned columnar crystals. Wei Qian *et al.* [8] developed an aerosol-liquid-solid spray method, producing oriented perovskite films and realizing an X-ray detector with high sensitivity of 1.48×10^5 μC Gy^{-1} cm^{-2}. Spray coating requires more time to prepare hundreds of micrometers thick film, and due to the large distance between the nozzle and the substrate, material utilization is comparatively low.

In a relatively short period, lead-halide perovskites have exhibited remarkable performance and demonstrated their application potential for X-ray imaging. Further advancements in printable lead-halide-perovskite radiation detectors have the potential to greatly enhance their performance, stability, and integration, ultimately fostering the growth of the radiation detection industry.

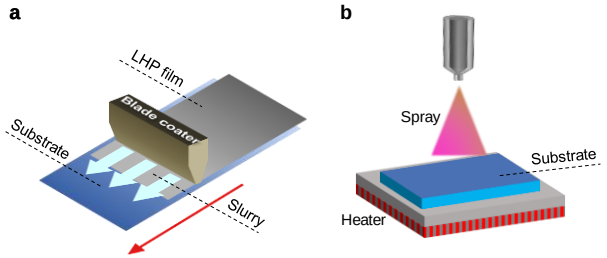

Figure 1 The schematic of doctor-blading (a) and spray coating (b) method for printable lead-halide-perovskite film fabrication. LHP: lead-halide perovskite.

Current and Future Challenges

Although lead-halide perovskites have shown promising results in the field of radiation detection, several challenges remain to be addressed, including composition and crystal structure exploration, film density optimization, dark current density inhibition, response speed improvement, and circuit integration.

Composition and crystal structure exploration. The composition and crystal structure of lead-halide perovskites directly influence their properties like carrier mobility, carrier lifetime, defect concentration, and ion migration activation energy [9], [10]. Currently, lead-halide-perovskite radiation detectors primarily rely on simple compositions, such as $MAPbI_3$ and $CsPbBr_3$, which exhibit poorer stability and lower carrier lifetime compared to their mixed lead-halide-perovskite counterpart. Learning from the development of perovskite photovoltaics, enhanced performance, and stability can be achieved by developing mixed-cation and mixed-halide perovskites.

Film denseness. During the annealing process of perovskite thick films prepared by solution doctor-blading, numerous pores form inside the film due to solvent evaporation. These pores severely negatively impact carrier transport, device uniformity, and degrade spatial resolution. Additionally, film density is a critical parameter in radiation detectors, and the presence of pores significantly reduces the attenuation efficiency of lead-halide perovskites for radiation.

Dark current density. The dark current density of lead-halide perovskites lead-halide-perovskite radiation detectors mainly ranges from 10^{-6} to 10^{-9} A cm^{-2} [11]. The dark current density directly impacts the devices' shot noise, leading to a decrease in the signal-to-noise ratio and a reduction in detective quantum efficiency (DQE) in X-ray imaging. Furthermore, due to the capacitance limitations of thin-film-transistor or CMOS arrays, the high dark current density can compress the imaging dynamic range [11]. The readout circuit requirements for the dark current density of lead-halide-perovskite detectors should be less than 10^{-10} A cm^{-2}.

Response time. Response time comprises rise time and fall time. Current research indicates that the rise and fall times of lead-halide-perovskite detectors are on the tens to hundreds of millisecond scale. This results in a significant lag in detectors, with over 10% lag after 35 ms [3], [12]. This lag far beyond commercial scintillators, and also worse than commercial α-Se detector (<0.5% @30 ms) [13]. Severe lag causes artifacts in X-ray imaging, rendering the detector unsuitable for dynamic imaging applications.

Integration. Integration with the readout array is a crucial issue that needs to be addressed for lead-halide-perovskite detectors in the future. This encompasses the robustness of integration and subsequent device packaging. The effective connection between lead-halide-perovskite detectors and the readout array directly influences signal readout and the number of defective pixels for the detectors. Packaging can prevent the performance degradation of lead-halide perovskites from water and oxygen erosion. Air-tight and radiation-robust packaging methods for lead-halide-perovskite radiation detectors still need to be developed.

Advances in Science and Technology to Meet Challenges

Figure 2 illustrates the strategies to meet several challenges, which we will expand on below.

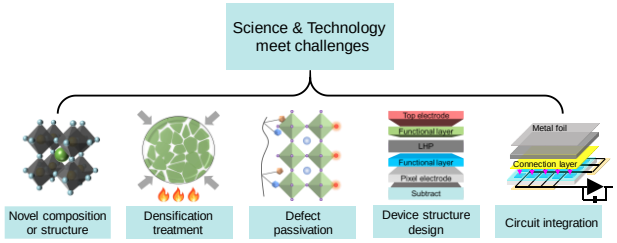

Figure 2 The schematic of main challenges and their solutions.

Development of novel lead-halide-perovskite materials. Previous studies have demonstrated that cubic phase lead-halide perovskites exhibit higher defect formation energy and shorter phonon lifetime, which can reduce defect density and increase the carrier lifetime of the lead-halide-perovskite film. Moreover, cubic phase lead-halide perovskites possess enhanced hydroxyl and thermal stability. Drawing on the research experience of perovskite photovoltaics, ideal cubic lead-halide perovskites can be identified and synthesized through the mixing of cations and halides. Yucheng Liu *et al.* [14] fabricated a $FA_{0.85}MA_{0.1}Cs_{0.05}PbI_{2.55}Br_{0.45}$ single-crystal X-ray detector, achieving a carrier lifetime of 6.4 μs and the highest sensitivity up to date of 3.5×10^6 μC Gy^{-1} cm^{-2}, emphasizing the importance of component and structural optimization of lead-halide perovskites.

In addition to 3D crystal structures, quasi-2D lead-halide perovskites also present a promising option. In quasi-2D lead-halide perovskites, 3D and 2D structures are arranged alternately. By selecting an appropriate number of 3D layers, high carrier mobility, and low ion migration can be achieved. Xin He *et al.* [15] fabricated a $PEA_2MA_8Pb_9I_{28}$ Ruddlesden-Popper type quasi-2D perovskite thick film, achieving an ion migration activation energy of 1.46 eV and exhibiting negligible device current baseline drift. However, the traditional wet chemistry method will lead to insufficient precursor reaction in the preparation of high-entropy perovskites, resulting in the uneven component distribution or phase separation. Haodi Wu *et al.* [16] employed a mechanochemical ball milling method to enable a complete precursor reaction, achieving high-purity, high-quality $FA_{0.9}MA_{0.05}Cs_{0.05}Pb(I_{0.9}Br_{0.1})_3$ over 1 kg per batch. They reported the first high entropy perovskite-based X-ray FPD with large $\mu\tau$ product (7.5×10^{-3} cm^2 V^{-1}), high sensitivity (2.1×10^4 μC Gy_{air}^{-1} cm^{-2}), and high spatial resolution (0.46 lp/pixel).

Densification treatment of the film. The densification in polycrystalline thick films can be effectively improved through the application of pressure. Menglin Xia *et al.* [5] applied a 2 MPa soft pressing on a TMTA-$MAPbI_3$ thick film, enhancing its densification. Scanning electron microscopy image further confirmed the removal of pores within the film. Ning Li *et al.* [17] used a hot-pressing method (100°C, 150 MPa) to promote grain fusion in the thick film, obtaining a smooth and dense film. The $\mu\tau$ product of the processed device was comparable to the single crystal-based detector, reaching 10^{-3} cm^2 V^{-1}. In subsequent work, hot isostatic pressing can be introduced to achieve more uniform pressure. Additionally, encouraging lead-halide-perovskite self-assembly is also an effective strategy. Ziyao Zhu *et al.* [18] demonstrated that $BaTiO_3$ ferroelectric dipoles strongly couple with lead-halide perovskites, fostering their growth in a dense, columnar structure aligned with the charge-carrier transport direction.

Defect passivation. Defect passivation is an effective method to address the lag of X-ray detector and suppress ion migration. Traditional semiconductor defect analysis methods, such as drive-level capacitance profiling (DLCP) and thermally stimulated current (TSC), can be employed to identify defect types in lead-halide-perovskite thick films. The defect passivation strategies in perovskite solar cells are worth learning from, where passivation by coordinate bonding, ionic bonding, or chemical conversion have proven effective in mitigating the negative impacts of defects [19]. Mature passivation recipes in lead-halide-perovskite photovoltaics can be applied in X-ray detectors with some necessary modifications.

Design of device structure. Effective device structure design can result in low dark current density and high response speed for lead-halide-perovskite radiation detector. Amlan Datta *et al.* [20] reduced the dark current density to 2.5×10^{-10} A cm^{-2} by introducing electron and hole-blocking layers. Yin Zhou *et al.* [21] constructed a heterojunction to effectively lower the device's dark current density (7.0×10^{-10} A cm^{-2}), enhancing the signal-to-noise ratio and enabling imaging under a low dose rate of 32.3 nGy_{air} s^{-1}. Additionally, by designing PN or Schottky device structures, the detector can operate under higher bias, achieving faster response speed ($t=d^2/\mu V$, where d is the thickness, V is the bias).

Integration. Generally, a pixel array has an uneven surface. A connecting layer is needed to establish a stable connection between the lead-halide-perovskite film and the array. Yong Churl Kim *et al.* [3]

used a polyimide layer to bond the lead-halide-perovskite film with the thin-film-transistor circuit. Sarah Deumel *et al.* [12] employed a grid-structured photoresist to achieve stable heterogeneous connections. It is crucial to develop methods that provide both excellent longitudinal conductivity and robust connections, and anisotropic conductive film (ACF) bonding may be a good choice. In terms of device packaging, metal foil with a low atomic number is the best choice, such as Be or Al, which can ensure perfect water and oxygen isolation and meanwhile minimized X-ray attenuation.

Concluding Remarks

Thanks to their solution processability, printable lead-halide-perovskite radiation detectors have achieved exciting results, such as high sensitivity, low detection limit, with large size and uniform performance. Some famous companies, like Samsung and Siemens, have also carried out research on printable lead-halide-perovskite radiation detectors. Further development requires addressing issues related to composition optimization, thick film densification, dark current reduction, response speed improvement, and circuit integration. Printing methods enable the fabrication of large-area lead-halide-perovskite radiation detectors with high sensitivity and high spatial resolution, and holds promise for medical, industrial, and security application.

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Section 3.3 – Printable lead-free perovskite-inspired radiation detectors

Ge Yang and Doup Kim

Department of Nuclear Engineering, North Carolina State University, 2500 Stinson Drive, Raleigh, NC, 27607-7909, United States of America

Status

Printable perovskite radiation detectors are a breakthrough technology that can enable low-dose and high-resolution ionizing radiation detection. Perovskite materials, which was first found by Russian researcher Lev Perovski in 1839, have recently sparked keen interest as a new class of radiation detector materials. Unlike conventional detectors that require expensive and complex fabrication processes, printable perovskites can be produced on large substrates using simple and low-cost methods. This makes them ideal for creating flexible and portable detectors that can be used for various purposes. The lead (Pb)-free perovskites, in which lead is replaced by comparable high Z-number materials, such as bismuth (Bi) and tin (Sn), have drawn special attention owing to their non-toxic nature to human being and the environment.

There are several typical methods for fabricating the printable lead-free perovskite radiation detectors. First, the spin-coating, in which perovskite precursors are deposited on the high-speed rotating substrate, is one of the most widely used ways to fabricate flexible perovskite thin films. Many high quality of perovskite films have been successfully produced using the spin-coating technique [1]. Second, blade-coating, a method that the blade can be used to spread the precursor uniformly, have been quickly developed thanks to its merits of fast printing and direct deposition [2]. Third, spray-coating, a technology that can print liquid and powder on the substrate, have been actively exploited thanks to their high deposition efficiency and flexibility in substrate selection [3].

Using environmentally friendly lead-free perovskite and various types of fabrication techniques, a series of radiation detection devices have been developed and some recent success are listed in Table 1. All-inorganic lead-free double perovskite $Cs_2AgBiBr_6$ film with high stability and ideal bandgap have been successfully deposited [4]. Zhang *et al.* reported a $Au/Cs_2AgBiBr_6/Au$ X-ray detector with excellent sensitivity of level of $10^4\ \mu C\ Gy_{air}^{-1}\ cm^{-2}$ and long diffusion length of $700\ nm$ [5]. Another X-ray detection device, $W/Cs_2AgBiBr_6/Pt$, with relatively high sensitivity of $487\ \mu C\ Gy_{air}^{-1}\ cm^{-2}$ was demonstrated by Haruta *et al.* [6]. The methylammonium cation-based perovskite $MA_3Bi_2I_9$ $(MA = CH_3NH_3)$ was investigated for X-ray detection by Dong et al. [7] and Xin et al. [1], revealing high resistivity and low detection limit. Another all-inorganic lead-free perovskite Cs_2TeI_6, which was fabricated by electrospray-coating, have shown suitable X-ray detection limit of $170\ nGy_{air}s^{-1}$ [8] and high sensitivity of $226.8\ \mu C\ Gy_{air}^{-1}\ cm^{-2}$ [9]. Jia et al. reported that hybrid perovskite $FACs$ $(FA = CH(NH_2)_2)$ has excellent detection limit of $3.5\ nGy_{air}s^{-1}$ [10].

Current and Future Challenges

In spite of many fascinating advantages, i.e., low toxicity, high resistivity, low detection limit, flexibility, and especially reasonable fabrication cost, the printable lead-free perovskites have several challenges to be overcome. At this point, the development of lead-free perovskite materials is still at a relatively early stage compared with their well-studied lead-based counterparts, and their performance and stability need to be further improved. The limitations of printable lead-free perovskite detector materials can be connected to both intrinsic factors of lead-free perovskites and unique characteristics of printable perovskites.

Ion migration. Similar to other types of perovskite radiation detector materials, printable lead-free perovskites, especially hybrid perovskites, have suffered from ion migration. Ion migration could potentially cause the degradation of material quality, affect the electrical properties, and lead to the instability of detector performance. For example, the representative printable lead-free perovskite

$MA_3Bi_2I_9$ film has an intrinsic tendency of ion migration, which comes from the movement of MA^+ cations inside the perovskite structures [12]. This kind of ion migration could cause the change of charge transport behaviour over time. Further studies are needed to address this issue.

Grain boundaries. Printable fabrication methods, such as spray-coating and blade-coating, have a chance to promote the formation of many grain boundaries, which directly influence charge transport and collection efficiency. Grain boundaries can act as charge traps, leading to the charge carrier recombination, which usually cause the degradation of whole detector device performance and deep level defects [13].Thus, it should be a big challenge to increase the grain size, while minimizing the number of grain boundaries during the printing the lead-free perovskites [2].

Need to extend detection range into higher energy. Most of printable lead-free perovskite radiation detectors have been focused on X-ray detection (less than 100 keV), while the reports of detecting higher energy radiation, i.e., gamma-ray (several MeV), using these detectors are relatively lacking compared to non-printable perovskites [14]. In order to detect higher-energy radiation, thick detector medium must be used to ensure sufficient absorption of incident radiation. However, most of the current fabrication methods are only capable of producing films on the order of several μm. The printable gamma-ray detector devices should be developed and investigated, which could offer an enabling technology in nuclear safety, non-proliferation inspection and homeland security applications.

Advances in Science and Technology to Meet Challenges

Doping. Many doping materials, such as Cl [15] and $MACl$ [7] have been investigated to increase the ion migration activation energy, which helps suppress the ion migration and improve the transport behaviours of charge [1]. In addition, adding appropriate additives in the lead-free perovskites can achieve the enhancement of crystallinity and morphology, which results in higher optoelectronic performance [10].

Large size cation-based perovskites. Because the cation size could influence the crystallinity and quality of the perovskite films [16], lead-free perovskite with larger size of cations could help obtain better radiation detection performance from suppressed ion migration and improved material quality. Most commonly used cation for fabricating printable lead-free perovskite should be MA^+ and Cs^+, whose sizes are smaller than FA^+ cation [17]. Adding some other additive cations with MA^+/Cs^+ and exploring the FA^+-based lead-free perovskites should be further explored.

Improved fabrication methods. The traditional methods for printable lead-free perovskites, such as spin-coating and blade-coating, have certain limitations that often hinder their capabilities to obtain compact, flexible, high-crystallinity, and low-defect of perovskite films due to the fact that the solvent molecules could break through the shell during the nucleation process [18]. Scalable spray-based methods, including mist deposition [Figure 1(a)], aerosol deposition [Figure 1(b)], and electro spraying, have an ability to proceed both nucleation and growth simultaneously, resulting in the fabrication of uniform and thick perovskite films [2]. These merits generally enable the generation of columnar grains, which lead to high mobility-lifetime product and reduced charge recombination [6]. Another promising printing technique, inkjet printing, has an advantage of forming thick and multi-layered lead-free perovskite [19][20]. It should be noted that the thickness of perovskites is essential for high-energy gamma-ray detection considering the effective attenuation of gamma-rays in the detector medium [14]. Spray-based deposition and inkjet printing methods can be applied on thin and flexible substrates, which help enlarge the application portfolios [8].

Concluding Remarks

Recently, the research of printable lead-free perovskite-inspired radiation detector has attained many remarkable achievements, e.g., demonstration of high-sensitivity and low-detection-limit on X-ray detection and versatile technologies to fabricate flexible lead-free perovskite detector devices. However, there are still some challenges that need to be addressed to further improve detector

performance. In this regard, ion migration, charge recombination at grain boundaries, and insufficient detector development for high energy gamma-ray detection are three representative issues. On-going efforts of material synthesis and device fabrication have made positive progress to help address the challenges to accelerate the development of printable lead-free perovskite detector technologies for enabling high performance radiation detection at competitive cost. Further systematic work is needed to improve their performance and stability.

Table 1 Recent research results of printable lead-free perovskite films and the fabricated X-ray detection devices.

Material (Detector device)	**Fabrication method**	**X-ray detection property**			**Reference (year)**
		Sensitivity (Bias) $[\mu C\ Gy_{air}^{-1}\ cm^{-2}]$	**Resistivity** $[\Omega\ cm]$	**Detection limit** $[nGy_{air}s^{-1}]$	
$\boldsymbol{Cs_2AgBiBr_6}$ $(Au/Cs_2AgBiBr_6/Au)$	Spin-coating	$1.8 \times 10^4\ (5\ V)$	-	145.2	[5] (2020)
$\boldsymbol{Cs_2AgBiBr_6}$ $(W/Cs_2AgBiBr_6/Pt)$	Mist deposition	$487\ (10\ V)$	1.0×10^{10}	-	[6] (2021)
$\boldsymbol{MA_3Bi_2I_9}$ $(Au/MA_3Bi_2I_9/ITO)$	Blade-coating	$100.16\ (15\ V)$	3×10^{11}	98.4	[7] (2022)
$\boldsymbol{MA_3Bi_2I_9}$ $(ITO/MA_3Bi_2I_9/Au)$	Spray-coating	$35\ (15\ V)$	5×10^{11}	140.0	[1] (2022)
$\boldsymbol{Cs_2TeI_6}$ $(FTO/Cs_2TeI_6/PTAA/Au)$	Spray-coating	$19.2\ (1\ V)$	4.2×10^{10}	-	[11] (2018)
$\boldsymbol{Cs_2TeI_6}$ $(PI/Cs_2TeI_6/Au)$	Spray-coating	$76.27\ (5\ V)$	1×10^{11}	170.0	[8] (2021)
$\boldsymbol{Cs_2TeI_6}$ $(PI/Cs_2TeI_6/Au)$	Spray-coating	$226.8\ (10\ V)$	1.9×10^{11}	-	[9] (2022)
$\boldsymbol{FACs}$ $(ITO/FACs/Cu)$	Spray-coating	$3433\ (-0.5\ V)$	-	3.5	[10] (2022)

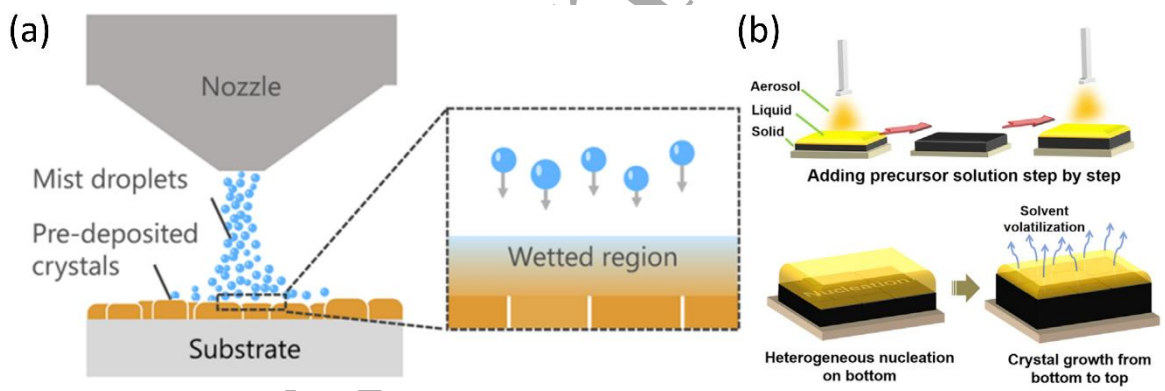

Figure 1 (a) Schematic illustration of mist-deposition technology using pre-wetted crystals [6]. (b) Aerosol-liquid-solid fabrication process and nucleation mechanism of deposited solution. Reprinted from [18], Copyright 2021, with permission from Elsevier.

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Section 3.4 – Printable organic semiconductor-based radiation detectors

Derek Dremann and Oana D. Jurchescu

Department of Physics and Center for Functional Materials, Wake Forest University, Winston Salem, NC 27109, United States of America

Status

Radiation detectors used in commercial applications typically consist of inorganic semiconductors such as silicon or germanium since their high atomic numbers (Z) result in a strong interaction with the radiation, making them very sensitive. This behaviour, however, is very different than that of the human body, which consists of low-Z elements. Consequently, in medical applications the recorded output must undergo corrections to match the response of a tissue-equivalent (water-equivalent) target.[1] The instrument calibration is dependent on the specifics of the setup, as well as the treatment regimen and the needs of the patient; such a complex protocol is inevitably prone to errors. Organic semiconductors have emerged as a viable solution to this problem given their similarity in response to that of the human body, which eliminates the need for extensive corrections, thus improving the precision and reducing the complexity of the equipment. The incorporation of organic semiconductors in radiation detectors brings several other advantages. First, their processing using solution or laser printing reduces the cost even further, also making them compatible with different form factors and with flexible substrates conformal to the human body.[2]–[4] The vision is to develop remote monitoring devices consisting of large-area arrays of discrete detectors that can be placed directly at the point of contact to provide precise, instantaneous feedback with high spatial resolution (Figure 1). Accurate control of the magnitude of the dose at every point of contact is critical in delivering the prescribed amount to the target, while preserving the bodily functions of surrounding and/or neighbouring organs and tissues. Second, the lightweight of organic devices makes them suitable for wearable electronics addressing worker radiation safety in high-exposure environments like nuclear plants, space and aircrafts, or hospital and research facilities using X-Ray sources. The incorporation of organic semiconductor radiation detectors in portable medical equipment, along with the lower cost, would lead to a more inclusive and affordable healthcare.

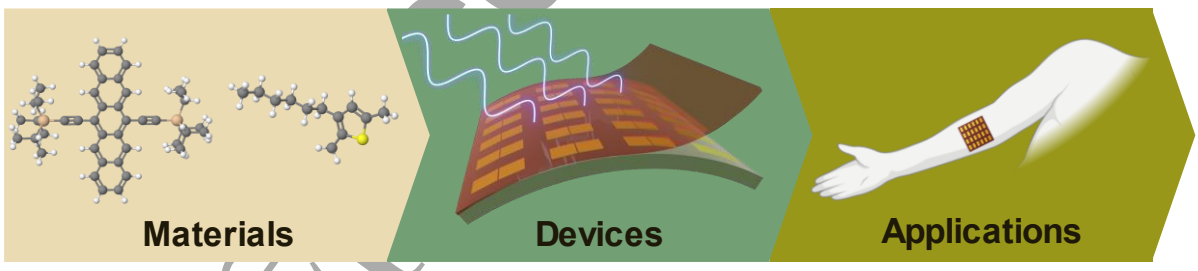

Figure 1 Organic semiconductor-based radiation detectors. a) Small molecules and polymers used in radiation detectors. b) Large-area arrays of radiation detectors enabled by organic semiconductors. c) Wearable radiation sensor.

These remarkable properties have been recognized early on and, as such, organic semiconductors were tested in various radiation detecting technologies. Small molecule and polymeric semiconductors have been incorporated in radiation detectors both as active layers to directly transduce the ionizing radiation into electrical signal, or in conjunction with scintillators for indirect sensing.[5], [6] The devices include diodes, photodetectors and transistors,[1], [7]–[9] and several demonstrations of integration with flexible substrates are already available; for more details please see the recent review on this topic by Posar *et.al.*[10] Notably, the sensitivity of organic radiation dosimeters has rapidly improved, reaching values of $1.3 \cdot 10^4$ μC/Gy·cm^2 along with minimum

detectable dose rates of 35 µGy/s.[11] While related to its sensitivity, the clinical utility of a detector has to be weighed among other factors relative to its intended purpose, therefore accuracy, detection limit, specificity are amongst additional factors that are taken into account.

Current and Future Challenges

Both radiation detectors and radiation dosimeters are crucial tools for understanding, exploiting, and managing the risks associated with ionizing radiation. However, they serve different purposes: while detectors provide information on the real-time intensity and type of radiation, dosimeters measure the cumulative absorbed dose over time.[12] Typically, the dose is normalized per unit mass and expressed in units of Gray (Gy = J/kg). In the medical field, detectors are incorporated in X-ray imaging in diagnostic radiology, while dosimeters provide radiation delivery verification for radiotherapy treatment of cancer, benign tumors or other conditions (heterotopic ossification, keloids, arteriovenous malformations, etc).

Organic semiconductors exhibit unique properties that are not present in any other class of materials employed in radiation detection, making them serious candidates for large-area detectors conformal to the human body. But to fully exploit this potential, it is critical that the mechanism for radiation detection is clarified; most likely, it will be dependent on the nature of the radiation, e.g. ions, neutrons, protons, X-ray, gamma. Several key questions should be addressed to allow a transition from the current trial-and-error approach to a rational design of materials and device structures efficient in radiation sensing. What determines the sensitivity of a device? Are there certain features in the organic semiconductors chemical structure or thin-film microstructure that can enhance the response, which would translate in a higher sensitivity? A large number of organic semiconductors became available and their environmental and operational stability now match the requirements for most optoelectronic applications.[13], [14] But is this stability maintained under radiation exposure? How can one distinguish between the effects resulting from interactions with radiation and other effects such as bias-stress or environmental degradation, which can also yield changes in electrical properties of the organic semiconductor films? The mechanical strain introduced during bending/flexing to address irregular shapes on the human body could also lead to reversible or even irreversible damage to the sensor. Due to the sensitivity of transport to the microstructure, another challenge that needs to be addressed is the areal uniformity in film properties, which is a pre-requisite for the incorporation in large-area detector arrays necessary to evaluate dose non-homogeneities. Therefore, controlling film formation on length scales relevant to real-life dosimeters, especially during high-volume processing, becomes critical. The spatial resolution is proportional to the number of devices (pixels) within the matrix and thus downscaling the detector size would result in better accuracy in the 2D mapping of the beam properties. Downsizing electronic devices, on the other hand, makes manufacturing more difficult and can result in reduced performance due to high contact resistance and less effective heat dissipation.

Advances in Science and Technology to Meet Challenges

The research efforts focused on organic semiconductors have spanned several decades and have generated a large number of materials which have been critical in establishing structure-property relationships for the development of high-performance optoelectronic devices. Similar lessons should now be developed in the context of radiation detection, and it is possible that an effective sensor response implies different material design strategies. This is a burgeoning area of research, which will take advantage of the rich chemical versatility of organic semiconductors to introduce functionalities tailored for each type of radiation, as well as for well-defined energy windows. But the rational design of new materials is dependent on the understanding of the mechanism responsible for radiation detection. Another possible outcome is that discarded materials which have been found to exhibit sub-par electrical properties can be revisited, by focusing on the requirements for response to radiation which may not include the need for a high charge carrier mobility.

Organic semiconductor film formation proceeds through stochastic crystallization via multiple and often competing pathways during solution drying, making microstructure control across large area surfaces not trivial. Fortunately, decades of research focused on programming film crystallisation for the development of transistors, diodes or solar cells provided an increased maturity in processing-structure-property relationships and generated the much-needed toolbox for controlling the film formation in the fabrication of radiation detectors/dosimeters.[15], [16] An alternative route is that of employing amorphous films, which offer isotropic properties, with no grain boundaries.

The device design will go hand in hand with material progress: for example, the sensitivity was found to be dependent on the gate-source voltage in RAD-OFETs (Radiation Detector Organic Field-Effect Transistors).[1] The resilience to mechanical stress upon bending is dependent on the nature of the consecutive device layers and the bending radius, both imposing challenges in considering multiple factors in device architecture to preserve the sensitivity. Encapsulation is an efficient way to increase the environmental and operational stability but choosing the encapsulant layer should also consider its response to radiation. Device downscaling provides higher resolution in mapping the spatial properties of the radiation beam, but it also exacerbates the contribution of the contact resistance to the overall device response, thus introducing errors.[17], [18] Contact resistance can be reduced through chemical tailoring the electrode surface with self-assembled monolayers, insertion of interlayers, doping, or adoption of organic contacts.[17] The latter brings the additional benefit of a more uniform radiation absorption in an all-organic device.

Concluding Remarks

Organic semiconductors could revolutionize the way that radiation interaction with the human body is detected and measured given the similarity in in the Z-number with that of tissue, greatly enhancing the precision and reducing the complexity of medical equipment. Low-cost, light-weight and mechanically well-matched interfaces for biological systems will allow sensor placement directly onto the human body to improve the quality and lower the cost of healthcare. New applications that are impossible to realize with the current technologies, like, for example wearable personal dosimeters, will greatly impact our wellbeing. Incorporation of organic semiconductors in radiation sensors, however, is dependent on a clear understanding on the physical processes taking place upon interaction of the organic semiconductors with radiation: development of new structure-property relationships in the context of radiation detection will result in precise and radiation type-selective response imbued by synthetically tuned molecular building blocks generated in new materials or, possibly, in revisited old compounds. Creative device designs, along with a thorough control of the mechanical and electrical properties and how they are affected by processing will accelerate the commercial readiness of printable organic semiconductor-based radiation detectors.

Acknowledgements

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Section 3.5 – Printable quantum-dot-based radiation detectors

Dmytro Bederak and Artem G. Shulga

QDI systems B.V, L.J. Zielstraweg 1, 9713 GX, Groningen, The Netherlands

Status

Colloidal quantum dots have emerged as a promising class of materials for printable radiation detectors. In particular, previous research was focused on using quantum dots as scintillators for indirect X-ray and gamma detectors due to their excellent optical properties and strong photoluminescence.[1] Moreover, heavy-metal based quantum dots can also be applied for the direct conversion detectors due to high radiation absorption and good charge transport properties in films. Due to the presence of heavy atoms, PbS quantum dots possess higher X-ray stopping power compared to traditional materials for the direct X-ray imagers such as Si and Se (Figure 1).[2] Another technological advantage of quantum dot material is the amorphous structure of quantum-dot-based layers. Typically, in an amorphous semiconductor, the diffusion distance of charge carriers is much smaller compared to drift, thus minimizing charge sharing between pixels and allowing for high-resolution sensors. In combination with the ease of deposition of quantum dot films from solutions by simple printing techniques, these advantages make quantum dot technology an important candidate for next generation X-ray detectors.

One of the first attempts of fabricating quantum-dot-based radiation detectors was based on a hybrid quantum dot/organic approach, where quantum dots were used as X-ray sensitizers, and organic heterojunction as charge transport material.[3] However, the efficiency of charge transport from quantum dots to the organic matrix limited the performance of the devices.

Other notable approaches are growing macroscopic crystals from quantum dot solution[4] or compressing quantum dot powder into pellets[5]. The compressing method can provide mm thick quantum dot pellets which are required for efficient stopping of high energy radiation. While these methods allow easy and straightforward fabrication of thick quantum dot radiation absorbers, production of large area flat-panel detectors using them remains challenging. Also, such methods are not suitable for printable sensors.

Recent progress in deposition of thick quantum dot films by printing techniques enabled prototyping X-ray sensors compatible with large-area manufacturing.[6] Lab-scale devices suggested that quantum dots demonstrate X-ray absorption and sensitivity potentially suitable for mammography application. These results encouraged further R&D efforts to demonstrate a quantum dot X-ray sensor, able to deliver high-resolution X-ray images (Figure 2).

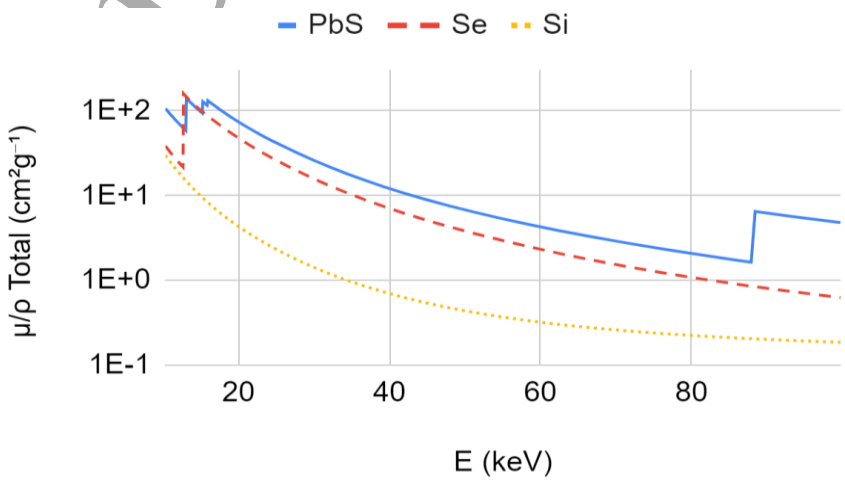

Figure 1 Mass X-ray attenuation coefficient for PbS, Se, and Si.

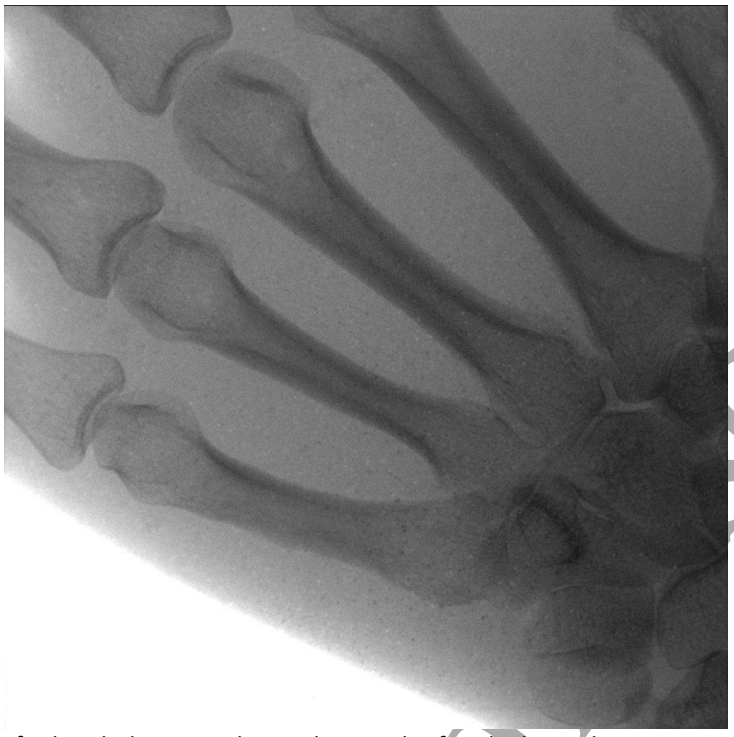

Figure 2 X-ray image of a hand phantom obtained using the first high-resolution quantum dot sensor. Image courtesy of QDI systems and Varex Imaging.

Current and Future Challenges

Ink fabrication. Fabrication of X-ray detectors requires significant amounts of quantum dots due to large area and film thickness. For example, a single medical X-ray detector requires tens of grams of quantum dots. Thus, an upscaled synthesis of quantum dots needs to be established to reliably produce high-quality material. After the synthesis, quantum dots are typically capped with long insulating ligands which should be replaced with shorter species to enable good electrical transport in deposited films.[7], [8] This is done by phase transfer ligand exchange and resultant inks can be printed by various solution-processable techniques.[9] This process is associated with complex processing and difficulties in scalable production and needs to be further developed for X-ray technology with high material demand.

Film deposition. The thickness of the quantum dot film for radiation detectors needs to be orders of magnitude thicker than submicron quantum dots films that are sufficient for IR detectors or solar cells. Deposition of such thick films uniformly on a large area is a tremendous challenge and information about this is scarce.

Stability. Environmental and operational stability of the quantum dots layer and the detector as a whole is crucially important for medical X-ray application. The device performance can degrade due to oxygen or water vapors, operation at high temperature or bias and prolonged exposure to ionizing radiation.

*Performance of the detectors. Q*uantum dot radiation detectors must meet a set of criteria to get a green light for the commercialization of the technology. These parameters include low lag (< 2% after 33 ms), low dark current (< 1 nA/cm^2), high conversion rate (> 0.24 μC/cm^{2}R for 20 keV photons), and high detective quantum efficiency (>65% at zero spatial frequency).[10] A future challenge can be the optimization of each of device performance parameters to the level where it will outperform current commercial detectors.

Cost. Quantum-dot-based sensors need to be competitive compared with well-established commercial technologies in terms of price. Being a highly-engineered material, quantum dots are

associated with higher material costs, however cost-efficient deposition process allows vendors to have an eventual competitive advantage.

Environmental impact. Quantum dot processing requires extensive use of organic solvents, heavy-metal containing chemicals and toxic reactive organic precursors. Thus, the environmental impact of large-scale production should be carefully considered and different measures need to be taken to minimize it.

Advances in Science and Technology to Meet Challenges

Ink fabrication. The synthesis of quantum dots can be scaled up and the industry leaders produce tens of tons of quantum dots for displays.[11] However, upscaling of the ligand exchange process still represents a challenge, with a few g of quantum dots (lab scale) batches demonstrated.[12] Nevertheless, it is necessary to upscale it even further for the fabrication of radiation detectors and decrease the associated cost. For that, continuous ink fabrication approach may be introduced, similarly to the continuous flow synthesis of quantum dots.[13]

Film deposition. Printing of quantum dot films with the right thickness for radiation detectors is still under development, nonetheless 140 µm thick quantum dot films were successfully demonstrated.[6] Typically, such thick films are deposited by ultrasonic spray coating method, which minimizes material losses and results in a good surface morphology.

Stability. The encapsulation layer is typically used in order to protect the quantum dot layer from environmental factors.[7], [14] Likewise, encapsulation might be utilized in X-ray sensors to increase the stability. However, more research is needed towards studying the sources of degradation of the device under the combination of temperature, humidity, voltage bias and X-ray exposure.

Performance of the detectors. It is difficult to summarize the performance of the detectors due to the low number of reports and various types of quantum dots and structures described in them. It was reported that a 140 µm thick spray-coated PbS quantum dot layer have sufficient X-ray absorption to be applied in mammography with X-ray sensitivity exceeding state-of-the-art amorphous selenium several times.[6] Here, it is useful to note that the performance of the pixelated sensors is more relevant and can vary greatly when compared to single area devices.

Cost. Modelling of the synthetic cost shows that the price of PbS quantum dots can potentially be decreased to the level of a few tens of USD/g.[15] Nevertheless, the commercial price of quantum dots on the market still remains high (hundreds or even thousands of USD/g).[16]

Environmental impact. The environmental impact of production of quantum-dot-based detectors should be reduced. All the chemical waste which is formed during the synthesis must be carefully disposed of in accordance to the regulations. Solvents can be recycled or substituted for greener alternatives, if possible. Solvent evaporation during the deposition of thick quantum dot films results in fumes, which can be scrubbed from the exhaust.

Concluding Remarks

The recent advances in quantum dot synthesis, ligand-exchange and deposition have resulted in lab-scale prototypes of printable quantum dot radiation detectors. A set of technological challenges need to be solved for the commercialization of this technology. They are associated with the upscaled quantum dot synthesis and ink fabrication, the deposition of thick quantum dot films on large areas and optimization of the performance and stability of the detectors.

Development of such detectors is a multidisciplinary R&D project and requires collaboration between scientists and engineers with different backgrounds and involvement of commercial partners, especially when it comes to the fabrication and characterization of the imaging devices. This is a relatively new and undeveloped field; therefore, it is difficult to predict the direction of its evolution and full technological potential. It is anticipated that one of the first niches for this technology will be

direct conversion medical X-ray sensors. Quantum-dot-based radiation detectors have a promising technological advantage for mammography applications, because of higher X-ray sensitivity compared to those of amorphous selenium.

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Section 4.1 – Introduction to printable mechanical sensors

Joseph Andrews[1,2]

[1] Department of Mechanical Engineering, University of Wisconsin – Madison, Madison, WI, 53716, United States of America
[2] Department of Electrical and Computer Engineering, University of Wisconsin – Madison, Madison, WI, 53716, United States of America

Electronic mechanical sensors can be defined as electronic devices that transduce a mechanical process into a measurable change in an electronic parameter. In terms of mechanical processes, the most sensed include strain and pressure, as depicted in Figure 1. These are often sensed using passive resistive[1,2] or capacitive components,[3,4] but there have been demonstrations of utilizing printed active components for increased sensitivity.[5,6] The realization of mechanical sensors has benefited several fields. Health care is a prime example, where strain sensors can be used to sense heartbeat or breathing cycles[7] and force sensors can be used to detect gait patterns.[8] Many other fields, including structural integrity monitoring[9] and industrial process monitoring[10] have also been impacted through the development of mechanical sensors.

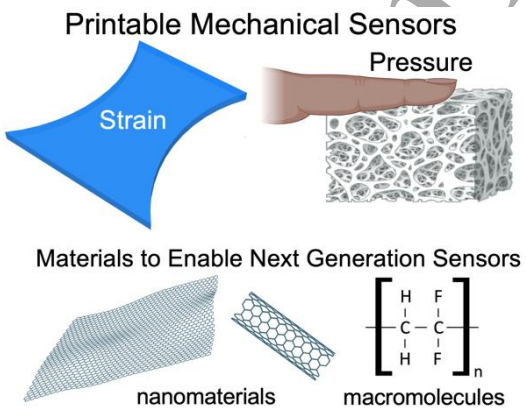

Figure 1 Overview of the primary parameters relative to mechanical sensing along with materials to enable next generation sensors.

Utilizing printed electronics to fabricate mechanical sensors can provide many advantages over traditional techniques. The freedom in substrate choice has led to the development of more stretchable sensing technologies for high strain applications. Another key advantage is the ability to fabricate non-traditional geometrical structures. One example incorporates curved patterning within a strain gage to drastically increase sensitivity due to localization of stress fields within serpentine conducting lines.[2] Lastly, printed electronics can offer the ability to generate large-area distributed sensing systems. This can enable spatially resolved sensing for parameters such as pressure. A prominent example of this utilized solution processed carbon nanotube thin-film transistors to create an active matrix, where capacitive sensors based on pressure sensitive rubber composites were interrogated spatially using minimum electrical connections.[11] Printed electronics can enable future sensing systems that require high conformability, customized geometry, and spatially resolved data capture.

Key benchmarking elements for mechanical sensors include sensitivity (also referred to as gage factor for strain sensors), specificity, and dynamic range. Gage factor for strain sensors can be defined as the percent change in resistance for a given change in percent strain. For a typical off-the-shelf commercial sensor consisting of evaporated constantan on polyimide substrates, one can expect a gage factor of approximately 2.[12] While sufficient for many applications, printable devices with unique geometries

including serpentine patterns, can achieve gage factors that are orders of magnitude higher, with on example approach 10^7.[2] Similarly, pressure sensors can be benchmarked related to their sensitivity, with highly sensitive devices needed for applications such as heartbeat monitoring. The sensing dynamic range is another key factor to consider for pressure sensors. There has been significant work to increase the range of capacitive sensors to allow for dynamic linear sensing ranges from 0 to 175 kPa.[8] Lastly, the time response of both sensing technologies is something that should be carefully considered. It is of note, however, that often the means of applying a mechanical impulse can indeed be slower than the response of the sensor. For example, a pressure sensor tested using a traditional load frame would have trouble loading the sensor at a rate that is slower than the pressure sensor response itself, precluding insight into the time response.

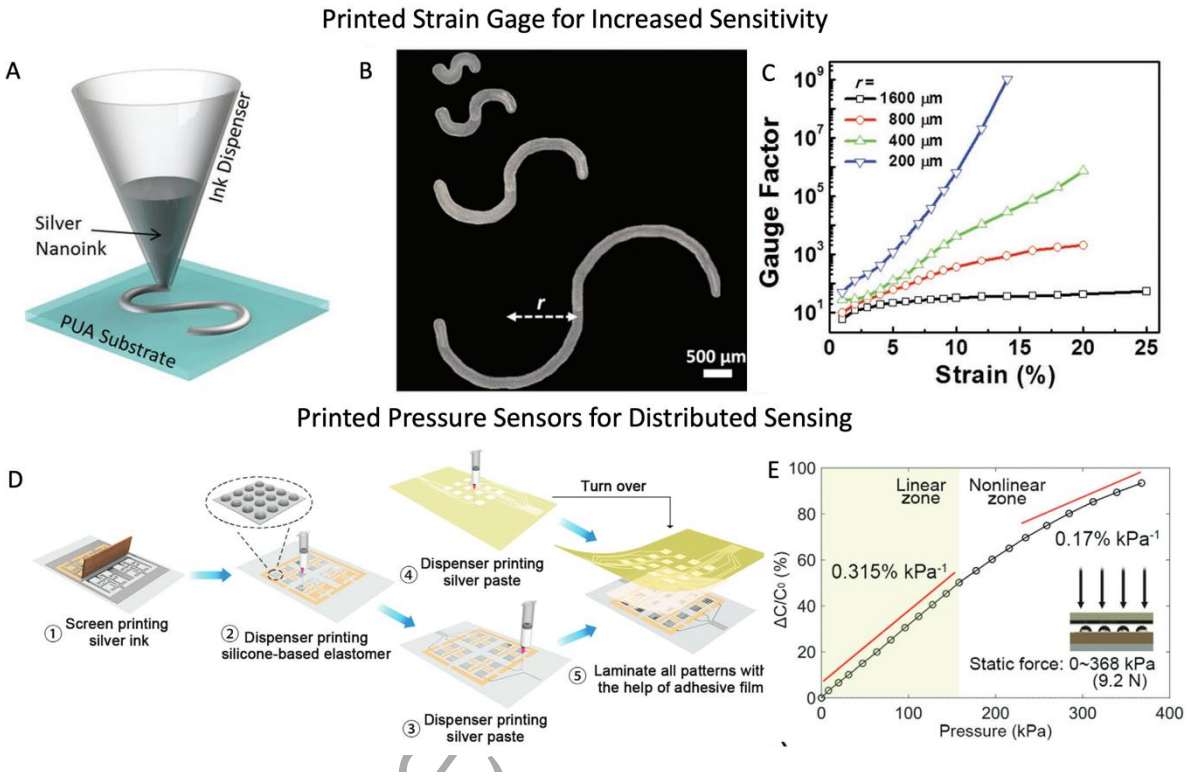

Figure 2 Examples of printable mechanical sensors including a printed strain gage (A-C) and a printable capacitive pressure transducer (D, E). (A) Extrusion printing of S shaped patterns, as displayed in (B) with the resulting strain sensing properties for varied radii of curvature (C). (D) Two substrate printing required for forming parallel plate capacitive structures separated by elastomeric domes for capacitive pressure sensing, including the results displayed in (E). (A-C) are adapted with permission from [2], and (D, E) are adapted with permission from [3].

Currently, printed sensors for mechanical transduction have been demonstrated using a wide variety of printable materials including polymeric materials such as PVDF, carbon nanocomposites, 2D materials, nanomaterials, and organic materials. In this section of the roadmap, each material will be discussed, specifically focusing on the challenges and potential advances to meet those challenges. Many of the challenges discussed in the following sub-sections relate to material processing challenges that preclude sensor yield and uniformity. One of the reasons that constantan thin-film strain gages are a main stay for strain and pressure (through integrated load cells) measurements is their consistency. In working with new materials and processes, the device-to-device uniformity must be improved through a more thorough understanding of the material processing parameters and the sensor working principles. Another key challenge to overcome is parameter cross sensitivity. Many of the printable materials used for their sensing properties, such as carbon nanomaterials or polymeric materials, are inherently sensitive to environmental parameters such as humidity or temperature.

Schemes must be addressed to allow for real-time calibration or elimination of cross-sensitivity all-together.

The field of printable electronic mechanical sensors is quite broad and therefore uses many different techniques for printing, with those techniques being distinguishable as enabling two dimensional technologies (inkjet, aerosol jet, gravure printing) and those that enable three dimensional structures (extrusion). Two-dimensional printing technologies are often used for strain gage fabrication, where thin conductive traces are used to transduce mechanical strain of a flexible substrate, however, three dimensional techniques are extremely attractive for developing compressible structures for pressure monitoring. Given the broad set of potential deposition techniques, the challenges of material processing are sufficiently broad, but contain broad themes related to material dispersibility, rheological optimization, and process uniformity. To compete with more mature, non-printing techniques such as physical vapor deposition, innovations are needed. For example, sensors that rely on small geometrical changes for transduction must have consistent print patterns, likely necessitating closed-loop control during the deposition process, an active area of research for many printing techniques.

The final challenge relevant to the broad area of printable mechanical transducers is the attachment of the sensor interrogation electronics. In a flexible hybrid electronic scheme where the sensor consists of a printed electronic device, but the data logging capabilities utilize rigid silicon ICs, the connection point is often the weakest.[13] This weak connection stems from the need to utilize low-temperature epoxies or other electrical connection schemes due to the low processing temperature requirements of flexible and stretchable substrates. This mechanical weak point must there be isolated or mitigated in some fashion to not influence the data transmission or recording of the sensor. This can be accomplished through mechanical affixation, stress-relieving passivation techniques, or initiating wireless data communication. Solving this challenge is critical in terms of transitioning the advantageous printed sensors from the lab to the real-world.

Overall, printed electronics technology is poised to have a significant impact on the future of mechanical sensing. Indeed, the field is already dominated by thin-film technologies, and the many important advantages of printing the transducers motivate their introduction into real-world sensing applications. The performance increase that is realized from using novel material sets, as discussed in subsequent sections, will also allow for new application spaces, such as wearable or even implantable technologies. In addition to the performance increase, the additive nature of printing processes is expected to allow for more sustainable manufacturing schemes, specifically if attention is paid to the full life cycle of the materials. These motivating factors will lead to the scientifically discovered solutions to the presented challenges, allowing for increased utilization of printing technologies for mechanical sensing.

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Section 4.2 – Printable pressure sensors based on poly(vinylidene fluoride) and its derivates

Pedro Costa[1], Nikola Perinka[2] and Senentxu Lanceros-Mendez[1,2,3]

[1]Physics Centre of Minho and Porto Universities (CF-UM-UP) and [2]Laboratory of Physics for Materials and Emergent Technologies, LapMET, University of Minho 4710-053 Braga, Portugal
[2]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain
[3]IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

Status

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer with high electroactive properties [1]. PVDF copolymers and ternary polymers have been developed (Table 1) in order to improve specific material characteristics, including the electroactive properties [2]. The main properties of PVDF-related materials for electromechanical conversion applications, include the piezoelectric coefficients d_{31} and d_{33}, the electromechanical coupling (k_{33}) and the dielectric constant (ε') are presented in Table 1. These characteristics are tailored to improve PVDF materials for applications as sensor and energy harvesting devices.

Table 1 Electroactive properties of PVDF based materials (left) and characteristics of the inks for specific printing technologies (right) [3].

Main Properties	d_{31} / d_{33}	k_{33}	ε'
PVDF	8-22/-24 -34	0.2	6-12
PVDF-TrFE	12 / -38	0.29	18
PVDF-HFP	30 / -24	0.36	11
PVDF-CTFE	- / -140	0.39	13
PVDF-TrFE-CTFE	-	-	40

Printing Technology	3D	Inkjet	Screen
Viscosity (mPa.s)	5 – 500,000	4 – 30	1,000-10,000
Resolution	50-200	20-100	30-100
Cost	Low	Moderate	Low
Speed	Low	Moderate	Low

PVDF can be reinforced with high-piezoelectric ceramics to be tailored for piezoelectric and capacitive sensing applications [4]. With respect to the mechanical characteristics, tensile stress and Young modulus are in the order of 35-55 MPa and 1-2 GPa, respectively, with maximum elongations up to 500 % [3]. Increasing filler content typically leads to an increase of the electroactive properties, at the cost of increasing Young modulus and decreasing maximum elongation. Moreover, PVDF composites have also been implemented as piezoresistive sensors by the incorporation of conductive fillers [1]. Accordingly, working principles for PVDF-based pressure sensors are divided into three main categories: voltage (piezoelectric), capacitance, and resistance transduction under the mechanical excitation.

Voltage variations in piezoelectric sensors are related with the piezoelectric coefficients (Table 1). For capacitive sensors, the dielectric constant, and geometrical factors ($area/thickness$) are altered when under pressure. For piezoresistive pressure sensors, materials with electrical conductivity close to the percolation threshold show a higher sensitivity. The sensitivity of the different sensors can be determined by $S = \delta(\Delta X/X_0)/\delta P$, where X is electrical response for the different types of sensors, typical values being 19 mV/kPa for piezoelectric transduction, ≈1 kPa^{-1} for capacitive transduction, and 67 kPa^{-1} for piezoresistive PVDF based pressure sensors [1, 5].

Focusing on the piezoelectric effect, the most representative sensing principle for PVDF, the typical sensor applications (Figure 1) include monitoring human signals, tactile sensing, and soft robotics. 2D printed devices have been mainly used for low pressures (from 10^{-5} to 10^{-1} N), whereas 3D-printed sensors have been also applied as self-powered devices and typically allow sensing higher pressure ranges (from 1 to 10^5 N) [6]. The main PVDF-related materials, printing techniques and sensitivity of the sensors are presented in Figure 1.

Active Material	Printing technique	Typical Force	Sensitivity	$\|d_{33}\|$ (pC/N)	Ref.
P(VDF-TrFE)	Screen	0.5-3 N	112 mV/kN	-	[7]
P(VDF-TrFE)	Bar coating	1-3 N	-	26.9	[8]
PVDF	Electrohyd rodynamic	3×10^{-5} N	0.2 mg	-	[9]
PVDF	DWP	50 N	443 mV/N	-	[10]
P(VDF-TrFE)	DIW	46 kPa	~2 V/kPa	130	[11]
BT/PVDF	DIW	500 kPa	61.6 mV/kPa	69.1	[12]
PVDF	FDM	2 N	4.8 V/N	47.8	[13]
PZT/PVDF	FDM	14 kPa	21 mV/kPa	-	[14]
IL/CNT-PVDF	FDM	2.5kPa	2.65 V/kPa	-	[15]
BT/PVDF-HFP	DIW/FDM	4.5 Kg/cm^2	20 $V/Kg/m^2$	-	[16]
G/BT/PVDF	FDM	1 N	-	30.2	[17]

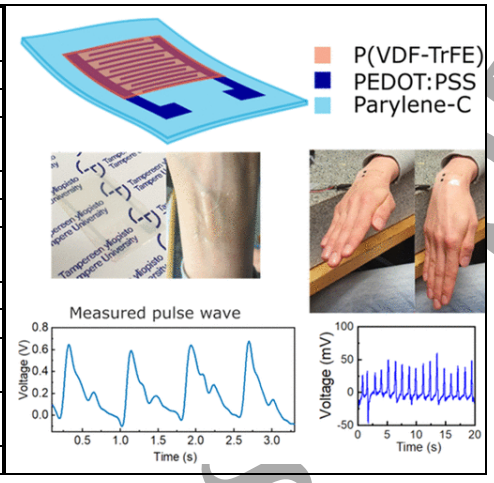

Figure 1 Left: typical parameters of printed PVDF-based pressure sensors. Right: Example of a printed transparent pressure sensor for bio-signal monitoring based on P(VDF-TrFE) [18].

Current and Future Challenges

PVDF-based materials are receiving increasing attention due to their allowance for simple fabrication, mechanical flexibility, chemical and radiation stability, and high-performance dielectric and piezoelectric properties. Using their intrinsic properties, these sensors can convert a pressure into an electrical response, with the advantages of simple fabrication, low-cost, wide frequency range, and high sensitivity [17, 19]. However, the conversion efficiency (electromechanical coupling factor increases with ceramic reinforcement) and the stability of the signal over time must be further improved. Capacitive and resistive pressure sensors are highly dependent both on intrinsic physical-chemical properties and geometrical factors variations (geometry variations leading typically to much lower sensor sensitivity than intrinsic variations), contrary to piezoelectric sensors. An important aspect for improving pressure sensitivity, response time, and linearity of piezoelectric sensors is the control of the β-phase crystalline content, which determines the piezoelectric response of the material.

Thus, a challenge relies on increasing the crystalline content of the PVDF without losing mechanical flexibility. Similar factors must be considered in composites, especially with large amounts of fillers, being critical a homogeneous dispersion and a low filler size. The β-phase content can be increased by means of nucleating agents, additives (including ceramics, ionic liquids and conductive fillers), or by employing specific processing strategies (e.g. application of specific temperatures or electric field) [1].

An interesting characteristic of PVDF pressure sensors is their multifunctionality, as the same material can act piezoelectric and capacitive, nevertheless, to identify the specific signal to the applied stimulus can be complex and specific electronics is required. Furthermore, self-power flexible devices have been also presented working without external power supply, though energy conversion efficiency and power output must be improved to obtain fully self-powered functional monitoring systems. The enhanced multifunctionality combined with self-power characteristics is one of the critical advantages of PVDF materials.

One important issue in soft materials is the interconnection of the flexible PVDF based sensors with the read-out circuitry, for which low resistance, highly adhesive electrode interconnects are ultimately required. Additionally, the sensing operation range must be addressed through specific geometrical designs of the sensor. Finally, the readout of weak signals (biomedical monitoring) and noise interference are still relevant challenges influencing sensitivity.

Advances in Science and Technology to Meet Challenges

There is continuous research for novel PVDF-based polymers, composites, and blends with enhanced electroactive properties and dielectric constant, allowing improved sensitivity and sensing range, among the most critical parameters for sensing applications (Figure 2). Copolymers and ternary polymers and composites allow higher piezoelectric coefficients, while also allowing tuning the degree of crystallinity. To improve the piezoelectric phase content, ceramic or nucleation agents (nanoparticles or ionic liquids) represent a suitable strategy, together with specific processing conditions including the application of poling and mechanical stretching. Ternary PVDF based materials lead to large dielectric constant suitable for capacitive sensors (linear, reversible, and fast response sensors), whereas piezoresistive sensors must increase cycling stability by improving polymer matrix interactions with the conductive network. Piezoresistive sensors critically depends on and therefore are tuned by the filler properties (geometry and conductivity) [2, 3]. Functionalized nanocarbonaceous allow to enhance the polymer-filler chemical interaction, and consequently, the sensor response [4]. With respect to the sensing response time, it is in the order of tens to few hundred milliseconds for piezoelectric, capacitive and piezoresistive sensors, being suitable for a wide range of applications. The hysteresis to recover can be large, but critically depends on the external stimuli given to the sensor.

Devices obtained through processes such as lithography are time-expensive, complex to process and involve high material waste. This is overcome by large area printing methods such as screen-, spray- or 3D printing methods. These methods allow for high customization, reduced number of manufacturing steps, minimized materials waste, and large-scale production of sensing devices. Developing inks for sensing applications typically implies including further additives to establish the necessary rheological qualities, requiring a post-treatment procedure for their removal. These materials should be common for different printing techniques to achieve uniform industrial processes.

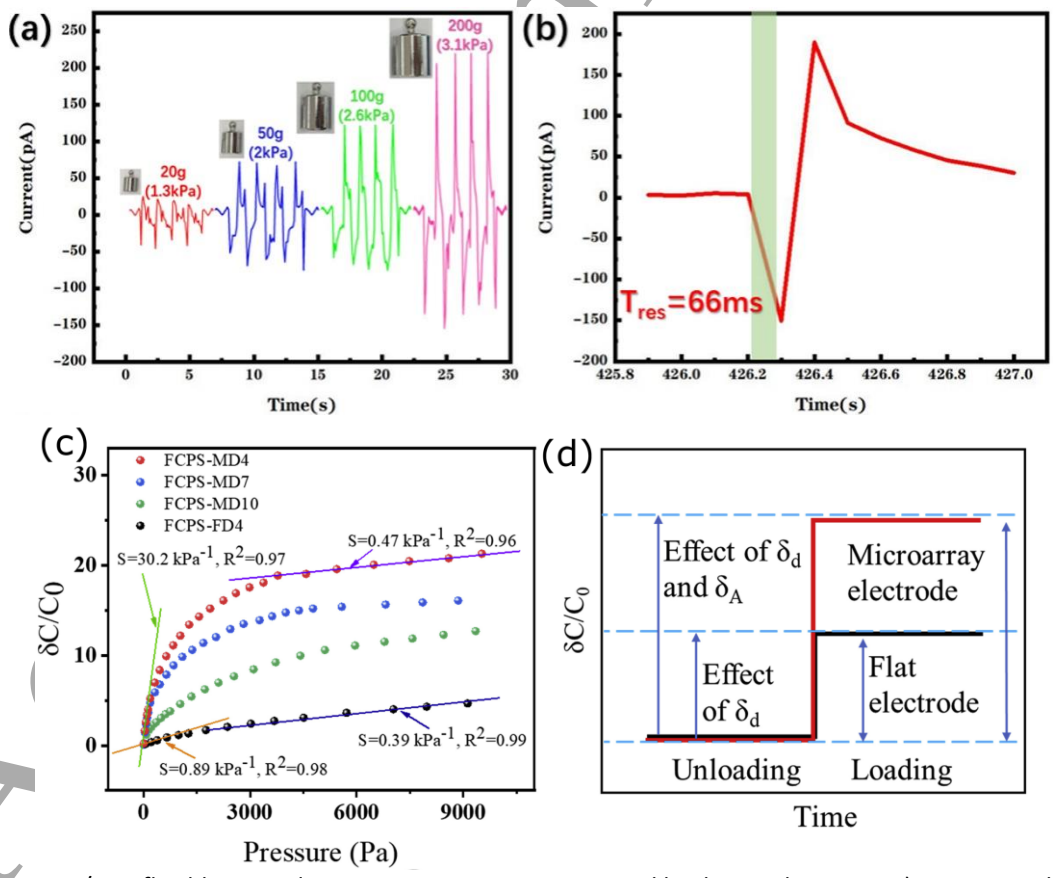

Figure 2 PVDF/CNT flexible piezoelectric pressure sensor processed by direct ink writing: a) measuring different weights and b) time response [19]. Capacitive PVDF sensor: c) sensitivity and d) response time [20].

Structured pattern and geometrical (area/thickness) factors can also be a key issue for improving sensitivity of the sensor. Thus, pyramidal assemblies present larger sensitivity even for low pressures, while pillar structures exhibit a larger and linear sensing detection area (Figure 2). Furthermore, porous structures show a lower detection limit and a larger deformation detection range due to softer mechanical properties of the material.

Ongoing research should be focused on achieving improved sensitivity, flexibility, and adhesion to substrates and between layers. Additionally, work is needed to improve cycling stability and to allow for implementation in harsh environmental conditions. Improving response sensitivity and sensing range in future PVDF pressure sensors is a challenge, as often improving one is detrimental of the other. The response time of the piezoresistive sensors, in the range of tens of milliseconds is suitable for a wide range of applications, though the recovery time can be slow (in the order of seconds), limiting fast dynamic applications. Therefore, to obtain a suitable balance for a specific application constitutes an important design challenge that must be addressed.

Concluding Remarks

PVDF-based materials present outstanding electroactive properties to enable flexible pressure sensors with transduction schemes including piezoelectric, capacitive and piezoresistive. PVDF copolymers and ternary materials allow for the improvement of electroactive and dielectric properties when compared to pristine PVDF, that can be combined with reinforcement fillers (nanocarbonaceous or high-dielectric ceramics) to further optimize specific properties for functional applications. There is a wide range of processing methods and geometries in which PVDF-based materials can be processed, allowing a wide range of applications with suitable integration into devices. Additive manufacturing technologies for the processing of PVDF-based materials hold great promise for the implementation of those sensors in the scope of the IoT. High-resolution printing compatible with specific polymer substrates and green chemistry allow an increasing the number of application areas.

The academic and industry continuous search to improve the intrinsic properties and processability of PVDF-based materials and devices allows foreseeing an interesting future due to their broad and easy processing, flexibility, low-cost, mechanical, thermal, radiation and chemical resistance. Human motion and health monitoring, artificial skin, smart and soft robotics are some of the relevant fields of applications of PVDF based materials for pressure sensing applications.

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4.3 Printable pressure sensors based on carbon nanocomposites

Alex Chortos

Purdue University, West Lafayette, IN, 47907, United States of America

Status

Due to their exceptionally low cost and chemical inertness, carbon-based conductors have been extensively used in both academic research and commercial development of deformation sensors. For example, as one of the first companies to develop printed flexible pressure sensors, Tekscan patented a pressure-sensitive ink formulation in 1999 based on carbon black [1].

In sensors based on intrinsic piezoresistance (varying the resistance due to changes in particle distributions within composites), carbon black has been used for decades [2], but these compositions typically suffer from hysteresis. Newer carbon allotropes such as carbon nanotubes (CNTs) and graphene with high aspect ratios have enabled composites with reduced hysteresis[3] and controlled temperature dependence [4]. With the explosion of interest in "electronic skin" in the mid 2010's, the use of contact resistance between elastic surfaces was re-popularized due to its advantages of higher sensitivity, thinner active layers, and independence from temperature. The roughness of the surface could be rationally tuned using micromachined templates [5]. Scalable, low-cost alternatives include templating carbon materials onto rough surfaces such as paper [6] and sandpaper[7], while regular structures such as steel meshes[8] provide better reproducibility. Directly printing the active layer enables the production of deterministic microstructures with customizable shapes that have not been possible previously.

The rapidly expanding interest in 3D printing has created new opportunities and challenges for carbon-based deformation sensors. For example, sensors can be created with active layers that include structures with variable heights or shapes to enable unprecedented sensitivities [9] and tailorable dynamic range [10]. Furthermore, 3D printing enables integration with emerging 3D device concepts such as soft robots [11].

Demonstrations of printed sensors can already achieve performance metrics (sensitivity, dynamic range, and response time) comparable to or larger than those of non-printed devices (Table 1). These performance metrics are sufficient for many of the envisioned applications, such as measuring the pressure distribution in shoe soles (which mainly requires high dynamic range) and measuring arterial pulse waveforms (which mainly requires high sensitivity. In some cases, printed sensors can achieve these performance metrics with reduced fabrication complexity. For example, there is often a trade-off between the sensitivity and dynamic range. One way to increase both metrics simultaneously is to increase the number of contact interfaces in the active layer. For conventional fabrication approaches, this can require elaborate fabrication approaches involving aligning and transferring multiple structures. In contrast, extrusion printing can directly produce active layers with the number of contact interfaces proportional to the number of print layers, enabling high sensitivity and dynamic range [12]. However, these printed devices often have reproducibility and uniformity much lower than the more mature techniques based on lithography and microfabrication.

Current and Future Challenges

Micron-sized carbon fillers such as carbon fibers can achieve reproducible random dispersions that correspond with theoretical predictions [15]. However, the unique lack of chemical groups on CNTs and graphene and their high surface areas make them unusually difficult to disperse, even compared to other nanomaterials with similar dimensions.[16] Chemical modification can improve dispersion at the cost of conductivity, while the use of surfactant dispersants can affect the properties of the

Table 1 Performance metrics of reference and printed pressure sensors. Sensitivity refers to the highest sensitivity within the sensing range (the sensitivity usually varies with pressure). Three micromolded devices are included as a reference to conventional fabrication approaches.

Device	Sensitivity (kPa^{-1})	Dynamic Range (kPa)	Reference	Year
Micromolded CNTs	15.1	25	[5]	2014
Micromolded graphene	14	10	[13]	2016
Micromolded graphene	2000	40	[14]	2019
Micromolding + CNT printing	20	1000	[8]	2020
Extrusion printed CNT composite	200	146	[12]	2020
Extrusion printed CNT/CB composite	212	400	[9]	2022
Extrusion printed graphene foam	3.1	400	[10]	2022

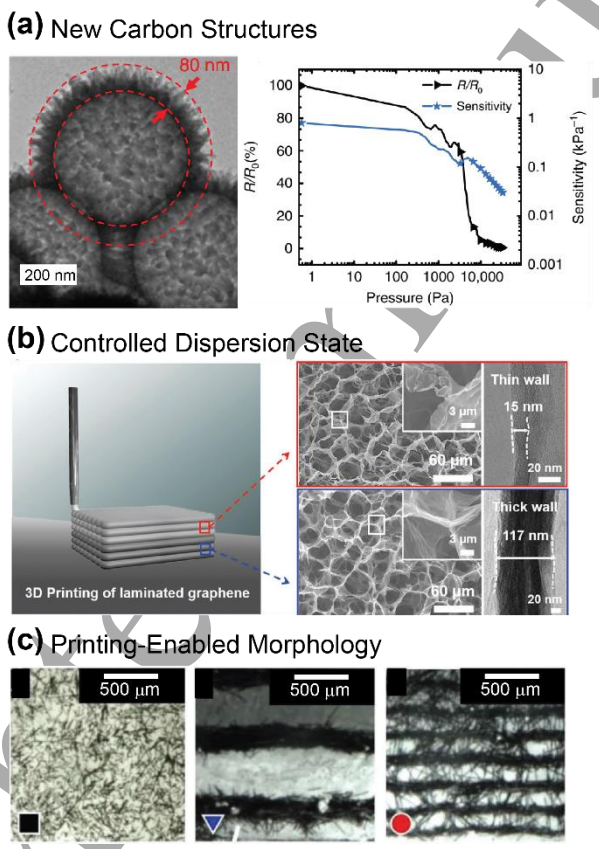

Figure 1 Opportunities for innovation include: (a) Design of new carbon fillers [18]. (b) Improved control over dispersion characteristics [10] (Reproduced with permission from Wiley-VCH). (c) Leveraging printing to tailor composite morphology [15] (Reproduced with permission from Wiley-VCH).

printing inks. The aggregation rate is highly sensitive to the surface chemical functionality, and achieving surface modification reproducibly between batches can be a challenge. Even commercial products sometimes have batch-to-batch variations in the surface energy, making it challenging to achieve reproducible devices.

In moving from lab-scale device demonstrations to scalable printing, the printing process becomes a critical factor in determining the composite performance. For example, when an ink is extruded through a nozzle, the resulting high shear forces modify the dispersion of fillers. After printing, those

fillers can redistribute before reaching a kinetically trapped state. In fused deposition modeling (FDM) printing, slow thermal cooling results in dispersions that are sensitive to many factors that include external temperature and print speed.[17] As a room temperature extrusion printing process with a very short time to kinetically trap the ink, direct ink write printing can achieve more reproducible printing processes.[10] Due to the proliferation of new printing methods, understanding how these printing processes affect composite properties is essential.

Few of the described device platforms are fully printed. For example, Wu *et al*. printed the silver electrodes and CNT active layer [8], but the critical step of patterning the microstructures was done manually using molding. Truly scalable fabrication will be enabled by printing all components of a device using a fully automated manufacturing process [19]. However, translating high-performance bench-scale device concepts into large-scale printed devices will require innovations in printing and ink designs.

Advances in Science and Technology to Meet Challenges

Initial work shows promising synergistic interactions between different carbon allotropes. For example, CNTs provide high conductivity and low percolation threshold while carbon black improves the dispersion of CNTs and the rheology of the printing ink [20]. Carbon structures with new morphologies can create unprecedented capabilities. For example, the preparation of carbon particles with sharp surface protrusions enables devices with high sensitivity based on Fowler-Nordheim tunnelling [18]. Continued exploration of new filler morphologies and combinations will enable improved device performance. In addition, most of these works were done on cast or molded samples, and studying the effect of aspect ratio and morphology in the highly dynamic non-equilibrium printing processes will be critical for fully printed devices.

Progress in understanding printing technologies can be leveraged to control the morphology of composites. For example, the “coffee ring effect” during the drying process of low-viscosity inks causes non-uniform distribution of the materials that has been exploited to increase the sensitivity to deformation [21]. Multimaterial printing processes can also be leveraged to control the aggregation of graphene to enable improved uniformity and conductivity [22]. In extrusion printing, the shear forces within the nozzle can align high aspect ratio fillers to tailor the percolation threshold and piezoresistance coefficient. Advances in the integration of acoustic stimulation into the printing process has been used to align carbon fibers to improve the reproducibility [15].

Concluding Remarks

Carbon allotropes are typically the lowest cost filler for piezoresistive sensors and have therefore remained in common use despite the proliferation of alternative nanomaterials. The precipitous drop in the price of CNTs and graphene over the last decade have enabled all carbon allotropes to be cost effective. Consequently, the primary discriminating factor between different carbon allotropes is now the performance and suitability for the application. Carbon materials have the largest versatility in dimensionality and structure, and further progress in the field will focus on finding synergies between the structure of the fillers and the processing characteristics of each printing technique.

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Section 4.4 – Printable strain sensors based on nanomaterial composites

Saurabh Khuje[24], Jian Yu[25] and Shenqiang Ren[24]

[24] Department of Materials Science and Engineering, University of Maryland, College Park, MD, 20742, United States of America
[25] DEVCOM Army Research Laboratory, Aberdeen Proving Ground, MD, 21005, United States of America

Status

Printable strain sensors are attractive for wearable electronics. To achieve high sensitivity and stretchability, printable nanomaterials and elastomers have been collated to develop composites for strain sensing applications. This can be achieved via printing conductive ink onto polymers or incorporating them together to print free-standing conductors [1]. The mechanisms of nanocomposite-based strain sensors depend on the strain propagation attributed to mechanical mismatch between supporting substrates [2], geometrical interface (stretching causes change in cross-sectional area due to Poisson's ratio) [3], electrical conduction or tunnelling [4]. In synergy with manufacturing, selection of appropriate materials is crucial for designing strain sensors. Conducting materials such as carbon (carbon nanotubes, carbon black, graphene) [5], metallic nanowires (NWs), nanoparticles (NPs) and nanofibers (NFs) [6], or conductive fabrics have been implemented as active sensing mediums. As per the percolation theory, a decrease in conductivity is observed as the spacing between the NPs becomes prominent during bending and stretching. To overcome this, NP conductive network can be preserved by adding NWs as conductive and flexible scaffolds subjected to strain [7].

Moreover, these active materials are incorporated in stretchable substrate materials including thermoplastic polymers [8], and silicone elastomers [5]. The interaction between the active materials and supporting materials significantly impact the sensing properties of the printed strain sensors. Table 1 lists the materials utilized, printing techniques, operating principle, and sensitivity of different strain sensors. Figure 1 depicts strain sensing mechanisms and certain on-body applications. Figure 2 illustrates certain materials for fabrication of strain sensors and uses for physiology applications. Reliability is another challenge pertaining to stretchable nanocomposite sensors. This can be mitigated via selection of an apt strain rate and operating range, as well as suitable cyclic loading profile to ascertain the settling down of nanomaterials and nanomaterial-polymer interface. Ensuring this minimizes (or eliminates) hysteresis and enhances cycling performance. In terms of non-linear sensing, the input/output stimuli can follow an algebraic function, thus deeming a stable, highly reproducible sensor performance with required number of loading/unloading cycles during application. Even

Material	Process	Substrate	Operating principle	Sensing range	GF/Sensitivity
CNTs, Ecoflex, PDMS	Micro-contact printing	Embedded	Capacitive	50% Tensile	GF: 0.5
PEDOT: PSS	Inkjet	PET	Piezoresistive	0.33%	GF: 165
Polyvinyl chloride/carbon black, Ag	Screen Printing	PI	Piezoresistive	0.14%	$GF_{tensile}$: 741 GF_{compre}: 1563
P(VDF-TrFE), Ag	Screen Printing	PI	Piezoelectric	0.5 – 4 N	0.05 V/N
PVDF, AgNPs	Inkjet	Embedded	Piezoelectric	3 N	2.8 ± 0.9 mV/N

Table 1 Comparison of strain sensors based on different sensing mechanisms [9].

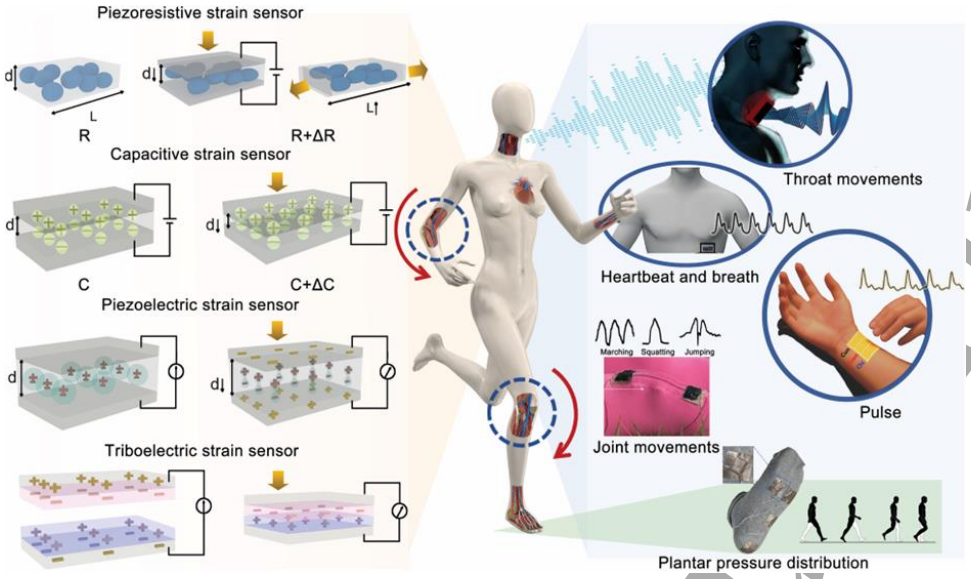

Figure 1 Schematic depicting the basic working principles of strain sensors and applications pertaining to physiological bio-signals in the body [15]. Reproduced with permission. Copyright 2022 Elsevier.

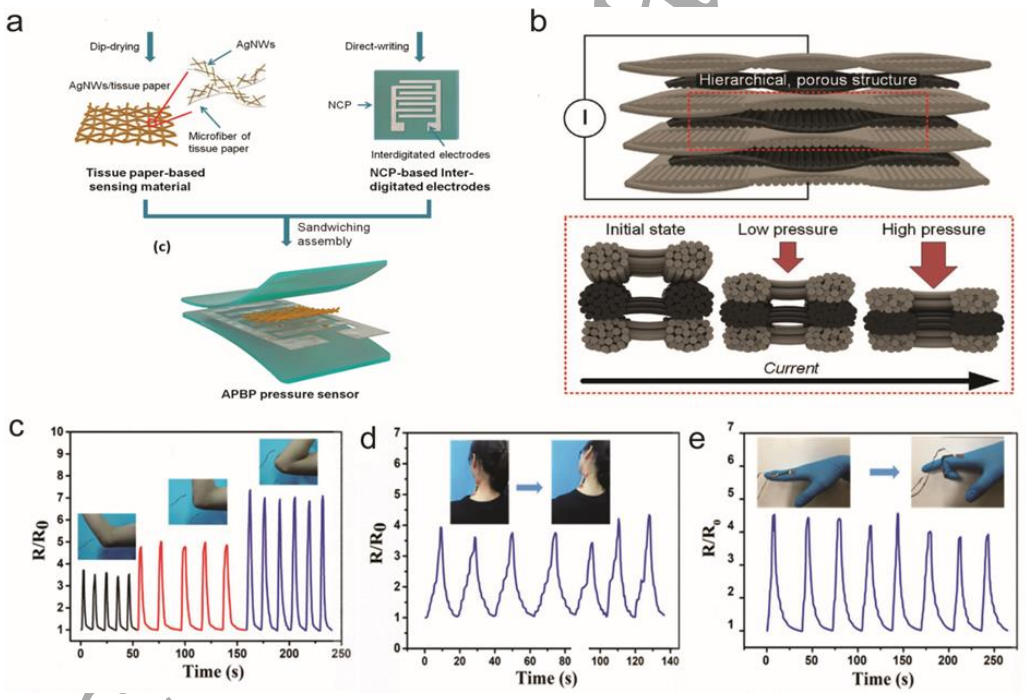

Figure 2 (a) Piezoresistive strain sensor based on Nanocellulose paper/AgNWs/Nanocellulose paper composite [16]. Reproduced with permission. Copyright 2019 American Chemical Society. (b) Schematic depicting strain sensor based on multi-layered CNT-fabric composite [17]. Reproduced with permission. Copyright 2019 John Wiley and Sons. (c-e) Plots depicting human motion detections including joint movements, neck movement and finger bending on a SiO_2/graphene-decorated electro-spun nanofiber sensor [18]. Reproduced with permission. Copyright 2019 Elsevier.

though there have been considerable advancements in strain sensors, further research is required to address prevailing issues such as non-linear behaviour, a small degree of hysteresis, poor reproducibility, and detection limits for promoting their practical applications further.

Polydimethylsiloxane (PDMS) consists of several comprehensive characteristics, namely better adhesion to other materials, good chemical inertness, and biocompatibility. Additionally, it has high compressibility, bendability, and stretchability, with low Young's modulus value in the range 0.4 – 3.5 MPa, thus enhancing its overall stretchability [10]. Eco-flex (soft silicone) has a simple preparation process, a tensile factor of ~600%, and is biocompatible with human skin [11]. For applications requiring high stretchability, eco-flex is more beneficial compared to PDMS and PVDF (a 1 mm thick film of Eco-flex is more stretchable than its PDMS counterpart with similar dimensions) [12]. PVDF also boasts of chemical inertness alongside good mechanical, thermal and physical characteristics such as piezoelectricity and piezoresistivity. Additionally, with hydrophobic capabilities, it is useful for applications necessitating anti-fouling or waterproofing [13]. For nanomaterials deposited on these substrates, drawbacks include susceptibility to delaminate and interfacial failure, because of mechanical mismatch between the substrate and nanomaterial of interest. Moreover, the viscoelasticity or plasticity characteristics of these substrates may cause performance degradation due to induced instability of deposited nano-structural materials, when subjected to high strain and loading frequencies. To attenuate these effects, strategies have been realized for ensuring substrate-nano-structural material compatibility based on the application requirement, an example involves tuning the substrate modulus [14].

Current and Future Challenges

It has been proposed that achieving a sensor with high stretchability ($\varepsilon \geq 100\%$), linearity and sensitivity ($GF \geq 50$) would pose a significant challenge [4]. Several efforts have been put forth for addressing these challenges, with the latest developments overcoming some of them, such as having high stretchability and sensitivity [19], low-hysteresis and high cyclic stability [20]. Although newly developed nanomaterial sensors target high sensitivity and stretchability, very few report details on reliability, a prerequisite for sensors to be utilized as actual gauges. Moreover, resolution monotonicity is another less unexplored area. The interaction between the conductive nanomaterials and polymers, as well as the viscoelastic nature of the latter contribute to the hysteresis of the printable nanocomposite sensors [4]. Additionally, the accuracy of the sensor is afflicted by numerous conditions including calibration, temperature, non-linear behaviour, and hysteresis resulting in inaccurate readings. Under dynamic conditions, thermally insulating elastomers may experience heat build-up, thus affecting their performance. These errors may happen under extreme temperature and can be alleviated by the circuitry and programming software applying specific compensations, which can lead to upwards of 99.557% measurement accuracy [1]. The deteriorating interface between the polymer substrates and nanomaterials or irreversible changes to the nanomaterial arrangement with increasing loading cycles adds to the increased resistivity, causing unreliability.

A nanocomposite strain sensor capable of measuring decoupled strain in multiple directions and deformations is challenging to implement, and studies need to be conducted to create a novel sensing network, such as metamaterials and 3D structures [21]. Strain sensors with stretchable characteristics (> 100%) are usually manufactured by embedding conductive fillers in stretchable matrices. However, the rigid conductive filler-based sensors could experience electrical failure when subjected to long-term stretching cycles. Metallic NPs show a lower working strain range (20%) compared to NWs (80%) attributable to the high aspect ratio of the latter. Moreover, a higher processing temperature (>150ºC) is required to eliminate the organics capping the NWs and grant desirable conductivity. This temperature is unfavourable for some polymer-based substrate materials as it deteriorates dramatically following high temperature processing. Hence, there is also a need for developing metallic ink nanomaterials that are processable at lower temperatures to prevent degradation of substrate materials. Additionally, metallic nanostructures exhibit low resistance to oxidation, resulting in deterioration of electrical performance over time.

Advances in Science and Technology to Meet Challenges

New materials with nanostructure designs and advanced packaging techniques are necessary for eliminating the obstacles described above concerning environmental factors. The temperature interference can be decoupled via a support structure that can compensate for the temperature variations. For humidity, hydrophobic coatings can be implemented to intercept water molecules from entering the strain sensing network. For addressing the weak adhesion of conformal strain sensors on human skin, gecko-inspired structures [22], pressure-sensitive additives [23] are being pursued. Materials that can conformally adapt to the skin roughness or integration with skin-composite microfibers would be beneficial. To prolong the life cycle of the strain sensor, self-healing materials may be considered, which will allow the supporting material to regress to their original shape with full or partial functional recovery after sustaining damage. This concept can be implemented for developing highly sustainable and durable strain sensors. An avenue to expand the operational lifetime of the strain sensors is to incorporate healing capability into electronic applications. A process that can achieve large-scale and economical synthesis of high-quality nanomaterials with uniform characteristic dimensions (e.g., length, diameter) would be beneficial for stretchable electronics. Moreover, to prevent oxidation, additional materials can be incorporated to coat the metallic nanostructures, thus prolonging their lifespan. For instance, when using copper nanostructures, graphene has shown to be effective for oxidation and corrosion-resistance [24].

Additional research is needed for integration of devices and 3D printing aimed towards multifunctional devices with efficient performance and elongated lifespans. Fabricating multifunctional strain sensors will provide an insight on the biological understanding which will enable the formulation of hypotheses for investigation of living organisms. On a similar note, soft sensing enabled by functional nanomaterial composites will assist with veterinary care and biomechanics overall. Besides developing sensor hardware, a software is required as an interface between the device and the user. Different transduction mechanisms outline different sensing capabilities, thus there arises a need for developing algorithms for processing and interpreting different signals from different transduction units. Figure 3 briefly highlights the healing mechanism, possible uses of strain sensors for physiological signal monitoring and system integration.

Concluding Remarks

As the modern technology extends in various sensor-based applications, rapid progress on strain sensors has been made in the last few years by coupling additive manufacturing with functional nanostructures, deeming the use of strain sensors in real-life applications a possibility. The thriving development of multifunctional nanomaterials, capable of additive manufacturing, has led to unprecedented advancement of strain sensors with quick response proficiency. Several methods including aerosol jetting, inkjet printing, direct writing and screen printing have been implemented for fabrication of strain sensing devices. Stretchable, wearable, and ultrasensitive sensors have emerged as a result as ideal candidates for several applications, enabling them to become a crucial component for upcoming flexible hybrid electronics. This progress affirms the concept that strain sensors may serve as an essential component for robotics, military, medical and industry sectors. Nevertheless, several challenges relating to the design of high-performing sensors, low dynamic response, a small degree of hysteresis, robust packaging, and conformal adhesion onto surface of interest still need to be taken into consideration. A comprehensive understanding of mechanical, electric, and thermal properties is a must for the sensors to be utilized in target monitoring applications.

Acknowledgements

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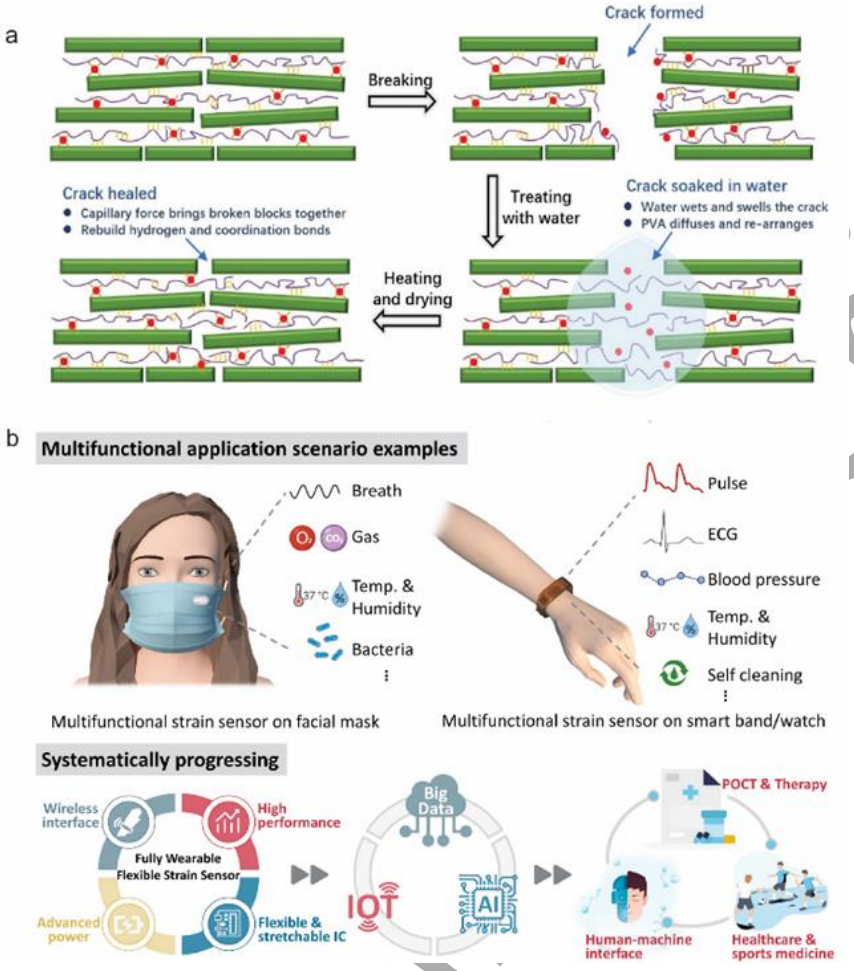

Figure 3 (a) Schematic depicting the water-initiated healing process of graphene oxide-AgNW/PVA-Ca^{2+} strain sensor [25]. Reproduced with permission. Copyright 2019 Elsevier. (b) Schematic depicting the prospects for flexible strain sensors in regards of physiological signal monitoring and integration of multiple systems [15]. Reproduced with permission. Copyright 2022 Elsevier.

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Section 4.5 – Organic semiconductors for mechanical sensing

Antonello Mascia, Mattia Concas and Piero Cosseddu

Department of Electrical and Electronic Engineering, University of Cagliari, Piazza d'Armi, 09123 Cagliari, Italy

Status

Organic semiconductor-based devices have attracted considerable interest in the last decades since they can be deposited on flexible plastic substrates through a low-cost and solution-based manufacturing process. However, due to the polycrystalline nature of most organic semiconductor thin films, their electrical properties are typically influenced by mechanical deformation.

In this context, very few examples of two-terminal devices based on organic semiconductors have been reported as strain sensors. In this configuration, the applied mechanical deformation affects the organic semiconductor conductivity, thus leading to a resistance variation of the thin film. A significant example was introduced by H.-j. Kim et al., who reported a two-terminal strain sensor obtained by a solution-processed rubbery elastomeric semiconductor nanocomposites (P3HT-NFs percolated in PDMS), with a gauge factor of about ∼32 and a uniaxial stretchability of 100% in a stretch and release repetitive test [1].

However, among the many device architectures introduced over the years, the most employed approach involves using Organic Thin Film Transistors (OTFTs), as in this case the transistors can be employed not only as mechanical sensor, but also to address the sensing elements in matrices/arrays and/or to locally amplify the sensor response, thus strongly simplifying the required readout circuitry complexity. Thin-film transistors can be employed as strain sensors by exploiting different effects, such as dielectric capacitance or contact resistance variations. Moreover, as also the charge carrier hopping mechanism across the active layer is generally affected by mechanical deformation, such conductivity changes induced by mechanical deformation in the active layer can be employed for the realization of flexible strain sensors [2]. In fact, it was found that, when working at deformations below 2% of surface strain, such behavior is generally reproducible and linear, therefore, different kinds of organic semiconductors have been employed over the years for the development of flexible mechanical sensors, mainly in the wearable electronics application field [3] [4]. Many works have been recently reported showing that a very large class of molecules can be employed, from pentacene and its soluble derivatives [5] to solution-processable perylene-based systems [2], as well as heptazole-based semiconductors, employed by P. J. Jeon et al. that reported the performance of a strain sensor based on a complementary inverter, achieving a gauge factor of up to 90% [6].

Cosseddu et al. demonstrated that Pentacene-TIPS OTFTs can be also employed as flexible strain sensors capable to detect strains up to 2% with remarkable reproducible performances [7]. More recently, J. Y. Oh et al. [8] developed a strain-sensitive, and autonomously self-healable semiconductor polymer capable of achieving a gauge factor of $5.75 \cdot 10^5$.

Such insights have allowed for the development of different applications in the field of wearable electronics. Recently, several research groups have reported about the development of OTFT-based printed matrices of tactile transducers for the development of artificial skin prototypes [9]. Lai et al. reported on the development of a smart glove for the detection of finger and wrist motion, whereas Someya's group reported on the development of highly sensitive pressure sensors that can be potentially employed for the fabrication of a smart glove for monitoring tissue hardness and eventually for early detection of breast tumors [10]-[11].

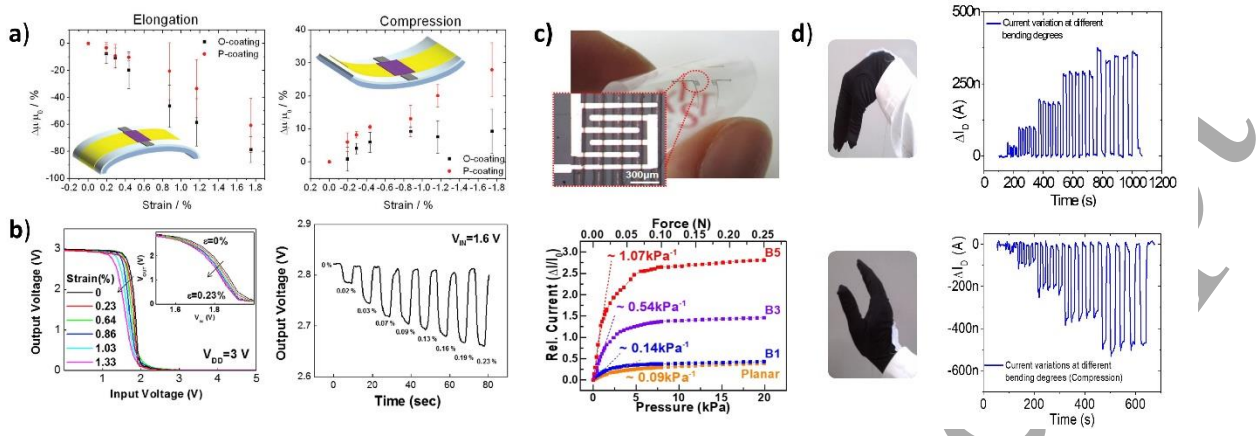

Figure 1 Some examples of recently reported mechanical sensors, strain and pressure, based on printable organic semiconductors (a), (b) and (c) and their application in the field of wearable electronics (d). Reprinted with permission [5][6][9][10].

Current and Future Challenges

Despite the many progresses that have been made in the development of novel materials and architectures, which allowed for the development of highly flexible mechanical sensors with remarkable performances, and many interesting applications in particular in the field of wearable electronics and robotics, there exist some important issues that are still limiting their actual diffusion into real products. First of all, the reliability of such systems is generally reduced by early aging effects due to moisture and oxygen contamination of the organic semiconductor. This issue is well known and very common to all flexible electronic devices based on organic semiconductors, as it is very difficult nowadays to develop and routinely fabricate over large areas flexible thin film packaging capable to act as efficient barriers for moisture and oxygen permeation. This issue represents a very important challenge as mobility variation, as well as threshold voltage shifts induced by contamination processes, can strongly influence the entire system's performance.

Moreover, it has also to be considered that in applications such as wearable electronics, where continuous deformations are applied to the entire flexible electronic system, such induced mechanical stresses could lead to unexpected issues in different layers/interfaces of the flexible devices. It has been recently demonstrated that continuous stress can lead to internal cracks in the metal layers and some organic semiconductor thin films [12] [13]. Furthermore, also delamination between the different layers forming the final device can take place thus leading to a failure of the device in the long term.

Last but not least, one more, often under-evaluated issue, regards the fact that flexible sensing systems require not only the sensing matrix but also a dedicated circuitry for local addressing and possibly amplification of the signals. Therefore, in this contest, it is necessary that in such systems only the sensing areas (matrices of sensors) respond to the mechanical stimuli, whereas all the other parts of the system (i.e. interconnections, local readout circuitry), must withstand the induced mechanical deformations, as a variation in the readout circuitry transistors mobility and/or threshold voltages will lead such circuitry to deviate from its ideal functionalities.

Advances in Science and Technology to Meet Challenges

There are several very promising ways which are being developed and optimized, in these past years, for efficiently overcoming the reported challenges. In particular, stability of organic semiconductor materials is an issue that involves all the possible applications in which such materials are required. Along the years, material scientists are spending huge effort to develop novel materials, with suitable energetic levels and a proper microstructure capable to minimise the interdiffusion and also chemical

reactions of contaminants into the active. Moreover, different examples of very promising multilayer flexible encapsulating solutions have been reported, capable to increase the shelf life of organic solar cells by several months. Similarly, such approaches can eventually be employed for a suitable packaging of flexible sensing systems [14]. A remarkable effort has been also made by researchers for finding new approaches for minimizing mechanical stress-induced reliability issues, as metal interconnection fracture and delamination. The fabrication of ultrathin, possibly also 2D, conductive layers, that have a much lower stiffness could better withstand such deformations, as well as proper engineering of their geometry can dramatically minimize this issue. For instance, several works reported that mechanical robustness can be also improved by a proper embedding of the entire device structure, as well as by using spring-like, kirigami, or serpentine-shaped electrodes [11]- [15].

Finally, novel solutions for alternative highly stretchable organic semiconductor systems have been also reported over the years. Very recently Shim et al. reported the development of a novel approach for embedding organic semiconductors into an elastomeric matrix, for the fabrication of highly stretchable transistors and logic circuits that can be stretched up to 50% without showing any significant loss in their performances [16].

Concluding Remarks

Solution processable organic semiconductors are without any doubt very good candidates for the development of flexible mechanical sensing systems as they can be processed over large areas, at relatively low temperature, thus compatible with the most used plastic substrates, and, most importantly, by using cost efficient technologies as different kinds of printing techniques. High performances and reproducible results have been recently reported allowing scientists to develop demonstrators in several application fields, from artificial skin patches for robotics and prosthetics, to smart garments for sportswear and also personalized healthcare, showing the huge interest that such technology has in the scientific community. However, there are still some bottlenecks, particularly concerning their long-term reliability, that must be considered to allow their commercialization. Recent findings and materials optimizations have shown that there are good chances to overcome such issues and possibly turn these devices and systems into real products soon.

Acknowledgements

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Section 4.6 – 2D materials for mechanical sensing

Robert J Young

National Graphene Institute and the Department of Materials, University of Manchester, Manchester M13 9PL, United Kingdom

Status

Layered crystals have a wide range of electronic, electrochemical and photonic properties but their true potential is only fully unlocked once they are exfoliated into 2D layers [1]. There was a massive increase of interest in 2D materials following the first isolation of graphene in 2004, that prompted a flood of research into its unique physical properties. It is now recognised that there is a whole family of 2D materials with a range of properties that can be prepared from different layered crystals that include hexagonal boron nitride, transition metal dichalcogenides, and MXenes [2]. One of the best ways of preparing 2D materials in large quantities is the exfolation of layered crystals in a variety of liquids [3] and this lends itself to the development of liquid-phase '2D inks' as solution-based media that can be used in different surface deposition methods such as spin coating, ink-jet printing, spray coating and drop casting [1]. The optimum solvents for liquid-phase exfoliation are not necessarily the best media for ink applications. The formulations of the 2D inks are therefore usually adapted for the type of 2D nanomaterial and the specific deposition technique being employed to optimise the rheology, drying behaviour wettability and adhesion to the substrate [1].

One of the main attractions of monolayer graphene is that it exhibits very high electrical conductivity (~10^6 S/m). When it is incorporated in an electrically-insulating polymer matrix to form a 2D nanocomposite, it can lead to the polymer being able conduct electricity as shown in Figure 1(a) [4]. The level conductivity of the nanocomposite is found to depend upon a number of factors such as the type of graphene, polymer matrix and graphene dispersion. The most characteristic feature is, however, that the conductivity first increases rapidly with the level of graphene loading (e.g. weight or volume fraction) until it reaches a critical value, known as the percolation threshold, at which point the conductivity reaches a plateau level [5]. The percolation threshold corresponds to the formation of a conductive network of the nanofiller particles and this phenomenon can be exploited for mechanical strain sensing [6]. If a nanocomposite with a composition near that of the percolation threshold is deformed it is found that its resistivity (R) changes with strain as shown in Figure 1(b). This is because the deformation causes a reversible change in the contacts between the conducting filler particles in the nanocomposites and shown schematically in Figure 1(c) [7]. The dependence of the change of resistivity (or conductivity) on strain is often linear, as seen in Figure 1(b), and is usually characterised in terms of the 'gauge factor' G defined as $G = (\Delta R/R_0)/\varepsilon$, where ε is the strain and R_0 the zero-strain resistivity. Conventional metallic resistance strain gauges have a value of G in the range 2-5. Semiconductor-based strain gauges, based upon boron-doped silicon or germanium, can have gauge factors >100 (depending upon the level of doping) and both types of strain gauge are also only capable of measuring strain at relatively low levels (<5%). The first strain gauges based upon spray-deposited percolative films of 2D materials reported gauge factors in excess of 150 and the ability to measure strain reversibly over 4000 cycles [6].

Current and Future Challenges

One of the main potential applications of strain sensors based upon printed 2D materials is in the area of stretchable, skin-mounted and wearable strain sensors for healthcare monitoring [8]. The challenge of this application is that it requires strain sensors with a high gauge factor, based upon flexible low-modulus materials that are capable of measuring high levels of strain and being cycled reversibly many times without significant levels of hysteresis [9].

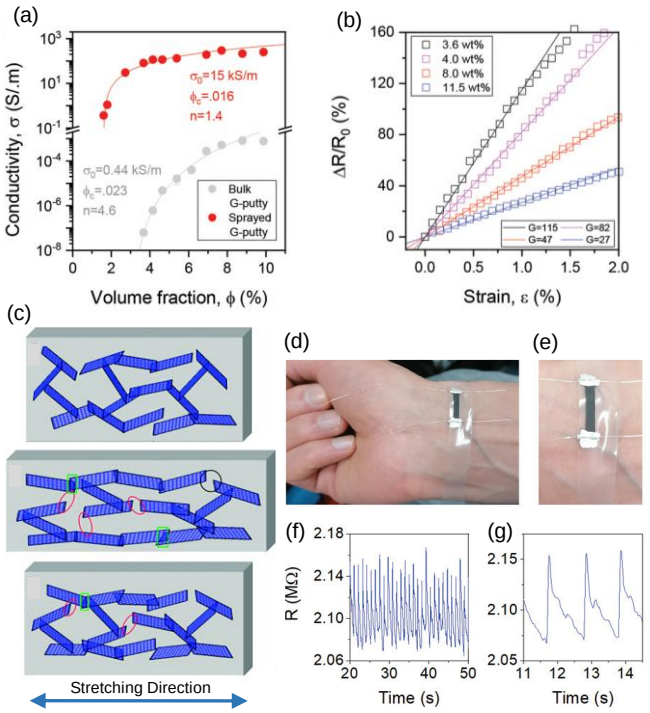

Figure 1 Strain sensors based upon printable graphene-based nanocomposites (G-putty). (a) Conductivity plotted as a function of graphene volume fraction comparing sprayed material compared to bulk G-putty [4]. Note that the conductivity scale is logarithmic. (b) Fractional resistance versus strain for sprayed G-putty for four different mass fractions [4]. It can be seen that *G* decreases as the graphene loading increases. (c) Schematic illustration of the change in the graphene network in a single cycle showing the original state, the state of the network following stretching and the state after the unloading process [7]. (d,e) Strips of G-putty screen-printed onto an elastomer film mounted on a wrist for pulse measurement [4]. (f,g) Variation of the resistance of the G-putty coated film with time showing a pulse rate of the order of 60 beats/minute [4]. Reproduced with permission of John Wiley and Sons and of the Royal Society of Chemistry.

The gauge factors of strain sensors based upon printed 2D nanocomposites are found to depend upon a number of factors and considerable effort is now being expended upon maximising the value of *G* and over a large sensing range for particular strain sensor systems [10]. The response of a strain sensor may also become non-linear over a range of high strains, which can be a challenge. Boland [10] introduced a parameter known as the working factor (*W*), the maximum strain to which the sensor response is linear, as a figure of merit defining the limitation of the mechanical response of a particular strain gauge system. He also pointed out that the Young's modulus (*E*) of the strain gauge is an important consideration in the performance of a strain gauge and suggested benchmarks of $G > 7$, $W > 1$ (i.e. 100%) and $E > 300$ kPa for the optimum sensing of motion in the human body. Figures 1(d)&(e) show the use of a graphene/polymer strain gauge for monitoring the pulse in a human wrist and the resistance changes monitored from the associated deformation of the skin are shown in Figures 1 (f)&(g). The strains involved in pulse monitoring are quite small (~2%) whereas much larger strains (≥100%) are associated with other applications such as the bending of joints, illustrating the challenges involved in healthcare monitoring.

One of the main drawbacks of employing resistance strain gauges is that they need to be wired into electrical circuits. Moreover, they measure only the average strain over the whole area of the strain gauge which may have dimensions greater than the of the order of many mm (e.g. Figure 1(d)). They are therefore not suitable for applications where more local strain measurement is needed or where electrical connections are not possible.

Advances in Science and Technology to Meet Challenges

One possibility of constructing different types of strain sensors using 2D materials is by employing Raman spectroscopy [11] whereby a laser beam is focused on the sensor and the scattered light monitored. 2D materials such as graphene undergo resonance Raman scattering such that a well-defined spectrum can be obtained from a graphene monolayer on the surface of a polymer substrate as shown in Figure 2(a). The resonance Raman scattering is so strong that it swamps any signal from the substrate or from the polymer matrix in a nanocomposite [11]. When the substrate is deformed there is a large shift in the Raman band positions as shown in Figure 2(a). Moreover, the band peak position undergoes a reproducible, linear and reversible shift with strain as shown in Figure 2(b), precisely the behaviour needed for strain gauge applications. Since the exciting radiation is delivered by a laser beam it can be focused to a spot of the order of 1 μm enabling strain measurements over regions of this size. An example of this is shown in Figure 2(c)&(d) where the local strains around a crack in a graphene monomer flake deformed on a substrate are monitored on the micron scale by Raman mapping [12]. Strain measurements with similar resolution can be undertaken in monitoring surface cracks in the polymer substrate under a 2D crystal [13]. An additional advantage of using Raman spectroscopy is that since the laser beam is polarised there is the possibility of using polarised Raman spectroscopy [14] to map strain in different directions.

This research upon carbon materials has been greatly facilitated through the development of improved hardware in the form of Raman microscopes that are essentially Raman spectrometers combined with optical microscopes [15]. They are more versatile and compact than conventional

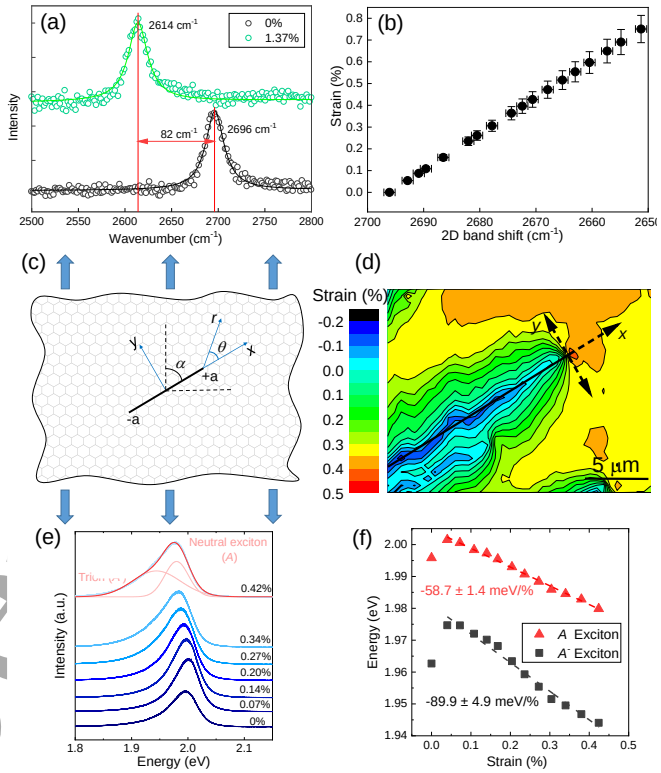

Figure 2 (a) The Raman 2D band of a monolayer graphene flake on a PMMA substrate before and after the application of 1.37% strain [12]. (b) Strain in the graphene determined from the band shift shown in (a) [12]. (c) Schematic illustration of a pre-crack along the armchair direction in a graphene monolayer crystal, on a PMMA substrate, under stress in the vertical direction [12]. (d) The measured strain distribution around the crack tip in the graphene at 0.33% applied strain [12]. Reproduced with permission of John Wiley and Sons. (e) Evolution of the PL spectrum of a monolayer WS_2 flake as strain increases [16] (CC BY 4.0 DEED). (f) The energies of A exciton and A^- exciton peaks as a function of strain, with the solid lines being the linear fits of the data points [16] (CC BY 4.0 DEED).

Raman spectrometers but implementation of these optical strain sensors will, however, require further developments of more compact Raman hardware such as hand-held systems that are not currently available. Some other 2D materials give rise to strong Raman scattering with well-defined strain-induced band shifts and so can be employed in a similar way to measure strain. An analogous technique that can be employed is the photoluminescence (PL) of monolayer 2D transition-metal-dichalcogenide crystals of WS_2 that are direct-gap semiconductors that give rise to strong PL, as shown Figure 2(e). Such PL spectra are obtained using similar spectrometers with focused laser beams and large, well-defined reversible shifts of the PL peaks are found with the application of strain [16] as shown in Figure 2(f).

Concluding Remarks

2D materials are often prepared by liquid-phase exfoliation and this lends itself to the preparation of inks containing 2D material particles that deposit well on surfaces. Resistance strain gauges containing 2D materials printed on a substrate are now well established based upon inks or polymer-based nanocomposites deposited through a variety of printing techniques. The factors that control the sensitivity and strain range of such sensors are now well established, particularly for applications such as in healthcare where a flexible strain gauge and wide range of strain measurement are needed. The possibility of developing a completely new generation of strain sensors based upon the strain-induced Raman band shifts of 2D materials has also been discussed. Such sensors would have the advantage of being able to monitor strain remotely in micron-sized regions with the possibility of directional strain measurement through employing a polarised Raman laser beam. Additionally monolayer transition metal dichalcogenides undergo strong photoluminescence with PL peaks that undergo large strain-induced shifts. This gives rise to an additional non-contact optical technique again based upon 2D materials in the form of printable inks or polymer-based nanocomposites.

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Section 5.1 – Introduction to printable temperature sensors

Tomoyuki Yokota and Takeo Someya

Department of Electric and Electronic Engineering, The University of Tokyo, Tokyo, Japan

Temperature is one of the most commonly encountered physical quantities in our daily lives. It is crucial in various aspects, from weather forecasts to body temperature monitoring for health reasons. Moreover, temperature considerations are crucial in the design of household appliances, such as computers, smartphones, and digital cameras, particularly to reduce the heat generated during their operation[1, 2]. Among the different types of temperature sensors available, resistance temperature detectors (RTDs)[3] and thermocouples[4] are the most commonly utilized. RTDs utilize a metal or semiconductor material whose resistivity changes with temperature. They are known for their ease of miniaturization and high accuracy. On the other hand, thermocouples generate an electromotive force by joining two different metals, creating a temperature difference between the contacts.

When evaluating temperature sensors, key benchmarking elements include sensitivity, linearity, response speed, and temperature range. Sensitivity refers to the percentage change in the output signal, such as the resistance, capacitance, and voltage, for a given percentage change in temperature. Metal-based RTDs typically exhibit constant sensitivity over a wide temperature range (for example, Pt RTDs exhibit good linearity from -200℃ to 600℃). In contrast, semiconductor-based RTDs exhibit high sensitivity within a specific temperature range and low sensitivity outside of this range. In the case of thermocouples, their sensitivity and temperature range are determined by the metals they comprise. A typical thermocouple utilizes a rhodium–platinum alloy and platinum, which provide stability. This thermocouple demonstrates a sensitivity of 5-15 μV/℃ and can effectively operate from 0℃ to 1600℃. Thermocouples exhibit a faster response compared to RTDs. The response speed is defined as the time required for a temperature sensor to respond to a 90% step change in temperature. The heat capacity of a sensor is crucial in determining its response time. The sensor structure should be carefully designed to increase response speed.

Compared with resistance thermometers, thermocouples possess a simple structure and are cost-effective. These temperature sensors have been successfully miniaturized as well, making it challenging to replace them with temperature sensors fabricated using printing processes. However, in recent years, novel applications have emerged that require flexibility[5, 6] and multi-point temperature measurements[7, 8] instead of conventional single-point temperature measurements (Figure 1). Many applications utilize a large area; one notable application is the use of artificial skin in robotics. For instance, it is asserted that the human palm contains approximately four temperature sensors per square centimeter[9]. Therefore, large-area multi-point sensors are crucial for realizing electronic skins. These applications require a high sensitivity of at most 0.1℃, temperature responsiveness similar to human sensory perception, and stability in various environments. Moreover, if the measurable temperature range can be increased, in the sensor can be employed in temperature regulation and quality assurance inspections within industrial production lines. A promising application is in healthcare sensors[10-12]. Because healthcare sensors are expected to measure body temperature over an extended period, placing a temperature sensor that adheres closely to the skin surface is crucial. This can be effectively achieved by utilizing a printing process to integrate the sensor onto a flexible substrate[13, 14]. Unlike conventional rigid substrates, flexible substrates are composed of soft materials, enabling the sensor to conform to the skin's contours and securely attach to it. This enables accurate monitoring of body temperature[15, 16]. In addition to monitoring body temperature, flexible temperature sensors also find valuable applications in wound monitoring[17]. The healing process involves increased blood flow, which results in a slight increase in body temperature. Therefore, the utilization of printed temperature sensors with multiple points allows for the tracking and mapping of wound conditions over time.

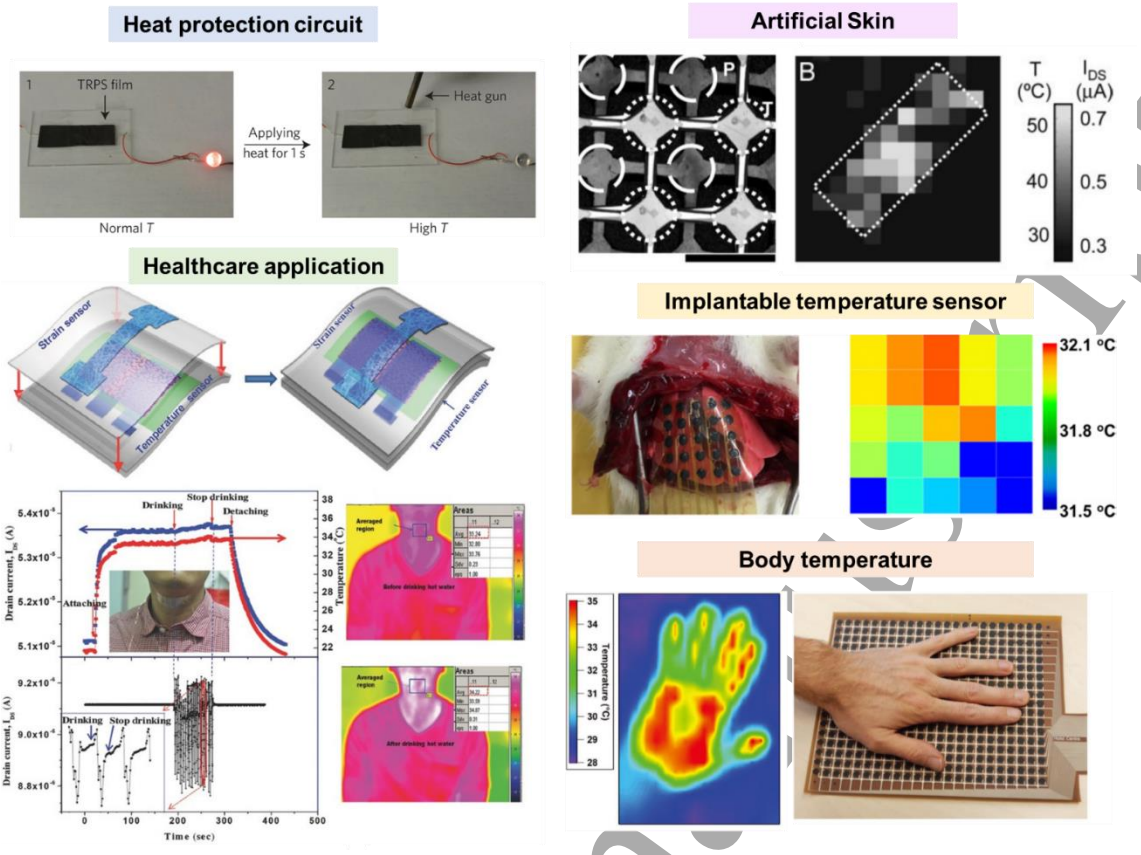

Figure 1 Application of flexible and printable temperature sensors[6, 7, 8, 13, 24]. Reproduced with permission. Copyright 2016 Willey-VCH, 2005 National Academy of Sciences, 2019 Willey-VCH, 2015 National Academy of Sciences, and 2016 Springer Nature.

Therefore, a significant number of temperature sensors that can be fabricated via printing have been developed in recent years. To fabricate a temperature sensor using a printing process, a functional ink that contains a material whose carrier mobility or crystal structure changes with temperature should be fabricated. A wide range of materials are being explored as potential candidates, including polymer materials (Section 5.2) and metals (Section 5.3), which are also utilized in conventional temperature sensors. In addition, next-generation semiconductor materials, such as organic semiconductors and carbon nanotubes (Section 5.4) as well as two-dimensional materials, like graphene and MXene (Section 5.5), are being utilized. The detailed reports on printed temperature sensors for each material are introduced in the following sections. These materials can be transformed into ink by dissolving them in a solvent or by dispersing pulverized nanoparticles or flakes in a solvent. Therefore, temperature sensors can be fabricated on various substrates, such as rubber and polymers by utilizing the printing process. Some printable temperature sensors exhibit properties comparable to those of conventional temperature sensors. For example, nickel ink-based resistance temperature detectors demonstrate a sensitivity of 0.44%/°C and exhibit high linearity within a temperature range of -60°C to 160°C [18]. Furthermore, screen-printed In_2O_3/ITO thermocouples exhibit a sensitivity of 44.5 μV/°C and can be effectively utilized across a wide temperature range from 25°C to 1270°C [19]. However, achieving the same characteristics as conventional sensors using functional inks poses a challenge owing to limitations in materials and processes. In addition, compared with the high-purity materials utilized in conventional temperature sensors, printable materials are limited in that, to process them into inks, organic substances (such as dispersants) adhere to the surface, resulting in poor crystallinity. Consequently, these printable temperature sensors exhibit lower temperature characteristics, lack long-term stability, and have a narrow temperature range owing to the influence of organic

substances. Therefore, technologies, such as the formation of high-purity thin films and the stable dispersion of nanomaterials in a solvent are crucial for industrialization.

Among the printed temperature sensors, flexible RTDs have been extensively investigated[20, 21]. As earlier mentioned, resistance thermometers utilize materials, such as conductive polymers or metals, which exhibit a linear change in resistance with temperature. Therefore, flexible temperature sensors employing silver electrodes[20] formed through a printing process or conductive polymers, such as poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS)[21] have been investigated. Other commonly reported products include thermistors utilizing organic semiconductor materials and oxides. Similar to RTDs, thermistors rely on changes in resistance with temperature. Compared with RTDs, thermistors exhibit a significant non-linear change in resistance[8]. Furthermore, flexible temperature sensors have explored a wide range of materials, such as organic semiconductors[22] and carbon nanotubes[23], providing a diverse selection compared with the aforementioned resistance thermometers. Another widely used printable temperature sensor is the thermistor made of a polymer material[13, 24]. This material is composed of a polymer blended with a conductive filler, which allows for easy viscosity adjustment and exceptional printability. Polymer thermistors are characterized by a large change in resistance near the glass transition temperature or melting point of the polymer. Beyond their application as temperature sensors, their application in protection circuits, such as thermal fuses, has been reported as well.

Concluding Remarks

As elucidated earlier, several studies on the development of printed temperature sensors are underway, with an increasing number of reports showcasing novel applications, such as temperature distribution measurements and measurements of body temperature in daily life. However, several issues regarding printed temperature sensors remain unresolved, such as device variation and the stability of sensor characteristics. To mitigate device variation, it is imperative not only to enhance the stability and uniformity of functional inks but also to enhance printing and drying methods. Another critical concern revolves around the impact of distortion on device characteristics. Unlike conventional sensors that remain solid, flexible substrate-based sensors undergo distortion when the substrate is bent, causing changes in their characteristics. This distortion-induced change is particularly significant for temperature sensors with minimal resistance fluctuations, such as resistance thermometers, rendering accurate temperature measurement unattainable. Furthermore, thermistors exhibit hysteresis in response to temperature changes. Therefore, this hysteresis should be minimized to a certain extent to achieve precise temperature measurements.

Acknowledgements

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Section 5.2 – π-Conjugated polymer-based temperature sensors

Sung Jae Jeon, Naixin Zhaon and Yuning Li

Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN) University of Waterloo, 200 University Ave West, Waterloo N2L 3G1, ON, Canada

Status

π-Conjugated polymers are a special class of polymers with an extended π-conjugated system that endows them with unique electronic properties and can be processed into inks for printed electronics. These polymers can be used for temperature sensors by exploiting their temperature-dependent electrical resistance. Conjugated polymer-based temperature sensors enable low cost, high throughput, and ease of large-scale fabrication, making them attractive for a wide range of applications.

Pristine conjugated polymers have very low conductivity, whereas after chemical, electrical or electrochemical doping they become conductors. In general, charge transport in moderately conductive conjugated polymers follows a variable range hopping model [1], and the resistance of conjugated polymers decreases with increasing temperature, exhibiting a negative temperature coefficient. These characteristics allow conjugated polymers to be used for thermistor type temperature sensors, where chemically doped conjugated polymers are used as the channel material between two electrodes [1–5]. The resistance of the device is measured as the output versus temperature, and the sensitivity is expressed using the temperature coefficient of resistance. Organic field-effect transistors based on pristine conjugated polymers can also be used as temperature sensors [6]. The conjugated polymer channel becomes conductive under a gate bias, and its conductivity varies with temperature in a manner similar to that of chemically doped conjugated polymers. Some conductive conjugated polymers are excellent thermoelectric materials, and their thermoelectric response can used to detect temperature changes [7]. Thermoelectric temperature sensors detect voltage changes caused by temperature fluctuations. Among them, the thermistor type temperature sensors are very simple and easy to fabricate and have been most widely studied. Representative conjugated polymers used for thermistor type temperature sensors are shown in Figure 1.

Conjugated polymer-based temperature sensors have potential applications in various fields, including smart packaging, electronic skin for robotics, biomedical sensing, and environmental monitoring. For example, they can be used to monitor the temperature of perishable goods during shipping and storage. In biomedical sensing, they can be used as smart patches and tattoos to monitor body temperature or detect temperature changes in biological samples. In environmental monitoring,

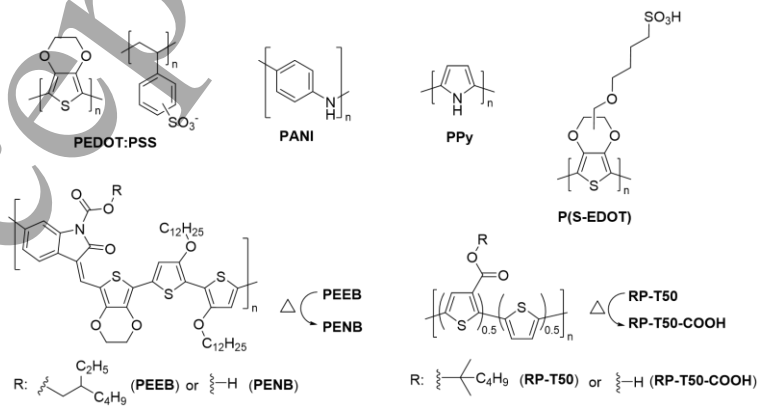

Figure 1 Representative conjugated polymers used for temperature sensors reported in the literature: poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS) [1], polyaniline (PANI) [2], polypyrrole (PPy) [2], P(S-EDOT) [3], PEEB/PENB [4], and RP-T50/RP-T50-COOH [5].

they can be used to monitor temperature changes in air and water. They can be integrated into electronic devices such as smartphones, smartwatches, and wearable technology. Although this research field is still in its infancy, with most of the work done within the past decade, conjugated polymer-based temperature sensors have shown great application potential and accelerated efforts are needed to commercialize this technology.

Current and Future Challenges

Despite their attractive features, conjugated polymer-based temperature sensors still face several challenges that need to be addressed before they become a commercial reality.

Insufficient sensitivity and accuracy. The sensitivity and accuracy of conjugated polymer-based temperature sensors may be affected by numerous factors such as the intrinsic properties of the material, material composition, device configuration, and processing conditions. When conjugated polymers are used as the sole sensing material in thermistor type sensors, the temperature coefficient of resistance of the sensors is typically <1%/°C, which is insufficient for achieving the high accuracy and reliability required for some applications such as monitoring the body temperature of patients.

Poor long-term stability and durability. Conjugated polymer-based temperature sensors are usually not as durable as inorganic material-based sensors, and can degrade over time due to environmental factors such as moisture and UV exposure. For example, PEDOT:PSS-based temperature sensors are extremely sensitive to the ambient humidity due to the highly hygroscopic nature of the dopant PSS. Small changes in the water uptake in PSS lead to microstructural changes, resulting in significant changes in the electrical resistance of PEDOT:PSS. The PEODT:PSS layer can be encapsulated with a hydrophobic polymer layer to improve the ambient stability of the sensor [8]. However, the long term stability of these encapsulated devices remains a concern especially for wearable devices.

Limited sensing temperature range. Conjugated polymer-based temperature sensors typically experience a significant decrease in sensitivity around 40–50 °C due to increased interchain distances in the conjugated polymer phase and/or expansion of the dopant phase at temperatures above this range. In addition, dopants may undergo irreversible phase separation or evaporation, leading to device performance degradation or even failure. The rather low upper sensing temperature of conjugated polymer-based temperature sensors will limit their applications.

Integration with other devices. Conjugated polymer-based temperature sensors need to be integrated with other devices to form a sensor system for real-time temperature monitoring in various applications. The fabrication of the conjugated polymer-based temperature sensors and their performance must be compatible with other devices in the system.

Biocompatibility and environmental considerations. Many conjugated polymer-based sensors will be used in wearable electronics, biomedical devices, and food and drug packaging, and all components of a temperature sensor must be biocompatible. The negative environmental impact of the production and disposal of electronic products is escalating, thus there is a strong demand for the development of green solvent processable and biodegradable temperature sensors.

Advances in Science and Technology to Meet Challenges

There are several advances in science and technology that are needed to meet the challenges associated with conjugated polymer-based temperature sensors.

New materials. The development of conjugated polymers with higher sensitivity, higher stability, and better environmental tolerance is essential to meet the sensor performance requirements. The thermal sensitivity of conjugated polymers is governed by the chemical structure, chain conformation, crystallinity, film morphology, etc. Further studies are required to better understand the structure-sensitivity relationship for developing conjugated polymers with enhanced sensitivity. The instability of the conjugated polymer-based sensors may be caused by the weak polymer-dopant interaction and hygroscopic nature of the polymer and/or dopant. Formation of more stable polymer-dopant charge

transfer complexes, use of non-hygroscopic dopants, strengthening intermolecular interaction, and attaching dopant groups to the conjugated polymer may improve the sensitivity, thermal stability, and long-term stability of the sensors [3–5]. Addition of nanofillers such as carbon nanotubes [9] to the conjugated polymer matrix may also be a viable approach to improving the sensitivity of the sensors.

Different types of polymers should be developed to meet the specific requirements of temperature sensors for various applications. Atom economy, synthetic complexity (or cost), green solvent processability, biocompatibility, and biodegradability should also be considered when developing conjugated polymers for temperature sensors.

Device fabrication and system integration. Traditional roll-to-roll printing techniques such as screen and gravure printing are ideal for manufacturing conjugated polymer-based sensors at low costs, but they may compromise the device performance. In addition, depositing other components (such as electrodes and encapsulation layer) may face issues such as poor compatibility, low resolution, poor registry, and high cost. Therefore, advances in fabrication methods such as additive manufacturing, microfabrication, and nanofabrication are crucial for improving the accuracy and precision of the sensors while reducing their cost and increasing their scalability.

Integrating a temperature sensor with other devices to form a sensor system is the final but crucial step in pushing the sensor to practical applications. The development of compatible interfaces and communication protocols is necessary for the successful integration of conjugated polymer-based temperature sensors with other devices. For example, building a sensor system to measure and store the temperature history of a package would require an antenna, a transponder, and a battery (Figure 2) [10]. The joint efforts from different disciplines are required to develop high-performance and cost-effective conjugated polymer-based temperature sensors for practical applications.

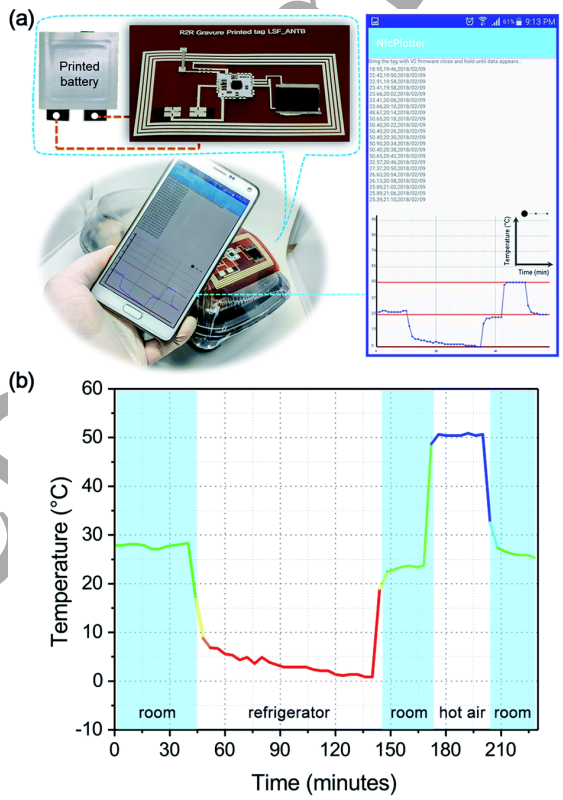

Figure 2 Real-time testing and validation of the time–temperature history monitoring system. (a) The smartphone displays the temperature history log extracted from the NFC thermistor attached to the chicken package. (b) Magnified view of the logged temperature data under different conditions [10]. Reproduced from Ref. [10] with permission from the Royal Society of Chemistry.

Concluding Remarks

Conjugated polymer-based temperature sensors have shown great potential in various emerging applications such as wearable electronics, electronic skin, biomedical devices, and food packaging. As the enabling materials, conjugated polymers play a vital role to meet the stringent requirements for accuracy, reliability, temperature range, mechanical properties, and cost of the sensors. Since this is a relatively new research area, only a limited number of conjugated polymers have been explored. PEDOT:PSS has been most widely used for conjugated polymer-based sensors. However, its high hygroscopicity leads to low sensor sensitivity and poor stability and additives are needed to increase the devise sensitivity. Therefore, there is an urgent need to develop new conjugated polymers with higher sensitivity and long-term stability to meet application demands. Biocompatibility, green manufacturing, and biodegradability are additional challenges in developing conjugated polymers for temperature sensors. The final step, integration of conjugated polymer-based sensors with other devices and elements to form high-performance, cost effective, and green sensor systems is also very challenging, which requires joint efforts of several disciplines. Nonetheless, the development of new materials, substrates, and fabrication techniques is expected to make conjugated polymer-based temperature sensors a commercially viable technology and widely used in various applications in the near future.

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Section 5.3 – Printed metals for temperature sensing

Darpan Shukla, Shuang Wu and Yong Zhu

Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC, 27695, United States of America

Status

Temperature measurement can be performed using thermocouples, resistance temperature detectors (RTDs), and thermistors (Figure 1). Thermocouples are constructed using two metals or metal alloys. They usually operate in a temperature range of −270 °C to 1600 °C with a Seebeck coefficient varying from 5 μV/°C to 40 μV/°C. Conventionally, thermocouples are fabricated by sputtering or microfabrication. Low-cost fabrication methods such as printing have been utilized for fabricating thermocouples. Printed thick thermocouples would lead to long response time. Hence, the recent focus has been on printing thin-film thermocouples. Platinum-gold based thin-film thermocouple was fabricated using screen-printing. The response time of the platinum-gold thermocouple was 8.6 μs, 10.1 μs, 11.2 μs, and 12.3 μs with thickness of 2.7 μm, 5 μm, 16 μm, and 20 μm, respectively.[1] High sintering temperature associated with printed metals for thermocouples such as platinum can hinder their use on polymeric substrates. Silver and nickel-based screen-printing inks were used to lower the sintering temperature to 200 °C; the silver ink included 70 wt% silver content and flake size of 1.5 to 4 μm, while the nickel ink had 62 wt% nickel content and particle size of 2 to 10 μm. The printed silver-nickel thermocouples demonstrated a linear response in the temperature range of 40 °C to 240 °C. It was also insensitive to the sintering level with a constant Seebeck coefficients of ~20 μV/°C for different sintering conditions.[2] In addition to lowering the sintering temperature, performance of the printed thermocouples under mechanical deformation and external environment such as humidity and oxidation should be stabilized. Flexible thermocouples were inkjet printed using liquid metal–organic decomposition materials, consisting of copper and copper-nickel particle-free conductive inks. The Seebeck coefficient for the thermocouple was recorded to be 20.6 μV/°C, insensitive to external stimuli, such as bending, humidity, and thermal cycling.[3] Understanding the influence of micro- and nano-structure of the printed film on the electrical and mechanical performance of the thermocouple is important. A thermocouple was aerosol jet printed on a flexible Kapton substrate using commercial copper and copper-nickel inks. The copper and copper-nickel nanoparticles have the size of 86 ± 4 nm and 140 - 210 nm, respectively. The Seebeck coefficient of the thermocouple varied with only 2.5% of its initial value (39.83 μV/°C) after 200 bending cycles with a bending radius down to 25 mm and 200 twisting cycles at an angle of 120°. The stable performance of the thermocouple under repeated mechanical load was attributed to the porosity of the sintered nanoparticles in the film. The fused copper and copper-nickel nanoparticles lowered the effective elastic modulus of the film by an order of magnitude when compared to the bulk. This allowed the film to reduce stress build-up during bending and twisting.[4] An inherent drawback of thermocouples is that small voltage signal that would require a signal amplification and translation circuit.

RTDs are characterized with positive temperature coefficient. They exhibit linear response and benefit from simplified sensor design. For RTDs, a high temperature coefficient of resistance (TCR) is preferred. Commonly used metals for RTDs are copper, nickel, platinum, silver, and gold among them nickel has the highest TCR. A commercial thermoplastic polymer/resin-based nickel flake ink was used as a sensing material for RTD. The ink was screen-printed on a flexible polyimide substrate followed by thermal curing at 130 °C for 15 min. The nickel-based RTD monitored temperature ranging from -60 °C to 180 °C with a TCR of 0.44%/°C, 3 times higher than the TCR of a printed silver-based RTD (0.1%/°C). It also showed good repeatability under dynamic heating and cooling cycles between -40 °C to 160 °C.[5] Nanomaterials such as nanoparticles and nanowires exhibit different properties from their bulk counterparts, offering great potential for printed temperature sensors. For instance, metal

nanoparticles have a significantly lower melting temperature than their bulk, allowing printing on polymer substrates. Stable platinum nanoparticle-based ink was inkjet printed for the fabrication of a resistive heater and an RTD. For printing, thiolate ligand-stabilized platinum nanoparticles with size ranging from 3 to 5 nm were synthesized. Then, a highly conductive ink with 15 wt% platinum nanoparticles dispersed in a toluene-terpineol mixture was formulated. Use of nanoparticles allowed the sintering temperate to be 200 °C, significantly lower than the conventional sintering temperature of the bulk platinum. The RTD showed linear resistance-to-temperature response from room temperature to 130 °C.[6] Additionally, nanoparticle-based metallic inks can permeate textiles, which can be used for the development of flexible wearable sensors.[7] However, the resistance change in wearable RTDs can be influenced by the human body motions. A Kirigami-inspired strain insensitive wearable RTD based on silver nanowires was fabricated by spray deposition. The sensor was characterized in the wearable temperature range of 25 °C to 60 °C. The designed Kirigami pattern accommodated large tensile strain up to 100% by out-of-plane rotation showing a negligible resistance change. TCR of the silver nanowire network embedded in polyimide film could be enhanced by increasing the nanowire density and annealing temperature, approaching TCR of bulk silver (3.8×10^{-3} /°C at 20 °C). For example, the sensor displayed a TCR of 3.32×10^{-3} /°C for silver nanowire density of 2.053 per μm^2 and annealing temperature of 200 °C. The silver nanowire-based wearable RTD was used to measure skin temperatures at the biceps and knee.[8] Thermal and electrical sintering of silver nanoparticle-based printed RTD enabled a TCR of 3.8×10^{-3} /°C at 22 °C. After printing, conditions for thermal sintering were optimized by in-situ resistance measurement on the aerosol jet printed silver pattern. Next, electrical sintering generated localized heat at the grain boundaries, increasing grain coalescence, and thus improving TCR. The printed RTD displayed reliable and linear response up to 70 °C.[9]

Thermistors can have either positive or negative temperature coefficient. They are typically fabricated using either ceramic-type semiconductor materials or polymer-based materials. Please refer to chapter 5.2 and 5.6 for polymer and ceramic based thermistors, respectively.

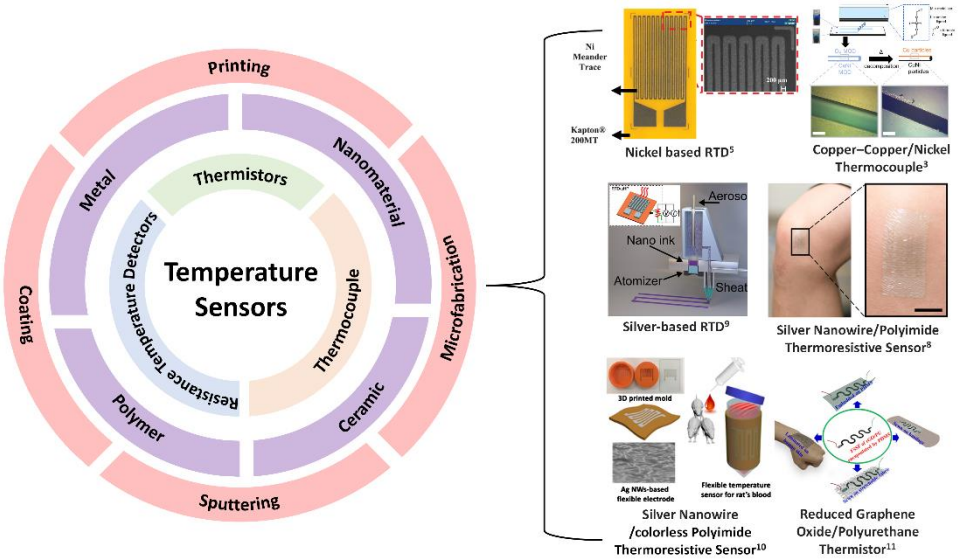

Figure 1 Schematic showing different types of temperature sensors, fabrication techniques, and sensing material. Inkjet printed copper and copper-nickel based thermocouple. Reprinted with permission from [3]. Copyright (2022) American Chemical Society. Screen-printed nickel based RTD on flexible polyimide substrate.[5] Aerosol jet printed silver based RTD. Reproduced with permission from [9]. John Wiley & Sons. © 2023 Wiley-VCH GmbH. Kirigami-inspired thermoresistive temperature sensor based on silver nanowires. Reproduced with permission from [8]. John Wiley & Sons. © 2019 Wiley-VCH GmbH. AgNW-colorless polyimide film-based temperature sensor for monitoring the temperature of blood packages. Reprinted with permission from [10]. Copyright (2018) American Chemical Society. Stretchable temperature sensor based reduce graphene oxide and polyurethane. Reprinted with permission from [11]. Copyright (2019) American Chemical Society.

Current and Future Challenges

Sensitivity. The higher the sensitivity in either voltage (thermocouple) or resistance change (RTD and thermistor), the smaller the temperature change that can be detected by the sensor. For health monitoring applications, the stable human body temperature usually ranges between 37 °C and 37.5 °C, which requires high sensitivity. To improve the sensitivity of printed metal enabled temperature sensors, choice of metal materials (platinum, copper, nickel, silver) nanostructure of metallic component (e.g., nanoparticles, nanowires, nano meshes) and fabrication processes are the main challenges. For example, compared with the classic Pt temperature sensor (TCR = 0.0055 K^{-1}), the TCR of Gr-PDMS composite material can reach up to 0.286 K^{-1}.[12]

Response time. Response time is related to the thermal response of the printed metal itself and reflects the rapid response ability of the sensor to temperature change. Challenge lies in applications such as real-time human body health-monitoring and wearable artificial intelligent elements with an instant response.[13] A Xene-AgNW-PEDOT:PSS-pp:TeNW temperature sensor exhibited a response time of 1.8 s, and a relaxation time of 6.5 s, which might not be sufficient for some real-time applications, for example, temperature-based respiration sensing.[14]

Accuracy. Most methods for measuring temperature require contact between the sensors and the subject. The quality of contact is hence the key to accurate temperature measurement. The printed temperature sensors provide some level of flexibility thus decent quality of contact with the subject. However, for high-precision temperature measurements, it remains challenging to develop highly conformable printed temperature sensors. The printed metal-based temperature sensors provide some level of flexibility. However, for high-precision temperature measurements, it remains challenging to develop highly conformable printed temperature sensors.

Stability. Stability means stable measurements against external stimuli and under prolonged, cyclic application. As mentioned above, some printed metals suffer from environmental degradation, such as oxidation and corrosion. It is important to maintain stable performance when other types of loadings are present such as mechanical deformation. Some progress has been made towards the durability of printed metal-based temperature sensors in harsh environments. For example, an oil/PDMS encapsulated sensor has shown good sensing performance under a 35 PSU salinity water environment.[15] It remains challenging to develop temperature sensors with excellent material and mechanical stability for long-term applications.

Additional challenges for wearable applications. For wearable applications, printed temperature sensors offer several advantages including softness, stretchability, and conformability. User comfort is a crucial issue for long-term temperature measurement. To improve the comfort, the substrate for printing should be thin, lightweight, conformal, and breathable.

Advances in Science and Technology to Meet Challenges

Printed metal-based temperature sensors have seen exciting advances. However, limitations exist including high sintering temperature, little resilience to external environment, low sensitivity, and poor mechanical robustness. Nanocomposite is a promising approach to improve the performances when compared to pure metal-based temperature sensors. In particular, it is promising to formulate a conductive hybrid ink which utilizes multiple nanomaterials in its formulation. In a recent example, a hybridized ink comprising of silver, copper, and nickel nanoparticles had the potential to increase the overall sensitivity of the printed temperature sensor by 300%.[16] Formulation of a hybrid ink will involve careful consideration of the compatible metallic nanoparticles, compatible solvent/additives with different nanoparticles, and a suitable printing method. Additionally, the concept of hybrid ink can also be extended to include carbon-based nanomaterials such as graphene and carbon nanotubes with the metallic nanoparticles. For example, incorporation of carbon-based materials could mitigate oxidation of metals like copper for high-temperature sensing.

For wearable applications, the effect of mechanical deformation on the performance of the temperature sensor must be eliminated. One approach would be to significantly increase the sensitivity of the temperature sensor such that the signal due to mechanical perturbation is negligible. The other approach is to create material/structure whose resistance or thermoelectric response does not change with mechanical strain. In addition to exploiting the intrinsic stretchability of the printed metallic nanomaterial, a variety of stretchable designs such as Kirigami, fractal, serpentine, mesh-shaped, and island-bridge can mitigate the mechanical effect.[17], [18], [19] Additionally, textile-based temperature sensors can seamlessly integrate with human bodies and offer the benefits of lightweight, conformal, and breathable wearable electronics.

Printing and postprocessing processes are key to the performance of printed temperature sensors. Sintering plays a key role for the nanomaterial-based temperature sensors.[20] Novel sintering methods that are compatible with low-thermal-budget substrates are in great need. For example, it was demonstrated that laser reductive sintering could increase the activation energy required for electrical conduction in nickel oxide, which in turn could increase the sensitivity.[21] Sustainable manufacturing is a promising direction to reduce the footprint of plastic-based substrates for printed temperature sensor. This can be achieved by utilizing biodegradable substrates and recycling of the metal nanomaterials used in the printed temperature sensors.[22]

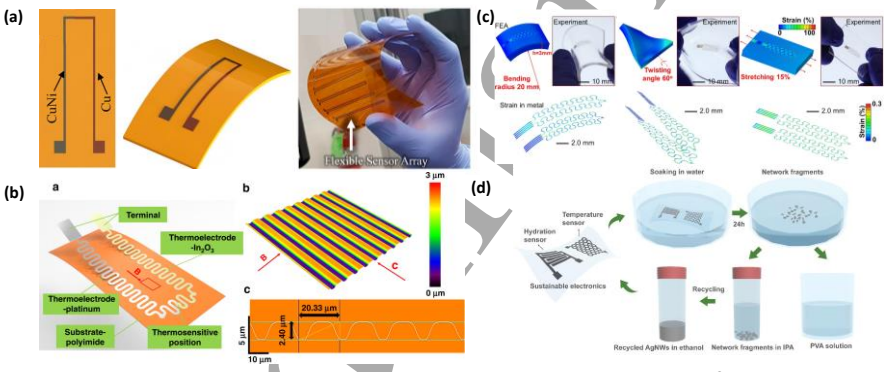

Figure 2. (a) Aerosol jet printed copper and copper-nickel temperature sensor on flexible Kapton substrates. Reprinted with permission from [4]. Copyright (2019) American Chemical Society. (b) Flexible sensor consisting of two temperature sensing curved electrodes, i.e., platinum and indium oxide (In_2O_3).[18] (c) Finite elemental analysis and optical images of a differential temperature sensor under various mechanical deformations such as bending, twisting, and uniaxial stretching. Reproduced with permission from [19]. John Wiley & Sons. © 2015 Wiley-VCH GmbH. (d) Recycling process for printed silver nanowire-based sensor. Reproduced with permission from [22]. John Wiley & Sons. © 2021 Wiley-VCH GmbH.

Concluding Remarks

Printing metals for temperature sensing has gained popularity due to their low-cost fabrication, high scalability, and less material wastage. The ability of the metallic nanomaterials to be dispersed in an ink or be constituted as conductive filers in a composite has provided better sensitivity, reliability, anti-oxidation, and superior mechanical performance. However, more research is needed for development of hybrid inks, hybrid composites, and hybrid printing processes to overcome the challenges presented by individual metallic nanomaterials and printing processes. Hybrid printing will allow the fabrication of printed metals on textiles, paving their way for wearable sensing. Since printed metals show a change in resistance with temperature, different structural designs such as Kirigami, serpentine, or fractal patterns need to be incorporated to decouple the influence of mechanical stimulus especially for wearable applications. Lastly, recyclability of the printed metals for temperature sensors is important for an eco-friendly manufacturing approach.

Acknowledgements
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Section 5.4 – Carbon nanotubes for temperature sensing

Kuniharu Takei

Graduate School of Information Science and Technology, Hokkaido University, Sapporo 060-0814, Japan

Status

Carbon nanotubes (CNTs) are a potential material for printed temperature sensors, owing to their mechanical flexibility and ease of mass-production at low-cost[1-7]. Furthermore, the ability to control CNT conductivity by selecting appropriate metals and semiconductors, which can be modified based on wall thickness, i.e., single-wall or multi-wall and chirality, is advantageous in designing sensors for specific applications. However, for printed sensors using CNTs, several things need to be considered. CNT networks or composite thin films can be formed on a variety of substrates at low-cost using mass fabrication processes. Without a networked thin film, electrical conductivity, which is an essential property of resistive temperature sensors, cannot be realized. To achieve conductivity, CNTs must be sufficiently concentrated when dispersed in an ink for uniform printing. If other polymer materials are used to form CNT network films, the concentration of CNTs needs to be about <10 wt% to prevent aggregation of CNTs in the polymer.

After considering material composition and formation methods, then the sensor can be characterized in terms of sensitivity, stability, and repeatability. Most cases using CNTs for temperature sensor application are to measure two-terminal electrical resistance by printing Ag or other electrode materials onto CNT-based films. This section focuses only on resistive-type temperature sensors to discuss sensing mechanisms, electrical performance, and challenges to practical applications.

Current and Future Challenges

Two main sensing mechanisms using CNT-composite materials are explained. The first is the use of CNT temperature coefficient of resistance (TCR) only. Every conductive material has a TCR function due to electron scattering or hopping in the material. Depending on electron behaviors, resistance increases or decreases as temperature increases. For example, a CNT and graphene oxide composite film has been reported to form a highly sensitive temperature sensor[7]. According to that report, single-walled CNTs (SWCNTs) show a high TCR of ~60×10^{-3} °C^{-1} compared to other CNT-based sensors [1, 3, 6]. In the foregoing case, resistance decreased as temperature increased. Graphene oxide served as a lubricant to prevent CNT aggregation in the ink, which is important for printed sensors. Another mechanism is electron hopping at the interface between CNTs and other conductive materials in the composite film in addition to TCR. One example is a mixture of SWCNTs and SnO_2 nanoparticles [4, 6]. Since the interface between these two materials detects temperature differences, sensitivity is varied by changing the ratio of SWCNTs and SnO_2. Notably, the TCR of SnO_2 nanoparticles, which is much larger than that of CNT, is negligible, because it has a much larger resistance than does CNT, such that sensor resistance is defined mainly by the CNT resistance. After optimizing the composition ratio, the sensitivity is ~2×10^{-3} °C^{-1}, which is relatively low compared to the CNT/graphene oxide system. However, although the sensitivity is low, it achieved long-term stability, which is a challenge for printed sensor applications.

For printed temperature sensors, reproducibility and stability of sensor output are two important parameters. Since a temperature sensor must output absolute values of temperature, it is unacceptable to have hysteresis or sensor output drift over time. However, due to the use of organic materials as ink lubricants or solvents, printed temperature sensors are often unstable for a long-term use. One approach using a CNT and SnO_2 composite film showed relatively long-term stability with an error less than 0.15°C in the period of about a week [6]. The study tried to remove organic solvent

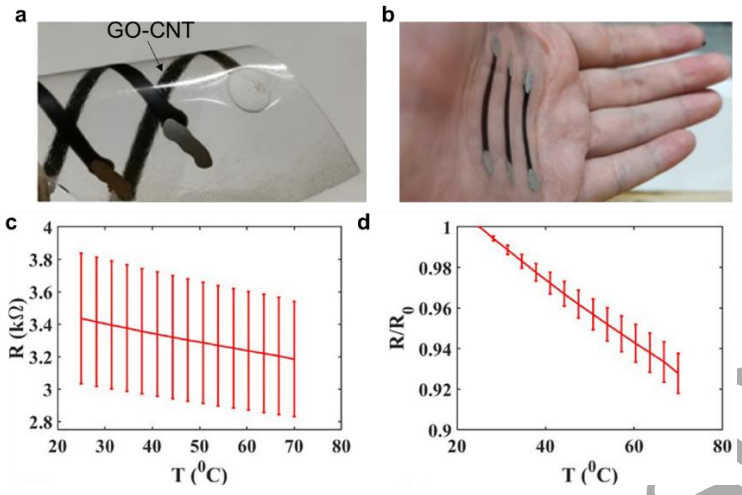

Figure 1 Graphene oxide-CNT temperature sensor. Photos of sensors (a) under bending and (b) on a hand. (c) Resistance and (d) normalized resistance as a function of temperature. Reproduced with permission. [7] Copyright 2021, American Chemical Society.

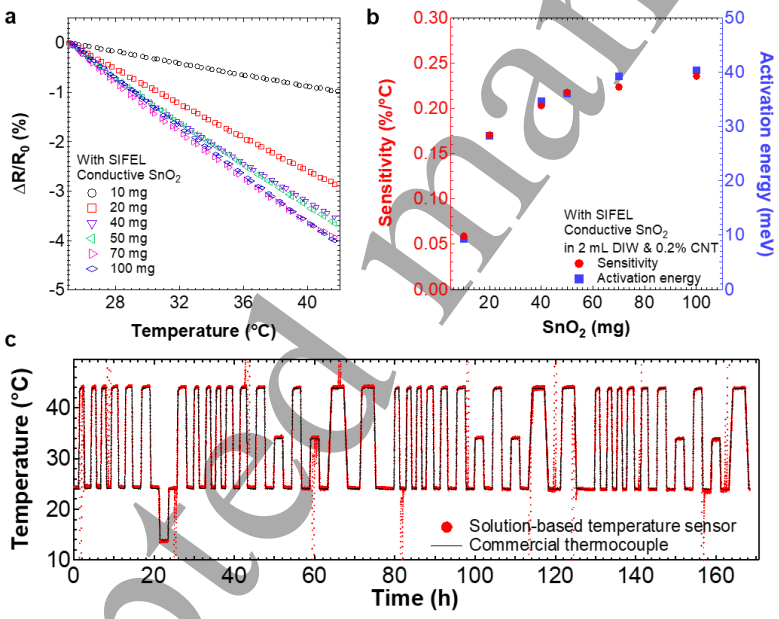

Figure 2 CNT-SnO_2 temperature sensor. (a) Resistance change ratio at different SnO_2 compositions in a CNT ink and at different temperatures. (b) Sensitivity and activation energy of the sensor with different SnO_2 compositions. (c) Long-term temperature monitoring compared to the output of a commercial thermocouple used in a temperature-controllable oven. Reproduced with permission. [6] Copyright 2019, John Wiley & Sons.

from the printed thin film by rinsing with hot water after pre-curing the materials. While at present this may be one way to achieve stability and repeatability of temperature detection, much more stable materials must be developed in the future.

Another important parameter is selectivity between temperature change and other stimuli. Printed CNT-based temperature sensors are often used in flexible sensors. Accordingly, mechanical flexibility and insensitivity to bending, i.e., strain, are required. Since CNTs have small diameters, strain distribution in single CNTs is small, in principle. However, by combining CNTs with polymers to form composite films, this strain needs to be considered. To minimize the effect of strain or bending of the

substrate, CNT-based temperature sensors are usually designed to be in neutral regions of strain against bending by adding a film substrate over the sensor. This protective layer also blocks other stimuli such as moisture, which would otherwise cause resistance changes. In fact, a CNT/SnO_2 temperature sensor was passivated to achieve highly stability using a fluorine elastomer to block moisture [6]. In consideration of these issues, device structures, including film lamination over the sensor, should be carefully considered when designing a sensor.

Advances in Science and Technology to Meet Challenges

In the future, the primary challenge in relation to CNT-based temperature sensors will be how to realize long-term stability and reliability, similar to commercially available thermistors, Pt temperature sensors, and thermocouples. To address this challenge, surface functionality of CNTs and other composites must be understood and must be developed based on a knowledge of surfaces and their modifications. Although sensitivity is also an important parameter for detecting small temperature changes in medical applications, without improving reliability, it may be difficult to use flexible sensors as temperature sensors.

Acknowledgements

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Section 5.5 – 2D materials for temperature sensing

Yubin Huang, Jean Spiece and Pascal Gehring

Institute of Condensed Matter and Nanosciences, Université catholique de Louvain (UCLouvain), 1348 Louvain-la-Neuve, Belgium

Status

2D materials offer significant opportunity for developing high-performance temperature sensors based on changes in their electrical resistance (resistance temperature detectors (RTD) and thermistors) and on thermoelectric effects (thermocouples). This is due to their high carrier mobility and high thermal conductivity leading to high sensitivity to temperature changes and fast response times. To this end, first demonstrators of RTDs based on single sheets of graphene (see Figure 1a) [1] show high sensitivity due to the low thermal mass, reaching that of commercial Platinum RTDs.

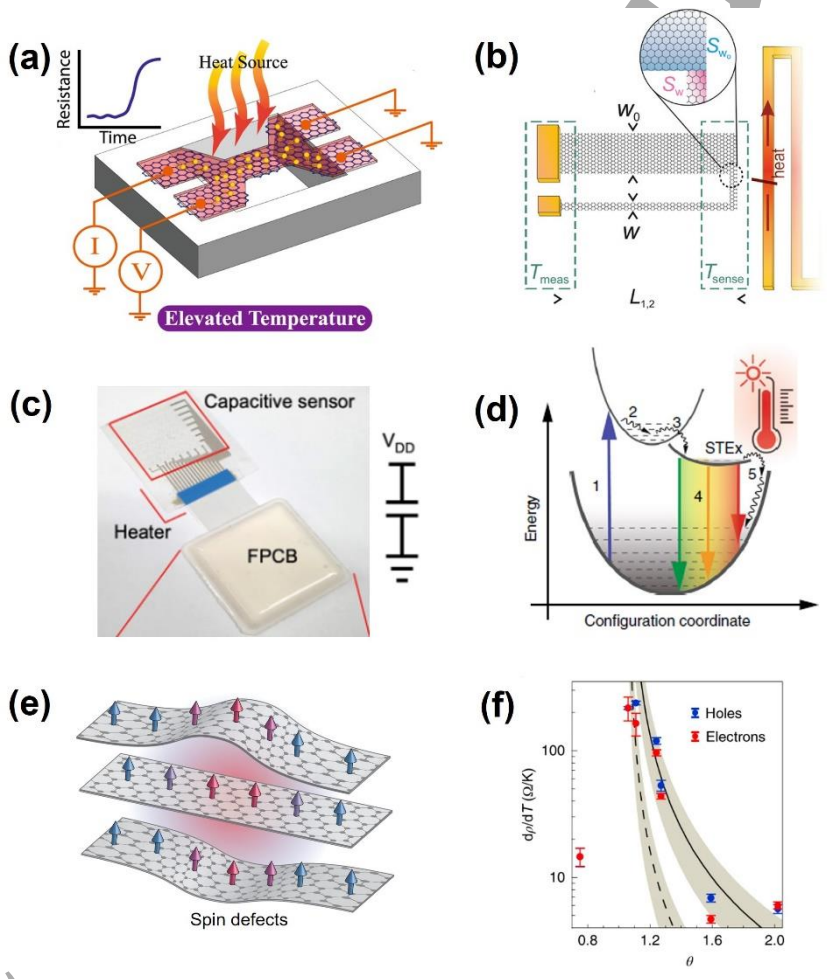

Figure 1 Temperature sensors based on 2D materials. Schematic view of (a) the single graphene thermoresistive sensor. Reproduced from [1]. (b) the U-shaped single-material graphene thermocouple. Reproduced from [5]. (c) the graphene/epoxy-based capacitive temperature sensor. Reproduced from [6]. (d) Energy diagram depicting the process of self-trapped excitons (STEs) with strong temperature dependence of the photoluminescence. Reproduced from [7]. (e) A local temperature increase causes the hexagonal boron nitride lattice to expande and produces detectable spins shift in the resonant frequency. Reproduced from [8]. (f) the dρ/dT curve of twisted bilayer graphene (tBLG) devices for different twist angles θ and carrier concentrations. Reproduced from [20].

Furthermore, other 2D materials like transition metal dichalcogenides, MXenes show high electrical conductivity and Seebeck coefficient, resulting in high thermovoltage output and sensing resolution [2, 3], ideal for thermocouple operation. In some 2D materials like graphene, the good sensing performance is preserved over wide working temperature ranges, and even in harsh environment, making them suitable for high-temperature sensing applications like fire alarms [4]. Besides their advantages, there are some properties specific to 2D materials that can limit their sensing performance. For example, a RTD based on a single layer graphene can be influenced by surface defects, edges or even its substrate [1].

Thermocouple-based sensors typically require a junction between two materials with different Seebeck coefficient which can be realized by stacking different 2D materials (*e.g.* MXene and graphene [2], WS_2 and $NbSe_2$ [3]) on top of each other, or by geometrically patterning a single material [5]. The latter has been applied to fabricate single material graphene thermocouples with a U-shaped pattern [5] (see Figure 1b), achieving a maximum sensitivity of $\Delta S \approx 39\ \mu V\ K^{-1}$. A few studies have also explored using other temperature-dependent physical quantities beyond the electrical ones to develop temperature sensors in 2D materials, which involves detecting changes in capacitance [6], photoluminescence intensity [7] and spin shift [8] and may offer other ways to temperature sensors (see Figure 1c-e).

Advances in fabrication technology have enabled researchers to accurately engineer the electronic band structures and geometry of 2D materials to improve temperature sensing performance. 2D material inks allow for making large-scale temperature sensing pathways or films. For example, a printed MXene temperature sensor based on thermally activated electron transport was formed on a flexible polymer substrate [9]. Lastly, 2D materials can be ultimately scaled to the single atomic layer limit. Such ultra-thin temperature sensors can be integrated into micro-/nanoelectronics, wearable devices and robotic systems [10]. Table 1 summarises and compares the performance of several 2D materials that have been used to fabricate temperature sensors.

Table 1 Performance of temperature sensors based on 2D materials.

Material	Sensor type	Temperature range	Sensitivity	Reference
Graphene single flake	RTD	10 to 30 °C	0.22% K^{-1}	[1]
MXene/Graphene film	Thermocouple	0 to 200 °C	53.6 μV K^{-1}	[2]
WS_2/$NbSe_2$ film	Thermocouple	10 to 60 °C	82-90 μV K^{-1}	[3]
Graphene oxide/polydopamine	Thermistor	100 to 350 °C		[4]
Graphene single flake	Thermocouple		39 μV K^{-1}	[5]
Graphene/SU-8 epoxy	Capacitance	10 to 60 °C	40.4 fF K^{-1}	[6]
Tin-halide perovskites	Luminescence	–100 to 110 °C	20 ns K^{-1}	[7]
hexagonal boron nitride film	Spin	5 to 350 K	-623 kHz K^{-1}	[8]
MXene film	RTD	20 to 55 °C	0.066% K^{-1}	[9]
Twisted bilayer graphene	RTD		7% K^{-1}	[20]

Current and Future Challenges

Fabricating a good 2D materials temperature sensor involves the preparation of high-quality 2D materials and their integration in functional devices. Some 2D materials are air-sensitive making them unreliable over time. Also, due to their large surface-to-bulk ratio, 2D flakes are prone to electrostatic changes of their electronic properties by the substrate, by the atmosphere/gases or by contaminants. This makes them highly susceptible to changes of their surrounding environment, which can then cause fluctuations in the temperature sensing signal. Finally, a thermocouple sensor usually requires two differently doped 2D materials. Even though some 2D materials naturally possess an intrinsic doping due to their fabrication process, it is desirable to control the type of majority carriers and their density precisely. This is however still a key challenge, because most doping methods developed for bulk semiconductors cannot be directly applied to 2D materials. What is more, methods that have been demonstrated to dope 2D materials – which include chemical vapor transport (CVT), charge transfer and plasma treatment – are time-consuming, unstable over time and can damage the crystal structure [11].

The integration of 2D materials into a single-flake temperature sensor requires to control precisely the position and alignment of the flakes, as well as the contacts on the 2D materials. However, it is hard to prepare high-quality 2D materials with large lateral sizes. When printing small 2D flakes, the electrical resistance (and its temperature dependence) of the resulting film is mostly dominated by the (often weak) electronic coupling between the 2D flakes rather than by the intrinsic properties of the single flakes themselves. Additionally, enabling a low access resistance to the thermometer requires making good ohmic contacts on 2D materials. This is inherently problematic for 2D semiconductors like MoS_2 or WSe_2 where often non-ohmic contacts and high Schottky barriers due to Fermi level pinning are observed [12].

Understanding heat transfer in a temperature sensor is essential to achieving precise temperature measurement. This depends on the material and geometric configurations. The low thermal conductance of some substrates like polymers can increase the response time. Meanwhile, ultrathin 2D flakes have low heat capacity, leading to a weaker electrical response to temperature changes. Additionally, the deformation of 2D material induced by thermal expansion or external mechanical forces may add strain on flakes, resulting in an alteration of their electrical and thermal properties, and in extra electrical signals caused by piezoelectric and flexoelectric effect [13]. Therefore, the current limits to their sensitivity may not be viable for some specific applications that require to detect tiny temperature changes, such as local heating in scientific research or biological processes.

Advances in Science and Technology to Meet Challenges

Further improvements are needed in mass production, doping techniques and surface functionalization. Often bulk sensors do not possess the high sensitivity found in mechanically exfoliated single crystalline flakes. To this end, the surface chemistry must be controlled to ensure a low contact resistance between individual flakes and to passivate them from their environment. Some 2D materials with reactive surfaces (e.g., MXenes, graphene oxide) might offer simple and scalable strategies for optimization [14]. 2D materials inks [15,16] allow researchers to develop large-scale temperature sensors by forming a network junction and uniform films with desired geometry on various substrates. Nonetheless, further efforts are needed to solve the self-stacking problem of 2D material inks [15]. Typical metal contacts on 2D materials often result in large access resistances, which can be improved by defect engineering [17] or thickness modulated doping [18]. Furthermore, some recent experiments [11, 12] have achieved low contact resistance using Sb and Bi contacts with van der Waals materials.

Encapsulation layers (e.g., hexagonal boron nitride, polymer coatings) and surface modification are being explored to improve the air- and moisture-stability of 2D materials. Although hexagonal boron nitride encapsulation has been demonstrated to successfully prevent highly air-sensitive materials from degradation over months, this method still lacks scalability.

The sensitivity of thermocouples depends on the difference of Seebeck coefficient of two materials. The magnitude of the Seebeck coefficient can be increased by introducing sharp changes of the DOS at the Fermi energy. To this end, it has been demonstrated that dilute isovalent sulfur doping of Bi_2Te_2Se flakes can alter the effective mass of charge carriers and thus almost double the Seebeck coefficient [19].

It is worth mentioning that – for devices consisting of single flakes – there are alternative proposals to reach high sensitivities. As an example, it has been demonstrated recently that by twisting two single layers of graphene [20], electron-phonon interactions could be increased. To this end, by engineering a twist angle of 1.24° between the two layers, sensitivities of up to 300Ω/K (≈7%/K) can be reached (see Figure 1f). Furthermore, optical temperature sensing (*e.g.,* photoluminescence [7]) and quantum-sensing technologies (*e.g.,* spin defects in hexagonal boron nitride [8]) allow to detect small temperature changes with high spatial resolution. The exciton emission lifetime of perovskites and resonance frequency of spin in hexagonal boron nitride are strongly temperature-sensitive, making them excellent temperature sensors. For temperature sensing down to mK temperatures, superconducting junctions of 2D materials [21] could serve as highly sensitive thermometers. Lastly, the temperature dependence of mechanical properties of 2D materials can be exploited to fabricate sensors based on membranes, where single layer graphene resonators showed a change of quality factor by one order of magnitude within 100 Kelvin [22].

Concluding Remarks

The field of 2D materials has grown rapidly over the past two decades, offering a great platform for printable devices in temperature sensing. Despite some reported progress in 2D materials for temperature sensing, only a limited number of 2D materials are currently available for large-scale applications. This stems mostly from the low control of inter-flake couplings in printed films which results in a large difference between single-flake and bulk-film behaviour. With respect to performance, 2D materials potentially enable high speed temperature read out due to their high electron mobilities and high thermal conductivities. Therefore, it is essential to combine theoretical, experimental, and computational methodologies to further study and optimize the performance of 2D temperature sensors by exploiting novel and unique functionalities like the tunability of 2D materials by defect engineering, van der Waals heterostructures, and twisted moiré systems.

Acknowledgements

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Section 6.1 – Introduction to Printable Gas/Vapour Sensors

Krishna C. Persaud

Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom

Gas or vapour sensors can be realised using many different materials, based on a variety of working principles. They are used in many applications, often related to health and security such as air quality monitoring (indoor and outdoor), vehicle emissions, toxic and hazardous gas alarms, personal healthcare - medical screening and diagnosis, food quality monitoring, agricultural and farming emission monitoring. Some sensors are designed for single use – such as smart food labels. Others are used for continuous monitoring of an environment or process. Electronic noses[1] utilise an array of different gas sensors that display broad overlapping specificity to different chemical families, to produce a response pattern that allows fingerprinting a complex mixture of compounds and discrimination of complex mixtures[2]. For these sensors to be successful they need to be sensitive to target volatiles, respond rapidly and reversibly, and have reasonable selectivity to gases or vapours of interest. Desirable features are low-manufacturing cost, stable operation over many cycles of use, and low power consumption.

Common gas sensor technologies include electrochemical redox gas sensors, chemoresistive sensors where there is a change in conductance proportional to the concentration of the target gas, capacitance based sensors, organic field-effect transistors showing a change in source-drain current in response to a gas, mechanical sensors such as quartz crystal microbalances, surface acoustic wave devices, micro and nano electro-mechanical Systems displaying a change in resonant frequency due to interaction of gases on a surface, together with optical gas sensors where the change in optical absorption may be measured. Target gases of commercial importance to the gas sensor industry include reducing gases such as CO, H_2, CH_4, oxidising gases such as O_3, NO_x, Cl_2, requiring detection limits in the ppm region, gases such as H_2S and SO_2 and NH_3 requiring detection at ppb levels, and others such as CO_2, alcohols, O_2 where very high concentrations (1% or higher) need to be detected. Electrochemical gas sensors are generally much more selective to target gases, but more expensive than other gas sensor technologies. Low-cost gas sensors based on metal oxides show lower selectivity and cross react with other potentially interfering gases and vapours. Printed gas sensors based on these materials show much the same performance as their counterparts manufactured traditionally[3]. Electronic nose applications have opened the need for sensors that can discriminate a large range of volatile organic chemicals such as aldehydes, ketones, esters, heterocyclic compounds, and others at concentrations of ppm to ppb levels required for environmental or food quality applications. This has opened new opportunities for sensors based on organic conducting polymers, 2D-materials or other, but many of these are experimental and still need to demonstrate robustness in practical applications. This is an ongoing challenge for printed gas sensors.

Chemoresistive and field-effect transistors type devices typically consist of a thin layer of sensing material deposited between two electrodes. Generally, the sorption (adsorption or absorption) of volatile molecules onto a sensitive surface is a prerequisite for triggering a transduction process in a gas sensor platform, and it is this sensitive surface that has been the focus for using printable materials. Other component parts, such as interdigitated electrodes, connectors and even first stage amplification are also amenable to printing. Of these technologies, metal oxide-based gas sensors have predominated the gas sensor market. Despite their disadvantages of high-power consumption, lack of selectivity and prone to drift, they are low cost and easy to mass manufacture. Screen printing techniques were applied early in gas sensor manufacture for metal oxide gas sensors promoting volume manufacture and increased reproducibility.

The development of soluble conducting polymer materials has allowed increased use of spin coating, inkjet printing, micro-drop dispensing, aerosol printing, or 3D-printing for sensor fabrication. This has facilitated development of more complex organic field effect gas sensors that provide higher sensitivity as well as more measurable parameters of gas adsorption such as change in field effect mobility, threshold voltage, on-current, and the subthreshold swing[4].

Figure 1 illustrates some of the perspectives of printable gas sensors going from a repertoire of materials available to a range of different devices with large potential applications. A new driver for printable gas sensors is the freedom to print gas sensors, heating elements, connectors and even associated electronics on flexible materials such as plastics, paper, or textiles – opening new product opportunities as well as sustainable manufacturing practices. Feeding into this is the increasing availability of two-dimensional materials such as graphene and graphene oxide (containing carboxyl, hydroxyl, epoxy groups) with a thickness of a few nanometres or less, allowing electron movement in a two-dimensional plane. These materials may be functionalised with other organic or inorganic materials, mixed with nanostructures such as carbon nanotubes, metal oxide nanoparticles, biological materials as well as organic semiconductors to confer unique gas adsorption properties. This flexibility allows formulation of new inks with unique properties for printing individual gas sensors as well as arrays of sensors with different selectivity to different gases or vapours[5]. Different categories of materials such as hydrogels that swell on sorption of a gas or vapour can now be easily printed[6,7]. Associated with this is the increasing use of biomimetic materials, aptamers, peptides, proteins as more selective molecular recognition elements in a gas sensor[8].

As a result, the repertoire of materials available for research and potential commercial application is increasing daily. Understanding the mechanisms of action of these materials is challenging. For example, one-dimensional materials with diameters comparable to the Debye length (a few to tens of nanometres) are potentially advantageous for achieving a high sensor response for 2-D materials, while creation of porous structures with large specific surface areas to enable enhanced gas adsorption and diffusion, increases performance.

With the emergence of new sensing materials and new methods of manufacture, the gas sensor field is being forced from convention to innovation and is on the verge of a paradigm shift in terms of manufacture as well potential applications. There are very few established manufacturers of gas sensors worldwide, and they only exploit traditional well proven materials and transducer platforms. They will only accept new manufacturing methods if they are robust and show a defined cost-benefit. This opens both opportunities as well as a myriad of problems. There are many potential applications of gas/vapour sensors each of which have widely different requirements in terms of sensitivity, selectivity, stability. Ideally a gas sensor should be reversible, molecules should not be chemisorbed onto the active surface, they should be robust, long lived, free from poisoning and long-term drift. Some applications may require single use sensors that may give a simple colour change when a particular gas or vapour is detected. Most of the new materials reported in the literature come from research laboratories where there have been limited characterisation of the robustness for applications. Many claims of selectivity to chemical species are exaggerated and are often dependent on a limited range of chemicals tested. Hence there are challenges to the research community to prove which materials and manufacturing processes should be adopted for printed gas sensors. Specification of materials, and application of recognisable standards are lacking. Choice of appropriate printing technology is dependent on the material selected as well as the potential market volume. These barriers need to be overcome for printable gas sensors to become adopted by manufacturers for routine production. Going from research, prototyping to manufacture requires risk analysis and market analysis of new and emerging markets likely to be opened by the availability of printable gas/vapour sensors.

The market for gas sensors is increasing rapidly due to critical industries releasing gases of concern into the environment. These include carbon monoxide, carbon dioxide, ammonia, hydrogen sulphide, and hydrocarbons driving the requirement for gas monitors to minimise effects on human health due

to excess emissions[9]. There are widespread applications of gas sensors in automobiles, air quality monitoring systems, and various consumer devices and increasing use of micro-electromechanical devices that are internet of things connected that put pressure on manufacturers to achieve competitive prices. The availability of cloud computing and big data processing now opens opportunities for deployment of large numbers of sensors covering wide areas creating environmental sensing networks that give real time 3-dimensional distribution of gas emissions[10,11].

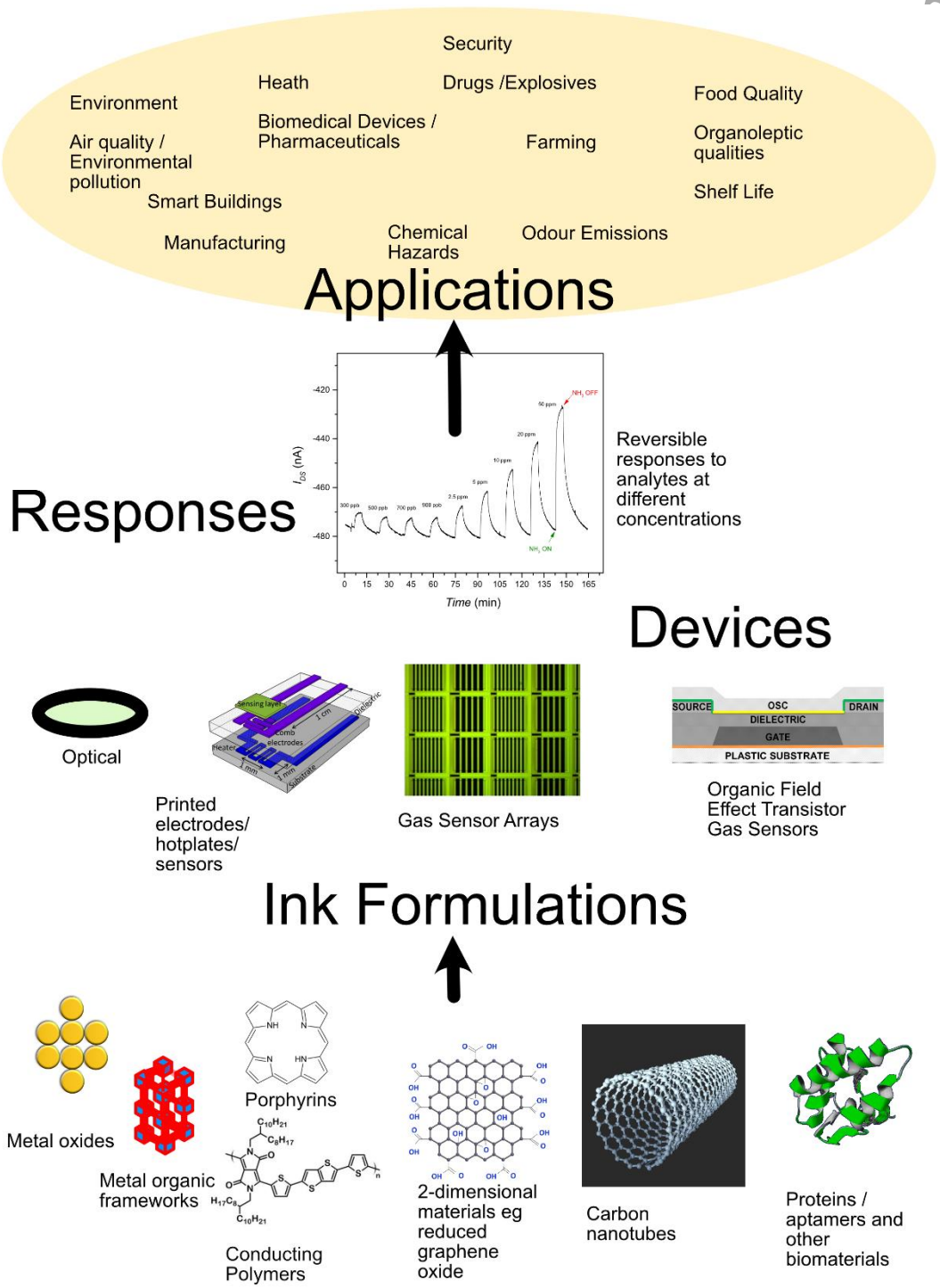

Figure 1 Perspectives for printable gas sensors.

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Section 6.2 – Printable gas/vapour sensors based on organic semiconductors

Eduard Llobet

Dept. of Electronic Engineering, Universitat Rovira i Virgili, Avda. Països Catalans, 26, 43007 Tarragona, Catalonia, Spain

Status

The development of fully printed, organic gas sensors has been fuelled by the evolution of the Internet of Things and the need of achieving flexible, stretchable gas sensing devices to meet the requirements of a wide spectrum of potential applications such as air quality monitoring, food logistics, industrial safety, security or health monitoring. Besides showing a semiconducting behaviour, the electrical conductivity of conjugated polymers such as polythiophene, polypyrrole, polyaniline, poly(p-phenylene vinylene), poly(p-phenylene sulphide), polycarbazole, polyacetylene, polydiacetylene, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate and their derivatives can be tuned via chemical doping. Conducting polymers have modifiable backbones, end groups and side chains, which enables tailoring their electrical properties and surface chemistry [1,2]. Gaseous species interact with organic polymers either via adsorption involving significant charge transfer or via weak intermolecular forces such as π-π interaction, hydrogen bonding or dipole-dipole interaction, which generate charge doping effects that modify electrical properties. Furthermore, conducting polymers can be hybridised with conducting fillers such as carbon nanomaterials, metal or metal oxide nanoparticles to further improve response intensity and dynamics at room temperature [3]. All this explains why these materials have been studied for developing organic electronic devices and, particularly, gas sensitive devices. Organic semiconductors have been used as the gas-sensitive channel in printed organic field

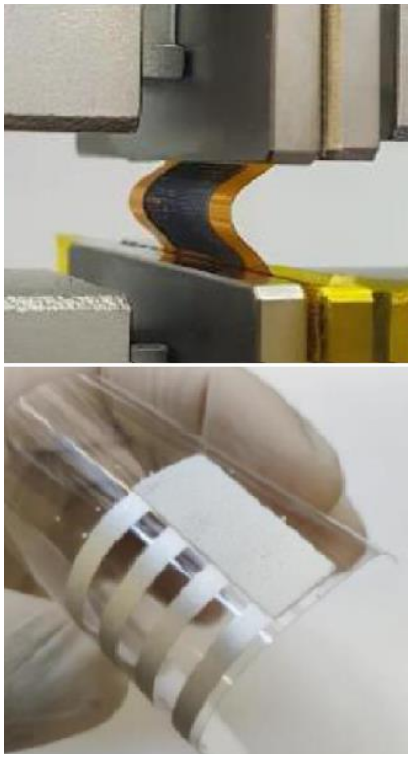

Figure 1 Printed chemoresistive gas sensor undergoing repeated automated bending tests for studying its reliability. Au Interdigitated electrodes are printed on polyimide by inkjet and the gas sensitive film consists of air-brushed polypyrrole nanoparticles supported on graphene flakes (top). Printed piezoelectric energy harvester on polyethylene. The piezoelectric film consists of polyvinyl acetate + poly(3,4-ethylenedioxythiophene) + ZnO.

effect transistors or in chemoresistive devices. While chemoresistors are simple but prone to suffer from temperature influence and moisture cross-reactivity, organic field effect transistors can be made more stable to environmental variables at the cost of requiring more involved fabrication processes, not always amenable to the desired fully printed approach. Printable sensors employing organic semiconductors are well suited for developing low-power, low-cost gas/vapour sensing devices for achieving ubiquitous gas sensing and for being integrated in autonomous, unattended IoT networks (Fig.1). Such sensors can be printed to polymeric, elastomeric, fibres, yarns or fabric substrates for becoming flexible and stretchable, thus enabling their use in smart packaging or in wearables. Current challenges are related to the low sensitivity achieved so far in the detection of some target molecules, the slow response dynamics often experienced with room-temperature operated devices, the limited stability of organic semiconductors when subject to operate under ambient conditions, and finally, the lack of selectivity, especially due to important ambient moisture cross-sensitivity. All these shortcomings currently hinder the high market potential of printed gas/vapour sensors in many application fields. These limitations and ways to overcome them are discussed in the next sections.

Current and Future Challenges

The development of printed organic semiconductor gas sensors faces many challenges that range from the production of heterogeneous materials, their integration in printing processes or meeting the required specifications for a broad range of applications. The production of organic nanomaterials and hybrids does not use always solution processed approaches, which would help achieving high quantities of nanomaterials for mass market manufacturing at low cost. Currently printed organic gas sensors have been developed for sensing different gases using polypyrrole (acetic acid, NH_3), polyaniline (CO, NO_2, NH_3, VOCs, H_2S), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (nerve agents, CH_2O, NH_3), poly(3-dodecylthiophene) (volatile organic compounds) [4,5]. The most promising results have been achieved for detecting NO_2 and NH_3. Chemoresistive or field effect transistor sensors employing the aforementioned materials show good sensitivities at ppm levels. While this is enough for some target gases, current sensitivity is not enough for CH_2O in indoor air quality monitoring (tens of ppb), for reliably detecting nerve agents in security applications (units of ppb) nor for detecting volatile organic compound biomarkers in health applications (units of ppb). In addition, selectivity remains an open issue as organic semiconductors, even when doped or functionalised, show a broad selectivity and respond to many gases and vapours, including ambient moisture. Their long-term stability under open-air operation conditions (a few months) is still poor compared to than that of inorganic semiconductors (up to two years). Printed organic semiconductor sensors operate at room temperature, which is highly advantageous for lowering power consumption, however, this often results in slow response dynamics (typically units to tens of minutes) and in lengthy or incomplete recovery (tens of minutes to hours). Such long response and recovery times are inappropriate for occupational safety and for security applications (units of second times). High performance organic field effect transistors currently use slow deposition processes and printed devices do not meet the high-frequency performance needed in radio frequency identification applications [6]. Indeed, advancing towards fully printed, passive and chip-less tags with gas sensing capabilities would help meet the stringent low costs needed in smart packaging for food logistics applications. With the development of suitable substrates for better printability, stretchability and breathability, and the amelioration of conductive inks for achieving stretchability of conductive paths and electrodes, there is a need for developing printed organic gas sensors with higher reliability upon bending and stretching (avoiding delamination of the gas sensitive organic semiconductor film). Finally, addressing self-healing properties of printed organic gas sensors for achieving better in-field performance [7] and re-use and designing for the recyclability and disposability are also challenges for the near future.

Advances in Science and Technology to Meet Challenges

For increasing selectivity several approaches need to be explored further and possibly combined. The main approach consists of modifying the surface chemistry of conducting polymers via engineering

doping, modifying their terminal groups and side chains to favour specific interactions with target molecules. Functionalisation effects in selectivity can be enhanced further by promoting modifications in the physical structure of the organic sensing films to favour the interaction with target gases. This could be achieved via using 3D printing or the design of sacrificial layers developed for controlling parameters such as porosity, film thickness, microstructure and the interphase with substrates and electrodes. A more sophisticated approach worth developing is the coating of the organic gas sensitive films with organic filters acting as molecular sieves. Printing superimposed films of hydrophobic polytetrafluoroethylene should be explored as a way to limit humidity cross-sensitivity or the printing of solution processed metal organic frameworks or covalent organic frameworks would enable boosting selectivity via tailored physicochemical interactions. Metal or covalent organic framework films may also help pre-concentrate target analytes, thus enabling the lowering of limits of detection and ameliorating response times (as lower response times are generally achieved at higher analyte concentrations). Finally, the hybridisation of organic semiconductors with carbon nanomaterials such as graphene [8] deserves to be developed further. The reason is twofold as carbon nanomaterials help extend the range of gases that can be detected (e.g., H_2) and may ameliorate the stability and sensing performance of organic semiconductors operated in humid environments (given the hydrophobic character of graphene). Besides improving gas sensitive materials, unconventional operating methods should be developed not only for improving selectivity, but also sensor recovery and baseline stability. Organic semiconductors have their electrical and optical properties modified upon gas adsorption and covalent organic frameworks show fluorescence properties. This should be explored for achieving multimodal sensors (e.g., electronically and optically interrogated) for enabling the orthogonal detection of target analytes in multi-gas mixtures. Light activation has been seldom used in organic semiconductor gas sensors and its use could help improving sensitivity and surface cleaning (i.e.,

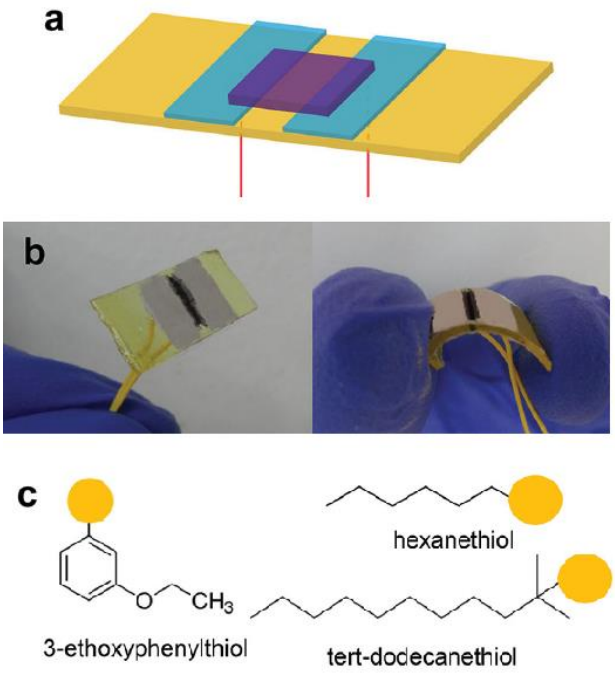

Figure 2 a) Schema and b) photograph of the self-healing chemiresistor consisting of a transparent (yellowish) self-healing substrate, self-healing organic polymer electrodes and jelly-like self-healing and pliable induced self-healing polymer filled with organic ligand caped AuNP film. c) Schema of the ligands coating the AuNPs. The self-healing substrate is a crosslinked polyurethane (sh-crl-PU) elastomer. This unique characteristic is due to the reversibility of hydrogen and/or covalent bonds that are formed inside the polymer. These are broken during scratching and recover in the self-healing process. Adapted from [7] ©2015 WILEY-VCH Verlag GmbH & Co.

improving recovery). Soluble acene crystals for solution processing and printing of organic field effect transistors with improved performance are under development [9]. Ameliorated devices should be used in the next years for achieving fully printed wireless tags with sensing capabilities, thus making an impact in food logistics. As new elastomer substrates are being developed with self-healing capability [7, 10] (Fig.2), a similar approach should be used for achieving gas sensitive organic films with self-healing properties matching those of substrates.

Concluding Remarks

The advantage of organic semiconductors for gas/vapour sensing lies in their versatile response mechanisms that comprise adsorption induced charge doping, proton doping and changes in conformation or orientation of molecular chains. Polymers can be easily functionalised for tailoring their surface chemistry, thus tuning their selectivity to some extent. Their conductivity can be improved via doping or by hybridizing with more conductive fillers such as carbon nanomaterials. Such materials are multifunctional, as they can be used in the near future not only as gas sensitive films, but also for developing the front-end electronics, conductive paths, energy storage capacitors or antennas for wireless communications. Organic materials and their hybrids can be solution processed, which makes them particularly suited for developing fully printed gas sensors on virtually any type of substrate (i.e., rigid, flexible, stretchable). Additionally, they can help avoiding the use of expensive metals and enable the development of self-healing sensors, thus enhancing inexpensiveness, re-useability, recyclability and disposability. Despite all these advantages, this roadmap has identified the currently existing issues with printed organic gas sensors and provides some directions on how research efforts should be directed for addressing them to help implement the translation of lab prototypes into marketable products.

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Section 6.3 – Printable gas/vapour sensors based on carbon nanotubes

Soufiane Krik, Sahira Vasquez, Martina Aurora Costa Angeli, Luisa Petti and Paolo Lugli

Faculty of Engineering, Free University of Bozen-Bolzano, Italy

Status

Carbon nanotubes are especially interesting for gas sensing, due to their high surface-to-volume ratios (1315 m^2/g), excellent electrical (107 S/m) and thermal (3500 W/mK) conductivity, notably high adsorption capacity (29.97 gCO_2/Kg adsorbent), and good sensitivity towards different analytes [1]. Particularly investigated is the high affinity of pristine carbon nanotubes towards NH_3, NO_2, SO_2, and O_2, besides the minor response to N_2, H_2, H_2O, and CO_2. Such good response is mainly due to the high number of active sites available for gas adsorption through the inner and the outer surface of carbon nanotubes. Upon adsorption, gases transfer charges on the nanotube sidewalls, leading to changes in their electrical properties. This phenomena takes place both in single and in multiple carbon nanotubes, also when these are randomly oriented in networks [2]–[6]. Despite the limited resulting specificity of such process, the capability of undergoing chemical modification through their sidewalls allows functionalizing carbon nanotubes and thus tuning their response and selectivity to targeted gases/vapours. Printed and functionalized carbon nanotube-based gas sensors have shown promising performance (down to ppb level in few seconds) for different gases/vapours (i.e., NH_3, ethanol, CO, formaldehyde, NO_2) with response time down to ~10 s, even at room temperature under both inert (e.g., N_2) and air atmosphere [7]. Printable carbon nanotube-based gas/vapour offer manyfold advantages, not only in terms of low-cost manufacturability, but also for their ability to operate at room temperature with low power consumption, as compared to metal oxide-based gas sensors that require operating temperatures typically above 200 °C. The versatility of using printing processes on unconventional substrates [8], makes these sensors appropriate as portable, disposable, conformable, and wearable devices [9], for applications such as the early identification of diseases [10], as well as the monitoring of food spoilage directly on the package [11]. Even if these sensors meet some of the features required, such as (i) high sensitivity for low concentrations, (ii) rapid response, (iii) low cost, and (iv) low power consumption, their technology readiness level is behind conventional counterparts (e.g., metal-oxides, electrochemical, and optical sensors), because they still lack (i) reversible operation, (ii) good selectivity, and (iii) stable operation over time. Nevertheless, the fact that commercial gas sensors are bulky and require high operating temperatures, pushes for further advancement with alternative materials. Furthermore, the detection of new gas/vapours in unconventional environments (e.g., in vitro systems modelling the gastrointestinal tract where traditional sensors fail due to the harsh acidic and anaerobic conditions) makes carbon nanotubes ideal materials to develop next-generation gas sensors [12].

Current and Future Challenges

The current challenges that still limit the use of printable gas/vapour sensors based on carbon nanotubes mainly involve the use of nanotubes as sensing material and the fabrication methods (i.e., printing) employed. Figure 1 provides an overview of the main challenges linked to the current research and development of printed carbon nanotubes gas/vapour sensors.

Fundamentally, one of the major obstacles is surely the low reproducibility and reliability of carbon nanotubes, with the difficulties in synthesizing carbon nanotubes with high purity (e.g., >99%), homogeneity in size (especially length), and further chemical functionalization [13].

Additional variability is also provided by the printing methods used to fabricate the sensors, which typically show a lower reproducibility compared to the conventional fabrication process. Consequently, the variability in the printed outcome as compared to the nominal layout can influence the homogeneity of the sensor performance. Even if experimental results show that carbon nanotubes

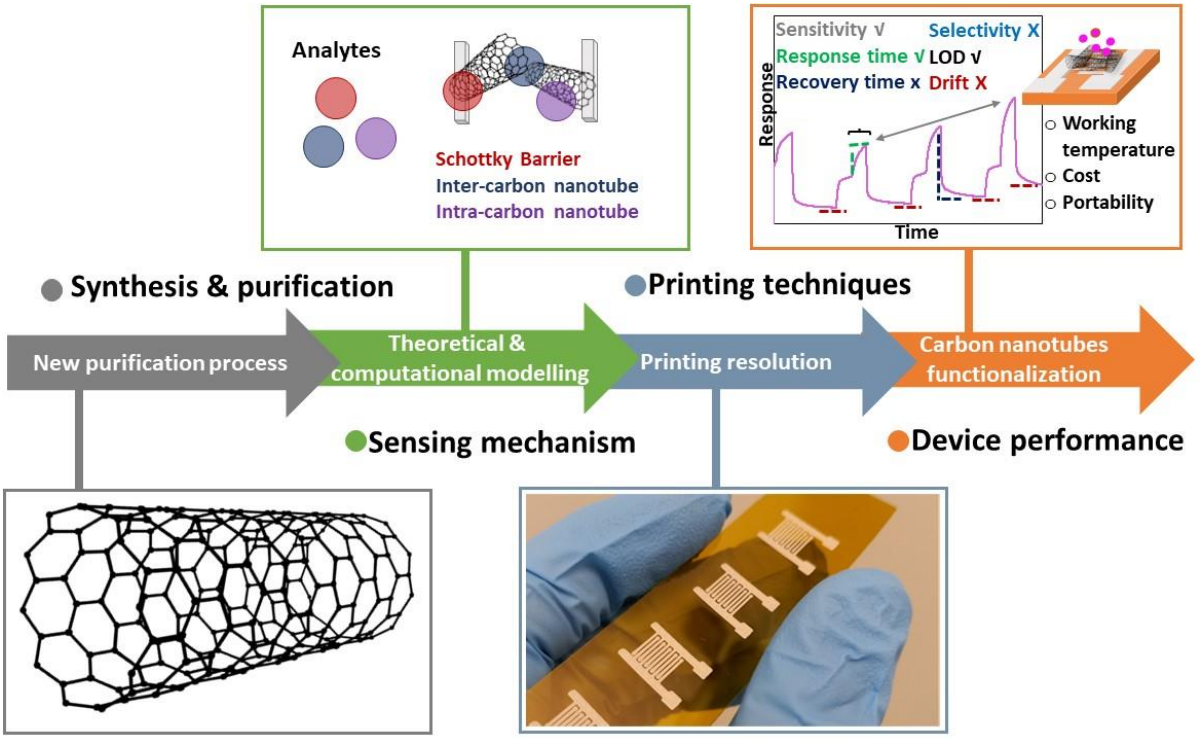

Figure 1 Overview of the main challenges related to printed carbon nanotube-based gas/vapour sensors, with key research directions required to advance the field.

are able to detect several gases, there are still a lot of unanswered questions regarding the fundamental processes underlying the working principle of carbon nanotubes. Specifically, in the complex sensing mechanisms (Schottky barrier, inter and intra carbon nanotubes) of carbon nanotubes-based sensors (Figure 1), the resolution of the contacts bridging the electrodes and the homogeneity of the conductive film plays a major role in the device operation [14].

Despite the high sensitivity, fast response time, and low limit of detection, key issues for the transition of these sensors from research to industrial scale are their limited selectivity, the slow recovery time at room temperature, and the drift over time (Figure 1). Over the past years, the functionalization of carbon nanotubes with metal nanoparticles (such as Au, Ag, Pd, and Pt), chemical groups or organic molecules, and innovative composites have remarkably strengthened both sensitivity and selectivity to some gas species (NH_3, NO_2, N_2, H_2, H_2S, CO) [15]. However, further progress is needed to comprehensively examine how carbon nanotubes contribute on the composite gas sensing performances and meet the technical criteria (reproducible specificity to target gas/vapour at a fast rate in the presence of high humidity and temperature variability) of real applications. In fact, carbon nanotubes may also be affected by environmental factors, such as temperature and humidity fluctuations, that can potentially interfere with the sensing mechanism.

Advances in Science and Technology to Meet Challenges

To address the abovementioned challenges, inter and multidisciplinary approaches in both basic and applied research and developments are required. First of all, efforts must be focused on the development of new and optimized carbon nanotubes synthesis and purification processes to enhance their purity and their quality (i.e., length and diameter), leading thus to gas/vapour sensors with better sensitivity and reproducibility. In addition, more basic research is required to better comprehend the principles behind the carbon nanotube sensing mechanism and serve as a guide for creating new strategies to boost the functionality of carbon nanotube-based sensors, opening thus

the possibility of exploitation of not yet explored transduction technologies. This could be done by working on theoretical and computational modelling methods, such as density functional theory. Carbon nanotube functionalization and hybridization with novel composites, along with suitable printing methods, is a further future direction expected to advance the performance of carbon nanotubes gas sensors at room temperature. For instance, it has been demonstrated that decorating carbon nanotubes with metal oxide nanoparticles or wrapping carbon nanotubes on conductive polymers that do not interact with interfering sources, allows enhancing both the sensitivity and the selectivity of carbon nanotubes-based gas sensors [16]. For example, as shown in Figure 2, a fully printed ethanol vapour sensor has been made by functionalizing carbon nanotubes with carboxylic acid or PEDOT:PSS, showing an improvement of the sensitivity compared to the pristine carbon nanotube sensor by 1.7X and 2.53x, respectively [17].

In parallel to the improvement of the sensing material itself, it is fundamental to work also on the integration of carbon nanotubes with printing techniques to realize reproducible devices. For example, improving carbon nanotubes' homogeneity and dispersion in solvents without the need of surfactants, combined with the adhesion of the printed pattern to the nominal design would surely enhance the reproducibility of the devices.

Besides this, most effort must be done towards data analysis through powerful computational techniques, such as machine learning, to compensate for the intrinsic limitations of the used materials and the technology (i.e., selectivity, time stability, and interference to environmental factors), enabling the advancement of the knowledge and potentially allowing predicting unseen situations in real applications.

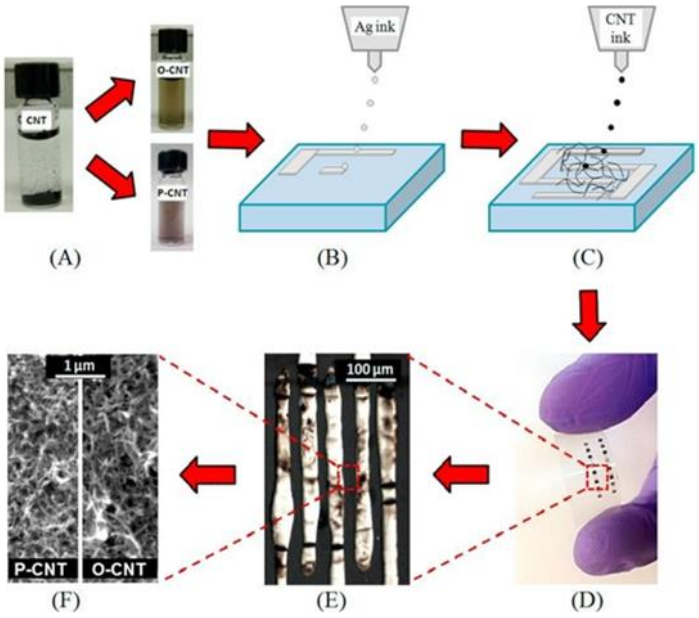

Figure 2. Fully printed and flexible carbon nanotubes-based gas sensor: (a) carbon nanotubes functionalization with carboxylic acid (O- carbon nanotubes) and PEDOT:PSS (P- carbon nanotubes); (b) printing of silver electrodes; (c) printing of carbon nanotubes; (d) photograph of the sensor on flexible substrate; (e) optical microscope image shows the printed silver interdigitated electrodes and (f) scanning electrode microscope image shows the printed carbon nanotubes. Reproduced with permission from [17].

Concluding Remarks

Printed gas/vapour sensors based on carbon nanotubes have demonstrated exceptional great promise for a variety of new applications in which state of the art commercial metal oxides and electrochemical sensors, as well as spectroscopic technologies are not suitable, due to their high operating

temperature (300-600°C) and resulting high power consumption, as well as their bulky size and high cost. Despite printable carbon nanotubes-based gas sensors are still in the early stages of development for practical applications and further efforts are required to employ them under realistic usage scenarios, the research has been making for more than two decades unremitting efforts to enhance the performance of these sensors. Although it is hard to anticipate the long-term impact on the market, the fabrication of printable gas/vapour sensors based on carbon nanotubes gives academics and business experts a sizable chance to progress in the field of gas sensing technology, by developing fresh and creative solutions to unconventional applications.

Acknowledgements

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Section – 6.4 Printable gas/vapour sensors based on metal oxides

Barbara Fabbri, Elena Spagnoli and Arianna Rossi

University of Ferrara - Department of Physics and Earth Sciences, via Saragat 1/C, 44122, Ferrara, Italy

Status

The idea of Brattain and Bardeen of using semiconductors as gas sensitive devices led to the discovery of a chemoresistive effect in metal oxides (Heiland, 1954). Namely, it was observed that the adsorption/desorption processes of gaseous compounds on the surface of a semiconducting material could change their electrical parameters, i.e., resistance, playing a key role in determining the presence of target analyte in the environment. The subsequent pioneering research reported in 1962 (Seiyama et al. and Taguchi) and the consecutive successful commercialization of gas sensors by Figaro paved the way to significant development efforts in this emerging field. Since the 70's, owing to their easy and simple synthesis manipulation, the metal oxides (e.g., SnO_2, ZnO, In_2O_3, and WO_3) have been established in the market as the standard printable functional films for gas sensors. In the late 80's, their primary revolutionary application was as alarm devices to prevent fires in homes through real-time monitoring of the amount of explosive and hazardous gases present in indoor environments [1, 2].

Nowadays, due to their tuneable physico-chemical properties and their robustness, metal oxides are still the most used functional materials for fabrication of printable solid-state gas sensors. Indeed, the global metal-oxide gas sensors market is expected to grow to USD 2.1 Billion by 2027, expansion attributed to the increasing requests in emerging applications, for instance, sewage treatment, medical, oil and natural gas, automobile industry, food industry, and smelting [3]. Smart cities and building automation are the main applications driving demand, which include weather stations and environmental monitoring in both public places and transportation (figure 1). The gases that can be detected most easily with metal-oxide sensors are ammonia, nitrogen dioxide, carbon monoxide, and volatile organic compounds, even if more research is needed to accomplish both applicative detection limits, i.e., for NO_2, and selectivity, e.g., breath contains over 3.500 volatile organic compounds [2].

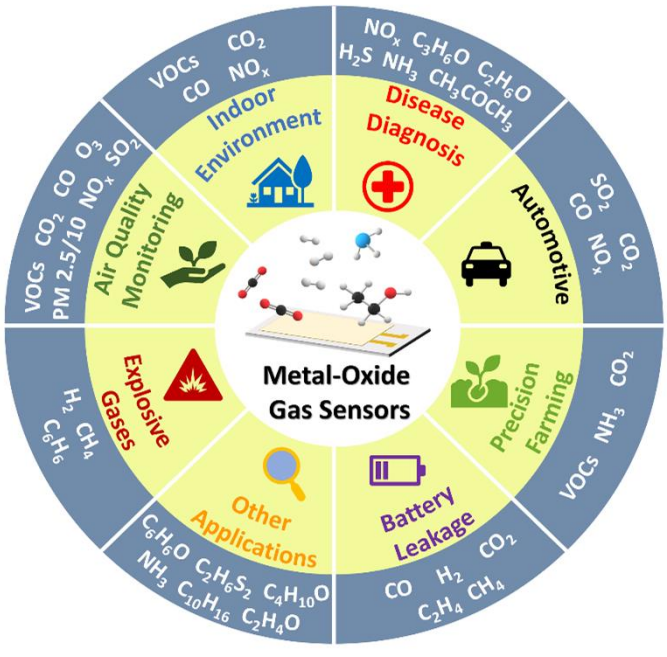

Figure 1 Application targets required by metal oxides-based gas sensors mass market and relative analytes of interest.

Therefore, the enhancement of already feasible features of metal oxides will result in both a gain of the sensing materials performance and a viable technological implementation of the devices. First, the availability of innovative strategies for structural engineering will pave the way for ground-breaking metal oxides, overcoming the significant disadvantages of standard ones, such as limited long-term stability and selectivity, and strong moisture interference. Moreover, starting from recent technological advances in miniaturization, further reductions in size, manufacturing cost, and power consumption will enable their future endorsement to the Internet of Things paradigm for large-scale applications [4]. Therefore, the combination of enriched physico-chemical properties and technological advances will corroborate such solid expertise developed on metal-oxide gas sensors so far.

Current and Future Challenges

The major shortcomings of metal oxide-based gas sensors are the short-term reproducibility of the response, the stability of conservative performance and the long-term signal drifts, which reduce the sensor life. Indeed, the structural properties of these materials can change during their usage over time because of poisoning gases, grain growth induced by elevated operating temperatures, changes in crystallographic faces, and point defects. Preventing such problems would simplify sensor calibration, avoid uncertain results and false alarms and extend sensor operation to commercially requested 5-10 years' service life (e.g., oxygen sensors).

Additionally, the activation of an effective sensing mechanism, based on gas-solid chemical reactions, represents a crucial hurdle for metal oxide-based gas sensors. Indeed, the reversibility of processes at the surface requires an activation energy, typically supplied by heating the sensitive layer at elevated temperatures (200-700°C). This condition is the main limitation for a wide-spreading of low-powered metal-oxide sensors and it inhibits their applicability in explosive/degradable environments [5]. Then, significant efforts aim to reduce the operating temperature without compromising the sensing performance in terms of kinetics and reversibility of the reaction mechanism.

Several attempts have been pursued to increase sensitivity exploiting the broad palette of precursors and synthetic techniques that enable metal oxides' compositional, crystallographic, and morphological properties to be tailored. Nevertheless, because of expensive reagents and sophisticated equipment needed, the large-scale technological transfer for the industry is commonly demanding. Moreover, despite the encouraging results obtained in controlled atmosphere, ambient temperature and moisture have shown to significantly contribute in determining the overall sensor performance. To date, the development of humidity-independent metal-oxide sensors for atmospheric real-time gas measurements is extremely challenging, e.g. O_3 sensors, because water can easily yield hydroxyl groups, negatively affecting the electrical properties of the sensitive film (response lowering >30%) while limiting target gas adsorption [6]. Additionally, the low selectivity of standard metal-oxide sensors, induced by kinetic competition in redox reactions between different gaseous species on the surface-active sites, is a crucial obstacle for the detection of the analyte in gas mixtures, especially when present at sub-ppm concentrations. The combination of unsuited sensitivity and selectivity restricts the range of gas detection and the sensor calibration linearity, which are widely regarded as essential parameters for challenging applications addressed both to monitor extremely low and remarkably high target concentrations. Detection constraints in the order of few ppm are required for air quality monitoring and toxic gases, e.g., SO_2 (1 ppm), NO_2 (10 ppm) and CO (25 ppm), while quantification of high gas content is appealing for industrial applications, e.g., CO_2 (>1000 ppm) and H_2 (~4% per volume of air) [7]. Among the difficult gases to detect with metal-oxide sensors, CO_2 and oxygen are the most critical. Indeed, to date, CO_2 has been inert for detection by metal-oxide semiconductors, while elevated temperatures (600-900 °C) of exhausts require oxygen sensors working in a harsh environment [8].

Along with the issues for commercialization of suitable metal oxide-based sensors, major challenges concern the more fundamental theoretical and experimental research to fill the lack of knowledge, which persists on the gas sensing mechanism, especially in photo-activation mode [9].

Advances in Science and Technology to Meet Challenges

The challenges mentioned above could be addressed through a multiscale strategy (Figure 2).

(i) Sustainable solutions aimed to lower long-standing metal oxides power consumption and to enhance sensitivity by cost-effective materials. The use of visible light to activate gas sensitivity in metal oxides is an attractive and unexplored alternative to thermal activation for harsh applicative demands. Visible light would be preferred over UV both to avoid possible affection of analytes, e.g. reducing NO_2 to NO, and to exploit better efficiency than UVB/UVC sources. However, metal oxides own bandgaps with energy higher than those of visible light photons, then they need to be sensitized, e.g. by doping or decorating with narrow-band semiconductors or plasmonic metal nanoparticles. Alkali metals have also long been predicted to be an ideal plasmonic material [10]. Moreover, they represent a cost-effective and affordable alternative to noble metals, since they can introduce defects in metal oxides, contributing to the appearance of impurity intra-band levels, which lead to the adsorption in the visible range.

(ii) New mechanistic studies leading to overcome lack of selectivity and to accomplish a feasible calibration. Enhanced sensitivity must be addressed by increasing porosity and surface-to-volume ratio of printable nanostructured sensing films, while improving metal oxides reactivity through heterojunctions or incorporating functional materials. Sensor selectivity can be achieved by (1) optimizing the device working temperature and/or the chemical composition of the active layer, to regulate the gas sensing reactions between targets and metal oxides, (2) using gas sensor arrays, in

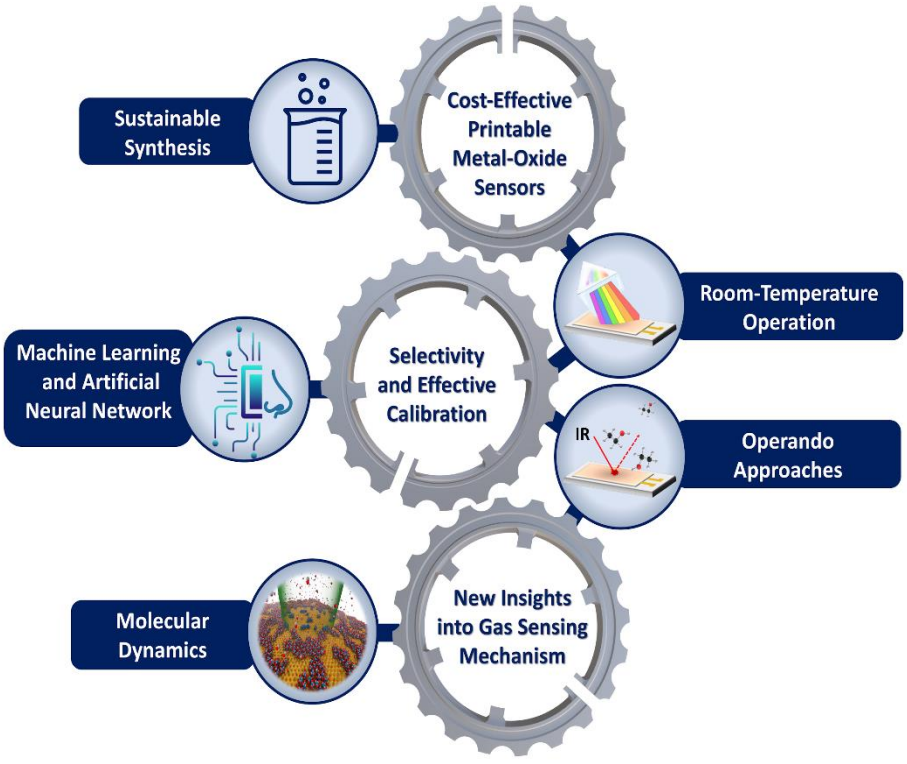

Figure 2 Overview of challenges and addressed cutting-edge strategies for printable metal oxide-based gas sensors. The molecular dynamics simulation image is reprinted with permission from ref. 12. Copyright 2016. With kind permission of The European Physical Journal (EPJ).

combination with sophisticated algorithms. Indeed, machine learning and artificial neural networks are pioneering data-processing approaches to improve selectivity and to compensate for signal drift and non-linear sensitivity, both establishing an effective calibration procedure and paving the way for Internet of Things.

(iii) Advanced theoretical and experimental techniques to provide new insights into gas sensing mechanisms. Operando approaches combine investigation on sensing transduction together with advanced characterization techniques (e.g. Diffuse Reflectance Infrared Fourier Transform spectroscopy), monitoring the metal-oxide film under its actual working, i.e. under device operation conditions. These effective and promising methods would allow us to examine reactions occurring at such rough-surfaced solid metal-oxide films, giving hints on the gas sensing mechanism [11]. However, reaction dynamics usually proceeds too fast to be determined by *operando* characterization, resulting in limited information. Therefore, simulations by molecular dynamics including chemical reactions in heterogeneous phase would be a valuable tool to support experimental analyses, studying the dynamics of physical/chemical adsorption of gaseous molecules on metal-oxide surface [12].

Concluding Remarks

The starring role earned by metal oxide-based gas sensors during the "sensor decade", the first of the 21st century, is out of discussion. Starting from the first printing technique used for the metal oxides, i.e., screen printing, significant efforts have been made to adapt existing printing methods to the fabrication of electrical gas sensors. Nowadays, the term "printable" is no longer limited to inks/pastes used for the sensing layer, but rather extended also to electrodes and substrates, then these three components are interdependent [2]. On the contrary to gas sensors manufactured using conventional methods, printed metal-oxide gas sensors could achieve the Internet of Things paradigm due to their low-cost, low-power consumption, and technological integrability. Besides the compatibility studies on materials and methods for electrodes and substrates, e.g. microfabrication techniques, diverse research directions are opening on metal oxides. If on one side the significant lacks on sensing mechanism will foster the development of new computational interfaces also addressed to tailor highly selective metal oxides, on the other side, we expect that the design of innovative *operando* systems for photoactivation studies will retrieve and exploit knowledge from other nearby areas, such as photocatalysis and photonics, and in addition will enable room-temperature operating metal oxide-based sensors.

Acknowledgements

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Section 6.5 – Printable gas/vapour sensors based on 2D materials

Luigi G. Occhipinti, Chenyu Tang, Wentian Yi, Dafydd Ravenscroft and Tharun R. Kandukuri

Cambridge Graphene Centre, Department of Engineering, University of Cambridge, 9 J J Thomson Avenue Cambridge CB3 0FA, United Kingdom

Status

Two-dimensional (2D) materials, including graphene and related materials, layered metal dichalcogenides, hexagonal boron nitride, and MXenes, the latter referring to $M_{n+1}X_nT_x$ (M = transition metal, X = C and/or N, and T = surface-terminating functional group like -F, -OH, or -O), have emerged as compelling gas sensing materials due to their unique physical and chemical properties [1]. These properties encompass atomically thin layered structures, tunable electronic and optical properties, and extraordinary mechanical strength. Furthermore, the inherent stability of 2D materials allows for long-term operation and robustness in harsh environments, making them suitable for real-life applications.

The gas sensitivity of 2D materials arises from their high surface-to-volume ratio and abundant active sites, rendering their charge transport susceptible to gas molecule adsorption [2]. The absorption of gas molecules with varying electron-doping or withdrawing abilities at the interfaces can induce bandgap alternations, generating resistance responses [1]. Typical analyte-material interactions in 2D material-based gas sensors encompass van-der-Waals interaction, charge transfer, π–π interaction, hydrogen bond interaction, and coordination. The strong noncovalent interactions induced by defects, atomic orbitals, and surface chemistry of 2D materials contribute to high sensitivity and selectivity at room temperature.

Printing of 2D materials presents an attractive option for cost-effective gas sensor fabrication [3]. Large-scale production of 2D material flakes with edge defects and active sites can be achieved through liquid-phase exfoliation. The dispersion of 2D flakes can then be formulated into inks for printing methods such as inkjet, screen printing, and gravure. Graphene oxide and reduced graphene oxide, with functionalized surfaces and better dispersity, can be easily prepared via Hammer's methods and are extensively reported for fabricating both capacitive and chemoresistive gas sensors. Additionally, graphene's high surface-to-volume ratio and excellent conductivity make it a promising scaffold for loading other active materials and providing conductive channels. Layered metal dichalcogenides, such as MoS_2 and SnS_2, possess tunable bandgaps and can interact with gas molecules through various noncovalent interactions. It is noteworthy that MoS_2 is intrinsically n-type doped but can be p-type doped in the form of exfoliated flakes, enabling gas sensor printing without additional doping or modification [4]. Pristine Ti_3C_2 MXene is a metallic 2D material with surface terminal groups. Analogous to graphene, its sensitivity and selectivity can be improved via an oxidation process [5]. Multiple heterojunctions of Ti_3C_2 and semiconducting TiO_2 can form Schottky barriers within the flakes, specifically enhancing the selectivity of nitrogen dioxide by an order of magnitude. AI-based data processing are effective methods to achieve accurate gas/vapour sensors based on 2D materials with high selectivity in complex gas mixtures and environments.

Current and Future Challenges

Current research on printed 2D material-based gas sensors focuses on extensively explored graphene and related materials and layered metal dichalcogenides in different applications ranging from personal exposure monitoring to toxic and polluting gases to washable textile-based sensors for wearable electronics applications with ultrahigh sensitivity, down to 20 or 100 ppb of NO_2 in dry and humid air respectively [6]. While several 2D materials, such as graphene and related materials, MXene and black phosphorous inks, have been formulated to fulfil printability requirements [7], there is a need for further research to optimize their use in gas sensor fabrication.

Commercially available chemoresistive gas or vapour sensors are generally based on heated metal oxides (e.g. SnO_2, ZnO, TiO_2, Cu_2O) to provide an estimation of the total volatile organic compounds (VOCs) in air or the concentration of toxic or polluting gases such as CO, NO_2, and others with concentration in the range of 1 part per million or higher. Compared to these, printed gas sensors operating at room temperatures generally exhibit slower response and recovery due the difficulty to promote desorption of gas molecules absorbed in the sensing layer. 2D material-based gas sensors have the ability to work at room temperature and to run at low-power consumption as required in portable and mobile device applications. Thanks to the high surface area (2630 m^2/g for graphene) and surface activity of 2D materials used as sensing layers 2D-materials based gas sensors are capable of ultra-high sensitivity and lower limit of detection (LOD), down to the part per billion (ppb), as required for detecting a large variety of gases and vapours, as well as odours, solvents, and other potentially toxic gases that are present in minute concentration in indoor or outdoor environment [3]. An expedient way to initialize the sensors is to apply pulsed high heat or UV exposure to accelerate the desorption of gas molecules. Additionally, the performance of printed layers of 2D materials for gas sensing is inevitably degraded compared to CVD-grown layers and single flake devices due to the disordered hopping transfer in the percolating network [8]. Conversely, the inherent defects in exfoliated flakes can dominate the electrical properties of 2D materials. Many effective strategies have been developed to enhance the performance of 2D material-based gas sensors, such as surface modification, heterostructure, and nanostructure [9]. Graphene exhibits poor sensitivity to gas molecules but can be enhanced through doping and chemical modification. There have been types of gas sensing diodes with increment on sensitivity based on single-flake or CVD-grown layered metal dichalcogenides. Consequently, a current challenge is the transferral of these existing strategies and the development of distinct strategies for solution-processed 2D materials.

The majority of reported printed gas sensors based on 2D materials can only generate single outputs. In the future, more complex tasks like recognizing mixtures of unknown gases will necessitate gas sensing arrays or multivariable gas sensors with multiple outputs [10]. CMOS gas sensors with printed 2D materials as active layers are a promising option for commercialization, but they still face challenges such as high manufacturing costs and poor device-to-device reproducibility [11].

One of the main challenges in utilizing AI for developing models of 2D materials-based gas/vapour sensors is the ability of the AI model to apply effectively in heterogeneous sensing environments, that requires model interpretability and explainability. While AI can assist in the design and fabrication of 2D gas/vapour sensors, determining the optimal material properties, sensor geometries, and fabrication processes, to achieve a specific sensing target, the AI model is often unable to provide a deep understanding of the underlying physical and chemical processes. This requirement is difficult to achieve with black-box neural network models [12].

A key aspect of 2D materials-based gas sensors is the slow desorption of gas molecules from the sensor surface, leading to prolonged recovery times. This issue stems from the strong adsorption forces between the gas molecules and the 2D material surface. Innovative approaches to mitigate this challenge include surface functionalization and the integration of hybrid and porous materials. Surface functionalization can alter the chemical properties of the 2D materials, thus weakening the adsorption forces and facilitating faster desorption. Moreover, the use of hybrid structures combining 2D materials with other nanostructures (e.g., metal oxides or polymers) can enhance gas molecule mobility and desorption kinetics. Further research in these areas could substantially improve the recovery times of these sensors, making them more viable for practical applications. [13]

Advances in Science and Technology to Meet Challenges

A promising approach for detection of gas and volatile organic compounds (VOCs) present both in outdoor and indoor environments encompasses the use of bio-inspired Murray materials, as hierarchical porous structures that control absorption and desorption of the different gas molecules present in air [14]. These materials can be manufactured by solution-phase additive manufacturing

techniques and are used to obtain self-assembled porous structures with nano- and micro-level pores that mimic the hierarchy of length scales found in xylems and leaf veins in plants. With multiple levels of interconnected channels, this universal structure has evolved over many million years to ensure mass transport (i.e., fluid permeation) with minimum energy expenditure through the preservation of volumetric flow rate. This approach (Figure 1) allows optimum through-flow of gases to the 2D material composite structure, providing a fast, highly sensitive and selective response [15].

AI methods used for classifying detected gases/vapours include classical machine learning methods, such as Principal Component Analysis (PCA), Support Vector Machine (SVM), Multilayer Perceptron (MLP) [16-18], and deep learning methods, such as Convolutional Neural Network (CNN) and Recurrent Neural Network (RNN) [19] (Figure 2). The former is suitable for use in application scenarios with relatively simple environments and single data modality, while the latter are better suited in situations where multiple complex gases/vapours are interrelated and data contain a certain degree of temporal complexity.

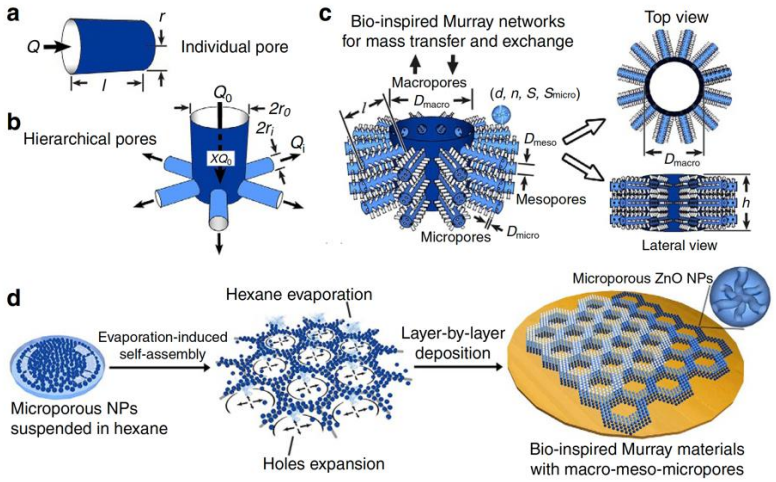

Figure 1 Hierarchically porous networks in Murray materials via self-assembly with macro–meso–micropores. Reproduced with permission from Zheng *et al.* [14].

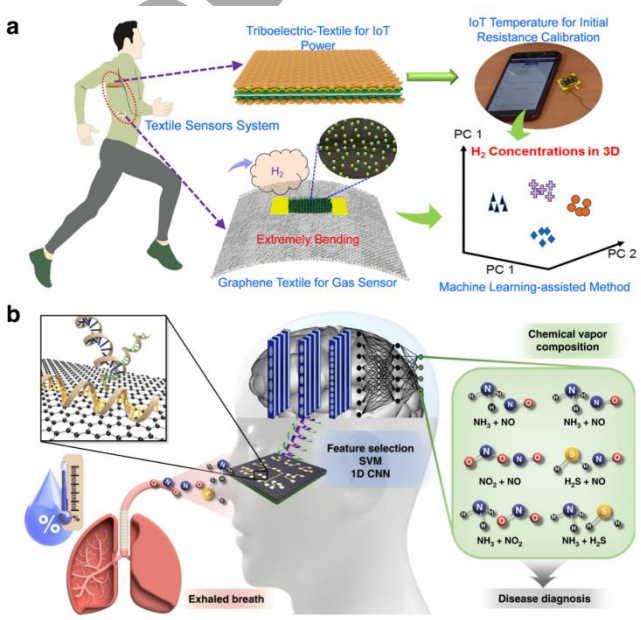

Figure 2 AI-based Gas Sensor Systems. (a) Wearable H_2 gas sensing on inkjet-printed graphene textiles with machine learning and IoT integration. Reproduced with permission from Zhu *et al.* [16]. (b) Schematic diagram of the human exhaled gas diagnostic process. Reproduced with permission from Hwang *et al.* [19].

Key to the success of printable gas/vapour sensors based on 2D materials operating at room temperature, is the integrated analysis of accurate gas classification and concentration regression. A fully inkjet-printed room-temperature gas sensor based on graphene-metal oxide hybrids and utilising a machine learning-assisted visualization platform, has been developed. It demonstrated high stability and reliability with a portable low-power design [20]. Transfer learning is a promising method to address the challenge of developing AI models that can be effectively utilized in heterogeneous sensing environments by leveraging knowledge gained from one environment and applying it to another related environment [21]. Explainable Artificial Intelligence (XAI) has the potential to address the challenge of model interpretability and explainability by providing insights into the underlying decision-making processes of AI models. For example, XAI techniques can provide explanations for specific model decisions, making it possible to understand why a particular material, geometry, or fabrication process was chosen or recommended by the AI model. This information can be used to fine-tune the model or validate its predictions against domain knowledge and expert intuition [22]. Local interpretable model-agnostic explanations (LIME) can be applied to deep learning models used in 2D gas/vapour sensors to identify the most relevant features and interactions responsible for the model's decisions [23].

Concluding Remarks

In conclusion, the application of 2D materials, beyond graphene and transition metal dichalcogenides, in printed gas sensor fabrication is still rare. While several 2D materials, such as MXene and black-phosphorus inks, have been formulated, there is a need for further research to optimize their use in gas sensor fabrication. Combining the ideal characteristics of 2D materials with bio-inspired printable 3D nano and mesoporous network structures designed for minimum-energy fluid permeation is a promising research area to achieve unprecedented levels of sensitivity in gas and vapour sensing. AI methods are utilized to assist both in the modelling and data analysis to achieve highly accurate and selective 2D materials-based gas and vapour sensor devices, as well as in the design of advanced sensor structures by modelling hierarchical porous structures and predicting the gases/vapours and surfaces interactions.

Acknowledgements

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Section 6.6 – Printable gas/vapor sensors based on halide perovskites and derivatives

Zain Ul Abideen[1], Zahra Azimi[2] and Antonio Tricoli[1,3]

[1] Nanotechnology Research Laboratory, Research School of Chemistry, College of Science, Australian National University, Canberra, ACT, 2601, Australia
[2] Research School of Physics, Australian National University, Canberra, ACT, 2601, Australia
[3] Nanotechnology Research Laboratory, Faculty of Engineering, University of Sydney, Sydney, NSW, 2006, Australia

Status

Metal halide perovskites have recently attracted significant attention in optoelectronics, contributing to numerous breakthroughs in applications, including solar cells, light emitting devices, photodetectors, sensors, and transistors [1], due to their favorable optoelectronic properties, such as high optical absorption coefficients and tuneable bandgaps. Moreover, compared to other printable semiconductors, they exhibit long carrier diffusion lengths, high carrier mobilities, and low trap densities [2]. Metal halide perovskites are commonly categorized into two groups based on their composition: inorganic metal halide perovskites and hybrid organic-inorganic metal halide perovskites. The hybrid organic-inorganic metal halide perovskites family has an ABX_3 structure, where 'A' is an organic cation, 'M' is a metal cation, and 'X' is a halide anion. Layer-structured two-dimensional perovskites follow instead the $(RNH_3)_2(A_3)_{n-1}M_nX_{3n+1}$ structure where RNH_3 represents bulkier alkyl ammonium cation, 'A' stands for small organic or alkyl metal cation, 'M' and 'X' represent the group IV metal cation and the halogen, respectively, and 'n' is the number of layers [3]. The semiconducting nature and favorable optoelectronic properties of metal halide perovskites, which can be easily tuned by altering A/X-site ions, make them also suitable for sensing gas molecules. Different types of perovskite materials, applications of halide perovskites in optoelectronics, their printing techniques, and the current challenges are illustrated in Figure 1.

Recently, the application of metal halide perovskites in gas/vapor sensing has shown promising performance in detecting various gases including volatile organic compounds, carbon monoxide, ammonia, oxygen, and nitrogen oxides (NO_x) [4]. The major benefits of perovskite-based gas sensors are their high sensitivity (currently in the range of parts per million to parts per billion) [4], fast response, and recovery times (less than a minute), and low detection limits (less than one parts per million) [3]. Transduction of their sensing response has been successfully achieved by a variety of methods, including photoluminescence, photo-electrochemistry, electro-chemiluminescence, and chemoresistive [5]. Furthermore, perovskites can be easily integrated into compact and low-cost devices, making them suitable for widespread use in various industries, including environmental monitoring, industrial process control, and healthcare. Despite this potential, perovskites are not without their challenges, such as high reactivity to ambient conditions such as oxygen, humidity, and temperature that negatively impact their long-term stability. However, recent progress toward the development of selective nitrogen dioxide, oxygen, and humidity sensors has been reported (Figure 2) [6, 7].

Despite progress on the fabrication of more stable perovskite gas sensors by laboratory-scale spin-coating methods, there has been less focus on their scale-up and commercialization [9]. However, extensive research has been conducted toward the scale-up of perovskite solar cells using a spray, blade, and slot-die coating, flexographic, inkjet, gravure, and screen printing [9]. Amongst these methods, inkjet printing as a low-cost, designable, reliable, and reproducible method has been used to fabricate gas/vapor sensors [10]. In inkjet printing, a printer is loaded with perovskite ink, which is then dispensed through a nozzle as small droplets onto a sensor platform. $CsPbBr_3$ perovskite films show a current degradation of only 12% after 200 cycles, indicating the excellent conductivity,

stability, and durability of the uniformly grown inkjet-printed perovskite films [11]. Similarly, the self-powered organic–inorganic hybrid heterojunction of *p*-type hybrid-halide perovskite and *n*-type InGaZnO prepared by inkjet printing demonstrated nitrogen dioxide sensitivity of 127.2% per part per million [7]. These recent results demonstrate that mass production of high-performance perovskite gas sensors may be possible by optimization of the ink formulation and inkjet printing parameters.

Current and Future Challenges

Printable gas/vapor sensors based on halide perovskites face numerous challenges [1, 4], including their limited environmental stability. Halide perovskites are sensitive to moisture and heat, leading to rapid structural degradation and sensor performance decay [12]. For example, the complete decomposition of $CH_3NH_3PbI_3$ takes more than 20 days at a relative humidity of ~50%, and less than 5 days at a relative humidity of over 90% [13]. Another standing challenge is the limited reproducibility of their sensor performance. The latter varies greatly depending on the synthesis method and experimental conditions, such as the area of the sensing film and electrodes [5]. The response of metal halide perovskites to a fixed concentration of as low as 10 parts per million of ammonia gas decreases by about 10% after the initial few cycles in a recent reproducibility study [14].

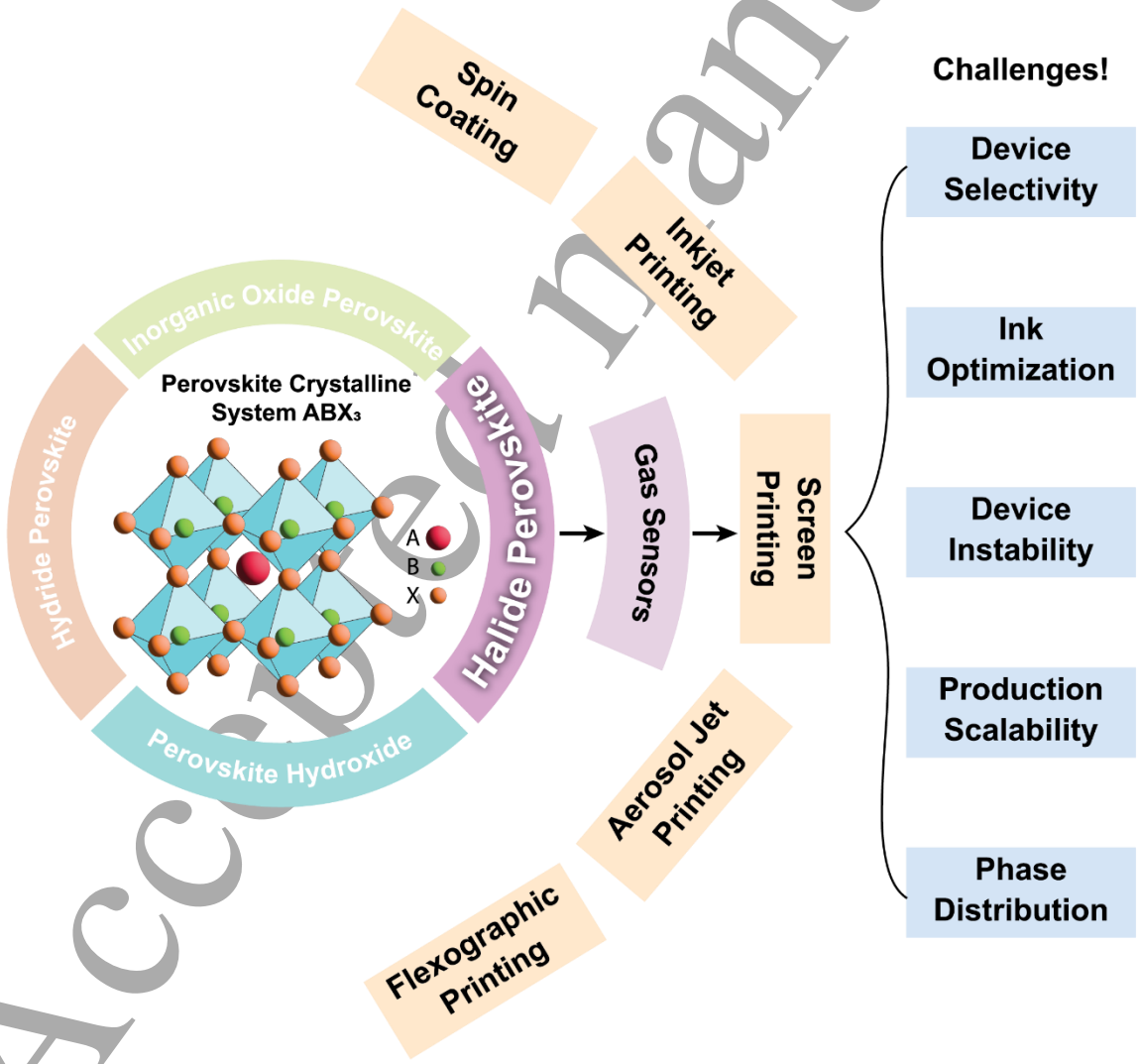

Figure 1 Schematic illustration of perovskite materials system types, their applications in various sensing areas, and their challenges.

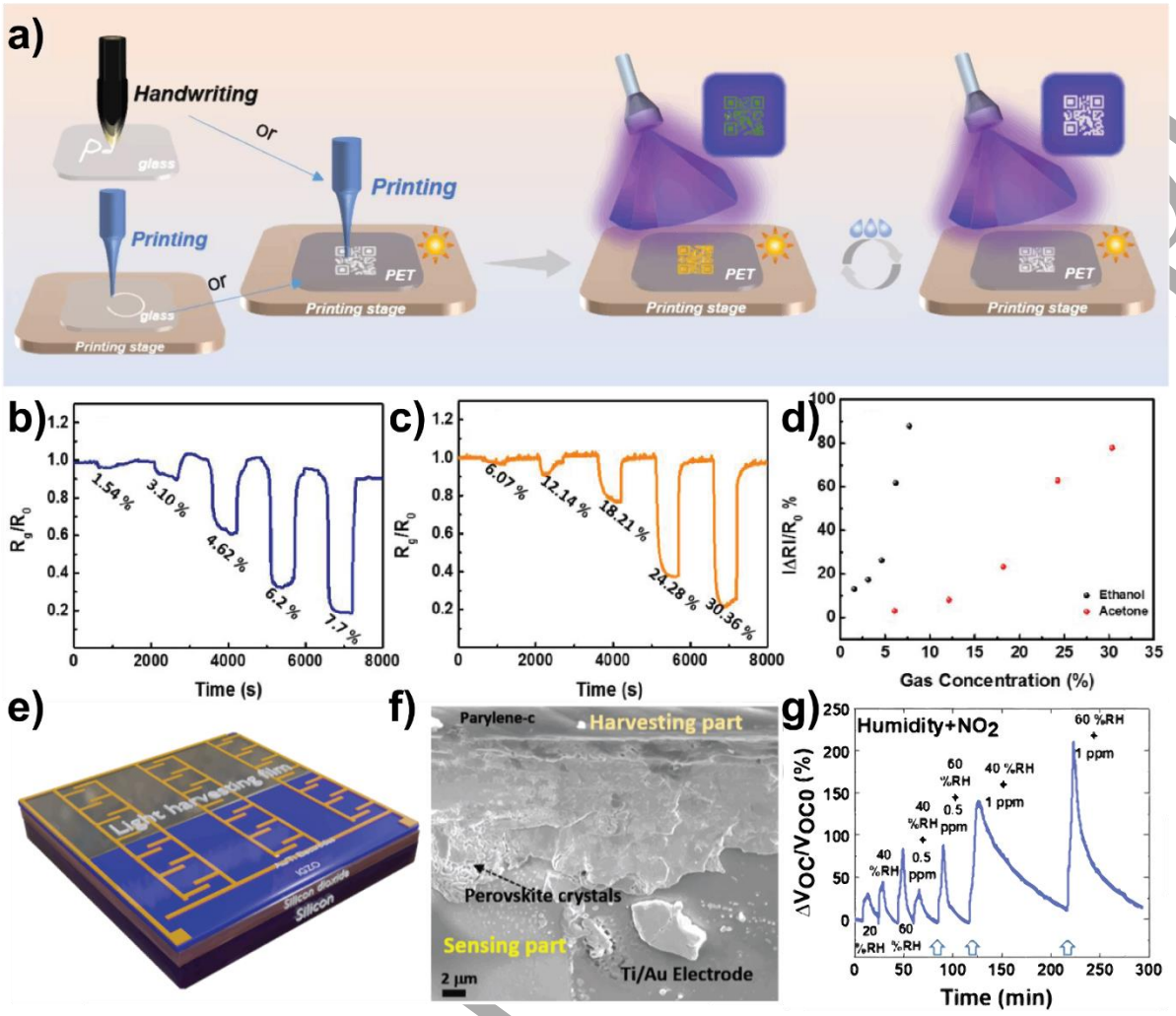

Figure 2 a) Schematic illustration of reversible fluorescent patterns on glass substrates and Polyethylene terephthalate substrates by handwriting or printing for printable humidity sensors based on perovskite composites. Reprinted by permission from [6]. b) Response of printed, flexible, and self-powered sensors to ethanol and c) acetone at room temperature. d) Sensitivities of printed sensors as a function of analyte gas concentrations. Reprinted by permission from [8], copyright 2018 John Wiley and Sons. e) Schematic drawing of organic-inorganic hybrid heterojunction based on halide perovskite and InGaZnO self-powered, highly selective nitrogen dioxide sensor. f) Cross-sectional scanning electron micrograph showing the interface of the energy harvesting part and the sensing part. g) transient response of the organic-inorganic hybrid heterojunction based on halide perovskite and InGaZnO self-powered, highly selective nitrogen dioxide sensor to various humidity levels and nitrogen dioxide gas in the presence of humidity. Reprinted by permission from [7], copyright 2021 American Chemical Society.

Currently, halide-based perovskite sensors can selectively detect only a limited range of gases, namely carbon monoxide, ammonia, oxygen, and nitrogen oxides [4], limiting the scope of applications. Furthermore, they generally have high cross-sensitivity to these gases, which challenges the accurate identification of the analyte [7], and their sensitivity and selectivity are insufficient for applications requiring the detection of the concentration of gases less than parts per billion, such as disease detection and monitoring by human breath analysis. The highest sensitivity reported so far using lead halide perovskite nanoparticles is 0.5 parts per million for hydrogen sulphide gas [15]. Therefore, improvements in the selectivity and sensitivity of halide-based perovskite sensors are also required for advanced healthcare applications.

Another existing challenge is to develop low-toxic perovskite materials for use in miniaturized sensing. Current halide-based perovskite materials' toxicity and environmental impact are of concern and limit their ability to be commercialized. Halide perovskites contain heavy metals such as lead and are processed with toxic solvents, both of which can be toxic to plants and animals. $MAPbI_3$-based perovskites consist of approximately one-third of their weight in lead and are soluble in water [16]. The consumption of lead can have detrimental effects on various organs including the liver, kidneys, nervous system, and other bodily systems [16]. Additionally, the instability of some halide perovskites under humid and/or high-temperature conditions can result in the release of toxic gases, such as hydrogen cyanide. Therefore, developing stable and robust halide perovskites is crucial for reducing their environmental impact and toxicity.

Currently, most halide perovskite sensors are produced through the spin coating method, which is difficult to scale up for mass production. Additionally, the process can be sensitive to the quality and purity of the starting materials, which can further complicate scaling up the production process. Inkjet printing has shown potential for producing high-resolution patterns and precise ink placement, which makes it the most promising method for printing perovskite sensors. However, the inkjet printing process is slower than other printing methods and has issues with ink viscosity, positioning accuracy, and print resolutions (current resolution is 1-100 µm), and yet not enough research has been conducted to print and commercialize highly reproducible and performing halide perovskite-based gas sensors [10].

Advances in Science and Technology to Meet Challenges

Printable gas sensors using metal halide perovskites and their derivatives hold promise for compact gas sensing devices in various applications. Recent advancements have been focused on sensitivity, sensing performance, and toxicity issues. However, further research is needed to tackle the remaining challenges including stability, reproducibility, selectivity, and fabrication scalability.

The current limited environmental stability of halide perovskite materials may be overcome by probing more stable perovskites through the surface and compositional tuning and encapsulation techniques. For instance, the incorporation of long-chain organic cations (Cu^{2+}, Mn^{2+}, and Sn^{2+}) in two-dimensional layered perovskites may demonstrate better stability against oxygen and moisture, offering improved performance and longevity when compared to three-dimensional perovskites.

The sensitivity and target gas selectivity of halide perovskite gas sensors can be improved by optimizing light absorption to stimulate chemical reactions, tailoring charge carrier generation using heterojunction architectures and defect engineering including interstitials and substitutional defects, and surface modification of the perovskite materials by exploring various nano structural configurations. Future endeavors should also be focused on optimized dopant concentration and distribution which are necessary to reduce cross-selectivity for applications requiring the detection of ultra-low gas concentrations (in the range of parts per trillion), including disease diagnosis through breath analysis. Achieving consistent and reproducible sensor performance is crucial for reliable gas sensing. By standardizing synthesis methods, optimizing the area of the sensing film and electrodes, and implementing rigorous quality control measures, the variability in sensor performance can be reduced.

Similarly, recognizing the environmental impact and toxicity concerns associated with lead-based halide perovskites, there is a dire need to develop low-toxic alternatives without sacrificing the sensing performance and stability. By exploring alternative cations such as non-toxic divalent e.g., Sn^{2+}, Ge^{2+}, Cu^{2+}, hetero-valent (other than di-valent) replacements, non-toxic precursor solvents, lead-free double perovskite derivatives, and incorporating environmentally friendly encapsulation techniques, substantial progress in reducing the toxicity and environmental impact of halide perovskite materials can be made. To facilitate cost-effective large-scale production of halide perovskites for gas sensing using inkjet printing techniques, additional research is necessary to customize ink compositions for specific and drop-on-demand printing methods, ensuring low-cost and high-speed processes, while

also achieving adequate electrical conductivity at lower temperatures without substrate and precursor inks degradation and damage.

Concluding Remarks

The development of miniaturized gas sensing devices based on perovskite materials is at its early stage and presents several opportunities for material and fabrication process discoveries. Open challenges include the development of new sensitive and selective materials with enhanced stability and tunability for portable gas sensing systems. Furthermore, combining the sensing properties of halide perovskites with their light-harvesting features has significant potential for the development of self-powered miniaturized gas sensor systems for application in distributed and wearable sensing. Establishing dedicated processes and solutions to produce halide perovskite gas sensors is a current bottleneck that will likely require different solutions than those opting for devices that can be hermetically sealed from the environment such as photovoltaic cells and photodetectors. Success in this task will lead to ample opportunities for fundamental and technological discoveries as well as for the translation and commercialization of halide perovskite-based gas sensing technologies.

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Section 6.7 – Printable gas/vapour sensors based on metal-organic-framework materials

Almudena Rivadeneyra[1] and Sara Rojas[2]

[1] Dept. Electronics and Computer Technology, University of Granada, Spain
[2] Dept. Inorganic Chemistry, University of Granada, Spain

Status

Compared with classic porous materials, the chemical versatility, regular porosity and diversity of their structures make metal-organic frameworks attractive for their potential use in different fields (catalysis, sensing, gas storage or drug delivery). Metal-organic frameworks are based on metallic nodes and organic linkers giving rise to a class of functional crystalline materials potentially porous. Remarkably, metal-organic frameworks can also hold other active guest molecules, enzymes, bacteria, and nanoparticles to promote their sensing properties. In addition, the fact that metal organic frameworks are porous materials easy to be functionalized facilitates the tuning of their selectivity by tailoring the size of the pores to the target molecules. Although many efforts have been concentrated in the preparation of novel metal-organic framework structures with different topologies, the integration and immobilization of these materials in functional devices is still in its infancy. In order to apply metal-organic frameworks in sensing applications, their deposition in a substrate with excellent surface coverage is highly desirable.

The preparation of metal-organic framework thin films on different nature substrates has recently drawn attention from the research and industrial fields. In this regard, metal-organic framework thin films have been fabricated by various approaches, such as spray layer-by-layer,[1] or the direct solvothermal synthesis.[2] Printed metal-organic frameworks have recently been proposed as an interesting approach to deposit metal-organic frameworks as it allows to directly create complex structural networks with much less waste than with other techniques. For example, metal-organic framework-74(Ni) and the University of Texas at San Antonio-16(Co) materials have been reported as 3D-printed monoliths for CO_2 adsorption,[3] or a 3D printable hydrogel ink containing Zeolitic Imidazolate Framework-8 anchored on cellulose nanofibers as drug delivery platform.[4]

Researchers have also explored the inkjet printing for creating metal-organic framework thin films for their use in signal sensors, chemical sensors, and selective membranes. In 2015, Júnior et al. pioneering reported a series of lanthanide metal-organic frameworks printed onto plastic and paper foils with a conventional inkjet printer, and open a new window for exploring printed metal-organic framework materials in technological applications, such as optical devices (lab-on-a-chip), proof of authenticity for official documents and sensing.[5] Other authors reported the deposition of metal-organic frameworks in screen-printed carbon electrodes,[6] drop-casting in the detection of nitrite[7] or ammonia,[8] or spin coating in the detection of *Escherichia coli*.[9] But not until 2021, the possible practical utility of printed metal-organic frameworks was demonstrated for sensing. Particularly, Deep et al. demonstrated the potential of printed Mn-1,4-benzenedicarboxylate and Tb-trimesate metal-organic frameworks on NH_3 detection over the range 5-80 ppm with a limit of detection of 0.3 ppm (much lower than already reported ammonia sensors) through colorimetry and photoluminescence, respectively.[10] Finally, in 2022 Ameloot et al. reported for the first time the use of aerosol jet printing for the deposition of the ultramicroporous metal-organic framework University of Texas at San Antonio-280 with CO_2 adsorption capacity and potentially useful in CO_2 sensing (Figure 1).[11]

Current and Future Challenges

Metal-organic frameworks have demonstrated their utility as coatings through the development of inks with different purposes. They are stable under high temperatures (*ca.* 300 ºC), so they can be

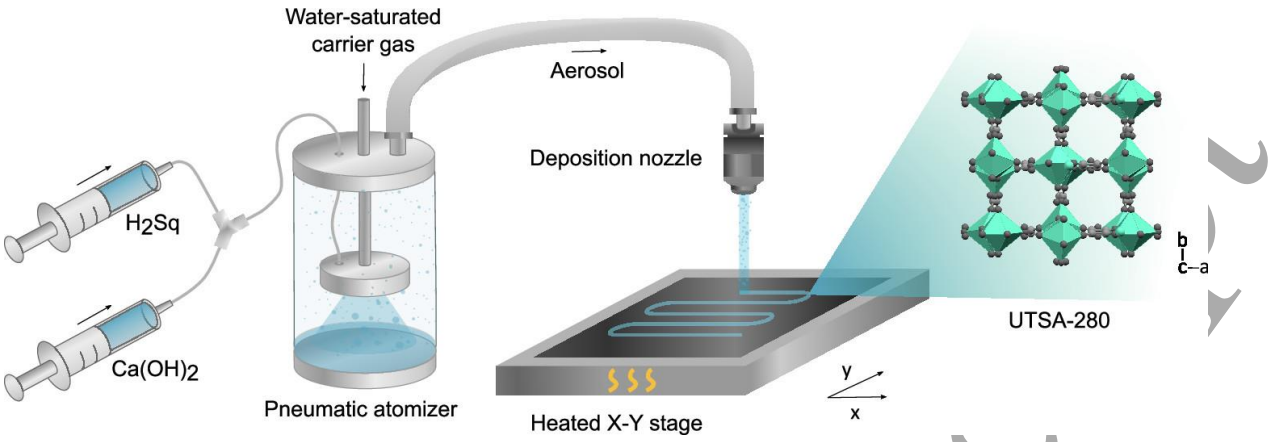

Figure 1 Schematic representation of the aerosol jet printing setup used to deposit University of Texas at San Antonio-280. [CaO_6] polyhedra are shown in green and C and O atoms are shown in grey. Reproduced with permission.[11]

printed using different technologies. Also, mechanical properties can be adapted by adjusting the composition and printing parameters. Thus, the printed materials have similar properties (adsorption, fluorescence) than the pristine metal-organic frameworks with better mechanical properties.

As a new class of porous materials, it is important to recognize that prior to the potential use of printed metal-organic frameworks as gas/vapor sensors, metal-organic framework's stability and aging or their fatigue/reusability is a major challenge. Most of the reported printed metal-organic frameworks applied in different fields, did not consider their reusability or it is only performed at short-term cyclability, remaining almost unknown the long-term reuse of these deposited solids. Further, considering their way from basic to industrial applications, novel synthetic routes with appropriate space time yield (kilogram of materials per cubic meter of reaction mixture per day), avoiding the use of expensive or dangerous reactants, using green and economic solvents, and favouring low pressure conditions are required.[12] If fact, the vast majority of deposited metal-organic frameworks are related with materials synthetized at room temperature (mainly Cu-trimesate or Zeolitic Imidazolate Framework-8).

Another important point is the optimal dispersion of metal-organic frameworks on the desired support. Dispersing metal-organic frameworks into polymer matrixes is an effective way to enhance the mechanical, electrical, optical, and mass transport properties. Thus, to control the dispersibility of metal-organic frameworks in these matrixes is basic for their optimum functionality. Metal-organic framework particles aggregation is a recurrent phenomenon, which is often indicative of poor interfacial compatibility, associated with a loss of mechanical and mass transport properties of the composites. Such aggregation is especially critical in the deposition of smooth and, therefore, reproducible printed layers. In this sense, metal-organic framework's surface modification has recently reported as an efficient alternative to avoid aggregation issues.[13]

Advances in Science and Technology to Meet Challenges

Metal-organic frameworks are impressive materials in terms of adsorption and chemical diversity. In the field of gas sensing, metal-organic frameworks are especially attractive because of the possibility of tuning their sensitivity and selectivity to a target molecule during their synthesis by incorporating in their porosity the proper functionalities (chemical groups, metallic particles, etc). For instance, the Pd-embedded in a Zr and dibenzo[*b*,*d*]-thiophene-3,7-dicarboxylate-5,5-dioxide metal-organic framework shows higher efficient and selective hydrogen sensing performance that the pristine metal-organic framework.[14] Upon exposure to H_2, the transient resistance curves of the gas sensor showed a 5-fold increased response when the Pd-based composite is utilized. Another example is the amino functionalized Universitetet i Oslo-66-NH_2 material in the effective chemiresistive sensing of acidic gases, such as SO_2, NO_2 and CO_2.[15] While the non-functionalized Universitetet i Oslo-66 showed no

detectable changes in resistance, Universitetet i Oslo-66-NH_2 demonstrated an attractive response of 21.6, 7.6 and 11.4% for 10 ppm SO_2, 10 ppm NO_2 and 5000 ppm CO_2, respectively. Thus, printed metal-organic frameworks are projected as a novel pathway to bust their applications in several important fields (chemical, food and energy industries, biomedicine, etc.) thanks to the combination of metal-organic frameworks' properties with the inherent advantages of printed electronic technologies. To advance into the realization of printed metal-organic frameworks, some important facts should be considered, like particle size, viscosity and surface tension, among other technological parameters to obtain stable inks/pastes. Regarding their manufacturing, significant advances should be achieved towards sustainable metal-organic frameworks. In spite of the synthesis of some environmentally friendly metal-organic frameworks, the majority of them require either high temperature (120-220 ºC) and/or high-pressure processes (using Teflon-lined autoclaves), hazardous solvents and/or the resulting synthesized metal-organic frameworks are not biodegradable.

Overall, some advances have been performed on the development of printed metal-organic frameworks, although their application in gas/vapor sensing is still in its early stages. Despite the outstanding performances of some metal-organic frameworks, their application in this field requires a further deep evaluation of crucial parameters (reusability, cost, industrial conditions, efficient deposition, etc.). Apart from the mentioned challenges with respect to the printability of metal-organic frameworks, another path to explore is the compatibility between metal-organic frameworks and pre-treatment (normally required for surface tension incompatibilities) and post-treatment processes (normally needed for activating the deposited layers) as sensing devices are composed of many different layers and metal-organic frameworks must not be used alone. Finally, besides metal-organic frameworks optimization, the existing perspective of 3D printable sensors is based on the capacity to create complex shapes, opening a set of opportunities to find uses in other diverse areas.

Concluding Remarks

Over and above, gas/vapor sensing printed metal-organic frameworks are conserved as multifunctional platforms, as they not only work as sensors, but also as adsorbents, and even as detoxifying agents. Apart from the outstanding features of metal-organic frameworks, their ease of functionalization during the synthesis process with respect to other commonly used materials for gas sensing, makes them perfect candidates to achieve selective sensing layers, which is one of the major, not yet resolved challenges, in this type of sensors. However, for their broader use in printing technology, science and technology should face the main weakness in the current state of the art: the formulation of stable dispersions.

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Section 6.8 – Printable gas/vapour sensors based on metal-sulfide materials

Andrea Gaiardo[1], Matteo Valt[1] and Barbara Fabbri[2]

[1]MNF—Micro Nano Facility, Sensors and Devices Center, Bruno Kessler Foundation, Via Sommarive 18, 38123 Trento, Italy
[2]Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy

Status

Metal sulfides have attracted great research interest due to the abundant choice of cheap materials. They are part of the current generation of sensing materials, holding a favorable position by virtue of their elemental composition, and progressing as possible cutting-edge alternatives to metal-oxide semiconductors. In fact, the absence of oxygen in the crystal lattice results in a distinct catalytic mechanism for the surface reaction, as well as representing a potential solution to the consistent signal drift experienced by metal oxides and attributed to in/out diffusion of oxygen vacancies. Moreover, metal sulfides possess high carrier mobility at low temperature when compared to other sensing materials, which allows a low energy consumption and then a low/room temperature operation, making them superior for a feasible technological integration [1]. In addition, their sizable and tuneable bandgaps enable the light activation in the visible range, involving both high energy efficiency of photoconversion and an effective room-temperature operation. However, only starting from the last decade metal sulfide semiconductors are receiving intense research interests for promising applications in gas sensing, demonstrating a range of unique properties that outperform those of other nanostructured semiconductors [2]. The possibility to tune the nanostructure morphology and crystal structure by using simple and inexpensive methods continues to push forward the usage of metal sulfides as functional 154ensingg materials. In particular, both theoretical and experimental investigations have highlighted that 2D metal sulfides are extremely efficient in gas detection due to their high surface-to-volume ratio, high conductivity, and surface reactivity, although the lack of control over their printing and the associated uncontrolled packing of 2D nanostructures limit reproducibility in their production.

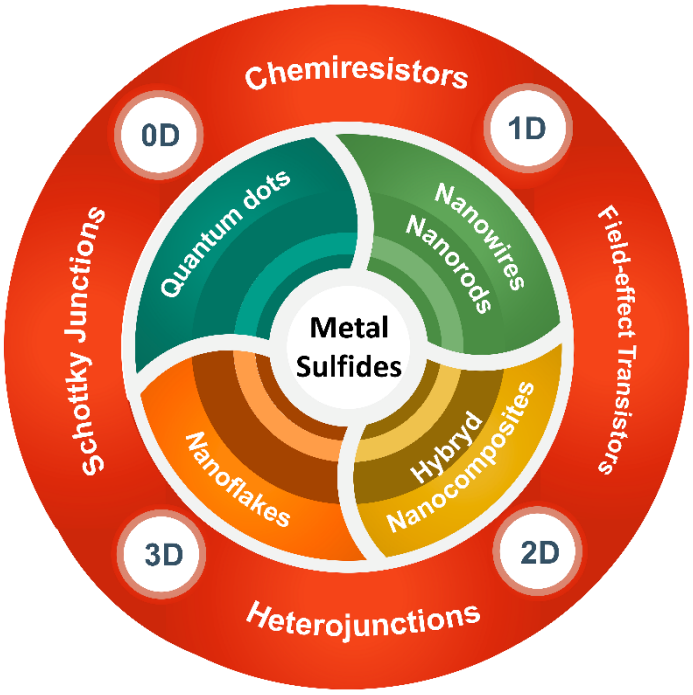

Figure 1 Metal sulfides-based devices and nanostructures.

Metal sulfides-based sensors can be classified into chemiresistors, Schottky junctions, heterojunctions, field-effect transistors, and optical and surface acoustic wave gas sensors (figure 1). Studies published so far highlighted that IV-VI metal sulfides show fast response and recovery time, within the range of a few seconds, while II-VI compounds have high response and selectivity to volatile organic compounds [3], especially in dry air, but at relatively high working temperatures (> 150°C). The use of functionalisations or hetero-junctions with other nanostructured semiconductors leads to a strong increase in the sensing performance of metal sulfides-based printed gas sensors, allowing to detect concentration of both organic and inorganic gases with a limit of detection compatible with application requirements, including air quality monitoring (e.g. NO_2 – 20 ppb, benzene – 0.1 ppm, NH_3 – 1 ppm, etc.) and detection of explosive gas leakages (e.g. H_2 – 1 ppm, etc.).

Current and Future Challenges

Research in this field still needs more knowledge in the deep understanding of surface phenomena that drives gas sensing performance of these materials since these topics are still unclear and several investigations need to be performed with the help of both theoretical and experimental investigations. As an example, efforts from a few research groups have been devoted to the study of sulfur defects and their impact on sensing properties. Developing synthetic methods and deposition techniques that enhance performance and signal reproducibility in analytical measurements is crucial and requires significant improvements. Indeed, it is well known that film thickness impacts on sensing performance, especially on 2D structures [4]. In fact, the number of layers affects the electronic properties of 2D materials. Therefore, developing deposition/printing methodology for optimal reproducibility and film thickness is becoming critical for the use of these materials. For instance, non-scalable thin-film techniques such as layer-by-layer deposition have so far led to the development of metal sulfide gas sensors with better performance than printed ones, stressing the need for improved printing techniques for these materials for the large-scale production of high-performing devices [3].

Although metal sulfides-based devices are sensitive to the same gases and vapours as metal-oxide gas sensors, they are less sensitive to specific gaseous compounds, including acetone, ethanol, H_2S and SO_2, which greatly compromises the widespread use of these materials in various application fields. In particular, their adoption is severely limited in cases where the required gas detection limit is in the ppt/low ppb range, such as in medical applications (e.g., breath analysis).

In addition, illumination and temperature have a significant impact on the characteristics of metal sulfide semiconductors, such as photoconductivity and limit of detection. Indeed, despite high melting temperatures, sublimation and material poisoning can occur at significantly lower temperatures. As a result, for the most stable sulfur-based compounds such as ZnS and CdS, working temperatures of gas sensors cannot exceed 300–350 °C, while other metal sulfides degrade at temperatures lower than 100°C [5]. This shortcoming, mainly due to surface oxidation, negatively impacts on the long-term stability of the material and the related sensor performance (e.g., signal drift and response reproducibility) [1]. Therefore, other activation modes need to be explored to achieve low/room-temperature operation overcoming the aforementioned phenomena. In this regard, the number of scientific papers pertaining to such systems is rapidly rising [3], suggesting that more research and development is necessary since metal sulfide semiconductors, at the current state-of-the-art, are still unable to address issues with selectivity and instability of gas sensors over time, especially under high-humidity conditions [1, 3].

Advances in Science and Technology to Meet Challenges

Elucidating the receptor and transduction mechanism is essential to understand and improve the performance of metal sulfides-based gas sensors for their potential use and commercialisation. Ab-initio computational analysis and quantum mechanical modelling have provided evidence of chemical and physical adsorption of gases on the surface of the sensing material. However, only the adoption

of advanced multiscale models in combination with in-situ/operando analysis can provide the entire panel of information required for a full understanding of the sensing mechanism [6,7].

To overcome the current challenges related to the production and printing of metal sulfides for gas sensing applications, the combined adoption of advanced bottom-up (hydrothermal synthesis, microwave-assisted method, etc.) or top-down (liquid phase or mechanical exfoliation) scalable strategies for materials synthesis with innovative material modification methods (heat treatment, plasma etching, functionalization,, etc.) is paving the way for the control of chemical (defects, etc.) and physical (conductivity, etc.) properties of nanostructured metal sulfides, which can be exploited for gas sensing as well [8,9]. Furthermore, new coating approaches under investigation, including molecular printing, light-based printing, and spray coating, are showing significant advantages in controlling the deposition thickness of films based on 2D nanostructures, facilitating the optimisation of deposition parameters for the specific application required [10].

Regarding the shortcomings shown so far by metal sulfides-based gas sensors in terms of performance, innovative software and hardware technologies are being investigated. To address the instability due to uncontrolled oxidation of the nanoparticle surface, the development of 2D layered amorphous metal-oxide nanostructures is leading to strong advantages for material stability, allowing the structural, morphological, and electrical properties of metal sulfides to be maintained over time, while increasing surface reactivity [11]. Furthermore, the exploitation of a mixed activation methods recently studied for other sensing materials (e.g., metal oxides), which includes dynamic temperature modulation and photoexcitation in the UV-visible range with ultra-low power radiation sources (µLEDs) [12], can lead to soft activation of metal sulfides-based gas sensors, allowing for increased device stability by limiting surface oxidation. Recent work has shown that the development of suitable Schottky junctions, heterostructures and functionalization allows for increased catalytic performance of metal sulfides, which can be exploited to improve sensing device performance, including limit of detection, selectivity, and sensitivity [3].

For the effective use of metal sulfides-based sensors on-field, which is still lacking today, it is crucial to increase knowledge on the performance of these devices in the long term, also by taking advantage

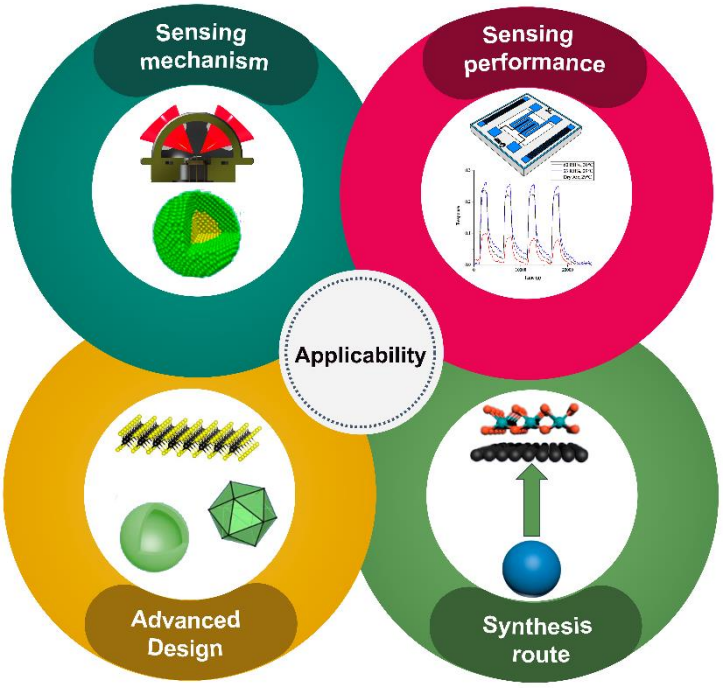

Figure 2 Overview of challenges and possible state-of-the-art strategies for printable metal sulfides-based gas sensors.

of innovative approaches such as rapid ageing tests. This will enable the above-mentioned new technologies to be combined with a data-driven approach for developing predictive models (using artificial intelligence methods) useful for optimising the performance of the devices and meeting the application requirements (Figure 2). Such a combined approach has brought significant benefits to other types of detectors (e.g., metal-oxides-based sensors), enabling their effective functional use in relevant environments.

Concluding Remarks

In these early years of research into the use of metal sulfides for the development of printed gas sensors, strengths, challenges, and weaknesses emerged. Thanks to their peculiar chemical-physical properties, metal sulfide gas sensors have shown superior sensing performance for the detection of various target gases compared to other widely used sensing materials. On the other hand, the lack of knowledge about their sensing mechanisms, the instability of metal sulfides over time due mainly to surface oxidation, and the strong impact of the deposition technique on their electrical and sensing performance have limited the study of metal sulfides-based devices to the laboratory environment, preventing their use in on-field applications. The current challenges on metal-sulfides-based gas sensors can be overcome tackled exploiting innovative state-of-the-art technologies, including: (i) multiscale models for simulation and in-situ/operando techniques to unravel sensing mechanisms; (ii) new methods for the synthesis of metal sulfide nanostructures with great control over their structure, composition, etc.; (iii) soft activation approaches, such as temperature modulation or low-power photoactivation; (iv) development of predictive models based on data-driven artificial intelligence techniques for data analysis. The combined adoption of these methods can bring the metal-sulfides-based sensors to the next level, paving the way for their future use in relevant environments.

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Section 6.9 – Printable gas/vapour sensors based on 1D/nanowires materials

Vardan Galstyan, Dario Zappa and Elisabetta Comini

Department of Information Engineering, University of Brescia & UdR INSTM of Brescia, via Branze 38, Brescia, Italy

Status

Currently, 1D nanomaterials have been recognized as suitable structures to replace the traditional thick films of polycrystalline metal oxide powders in gas sensing devices. Variations in their dimensionality, shape, and composition provide a wide range of possibilities for the research and development of gas sensors with enhanced sensitivity and selectivity, as well as fast response and recovery times. Great progress was achieved in the synthesis of nanowires thanks to technological advances in deposition techniques. Significant efforts have been made for the integration of these materials into printable sensing devices and the identification of gaseous compounds by using different detection approaches (mainly electrical, optical, colorimetric, acoustic, thermocatalytic, gravimetric, and capacitive, [1]). Herein, the nature of analyte molecules, low dimensionality, and the type of material, as well as the interface between nanowires are crucial factors that affect the excitation, surface reactions, charge distribution, and emission.

Many works explored new composites and heterojunctions, where the synergy effect between different materials enhances their sensing performance. The most investigated sensing materials in the form of nanowires are metal oxides (SnO_2, ZnO, WO_3, and TiO_2), semiconductors (Si and SiC), perovskites, and metals (Au, Ag, and Pd). The synthesis procedures have been well developed concerning vapour and liquid phase methods, such as chemical/physical vapour deposition, pulsed laser deposition, thermal oxidation, electrospinning, electrochemical synthesis, hydro- and solvo-thermal, sonochemical, surfactant and template-assisted techniques [2]. However, there are no comprehensive investigations on the integration of nanowires into printable gas sensing devices.

Electrical gas sensors (conductometric, Schottky, and field-effect transistors), where the properties of working materials are changed due to their interaction with gaseous compounds and vapours, are one of the most investigated architectures for the fabrication of printable gas sensors. Herein, the longitudinal domain structure in the nanoscale provides an extremely large surface-to-volume ratio enhancing the diffusion of analyte molecules towards the surface and the interaction. ZnO is one of the most studied metal oxide nanowires for the fabrication of electrical sensors, where the response of the material increases about forty times compared to thin film devices [3]. The charge transfer is enhanced due to the adsorption of analyte molecules to the surface of low-dimensional nanowires, and the response time of the ZnO-based sensor is reduced from 287 to 67 s. This is an important parameter for the fabrication of fast sensors and the real-time detection of gases.

In a similar fashion, capacitive sensors are normally based on the gas-dependent dielectric constant of sensitive nanowires. These devices are frequently designed to detect humidity at room temperature and are mostly based on Ag, ZnO, and other semiconducting nanowires. However, they require more complex interface electronics compared to conventional conductometric or field-effect transistor-based devices.

Optical gas sensors based on 1D nanowires mostly rely on two transduction mechanisms upon interaction with a specific analyte: a change of their optical transmittance or the quenching and shifting of their photoluminescence. Silicon, silver, and metal oxides have been widely studied. As an example of superior performances of 1D nanostructures, hierarchical nanowire-based WO_3 films exhibited shorter response time and higher transmittance change ($t_{80\%}$ = 24.8 s, ΔT_{1500nm} = 65.1%) than porous films ($t_{80\%}$ = 66.3 s, ΔT_{1500nm} = 28.6%) [4].

In surface acoustic wave sensors, the adsorption of the gas molecules on the sensitive interface modulates their propagation properties. They are largely used for hydrogen and humidity monitoring, typical materials are Pd-based, Ag, SnO_2, and ZnO. As a comparison, a ZnO thin-film sensor was reported to detect hydrogen concentrations approaching 0.2%, while an equivalent nanowire sensor was capable of measuring concentrations one order of magnitude lower [5]. Gravimetric sensors measure the change in weight. The active material is deposited on a mechanical resonator and the gas adsorption may induce a shift in its resonant frequency. Quartz crystal microbalances have been used as sensors at room temperature with ZnO, Au, and Ag or IrO_2 nanowires for the detection of ammonia, humidity, acetone, other vapours, and odours including alcoholic beverages.

In colorimetric gas sensors, the response is based on the colour change due to the chemical reactivity of the indicators and usually exploits nanomaterials, but no relevant research has been done on gas phase detection using nanowires. In thermocatalytic-type sensors, the combustible gaseous compounds burn on the catalytic material increasing the temperature of the sensing structure and in turn its electrical resistance [6]. In this case, metal oxide nanowires with their stable thermal properties seem effective replacements for the conventional metallic layers, in which thermal instability affects their functionality. However, metal oxide nanowires have not yet been integrated into such gas sensors and studied in detail.

The continuous research works and further advances in synthesis technologies of nanowires with desired composition and dimensions, the proper analysis and choice of detection approach for each gaseous compound will lead to the manufacturing of gas sensing systems that meet target applications.

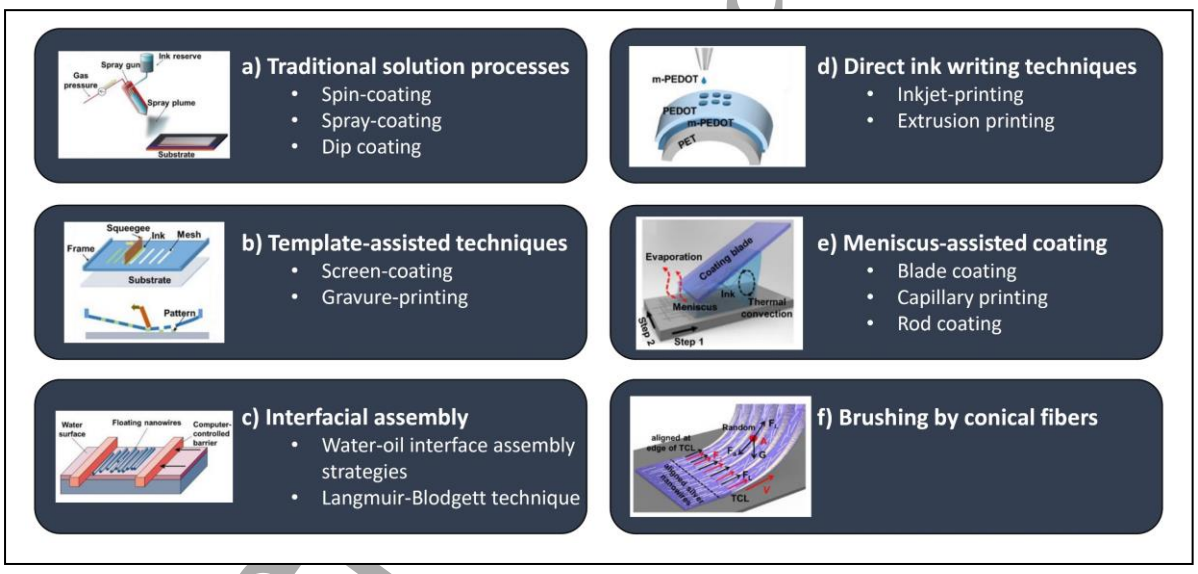

Figure 1 Schematics of various solution processes. Figures: (a) spray-coating. Reproduced with permission from ref. [7]. Copyright 2016 Wiley-VCH VG&CK, Weinheim. (b) Screen-coating. Reproduced with permission from ref. [8], under the terms of Creative Commons CCBY License. (c) Langmuir–Blodgett technique. Reproduced with permission from ref. [9]. Copyright 2019 American Chemical Society. (d) Inkjet printing. Reproduced from ref. [10]. Copyright 2013 American Chemical Society. (e) Blade-coating. Reproduced from ref. [11]. Copyright 2016 American Chemical Society. (f) Brushing by conical fibers. Reproduced with permission from ref. [12]. Copyright 2018 Wiley-VCH VG&CK, Weinheim.

Current and Future Challenges

Printable sensing technologies require the preparation of inks composed of 1D nanowires. Their formulation is crucial for the device performance and should not be underestimated. It also strongly depends on the patterning technique used for the dispersion of nanowires on a substrate [13]. Inks composition and properties, such as viscosity, surface tension, and solvent chemical nature, are

pivotal for achieving high printing accuracy and resolution. In particular, the choice of solvents and binders/additives is fundamental for the nanowires final electrical, optical, and sensing properties: their permanent binding to the nanowires surface may reduce the interaction with the surrounding atmosphere thus affecting sensor performance dramatically. Moreover, ideally, these inks should be inexpensive, easy to prepare, environmental-friendly and stable against aggregation and precipitation. For ink preparation, the easiest approach is the synthesis of nanowires directly in the form of powder compared to their growth on support, which requires a challenging detachment and transfer.

Electrical, optical, and transduction properties are strongly correlated with the coverage and micropatterns of the 1D materials, which makes them critically important for high-performance sensors development. Various solution processes capable of making micropatterns have been proposed, each one with its unique advantages and disadvantages [14]. Moreover, the choice of substrate for printing is fundamental. Adhesion, homogeneous size and distribution of nanowires, chemical stability with the ink solvent, and wettability are affected by the combination of substrate material and ink. Furthermore, it should satisfy required sensor specifications, while being compatible with conventional electronics when integrated into small and portable monitoring systems.

Alignment of the deposited nanowires is another challenge, as solution-based processes do not guarantee precise arrangement. Despite alignment is not strictly required for gas sensors, in some cases (such as surface acoustic wave sensors) it may affect their performance. In this regard, a few techniques can be adopted, for example, electrophoresis. Although nanowires exhibit versatile functionalities for the detection of gases, they suffer from poor selectivity. Hence, the realization of materials with appropriate compositions and dimensions for the selective detection of a specific analyte is an important challenge. Moreover, if the volatile compound to be detected is poorly interacting with the material surface, such as in the case of CO_2, nanostructuring the surface may provide only limited effects.

Even though great advancement has been achieved in the application of nanowires in printable sensing technologies, their stability and reproducibility need detailed studies. Most of the devices have been developed at the laboratory level (low technology readiness level). Therefore, further advances are required for a high-throughput and large-area uniformity fabrication of printed sensors, maintaining low production costs. Despite the huge advances in the field, the interaction mechanism between specific volatile molecules and nanowires surface is not fully understood, and further studies are required to optimize the relation between sensing material and target analyte. Moreover, some sensing architectures have intrinsic limitations due to the nature of the transduction mechanism. For example, in optical sensors, the quenching of the photoluminescence signal limits the sensitivity up to specific gas concentrations, and colorimetric may give just an ON/OFF status.

Advances in Science and Technology to Meet Challenges

Concerning ink preparation, more attention should be given to environmental sustainability by selecting green procedures and solvents. The specific toxicity of nano-sized materials and deposition techniques should be considered. It has been proven that 1D nanomaterials can induce pathologic injuries and are more biologically harmful than other morphologies (nanoparticles for example) [15].

In sensor fabrication, specific surface treatments, such as plasma, functionalization, wet chemical, and temperature control, may improve surface adhesion and wettability mostly on soft and flexible substrates. Improved substrate adhesion is essential under mechanical deformations or at extreme operating conditions (temperature, humidity, gas flow, and aggressive atmospheres). Rational optimization of the devices may be achieved by understanding sensing principles, which require *operando* measurements (such as diffuse reflectance infrared Fourier transform spectroscopy, attenuated total reflectance-Fourier transform infrared spectroscopy, and near ambient pressure-X-ray photoelectron spectroscopy) that provide accurate information on the surface chemistry during the operation in real working conditions [16].

Several nanowires have been successfully applied in printable electrical gas sensors using various techniques. While the achievements in thermocatalytic-type sensors suggest that 1D nanowires can be used in the aforementioned monitoring systems for the selective detection of combustible gases. However, there is no progress in this field and further investigations are required to evaluate the integration of semiconductor nanowires in thermocatalytic-type gas sensors. The interaction of nanowires with smaller and simple molecules of analytes (for example, hydrogen) can be improved by the modification of the dimensions of the material and the application of catalytic layers. Instead, the adsorption of large and complex molecules (for example, acetone) on nanowires requires higher energies, and therefore the sensors operate at relatively elevated temperatures. Thus, more research studies are required for the development of composites and heterojunctions with precise control of the composition and size of nanowires, which may enable the tuning of their sensing response and selectivity to complex gaseous compounds. Furthermore, their combination with selective filters/membranes could be another efficient way to enhance selectivity. Lately, some interesting approaches have been proposed, such as novel surface molecular imprinting strategies for selective control in heterogeneous catalysis. These procedures can be integrated into gas sensing devices to achieve the required selectivity. The concept relies on a template-assisted selective passivation of the active surface. Upon removal of the template, unpoisoned sites provide size, shape, and functional group compatibility with the target analyte. This strategy enables selective catalytic reactions by proper selection of the template, poisoning molecules, and design of the imprinting process [17].

Another strategy largely adopted to overcome selectivity issues in traditional gas/volatile sensors is the integration of multiple devices forming an array. The challenge, however, remains the combining of different sensing principles in one single system, due to the variety of requirements of each element forming the array. At the same time, machine learning algorithms and artificial intelligence could provide valid support for the discrimination of analytes in a noisy environment.

Concluding Remarks

Overall, significant advances in the synthesis methods of nanowires with various dimensions have boosted their application in printable sensing technologies. Simultaneously, new processing methods for nanowires with complex compositions continuously enhance their sensing performances. The preparation of inks with appropriate chemical stability is important for the development of printable sensing devices. The understanding of the adhesion mechanism of materials on the substrate remains a significant factor to be examined. Thus, the accuracy of printing methods including the ink properties should be a topic for further studies. Moreover, appropriate technical procedures for transferring nanowires from the support material to the ink solvents must be developed. Considerable advancements have been made in the application of nanowires in electrical and optical printed gas sensors. Instead, the integration of nanowires in printed sensing devices based on other operation technologies, such as surface acoustic wave, gravimetric, colorimetric, and thermocatalytic is still in its early stage of development.

The current research studies suggest that printed sensing devices will open a new era for the manufacturing of flexible and stretchable gas/vapour sensors for real-time monitoring of human health and the environment. Nowadays, the reduction of adverse effects of technological processes on human life and the environment is highly required. Therefore, eco-friendly fabrication procedures and the application of nontoxic precursors and materials in the development of printable technologies and sensing devices should be considered.

Acknowledgments

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CN00000023), Spoke 5 “Light Vehicle and Active Mobility”. This manuscript reflects only the authors’ views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

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Section 7.1 – Introduction to printable chemical sensors for non-biological analytes in solid/liquid media

Vincent Noël, Giorgio Mattana and Benoît Piro

Université Paris Cité, ITODYS, CNRS, F-75006 Paris, France

Printable materials for chemical sensing are of course needed to make electrical contacts (in this case, metal inks are the most common, e.g., silver, gold and, more recently, platinum), but are also needed to make the functional parts of chemical sensors, e.g., conducting polymers, nanostructured oxides, organic or inorganic semiconductors, graphene or carbon nanotube derivatives... These materials are already available as inks, but their use as thin functional films often involves complicated and/or non-reproducible procedures. Printing (inkjet printing, screen printing, aerosol printing, to name the most common techniques) allows the deposition of thin films in a very reproducible way and is one of the most credible methods for the fabrication of sensors in laboratories, but also on an industrial scale.

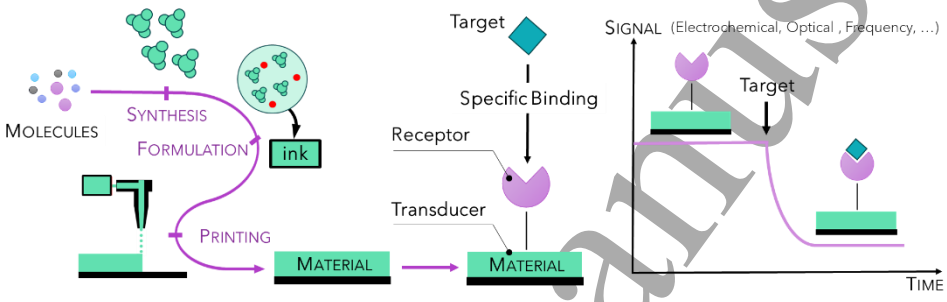
Like all chemical sensors, those for non-biological analytes contain two functional parts: a receptor and a transducer. A chemical event (a reaction, the binding of a target molecule to a probe, a change in refractive index, in pH, in capacitance, etc.) occurring at the (molecular) receptor is translated by the transducer into an analytical signal, which is generally optical (absorbance, fluorescence), electrical (potential, current), or both (e.g., electrochemiluminescence). Non-biological analytes that can be addressed by printed chemical sensors are, for the most commonly reported ones, toxic ions (e.g., heavy metals, chromium, arsenic), organic pollutants such as pesticides or even nanoparticles such as nanoplastics, in soils or surface, drinking or sea water. The most promising device configurations for such types of analytes now seem to be conductivity sensors and thin-film transistors, both of which can be easily fabricated by printing technologies such as screen printing [1] (but for relatively thick - tens of micrometers - layers with limited lateral resolution, 100-200 µm), inkjet printing [2], extrusion [3], but also capillary printing [4] and nanoprinting [5], which allow the design of much smaller functional parts, down to a few tens of nanometers in size as well as thickness. Different types of substrates can currently be used for device fabrication, but the most interesting (because of their low cost, flexibility, and light weight) are plastic films and, more recently, paper [6].

Currently, printed chemical sensors designed for non-biological analytes such as organic pollutants or metal ions, make use of a wide variety of active materials, including metal oxides, conjugated polymers, carbon nanotubes, graphene, metal organic frameworks, amongst others. These materials can be prepared or functionalized through soft chemical processes known as “chimie douce”. Such processes can be achieved through inkjet printing. Each droplet jetted on the substrate can mix and react with a previous jetted droplet, effectively creating pL reactors within the droplets. Although not yet reported, this process could enable the fine control and localization of reactions within pL droplets, on a µm-scale.

When it comes to performance expectations, printed chemical sensors are not significantly different from chemical sensors produced using conventional techniques [7]. The response time is not usually a limiting factor, but high levels of both selectivity and sensitivity are needed, with limits of detection (LOD) ranging from the nanomolar to the femtomolar (nM to fM) levels. The desired sensitivity is achieved through a high density of high-affinity capture probes attached to the sensor surface. Proper immobilization of purpose-designed molecular probes, exhibiting lock-and-key recognition properties (i.e. steric effects coupled with weak-bond interactions), provide the desired selectivity while small active areas provide the low LOD. Printing technologies enable the achievement of these goals because the capture probes, antifouling agents, protective membranes, or other sensor components can be deposited in a precisely controlled manner, on tiny areas. This process can be executed layer by layer, with lateral resolution that extends down to the micrometer scale.

As mentioned above, the active materials used for detection of non-biological targets must include a recognition function and have physico-chemical properties capable of translating the presence of the target into the variation of a given physical signal, ideally proportional to the quantity of the analyte detected, as it is needed for any kind of sensor. A schematic view of how an active recognition layer can be printed for being used in a chemical sensor is given on Scheme 1 below.

An important criterion concerns the stability of the materials. Indeed, unlike sensors dedicated to the detection of biological compounds used in aqueous medium (often neutral pH, i.e. biological fluids), materials for the detection of non-biological chemical compounds can be in contact with aggressive environments (high pressure, high temperature, corrosive environment, low or high pH, etc.) [2]. It is therefore necessary to anticipate this aspect in the design of the device and to use materials capable of withstanding the analysis conditions. For these reasons, post-processing of the printed layers is often mandatory, for example to induce crosslinking or crystallization of the materials.



Scheme 1 How an active recognition layer can be printed, on any kind of substrate, for being used in a chemical sensor. Note that the receptor can be printed as well.

Another issue that must be addressed is the environmental impact of printed chemical sensors. Reducing the amount of active material deposited on a sensor is the primary objective, which digital printing technologies like on-demand inkjet printing with each droplet having a volume of merely a few pL, perfectly address. Another crucial issue is the use of toxic chemicals, specifically solvents, given that printing is a wet procedure; hence, the use of water as a solvent or vehicle is of utmost importance [8]. Finally, today's consideration of recyclability is vital. Once again, the layer-by-layer addition of functions that can be detached from one another at the product's end-of-life, printed on natural or recyclable substrates (e.g., textile, paper, recyclable polymers...), make printing technologies a highly appealing and scalable solution for industrialization. It is generally agreed that environmental impact is best evaluated in terms of Life Cycle Assessment (LCA), which is able to provide an estimation of how a given technology affects the environment (in terms of energy consumption, utilization of rare and nonrenewable resources, emissions and recyclability). While LCA analysis has been applied to specific printed materials (polymeric films used for photovoltaic applications) or devices (antennas) [9], to the best of our knowledge a comprehensive evaluation of the environmental impact of printed chemical sensors for non-biological analytes is still missing and would be strongly needed in order to set up fabrication strategies capable of obtaining devices with reduced carbon footprint.

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Section 7.2 – Printable chemical sensors for non-biological analytes in solid/liquid Media based on organic semiconductors

Elliot Strand, Eloise Bihar and Gregory L. Whiting

University of Colorado Boulder, College of Engineering and Applied Science, 4001 Discovery Drive, Boulder, CO, 80303, United States of America

Status

For printable chemical sensors used for non-biological analytes in solid and liquid media, organic semiconductors hold particular promise due to their ease of fabrication, biocompatibility, customizable functionality and mechanical flexibility. Among the various available organic semiconductors, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate is the most widely used due to its ease of processing, stability in aqueous environments, high conductivity, and compatibility with printing techniques (Figure 1) [1]. Over the past decade, several reports have demonstrated the successful use of solution-processable semiconductors with printing processes for developing organic chemical sensors for non-biological analytes in solid and liquid media. Examples include coupling printed organic semiconductors with ion-selective membranes for detection of ions like sodium and potassium, or using pH-sensitive dyes alongside organic semiconductors for proton uptake measurements [2,3]. Other approaches have associated organic semiconductors with inorganic materials for monitoring oxidation reactions (e.g., hydrazine detection) [4], utilized selective mediators and enzymes for ethanol detection [5], and incorporated fluorinated polymers for temperature sensing [6].

Organic semiconductors can offer significant advantages over traditional microelectronic materials in this case. For example, organics are well suited for use in various natural environments, enabling tight integration with various media over long durations. In addition, organic materials are mixed ionic/electronic conductors that can transport both ions and charge carriers throughout the volume

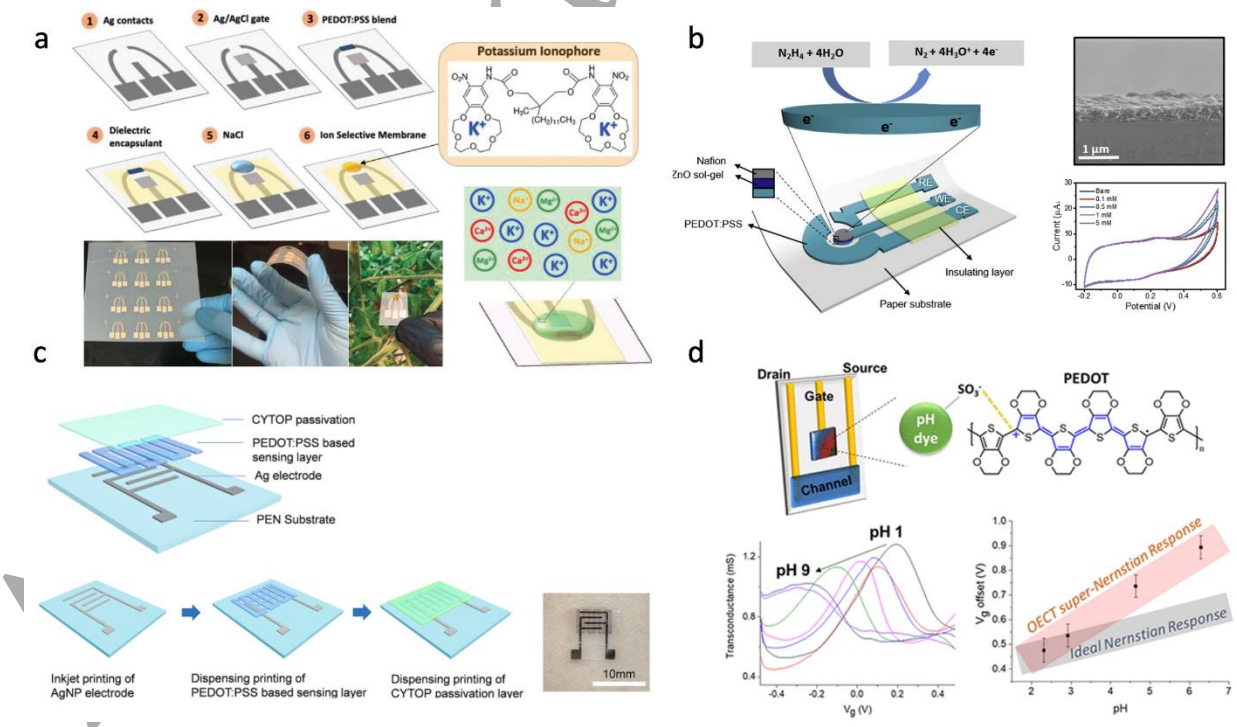

Figure 1 Printed chemical sensors for **a** ion, **b** hydrazine, **c** temperature and **d** pH sensing. **a–d** adapted with permission from references (2 ,4, 6, 7).

of their structure. Hence, they exhibit capacitance values that are orders of magnitude higher than conventional semiconductors or noble metals that are limited by their surface area due to the double layer capacitance. As a result, printable chemical sensors based on organic semiconductors can achieve high sensitivities (> 59mV/dec) compared to many established sensing devices that are limited by the Nernstian slope. The electronic and structural properties of organic semiconductors can also be readily tuned using organic chemistry, which makes them extremely versatile, label-free sensors. Secondary doping techniques involving organic solvents like ethylene glycol, dimethyl sulfoxide, or glycerol have demonstrated the ability to enhance conductivity. The addition of counter ion polyelectrolytes, such as poly(styrene sulfonic acid), not only contributes to aqueous solubility but also enables substitution with other counterions like Tosylate, which can modify sensing capabilities. For example, Mariani, *et al*. explored the synthesis of poly(3,4-ethylenedioxythiophene) doped with pH-sensitive dyes (bromothymol blue and methyl orange), tailoring the sensing application specifically for pH detection [7]. Similarly, Culebras, *et al*. synthesized poly(3,4-ethylenedioxythiophene) doped with various counterions (perchlorate, hexafluorophosphate, and bis(trifluoromethyl sulfonyl)imide) via electro-polymerization to fine-tune its thermoelectric properties for use in thermoelectric generators [8].

Current and Future Challenges

While organic semiconductors offer numerous advantages for chemical sensing applications, they also present certain challenges. One significant challenge lies in achieving sufficient stability, as organic materials tend to be more susceptible to degradation in most solid and liquid environments compared to their inorganic counterparts and can be prone to complex interference from environmental factors. The specific needs and performance characteristics for such sensors depend closely on the application space they are to be used in. For example, if one-time use disposable test strip like devices are being made, which printed organic materials are particularly well suited to, then long term operation is not required, and minimizing device-to-device variability will be a critical concern. It can be challenging to achieve high reproducibility in the fabrication and integration processes of organic semiconductors, which requires careful control over manufacturing methods and device structures in order to achieve consistent and optimal performance metrics. On the other hand, if the sensor is to be installed and provide continuous readout over weeks or months, for example for in-situ monitoring of factors such as pH, temperature, analyte concentration, and electrical conductivity, then the main operational concern is likely to be addressing drift and degradation of the sensor signal over time. This is of particular concern in complex liquid media that may contain materials that foul, damage, or dissolve the materials that the sensor is made of and will limit useful lifetimes. It should be noted that in some cases that degradability of the sensor materials can be a desirable feature, enabling transient electronic systems that provide reduced waste and allow for wide dispersion of sensors into the environment for monitoring natural systems such as agricultural soils [9,10], however this can further exacerbate issues of signal drift over time.

Sensor selectivity is another significant concern. Organic semiconductors tend to respond to a wide range of other analytes, and this cross-reactivity can limit their utility. For example, chemical sensors for determining concentrations in liquid media, will likely respond to other similar interfering compounds, as well as differences in factors such as temperature and pH. As such new materials for sensors, including materials for selective membranes are needed. Other approaches to providing selectivity such as read-out methods and biasing schemes, packaging approaches, and data analytics all need to be further developed to enable the use of these sensing devices. Overcoming these challenges will be crucial for advancing practical application of organic semiconductors for chemical sensing for non-biological analytes and for expanding their capabilities in real-world scenarios.

Advances in Science and Technology to Meet Challenges

In general, the importance of packaging and encapsulation for chemical sensors based on organic materials has not been emphasized, but these features are critical for gathering meaningful data from

the application environment, particularly in natural systems, to ensure longer term operation by minimizing fouling and sensor drift over time. There is also great promise in the development of new materials for printed chemical sensors rather than relying on traditional organic semiconductors such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate. The synthesis of novel semiconducting polymers is crucial to expound important structure-property parameters required, for example, for accumulation mode organic electrochemical transistor operation [11,12]. Since organic electrochemical transistors based on these polymers operate in accumulation-mode, they could be functionalized to detect anionic species (such as nitrate - important for environmental monitoring) through a doping mechanism. The ability to detect both positively and negatively charged ions with printed organic electrochemical transistors would expand the range of sensing applications for these devices.

Concluding Remarks

The development of printable chemical sensors based on organic semiconductors is a promising pursuit in the advancement of sensing technology. These devices offer numerous advantages such as mechanical flexibility, biocompatibility, physical and chemical customizability, compatibly with additive print-based fabrication techniques that enables low cost and low energy production of large numbers of devices that are largely free from areal constraints, and the ability to detect a wide range of analytes in solid and liquid media. There are a wide range of exciting use cases for printed organic chemical sensors, alongside significant research challenges, particularly surrounding long-term stability, device-to-device variability and reliability, and selectivity that need to be addressed before widespread use can become common. Material design and device engineering will be essential for the future progress of printable chemical sensors. Both hardware (e.g., packaging) and software (e.g., data analytics) approaches are exciting methods to improve long term device function. The synthesis of novel organic semiconductors will also play a role in improving device performance as well as the range of analytes that can be monitored. Overall, there is immense potential for printable chemical sensors based on organic semiconductors to solve real-world problems that require the monitoring of various environments.

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Section 7.3 – Printable chemical sensors for non-biological analytes in solid/liquid media based on carbon nanotubes

Bajramshahe Shkodra, Mattia Petrelli, Martina Aurora Costa Angeli and Luisa Petti

Faculty of Engineering, Free University of Bozen-Bolzano, 39100, Bolzano, Italy

Status

Nanomaterials are often used to improve the sensitivity of chemical sensors by amplifying their conductivity and catalytic activity. Among the different nanomaterials employed for the detection of non-biological analytes (e.g., ions, heavy metals, and organic pollutants), carbon nanotubes offer particularly advantageous structural and optical characteristics. With a diameter that varies from 0.4 to 100 nm and a length up to tens of micrometers, carbon nanotubes have high aspect ratios that enhance their sensing performance. They are also characterized by excellent electrical properties (e.g., conductivity one order of magnitude more than copper), mechanical properties (e.g., 100 times more resistant and 6 times lighter than steel), and thermal properties (up to 250°C in air and >2600°C in vacuum) [1]. Furthermore, the solution processability of carbon nanotubes makes them fully compatible with commercially available printing and coating techniques, such as inkjet, screen-printing, and spray-coating [2][3]. The combination of these properties enables sensitive chemical sensors for the detection and quantification of a wide range of non-biological analytes.

In particular, solution processable carbon nanotubes are combined with different chemical sensing transducing platforms, such as electrochemical sensors, electrolyte-gated field-effect transistors, and chemiresistive sensors (see Figure 1). In the case of electrochemical sensors, carbon nanotubes are employed to modify the surface of the working electrode, while for transistor-based and chemiresistive sensors the carbon nanotubes constitute the sensing layer. By combining these platforms with ionophores or other recognition elements selective detection of Zn^{2+}, Pb^{2+}, Cd^{2+}, nitrogen compounds like NH_3, NO_3^-, NO_2^-, and organic compounds (dimethyl methylphosphonate, bisphenol) can be achieved [3]–[8].

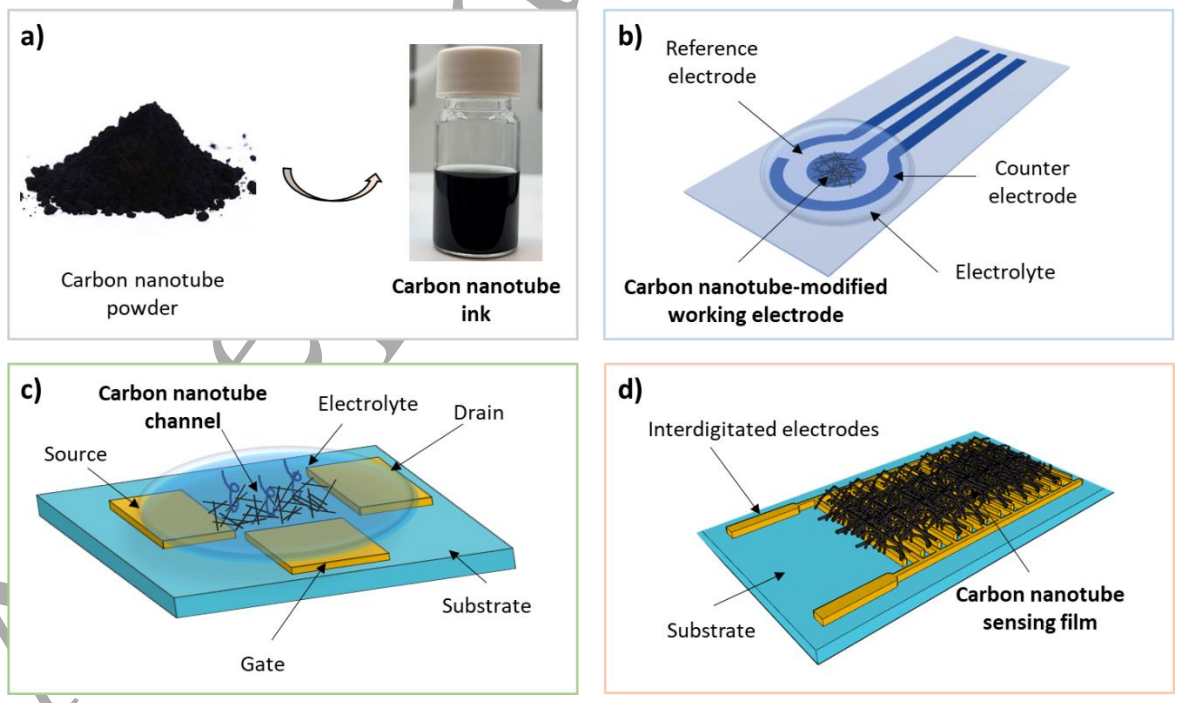

Figure 1 a) Printable carbon nanotubes for: b) electrochemical sensors, c) electrolyte-gated field-effect transistor-based sensors, and d) chemiresistive sensors.

Recently, fundamental and application-oriented studies on hybrid carbon nanotube-nanomaterials are being explored [9]. Hybrid carbon nanotube-nanomaterials are valuable materials that combine the unique physicochemical properties of different components, potentially yielding novel properties through component interaction [10]. In a recent study, an electrochemical sensor with carbon nanotube-copper modified screen-printed electrode was reported to detect NO_3^- [11]. Similarly, a screen-printed electrode modified with carbon nanotubes functionalized with silver-doped zinc oxide nanoparticles was reported for bisphenol detection [12].

The combination of carbon nanotubes' high compatibility to metals, polymers, and nanoparticles with their solution processibility is indeed expected to push toward the technological advancements of printed chemical sensors. This will lead to significant improvements in the monitoring of the health of the environment, humans, animals, and plants, enabling new fields of applications until now not accessible through standard fabrication techniques.

Current and Future Challenges

Although significant achievements have been reached (e.g., sensitive detection down to nM concentration), most of the carbon nanotube-based chemical sensors are at laboratory stage and need further development before being ready for commercialization and production [13].

When bringing these devices from the laboratory to the real-world environment (i.e., complex biological environments with a wide range of fluctuating parameters such as temperature, pH, and liquid compositions), these sensors lack indeed in reliability and accuracy.

Another major issue that appears when testing such sensors in complex biological environments is the non-specific binding i.e., the lack of selectivity to the specific target analyte even when exposed to non-specific interactions [14]. Even though numerous technological advancements (e.g., functionalization with biorecognition elements) have been demonstrated, non-specific binding remains a critical bottleneck.

Particular attention must be given also to device-to-device variability and time stability, which strongly limit sensor reliability, hindering as a consequence a wider applicability. The device-to-device variability is related to both the composition, homogeneity, and uniformity of the carbon nanotube based-ink used, as well as to the printing technique employed for its deposition.

A further challenge regards the ability to sense multi-analyte in a single device, which is fundamental for the development of smart and interactive sensors for wearable and point-of-care applications.

Finally, in terms of the use of carbon nanotubes, the synthesis cost needs to be lowered and their environmental effects should also be carefully assessed. Indeed, some studies have revealed that carbon nanotubes, depending on their size, shape, surface area, and chemical composition, may have possible health impacts on the environment and humans [2].

This is why more research is needed especially in the following areas:

1) improvement of the sensing performance (e.g., sensitivity and specificity);
2) enhancement of the printing technique, as well as optimization of the carbon nanotube-ink composition, to lower the device-to-device variability;
3) development of transducer platforms that allow multiple-stimuli detection in a single device (e.g., arrays);
4) development of mathematical algorithms to minimize sensor drift.

Advances in Science and Technology to Meet Challenges

To achieve desirable performance of chemical sensors based on carbon nanotubes, i.e., in terms of sensitivity (which depending on the application should be as low as 10 µg/L, as in the case of arsenic in water [15]), selectivity, stability over time (i.e., minimal sensor drift), a thorough optimization of the

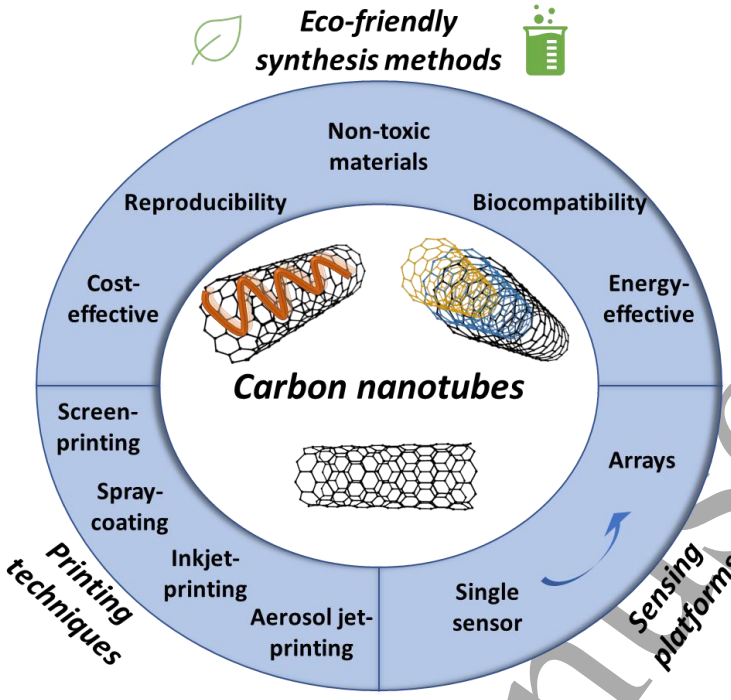

Figure 2 Advances in science and technology required to meet the main challenges in the field of printable carbon nanotube based chemical sensors for non-biological analytes in solid/liquid media.

entire sensing platform is required. When looking at chemical sensing platforms (see Figure 1), one can in fact distinguish between the sensing layer (i.e., the carbon nanotube-ink) and the transducing element (i.e., metallic or carbon nanotube-modified electrodes). In this regard, research should focus on the optimization of the formulations of carbon nanotube inks to be used as sensing or modification layers, as well as on the printing technique employed to integrate the carbon nanotube ink into the sensing platform (see Figure 2).

First of all, dedicated efforts on carbon nanotube ink preparation are crucial to achieve the desirable performance of chemical sensors. An ideal carbon nanotube ink is represented by a homogenous dispersion of nanotubes in the solvent, resulting in a bundle-free film. In fact, the currently poor dispersion of carbon nanotubes in solvents greatly limits their applicability in the fabrication of chemical sensors. To overcome this, polymer modification or biosurfactants could be used to enhance the homogeneity and lead thus to improved performance in terms of sensitivity, device-to-device variability, and time stability [16]. Furthermore, homogeneous nanotube ink composites are ideal materials for flexible and printed electronics, with the potential for integration into printing techniques, including screen-printing, spray-coating, inkjet-printing etc.

Secondly, the printing technique used to integrate nanotubes' ink into the sensing platforms, must fulfil several requirements e.g., uniform deposition, reproducibility, controlled thickness. Here to further extend the spectrum of possibilities of printing, the integration of different techniques can bring innumerable benefits, and let the designers exploit the advantages of each method, e.g., screen-printing of electrodes (i.e., transducing element) and spray-deposition of few nm thick carbon nanotube networks (i.e., sensing layer) [17]. However, a thorough examination of printing processes on nanotube ink distribution must be performed to understand and improve the electrical properties of the printed patterns.

Finally, a dedicated effort for the development of carbon nanotubes chemical sensor arrays is needed. The use of chemical sensor arrays in combination with mathematical algorithms (e.g., chemometric techniques) for data analysis is the key to truly assess the sensor performance and open new applications horizons e.g., electrochemical arrays for detection of several analytes simultaneously.

Concluding Remarks

The last two decades of research have highlighted the strengths, challenges, and weaknesses related to the use of carbon nanotubes for printed chemical sensors. Thanks to their nano dimension and their chemical properties, carbon nanotubes have shown high versability for detecting various non-biological analytes in solid/liquid media. However, the instability of carbon nanotubes over time, the strong impact of the ink composition and deposition technique on the sensing performance have limited the use of these devices at the laboratory scale. The current challenges can be tackled by focusing on: (i) improving the sensing performance (e.g., sensitivity and selectivity), (ii) enhancing the printing technique, as well as optimizing the carbon nanotube-ink composition, to lower the device-to-device variability, (iii) developing transducer platforms that allow multiple-stimuli detection in a single device (e.g., arrays), and (iv) working on the data analysis through chemometrics models.

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Section 7.4 – Printable chemical sensors for non-biological analytes in solid/liquid Media based on 2D materials

Giulia Moro, Ada Raucci, Antonella Miglione and Stefano Cinti

Department of Pharmacy, University of Naples "Federico II", Via Domenico Montesano 49, 80131 Naples, Italy

Status

Since the discovery of graphene and the advent of single- and multiple-layer materials in the early 2000s, 2D materials have been widely applied in electrochemical sensing platforms, especially in portable electroanalytical devices for in-situ monitoring [1]. By enhancing the electrochemically active area, the conductivity and/or promoting different interactions with the target molecules, such as π-π ones, these materials enable improving the analytical performances of the electrochemical sensors. Their high compatibility with metals and carbon-based materials, together with their mechanical strength and flexibility contribute to the technological advances of printed electrochemical sensors, especially wearable ones [2]. Characterized by a single-layer structure with a thickness of few nanometres, 2D materials for sensing represent a branched family, as summarised in Figure 1.

In printed sensors, graphene-based materials, i.e., graphene oxide, reduced graphene oxide, etc. have been used as electrode modifiers or incorporated the conductive inks. Their electrocatalytic properties might be also improved by adding electrocatalysts or doping agents [5]. By combining graphene-based

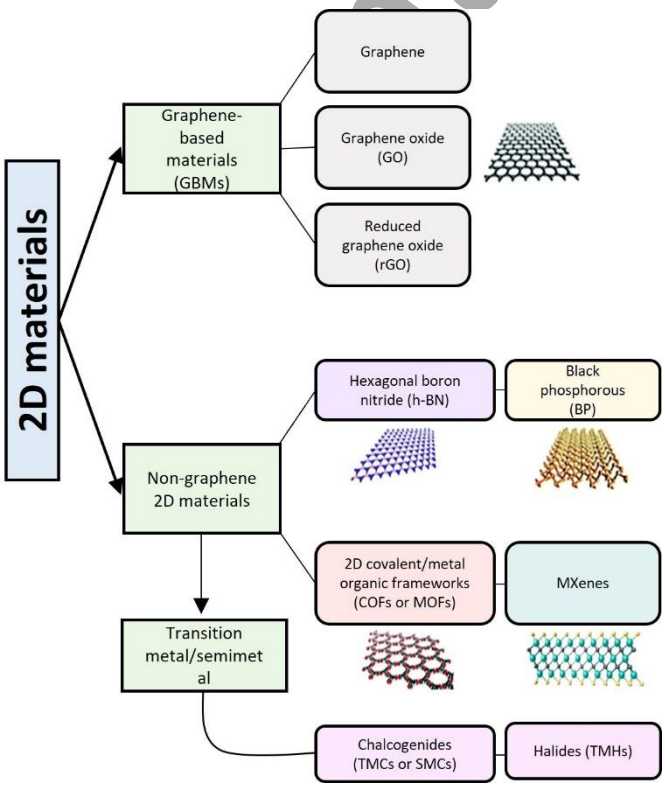

Figure 1 Summary of the main 2D materials applied in printed electrochemical sensing over the last 20 years. Adapted with permission from reference [3] Copyright 2019, American Chemical Society; MXene is adapted with permission from reference [4] Copyright © 2022, Springer Nature. GBMs: graphene-based materials; GP: graphene oxide; rGO: reduced graphene oxide; h-BN: hexagonal boron nitride; BP: black phosphorous; TMHs: transition metal halides; COFs/MOFs: covalent/metal organic frameworks; TMCs/SMCs: transition metal or semimetal chalcogenides.

materials with several species, namely ionophores, ionic liquids, polymers, they have been used to modify screen-printed electrodes (SPEs) for the simultaneous detection of metal ions (Zn^{2+}, Cd^{2+}, Pb^{2+}), drugs, and neurotransmitters with optimal recoveries and enhanced sensitivity/selectivity in real samples analysis [6-9]. Also non-graphene 2D materials (Figure 1) have been largely tested as electrode materials or modifiers, from hexagonal boron nitride, black phosphorous, transition metal or semimetal chalcogenides, and transition metal halides until 2D covalent/metal organic frameworks and MXenes [2,10]. The hetero-metal synergism of bimetallic metal organic frameworks has been found to promote selectively the adsorption of pesticides resulting in SPEs-based sensors with simple architectures and detection limit of ca. 0.3 ppb [11,12]. Nowadays, the graphene analogous Xenes and MXenes represent the cutting edge 2D materials for sensing application [13]. Singh *et al.* combined MXene-Co_3O_4 nanocomposite with portable sensors to follow H_2O_2 production in in cancer cell-lines paving the way for real time monitoring of biological system changes [14]. Recently, MXenes/reduced graphene oxide composites have been synthetised with a green approach for the detection of pesticides [15]. During the last two decades, the properties of the 2D materials have been further enhanced by creating hybrids with other nanomaterials varying from 0D to 3D architectures.

Current and Future Challenges

Aiming at bridging the gap between lab-scale fabrication and industrial-scale production with field applicability of 2D material-based electrochemical sensors, further challenges need to be addressed: (*i*) the in-depth understanding of the interaction at emerging 2D materials, (*ii*) the application of green approaches in the synthesis of 2D material-based modifiers, and (*iii*) the improvement of technological transfer processes with a specific focus on ink formulations and fabrication techniques.

A better understanding on how 2D materials interact with different substances may provide further excellent opportunities to explore sensors in terms of selectivity and sensitivity [16]. Each emerging 2D material has unique advantage, but its flaws cannot be ignored. The construction of hybrid nanomaterials including, but not limited to, the 2D materials themselves, is an effective way to avoid the former limitation: in fact, mutual hybridisation of materials can also lead interfaces with synergic properties, which can help increasing the sensitivity of the analytical device, while avoiding material defects [17]. In addition, 2D materials must be thoroughly evaluated with regards to biocompatibility, environmental stability, and long-term toxicity, because most of the currently used protocols for the synthesis of these materials, and related inks, include toxic substances and harmful processes [18, 19].

As anticipated in the previous section, functional materials can be formulated into inks that act as active printing materials at temperatures compatible with flexible substrates [20]. The excellent solution-processability of 2D materials enables potentially scalable manufacturing of printable sensors based on the techniques summarised in Figure 2.

For large-scale production, techniques based on chemical vapor deposition, inkjet printing, and lithography have shown a strong potential. The more established materials such as graphene, graphene oxide, and transition metal dichalcogenides, are ready to move forward to this stage, while the newer materials still need more basic research. Although same examples are reported, including inkjet-printed MoS_2/polyvinylpyrrolidone-based sensors showed an ultra-fast response to moisture, spray-coated black phosphor to determine H^+ ions and 3D-printed graphene/poly(lactic acid) to detect heavy metal ions [21], the analytical devices containing 2D materials available on the market are limited. Further improvements which will be focused on reliable product design, scalability and low-cost manufacturing are required to reach the market.

Advances in Science and Technology to Meet Challenges

Even if the application of emerging 2D materials is enriching the toolbox for electrochemical sensors' modifiers, the study of green approaches for the "*redesign*" of 2D synthesis is wiping off previous synthetic paths. In this scenario, biosynthetic paths allowing for the synthesis of 2D materials in

Figure 2 Overview of the most promising printing technologies compatible with 2D inks. Ink-jet Printing, drop casting, flexographic printing, spray coating and gravure printing are adapted from reference [21], Copyright © 2022, Springer Nature; extrusion printing is adapted from reference [22], Copyright © 2020 Cheng, Shi, Jiang, Wang and Qin; spin coating is adapted from reference [23], Copyright © 2017 ISTE Press Ltd. Published by Elsevier Ltd; screen printing is adapted from reference [24], Copyright © 2016 Elsevier B.V.

microorganisms with the by-production of biodegradable and non-toxic waste represent the most appealing alternative. Nowadays, biosynthesis is applied only to nanoparticles (NPs) synthesis, such as silver NPs, but the advances in the field of biotechnologies might allow to extend its applicability to 2D materials [18]. In the short term, the decrease of toxicity might be achieved by designing devices which can be regenerated, selecting the 2D modifiers based on both their performances and potential impact on human health and using nanomaterials derived from biomasses.

At the frontier of printing technologies, the development of new ink formulations compatible with different printing techniques, such as screen, gravure, inkjet, and extrusion-based printing (Figure 2) might play a major role. In these cases, 2D materials are uniformly dispersed in a solvent for ink formulation as the active component for the printing of smart flexible electronics [20]. So far, the most promising technique for making functional inks is liquid-phase exfoliation: the good dispersibility of the resulting nanosheets facilitates mixing of additional materials, allowing the formulation of hybrid inks. The liquid-phase processing of 2D materials is an attractive production method, adaptable to a

wide range of deposition techniques. Its development has led to the general production of stable 2D inks that are often applied for several non-patternable and patternable deposition methods, such as inkjet-printing, spin coating and drop casting. Indeed, 2D inks are no longer limited to academic research: graphene inks are already commercially available for screen-printing [21].

These technological advances should be further combined with biocompatible substrates for the development of more sustainable analytical devices. In this regard, the possibility to develop fully paper-based sensors using 2D inks might represent an important step forward in the design of chemical sensors [25]. By overcoming the poor stability of 2D materials and improving the analytical performance (especially in terms of reproducibility), these platforms will answer the market needs allowing the design of point-of-care diagnostics, remote sensors for the monitoring of pollutants as well as precision agriculture.

Concluding Remarks

The technological advances in 2D materials-based sensors shaped the world of electroanalysis allowing to design high performing platforms, from point-of-care to wearable devices. From the first GBMs to latest MXenes-modified electrodes, 2D materials have been successfully combined with chemical sensors to detect metal ions as well as organic molecules and macromolecules, combining the advantages of printed sensors with the exclusive properties of single-layer materials. However, 2D material-based sensors must be considered as at their starting point. Their analytical performances should be further improved especially in real sample analysis, their biocompatibility should be fully assessed, and their fabrication should match large-scale production requirements as well as green chemistry principles. The recent advances in 2D inks will surely help filling the gaps towards a progressive simplification of the sensor's architectures and the fabrication procedures. In this perspective, the selection of biodegradable 2D materials combined with paper-based supports might represent an important step forward.

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Section 8.1 – Introduction to printable biosensors

Alexander J. Casson, Zixin Wang, David Bird and John C. Batchelor

Department of Electrical and Electronic Engineering, School of Engineering, University of Manchester, Manchester, M13 9PL, United Kingdom

Significance and ambition

Biosensors aim to act as transducers, detecting and potentially quantifying the presence of a biological agent or signal [1–5]. Target analytes can range from small molecules and hormones, such as cortisol, to DNA and RNA, to lactate, and other markers in biological samples such as sweat. Printed approaches to manufacturing biosensors [6, 7, 8] are particularly promising as they provide a potential route to scalable manufacturing, allowing mass deployment, and allowing high-cost materials to be used as efficiently as possible, saving cost for device fabrication.

While elements of printed biosensors have been in commercial use for some time, the exciting trend in recent years has been the shift towards electronic biosensors, giving an electronic readout in addition to colorimetric approaches, which need to be inspected visually. Emerging printed electronics approaches can thus allow potential quantification of the analyte present, not only presence detection.

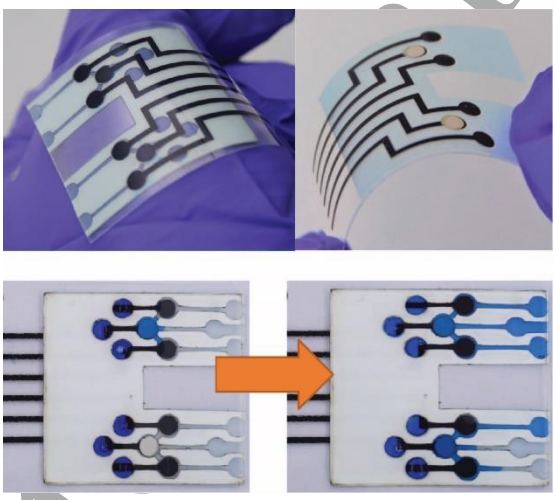

Figure 1 (Top) Example of a flexible screen printed biosensor with carbon tracks and an Ag/AgCl sensing electrode. Based upon [9]. (Bottom) A laser-cut microfluidics channel draws a liquid, dyed blue here, across the sensing site. In part © 2022 IEEE. Reprinted, with permission, from [9].

There are many types of biosensors (e.g. optical, piezoelectric, pyroelectric, etc.) but in general two main modes of operation for printable biosensors: Field Effect Transistor (FET) based, and electrochemical based. Both approaches are discussed in detail in the sections contained in this chapter. Electrochemical approaches, as shown in Fig. 1, are usually based upon either a three-electrode potentiostat measurement of an electrochemical cell (e.g. via cyclic voltammetry), or a two-electrode measurement of the open-cell potential. The base printed parts are conductive elements, often carbon, silver, or silver/silver chloride, with a sensing membrane to make the detector selective. This may be an ion selective membrane (as used in sweat sensors [1–3] to detect sodium or potassium ions, for example), or enzymes, antigens or other bodies for the target analyte to bind with. In FET based approaches, the sensing membrane is (typically) deposited on the gate of a printed transistor. In general, FET based approaches are more sensitive, as the transistor inherently includes electronic amplification. However, printing a transistor is substantially harder than printing the conductive tracks

required for electrochemical approaches, and printed FETs can be highly variable in their performance [10, 11].

The COVID19 pandemic highlighted the need for biosensors, with lateral flow tests being widely used, but in general not incorporating printed electronics and quantification. There is now a growing realisation that there are many potential uses of point-of-care and wearable biosensors, both for clinical use, and for sports and wellbeing applications [1–8]. Current wearable devices, measuring 'dry' modalities, such as activity and heart rate, have had a substantial impact on health and wellbeing applications. One ambition for printed biosensors is to allow many more 'wet' modalities to be as easily monitored and as widely used. One of the greatest challenges of the mid-21st century will likely be the significantly aging population, with people living with complex and multiple long-term conditions, such that simultaneous treatments may have conflicting effects. Therefore, optimising the efficacy of therapeutic approaches, and how our bodies are performing, will require substantially more monitoring. The metabolites and biomarkers of therapeutics will also be increasingly monitored to enable more tailored dosing of drugs.

Fundamental performance metrics and performance limits

For a printed biosensor, the performance factors of interest, and the challenges in advancing the state of the art, can be broken into two aspects: the printed parts themselves, and the sensing performance. For the printing state of the art, the considerations will be similar across the many different types of sensors considered in this roadmap (gas, temperature, and similar). There are key challenges in making high quality, mechanically robust prints which can be mechanically cycled many times, potentially at different temperatures and humidities to represent usage in different parts of the world. Low temperature, or low energy, curing is important for using thin and flexible substrates, which may decolour or change mechanical properties when they are (say) heated. Cost and yield are important performance metrics, particularly as the aim of using a printed approach is often to be scale-up compatible.

Focusing on performance factors specific to biosensors, there are many to consider. In principle a great many different analytes can be detected successfully and have been shown in the academic literature [1–9]. However, fundamental detection is only one factor, and does not guarantee sufficient robustness for real-world use. Fig. 2 illustrates some key biosensor performance metrics, with the precise form of these sketches depending on the actual biosensor, its target, and mode of operation. The Limit of Detection (LoD) and sensitivity are the two key metrics usually targeted first for improvement. The LoD shows the smallest amount of analyte that can be detected with a given level of confidence, compared to a blank sample, and the sensitivity shows how big the output change is for a change in the analyte concentration. Specificity is also important to demonstrate, showing that the sensor only responds to the analyte of interest, with a minimum of interference or crosstalk when complex solutions, such as saliva, are placed on the sensor. For some applications, response time will be important, particularly if a chemical reaction or binding event is involved. In some situations, it may be beneficial to have a less sensitive and less specific, but faster, output to allow initial screenings. Shelf-life and storage requirements are also important performance factors. Particularly for the sensing membranes used, there may be a limited usable lifetime, and this can substantially affect the practical usability and translation potential of early-stage investigations. This includes the potential for the sensing to be reversible/reusable, noting that hysteresis could be present.

In general, the electronic performance factors, such as input referred noise, power consumption, and amplifier linearity, are less critical for demonstrating operation, particularly if the target is a point-of-care device rather than a wearable one, but substantially affect the overall performance. Low power, miniature electrochemical readout chips, such as the Analog Devices MAX30131, are now becoming widely available (if rigid, off-the-shelf electronics are suitable for the application).

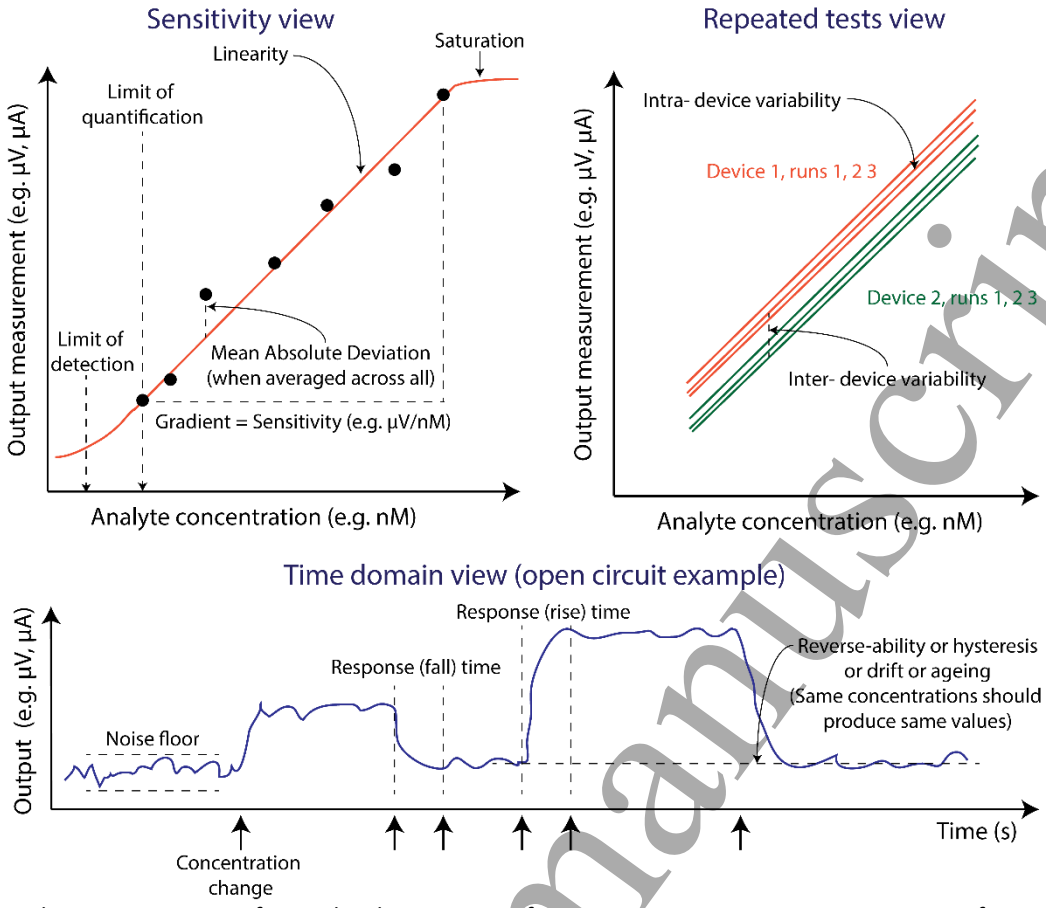

Figure 2 Schematic overview of some key biosensor performance metrics. Measurements are performed in the time domain, and may, or may not, be single-shot measurements, and may be cyclic voltammetry (or similar) or chronoamperometry (or similar), rather than the direct time course shown above (in which cases the time domain views will look very different to the above). The change in output (e.g. voltage) with respect to the amount of change in the analyte is extracted from the measurement (possibly after filtering to remove noise and other artefacts or interference sources) to calculate the sensitivity, limit of detection, and other performance factors.

Important to consider, particularly for reusable sensors, is the variability present. Often considerable variability is present in printed biosensors; whether due to the sensing elements, or the printed electronic components; and whether due to intrinsic variances between devices, batch-to-batch variances, or variances in a single device over time. Decreasing variability is an important research direction, which may be addressed by improving manufacturing processes, or adding circuitry for self-calibration, and cross-testing. An open challenge is in reducing the need for calibration through the design of the sensing device itself, ideally so that the sensitivity can be known through non-destructive tests such as optical inspection.

Overall, there are many performance factors determining performance, likely enough to fill a complete chapter in their own right. Only some are listed here. The REASSURED criteria [12], building on the World Health Organisation's ASSURED criteria [13], aim to give a framework for considering, and reporting of, performance factors. It is difficult in early stage works to holistically consider all of them, and this needs to be kept in mind, both when carrying out and reporting, and when evaluating, early stage works.

Open challenges and research directions

There are many potential avenues for further investigations, beyond only investigating the detection of additional analytes past those already reported. Conductive and dielectric inks, and substrate formulations for printability, are of course core. A major focus in manufacturing is on lifecycle analysis

and sustainability, giving devices which can be reused, recycled, or which naturally biodegrade for minimising electronic waste [8]. For example, many printed electronics have historically used plastic based substrates, such as PEN and PET. Degradable alternatives, such as NatureFlex™ and Ecoflex™, are now being investigated. Sustainability is particularly important for biosensors, as the analyte involved means the core sensing may intrinsically be single use only. Strong co-working with users and clinical partners is important to understand the trade-offs involved – it is unlikely that the ultimate aim is a lower LoD in every case. A slightly higher LoD with much better sustainability may be more desirable, but needs careful co-design with users and standards forming efforts. This includes consideration of the accuracy of non-invasive biosensors compared to clinical data which would be obtained through invasive tests.

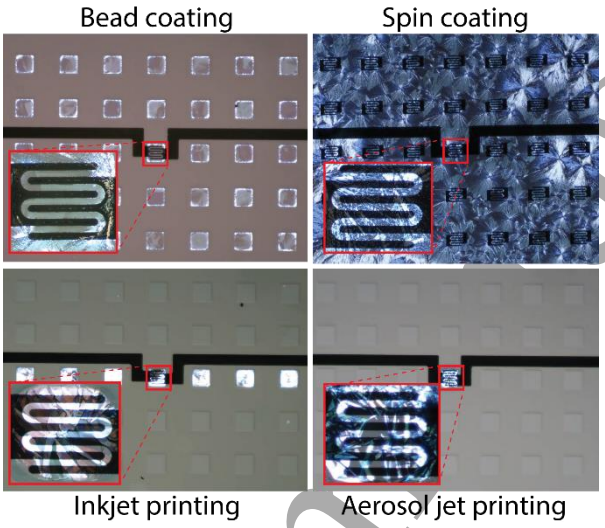

Figure 3 Different deposition techniques used to manufacture a transistor (viewed under an optical microscope). Very different morphologies and therefore performances can be achieved with the same underlying materials depending on the printing method used. Photo credit: CPI, author DB.

The route to scale-up and mass manufacturing, whether a roll-to-roll or batch fed process, or something else, is an equally important open challenge, which will interact with the above factors. As shown in some of our internal work in Fig. 3, very different manufacturing performances can be obtained with the same material, showing that the materials and manufacturing challenges need to go hand-in-hand.

The counterpoint to scale up is personalisation. Screen printing-based approaches use predefined masks and can be highly scalable, while inkjet and other approaches are digitally driven and can be changed, at least in principle, on-the-fly to give customised designs for different situations. While many printed biosensors have been demonstrated with both of these, and other, printing approaches, really exploiting personalisation is an open opportunity. Fabrication of devices through printing enables multiple sensing types to be incorporated onto the same substrate, which may enable the same sample to be used for multiple measurements. Personalisation of the sensing modalities may thus be possible, whilst also reducing the sample volume required, both to the benefit of the user. Moreover, reducing health inequalities is a major priority. Printing approaches to allow personalised biosensors (e.g. different sizes, shapes, analytes) may be an essential contribution for tackling these important health inequality challenges in biosensors, ensuring that biosensors are suitably available for all.

Finally, there are many open challenges in the wider flexible electronics aspects of a compete biosensor [14]. Fig. 1 shows an example of the core sensing element, but this needs to be connected to instrumentation, filters, calibration electronics, and data transmission and analysis components. Data transmission stages in particular, require high frequency, complex electronics, far beyond the

current state of the art to fully print. Whilst plastic electronics rather than printed electronics, there are exciting developments in this area from UK based company Pragmatic Semiconductor who are creating fully flexible microcontrollers [15], allowing flexible sustainable electronics to match the flexible sensor element. In the meantime, most approaches, assuming they do not simply use FR4 or Kapton based PCBs (Printed Circuit Boards), take a 'sea of rigids' approach, with the sensing element connected to conventional microchips mounted on flexible substrates with printed interconnects. Components are typically mounted with isotropic and anisotropic conductive pastes as it is very difficult to use low temperature solder with printed silver tracks. However, this limits the use of dense microchips, in packages such as BGAs (Ball Grid Arrays). With conductive pastes, flat bottom packages such as QFN (Quad-Flat No-leads) are typically much easier to mount, but many state-of-the-art microchips are now only available in BGA packages. The ability to robustly mount packages such as BGA as part of printed biosensors would allow a major step forward in improving overall electronic performance. Combining all these challenges, there are many exciting materials, sensing, electronics, and printing avenues to explore in future years.

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8.2 – Printable electrophysiology sensors

Alexander J. Casson[1], Le Xing[1], Liam S. J. Johnson[1], Zixin Wang[1] and Aula A. Alwattar[2]

[1]Department of Electrical and Electronic Engineering, School of Engineering, University of Manchester, Manchester, M13 9PL, United Kingdom
[2]Department of Chemistry, School of Natural Sciences, University of Manchester, Manchester, M13 9PL, United Kingdom

Status

Electrophysiology is the process of studying the electrical activity that occurs within biological tissues and the human body. Best known is the electrocardiogram (ECG), where electrodes on the chest or arms monitor the electrical activity of the heart, with this now integrated into many commercial smart watches. Electrical activity is in fact present across many different scales, which can be studied with electrophysiology approaches. There are cell membrane potentials, which can be monitored via patch clamping. Action potentials in nerves, which can be monitored with cuff electrodes. Electrical activity within the brain can be monitored with depth electrodes, placed deep inside brain tissues, or with electrocorticography (ECoG) electrode arrays placed on the surface of the brain. Non-invasively, many different electrical signals are present depending on where the electrodes are placed – with electrocardiography (ECG) for the heart, electromyography (EMG) for the muscles, electrooculography (EOG) for the eyes, and electroencephalography (EEG) for the brain (placing electrodes on the scalp) being the main modalities. This non-invasive sensing has many uses, from rehabilitation monitoring and control of prosthetic limbs via EMG [1], to epilepsy diagnosis and monitoring via the EEG [2].

It is in these non-invasive applications of electrophysiology where there has been the most interest in printing-based approaches for sensors. Traditional non-invasive electrodes have been made from sintered silver/silver chloride (Ag/AgCl) – that is, a sold metal disc – as silver/silver chloride obtains a low noise and low drift connection to the body [3]. (Gold and tin electrodes are also relatively common.) However, as a solid metal disc these electrodes are not physically flexible, an obstacle which potentially could be overcome by using printing based approaches. Printing allows layering of conductive materials onto soft substrates which better match the properties of the skin. This enables monitoring over longer periods of time, and even overnight [4]. Printing based manufacturing may also allow alternative materials to be used, such as PEDOT:PSS based materials. Despite being more resistive than Ag/AgCl, PEDOT:PSS has much better flexibility, elasticity and skin-conformity, which in turn facilitates a better connection with the body. Alternatively, usually silver/silver chloride electrodes are applied with a gel or hydrogel overlay to act as an electrolyte and improve the connection to the body. However, gel can dry out over time, limiting the recording time/quality, and, particularly for EEG, leaves a mess in the hair which needs removing at the end of a recording. While the need for a gel can be reduced somewhat, but not completely, by using an active electrode where a buffer amplifier is placed directly on the electrode itself, there has been much attention in the research literature towards making *dry* electrodes which obtain a good contact quality without requiring a gel [5]. Flat, skin compliant, capacitively connected electrodes provide a promising potential route for this in non-haired regions [6]. There is also substantial interest in smart textiles with integrated, say, printed ECG and EMG electrodes [7] to allow very long term and unobtrusive monitors embedded into clothing.

Lastly, there is an increasing awareness of the need for personalisation, that a solid metal disc will not always get the best connection to all different types of skin and through all different types of hair. Systematic racism has been highlighted in EEG [8], as current electrodes are one size fits all. Printing based manufacturing approaches allow, at least in principle, different electrodes to be made for different people, and different parts of the body, at different points in time. Printed electrophysiology

electrodes are more customizable and flexible, with a wide range of form factors possible. Some printing approaches, such as screen printing, can be readily scaled to produce large numbers of electrodes. As a result, there are many potential benefits over traditional sensing approaches.

Current and Future Challenges

From the application point of view, hair is the primary challenge in making electrophysiology sensors, with different approaches required depending on the amount of hair present at the desired recording site. For ECG on hairy chests, chest shaving is commonly done, but this is generally not acceptable for other modalities such as EEG on the head. For monitoring haired regions on the head with dry electrodes, *fingered* electrodes, as shown in Fig. 1 are often used. The fingers are intended to part the hair such that the tips can make direct contact with the scalp when held in place with a cap or adhesive. The electrodes in Fig. 1 are manufactured by printing a base structure, with flexible base structures now possible, which is then coated with a silver/silver chloride layer [9]. Many screen printable and dip coating silver/silver chloride inks intended for electrophysiological monitoring are now available from major ink suppliers. There are many degrees of freedom in the design of such a fingered electrode, from the number of fingers, to the thickness of the fingers, to the tip profiles, and there is an ongoing challenge to devise suitable design rules for picking the best shapes in any given situation, potentially driven by a 3D scan of the area the electrode is to attach to. A future challenge is to enable alternative printed materials to silver/silver chloride, with some directly conductive printed electrodes now starting to emerge [10, 11]. As no coating process is required these can potentially be both faster and cheaper to manufacture.

For non-haired regions there is much interest in conformal *epidermal electronics* where very thin structures are used such that they can follow the micro-contours of the skin and obtain a very high quality connection [12]. Both printed and non-printed based manufacturing of such structures are possible, see for example [4] and [13] respectively, with printed approaches having the advantage again of potential for personalisation, or being compatible with routes to scale up manufacturing. For example, roll-to-roll mass manufacturing of printed ECG electrodes has already been demonstrated [14].

Depending on the level of flexibility and conformality required, some electrodes take a similar approach to the fingered electrodes of Fig. 1 – screen printing a silver/silver chloride layer onto a standard flexible substrate used in printed electronics (e.g. Polyimide / Kapton / PEN / PET). Other works are exploring alternative materials for increased flexibility and stretchability, with for example PEDOT:PSS based electrodes [4, 15] and polyurethane based substrates [4, 16]. A number of examples of printed flat electrodes are show in Fig. 2. These are a very promising direction, and there are still a wide number of investigations possible, and needed, to optimize, scale-up, and translate these approaches to next generation electrodes.

Figure 1 A flexible silver/silver chloride EEG electrode with *fingers* for passing through the hair. Work reported in [9, 10].

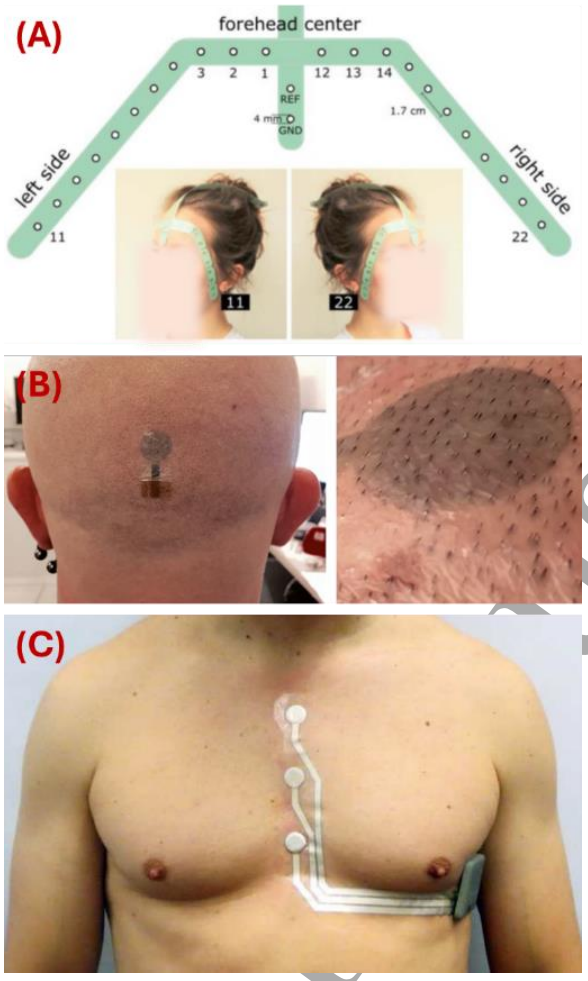

Figure 2 Examples of printed electrophysiology sensing electrodes on flat substrates for use in hair-free regions. (A) Forehead EEG array using Ag/AgCl ink [17]. Reprinted under CC-BY license. Modified for crop and blurred region. (B) Temporary tattoo electrode for EEG, inkjet printed using PEDOT:PSS based ink on a polyurethane substrate [4]. Reprinted under CC-BY license. Modified for crop. (C) Chest ECG array using Ag/AgCl ink on a polyurethane substrate [16]. © 2016 IEEE. Reprinted, with permission, from [16].

Advances in Science and Technology to Meet Challenges

In general, many electrophysiology electrodes are disposable, and so factors such as re-usability and being autoclavable post-use for sterilization are not critical to development. That said, there is of course growing importance in sustainable approaches, which motivate further investigations in this direction. In principle, printed approaches should be well suited for sustainability, with the additive manufacturing approach helping to minimise waste. This is particularly important if bespoke person-by-person electrodes are to be made. As noted previously, there are many potential benefits offered by printing approaches for personalisation, but much work is still required to realise the potential, and should be a priority for helping to reduce health inequalities. Important to note is that this does not necessarily involve changing the electrode itself. For example, [18] printed a novel electrode holder to connect to thick curly hair, giving a better connection compared to standard cap based holders or collodion adhesives, while keeping the fundamental electrode a circular shape.

Further, most of the electrodes discussed so far are passive ones, requiring wiring to connect them to instrumentation electronics. Emerging printing technology is allowing standard electronic components to be mounted directly onto printed structures, allowing the creation of active electrodes which are more robust to interference sources. For example, printers from Nanodimension [19] and Neotech AMT [20], and others, can 3D print circuit boards, including the pick-and-place of

microelectronic components, which may allow the active electrode circuitry to be added directly on top of one of the printed electrodes shown in Fig. 1, with all of the parts printed at the same time. A wide number of 3D printed EEG headsets to hold the electrodes are already available (e.g. [21, 22]), and so it is now possible to foresee entire systems being printed, not only the electrodes or electrode holders. The potential benefits of this in terms of signal quality, recording comfort, and other factors, vs. time and cost, need to be determined, but the technology advances allowing electronics to be integrated onto printed platforms clearly opens many opportunities for exploration.

Finally, the counterpart to electrophysiological monitoring of the electrical systems in the body is the stimulation of the electrical systems in the body, via magnetic, electrical, or other means. Non-invasive stimulation is a very wide area, but one where there may be potential for printed electrodes, similar to electrophysiology. For example, in transcranial electrical stimulation, typically conductive rubber electrodes soaked in saline sponges are used to inject a small current for neuromodulation purposes. The ways in which recording electrodes and stimulation electrodes operate, and are optimized, are very different, but there may be similar opportunities for printed stimulation electrodes as a complement to recording electrodes. These may act as an enabling part of future closed loop systems [23], which not only sense data but can sense and actuate and tailor the actuation based upon the currently sensed data.

Concluding Remarks

While electrophysiology, in all its many forms, is an established technology which is widely used both clinically and non-clinically, there remain many opportunities for improvement. These range from improving wearing comfort, to improving sustainability, to making personalised devices, to enabling more discrete and socially acceptable monitors. Printed electronic materials are already being incorporated into a wide number of electrode approaches, and there is much potential for the increased utilisation of printing-based approaches to enable next generation devices. We can expect to see even greater improvements in the functionality of printed electrodes as the technology continues to advance.

Acknowledgements

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Section 8.3 – Printable transistor biosensors based on organic semiconductors

Adrica Kyndiah[1], Fabrizio Antonio Viola[1,2] and Mario Caironi[1]

[1]Center for Nano Science and Technology, Istituto Italiano di Tecnologia, Via Rubattino 81, 20134 Milano, Italy
[2]Università degli Studi di Cagliari, Dipartimento di Ingegneria Elettrica ed Elettronica, Via Marengo 3, 09123 Cagliari, Italy

Status

Biosensors based on organic transistors combine high sensitivity with biocompatibility of materials and flexibility of devices, which can be manufactured using cost and energy-efficient printing techniques. Electrolyte-Gated Organic Transistors (EGOTs) are the building blocks of most biosensing applications, since they can be operated in biological solutions that host cells, tissues and target analytes. EGOTs are three-terminal devices where the electrical conductivity of the organic semiconductor, bridging the source and drain electrodes, is modulated by a third gate electrode in contact with the electrolyte [1]. Depending on the permeability or the impermeability of the organic semiconductor to ions in the electrolyte, EGOTs can be divided into Organic Electrochemical Transistors (OECTs) or Electrolyte-Gated Organic Field Effect Transistors (EGOFETs), respectively. In EGOT biosensors, either the semiconductor/electrolyte or the gate/electrolyte interface can be used for sensing, as shown in Figure 1. For example, the organic semiconductor poly(3-hexylthiophene-2,5-diyl) (P3HT) functionalized with a supported biotinylated phospholipid bilayer was shown to detect streptavidin [2], while procalcitonin (PCT) could be detected when functionalized with anti-PCT [3]. An alternative powerful strategy, decoupling the optimization of the semiconducting layer and of the receptors, is based on the functionalisation of the gate electrode with antibodies, proteins or enzymes that can selectively detect a target biomarker. The main advantage in using EGOT-based biosensors, compared to available electrochemical sensors, is the possibility of exploiting an amplification mechanism, potentially producing a higher signal-to-noise ratio. EGOTs can transduce small input modulations of V_{GS} (i.e., few µV) into easily measurable modulation of the output current (I_{DS}) thanks

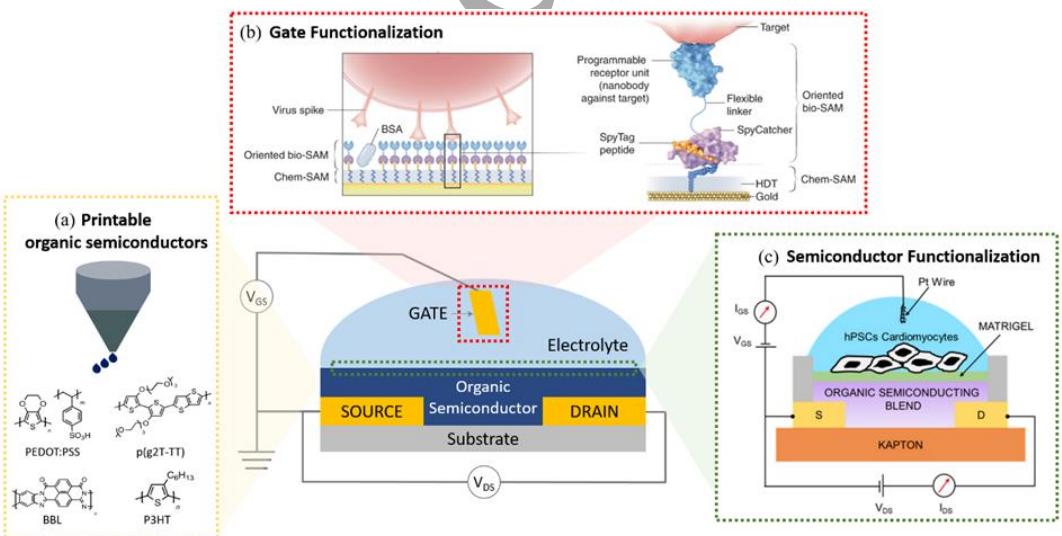

Figure 1 Schematic of printed FET based biosensors based on Electrolyte Gated Organic Transistors EGOTs. (a) Some examples of printable organic semiconductors. (b) Bio functionalization of gate electrode using chem- and bio-Self-Assembled Monolayer (reproduced with permission from [5]) (c) EGOTs as electrophysiological recording platform for Cardiomyocytes (reproduced with permission from [9]).

to large transconductance values (mainly due to large gate capacitance, reaching ~10 µF/cm^2 and ~1 mF/cm^2 in the case of EGOFETs and OECTs, respectively) [1]. Remarkably, EGOT-based biosensors capable of detecting biomarkers and pathogens (such as Immunoglobulin-G IgG [4] and coronavirus-2 (SARS-CoV-2) [5]) at single-molecule level detection have been recently reported. EGOTs biosensors have also been successfully employed for real time monitoring of cell growth and proliferation and as well as impedance biosensors[6]–[8]. In addition, they have also been used both for *in vitro* and *in vivo* electrophysiological recordings of electrogenic cells [9]–[12]. OECTs were adopted to record "extracellular" fields of cardiomyocytes action potential, [11], [13], i.e., the derivative of the action potential, as obtained with commercial microelectrode arrays (MEAs). Interestingly, "intracellular-like" signals could be recently recorded with EGOFETs [12].

Increasing efforts have also been devoted to manufacturing EGOTs at drastically reduced costs by high-throughput, large-area, additive techniques, such as printing methods (e.g., inkjet, screen-printing). The adoption of such methods reduces the waste of materials and enables both the fabrication of highly dense arrays [14] as well as sparse ELISA-like arrays, where subtractive techniques would produce excessive waste [15]. Moreover, organic materials typically require low processing temperatures, compatible with cheap, flexible substrates.

Current and Future Challenges

One of the core challenges in the development of printed EGOT-based biosensors is related to the stability of the functionalized interface of the capturing layer, which depends on many factors. One aspect is related to the strategy used to immobilize the biomolecules onto the gate electrode, such as the use of chemical self-assembled monolayers or the use of proteins [16]. Such a strategy can also strongly influence the device sensitivity, although a clear and general understanding is not yet available, as recent findings point to the possibility to adopt simpler physisorption protocols while maintaining sensitivity. It should also be noted that biorecognition elements are highly susceptible to changes when exposed to real biological environments, such as whole blood. In this case, they could denature rapidly (owing to values of pH or mineral concentrations) or due to the interaction with electroactive species, such as uric acid and ascorbic acid in blood plasma [17]. Another challenge is related to the device stability when exposed to aqueous environments for electrophysiology measurements and analytes sensing. EGOT stability should be guaranteed for a timeframe compatible with applications, such as weeks in the case of cell-based biosensors in order to achieve a confluence of cell cultures. Reproducibility, i.e., the achievement of uniform electrical performance among different devices, is a key aspect and may become a limitation when large-area printing techniques are adopted to pattern semiconductors due to a more difficult control over films microstructure over large-areas.

While proposed applications of EGOT-based biosensors are quickly expanding, the general understanding of their specific transduction mechanism, however, is still largely lacking. When the target analyte is detected by the biological layer attached to the gate, the questions arise as to how the specific interaction of the target species with the biorecognition layer or redox interactions are being transduced by the transistor. When it comes to electrophysiological recording of cells, few reports have demonstrated the ability to reliably record bioelectronic signals like the action potential of cardiac cells. EGOTs based on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) active layer have mainly been the choice for such applications due to their high transconductance and easy accessibility of the semiconductor. Yet, the signals acquired, for example from cardiac cells cultures [11][13], are still not on par with state-of-the-art electrophysiology techniques, like the patch clamp or poration methods.

Advances in Science and Technology to Meet Challenges

Interfaces in EGOT biosensors are critical for transducing of biological signals to ensure efficient and accurate detection. For analyte detection, a stable, compact capturing layer with proper orientation

would ensure a more reproducible limit of detection from one sensing test to the other. Normally, the biofunctionalized layer is characterised independently using optical techniques such as Surface Plasmon Resonance (SPR) or Quartz Crystal Microbalance with Dissipation (QCM-D). An *in-operando* study of the biolayer interface with gate electrode using either SPR or QCM-D during the sensing measurement would shed light on the stability issue of the interface layer due to dissociation or unwanted bindings in complex biofluids. Suitable device architectures, such as the floating gate geometry proposed by Frisbie and collaborators [18], should be considered when real-time monitoring of analytes in bodily fluids like blood is required, since, in this case, the transducer consisting of the fragile organic layer is physically decoupled from the sensing area.

To improve the stability of EGOTs, the first action is to set a "conditioning" protocol, which typically consists of cycling the transfer characteristics of the transistors for some time prior to sensing until a stable output current response is reached. Furthermore, the chemical properties of the organic material itself can be tailored to facilitate ion transport, promote electrochemical doping and water stability. In this context, glycol side chains were commonly used in polymers to enhance water penetration, resulting in facile bulk doping and, therefore, efficient modulation of transistor channel conductance. However, recent studies suggest that excessive water penetration can affect the electronic mobility of the semiconductor. For this reason, other strategies have been investigated to improve the EGOTs performance in water without affecting the stability. For instance, very recently, Inal's and Fabiano's group showed that the side-chain-free poly(benzimidazobenzophenanthroline) (BBL) achieved an impressive volumetric capacitance and stability, when exploited as active layer in an n-type EGOTs, with overall performance very close to that reported for p-type devices [19], [20]. A further investigation of the interplay between ionic transport, hydration and electronic properties of EGOTs would pave the way to advanced and tailored molecular designs thus enriching the library of organic materials that can be used for sensing applications. The reproducibility and uniformity issues, particularly relevant when high-throughput printing techniques are employed, could be tackled and addressed if the manufacturing process can be carried out within a controlled environment, such as Class 1 cleanrooms, and by using scaled tools and instrumentations already developed at R&D or industrial level.

Understanding the transduction processes at the analyte-receptor binding site is key for the further development of the field. Efforts should be dedicated towards unravelling the transduction mechanism by combining experimental data with theoretical models to relate the biochemical events during sensing to the changes in transistor parameters (such as threshold voltage, capacitance, and output current). Electrophysiological recording applications, on the other hand, rely on the sensitivity of the transistor to pick up weak but fast transient bioelectronic signals during the opening and closing of the ion-channels. Available cell-transistor coupling models are mainly based on CMOS FETs and a direct translation of these models to EGOTs should be carefully evaluated in order to provide a suitable theoretical description of the transduction mechanism at the cell membrane/semiconductor interface.

Concluding Remarks

Printed EGOTs-based biosensors are undoubtedly one of the most promising candidates for the next generation of highly performing, cost-effective biosensors that can be manufactured by means of large area and high-throughput fabrication processes. If the current challenges are tackled and key advancements are obtained in the next future, then printed organic biosensors could have a huge impact on clinical assays for fast diagnosis of diseases assaying real body fluids such as blood, urine or saliva, with high selectivity and sensitivity. Therefore, they could enable timely and effective therapeutic interventions, with benefits for the healthcare system. Moreover, they could be deployable at point-of-care (POC) sites (such as patient's house) delivering output results, such as specific diagnoses, directly to the patient with fast time-to-results or directly to the doctor if the devices are endowed with real-time connectivity. Another possible application of this technology is the development of high-quality, non-invasive electrophysiological recording platforms that monitor

the effect of drugs in electrogenic cells. Last but not least, further technological advancements for the manufacturing process, required to tackle present drawbacks (such as reproducibility), could open the opportunity for an actual commercialization of printed organic biosensors technology.

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8.4 – Printable FET biosensors based on carbon nanotubes

Faris M. Albarghouthi[1], Brittany N. Smith[1] and Aaron D. Franklin[1,2]

[1] Department of Electrical & Computer Engineering, Duke University, Durham, NC, 27708, United States of America
[2] Department of Chemistry, Duke University, Durham, NC, 27708, United States of America

Status

The goal of electronic, compact, low-cost, and customizable biosensors requires a distinct combination of specific material properties and appropriate processing. At the least, the electronic material transducing the detection signal must be highly sensitive while also being compatible with versatile fabrication approaches. Semiconducting carbon nanotubes (CNTs) offer relatively high mobility in a thin film, availability of all atoms on the surface for ultrasensitivity, and compatibility with solution-phase processing (e.g., printing) [1]. Carbon nanotube field-effect transistor (FET) biosensors – also known as CNT BioFETs – are transistor-based biosensors that make use of semiconducting CNTs to transduce binding events between analytes and receptors (Fig. 1A), and present one of the most promising approaches to point-of-care electronic biosensing [2]. While CNT BioFETs have been extensively investigated, most demonstrations in the literature rely on fabrication techniques for the CNT thin film that are costly and complex and/or have limited scalability, with few demonstrations

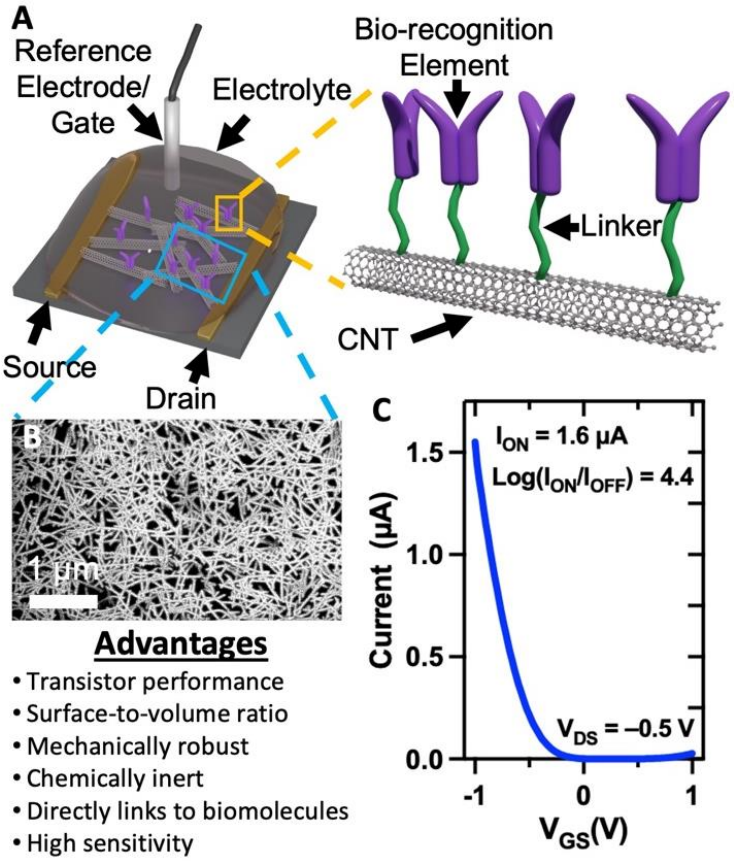

Figure 1 Printed CNT BioFET Overview. (A) Representative schematic of one type of printed CNT BioFET where the channel is solution-gated and the CNTs are linked to bio-recognition elements directly. (B) Scanning electron microscopy (SEM) image of CNT film, highlighting the single-layer film formed by printing a CNT ink. (C) Transistor data from a solution-gated CNT BioFET with a printed CNT channel showing high on-current and on/off-current ratio. Several key advantages of printed CNT BioFETs are also highlighted.

harnessing the versatility of printing [3]. Broad substrate compatibility, enhanced repeatability, lower fabrication cost, and rapid prototyping are all advantages that can be leveraged using printing techniques. Printed thin-film FETs with CNTs include a monolayer of nanotubes in a percolating network that offers a high surface-to-volume ratio (Fig. 1B), making it especially sensitive to biomolecular interactions [4]. Notably, these CNT-based devices show strong transistor performance – arguably the highest performing fully printed transistors [5] – using several different gating methods including solution-gating, as shown in an example transfer curve in Fig. 1C, with an on-current of 1.6 μA and an on/off-current ratio of 10^4.

While there are numerous demonstrations of fully printed CNT-based thin-film transistors [6]–[8], there are relatively few examples of printed CNT BioFETs. Zamzami et al. used inkjet printing of CNTs onto lithographically defined contacts to create a SARS-CoV-2 BioFET sensor that could detect antigen levels down to concentrations of 0.1 fg/mL [9]. Similarly, Molazemhosseini et al. created a rapidly stabilizing BioFET with an inkjet-printed CNT channel that detects biotin-streptavidin interactions at a limit of detection (LOD) of 1.47 nM [10]. Though promising, these and most other demonstrations still rely on a combination of printed and cleanroom-based techniques for device fabrication, meaning that further development is still necessary for all-printed CNT BioFETs. There also remain a diverse assortment of CNT BioFET configurations, from direct solution-gated to extended gate approaches [11]; while the variety of options is promising, there is a lack of clarity regarding which is best suited for certain application needs.

Overall, combining the ultrasensitive nature of CNTs with the many advantages of printing brings us closer to the widespread and low-cost realization of point-of-care electronic biosensors, which would undoubtedly have a significant impact on the commercialization and availability of diagnostic tools.

Current and Future Challenges

CNT BioFETs face several key challenges (Fig. 2A), the most relevant of which are generally applicable to all solution-gated BioFETs, including Debye length screening in complex media and temporal effects resulting in signal drift [12], [13]. One significant issue for BioFETs generally – with particular impact for CNT films – is instability stemming from improper passivation in an ionic solution environment. Encapsulation of the semiconducting channel and conductive metal electrodes can improve yield, stability, and performance of transistors in solution [14], though the process typically relies on cumbersome cleanroom-based techniques, which increase fabrication complexity and cost, effectively negating the benefits provided by printing. Aerosol jet printed SU-8 has been shown to decrease leakage current in solution [15], but the reliability of printed encapsulants for biosensing applications is still in question and warrants further investigation. In a similar vein, current demonstrations of printed CNT BioFETs use costly traditional cleanroom-based techniques for metal electrode deposition, despite a few advances demonstrating all-printed FETs [15].

With regards to the printing of the CNT channel itself, binder (e.g., surfactant or polymer) removal, CNT thin-film density, and semiconducting purity are all key considerations, with device-to-device variability resulting from these challenges. Printable CNT inks rely on the use of binders to improve dispersion in solution and prevent tube aggregation, though these materials greatly hinder CNT conductivity, making their efficient removal essential to achieving the performance necessary for biosensing. However, commonly used removal techniques like UV curing, thermal annealing, and thorough rinsing limit the types of substrates that could be used with these printable devices. While water rinsing could be used to remove certain binders, the density of nanotubes may be compromised with each rinse at non-uniform levels, requiring multiple print passes to deposit a sufficiently dense film and inviting a level of variability between devices [17].

Importantly, CNT density within the channel is a critical factor as it has been shown to influence BioFET sensitivity, with lower (but sufficient) tube densities offering the greatest magnitude of signal change and lowest detection limits [18], as tube-to-tube junction resistance plays a major role in sensitivity.

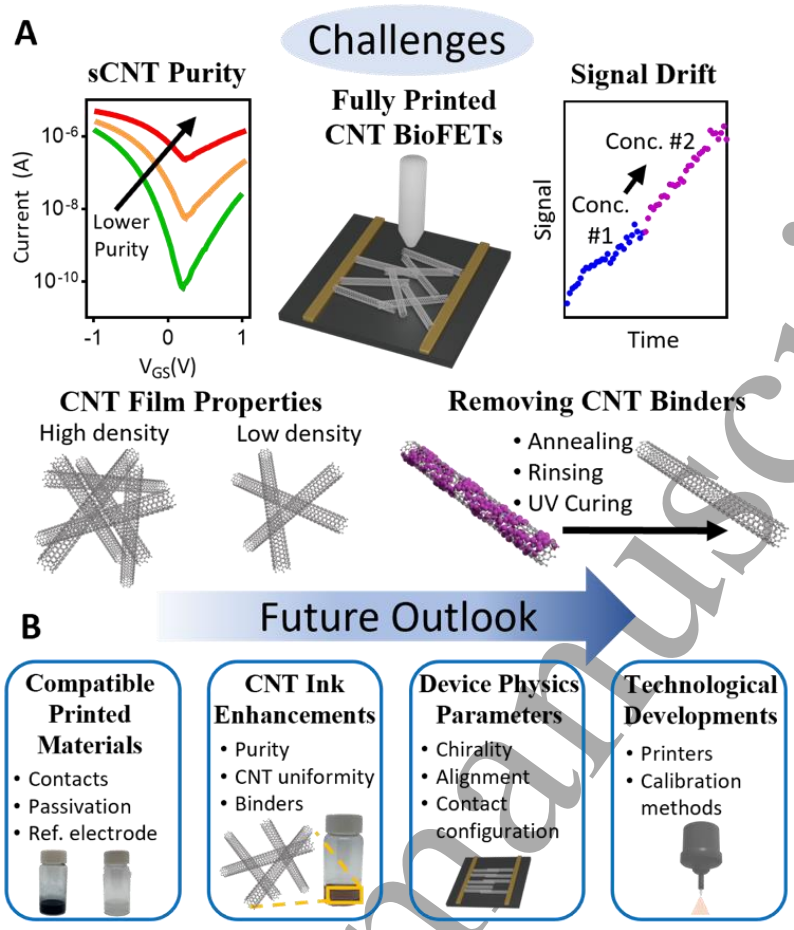

Figure 2 Challenges and Future Outlook. (A) Challenges for printed CNT BioFETs include CNT purity, removing binders, signal drift, thin-film properties, and fully print-based processing. (B) Future outlook for printed CNT BioFETs, including finding compatible printed materials, enhancing CNT ink formulations, understanding device physics parameters, and technological developments.

Similarly, the semiconducting purity of a CNT film affects FET performance. As one-third of CNTs are metallic by nature, separation of metallic CNTs from semiconducting ones is essential. Though there have been major advances in CNT separation techniques, even low concentrations of metallic tubes in a thin-film transistor (<1%) could dominate device transport and hinder sensitivity [19].
Altogether, the challenge of variability makes it difficult to accurately quantify the biosensing capability of ostensibly identical BioFETs, since an equal target analyte concentration in both devices could yield different magnitudes of response.

Advances in Science and Technology to Meet Challenges

To overcome the challenges listed above, several advances are needed (Fig. 2B). There is a need for extensive BioFET-specific examination of printable metal electrodes and passivation materials – for both the metal contacts and the channel itself – to increase stability, performance, and yield, while driving down fabrication complexity and cost. This could be done through parametric stability-focused comparisons of conductive (e.g., silver nanoparticles, graphene) and insulating (e.g., epoxies, high-κ dielectrics) components in physiologically relevant media and examining their performance over time. Technological developments in printing techniques focused on improving deposition consistency are crucial to mitigate the inherent sample-to-sample variability caused by the printing process itself. This also encompasses the development of CNT-based inks with enhancements in semiconducting purity, tube uniformity (size, chirality, etc.), and binder removal, all of which impact BioFET performance.

Further studies on the role of CNT chirality and alignment, metal electrode choice, and other device physics parameters as they pertain to biosensing could unveil additional factors that may improve device design moving forward.

Given that there are several device-specific considerations that contribute to variability, individual investigation into each of the factors mentioned above is necessary, as well as exploring off-chip methods of mitigating variability effects. One potential avenue for variability reduction would be to incorporate post-processing calibration methods, such as making use of current advances in machine learning algorithms to mitigate device-to-device inconsistencies [20].

In general, there is a need for a greater volume of work in printed CNT BioFETs to get the scientific community closer to a consensus on design. There is such great diversity in design and architecture (e.g., channel dimensions, metal electrode choice, passivation materials, gating configuration) for BioFETs that it is difficult to define a foundational starting point. Parametric studies comparing each of these variables are necessary to know how to better design printable CNT transistors for biosensing-specific applications.

Concluding Remarks

Despite significant progress in additive manufacturing and electronic biosensing, the strengths of printing have yet to be truly harnessed for CNT BioFETs. Though they have shown great potential as printed biosensors owing largely to the CNT thin film's innate electrical and mechanical properties, there remain several obstacles to overcome. Notably, device-to-device variability issues and the need for strictly print-based fabrication are in need of further work to realize all-printed CNT BioFETs. Yet, progress to date suggests that continued effort from the greater scientific community aimed at solving these pertinent issues has a high probability of success. Considering their compatibility with a wide range of solution-phase processing, all-surface conduction for high sensitivity, and extraordinary electrical properties (even in a thin film), CNTs offer one of the most encouraging paths to a low-cost, electronic biosensing technology, which would have a transformative impact on diagnostic medicine.

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Section 8.5 – Printable FET biosensors based on 2D materials

Arnab Pal and Kaustav Banerjee

Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA, 93106, United States of America

Status

Field-effect-transistor(FET)-based biosensors are highly promising due to their high sensitivity, low power consumption, and label-free detection capabilities. Either the channel or the dielectric of the biosensor FET is functionalized with specific receptors to bind analytes (Fig.1a), which causes a change in the channel potential. This change is detected as a variation in the transistor current, with the transistor typically biased in the subthreshold regime for maximum sensitivity, Fig.1b. An electrolyte solution atop the channel facilitates biomolecule/bioanalyte movement, while a reference electrode maintains a stable potential (Fig.1a).

Emerging 2D materials can improve the performance of FET biosensors [1]. Due to their ultra-thin nature, these materials offer excellent electrostatics and large surface-area to volume ratio (Fig.1c), facilitating enhanced interaction with biomolecules via the gate dielectric. Additionally, the high mechanical strength and flexibility of these materials, which can be exfoliated or synthesized into small flake sizes and thicknesses, enables seamless integration with existing printing technologies for various sensor platforms. Furthermore, the tunable bandgap of these materials allows precise customization of biosensor performance and design. This extraordinary promise of 2D materials for FETs, and hence FET biosensors, can be recognized from the pioneering work on scalability analysis of such devices [2][3], starting with one of the earliest demonstration of a MoS_2 FET biosensor [4], where pH and protein sensing sensitivities of 713 and 196 (even at 100 femtomolar concentration) respectively were observed. This highlighted that FETs based on large bandgap 2D transition metal dichalcogenides (TMDs) can outperform Si and graphene counterparts in sub-10 nm channel lengths, thereby enabling higher sensitivity, lower detection limits, and improved signal-to-noise ratio for next-generation biosensors. To improve the sensitivity beyond the limit imposed by FET subthreshold swing (SS), changing the device architecture/physics to steep-slope tunnelling FETs (TFETs) was proposed [5], resulting in predicted sensitivity improvements of up to two orders of magnitude compared to state-of the-art FETs. Further improvements in the performance and energy-efficiency of TFET biosensors can be achieved through a suitable heterojunction with 2D materials [6] to optimize the band-offset and improve the ON-current and SS, as was experimentally demonstrated in [7], where a Ge-MoS_2 vertical heterojunction TFET exhibited an ultra-low SS of ~31 mV/decade, one of the lowest among all demonstrated TFETs. The ultra-scalability and sensitivity of 2D-TFET sensors can be leveraged to design a revolutionary new class of biosensors capable of single-molecule detection. However, conventional fabrication methods for 2D-FET/2D-TFET biosensors have involved high-temperature, expensive, and complex growth and fabrication processes (e.g., CVD and ALD). Therefore, printing techniques (Fig.2a) offer an attractive solution for the precise deposition of 2D layers onto conformable substrates, enabling the manufacture of high-performance biosensors with enhanced sensitivity, selectivity, and stability.

Furthermore, printing from a substrate functionalized with specific biomolecules (e.g., antibodies, enzymes, and DNA probes) imprints the same functionalization onto the printed 2D materials, thereby enabling targeted detection of specific bioanalytes. Additionally, simplified integration of printed 2D materials with other electronics and communication technologies enables real-time and remote monitoring, while their low-cost of development makes them disposable, minimizing cross contamination. Despite limited progress in realizing printable 2D-FET biosensors due to the current immature processes for printing 2D materials [8], significant recent advancements include

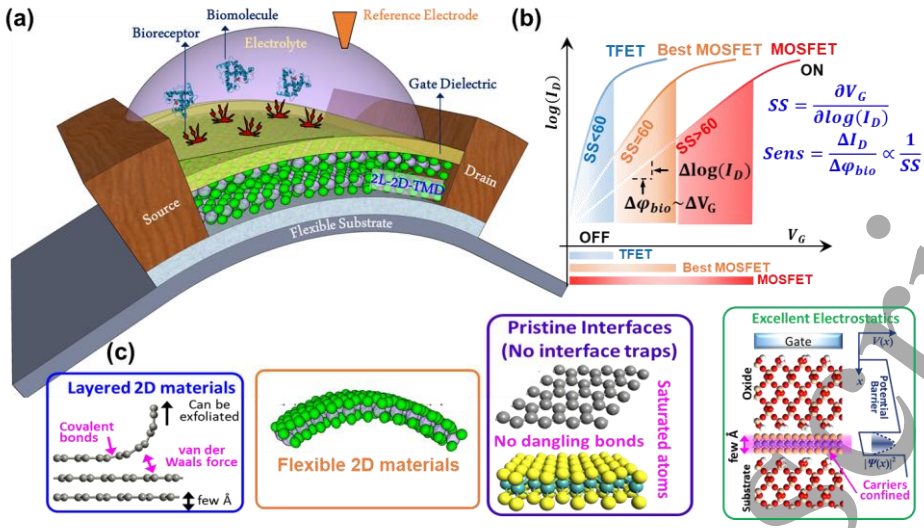

Figure 1 (a) Schematic of a top-gate 2D-FET biosensor on a flexible substrate, implemented with a bilayer (2L) 2D transition metal dichalcogenide (2D-TMD). (b) Comparison of I_D-V_G characteristics of TFETs, and common- and best-case-MOSFETs. Highest sensitivity is obtained in the subthreshold regime, which is marked in solid color. SS is inversely proportional to the biosensor sensitivity (*Sens.*), thereby making TFET biosensors the most sensitive. I_D and V_G are the drain current and applied gate voltage, respectively, and $\Delta\varphi_{bio}$ is the FET-channel potential change induced due to conjugation with the biomolecule. For 2D-FET biosensors with near ideal electrostatics, $\Delta\varphi_{bio} = \Delta V_G$. (c) Advantages of 2DM that help with implementing high-sensitivity flexible biosensor FETs.

demonstrations of printed graphene [9], 2D heterostructures [10][11], and transistors designed with inkjet-printed graphene and hexagonal boron nitride [12], and WSe_2 [10], and a demonstration of 2D-material-based printed glucose sensor employing screen-printed reduced graphene oxide [13].

Current and Future Challenges

Despite the promises offered by printable 2D-FET biosensors, there are several challenges to be overcome for use in practical applications. The primary challenge remains the reliable and high-quality printing of wide varieties of 2D materials on several substrates (Fig.2a), including flexible substrates, while being biocompatible and still providing high selectivity and sensitivity. High-resolution printing (Fig.2b) is also necessary to achieve smaller channel length transistors (important for detection of smaller biomolecules with higher sensitivity) and suitable heterojunctions for optimized FET biosensor performance. Additionally, optimizing the printing process to deposit diverse biorecognition elements with high stability on either the 2D-semiconductor channel or the gate-dielectric is paramount for the target analyte specificity and performance of biosensors. Development of standardized printing protocols and quality control measures are also essential to ensure reproducibility, as FET biosensor quality heavily depends on the printing process and variations can lead to difference in performance. Dielectric and contact engineering (Fig.2b) are also paramount to ensure optimal gate electrostatic control (offering large sensitivity for biomolecule detection), and efficient charge injection/extraction, respectively, critical to ensure correct biosensor operation. Particularly, optimizing the thickness, permittivity, and surface chemistry of the gate-dielectric material is crucial, since it affects the sensitivity, stability, and response time of the biosensor by influencing the charge transfer from the bioanalyte to the FET channel, while simultaneously minimizing the electronic noise and interference with the environment. Contact engineering which ensures optimum stability, sensitivity, and response time of the FET biosensor, can be optimized by appropriately choosing contact metals [14][15][16] and their contact configurations [17]. Surface fouling caused by the adsorption of non-specific biomolecules can interfere with the binding of the target analyte to the biorecognition element, posing another challenge in practical applications for 2D-FET biosensors [18]. The large surface-to-volume ratio of 2D materials exacerbates this issue, necessitating the development of antifouling

block layers (bovine serum albumin and zwitterionic polymers [19]) for coating the channel. Finally, the Debye length – the thickness of the electrical double layer formed at the electrolyte-dielectric interface (Fig.1a), which determines the minimum sensing distance – must also be increased to enhance the interaction between the target analyte and the FET biosensor, thereby improving sensitivity.

Advances in Science and Technology to Meet Challenges

To enable the design and production of printable high-performance 2D-FET biosensors at large scale, improvements in printing technology are paramount to enable low-cost fabrication of biosensors that are flexible and can conform to the body's shape, enabling continuous monitoring of vital signs. Among the several standard printing processes of inkjet, screen, roll-to-roll gravure, and flexographic printing (Fig.2a), the latter two techniques enabling large-scale, high throughput, low-cost, and scalable printing of 2D materials onto various substrates need to be particularly optimized for high-resolution printing (as fine as sub-500 nm). This can be achieved through development of application-specific, highly concentrated, and electrically conductive low-cost 2D-materials inks at large-scale, containing monodispersed 2D flakes of uniform flake size, thickness, and electrical conductivity (doping) to ensure uniform and pristine material properties of the printed 2D materials. Specifically, the ink formulations (Fig.2b) along with optimum binders and solvents, need to be optimized to render optimal ink physical properties for the specific printing technology and the targeted substrate. Contact and dielectric engineering of the 2D-FET biosensors also needs to be realized to ensure optimum performance, sensitivity, level-of-detection, and robustness. Specifically, solutions to reliably achieve Ohmic contacts to printed 2D materials with low-contact resistance (sub 1 kΩ.μm) needs to be realized through optimum selection of the metal for the specific 2D materials with appropriate contact geometry, along with appropriate dielectrics to ensure optimal electrostatics while minimizing hysteresis, noise, and spurious interaction with the environment. Furthermore, specific antifouling techniques that do not harm the sensitivity for the targeted bioanalyte while still providing adequate rejection of nonspecific bioanalyte adsorption, needs to be developed for operation with simultaneously high sensitivity and selectivity. Surface functionalization (Fig.2b) of 2D materials [20], through appropriate functionalizing molecules and techniques, is also crucial for improving the selectivity and sensitivity of 2D-FET biosensors to specific bioanalytes. While covalent functionalization, achieved through ligand conjugation of functional group with either chalcogen atoms or vacancies, results in more efficient charge transfer, and non-covalent functionalization techniques expand the range of materials that can be combined with 2D TMDs for detection of various bioanlaytes without significantly altering the properties of 2D materials (delivers clean interfaces without bonding), hybrid functionalization techniques combining both approaches result in both physically and chemically stable biosensors. Therefore, development of appropriate functionalization techniques with a variety of functionalizing molecules – both organic and inorganic, with appropriate techniques – must be achieved to reliably fabricate and demonstrate such biosensors. Techniques to improve the Debye length for larger sensitivity (with simultaneously lower noise) must also be explored without resorting to nanoscale FET channel bending and deformation [21], which can potentially degrade biosensor performance. Additionally, advances in integration techniques of 2D-FET biosensors with communication technologies for real-time monitoring, improved signal processing techniques for reliable performance in noisy environments, and safe and efficient biocompatible power supply solutions with minimal interference, must be achieved to realize the full potential of printed 2D-FET biosensors. Finally, advancements in machine learning-based AI algorithms are desired to aid biosensors in disease diagnosis by identifying disease patterns.

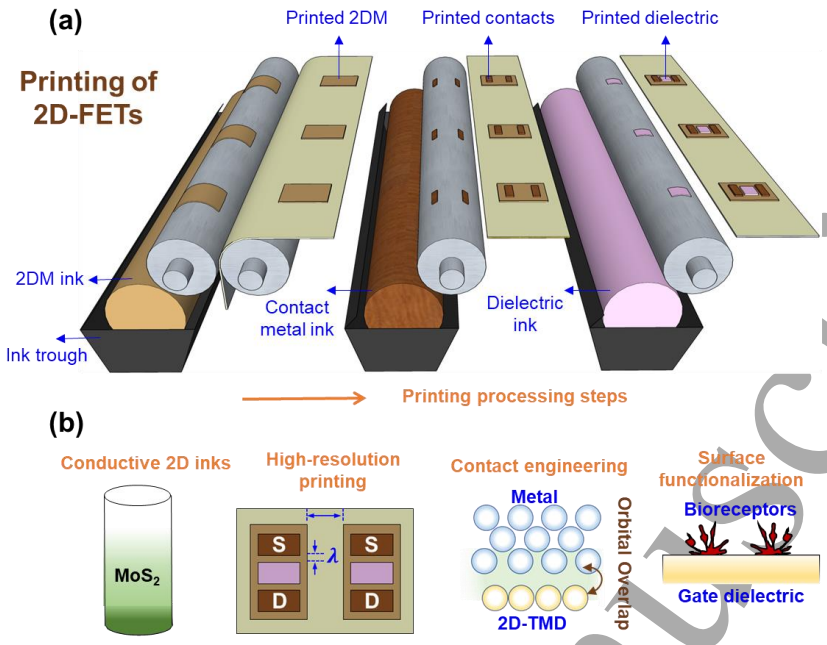

Figure 2 (a) Flexographic printing of 2D-FETs for biosensors. Rollers containing functional 2D-material inks for channel, metal inks for source/drain contacts, and dielectric ink for gate-dielectric. (b) Some practical challenges for implementing printed 2D-FET biosensor: finding suitable conductive 2D-material inks for decreasing source/drain/channel resistance, high-resolution printing to maximize throughput and reduce device-to-device variability, contact engineering through optimal contact metals (determined by orbital overlap with 2D-TMD for efficient current injection, and surface functionalization to ensure biorecognition with a diverse set of biomolecules with high sensitivity and selectivity.

Concluding Remarks

Printable biosensors based on 2D materials have immense potential for revolutionizing healthcare by enabling fast/low-cost, continuous, real-time, and non-invasive monitoring of vital signs and early disease detection. The use of 2D materials with high surface-area-to-volume ratio and the ability to functionalize their surface (or the gate dielectric) leads to biosensor designs with high sensitivity and selectivity to specific bioanalytes. Moreover, the printable technology allows producing biosensors that can be fabricated at low-cost in high volumes on a variety of surfaces, including flexible substrates, making them bio-compatible and able to conform to the skin contours or body's shape for continuous vital sign monitoring. Therefore, the integration of 2D materials with printable biosensors brings numerous benefits, such as improved sensing performance, reduced cost, and increased scalability. Moreover, advancements in printed 2D electronics can be leveraged to permit 3D heterogeneous integration of 2D materials with silicon and other conventional electronic materials **[22]**, thereby allowing ultra-compact and low-cost 3D integrated sensor electronics. While challenges remain in the development of high-performance 2D-materials-based biosensors, significant advances made in 2D materials synthesis, printable electronics, and surface functionalization hold great promise in improving the performance, reliability, and scalability of printable 2D-materials-based biosensors. With the continued progress in lithography techniques, signal processing, and integration with wireless communication technologies, the production of 2D-materials-based nanoscale biosensors with real-time monitoring of vital signals are expected in the near future, making them ubiquitous in the domain of accurate and real-time health monitoring for individuals, thereby bringing significant benefits to the healthcare industry and improving the overall quality of life.

Acknowledgements

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8.6 – Printable electrochemical biosensors based on 2D materials

Zachary T. Johnson and Jonathan C. Claussen

Iowa State University, Ames, IA, 50011, United States of America

Status

Electrochemical biosensor circuits are simple two or three electrode designs functionalized with biorecognition agents such as enzymes, antibodies, DNA or ionophores. These circuits that can be miniaturized to the microscale, are consequently well-suited for multiplexed sensing applications with small sample volumes even down to the nanoliter range [1]. Furthermore, these biosensors exhibit remarkable adaptability in sensitivity, enabling them to selectively detect a broad spectrum of concentrations, from attomolar levels of nucleic acids and micromolar quantities of blood glucose to picomolar amounts of salivary oncoproteins and millimolar levels of sodium in sweat [2], [3], [4], [5]. These sensors yield rapid, quantifiable concentration results even in turbid solutions which make them more amenable to testing in actual biological field samples than optical-based sensors. Moreover, electrochemical biosensors are becoming attractive for future integration with the Internet of Things (IoTs), and in a broader sense with Industry 4.0, especially since they can provide real-time and continuous monitoring of chemical/biochemical analytes in aqueous suspensions in the field [6] (Figure 1). Such sensor capabilities coupled with artificial intelligence updated and managed through the IoTs could enable the solutions we need to tackle the complex and multifaceted challenges associated with health, environment, climate, food, and water on the local and global scale, as well as on the individual and the population scale [7]. Traditionally, electrochemical sensors have been fabricated using noble metals or carbon materials. These materials are not only costly but frequently lack the antifouling properties and high surface area required for selective sensing and calibration-free operation in field applications. These performance limitations are beginning to be addressed with nanomaterials and particularly with 2D materials.

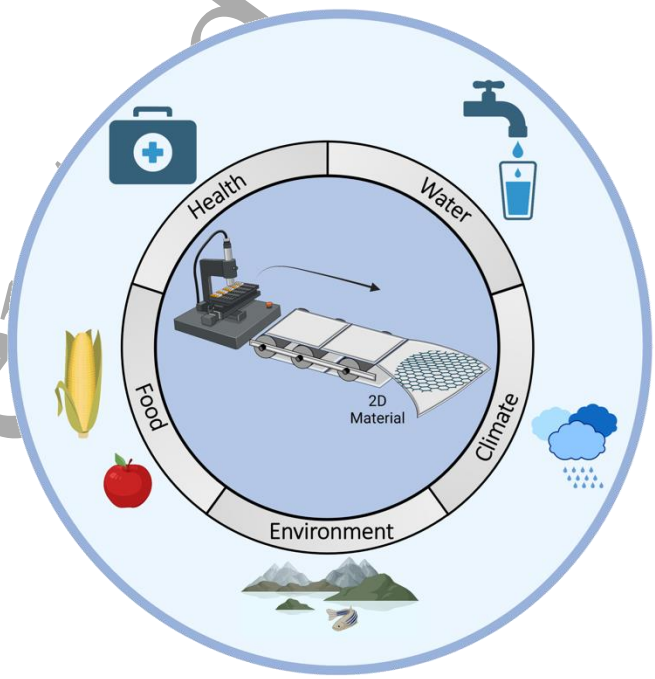

Figure 1. The wide-ranging impact printed electrochemical biosensors are expected on the fields of health, environment, climate, food, and water through the Internet of Things (IoT) and Industry 4.0.

Such 2D materials, led by graphene and followed by more recent advancements in Transition Metal Dichalcogenides such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2); MXenes such as titanium carbide (Ti_3C_2Tx); and even to some extent black phosphorous and boron nitride, provide remarkably high surface-area-to-volume ratio, mechanical strength and flexibility, and tunable properties that are relevant to sensing such as conductivity, surface wettability, and capacitance [8]. Electrochemical sensors that incorporate such 2D materials have exhibited improved performance characteristics, for example, electrodes modified with graphene have shown to improve the faradaic current by 20 times and the sensitivity of enzymatic sensors by 4-fold [9], [10]. Moreover, the concomitance of unique mechanical and tunable properties combined with recent advancements in scalable synthesis (e.g., batch chemical/physical exfoliation) and electrode fabrication (printing) make these materials more attractive than conventional nanomaterials, such as expensive precious metals like platinum, gold, and ruthenium or nanomaterials grown through expensive/low-yield processing such as chemical vapor deposition or laser ablation (e.g., carbon nanotubes).

Current and Future Challenges

The scalability and relatively low-cost of 2D electrochemical biosensor fabrication is being realized through high-yield fabrication processes such as chemical, mechanical, or even electrochemical exfoliation processes, which enable fabrication of 2D materials that are later combined with binders and solvents to form solution-phase inks that can be cost effectively 2D printed through rapid prototyping (ink jet and aerosol jet printing) and high-yield printing processes (screen and gravure printing) [11]. However, the challenge of using printed 2D materials for electrochemical sensing is that the surface properties of the as-printed electrodes are often not suitable for the continuous and real-time sensing needed for Industry 4.0.

Printing 2D materials requires that exfoliated material be broken down into micron scale flakes with nanoscale thickness through physical techniques such as sonication, ball milling, shear mixing or through additional chemical or liquid-phase exfoliation to render the flakes sufficiently small for printing processes [12]. Additionally, non-conductive binders (e.g., ethyl and nitrocellulose) and solvents are added to the material flakes so that that ink adheres well to the printed surface. The resultant printed 2D materials leave patterns that are smooth, well-defined and in many cases flexible. Finally, the binders and solvents in the inks are carbonized or removed from the printed circuits typically through high-temperature annealing, pulsed light treatment, or by chemical treatments. These post-print treatments render the print sufficiently electrically conductive for numerous applications including electrochemical sensing but do not tune surface properties such as surface area, wettability, and capacitance that can make the sensors truly capable of real-time and/or continuous field sensing applications. For example, they do not contain the surface area necessary for enhanced biorecognition agent loading and heterogeneous charge transport; the surface wettability needed to prevent biofouling, assist in humidity adsorption, or prevent a water layer building up between a sensing membrane and the underlying electrode; and the electrochemical capacitance to improve charge transfer kinetics and improve the overall sensor performance.

Finally, in-field monitoring will in many cases require the use of microfluidics to transport fluid to the electrochemical sensor surface (e.g., microneedles transporting interstitial fluid to wearable sensor) and/or to divide fluid samples to distinctly functionalized sensing regions to enable multiplexed biosensing [13]. As with the sensors, microfluidics need to be formed and patterned in a low-cost and scalable fashion for widescale deployment and ubiquitous use.

Advances in Science and Technology to Meet Challenges

A key approach to enabling large-scale deployment of printed 2D material electrochemical sensors involves developing techniques for creating a micro-structured surface finish on 2D prints, which enhances their performance in electrochemical biosensing applications. This micro-structured surface not only provides the high surface area required for highly sensitive electrochemical sensing but also allows for tuning of surface wettability and capacitance, essential for continuous, in-field applications.

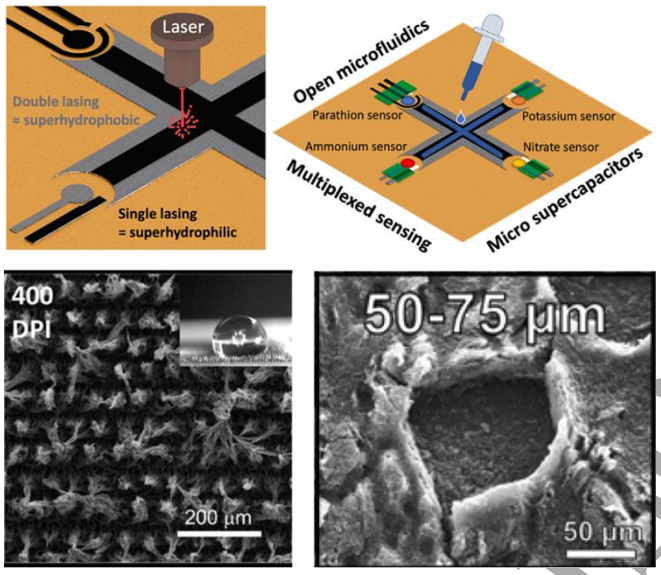

Figure 2 Top Row: Printed laser induced graphene electrochemical sensors and open microfluidics being created and patterned from the same lasing process. Bottom Row: Scanning electron microscopy (SEMs) micrographs showing surface morphology of (left) laser induced graphene (Inset: water contact angle measurement) and (right) volcano-like micropore left after removal of salt porogen from printed graphene. Figures are reprinted with permission from Royal Society of Chemistry and the American Society of Chemistry [14] and [16] respectively.

Furthermore, it can be further adapted to develop 2D material-based open microfluidics, facilitating fluid transport to the biosensors.

These advancements are being achieved through the development of inks and post-print processing techniques that inherently produce or promote the formation of micro- and nano-structured surfaces on 2D printed sensors (Figure 2). For example, salt porogens added to graphene can leave superficial micron-sized volcano-like pores after removal via laser irradiation that result in enzymatic electrochemical biosensors with double the sensor sensitivity [14]. This dramatic increase in sensitivity was due to increased reactive area for catalysis of electroactive species but also may stem from the developed superficial microenvironment that is more suitable for enzyme function, stability, and retainment all of which would be essential for repeated use in the field. In another example, a laser was used to etch microscale groves into printed graphene to create superhydrophobic tracks surrounding hydrophilic graphene to transport and split water across the surface (i.e., open microfluidics) to sensor locations [15]. These graphene-based open microfluidics enables the creation of the sensors and microfluidics from the same 2D material printed at the same time. This concept was further explored with laser-induced graphene (LIG) (graphene synthesis and patterning performed with a laser), where multiplexed electrochemical sensors for fertilizer ion and pesticide detection connected via open microfluidic pathways were fabricated on a single substrate [16]. These LIG-based electrochemical biosensors not only possess the electrocatalytic surface area and microenvironment necessary for highly sensitive enzymatic pesticide detection (achieving picomolar detection limits) but can also be engineered to exhibit hydrophobic surface wettability. This reduces or prevents water layer accumulation between the ion-selective membrane and the electrode surface, minimizes electrode fouling, and enables stable, continuous ion sensing in environmental samples for months. [17], [18]. These examples represent just a glimpse of the potential for micro-structuring 2D printed materials. As research into other 2D materials beyond graphene continues to mature, we can expect even more innovative approaches in the coming years.

Concluding Remarks

Electrochemical printed 2D biosensors will invariably have a significant role to play with Industry 4.0 as they help enable the IoTs in keeping our food safe, our water clean, and our bodies healthy. The use of 2D materials is enabling the high sensitivities, sensing ranges, and low detection limits needed to make rapid assessments of chemical and biochemical analytes in the field and the use of scalable 2D printing methods will make them affordable for ubiquitous use. However, to meet the IoT's demands for continuous or calibration-free sensing, researchers must innovate to micro- and nano-structure the surface of printed 2D materials. The goal is to create defect-rich and highly electrocatalytic surfaces without relying on noble metals, while also achieving the necessary surface wettability and capacitance to enhance sensor stability and longevity. Developing sensors and microfluidics for multiplexed biosensing entirely from 2D materials, eliminating the need for metals and non-degradable polymers, not only promises widespread implementation but also fosters the creation of sustainable analytical devices that can be recycled or discarded with minimal impact to the environment.

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Section 8.7 – Printable electrochemical biosensors based on conjugated organic compounds

Akshay Moudgil[1,2] and Wei Lin Leong[1]

[1] School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
[2] Department of Electrical Engineering, Indian Institute of Technology Jodhpur, Karwar 342030, Jodhpur, India

Status

Printable electrochemical biosensors based on conjugated organic compounds have gained significant attention due to their potential to provide a low-cost, easy-to-use, large-area, environment-friendly, and portable disease diagnosis, and health monitoring platform [1]. The active incorporation of conjugated organic compounds has unique properties, such as high electrical conductivity, good electrochemical activity, easy processability, and biocompatibility that make them excellent choice for biosensing applications [2], [3]. For example, conjugated polymers such as poly-3,4-ethylenedioxythiophene:poly-4-styrenesulfonate (PEDOT:PSS), poly(3-hexylthiophene) (P3HT), and polyaniline (PANI) are widely used in organic bioelectronics. The advantages of using these conjugated polymers include (i) tunable properties, in terms of their chemical structure and composition, allowing tailoring of their properties to match specific sensing requirements. By modifying the conjugated backbone, side chains, or doping agents, the polymer's electronic, optical, and sensing properties can be finely tuned; (ii) good electrical properties, where the presence of delocalized π-electrons in conjugated polymers imparts high electrical conductivity, making them excellent candidates for transducing the chemical information of analytes into electrical signals and (iii) facile functionalization, enabling the attachment of various functional groups, biomolecules, or nanoparticles that enhance the polymer's selectivity, stability, and compatibility with different analytes, making it suitable for diverse sensing applications. There are still some challenges in this class of materials. For instance, conjugated polymers are susceptible to environmental factors such as oxygen, moisture, and light, leading to degradation and loss of their sensing performance over time. Redox-active species in the sample matrix can also interfere with the electrochemical response of conjugated polymers, leading to false signals or reduced selectivity.

Printable electrochemical biosensors use various device structures, including two-electrode and three-electrode configurations with transducing principles (cyclic voltammetry, electrochemical impedance spectroscopy, and open-circuit potentiometry) where the three-electrode is typically preferred for more accurate measurements, as it allows better control of the electrochemical potential of the working electrode. These electrochemical methods offer distinct advantages, such as rapid and simultaneous analysis, qualitative and quantitative analysis, non-destructive and label-free analysis, simple and cost-effective, and long-term stability monitoring. However, challenges related to overlapping peaks, limited chemical selectivity, complex data analysis, data interpretation, electrode stability, and quantitative analysis must be considered for reliable and accurate measurements. Understanding the strengths and limitations of these methods facilitates their appropriate selection and optimization for various sensing applications. For instance, a label-free microfluidic paper-based electrochemical aptasensor for the multiplexed detection of cancer biomarkers was fabricated through wax printing and screen printing [4]. The sensor detected two cancer biomarkers, carcinoembryonic antigen (CEA) and neuron-specific enolase (NSE), which exhibited good linearity in ranges of 0.01–500 ng mL^{-1} for CEA (R^2 = 0.989) and 0.05–500 ng mL^{-1} for NSE (R^2 = 0.944), respectively. The limit of detection (LOD) was 2 pg mL^{-1} for CEA and 10 pg mL^{-1} for NSE.

Printed biosensors are advantageous for practical biosensing applications as they can conform to complex geometries, which is not possible with rigid material-based electronics. However, the device must be comfortable for specific applications, such as physiological metabolite detection, body

temperature monitoring, blood flow, pressure monitoring etc. Therefore, developing efficient and reproducible processing methods on the biodegradable or compostable substrate with low power consumption for these biosensors remains a critical challenge and opens new avenues, as illustrated in Figure 1.

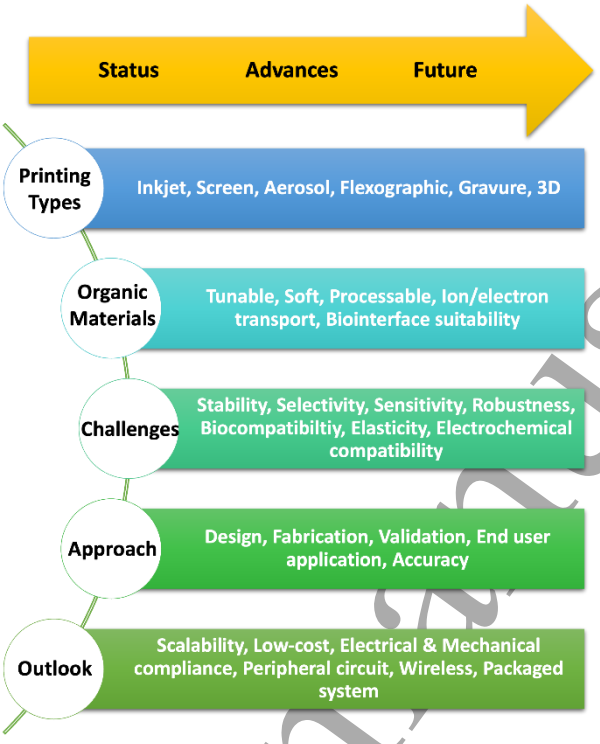

Figure 1 A schematic illustration of future roadmap for printable electrochemical biosensors based on conjugated organic compounds.

Current and Future Challenges

There is a growing need for developing new materials and printing technologies to address many challenges. Some of the key challenges are discussed below.

Materials. One of the main challenges in printable electrochemical biosensors based on conjugated organic compounds is the limited stability and lifetime (few hours to days) of the devices. The sensitivity of these materials to environmental factors such as temperature, humidity, oxygen, and oxidation/reduction processes during sensing can affect their performance over time (up to 50%), leading to sensor signal drift, sensing range variation, and reduced accuracy.

Device fabrication. Another challenge is optimizing the processing methods to improve their reproducibility and scalability. Some of the key challenges include:

- Materials compatibility: Choosing suitable materials is crucial for achieving high-quality printed devices, as different printing techniques require specific materials, and not all materials are compatible with all techniques. Therefore, to ensure the device's proper functioning and mitigate issues related to interfacial compatibility of the electrode and active sensing layer, soft-hard interfaces, and corresponding fatigue resistance, it is essential to select appropriate materials with appropriate chemical and physical properties, including surface energy, reactivity, and compatibility with the printing process.
- Deposition uniformity: Achieving uniform deposition of the functional materials is challenging, particularly for large-area printing. Non-uniform deposition can result in variations in device performance, which is undesirable for applications that require high sensitivity and accuracy.

- Resolution and feature size: The low resolution (20-50 μm) and large feature size (50-250 μm) achievable by printing techniques are limited by ink viscosity, nozzle size, and substrate properties.
- Post-processing requirements: Annealing, curing, and surface treatments are often required to improve the performance of printed devices. These steps are time-consuming and require specialized equipment, increasing the overall cost of the process.
- Device reliability and stability: Printed devices are often less stable and reliable than conventionally fabricated devices due to material degradation, electrode detachment, mechanical instability, elastic range variation, and strain effect decoupling.

Biosensor performance. One of the main challenges is the development of new materials with improved sensing properties, including higher sensitivity, selectivity (as high as possible with less standard deviation), stability (minimum 3 years for commercial use), and reproducibility (lower coefficient of variation <5%) along with lower limit of detection (up to single target entity with a certain level of confidence). Their sensitivity and selectivity need to be at the level of conventional biosensors, hence, sensor-biology interface optimization for specific analyte detection is required.

Practical application. Developing and integrating printable electrochemical biosensors have significant challenges, and critical factors are integration density, crosstalk, signal-to-noise ratio, power consumption, latency, and design complexity. Integrating these single or multiple biosensors onto a single printed platform with electronic circuits, signal amplifiers, and wireless communication systems is crucial for real-time monitoring and data analysis in various applications.

Looking into the future, developing stable and robust materials for the active layer, optimizing the printing process along with device-to-device variation, large-scale testing, standardization, and benchmarking, are required to overcome these challenges.

Advances in Science and Technology to Meet Challenges

The advances in materials innovations focus on developing new conjugated organic compounds with improved electronic properties, stability, multifunctionality, and dynamic performance studies [5]–[7]. Nanomaterials, such as conducting polymers, two-dimensional materials, and metal nanoparticles, are expected to enhance the electrochemical activity and biocompatibility of the active layer in a hybrid manner. At the same time, advances in form-factor innovations consist of ultrathin films and lightweight and customized textiles. Developing new printing techniques, such as reverse offset printing, and 3D printing is one of the promising approaches to improve the reproducibility and scalability of the biosensor fabrication process as these techniques can precisely control the active layer morphology and composition. Specifically, reverse offset printing and nano dispensing offer low feature sizes (5 μm) and high resolutions (1 μm) with excellent accuracy and repeatability, even on materials with poor porosity or irregular surfaces [8]. A further step is being targeted to optimize the printing process by i) controlling the ink transfer, ii) accurate positioning with low latency, and iii) surface energy of the used materials, iv) perfect matching between stretchable substrates and inks. For example, the inkjet-printed PEDOT:PSS electrodes thinner than 1 μm work well for electromyography and electrocardiography; even when facial hair grows through the electrode, they remain functional (Figure 2) [9]. Further, printing encapsulation materials and protective coating such as UV-curable polymers or dielectric layers is expected to enhance stability by preventing direct contact with ions or water.

Since biosensors rely on organic conjugated materials as the active and sensing element, surface functionalization is critical to improving their stability and selectivity. Developing novel conjugated organic materials with tailored properties and functionalities can provide new opportunities for highly sensitive and selective biosensors. Using aptamers or antibodies as sensing elements is a promising method, but there are currently no standard protocols available for printing these biomarkers. One approach can be using molecularly imprinted polymers (MIPs), which are synthetic polymers designed to selectively bind to specific molecules or ions, similar to how antibodies bind to antigens [10].

Furthermore, integrating microfluidics is a promising technique for enhancing electrochemical biosensor's sensitivity, selectivity, and reproducibility since it can enable precise control of sample delivery and manipulation. Going ahead, integrating printable biosensors with peripheral electronic devices (microcontroller, resistor, capacitor etc.) and wireless communication technologies will enable the development of wearable and implantable biosensors for continuously monitoring physiological parameters. The performance of biosensors can be improved by incorporating machine learning algorithms and artificial intelligence (AI) to optimize sensor design, reduce sensor drift, improve the accuracy of readout technologies, and analyze large datasets for identifying disease biomarkers and facilitating early diagnosis.

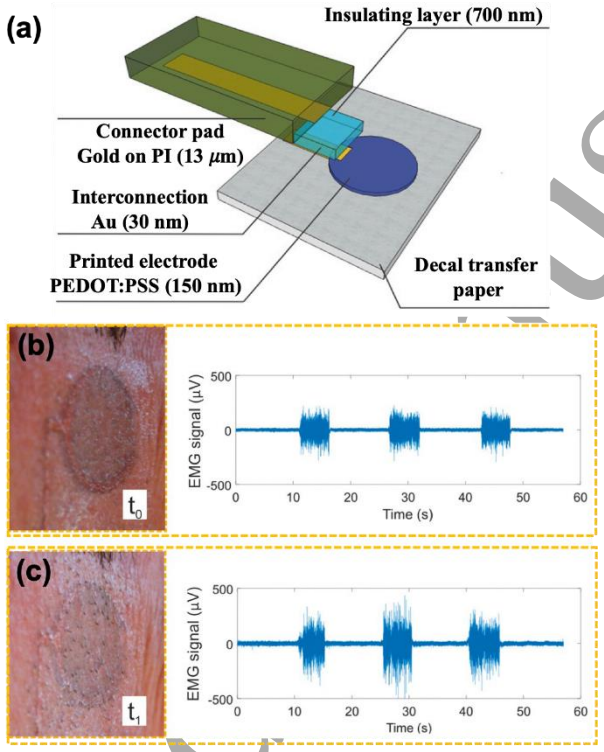

Figure 2 The proposed method involves temporary tattoo electrodes that are layered onto the skin. (a) A schematic of view of multilayer assembly of temporary tattoo electrode. The multilayer assembly includes two circular tattoo electrodes placed on the mandibular muscle of a subject. Surface electromyography recordings are taken at each time point to monitor performance. The functionality of the electrodes is assessed at two different time points: (b) t_0, which is 3 hours after shaving, and (c) t1, which is 27 hours after shaving, to observe hair growth through the tattoo electrodes [9].

Concluding Remarks

In summary, the development of printable electrochemical biosensors based on conjugated organic compounds is a rapidly growing field with numerous advantages such as low-cost, large-area, and flexible fabrication and possesses significant potential for revolutionizing disease diagnosis and monitoring application including point-of-care diagnostic devices, personalized healthcare, physiological analyte monitoring, and fitness tracking. The future roadmap can be chalked out in terms of innovation in materials, device printing techniques (inkjet, EHD, 3D), dimensional scaling (feature size, aspect ratio, aerial scaling), electrical performance (conductivity, mobility), mechanical robustness (elastic modulus, stiffness, viscoelasticity, self-healing), form factors (compact, hybrid printed circuits, wireless) and packaged system. However, several challenges must be addressed to realize their full potential by developing new materials, optimizing printing processes, and exploring novel approaches such as 3D printing and self-assembly. Advances in science and technology are

vouched for developing more efficient, reliable, and cost-effective printable electrochemical biosensors based on conjugated organic compounds. Further research is still required to optimize the performance of these biosensors for various applications and to address the challenges posed by complex biological samples. Future research should focus on developing more stable and reliable materials, improving the readout technologies, integrating multiple biosensors onto a single platform, and incorporating machine learning and AI techniques.

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