Flexible and Printed Electronics

ROADMAP • **OPEN ACCESS**

The 2025 PEDOT roadmap

To cite this article: Fabio Cicoira *et al* 2026 *Flex. Print. Electron.* **11** 032501

Flexible and Printed Electronics

OPEN ACCESS

RECEIVED
8 July 2025

REVISED
15 May 2026

ACCEPTED FOR PUBLICATION
24 June 2026

PUBLISHED
20 August 2026

ROADMAP

The 2025 PEDOT roadmap

Fabio Cicoira[1,*], Magnus Berggren[2,3,4], Erica Colaprico[2], Reverant Crispin[2,3,4], Isak Engquist[2,3,4], Drew Evans[5], Simone Fabiano[2,3,4], Jiaxin Fan[1], Zijing Guo[6], Guoying Gu[7,8], Amali G Guruge[9], Ryohei Ikeda[6], Magnus Jonsson[2,3,4], Laure V Kayser[10], Sadaf Khoomortezaei[1], Chi-hyeong Kim[1], Jinsil Kim[1], Jeonghun Kwak[11], Renee Kroon[2,3,4], Junghyun Lee[10], Jinhao Li[7,8], Baoyang Lu[12], George G Malliaras[13], David C Martin[10], Masakazu Mukaida[14], Tatsuya Miyamoto[15], Stephen J K O'Neill[16], Hiroshi Okamoto[6,17], Tetsu Sato[18], Oren A Scherman[16], Alexandra Sandéhn[2,3], Daniel T Simon[2,3,4], Jeong Han Song[11], Eleni Stavrinidou[2,3,4], Jun Takeya[6,19], Jadranka Travas-Sejdic[20], Alessandro Troisi[9], Klas Tybrandt[2,3,4], Qingshuo Wei[14], Meijing Wang[1], Shun Watanabe[6], Yuhang Wu[10], Bicheng Zhu[20] and Igor Zozoulenko[2,3,4]

[1] Department of Chemical Engineering, Polytechnique Montreal, Québec, Canada
[2] Laboratory of Organic Electronics, ITN, Linköping University, SE 60174 Norrköping, Sweden
[3] Wallenberg Wood Science Center (WWSC), ITN, Linköping University, SE 60174 Norrköping, Sweden
[4] Wallenberg Initiative Materials Science for Sustainability (WISE), ITN, Linköping University, SE 60174 Norrköping, Sweden
[5] Future Industries Institute, Adelaide University, Adelaide, Australia
[6] Department of Advanced Materials Science, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277–8561, Japan
[7] Robotics Institute and State Key Laboratory of Mechanical System and Vibration, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[8] Meta Robotics Institute, Shanghai Jiao Tong University, Shanghai, People's Republic of China
[9] Department of Chemistry, University of Liverpool, Liverpool L69 3BX, United Kingdom
[10] Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, United States of America
[11] Department of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, and SOFT Foundry Institute, Seoul National University, Seoul, Republic of Korea
[12] Jiangxi Provincial Key Laboratory of Flexible Electronics, Flexible Electronics Innovation Institute, Jiangxi Science and Technology Normal University, Nanchang, People's Republic of China
[13] Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 JJ Thomson Ave, Cambridge CB3 0FA, United Kingdom
[14] National Institute of Advanced Industrial Science and Technology (AIST)—University of Tokyo, Advanced Operando-Measurement Technology Open Innovation Laboratory (OPERANDO-OIL), AIST, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277–8589, Japan
[15] Department of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466–8555, Japan
[16] Melville Laboratory for Polymer Synthesis, Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
[17] Department of Physics, Nihon University, 1-8-14, Kanda-Surugadai, Chiyoda-ku, Tokyo 101–8308, Japan
[18] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980–8577, Japan
[19] Internation Centre of Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba 305–0044, Japan
[20] Centre for Innovative Materials for Health, School of Chemical Sciences, Waipapa Taumata Rau—The University of Auckland, 23 Symonds Street, Auckland, New Zealand and MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Wellington, New Zealand
[*] Author to whom any correspondence should be addressed.

E-mail: fabio.cicoira@polymtl.ca

Keywords: conducting polymers, PEDOT, bioelectronics, processing, modeling

Abstract

This roadmap presents key advances and future directions in the field of the conducting polymer polyethylene dioxythiophene (PEDOT), with a focus on its role as multifunctional material in emerging electronic applications. It covers a broad spectrum of topics, including self-healing materials, plant bioelectronics, energy harvesting and storage, and neural interfaces. The roadmap also addresses recent progress in the synthesis and functionalization of PEDOT derivatives, as well as insights from molecular dynamics simulations and transport physics. Emphasis is placed on a

range of processing techniques, such as electropolymerization, vapor phase polymerization, and 3D printing, and their implications for device performance. Specific applications explored include thermoelectrics, biosensors, organic electrochemical transistors, and advanced bioelectronic platforms for neuromodulation, stretchable electronics, and neuromorphic computing. This collective effort aims to serve as a comprehensive resource outlining the current state of PEDOT research and identifying challenges and opportunities for its integration across diverse electronic technologies.

Contents

Introduction

Fabio Cicoira[1], *Jadranka Travas-Sejdic*[2], *George Malliaras*[3]
[1]Department of Chemical Engineering, Polytechnique Montreal, Québec, Canada
[2]Centre for Innovative Materials for Health, School of Chemical Sciences, Waipapa Taumata Rau—The University of Auckland, Auckland, New Zealand and MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Wellington, New Zealand
[3]Electrical Engineering Division, Department of Engineering, University of Cambridge, Cambridge CB3 0FA, United Kingdom

Flexible and printed electronics have emerged as a highly multidisciplinary field at the interface of materials science, chemistry, physics, engineering, and health sciences, enabling the development of lightweight, conformable, and low-cost electronic systems for applications ranging from healthcare monitoring to soft robotics and energy harvesting. Progress in this field relies on the integration of advances across the full innovation chain—from molecular design and fundamental transport physics to device engineering and scalable manufacturing—alongside regulatory considerations and pathways to real-world clinical, industrial, and societal applications.

Within this context, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives, most notably PEDOT:PSS, have emerged as cornerstone materials for organic electronics and bioelectronic interfaces. Their unique combination of mixed ionic–electronic conductivity, solution processability, mechanical flexibility, and biocompatibility has enabled a wide range of technologies, including biosensors, wearable and implantable health monitoring devices, neural interfaces, organic electrochemical transistors (OECTs), flexible and stretchable circuits, energy storage devices (such as supercapacitors), and platforms for drug delivery and tissue engineering. Despite these advances, key challenges remain in understanding and controlling charge transport mechanisms, improving long-term stability, and expanding functionality while maintaining compatibility with scalable and sustainable fabrication methods.

Recent research efforts are increasingly focused on extending PEDOT-based systems beyond conventional device paradigms. These include the development of materials and processes for energy harvesting and thermoelectrics (TEs), the use of advanced fabrication approaches such as vapor phase polymerization (VPP), electrodeposition, and 3D printing, and the integration of computational tools, such as molecular dynamics (MD) simulations, to better understand structure–property relationships. At the device level, innovations in OECTs, biosensors, neural implants, and neuromodulation platforms are opening new opportunities for interfacing electronics with complex biological environments.

This roadmap brings together contributions from leading researchers to provide a comprehensive overview of the current status, key challenges, and future opportunities for PEDOT-based materials and technologies. Following the established roadmap format, each section discusses the state of the art, identifies critical limitations, and outlines the advances required to address them.

The roadmap is organized around key thematic areas spanning PEDOT-based materials, fundamental physics, device architectures, and manufacturing strategies. It includes dedicated sections on synthesis and fabrication strategies, such as electrodeposition and VPP, alongside emerging approaches including 3D printing. Fundamental aspects are addressed through discussions on charge transport physics and MD simulations, providing insight into the mechanisms governing device performance. Application-driven sections cover energy harvesting and TE systems, biosensors, neural implants, and neuromodulation technologies. Device-level perspectives focus on OECTs and related architectures, highlighting their role in bioelectronic interfaces. Together, these contributions provide a cohesive view of the field, linking fundamental understanding to technological implementation.

By integrating these perspectives, this roadmap aims to define the directions that will shape the next generation of PEDOT-based electronic and bioelectronic systems. Achieving progress across these interconnected domains will be essential to fully exploit the potential of conducting polymers in scalable, high-performance, and sustainable technologies. Looking ahead, by outlining key challenges and opportunities, this roadmap aims to facilitate the translation of these advances beyond the laboratory and toward deployment in clinical and industrial contexts.

1. PEDOT:PSS based self-healing materials

*Jinsil Kim, Sadaf Khoomortezaei and Fabio Cicoira**
Department of Chemical Engineering, Polytechnique Montreal, Québec, Canada

*Email: fabio.cicoira@polymtl.ca

Status

Wearable and flexible electronics are attracting significant attention due to their potential applications in healthcare monitoring [1], electronic skins [2], soft sensors [3], and energy harvesting systems [4]. Unlike conventional rigid electronic devices, soft electronics systems, including wearable, implantable, and stretchable devices, can conform to complex surfaces and integrate seamlessly with the human body. However, their mechanical compliance also makes them vulnerable to physical damage during prolonged use and repeated deformation. To address this challenge, self-healing materials have emerged as a promising strategy to restore functionality and enhance device durability [5, 6].

Self-healing materials have recently been integrated into soft electronics systems to improve their reliability and extend operational lifetimes. Among the many candidate materials, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), stands out as a leading conducting polymer due to its mixed ionic–electronic conductivity, biocompatibility, ease of processing, stretchability, and its ability to exhibit water-assisted or extrinsic self-healing behavior [7, 8]. In this material, PEDOT provides the electrically conductive backbone, while PSS acts as a polyelectrolyte dopant and dispersant that stabilizes PEDOT in aqueous dispersions and enables solution processing.

Self-healing mechanisms are generally classified into two categories: autonomic healing, which occurs without external stimuli, and non-autonomic healing, which requires external inputs such as heat, light, or humidity. As an example, PEDOT:PSS exhibits a rapid, non-autonomic healing mechanism when water is applied to damaged areas (figures 1(a)–(d)). In this process, the PSS chains swell, effectively filling the gaps caused by damage and facilitating nearly complete recovery of the material's structural, mechanical, and electrical properties [8].

The phase-separated morphology of PEDOT:PSS plays a key role in this healing process. The soft, hygroscopic PSS matrix absorbs water and swells, increasing polymer chain mobility and enabling rearrangement of the polymer network at the damaged interface. At the same time, the conductive PEDOT-rich domains reconnect, restoring the electrical percolation pathways and enabling recovery of electrical transport once physical contact between domains is re-established. In many reported systems, the electrical conductivity (EC) of damaged PEDOT:PSS films can recover up to 90%–100% of the initial value within seconds to minutes, depending on the film thickness and the size of the damaged region [4].

Several strategies have been explored to further enhance the self-healing capabilities of PEDOT:PSS-based materials. These include intrinsic healing enabled by the hygroscopic PSS phase, blending PEDOT:PSS with stretchable self-healing polymers, and incorporating dynamic bonding interactions within polymer networks. While many studies have focused primarily on restoring EC, achieving simultaneous recovery of both electrical and mechanical properties remains challenging. Developing materials that combine stretchability, mechanical durability, and efficient self-healing is therefore critical for advancing PEDOT:PSS-based systems for flexible and wearable electronics.

Current and future challenges

Despite the promising flexibility and self-healing ability of PEDOT:PSS, significant challenges remain regarding its mechanical durability and self-healing performance, particularly in applications involving repeated mechanical deformation or severe damage (e.g. scratches, cuts, tears or punctures) [10]. While PEDOT:PSS can recover from minor cuts (typically up to 20 μm), recovery of both electrical and mechanical properties becomes limited when larger damage occurs. This limitation is particularly critical for wearable, implantable, and soft electronic devices that must maintain reliable performance over prolonged usage under dynamic conditions.

Another major limitation is the degradation of PEDOT:PSS EC under repeated bending, stretching, or twisting, which can lead to device failure over time. In addition, practical soft electronics systems require autonomous healing, ideally at room temperature, so that functionality can be rapidly restored after damage. However, the lack of autonomous healing capabilities and the susceptibility of PEDOT:PSS to mechanical fatigue limit its use in applications requiring long-term stability.

To address these limitations, several strategies have been explored, including blending with additives or polymeric components such as polyethylene glycol (PEG), polyurethane diol, tannic acid, and Triton X-100 to improve stretchability and enable autonomous healing [9]. PEG-based blends exhibit autonomous self-healing behavior without external stimuli, as demonstrated by repeated cut–healing cycles and time-resolved electrical measurements

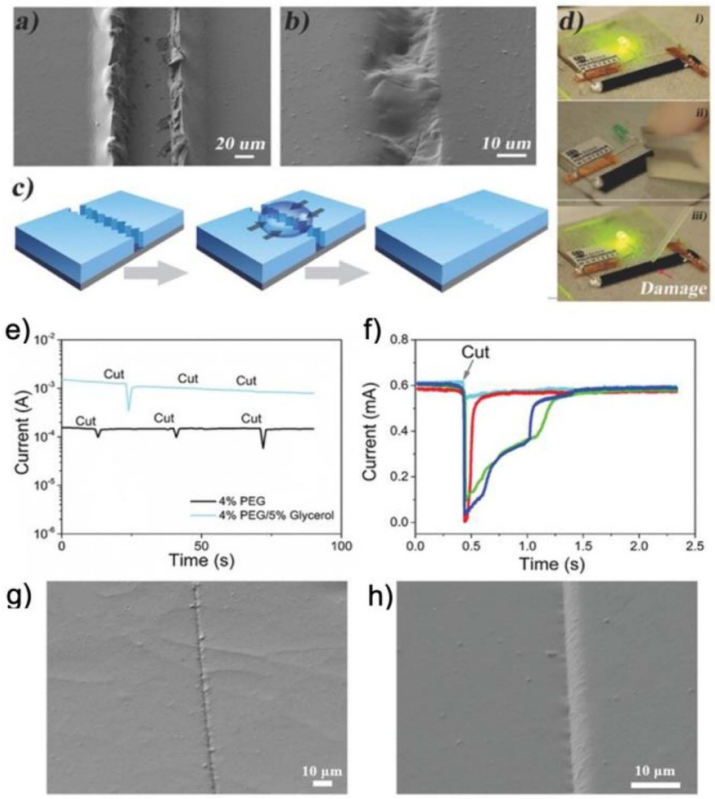

Figure 1. SEM images of the damaged area of a PEDOT:PSS film containing glycerol (thickness: 10 μm; width: 4 mm; length: 20 mm); before (a) and after (b) healing with deionized water; (c) schematic representation of water-induced mechanical and electrical healing; (d) demonstration of the damage and healing effect on a PEDOT:PSS film connected in a circuit with a LED bulb at a constant voltage of 3 V. [8] John & Wiley & Sons. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; (e) current versus time plots showing autonomous healing during several cuts in different regions of films processed from mixtures containing PEDOT:PSS and 4% PEG-400, with or without glycerol; (f) time-lapse current measurements during the cut/healing process for four different films; (g), (h) SEM images of the cut and healed region with different magnifications. The thickness of the films was ≈15 μm. The voltage applied during the healing test was 0.2 V. [9] John Wiley & Sons. © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

showing recovery of conductivity (figures 1(e)–(h)). Although these systems show promising properties, quantitative evaluations of fatigue resistance under cyclic deformation, crack propagation behavior, and electrical stability after repeated healing cycles remain limited. Developing advanced PEDOT:PSS blends incorporating novel additives or self-healing polymers will therefore be crucial to achieving materials that simultaneously combine high EC, stretchability, mechanical durability, and autonomous healing capability.

Advances in science and technology to meet challenges

Several strategies have been proposed to tailor the self-healing performance of PEDOT:PSS-based materials, including the incorporation of dynamic additives [11], post-treatment of PEDOT:PSS films [12], blending with stretchable self-healing polymers [13], and the design of composite systems incorporating dynamic bonding networks [14]. In particular, blending PEDOT:PSS with tannic acid and ethylene glycol (EG) promotes both mechanical and electrical recovery, as demonstrated by repeated cut–stick healing cycles, with restored EC and visual confirmation using an LED indicator (figures 2(a)–(d)) [11].

Addressing the coupled challenges of maintaining high EC, mechanical durability under repeated deformation, and efficient self-healing requires innovative material design strategies, particularly through the integration of stretchable self-healing polymer matrices such as polyurethanes (figure 2(e)) [15]. Stretchable polymers, such as polydimethylsiloxane (PDMS), polyurethane (PU), polyacrylate (PA), poly(vinyl alcohol) (PVA) [16], can exhibit self-healing behavior through dynamic covalent bonds (e.g. disulfide bonds, imine bonds and Diels–Alder reaction) or non-covalent interactions (e.g. hydrogen bonds and ionic bonds). When combined with PEDOT:PSS, these polymers enable the material to recover itself after mechanical damage while improving mechanical stability.

The efficiency of these self-healing interactions is often influenced by the glass transition temperature

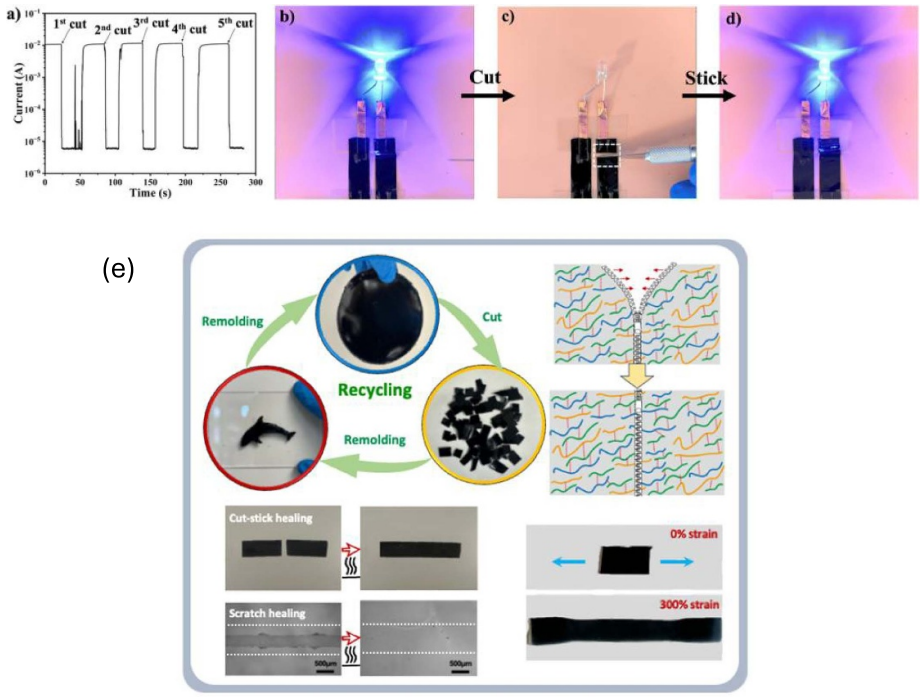

Figure 2. Electrical cut-stick healing process of PEDOT/EG/TA-3 films: (a) current versus time measurements under a constant voltage of 3.2 V after repeated cut-stick healing cycles; (b)–(d) visualization of the healing effect with an LED indicator: (b) original (closed), (c) cut (open), and (d) healed (closed). Reproduced from [11] with permission from the Royal Society of Chemistry. (e) Schematic illustration of self-healing and recyclable PEDOT:PSS/polyurethane blends illustrating recycling, cut-stick and scratch healing and stretchability. Reproduced with permission from [15]. CC BY-NC 3.0.

(T_g) of the polymer matrix. By adjusting parameters such as the crosslinking density, monomer selection or polymer blending the T_g can be tuned to enhance polymer chain mobility and enable healing at room temperature. For example, flexible backbone, linear monomers, or reduced crosslinking density can lower the T_g, and promote autonomous self-healing.

A key challenge in these systems is maintaining high EC, as most self-healing polymers are electrically insulating. To mitigate this issue, inclusion of conductivity enhancers such as glycerol, PEG, EG has been used to improve the charge transport within PEDOT:PSS. Achieving optimal performance therefore requires balancing EC, mechanical durability, and healing capability through careful control of material composition and structure [17].

Both chemical and physical compatibility between the components is critical. Chemically, the functional groups in the self-healing polymer (such as hydroxyl, carboxyl, or amine groups) interact with PEDOT:PSS, enabling dynamic bonding or supramolecular interactions that facilitate self-healing without compromising conductivity. Physically, the self-healing polymer and PEDOT:PSS should complement each other's mechanical properties to ensure that the material retains its structural integrity (i.e. the ability to recover shape, and mechanical performance after damage) and durability while also enabling repair of the damaged areas. Ultimately, combining self-healing polymers with additives in PEDOT:PSS offers a promising strategy to address challenges related to mechanical durability, self-healing and conductivity in wearable, bioelectronic, implantable devices, as well as soft robotics. By focusing on achieving a balanced integration of these materials, researchers are advancing toward the development of more durable, self-repairing, and electrically efficient materials, which are essential for next-generation devices [18].

Concluding remarks

PEDOT:PSS as a leading candidate for flexible, stretchable, and self-healing electronic devices, faces critical challenges in maintaining mechanical durability and self-healing performance, particularly under repeated stress or severe damage such as scratches, cuts, and punctures, which commonly occur in soft electronics. These limitations compromise its long-term stability and reliability in demanding environments. Through the utilization of dynamic bonding mechanisms, supramolecular interactions, and conductive additives, researchers are working to enhance PEDOT:PSS's stretchability, autonomous healing at ambient conditions, and electrical performance. Achieving the optimal balance between these elements is key to unlocking its full potential. With ongoing advancements in material

design and interdisciplinary research, PEDOT:PSS holds immense promise in shaping the next generation of resilient, efficient, and sustainable electronic devices, paving the way for transformative applications, including wearable electronics, health monitoring systems, bioelectronics, soft robotics and energy harvesting systems.

Acknowledgments

J K is grateful for the Fonds de recherche du Québec—Nature et technologies (FRQNT) for a PhD scholarship. S K acknowledges support from the NSERC Vanier Canada Graduate Scholarship for a PhD program.

2. PEDOT-based plant bioelectronics

Erica Colaprico[1], *Alexandra Sandehn*[1,2], *Eleni Stavrinidou*[1,2,3,*]

[1] Laboratory of Organic Electronics, ITN, Linköping University, SE 60174 Norrköping, Sweden

[2] Wallenberg Wood Science Center (WWSC), ITN, Linköping University, SE 60174 Norrköping, Sweden

[3] Wallenberg Initiative Materials Science for Sustainability (WISE), ITN, Linköping University, SE 60174 Norrköping, Sweden

*Email: eleni.stavrinidou@liu.se

Status

Plants are an essential part of our ecosystem and vital for human survival and prosperity. Plant bioelectronics targets the development of technologies for plant interface with two main goals: gaining a deeper understanding of plant functions at a fundamental scientific level and creating innovative solutions for smart and sustainable agriculture. Plant bioelectronics is an emerging research area, as bioelectronic technologies have traditionally been developed for biomedical applications. However, the challenges posed by climate change and a growing global population call for plants with greater resilience to environmental stress and higher productivity. Therefore, there is a pressing need to develop advanced tools that enhance our understanding of plant functions and tools that can be applied in agriculture and forestry to facilitate more sustainable practices.

PEDOT, often doped with PSS (PEDOT:PSS), has been the most widely used active material in organic bioelectronics. PEDOT:PSS offers several desirable characteristics for bio-interfacing, including efficient mixed ionic-electronic conduction, stability in aqueous environments (after crosslinking), biocompatibility, and solution processability. Additionally, its commercial availability has accelerated its adoption and exploration in diverse bioelectronic applications. Although the field of plant bioelectronics is relatively new, numerous PEDOT-based devices have already emerged (figures 3 and 4), in many cases drawing inspiration from successful demonstrations in mammalian systems.

Electrical signals in plants mediate long-distance signaling and are correlated with plant movements and responses to stress [18]. These signals have been studied using bulky metal electrodes that have a clear mismatch in form and mechanical properties with the plant tissue [27]. To address this mismatch, PEDOT-based conformable epidermal electrodes and multielectrode arrays have been developed for plant electrophysiology. PEDOT:PSS tattoo electrodes had a conformable and stable interface with plant leaves, enabling high-quality recordings of both fast and slow electrical signals in Venus Fly Trap and Arabidopsis and respectively (figure 4(B)) [22]. Despite this advancement, a major limitation for decoding electrical signals in plants lies on the low spatial resolution of the recordings, with typically one or few electrodes used. To overcome this, conformable multielectrode arrays based on PEDOT:PSS were developed to map the action potential in Venus flytrap, a model system for studying rapid electrical signals in plants (figure 4(A)) [21]. The study revealed key properties of signal propagation characteristics, demonstrating the advantage of such arrays for plant electrophysiology. In addition to monitoring electrical signals generated by stress or mechanostimulation, tissue impedance can also provide valuable physiological insights. The versatility of PEDOT synthesis enabled the direct fabrication of electrodes on leaves through vapor-phase polymerization, thus enhancing electrode integration and ensuring long-term stability [28]. Tissue impedance measurements were successfully employed to detect early-stage ozone damage in grape and apple leaves that could be relevant for preventing loss of harvest [29].

PEDOT-based implantable biosensors have been developed for monitoring of metabolites and nutrients. Sugars are synthesized during photosynthesis in the leaves and then transported via the vascular tissue to all parts of the plant to cover its energy demands. Glucose and sucrose biosensors based on OECTs were used for *in vivo* real time monitoring of sugar transport along the stems of young Hybrid Aspen trees, revealing previously uncharacterized diurnal fluctuations in sugar concentration (figures 3(A)–(C)) [19].

However, implanting sensors into plant tissue can trigger scar tissue formation. One approach that aims to minimize the wound response involved embedding PEDOT-based electrodes and OECTs in cryogels that swell upon implantation [20]. The devices were implanted in tomato stems and were used to monitor the ionic content and drought response of the plants (figures 3(D)–(F)). Yarn-based PEDOT OECTs have also been demonstrated as phytocompatible devices for monitoring changes in ionic concentration in Arundo donax stems and for detecting salinity stress [30]. To enable specific ion detection in xylem sap, ion-selective OECTs (IS-OECTs) have been developed for potassium monitoring in young pine trees [31]. Potassium selectivity was achieved by integrating a membrane containing potassium ionophores on the transistor channel.

In addition to physiological parameters, physical parameters are also crucial for plant monitoring. A wearable growth sensor based on PEDOT, modified for stretchability, enabled automated tracking of leaf elongation, in oat plants, providing insights into growth patterns influenced by light conditions [32]. The device's transparent and ultralight design ensured minimal impact on the leaf. Another example had a leaf patch form that

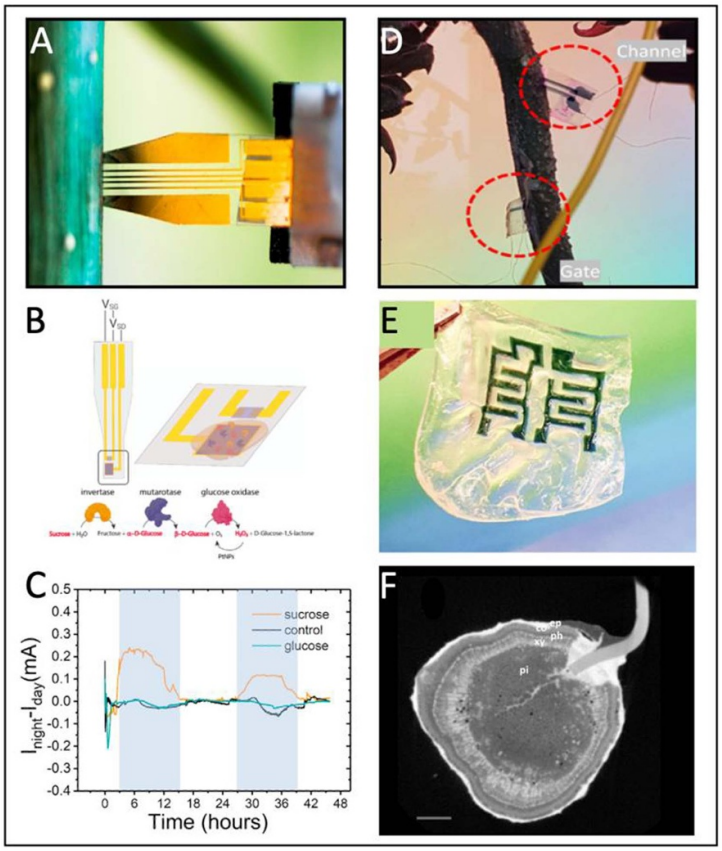

Figure 3. Examples of implantable plant bioelectronics. (A) Implantable OECT for glucose and sucrose monitoring in the vascular tissue of plants. (B) OECT schematic and functionalization with enzymes for sucrose sensitivity. (C) Real time monitoring of sucrose and glucose variation in young hybrid aspen trees—given as the change in channel current between night and day. (A)-(C) Reproduced with permission from [19]. CC BY-NC-ND 4.0. (D) Cryogel-OECT implants for monitoring nutrients in a tomato plant stem. (E) Cryogel-based device. (F) X-ray CT image of tomato plant stem with cryogel-OECT 1 week after implantation. (D)–(F) Reproduced from [20]. CC BY 4.0.

combined PEDOT-based strain and temperature sensors for multi-sensing capabilities as demonstrated in Brassica rapa (figure 4(C)) [23].

Plants, being sessile organisms, must adapt their growth to their environment. To optimize growth conditions, it is essential to monitor air and soil and correlate it with the plant status. Screen-printed PEDOT-based OECT sensors were developed for EC (that relates to the nutrient content) and temperature monitoring in growth media of tomato plants (figure 4(F)) [26]. Finally, devices that stimulate plant growth can serve as active scaffolds in hydroponics cultures. The aqueous processability of PEDOT:PSS enables the fabrication of 3D porous scaffolds through freeze-drying. The eSoil, a porous scaffold composed of PEDOT:PSS and nanofibrillated cellulose, induced a 50% increase in barley seedlings biomass upon electrical stimulation, highlighting the potential of these materials for enhancing plant growth (figure 4(E)) [25].

Current and future challenges

Plant bioelectronics is an emerging research field, and the development of design guidelines for implantable and wearable devices, along with protocols for interfacing these technologies with various plant tissues, remains in its early stages. A major concern for implantable technologies is the tissue response. Ensuring long-term device stability is also critical, which includes preserving the properties of electronic and biofunctionalized layers, a challenge shared with biomedical applications. Plants often induce necrosis in injured tissues, which can isolate the device from living tissue, further complicating long-term studies. Targeting specific tissues for sensing and delivery presents additional difficulties due to limited examples of interfacing methods.

For wearable devices, a key factor is to effectively interface the device's active area and the target tissue. Plant epidermal tissues are highly diverse and species-dependent, exhibiting varying morphologies, such as the presence of trichomes, and physicochemical properties, like hydrophobicity. Moreover, since leaves are the primary organs for photosynthesis and transpiration, leaf patch devices must not influence light penetration and gas exchange, while remaining lightweight, to avoid adding mechanical load.

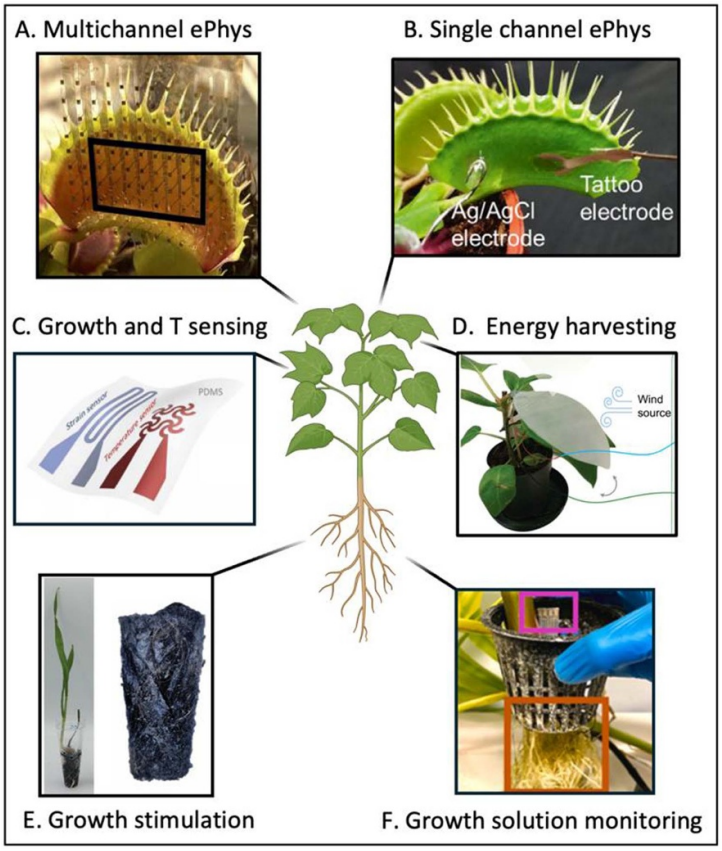

Figure 4. Examples of wearable plant bioelectronics. (A) Conformable multielectrode array for plant electrophysiology, Reproduced with permission from [21]. CC BY-NC 4.0. (B) PEDOT-tattoo electrode for plant electrophysiology, Reproduced from [22]. CC BY 4.0. (C) Leaf patch for strain and temperature monitoring, Reproduced with permission from [23]. CC BY-NC 4.0. (D) Artificial leaf coupled to living leaf for energy harvesting via triboelectric phenomenon, Reproduced from [24]. © 2024 The Author(s). Published by IOP Publishing Ltd CC BY 4.0. (E) E-Soil for enhancing plant growth via electrical stimulation, Reproduced with permission from [25]. CC BY-NC-ND 4.0. (F) Screen printed OECTs for monitoring EC and T in growth solution, Reprinted from [26], Copyright (2023), with permission from Elsevier.

When considering the type of application, several important aspects must be addressed. For devices intended for field use, whether in open-field or controlled-environment agriculture, stability in harsh conditions is a primary concern. Additional considerations include remote operation of the device, data logging and transfer, power supply, and the deployment of large number of devices. Electronic waste must also be considered, especially when deploying many devices in open fields. The impact on ecosystems is potentially significant, for instance, if animals accidentally consume these devices, or if devices in the soil disrupt plant symbiotic organisms, like bacteria and fungi that are essential to plant health. Another significant challenge lies in developing algorithms capable of analyzing large datasets and providing useful insights to the farmers. In the context of basic plant science, it is crucial to identify which research questions can be addressed using bioelectronic technologies and how bioelectronics can be combined with genetic tools, -omics platforms and advanced imaging techniques that are commonly used in plant science.

Advances in science and technology to meet challenges

Wound signaling in plants is studied mostly in the context of herbivore attack and therefore systematic implantation studies are necessary to establish design guidelines for optimal device geometry, form factor, mechanical properties, and materials selection. Such insights will also facilitate the development of techniques for targeting specific plant tissues with minimal invasiveness. Inspiration can also be drawn from nature, for example by mimicking how various organisms invade or form symbiosis with plants without triggering a systemic response.

For wearable devices, the development of breathable and transparent substrates that enable gas exchange and allow the transmission of wavelengths essential for photosynthesis should be a primary focus. Stretchability is also crucial, as plant tissues can grow significantly during the period of interest. Additionally, device encapsulation must address harsh environmental conditions such as exposure to water, UV light, and dust. Many of these challenges have been extensively studied in

biomedical applications, providing a strong foundation for adapting these solutions to plant bioelectronics. Furthermore, the active components of wearable devices should be customized to accommodate the complex morphology of plant tissues, transitioning from thin films to 3D or morphable architectures.

Pilot studies are essential for applying these technologies in agriculture. These can often be conducted through industrial collaborations or by spinning out technologies to transition lab demonstrations into commercial products. To minimize electronic waste, materials that degrade after their intended use, such as bio-based alternatives, can be adopted. Plant-based materials, for example, show promise for use as substrates and encapsulation. For power supply, many sensors require minimal energy, which can be harvested from plants. While plant-based biofuel cells have limited lifespans [33], alternatives including triboelectric energy generation from leaf movements [24] (figure 4(D)) or TE modules for environmental energy harvesting could offer more robust solutions. Furthermore, the rise of robotics could enable automation not only for deploying devices in the field, but also for retrieving them after harvest.

To advance basic plant science, fostering greater collaboration between engineers, materials scientists, and the plant science community is essential. Such partnerships will enable the joint design of studies that integrate bioelectronic tools with existing methodologies, maximizing their potential to address important questions in plant science.

Concluding remarks

PEDOT's properties and versatility allow it to support a range of plant bioelectronics applications, from *in vivo* monitoring and microclimate tracking to plant growth stimulation. However, most studies remain at the proof-of-concept stage, underscoring the need for further research to establish these technologies in plant science and agriculture.

Acknowledgments

The authors acknowledge support from the Swedish Foundation for Strategic Research (FFL18-0101), the Swedish Research Council (VR 2022-03507), The Wallenberg Wood Science Center (KAW 2018.0452), the European Union (ERC-2021-STG, 4DPhytoHybrid, 101042148) and the Swedish Government Strategic Research Area in Materials Science on Advanced Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971). Plant schematic in figure 4 is Created in BioRender. Stavrinidou, E (2025) https://BioRender.com/h44h975.

3. Challenges and opportunities in the synthesis and covalent functionalization of PEDOT and PEDOT:PSS

*Laure V Kayser**
Department of Materials Science and Engineering, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, NJ 19716, United States of America

*Email: lkayser@udel.edu

Status

The synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) was first described over 30 years ago in a 1988 patent attributed to Bayer AG, which also included many other C^1-C^4 substituted polythiophene derivatives. PEDOT rapidly became very popular because of its stability in the oxidized state, high conductivity, and transparency in thin films. For more details, we direct you to an excellent review by Groenendaal *et al* to learn about the synthesis of the EDOT monomer, and the early days of PEDOT and its derivatives [34]. In the initial patent, PEDOT was synthesized by oxidative chemical or electrochemical polymerization of the EDOT monomer. However, this process led to insoluble PEDOT which complicated manufacturing, distribution, and use. Shortly after, a patent describing a water-dispersible preparation comprised of PEDOT and poly(styrene sulfonic acid) (PSSH) was released. The synthesis involved the chemical oxidative polymerization of EDOT, to form $PEDOT^+$, in the presence of PSSH in water, ultimately leading to the polyelectrolyte complex $PEDOT^+$:PSS^-as a stable colloidal dispersion in water (figure 5). This scalable process is still used today to prepare commercial and lab-made formulations of PEDOT:PSS.

PEDOT:PSS is arguably the most successful of organic electronics with several commercial applications and a growing number of publications averaging a thousand per year in the last 5 years (Web of Science). In most of these mentions, the study or application rely on commercial formulations of PEDOT:PSS. Different formulations of PEDOT:PSS in water, glycols or organic solvents can be purchased at Heraeus (Clevios™), Agfa (ORGACON™), Xi'an Polymer Light Technology Corp., or Sigma Aldrich, with varying viscosity and sheet resistance. Formulations with a high sheet resistance are aimed at applications in antistatic coatings and OLED/QLED displays, while the low resistance ones (e.g. Clevios™ PH 1000) are for photovoltaics, smart displays, touch sensors, wearable electronics, and most recently bioelectronics.

As advanced applications of PEDOT and PEDOT:PSS are emerging, there is an increased need for functionalizing these polymers through covalent and supra-molecular chemistry. These functional groups may be aimed at improving the electronic and mechanical performance, selectivity or stability, enabling unique deployment methods *in vivo*, or providing more sustainable alternatives.

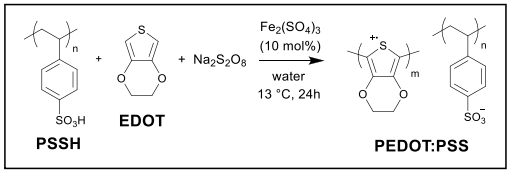

Figure 5. Synthesis of PEDOT:PSS as a colloidal dispersion in water by oxidative polymerization of EDOT in the presence of PSSH.

Current and future challenges

In the last decade or so, much attention has been placed on tuning the mechanical properties of PEDOT and PEDOT:PSS toward flexible and stretchable electronics for applications in human-machine interfaces [35]. This focus has led to many solutions to make PEDOT and PEDOT:PSS mechanically resilient to strain, provide softer interfaces for biological tissues (down to the Pa regime for conductive hydrogels), achieve stability in water, and enable self-healing electronics. Several synthetic approaches have been taken to achieve mechanical tunability, including the use of plasticizers, crosslinkers, copolymers, and the large majority of studies employed commercial PEDOT:PSS. One may therefore argue that the mechanical properties challenge has been largely solved. Below, we provide an overview of outstanding challenges on the synthesis and functionalization of PEDOT and PEDOT:PSS.

Given the popularity of commercial PEDOT:PSS, it is rather surprising that beyond the ratio of PEDOT:PSS (1:2.5 or 1:6 for low and high conductivity, respectively) and the solid content in water (generally between 0.8 and 4 wt%), not much is known about the molecular or processing parameters involved in manufacturing PEDOT:PSS and its different formulations. Presumably, trade secrets such as the molecular structure of PSSH (molecular weight, dispersity, degree of sulfonation), catalysts, synthetic conditions, additives, and post-processing all play a role in obtaining different grades of PEDOT:PSS. This reliance on commercial PEDOT:PSS poses several challenges:

(1) These parameters and the complexity of PEDOT:PSS are presumably to blame for the varying batch-to-batch reproducibility that has been anecdotally noticed by researchers.

(2) The study of structure-property relationships in PEDOT:PSS is hampered by the lack of information on its molecular structure and processing parameters. Establishing these relationships

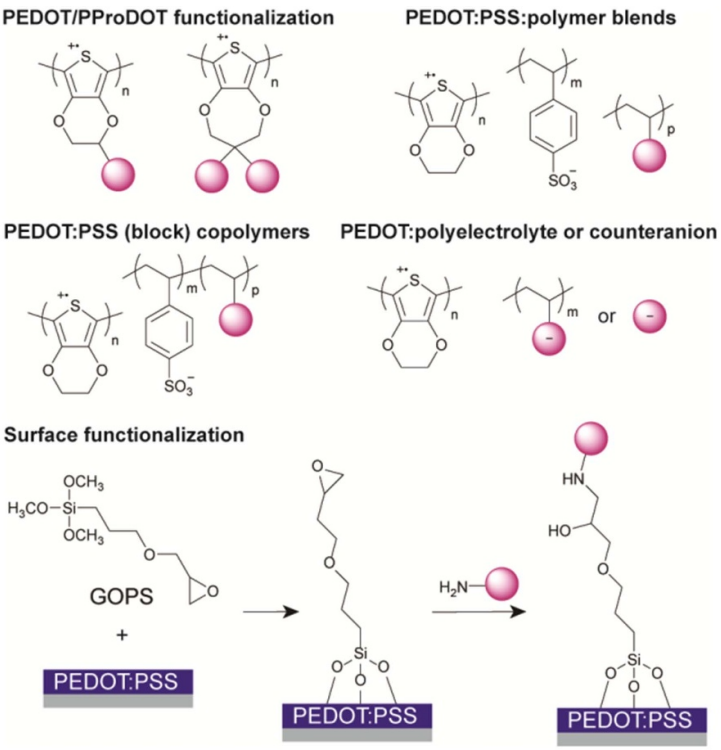

Figure 6. Common approaches for the covalent or electrostatic functionalization of PEDOT and PEDOT:PSS.

is crucial to understanding charge transport and potentially optimizing the materials for a particular application.

(3) PEDOT:PSS (particularly PH 1000) is increasingly used for bioelectronics applications. However, its synthetic complexity may impede its approval (e.g. by the FDA or EMA) for human-machine interfaces, as each formulation would have to be clearly defined and approved [36].

(4) With the exception of the sulfonate group, no synthetic handles are available to covalently functionalize commercial PEDOT:PSS. The ability to functionalize PEDOT or PEDOT:PSS is particularly important for bioelectronics and healthcare applications which may require biofunctionalization to achieve selectivity, specificity, or biocompatibility.

(5) Lastly, PEDOT and PEDOT:PSS have found applications in the area of sustainability as TE materials for energy harvesting, (super)capacitors for energy storage, and hole transport layers or transparent electrodes in photovoltaics. As we think about sustainable energy, it is important to remember that PEDOT and PSS are derived from depleting petroleum sources. Similarly, little is known about their (bio)degradation or recycling options. Alternatives for their synthesis and sourcing, and post-consumer fate must therefore be considered to address sustainability concerns.

Advances in science and technology to meet challenges

To address the challenges outlined above may require moving away from commercial formulations of PEDOT:PSS. We are already seeing several studies highlighting the importance of the chemical structure of PSS on the electronic properties of lab-made PEDOT:PSS. Continuing these fundamental structure-property relationship studies with precise control over the chemical structure will enable advances in our understanding of this complex material and provide new avenues for tuning it toward a specific application. We expect that the recent advances in characterization techniques [37] and computation will accelerate discoveries, similar to those that have been made to understand the role of small molecule additives (e.g. DMSO) on enhancing the EC of PEDOT:PSS [38].

Beyond PEDOT and PEDOT:PSS used by themselves or with secondary additives [39], there is also a need for developing strategies to functionalize them covalently or electrostatically. Several synthetic strategies have been successfully implemented such as the functionalization of the EDOT (or ProDOT) side chain, the use of epoxysilanes reacting with the sulfonate group of PSS on the surface of PEDOT:PSS, (block) copolymers of PSS with 'functional' monomers/polymers, the replacement of PSS with another counteranion (polyelectrolyte or small anion), and blending PEDOT:PSS with another 'functional' polymer (figure 6) [40]. What we

have yet to see, however, is a general approach for (bio)functionalization that allows for versatility and high degrees of functionalization, without negatively affecting the electronic properties.

We would also encourage the readers to think about methods to address sustainability concerns by finding alternatives to the direct use of petroleum-based starting materials. Current examples in this direction include sulfonated lignin [41] and expanded polystyrene foam from waste stream [42] as matrices for PEDOT. Additionally, more studies are needed to study the (bio)degradation of PEDOT and PEDOT:PSS derived polymers. As the backbone of PEDOT is made of strong π-conjugated carbon bonds, it is unlikely to degrade. There is therefore an opportunity to develop highly conductive polymers (CPs) whose backbone can be degraded or recycled, perhaps using hydrolysable imine bonds [43].

Concluding remarks

PEDOT and PEDOT:PSS continue to be essential materials for progress in science, technology, healthcare, and sustainability. As applications become more complex and specialized, there is an increased need for understanding their fundamental structure-property relationships and functionalizing them. Achieving these goals may require moving beyond commercial PEDOT:PSS and developing new synthetic tools for their covalent, efficient, and versatile functionalization.

Acknowledgments

L V K acknowledges funds from a CAREER award from the National Science Foundation (NSF) under Grant Number DMR-2237888.

4. PEDOT in energy harvesting and storage applications

Igor Zozoulenko[1,2], *Reverant Crispin*[1,2,3], *Renee Kroon*[1,3], *Isak Engquist*[1,2], *Magnus P Jonsson*[1,3,*], *and Magnus Berggren*[1,3]
[1]Laboratory of Organic Electronics, ITN, Linköping University, SE 60174, Norrköping, Sweden
[2]Wallenberg Wood Science Center (WWSC), ITN, Linköping University, SE 60174, Norrköping, Sweden
[3]Wallenberg Initiative Materials Science for Sustainability (WISE), ITN, Linköping University, SE 60174, Norrköping, Sweden

[*]Email: magnus.berggren@liu.se

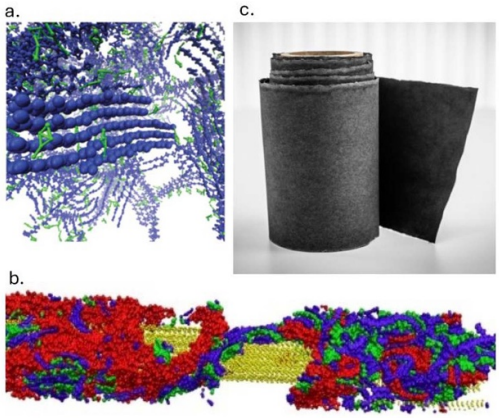

Figure 7. (a) Molecular dynamics (MD) simulations of PEDOT:TOS morphology showing formation of π-π stacked chains (adapted from DOI: 10.1039/c8cp02902d). (b) A snapshot of MD simulation of a cellulose nanofibril covered by PEDOT:PSS (adapted from DOI: 10.1021/acsaem.9b00307). (c) A paper electrode composed of activated carbon, PEDOT:PSS and cellulose exhibiting a specific capacitance of 30 F g^{-1}.

Status

PEDOT(:PSS) is a commercial success story in the field of organic electroactive materials, owing to its facile synthesis, water-processability, and high mixed ionic-electronic conductivity. These features have resulted in that PEDOT:PSS is a staple material for many different applications, ranging from transparent electrodes to charge-storage devices and OECTs. Below, we forward a few considerations on PEDOT-based materials targeting energy harvesting and storage applications.

Current and future challenges

Modern materials and device engineering, especially of importance for energy technologies, increasingly rely on simulations and modeling. Unfortunately, their usage is still underdeveloped and limited while studying PEDOT-materials, and consequently, limited theoretical understanding leaves many key aspects of, e.g. PEDOT:PSS overlooked in current literature. For instance, while PEDOT:PSS is described as having PEDOT- and PSS-rich regions, critical details about their composition and chemical structure, such as distribution of PEDOT within PSS-rich regions or the specific chemical form of PSS (i.e. PSS- vs PSSH), or identifying regions providing ion diffusion paths, remain brushed under the carpet. Only in recent years theoretical studies have begun to emerge employing Density Functional Theory, MD (see figure 7 for illustration), multi-scale calculations and machine learning (ML) [44] to address the fundamentals of PEDOT:PSS and molecularly doped PEDOT (e.g. PEDOT:TOS), including electronic structure, charge carrier nature (polaron/bipolaron), morphology, granular structure, swelling, coupled electronic-ionic transport, thermal conductivity and device modeling [45], which all are of great importance for energy technology relying on ion-electron interaction.

One example where fundamental modeling is critical, is morphology modulation of PEDOT:PSS using 'secondary doping' which impacts electronic charge transport. More recently, photoexcitation-based phase-volume ratio photo-tuning [46] was proposed to gain fine control over the polymer morphology. Here, the polymer is doped with hexa(arylthio)benzenes (HAB), which are well-known compounds demonstrating photoinduced aggregation but also the ability to bind to polymer chains. Under photoirradiation doped HAB molecules form different aggregate geometries depending on the chemical structure of dopant. The advantage of this approach is that the irradiation dose provides reversible tunability in controlling the overall morphology, and thus the charge transport of PEDOT:PSS.

To reduce the PSS content (as prepared typically ∼65 wt%) as an approach to achieve even higher EC, self-compensating materials such as S-PEDOT and the more soluble PEDOT-S have been developed, where the latter material provides an EC of ∼1000 S cm^{-1}. Combinations of PEDOT with other materials for charge storage and other energy applications have been extensively researched. To increase both conductivity and capacitance, different forms of carbon (activated carbon (AC), graphite/graphene) can be added. For improved mechanical properties and self-supporting films, cellulose/nanocellulose composites with PEDOT:PSS have proven useful. PEDOT interacts favorably with cellulose nanofibrils (CNF), promoting the formation of crystalline PEDOT domains. By casting, printing or spinning, self-supporting PEDOT-CNF films and filaments can be produced, and it has also been demonstrated that a mix of mainly cellulose, PEDOT:PSS and AC can be used in roll-to-roll paper machine manufacturing of charge-storage paper electrodes. For all these materials, secondary doping with, e.g. DMSO or EG, either

in the original mix or as post treatment, improves electrical properties. Combinations with lignin in different forms have also been explored, due to the natural occurrence of lignin in wood and its capability for additional charge storage through redox reactions. Recently, and expected even more so in the future, the synergistic combination of PEDOT:PSS and S-PEDOT is used to interface with lignin in native wood, which can then be accessed to boost the charge-storage capacity of corresponding conducting wood-based devices [47].

The redox-tunable properties of PEDOT:PSS have enabled a multitude of important optical applications including for energy applications. This includes energy-regulating surfaces where dynamic control of thermal infrared radiation enables active control of radiative cooling [48]. Future work in this and related directions may leverage recent work showing that PEDOT can be optically metallic in its oxidized state and switched to a low-conducting optically dielectric state. This has opened a new field of polymer-based tunable plasmonics and flat metasurface optics [49, 50], including for the infrared thermal range. The research directions of PEDOT-based metasurfaces and long-wavelength light control reaching into the terahertz (THz) radiation range, are in their early stages and have the potential to result in many important findings and applications during coming years. These will in part be related to dynamic tuning but also benefit from other peculiar opportunities such as inducing anisotropy by alignment [51].

Historically, PEDOT:PSS was first considered for symmetric supercapacitors, where only cation transport occurs during the charge/discharge process. However, PEDOT:PSS exhibits rather low specific capacitance ($C \sim 40$ F g^{-1}), in part due to that substantial mass fractions of included PSS is inactive in charge polarization. Even though PEDOT:PSS has a low C, it still offers an attractive material platform for printed energy devices. One strategy to increase C of PEDOT:PSS includes to replace inactive PSS with a polyanion balancing the positive charge of PEDOT but carrying redox-active groups also participating in charge storage, such as catechol groups. To further increase C, polymeric counterion (e.g. PSS$^-$) can be substituted with atomic counterions (e.g. Cl$^-$), which can increase the specific capacitance to 200 F g^{-1} [52]. C of a conducting polymer is related to the concentration of charges and the mass of the charge-storing unit of the conjugated system. Since EDOT is relatively heavy (142 g mol^{-1}) compared to other monomers (e.g. pyrrole ~67 g mol^{-1}), PEDOT inherently displays relatively lower C values. Another strategy to improve PEDOT's C is then to attach redox-active molecules directly onto the polymer chain, however, this impacts redox activity which then further dictates the anodic-cathodic nature the resulting electrode. Beyond energy density, another critical feature of PEDOT-based supercapacitors is self-discharge. Supercapacitors with aqueous electrolytes exhibit rapid self-discharge due to side reactions [53], typically within a few hours, whereas those with organic electrolytes can extend the self-discharge period to several days.

PEDOT:PSS is one of the most widely investigated ITO-free transparent electrodes for solar cells owing to its solution processability, high optical transparency, tunable work function (≈4.8–5.2 eV), and excellent mechanical flexibility. While pristine PEDOT:PSS films exhibit very low EC (<1 S cm^{-1}), extensive work has demonstrated that secondary-solvent treatments and acid doping (e.g. H_2SO_4, CH_3SO_3H, $HClO_4$) induce strong phase separation between PEDOT-rich and PSS-rich domains, increase chain planarity, and dramatically enhance charge transport. As a result, conductivities exceeding 4000 S cm^{-1}, sheet resistances below 30 Ω sq^{-1}, and optical transmittance around 90% at 550 nm have been achieved, approaching the performance of ITO deposited on glass. These advances enabled PEDOT:PSS electrodes to support increasingly competitive organic solar cells (OSCs) with efficiencies above 16% using $HClO_4$-doped PEDOT:PSS electrodes in PM6:Y6-based devices [54] as well as perovskite solar cells (PSCs) reaching power conversion efficiencies above 20% [55]. In particular, ionic dopants such as NaCl and RbCl incorporated into PEDOT:PSS have enabled ultra-high fill factors and enhanced operational stability in high-efficiency inverted PSCs.

Advances in science and technology to meet challenges

Fundamental questions remain unanswered regarding modeling and simulations, most notably, addressing the theoretical limits of maximum mobility and intrinsic (volumetric) capacitance of PEDOT materials. Further, theoretical understanding of polymerization, degradation mechanisms and charge injection at the PEDOT/metal interface is lacking. Additionally, intrinsic capacitance and density of states (DOS) calculations should consider realistic morphologies. Also, multi-scale simulations could advance insights into ion diffusion, electron mobility, electron-ion coupling with emerging artificial intelligence (AI) techniques. Modeling of PEDOT-based devices, such as supercapacitors, transistors and TE generators utilizing Nernst–Planck–oisson formalism, is currently emerging, however, further efforts are needed to transform these results into predictive device models. An improved understanding of the interaction between PEDOT and other important materials in charge-storage composites is needed to optimize energy and power density of these materials, while used in energy technologies. This includes AC, graphite, other conducting polymers, lignin, but also template materials such as cellulose and nanocellulose.

Specific PEDOT copolymers with redox pendant groups and proton trapping groups have been designed to enable proton-coupled electron transfer at the PEDOT electrode while working in organic electrolytes [56]. Upon design of an asymmetric supercapacitor or battery, PEDOT can be used as both electrical conductor and charge storage medium only in the range of potential where PEDOT is in its conducting state. PEDOT could potentially be combined with a redox polymer polyantraquinone to make a nanocomposite electroactive at −0.2 V vs Ag/AgCl; while PEDOT can be combined with polycatechol to make in a nanocomposite electroactive at +0.5 vs Ag/AgCl. Hence, PEDOT cannot be seen as an attractive material for large scale supercapacitors, but rather for thin, flexible and even stretchable supercapacitor or batteries.

To further improve electrical performance and mitigate the intrinsic conductivity–transparency trade-off of polymer OSC electrodes, hybrid transparent electrodes combining PEDOT:PSS with metal nanowires (primarily Ag nanowires) have been widely explored [57]. Despite their advantages, a critical limitation of PEDOT:PSS/metal-nanowire hybrid electrodes is the chemical instability arising from the acidic and hygroscopic nature of the PSS component. Direct contact between PSS and metallic nanowires—particularly Ag and Cu—can induce corrosion, oxidation, and junction degradation, leading to increased sheet resistance and long-term performance losses [58]. Thus, the PEDOT:PSS/metal-nanowire hybrids are a powerful but chemically delicate electrode platform, where continued control of interfacial chemistry is essential to simultaneously achieve record efficiency, mechanical flexibility, and long-term stability in next-generation flexible organic photovoltaics.

Concluding remarks

PEDOT:PSS possess several critical physical, chemical and processability characteristics, and have demonstrated a range of performance parameters, making them attractive for energy applications. However, further improvement of energy density and conductivity, for example, along with better understanding of its fundamentals are needed to make PEDOT:PSS successful beyond polymer capacitors. PEDOT:PSS has also progressed into a highly competitive ITO-free transparent electrode for photovoltaics, where long term chemical stability—particularly related to the acidic and hygroscopic nature of PSS and its interaction with metals—remains a key challenge.

Acknowledgments

We acknowledge financial support from Knut and Alice Wallenberg Foundation (KAW), The Swedish Foundation for Strategic Research (SSF), and VINNOVA.

5. Molecular dynamics simulations of PEDOT-based polymer blends

*Amali G Guruge and Alessandro Troisi**
Department of Chemistry, University of Liverpool, Liverpool L69 3BX, United Kingdom

*Email: a.troisi@liverpool.ac.uk

Status

Poly(3,4-ethylenedioxythiophene) (PEDOT)-based polymers are highly valuable materials for bioelectronic applications [36]. Owing to their complex and heterogeneous nature, obtaining detailed atomistic-level insights into their mechanical and charge transport properties through experimental investigations alone is challenging and often limited. In this context, MD simulations have emerged as a powerful complementary computational tool capable of probing such details and supporting the rational improvement of these materials. A significant portion of the remarkable properties of PEDOT-based polymer blends discussed in this paper originates from their microstructure and how it undergoes structural changes or governs specific interactions, all of which determine the mechanical and charge transport properties of the material [38, 59–66]. MD simulations have played a central role in building realistic models that support experimental interpretations and provide mechanistic insight across atomistic and mesoscopic scales in PEDOT-based systems. Specifically, MD has been widely used to explore the morphology of PEDOT-based polymer blends, particularly poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and poly(3,4-ethylenedio xythiophene):tosylate (PEDOT:Tos), as well as their behavior under various conditions [38, 59, 60, 62–68]. These conditions include exposure to water [63, 65, 66], solvents [38], ionic liquids [60], biological molecules [68] and pH variations [62]. Such studies provide detailed information on the structural arrangement of polymer chains and dopants, as well as the specific interactions that arise under these conditions and modulate material properties, which are ultimately important for various bioelectronic applications.

The success of existing studies inspire confidence in the feasibility of developing reliable MD models for complex PEDOT-based systems, offering insights that are difficult to access through other approaches. For example, atomistic models of PEDOT:PSS have shown that water permeation, compared to the dry state, leads to formation of smaller, less ordered, and more distantly located lamella crystallites (see figure 8). This structural change likely reduces conductivity, providing a plausible explanation for the experimentally observed low conductivity in PEDOT:PSS hydrogels or in water [66]. Another atomistic model demonstrated that at the interface of PDOT-rich and PSS-rich phases, larger and more oriented lamellae with a better interconnected PEDOT network form within conductive grains compared to the less-conductive PSS-rich phase. This finding explains why improved intra-grain conductivity arises from a marginal enhancement in phase separation between PEDOT- and PSS-rich domains [59]. More recently, atomistic simulations of PEDOT:PSS have shown that dopamine forms hydrogen bonds with PSS while simultaneously reducing inter-lamellar connectivity [68], indicating a modification of the polymer morphology and, consequently, the charge transport pathways within the material. These structural modifications offer a consistent explanation for the increased short-term plasticity relaxation time observed in the neuromorphic PEDOT:PSS sensors [69]. Coarse-grained (CG) models have also provided valuable insights. For instance, simulations have shown that solvent treatment followed by drying causes PEDOT-rich regions to move closer to each other, with a part of the PEDOT chains penetrating into PSS-rich regions. This enhances the coupling between PEDOT chains and further explains the morphological reorganization responsible for the conductivity enhancement observed after solvent treatment of PEDOT:PSS [38]. Both atomistic and CG simulations of other PEDOT-based polymer systems have similarly provided molecular- and atomistic-level insights that are difficult to access using conventional experimental approaches [64, 65, 67].

Given the significant potential to leverage this technique in future investigations over the next decade, it is an opportune time to address the challenges associated with applying MD to PEDOT-based polymers in order to meet the growing demand for next-generation bioelectronic applications.

Current and future challenges

Atomistic MD simulations are well-established for investigating complex polymers, including CPs. These models are highly effective in resolving monomer-level polymer arrangements and intermolecular interactions within polymer systems, thereby providing detailed insights into the behavior of PEDOT-based systems under various conditions and how these behaviors influence their properties [59–61, 66]. However, typical atomistic simulations are limited to nanoseconds timescales or, at most, a few microseconds. As system size increases, such as when modeling the granular structure of PEDOT:PSS, which exhibits average grain diameter in the range of 50–80 nm and consists of a PEDOT-rich core surrounded by a 5–10 nm thick PSS-rich shell, atomistic models face significant computational challenges and remain beyond practical reach. Even with the latest high-performance computing (HPC) resources, current atomistic models typically simulate either individual phases (i.e. PEDOT-rich or

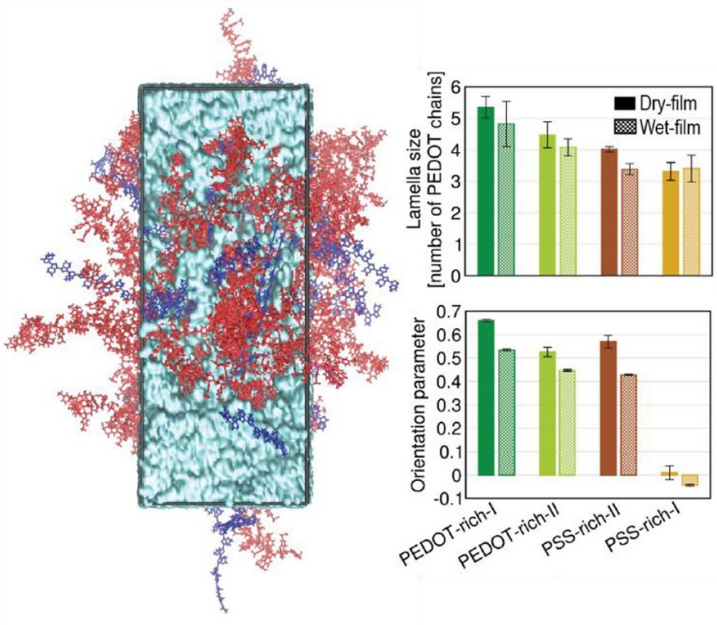

Figure 8. A simulated molecular dynamics system showing water (cyan) permeating the PEDOT:PSS structure (PEDOT in blue and PSS in red) is depicted on the left. The graphs on the right illustrate MD insights into changes in lamella crystallite morphology, including variations in average lamella crystallite size and orientation parameters caused by water permeation, compared to the dry state. Reproduced from [66]. CC BY 3.0.

PSS-rich) or simplified two-phase interfaces. On the other hand, equilibrating atomistic PEDOT-based models often requires multiple annealing cycles [59, 61, 66] to ensure sufficient relaxation of the polymer structure. For example, PEDOT:PSS systems typically require multiple annealing steps, largely due to the relatively high glass transition temperature (T_g) observed in MD simulations (approximately 1050 K) [61]. The elevated T_g necessitates extensive annealing procedures and longer simulation times to achieve proper equilibration, thereby substantially increasing the overall computational cost.

CG models offer an efficient solution for modeling larger systems over longer timescales. In CG representations, selected atoms within a monomer, an entire monomer, or even multiple monomers are combined into a single 'bead', thereby reducing the number of degrees of freedom. An example of a Martini CG model representation of PEDOT:PSS is shown in figure 9. This simplified representation accelerates equilibration and significantly reduces computational time compared to atomistic models. The Martini CG framework, widely applied to PEDOT:PSS, and PEDOT:Tos systems has effectively captured and reproduced experimental behaviors, such as swelling [63], conductivity enhancement following solvent treatment [38], and morphological changes induced by pH variations [62], while also providing theoretical insights in situations where experimental investigations are challenging [64]. These models have achieved simulation dimensions of PEDOT- and PSS-rich regions ($\geqslant$10 nm), approaching experimentally observed grain sizes [38, 62]. Long polymer chains have also been incorporated, including a PSS chain containing 2200 styrene sulfonate monomers in PEDOT:PSS [63], as well as large number of PEDOT chains with experimentally relevant chain lengths in PEDOT:Tos systems [64]. Despite these advantages, CG models have limitations such as intermolecular interaction strengths depend strongly on the selected bead types (e.g. in the Martini framework), and their simplified bead-level representation may fail to resolve critical interactions, such as polymer-water interactions during water diffusion. Additionally, entropy-enthalpy compensation in CG models, such as in Martini, can affect the accuracy of temperature-dependent properties in PEDOT-based systems [70].

The inclusion of additives in PEDOT-based polymer systems can significantly alter their properties, such as enhancing conductivity, stretchability and self-healing capabilities. Investigating these enhancements using MD simulations provides atomic-scale insights into the mechanisms underlying these changes, supporting the rational optimization of PEDOT-based polymer properties. However, when modeling PEDOT-based systems containing additives, equilibration protocols designed for additive-free PEDOT-based system may not be directly applicable. For example, high-temperature annealing that is effective for equilibrating atomistic models of additive-free PEDOT:PSS [59] can cause substantial volume fluctuations in PEDOT:PSS containing water due to superheating, ultimately disrupting proper equilibration of water within the polymer [66]. Adopting a lower-temperature equlibration

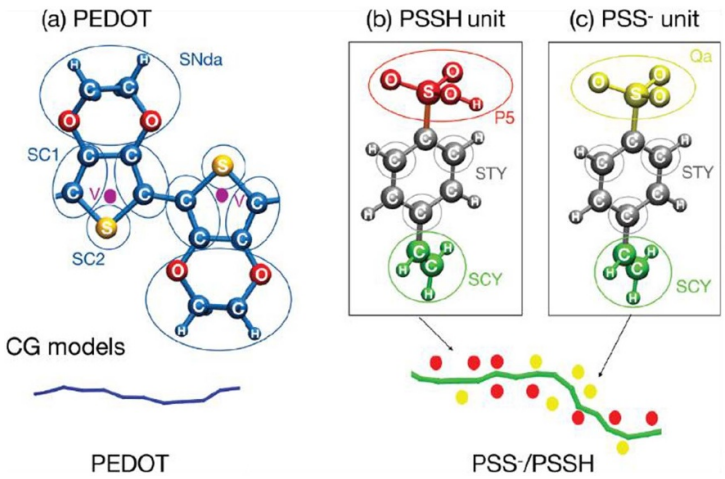

Figure 9. Martini CG models for (a) PEDOT, (b) deprotonated and (c) protonated monomers of PSS (PSS- and PSSH respectively), with Martini beads represented by grouping of multiple atoms. Each oval represents the atoms grouped together to form a specific bead. Reprinted with permission from [63]. Copyright (2020) American Chemical Society.

protocol for atomistic PEDOT:PSS with water can mitigate these volume fluctuations. However, this approach may fail to achieve sufficient water diffusion into PEDOT:PSS within accessible simulation times, giving the material's high *Tg* [66].

After equilibration of PEDOT-based polymer systems, validation against experimental data, such as grazing-incident wide-angle x-ray scattering or other relevant experimental data is essential before making predictive claims. This validation process ensure that simulations accurately reflect experimental observations, thereby establishing confidence in the reliability of the model (whether atomistic or CG) for predictive insights, which is a critical requirement for any PEDOT-based model. However, the lack of experimental data for certain PEDOT-based systems can complicate the validation process. Reusing already validated atomistic or CG models can save time and computational cost in future investigations. However, these models can exhibit limitations, such as slow water diffusion at 300 K [59, 66] and failure to adequately replicate experimental water intake [63, 66] (i.e. both atomistic and CG models), which are likely due limitations in force field parameters that govern the intermolecular interactions between water and PEDOT and dopants (e.g. PSS).

PDOT-based polymer materials exhibit metal-like behavior with fast electronic charge reorganization, which can lead to variable net charges on individual PEDOT chains. Classical all-atom forcefields, such as the generalized amber force field (GAFF) [59, 65], and optimized potentials in liquid simulations (OPLS) force field [60], as well as the CG Martini force field [38, 63, 64], have been widely used to model PEDOT-based polymers. However, these classical force fields treat the charge on PEDOT as fixed throughout the simulation and therefore do not account for dynamic variations in net charge (i.e. charge transfer ability). Moreover, polarizable force fields are currently unable to capture such dynamic charge redistribution. A study using quantum mechanics/molecular mechanics (QM/MM) approaches developed a method to model classical dynamics of polymer in an electrolyte while allowing excess charge on polymer chains to rearrange in response to external electrostatic potential [71]. However, this approach remains limited in reliability for modeling PEDOT-based polymers at high doping levels.

Advances in science and technology to meet challenges

To enable future atomistic simulations of larger-scale PEDOT-based polymer systems (e.g. granular structure of PEDOT:PSS) with long timescales, increased access to HPC systems equipped with advanced graphics processing units (GPUs) will be required to handle the intensive calculations involved in MD simulations. Currently, HPC platforms such as Anton 3 are advancing atomistic simulations in fields including biological research and drug discovery, achieving performance levels capable of simulating systems containing up to one million atoms over timescales approaching 100 μs per day [72]. Continued advancements in HPC technologies, including heterogeneous parallel computing architectures, improved algorithms for GPU task scheduling, optimized CPU workload distribution, and communication pathways (e.g. GPU-GPU data transfer), together with the development of GPU accelerated MD algorithms [73] specifically tailored for PEDOT-based polymer systems can substantially reduce the computational costs of future MD simulations. Until such advancements

are implemented, computational material scientists may adopt hybrid approaches that integrate atomistic and CG models in MD simulations of PEDOT-based systems. This approach enables efficient simulation of large PEDOT-based systems using CG models, where full atomistic models may be computationally impractical, while still retaining atomistic-level resolution when detailed mechanisms and molecular interactions needed to be examined. In addition, united-atom force fields offer an intermediate modeling approach between all-atom and CG representations, where hydrogen atoms are grouped with their respective parent atom. This representation is not as simplified as CG models, yet not as detailed as atomistic models. Developing united-atom models for PEDOT-based polymer systems could potentially reduce the computational costs associated with all-atom simulations while preserving a higher level of atomic detail compared to CG models. Encouragingly, a united-atom model has been already developed for poly(sodium p-styrenesulfonate) with ten repeating units, incorporating a united atom backbone and a fully atomistic pendant group (ring) [74]. A combination of such united-atom models with atomistic PEDOT representations, is feasible in future studies, similar to approaches that have been successfully applied to investigate morphology and ion transport in thin-film blends of polythiophene derivatives [75]. Apart from those, considering the complexity of model parameterization, computational costs associated with quantum mechanical calculations and force field refinement, and the extensive validation required for accurate PEDOT-based polymer modeling, making validated models publicly available in shared repositories could significantly expedite future research. Additionally, equilibration protocols developed to address system-specific challenges in PEDOT-based polymer systems, such as overcoming the high T_g of PEDOT:PSS [59], or the slow diffusion of water into PEDOT:PSS at low temperatures [66] should also be further validated across different PEDOT-based polymer systems and environmental conditions.

Even though classical force fields typically fail to capture the charge transfer ability of PEDOT, potential solutions may arise by adopting simplified model Hamiltonians [76] or by introducing new potentials that account for the metallic screening of charges. Such advancements could improve the description of the material's structural and dynamical properties, further facilitating the exploration of operando characterization, which captures dynamic changes and reveals structure-property relationships during device operation, ultimately crucial for the operation of bioelectronic devices.

Concluding remarks

Methodologically, we anticipate advancements in the accuracy of MD models, driven by the integration of CG and atomistic simulations, alongside improved validation against a broader array of experimental characterization data. These enhancements will lead to more robust simulation protocols, enabling a comprehensive and systematic exploration of PEDOT-based polymer physics, including the effect of additives, mechanical property modulation, and microscopic changes associated with de-doping or interfacing with different environments.

Acknowledgments

The authors thank support from the European Research Council (Grant No. 101020369).

6. PEDOT:PSS for neural implants

Stephen J K O'Neill[1], *Oren A Scherman*[1], *George G Malliaras*[*2]
[1]Melville Laboratory for Polymer Synthesis, Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
[2]Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 JJ Thomson Ave, Cambridge, CB3 0FA, United Kingdom

[*]Email: gm603@cam.ac.uk

Status

Neural implants, with the ability to monitor and regulate physiological processes, have gained considerable attention as a treatment method toward neurological diseases such as epilepsy, stroke and Parkinson's. The conducting polymer complex poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is a highly suitable material for these implants, forming an ideal interface between implantable electronics and neural tissue. In comparison to metals, PEDOT:PSS has a low Young's modulus (<1 GPa) enabling improved conformability and biocompatibility with soft and wet biological tissues [35]. The volumetric capacitance of PEDOT:PSS reduces the electrode-tissue interfacial impedance, giving rise to superior recording precision and high charge-injection currents for stimulation. A pioneering work by Khogagdy *et al* [77] used PEDOT:PSS on top of parylene-C and gold microelectrodes to enable single-neuron recordings from a rat's brain. Termed 'Nuerogrid', the 256-channel conformable neural interface array could record both local field potentials and action potentials from superficial cortical neurons without penetrating the brain surface. Another approach has involved integrating PEDOT:PSS in OECTs. The ionic-electronic conduction properties of PEDOT:PSS (hole mobilities of 1–10 $cm^2\ V^{-1}\ s^{-1}$) gives rise to high transconductance and superior signal-to-noise ratio for *in-vivo* brain recordings [78]. Such initial works paved the way for PEDOT:PSS neural implants, with subsequent studies improving both the material properties and device fabrication processes. Continuous advances in the field are rapidly leading toward higher-resolution mapping and improved stimulation capabilities, driving us closer to widespread clinical realization of neural implants.

Current and future challenges

Despite the benefits of PEDOT:PSS compared to metallic electrodes, the material faces an intrinsic trade-off between simultaneously achieving high conductivity and desirable mechanical properties (tough, soft, stretchable). Achieving high stretchability and softness is key for long term stability of implantable electrodes, preventing tissue delamination and maximizing conformability. Small molecule and ionic additives have been shown to improve the conductivity and stretchability of PEDOT:PSS through inducing crystallization of PEDOT domains [7]. For neural implantables, however, such non–cross-linked additives can be washed away within the body and the conductivity drops substantially. Macromolecules such as PEG have less tendency to be washed away and can enhance conductivity through morphological effects, however, the stretchability of the materials is limited [79]. As an alternative method to achieve desirable mechanical properties, PEDOT:PSS hydrogels have gained attraction on account of their high-water content and tissue-like softness. For instance, Liu *et al* [80] used an ionic liquid additive to form a PEDOT:PSS hydrogel with a water content of 82%, to achieve a Young's modulus as low as 10 kPa (figure 10(a)). Integrating the material onto a perfluoropolyether substrate enabled localized low-voltage electrical stimulation of the sciatic nerve in live mice. Another study by Lu *et al* [81] used DMSO for the formation of hydrogels with high stretchability (35%) and charge injection capacitance (8.3 mC cm^{-2}). Generally, however, limited electronic conductivities (<50 S cm^{-1}) and inadequate patterning strategies have restricted hydrogel electrodes to feature sizes greater than 100 μms, too large for single-neuron recordings.

Advances in science and technology to meet challenges

Advances in materials chemistry have the potential to address the limitations of PEDOT:PSS, either through the development of new property-enhancing additives, or, through the synthesis of new PEDOT-based derivatives. A fast-developing field is that of supramolecular chemistry toward bioelectronics. Jiang *et al* [79] recently developed a PEDOT:PSS additive consisting of a supramolecular polyrotaxane, composed of a PEG backbone threaded by cyclodextrin macrocycles. The threaded cyclodextrin reduced the materials crystallinity, thereby improving the stretchability of the PEDOT:PSS blend. As such, high conductivity was achieved even at high strains (6000 S cm^{-1} under 100% strain), leading to effective neural stimulation on the brainstem of a rodent model (figure 10(c)). Furthermore, functionalizing the cyclodextrin with PEG methacrylate gives rise to photopatterning abilities. A following work leveraged the same materials for continuous intraoperative neurophysiological monitoring during microsurgery [82]. Advances in supramolecular crosslinking interactions have further given rise

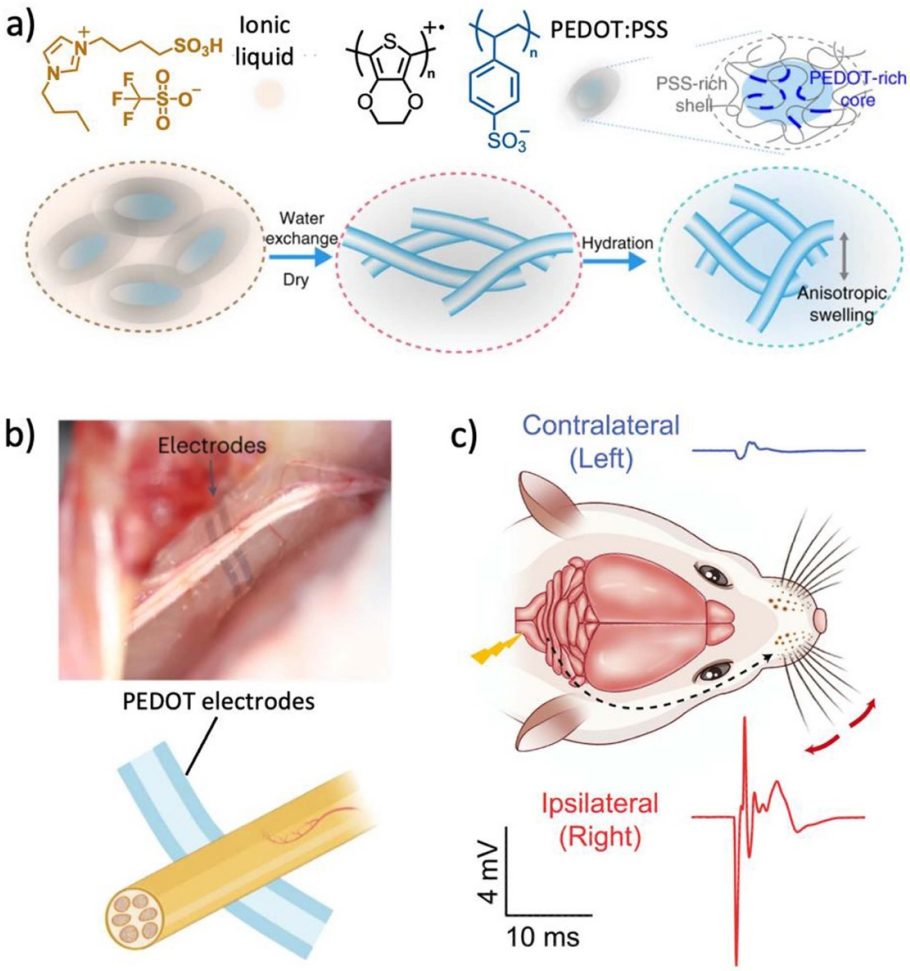

Figure 10. (a) Schematic of PEDOT:PSS hydrogel synthesis using an ionic liquid (4-(3-butyl-1-imidazolio)-1-butanesulfonic acid triflate) additive. Reproduced from [80], with permission from Springer Nature. (b) Schematic and photo showing the implantation process of soft PEDOT:PSS electrodes. A stable interface is achieved by wrapping the soft PEDOT electrodes around the sciatic nerve. Reproduced from [82], with permission from Springer Nature. (c) Schematic diagram and representative data traces showing the side specificity of brainstem stimulation in a live rat. From [79]. Reprinted with permission from AAAS.

to PEDOT:PSS materials exhibiting a Young's modulus similar to that of brain tissue (<5 kPa) and ultra-high stretchability (>500%) [83]. On the other hand, molecular modifications of PEDOT have also shown promise, whereby a sulfonic acid group can be directly functionalized onto the PEDOT backbone to enable high conductivities (1000 S cm^{-1}) without requiring blending with additives [84]. Improving the stability of PEDOT:PSS *in-vivo* is also an important consideration, with several studies highlighting that careful PEDOT counterion selection can reduce polymer degradation [85]. Further developent of the molecular structure of EDOT monomer side-chains, as well as optimization of their polymerization and counterion, has the potential to simulaneously improve conductivity and mechanical properties through control of crystallinity and molecular weight.

Concluding remarks

PEDOT:PSS neural implants have the potential to provide innovative treatments for neurological diseases, through exceptional stimulation capabilities and high-resolution mapping of the neural system. Notably, however, all the *in-vivo* experiments disused in this section have been performed in small animal models. The transition to humans will undoubtedly present greater challenges and require further optimization of tissue-interfacing materials. The human brain typically experiences much larger head motions (5%–10% in humans compared to 2%–3% in rodents), with higher applied forces on the devices. As such, the mechanical integrity of the materials will be vital when moving into human clinical trials, following suit from the suture-like neural probes currently being tested.

7. Fundamental transport physics of PEDOT:PSS

Hiroshi Okamoto[1,2*], *Zijing Guo*[1], *Tetsu Sato*[3], *Ryohei Ikeda*[1], *Tatsuya Miyamoto*[4], *Shun Watanabe*[1], *Jun Takeya*[1,5], *Qingshuo Wei*[6], *and Masakazu Mukaida*[6]

[1]Department of Advanced Materials Science, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277–8561, Japan

[2]Department of Physics, Nihon University, 1-8-14, Kanda-Surugadai, Chiyoda-ku, Tokyo 101–8308, Japan

[3]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980–8577, Japan.

[4]Department of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466–8555, Japan.

[5]International Center of Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba 305–0044, Japan.

[6]National Institute of Advanced Industrial Science and Technology (AIST)-University of Tokyo Advanced Operando-Measurement Technology Open Innovation Laboratory (OPERANDO-OIL), AIST, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277–8589, Japan.

*E-mail: okamotoh@edu.k.u-tokyo.ac.jp

Status

In PEDOT:PSS, holes are doped during the oxidative polymerization of PEDOT. Doped PEDOT oligomers form clusters, and macroscopic electric transport occurs via the transfers of hole carriers between these clusters [86]. PEDOT oligomers and insulating PSS long-chain polymers complexed by electrostatic attraction assume a colloidal state, containing high concentrations of PSS, where PEDOT clusters are fragmented by PSS, and hole transfers between the clusters is inhibited [87, 88]. Therefore, DC conductivity, σ_{DC}, of PEDOT:PSS films prepared from simple aqueous solutions by the spin-coating method (untreated films) is in the order of 10^1 S cm^{-1}. Attempts have been made to remove PSS; for example, films prepared by the spin-coating method using aqueous solution including a polar solvent such as EG (EG-added films) facilitate the elimination of PSS and improve σ_{DC} [89–91]. Furthermore, in EG-added films dipped into EG (EG-treated films) or films with drops of sulfuric acid (HS-treated films), PSS molecules are further eliminated resulting in high σ_{DC} exceeding 1000 S cm^{-1} (figure 11(a)) [92]. In particular, in HS-treated films, protonation of PSS accelerates the PSS elimination, increasing σ_{DC} up to 4000 S cm^{-1} [93, 94] The clarification of the carrier-transport mechanism reflected by such changes in σ_{DC} is important for the development and application of PEDOT:PSS and other conducting polymers including disorder and inhomogeneity.

Current and future challenges

In general, materials exhibiting band transport show Hall effects. In PEDOT:PSS films with high conductivity, e.g. ~800 S cm^{-1}, Hall effects were observed, while the carrier density calculated from the Hall coefficient R_H is more than two orders of magnitude higher than the actual value [96, 97]. In the same film, however, σ_{DC} decreases below 250 K and its temperature dependence cannot be explained by thermal-activation type nor variable-range-hopping type transport. Thus, it is difficult to clarify the nature of carriers and their transport properties from DC-conductivity and Hall-effect measurements alone. An effective approach to investigate the carrier-transport mechanism is to measure the complex optical conductivity ($\tilde{\sigma} = \sigma_1 + i\sigma_2$) spectra on the same film over wide frequencies covering from THz to visible region [95, 98], while their quantitative evaluations and analyses have not been performed.

Advances in science and technology to meet challenges

If the carriers exhibit band transport, $\tilde{\sigma}$ follows the Drude model (DM) expressed by the following formula.

$$\tilde{\sigma} = \frac{\omega}{i}\left[(\varepsilon_\infty - \varepsilon_0) - \frac{\varepsilon_\infty {\omega_p}^2}{\omega^2 + i\gamma\omega}\right] \quad (1)$$

$$\sigma_1 = \frac{\varepsilon_\infty {\omega_p}^2 \gamma}{\omega^2 + \gamma^2},$$

$$\sigma_2 = (\varepsilon_0 - \varepsilon_\infty)\omega + \frac{\varepsilon_\infty {\omega_p}^2 \omega}{\omega^2 + \gamma^2} \quad \left[\omega_p = \left(\frac{Ne^2}{\varepsilon_\infty m^*}\right)^{\frac{1}{2}}\right] \quad (2)$$

N, m^*, and γ are the carrier density, effective mass, and scattering rate of carriers, respectively. ε_0 and ε_∞ are the vacuum permittivity and dielectric constant in the high-frequency region. ω_p is the plasma frequency. e is the elementary charge. Typical spectra of $\tilde{\sigma}$ for $\varepsilon_\infty = \varepsilon_0$ is shown in figure 11(b). σ_2 shows the maximum at frequency γ. As the frequency decreases, σ_1 increases near γ and then reaches a constant value. On the other hand, if a material contains disorder or inhomogeneity, and the carriers are backscattered and localized for example by grain boundaries or defects, the $\tilde{\sigma}$ spectra could often be reproduced by

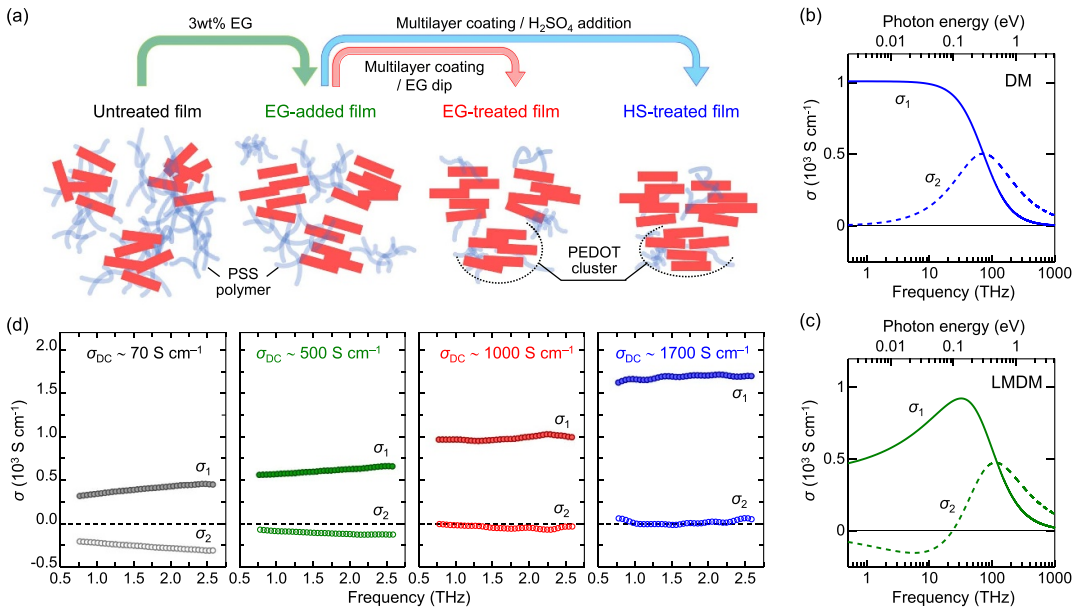

Figure 11. (a) Schematic structures of various PEDOT:PSS films [95]. (b), (c) $\tilde{\sigma}$ spectra with $\varepsilon_\infty = \varepsilon_0$, $\hbar\omega_p = 1.5$ eV, and $\hbar\gamma = 0.3$ eV in (b) DM and (c) LMDM. The localization parameter $Ck_F^{-2}\nu_F^{-2} = 3\,\mathrm{fs}^2$ is introduced in (c). (d) $\tilde{\sigma}$ spectra of PEDOT:PSS films shown in (a) at 294 K. (a), (d) Reproduced from [95]. CC BY 4.0.

the Drude-Smith model [99] or localization modified DM (LMDM) [98, 100] of phenomenological models in each of which a modified term is added to DM. Figure 11(c) shows $\tilde{\sigma}$ from LMDM, where $Ck_F^{-2}\nu_F^{-2}$ is a parameter characterizing the degree of carrier localization. In the low-frequency region, σ_1 decreases and σ_2 becomes negative. Thus, by analyzing the $\tilde{\sigma}$ spectra, quantitative information about the carrier-transport mechanism should be obtained. The study on PEDOT:PSS films using this approach is reviewed below.

Figure 11(d) shows the $\tilde{\sigma}$ spectra measured by terahertz time-domain spectroscopy (THz-TDS) for four types of films: untreated film, EG-added film, EG-treated film, and HS-treated film [95]. For all the films, the σ_1 value extrapolated to zero frequency is approximately equal to σ_{DC}. For the untreated and EG-added films, σ_1 decreases toward lower frequencies, indicating carrier localization. On the other hand, σ_1 for the EG- and HS-treated films shows no frequency dependence, being nearly constant. These behaviors are characteristic of DM in the low-frequency region (figure 11(b)), suggesting that carrier localization is very weak and γ is located at a higher frequency than the measurement region. To demonstrate their band transport, it is necessary to evaluate the higher frequency $\tilde{\sigma}$ spectra.

In the high-frequency region, optical reflectivity (R) spectroscopy is useful. Figure 12(a) shows the R spectrum of the HS-treated film; R below 2.6 THz (11 meV) was calculated from $\sigma_{1,2}$ directly obtained by THz-TDS [95]. As photon energy decreases from the visible region, R sharply increases around 1.15 eV. It shows fine peak structures due to phonons from 0.2 to 0.05 eV and then increases further nearly equal to 1. $\sigma_{1,2}$ obtained by the Kramers–Kronig transform (KKT) of the R spectrum are shown in figures 12(b) and (c) (black lines). $\sigma_{1,2}$ in the THz region accords with $\sigma_{1,2}$ obtained from THz-TDS (green circles), assuring that KKT was accurately performed.

As the photon energy decreases, σ_1 increases from ~1 eV, showing peaks due to multiple phonons around 0.1 eV, and finally flattens. σ_2 monotonically increases and saturates around 0.3 eV, and finally decreases to almost zero after showing sharp multiple phonon structures. The red dashed lines in figures 12(b) and (c) show the fitting curves by DM (equations (1) and (2)), which roughly reproduce the broad structures of $\sigma_{1,2}$. The red solid lines show the fitting curves obtained by adding 10 Lorentz oscillators to equations (1) and (2) for vibrational structures (Drude–Lorentz model (DLM)), which reproduce the experimental spectra well using $\bar{h}\gamma = 0.25$ eV. σ_2 becomes negative around 0.04 eV, which is attributable to the presence of phonons in the high-energy side. The fact that the carrier responses are reproduced by DM confirms that the HS-treated film exhibits band transport. The $\sigma_{1,2}$ spectra of the EG-treated film were also reproduced by DLM, although the magnitudes of $\sigma_{1,2}$ are smaller than those of the HS-treated film.

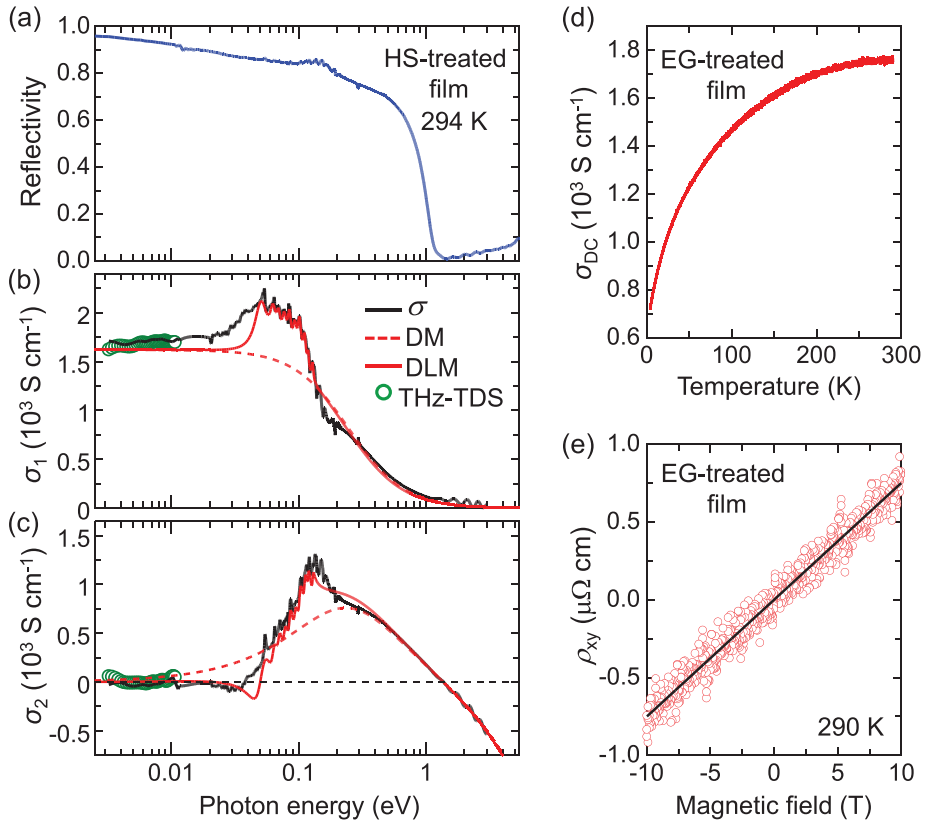

Figure 12. (a)–(c) Broadband optical spectra of the HS-treated film. (d) Temperature dependence of σ_{DC} and (e) Hall resistivity ρ_{xy} as a function of applied magnetic field in an EG-treated film. Reproduced from [95]. CC BY 4.0.

The evaluation of the absorption of PSS in the visible region revealed that the amount of PEDOT relative to PSS, $\delta_{PEDOT/PSS}$, increases as 1/2.5 (untreated film), 1/1.85 (EG-added film), 1/1.57 (EG-treated film), and 1/1.28 (HS-treated film). This suggests that as PSS is excluded, hole carriers are more easily transferred not only within each PEDOT cluster but also between clusters, and eventually band transport occurs in the EG- and HS-treated films.

Evaluating the values of mobility μ and m^* is an important issue. The x-ray photoelectron and IR-vibrational spectroscopies, and theoretical calculations revealed that the hole density per EDOT unit was approximately 1/3 [101, 102] and independent of film preparation methods. Assuming this, N can be calculated from $\delta_{PEDOT/PSS}$, μ is determined from $\sigma_{DC} = Ne\mu$, and m^* is obtained from $\mu = \frac{e}{m^*\gamma}$. In this framework, μ and m^* were evaluated to be 10.7 (7.1) $cm^2\ V^{-1}\ s^{-1}$ and 0.45 (0.49) m_0 (m_0: free electron mass) in the HS(EG)-treated film, respectively. It is reasonable to consider that the decrease in PSS increases the overlap of wavefunctions between adjacent PEDOT clusters, thereby decreasing m^* and increasing μ. However, since PEDOT:PSS contains disorder and inhomogeneity, how evaluated μ and m^* reflect those effects should be carefully investigated.

In an EG-treated film with $\sigma_{DC} \sim 1700$ S cm^{-1} (figure 12(d)), the Hall effect was observed (figure 12(e)), while N calculated from R_H is still an order of magnitude higher than the actual value [95]. This is likely due to the fact that in addition to holes responsible for the Drude response and Hall effect, holes exhibiting hopping transport exist and suppress R_H [96]. Because the experimental $\sigma_{1,2}$ spectra were reproduced with DM, the localized carriers do not contribute to the optical response in the infrared region and are strongly localized due to defects or disorder. The decrease of σ_{DC} below 250 K (figure 12(d)) shows that holes responsible for band transport also tend to localize. It is probably because the macroscopic transport includes the hole transfers through the boundaries between PEDOT clusters.

Concluding remarks

An important issue is to evaluate the spatial distribution of PEDOT clusters and PSS molecules in films and to quantitatively evaluate the interrelation between structural features and transport properties obtained from optical and transport measurements. For this purpose, it is necessary to examine

microscopic structures with a probe such as transmission electron microscope and scanning tunneling microscope that can provide nanoscale information [103, 104]. It is also significant to establish a theoretical analysis method for Hall effect measured in materials containing both free and localized carriers. PEDOT:PSS is a textbook material for understanding the transport properties of conducting polymers. Future studies of PEDOT:PSS will continue to play an important role in elucidating physical carrier-transport mechanisms in various complex polymers.

Acknowledgments

The authors thank the support from Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) (JP21H04988, JP18H01166, JP20K03801, JP22H04959, JP26K00648), and CREST, Japan Science and Technology Agency (JPMJCR1661, JPMJCR21O3). They also acknowledge Y Takahashi and M Ogino for the collaboration in THz-TDS measurements. Z G thanks the support from the Program for Leading Graduate Schools (MERIT-WINGS).

8. Electrochemical deposition of PEDOT

David C Martin, Yuhang Wu, and Junghyun Lee
Materials Science and Engineering, The University of Delaware, Newark, DE 19716, United States of America

Email: milty@udel.edu

Status

Conjugated polythiophenes such as poly(3,4-ethylene dioxythiophene) (PEDOT) are of considerable current interest for a wide variety of applications including energy storage, transistors, biomedical devices, and chemical sensors [34, 105, 106]. They are particularly valuable at the interfaces between solid-state electron/hole conductors and ionically-conducting electrolytes. Films of PEDOT are typically prepared by casting and drying an aqueous suspension (∼2 wt%), with poly(styrene sulfonate) (PSS) used as a solubilizing counter-anion. This process results in a PEDOT+:PSS- complex, with a net positive charge on the PEDOT about every 3 monomer units [45]. Spun-cast PEDOT:PSS films are often stabilized with a crosslinking agent ((3-glycidyloxypropyl)trimethoxysilane, GOPS) to improve their long-term mechanical and chemical stability in water or biological media.

A convenient alternative method for precisely forming thin films of PEDOT is by direct electrochemical deposition from solutions of the EDOT monomer and an appropriate counterion [107, 108]. The electropolymerization reaction involves oxidation of the EDOT thiophene ring at about +1.2 eV, with the loss of the thiophene hydrogens and corresponding formation of the extended conjugated polythiophene molecular backbone. The PEDOT polymer deposits on the anode as it becomes insoluble in the reaction mixture. The electrodeposition can be precisely controlled, either at constant voltage (potentiostatic), constant current (galvanostatic), or by cyclic voltammetry [109]. The result is a film with a desired thickness grown directly on the surface of the working electrode. The ultimate surface morphology can be tailored to be either smooth or rough depending on the needs of the particular application (figure 13) [110].

Another advantage of electrochemical deposition method is that it can be readily adapted for use with other EDOT monomers (EDOT+), resulting in correspondingly functionalized PEDOT polymers (PEDOT+) [111]. There are number of examples of useful EDOT+ monomers that have been described including carboxylic acid [112, 113] and maleimide side groups [114].

By changing the composition of the reaction mixture, it is possible to tailor the ultimate properties of the deposited films. In the example shown schematically in figure 13, PEDOT-carboxylic acid (PEDOT-COOH) is used as an adhesion layer to strongly bind the film to the solid substrate, with a subsequent rough PEDOT film providing a high-surface area, low impedance coating [115]. The PEDOT is then modified with maleimide (PEDOT-MA) on its outermost surface [114], providing a means to attach specific biofunctional agents (such as antibodies) that might interact in a known way with a target analyte (such proteins). This general approach has been used to create PEDOT-based VEGF impedance sensors, for example [116].

Macroscopically, the working electrodes becomes darker as the PEDOT polymer is deposited. Scanning electron microscopy (SEM) shows that the films become rougher as their thickness increases (figure 14). Impedance spectroscopy reveals a dramatic drop in the magnitude of the charge transfer resistance through the film (by a factor of 10^2–10^3), particularly in the low frequency range (less than 10^3 Hz) of interest for improving the signal sensitivity and energy requirements of many biomedical devices.

Current and future challenges

To further optimize performance for specific applications, it is possible to design EDOT monomers with a wide variety of side-group functionalities using so-called 'click' chemistries [117, 118]. Such modifications often require a change in the choice of solvent used during processing. If the PEDOT polymer product is too soluble in the solvent, it may not deposit well on the surface of the metal substrate. Examples of side groups that have been previously explored include carboxylic acids, maleimides [114], and cholesterol. Some multi-branched EDOT monomers have also been used [119], resulting in improved mechanical properties and control of surface morphology and charge transport behavior. A wide variety of different counterions can also be explored to further tailor the ultimate film structure and properties [120].

Advances in science and technology to meet challenges

Although experimentally challenging, *in-situ* transmission electron microscopy has recently been used to monitor the PEDOT electrodeposition process at near molecular resolution. By using a special sample holder with a liquid cell and electrical connections, it was revealed that the PEDOT electrochemical deposition process occurs through a series of intermediate states as the polymer molecular weight increased [121]. The specific nature of these intermediate states were identified and associated with their liquid- or solid-like state during the solidification process. The EDOT oligomer droplets became more irregular in shape and darkened as their molecular weight increased. They also showed characteristic variations in their dissolution and coalescence behavior. Liquid-like droplets were smooth and could redissolve into the reaction mixture, while solid-like

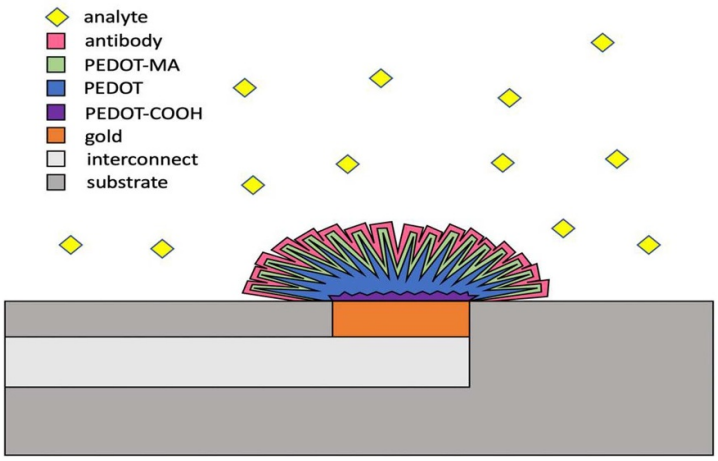

Figure 13. Schematic of multi-layer PEDOT film deposited on the surface of a solid substrate (not to scale). The PEDOT film grows off the gold metal electrode in a controlled manner due to the current that is provided from an external source via an interconnect. Here the first layer is shown as a carboxylic-acid variant (PEDOT-COOH) that provides enhanced adhesion to the substrate. The bulk of the film is PEDOT, grown in a way that leads to a high surface area, low impedance coating. The outer layer of the PEDOT is modified with maleimide (PEDOT-MA). The PEDOT-MA is reacted with some sort of specific binding agent, such as an antibody. The result is a device that reacts in a controlled manner with a target analyte.

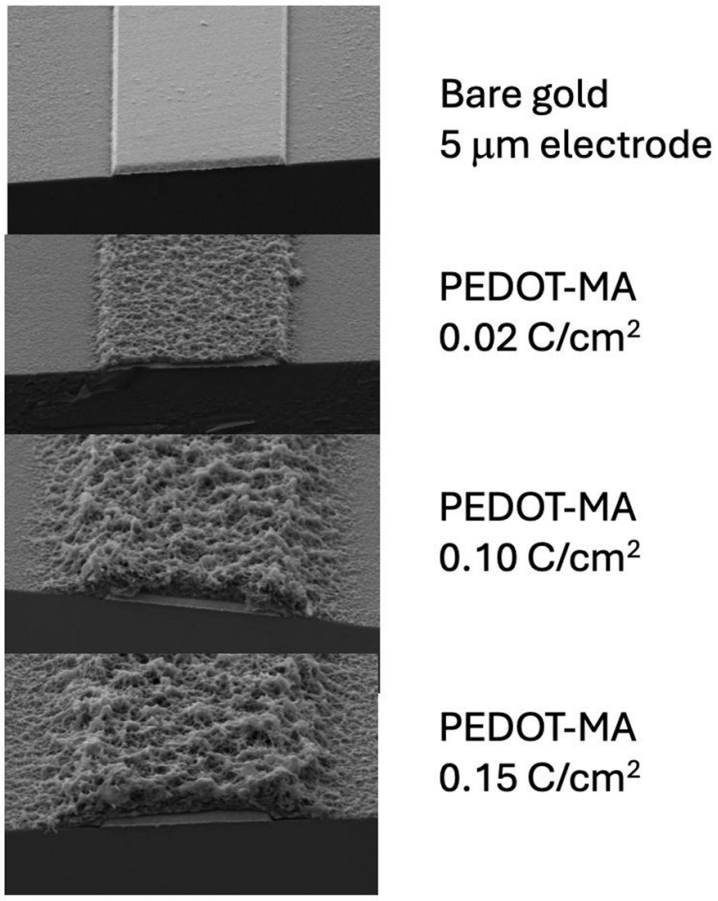

Figure 14. Cross-section scanning electron microscopy (SEM) images of a gold electrode with increasing amounts of PEDOT-maleimide (PEDOT-MA) electrodeposition. 2a: Bare gold electrode, 5 μm wide, 250 nm thick; 2b, 2c, 2d: PEDOT-MA films electrodeposited at 0.02 C cm^{-2}, 0.1 C cm^{-2}, and 0.15 C cm^{-2} total charge density.

droplets were stable and did not redissolve or coalesce. These droplets and fibrils evidently correspond to the bumpy surface structures seen in SEM images of electrodeposited films (figure 14).

Electrochemically deposited films based on PEDOT have recently been approved (FDA, CE Mark) for commercial use in certain biomedical device applications. These films were originally

developed by Biotectix LLC, and are currently distributed by Heraeus Medevio under the trade name AmpliCoat [122].

Concluding remarks

The electrochemical deposition of PEDOT and PEDOT derivatives provides a convenient means for the direct functionalization of metal microelectrodes used in a wide variety of applications, particularly those that involve the direct interfacing of rigid, solid, electronic components into soft, wet, electrolytically active matrices. Electrochemistry makes it possible to precisely control where and how much PEDOT is deposited, and facilities the use of alternative EDOT monomers and counterions. These coatings substantially lower the low-frequency impedance of these electrodes and facilitate subsequent biological surface treatments.

Acknowledgments

This research was funded in part by the National Science Foundation (NSF), the National Institutes for Health (NIH), the Air Force Office of Research (AFOSR), the Waters Corporation, and the University of Delaware.

9. PEDOT-based electrochemical biosensors for healthcare monitoring

*Bicheng Zhu and Jadranka Travas-Sejdic**
Centre for Innovative Materials for Health, School of Chemical Sciences, Waipapa Taumata Rau—The University of Auckland, 23 Symonds Street, Auckland, New Zealand and MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Wellington, New Zealand

*Email: j.travas-sejdic@auckland.ac.nz

Status

Electrochemical biosensors are devices that detect biological or chemical substances by converting biological responses into measurable electrical signals. These sensors have diverse applications across healthcare, environmental monitoring, food safety and biotechnology. Recent advancements in organic (semi)conductors have enabled the development of soft, stretchable, transparent and adhesive biosensing electrodes that interface seamlessly with skin and tissues [123]. This not only enhances biosensing performance but also minimizes disruption to normal tissue function, opening exciting new possibilities in healthcare monitoring. Among organic (semi)conductors, the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) stands out for its unique combination of properties (figure 15(A)), including aqueous processability, biocompatibility, stability and high conductivity, making it a particularly promising material for advanced biosensing applications. Commercially available aqueous dispersions of PEDOT:PSS (PSS-polystyrene sulfonate) provide processability and feature PEDOT:PSS nanoparticles with $PEDOT^+$ rich cores and PSS^- rich shells; however, the materials produced are brittle and rigid. The availability of PEDOT:PSS dispersion, fortunately, allows for preparation of composites with various additives, enhancing its stretchability and mechanical flexibility, making it suitable for innovative sensing applications in flexible and stretchable, implantable and wearable bioelectronics. Wearable sensors are designed to adhere comfortably to the skin, can monitor metabolites like glucose, or vital health signs such as heart rate, over extended periods. Implantable sensors, on the other hand, are either partially or fully introduced into the body, providing more direct access to biological signals with minimal discomfort to the patient. Advancements in microfabrication of conducting polymers [124] also facilitate such opportunities, providing means to manufacture various formats of PEDOT-based biosensors, such as microelectrode arrays (MEAs) or OECTs, at scale, reducing costs.

The applications of PEDOT in wearable biosensors cover a wide range of health parameters (figures 15(C) and (D)), from sensing biomarkers for diseases to mechanical forces and recording electrophysiological signals. These various sensors may operate on different sensing principles. Tactile and strain sensing, for example, often utilize capacitance or resistance changes as sensing readouts. Detecting metabolites and biomarkers form body fluids, such as sweat, saliva and blood, require different approach. Certain metabolites, like glucose, uric acid and dopamine, possess unique redox properties that can be directly exploited for selective sensing, either through their inherent properties or with the assistance of an enzyme immobilized on the sensor. The detection of biomarkers, such as mutated genes or specific cancer markers [125], often involves the conjugation of specific recognition probes, like aptamers or antibodies, to the surface of the sensor. This ensures selectivity and triggers an electrochemical change upon binding to the target, which is then recorded as the sensor's response. That requires derivatization of PEDOT with side chains carrying functional groups to enable attachment of the bioprobes [126]. Signal amplification methods are sometimes needed to achieve clinically relevant detection levels, that may utilize various nanoparticles or further redox reporters, as well as appropriate device configurations, such as OECTs and OFETs (organic field effect transistors).

The outstanding features of PEDOT make PEDOT-based biosensors highly promising for further development in wearable, integrated, noninvasive and real-time diagnostics and personalized health monitoring, as well as for a wide range of other applications.

Current and future challenges

PEDOT-based biosensors, however, face several challenges that must be addressed for broader adoption. The long-term stability of PEDOT can be compromised by environmental factors such as humidity, temperature and exposure to biological fluids, leading to performance degradation. Additionally, the potential leaching of small molecular additives that enhance the stretchability and flexibility of PEDOT:PSS could pose issues for long-term use, requiring further investigation. In biosensors that incorporate bioprobes, the stability of these probes is also a key consideration.

Commercially available PEDOT:PSS lacks functional groups for bioprobe conjugation, making the development of reliable and simple synthesis methods for functionalized PEDOT essential.

Non-specific fouling of sensing surfaces is a significant challenge in biosensor design, including PEDOT-based biosensors, particularly in applications involving body fluids with diverse components. Implantable sensors, which come into direct contact with internal tissues, may offer enhanced sensitivity and more accurate signal recording but are

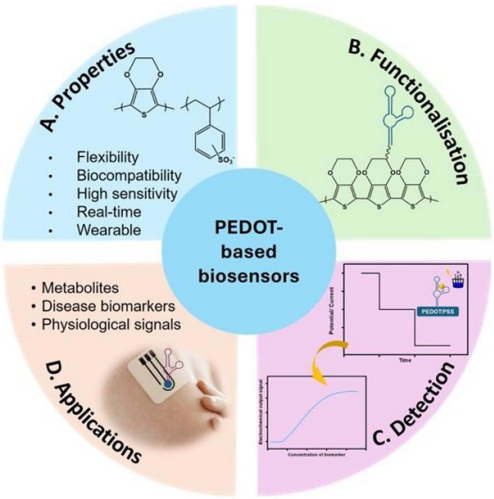

Figure 15. PEDOT-based biosensors. (A) Structure of PEDOT and PSS. (B) Functionalization of PEDOT for selective detection of target analytes. (C) PEDOT-based electrochemical detection generates a variety of electrical signals depending on the device design and readout platform. (D) Applications of PEDOT- biosensors in wearable and implantable health monitoring.

particularly susceptible to this issue. To be successful, implantable sensors must also exhibit improved mechanical compliance with biological tissues to ensure comfort and reliability.

Despite significant advances in PEDOT:PSS fabrication, the scalable production of miniaturized PEDOT-based biosensors, along with their integration into other microelectronics and potentially microfluidics, remains a challenge for the successful deployment of PEDOT biosensors in real-world applications.

In future long-term health monitoring applications, data processing and management must be considered from the early stages of sensor development. AI [127] and ML [128] are poised to transform biosensing technologies in healthcare. By integrating PEDOT-based biosensors with AI and ML algorithms, these technologies can enable personalized health management and facilitate the early detection of diseases.

Advances in science and technology to meet challenges

Achieving high sensitivity and selectivity in PEDOT-based electrochemical biosensors, while maintaining flexibility and stretchability for wearable applications, is crucial for accurate biosensing. Ongoing efforts focus on advancing PEDOT derivatization chemistries to enhance specificity through bioreceptor conjugation (figure 15(B)), optimizing device designs for signal amplification, and refining fabrication techniques to meet these objectives. For example, functionalisation of both PEDOT:PSS and EDOT for the detection of inflammatory cytokine interleukin 6 in an OECT device format were reported, that utilized diazonium chemistry to couple an aptamer probe to sulfonate moieties on the PSS of the PEDOT:PSS [125]. Instead of using PSS as the dopant, alternative dopants containing functional groups, such as zwitterionic polypeptides, have been investigated to anchor bioprobes via EDC/NHS chemistry for the detection of the breast cancer marker BRCA1 [129]. Functionalized EDOT monomers bearing carboxylic acid groups [130] and aldehyde groups [131] have also been synthesized for the attachment of lactate dehydrogenase and alpha-fetoprotein-specific antibodies through EDC/NHS coupling and Schiff base reactions, enabling the detection of lactate and alpha-fetoprotein. In another example, a simple, yet effective and rapid, conjugation chemistry was developed utilizing thiol-functionalized EDOT and thiol–hiol electrochemical oxidative coupling [132] that is generalizable to a variety of bioreceptors conjugation to PEDOT sensing surfaces. Functionalization of EDOT with EG side chains, polyzwitterions or other antifouling polymers may impart effective antifouling properties to PEDOT-based sensors. Additionally, other functionalization strategies have been explored to improve additional properties of PEDOT-based polymers in biosensors, such as hydrophilicity and biocompatibility [133].

Most current PEDOT electrodes for biosensing are in thin film format, typically deposited on metal substrates, such as in MEA formats. Recent advancements in fabrication techniques are focusing on both miniaturizing PEDOT sensing elements across all PEDOT-based devices and developing 3D PEDOT electrode arrays. These innovations aim to enhance the signal-to-noise ratio [134], which is particularly crucial for implantable biosensors that monitor electrophysiological signals or biomarkers from tissues such as the brain, heart and gut. A study reported the fabrication of 3D PEDOT:PSS pillars of 250 ± 10 μm height and diameter of 5 ± 0.5 μm by 'direct writing' of PEDOT:PSS ink on MEAs (figure 16(A)) and their application for recording extracellular potential signals generated by cardiac tissue [134] (figure 16(B)). The PEDOT:PSS pillars were robust and highly flexible, which was demonstrated by the reversible loading–unloading by a probe (figure 16(C)) and bending with the contraction and relaxation of the cardiac microtissue (figure 16(D)). The extracellular potential of cardiac tissue was successfully detected by these 3D CP microelectrodes.

PEDOT-based MEA biosensors offer exciting opportunities for detecting multiple analytes or different types of signals—such as biological markers, electrophysiological signals, temperature and mechanical forces—on a single array. This capability will enable comprehensive health status monitoring, facilitating more integrated and real-time assessments. For implantable biosensors applications, these would benefit from (on-demand) biodegradability and bio-absorbability. A progress in conjugated

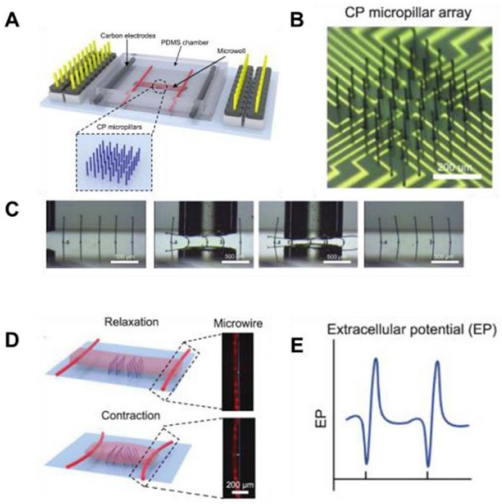

Figure 16. (A) Schematic illustration of the device that include a 3D conductive polymer (CP) microelectrode array (blue) for extracellular potential recording from cardiac microtissue, a microwell for seeding cardiac tissue and carbon electrodes (dark gray) for electrical stimulation of cardiac tissue. TPE/QD nanocomposite microwires (red) were used for force sensing (also shown in D). (B) A microscopy image of the CP microelectrode array (scale bar, 200 μm). (C) 3D CP pillars were bent by a probe and flexed back. (D) 3D CP microelectrodes bent with the contraction and relaxation of the cardiac microtissue. (E) Schematic of the extracellular potential detected by the CP MEA. Reproduced from [134]. © The Author(s). Published by IOP Publishing Ltd CC BY 4.0.

polymers-based transient electronics was reviewed recently [135]. PEDOT-based transient biosensors would be beneficial where temporary sensing functionality is desired, but also from the environmental point of view to deal with future increase in volume of skin and wearable electronics. However, controlling transience while preserving function until the desired point of degradation, is currently challenging.

Concluding remarks

PEDOT-based electrochemical biosensors hold great promise for wearable and implantable bioelectronics, enabling non-invasive, real-time health monitoring. With its biocompatibility, flexibility and conductivity, PEDOT is ideal for sensing a range of biomarkers, metabolites and physiological signals. However, challenges remain, including long-term stability, non-specific fouling and the need for functionalized PEDOT for bioreceptor conjugation. Future research should also focus on improving sensors' sensitivity, selectivity, scalability in fabrication and addressing need for material degradation. Additionally, integrating PEDOT-based biosensors with AI and ML could revolutionize personalized health management and disease detection. As advancements in flexible, stretchable and transient PEDOT devices continue, their potential in healthcare and other applications is expected to grow. This interdisciplinary field relies on contributions from many disciplines, including chemistry, physics, electrical engineering, biology and medicine.

Acknowledgments

The authors thank Waipapa Taumata Rau | The University of Auckland and the MacDiarmid Institute for Advanced Materials and Nanotechnology for their continuous support and research facilities.

10. PEDOT for thermoelectrics

*Jeong Han Song and Jeonghun Kwak**
Department of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, and SOFT Foundry Institute, Seoul National University, Seoul, Republic of Korea

*Email: jkwak@snu.ac.kr

Status

TE devices that can convert heat into electricity hold great promise as a sustainable means of reusing waste heat from industrial processes and the human body. The TE conversion efficiency is generally assessed by its dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α, σ, T and κ denote the Seebeck coefficient, EC, absolute temperature, and thermal conductivity, respectively. For practical applications, a high TE power factor (PF $= \alpha^2\sigma$) must be combined with low κ to at least achieve $ZT > 1$ near room temperature. Yet, each parameter has a trade-off relationship with the carrier concentration (n). The σ and κ increase with n, whereas the α shows the opposite trend, complicating the optimization of PF and ZT [136].

CPs have garnered attention as next-generation TE materials due to their inherently low κ, which can offset the loss of ZT. Additionally, they possess superior flexibility compared to their brittle inorganic counterparts, making them ideal candidates for powering future wearable devices and the internet of things. In particular, PEDOT:PSS has been extensively studied owing to its easy doping tunability, non-toxicity and solution-processibility that allows scalable production. Nevertheless, pristine PEDOT:PSS generally exhibits poor σ ($<$1 S cm^{-1}) and α (15–18 μV K^{-1}), necessitating secondary doping to achieve a high PF.

The most common approach to optimize PF of PEDOT:PSS is solution-based sequential post-treatment [137, 138]. This method achieves high σ by firstly forming highly crystalline PEDOT network through the partial removal of insulating PSS chains, followed by modulating the α through a chemical de-doping process. The use of polar solvents, acids and ionic liquids has been proposed to effectively remove PSS by weakening its ionic interaction with PEDOT chains or replacing PSS with counter-anions, allowing PEDOT:PSS to achieve high σ over 1000 S cm^{-1}. Subsequent base and reducing agent treatments can then improve α with sacrifice of σ by lowering the oxidation level of PEDOT chains, enabling optimization of PF. Under optimal post-treatment conditions, a high PF over 500 μW m^{-1} K^{-2} near ambient conditions has been reported (figure 17(a)).

Alternatively, embedding organic and/or inorganic fillers into PEDOT:PSS matrix has demonstrated significant improvement in α through energy filtering effects [137, 138]. By forming energy-level mismatch at the interface with fillers, low energy carriers in PEDOT:PSS are scattered by the energetic barriers, often resulting in larger improvement of α compared to sequential post-treatments (figure 17(b)). Beyond these conventional approaches, novel strategies have been proposed to engineer the TE properties of PEDOT:PSS. Representative examples include polaron level splitting [139] and interfacial energetics engineering [140], both of which modulate the DOS of PEDOT:PSS to enhance α with minimal compromise in σ. Moreover, non-chemical approaches employing light irradiation have been explored to improve the PF. These strategies rely either on micro-annealing effects that selectively remove PSS or on light-responsive materials that induce charge transfer to PEDOT:PSS [141]. Forming a multilayered structure has also proven effective in enhancing TE performance. By sequentially depositing secondary organic or inorganic layers onto PEDOT:PSS films, a combination of efficient electronic transport and interfacial carrier scattering can appear, leading to improved PF [142].

In addition to developing doping strategies to maximize the PF, various device architectures have been proposed to enhance the TE output power. The maximum output power (P_{max}) of a TE device is defined as $P_{max} = (\alpha\Delta T)^2/4R_{in}$, where ΔT and R_{in} denote temperature difference and the internal resistance of the device, respectively. Since ΔT is exponentially dependent on P_{max}, maximizing ΔT across the TE device is crucial to achieving high efficiency. However, organic TE devices typically have a planar structure, which is inefficient for generating a significant in-plane ΔT when attached to an out-of-plane heat source. This structural limitation hinders their ability to fully harness the thermal gradient available from such heat sources. To address this, extensive research has focused on designing novel TE device form factors (e.g. rolled, corrugated, and vertical structures). By reconfiguring the device geometry to better align with the direction of the thermal gradient. By doing so, they not only maximize ΔT but also improve the output power density and overall device performance, making organic TE devices more viable for practical applications such as wearable electronics and energy harvesting systems [140].

Current and future challenges

Since CPs exhibit a different charge conduction mechanism compared to inorganic materials, understanding their charge transport properties to minimize the trade-off relationship between σ and α upon doping is crucial. Achieving high σ for a given α in PEDOT:PSS depends on optimizing several nano-/micro-structural factors: (i) maintaining planar quinoid structure, (ii) lowering π–π stacking distance, (ii) enhancing high crystal correlation length, and (iv) achieving a fibrillar morphology of PEDOT chains [137]. This is because these factors result in

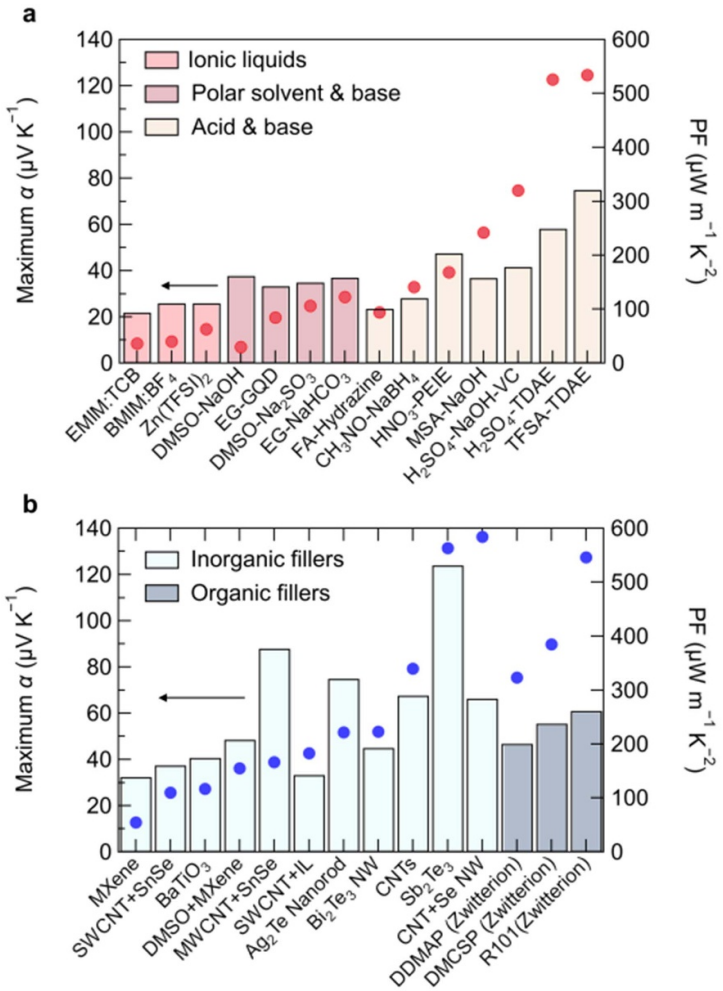

Figure 17. Representative maximum α (bars) and optimal PF (solid circles) of PEDOT:PSS films achieved using (a) secondary dopants and (b) inorganic or organic fillers in recent years. Data are sourced from literature, tables, and graphs in [137–145]. (EMIM:TCB: 1-ethyl-3-methylimidazolium tetracyanoborate; BMIM:BF4: 1-butyl-3-methylimidazolium tetra-fluoroborate; $Zn(TFSI)_2$: zinc di[bis(trifluoromethylsulfonyl)imide]; DMSO: dimethyl sulfoxide; EG: ethylene glycol; FA: formic acid; PEIE: polyethylenimine ethoxylated; MSA: methanesulfonic acid; TDAE: tetrakis(dimethylamino)ethylene; TFSA: trific acid; SWCNT: single-walled carbon nanotubes; MWCNT: multi-walled carbon nanotubes; NW: nanowires; DDMAP: N-dodecyl-N,N-dimethyl-3-ammonio-1-propane-sulfonate; DMCSP: 1-(N,N-dimethylcarbamoyl)-4-(2-sulfoethyl) pyridinium hydroxide; R101: rhodamine 101).

superior intra-/inter-grain transport, and therefore the improved carrier mobility (μ), that selectively contributes to σ. However, during blending or post-treatment process of PEDOT:PSS to enhance α, these structural parameters often get deteriorated, which leads to larger unwanted sacrifice of σ and a resultant limited improvement of PF [143].

Fundamental frameworks such as Kang–Snyder (K–S) model that describe the α–σ relationship of CPs have little been explored in PEDOT-based films. The K–S model proposes an empirical power law, $\alpha \propto \sigma^{-1/s}$, where s is a transport parameter that characterizes the energy dependence of carrier transport. In this framework, both α and σ scale with a temperature-dependent but energy-independent transport coefficient, $\sigma_{E0}(T)$, which can be interpreted as a weighted mobility reflecting the degree of percolation within the film. Achieving a low transport parameter, ideally $s = 1$, is beneficial because it typically corresponds to a higher σ_{E0} enabling greater σ at a given α [136]. Nonetheless, most CPs exhibit $s = 3$ (or 4), originating from their high structural disorder and hopping behavior, with only a few semi-crystalline or semi-metallic CPs exhibiting $s = 1$. For PEDOT:PSS, its inherently amorphous and disordered microstructure makes attaining $s = 1$ relation with high σ_{E0} challenging [143], while the underlying charge-transport mechanisms required to maximize σ_{E0} at a low doping level remain unclear.

To fully harness the material TE performance, challenges in efficient device design must also be addressed to maximize the output power. Although PEDOT:PSS is currently the leading organic TE material with a high PF, its output power after modularization remains in the nanowatt range, which is insufficient for practical device powering. As organic TE materials are typically intended for wearable devices, achieving a stable milliwatt-scale output power under

a small ΔT between the body and ambient temperatures is necessary. Increasing the number of PEDOT:PSS legs in series within a lateral module can boost the output voltage, but it simultaneously raises R_{in}. Therefore, careful optimization of the number of legs, geometry, and thickness of the PEDOT:PSS component is crucial to maximizing the module's P_{max}.

Beyond enhancing the TE performance, several additional factors should be considered particularly for wearable applications. Firstly, the device's TE performance must remain stable under continuous strain from the human motion. With human skin typically experiencing ∼30% strain from bending or stretching, the TE device should maintain high performance even after repeated cyclic exposure to such strains. Furthermore, biocompatibility of the device should be carefully evaluated. Traditional methods for fabricating TE devices often involve the use of acid, base, or inorganic particles, many of which can introduce toxicity concerns [144]. Hence, achieving high TE performance via biocompatible dopants or nanocomposites is an important issue that needs to be addressed. Lastly, more extensive research on the stability of TE devices needs to be conducted, particularly given that PSS is hygroscopic [145]. Since a continual power supply is essential for bioelectronic applications (e.g. healthcare monitoring), TE devices must function reliably under both ambient and humid conditions without experiencing significant performance degradation.

Advances in science and technology to meet challenges

Development of innovative doping strategies of PEDOT:PSS is required to mitigate the trade-off relationship among TE parameters. Since achieving high crystallinity with long-range order transport is key to realizing $s = 1$ transport, exploring effective dedoping strategies that minimally affect the polymer microstructure is crucial. Applying such strategy with green dopants or in the presence of plasticizer that makes film mechanically stable would be more desirable for bioelectronic applications.

Furthermore, since R_{in} can be significantly reduced by increasing the thickness of the PEDOT:PSS films, studies on the TE performance of sub-micrometer PEDOT:PSS films would be valuable for high P_{max}. Solution-processible film deposition techniques such as 3D printing must be simultaneously developed to produce scalable, and relatively thick PEDOT:PSS films for modulization.

Concluding remarks

To advance high-performance PEDOT:PSS-based TE devices, it is crucial to focus on the following key areas: (i) developing innovative doping strategies that minimize the inherent trade-offs among TE parameters, (ii) exploring the underlying charge transport physics that govern the α–σ relationship, and (iii) optimizing device engineering to maximize the output power density. Continued research and development in these domains will unlock the full potential of PEDOT:PSS for TE applications, particularly in wearable and bioelectronic devices that require practical levels of TE conversion efficiency.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIT) (No. 2022R1C1C1010152)

11. Vapor phase deposition of PEDOT

Drew Evans
Future Industries Institute, Adelaide University, Adelaide, Australia

*Email: Drew.Evans@unisa.edu.au

Status

Conducting polymers are fast approaching 50 years of research, since their initial discovery in the late 1970's [146]. An integral part of this research effort has been the development of methods to synthesize these polymers and fabricate them into useful films and structures. As the early-stage research becomes more mature these methods grow in importance as a bridge to commercial products and applications [147]. At their core, these synthesis methods are overcoming the challenge of conducting polymers being rigid, insoluble polymers. The deposition of conducting polymers from the vapor phase is one means to achieve high quality films and structures [148, 149]. The vapor phase deposition can be separated into two variants—oxidative chemical vapor deposition (oCVD) and VPP. In oCVD the monomer and initiator (oxidant) are fed into a reaction chamber as gases and reacted at or on the surface of the substrate [148]. Conversely, as depicted in figure 18, in VPP a thin film of oxidant is deposited on the substrate of choice, which in turn is exposed to monomer vapor within the reaction chamber (leading to polymerization at the oxidant surface) [150]. Both methods offer a means to coat conducting polymers over large areas, on a variety of substrates—including non-planar and complex geometries. Further advances herein would link deposition parameters with function and performance, giving control over the polymer properties uniformly across large areas. With many commercial products on the market that employ other (semi)conducting materials manufactured using vapor deposition processes, it stands to reason that oCVD and VPP are potential ways to bridge conducting polymer research with their commercial products.

Current and future challenges

The overwhelming majority of studies using vapor deposition focuses on poly(3,4-ethylenedioxythiophene) (PEDOT). Using either oCVD or VPP has afforded researchers some chemical flexibility though—using doping counterions other than polystyrene sulfonate (PSS), such as tosylate (Tos) and chloride (Cl). Bubnova *et al* demonstrated the value of evaluating different doping anions by showing VPP PEDOT:Tos is semi-metallic opposed to the semiconducting behavior of PEDOT:PSS [151]. Aligned with this, the primary property of interest to most researchers is the EC of the resultant doped-PEDOT material. The early work of Winther-Jensen and co-workers achieved conductivity on the order of 1000–1500 S cm^{-1} [152, 153]. From this starting point, conductivities comparable to conducting metal oxides and approaching metals have been led by Fabretto and co-workers (3000 S cm^{-1}) [154], Gueye and co-workers (4500 S cm^{-1}) [155], and Cho *et al* (7800 S cm^{-1}) [156].

When setting the ambition of conducting polymer-based commercial products, it is possible to identify several challenges. Firstly, the diversity of possible commercial products will rely on conducting polymer properties beyond their EC. For example, for TE devices it is necessary to study the electrical and thermal conductivity as well as the Seebeck coefficient. In OECTs, additional properties such as transductance become important. Optoelectronic applications such as electrochromic displays rely on the coloration efficiency and optical memory of the conducting polymer. Therefore, the research field must overcome the challenge of identifying and defining the property shortlist that would define performance in the intended application. Identifying the best application to benefit from the unique properties of conducting polymers is needed.

Secondly, the potential commercial products will necessitate particular substrates and geometries—unlikely to be generic glass microscope slides. For example, flexible and printed electronic devices utilize substrates having very different mechanical and thermal properties compared to glass. Compatibility of the vapor deposition process with these flexible, compliant, often stretchable, and thermally sensitive substrates presents as a challenge to overcome. Moreso, how to maintain the polymer properties achieved on glass when transferring over to these substrates? In the context of EC, the conductivity of doped PEDOT is typically one order of magnitude lower when deposited on plastics opposed to glass.

Finally, a deeper understanding of the vapor deposition process is required. It is important to understand how to control the growth of the polymer using various deposition parameters. This understanding would lead to control over the growth rate aimed at decreasing deposition times without comprising the polymer properties. This particular challenge is important when considering scaling up new products and making it industrially attractive to manufacture.

Advances in science and technology to meet challenges

In order to meet the challenges, there is a need to connect aspects of the global research effort together. One main opportunity is to link advances in computational studies (such as those led by Zozoulenko and co-workers [157]) with experimental results to glean deeper insights about the polymer synthesis and properties. Figure 19 presents the output from CG molecular dynamic simulations of PEDOT doped

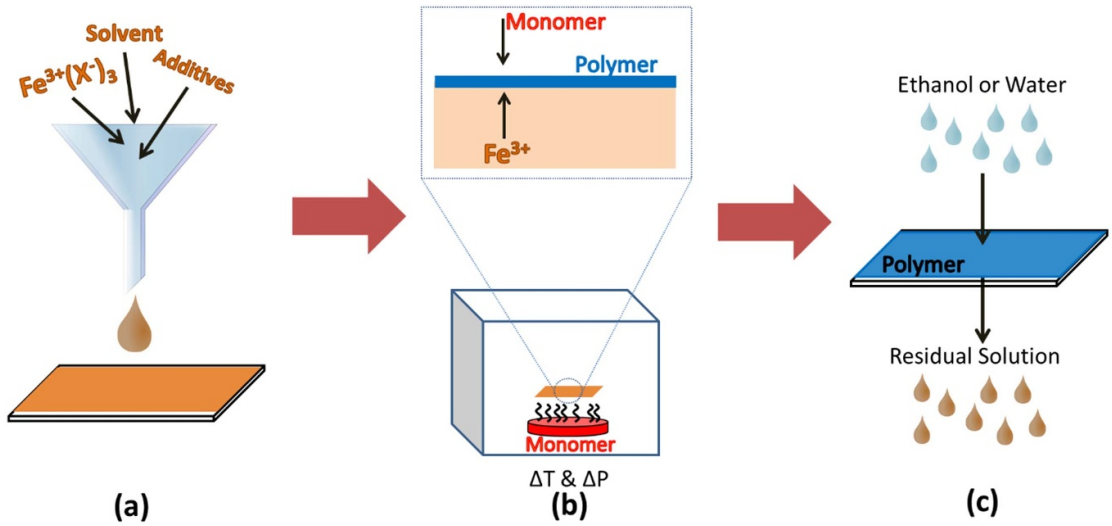

Figure 18. The VPP process involving (a) deposition of the oxidant solution commonly containing an Fe3+ salt in a solvent (typically an alcohol such as ethanol) with possible additives, (b) exposure of said oxidant to monomer vapor at a given temperature (T) and pressure (P), where (c) oxidant/monomer is transported/condensed at the interface to initiate polymerization, and (d) washing away excess oxidant and monomer to yield a ICP thin film. Reprinted from [150], Copyright (2017), with permission from Elsevier.

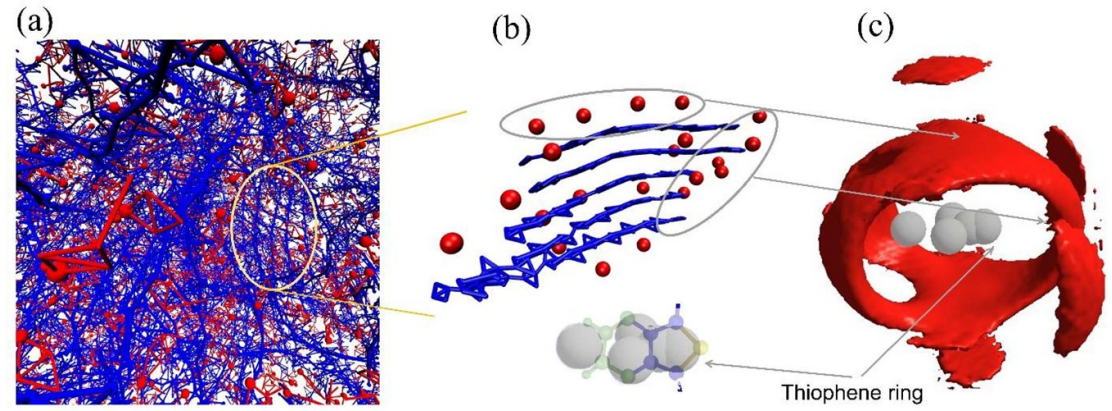

Figure 19. (a) The snapshot of the coarse-grained molecular dynamics simulation of the dried PEDOT:Tos film. The PEDOT chains and Tos molecules are in blue and red color, respectively. For a better presentation, the PEDOT skeleton is visualized by connecting the beads in the coarse-grained molecular dynamic model. (b) A typical PEDOT stacking with surrounding Tos molecule (For Tos molecules, only a sulfonate group is visualized). (c) The calculated spatial distribution function for Tos molecules around a PEDOT monomer. 'Tos 1' and 'Tos 2' refer to two tosylate populations. Reproduced from [157]. CC BY 4.0.

with Tos. Note that these simulations are for the general oxidative polymerization process—not specifically VPP. The relevance herein is that studies indicate that the EDOT monomer solubilizes into a surface layer of the oxidant and polymerization proceeds via liquid-phase oxidative routes confined near the vapor-liquid interface [158] and templated by additives in the oxidant layer [159, 160]. Such simulations show the likely presence of two discrete populations of Tos doping anions within the PEDOT structure—which was corroborated from detailed x-ray photoelectron spectroscopy analysis. New insights such as this go a long way to unlocking the underlying chemistry and physics of conducting polymers. Increased computational capacity is needed to allow for more complicated simulations, such as simulating the actual VPP process that occurs at the vapor-liquid interface. With advances in high performance computing allowing for more complicated and detailed models and simulations to be conducted there is opportunity for a deeper understanding to be developed faster than previously imagined.

Further to this, researchers are taking advantage of advances in characterization tools to gather new insights into conducting polymer properties. While in the early days using classic III–V semiconductor physics to describe the behavior of conducting polymers was sufficient, it has become evident

these polymers warrant their own description. This will be enabled by advances in a variety of techniques, from Hall effect measurements to photoelectron spectroscopy to a range of synchrotron-based scattering techniques. The connection of advanced characterization with the aforementioned computational studies will have impact on all dimensions of conducting polymer research. More specifically, in the case of vapor deposited PEDOT this connection will provide the understanding and control to underpin scaling-up of the proposed PEDOT-based devices.

From a technology perspective, the vapor deposition of PEDOT (and other conducting polymers) will be enabled by advances in other vapor deposition techniques. The broader chemical vapor deposition technology, as well as variants such as atomic layer deposition, are making their own advances regarding control of temperature and reacting/carrier gases to yield nanoscale control of growing thin films on a range of substrates. This level of technological advancement will be critical for the vapor deposition of PEDOT, once candidate end applications and fit-for-purpose devices are identified. The likely pathway forward for vapor deposited conducting polymers will be the adaptation of commercial chemical vapor deposition systems to conduct oCVD or VPP processes at scale.

Concluding remarks

The journey of a newly discovered material into commercial product(s) is often quite long, such as the pathway from discovery of conjugated molecules that emit light into the variety of large area electronic displays now ubiquitous in our daily lives. Backed by almost 5 decades of research, conducting polymers are set to make a similar transition into commercial products. To enable this is the need for industrially useful, and readily scalable, methods of producing high quality conducting polymers. Vapor deposition, especially for the doped PEDOT variant of conducting polymers, represents one leading candidate method. Realizing this requires the research sector to capitalize on advances in both experimental and computational techniques, while working with industry to identify the most probable market opportunity.

12. 3D printing of PEDOT

Jinhao Li[1,2], *Baoyang Lu*[3,*], *Guoying Gu*[1,2,*]
[1]State Key Laboratory of Mechanical System and Vibration, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[2]Shanghai Key Laboratory of Intelligent Robotics, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
[3]Jiangxi Provincial Key Laboratory of Flexible Electronics, Flexible Electronics Innovation Institute, Jiangxi Science and Technology Normal University, Nanchang, People's Republic of China

*E-mail: luby@jxstnu.edu.cn and guguoying@sjtu.edu.cn

Status

Three-dimensional printing facilitates PEDOTs-based patterns and structures via extrusion-based sol-gel transition or beam-based photopolymerization. Beyond conventional 2D manufacturing techniques like coating and lithography, 3D printing revolutionizes the production landscape by offering computer-controlled dimension-raising customization. 3D-printed PEDOTs, started with jet-printing in 1999 for patterned transparent electrodes [161], have grown to leverage recent advances in material designs and fabrication techniques. Notably, the introduction of polystyrene sulfonate (PSS) as the charge-balancing dopant yields a soluble derivative (PEDOT:PSS) and significantly increases the processibility for 3D printing.

The low-density polymer network of precursors and resultant weak intermolecular interactions are long-standing challenges to the free-form fabrication of high-performance PEDOTs. To address these issues, recent efforts have been devoted to ink-solute regulation and field assistance for 3D-printable PEDOTs [162, 163]. For example, material design strategies from molecular engineering, and phase engineering to morphology modulation provide shear-yielding properties or free radical polymerizations. By introducing supporting baths and physical fields, as-developed novel printing mechanisms enable cross-scale 3D architectures against capillary- and gravity-driven instability.

To date, 3D printing has been one of the most important approaches to PEDOTs-based architectures with geometrical complexity [124]. This technique raises sophisticated functions (conduction [134], stimuli-response [164], iontronic communications [165], etc.) to three dimensions, accelerating integration and miniaturization in electronic and robotic applications. The programmable fabrication also allows tailored shape forms and structural properties for task-specific applications, such as personalized healthcare and human-machine interactions. For example, PEDOT:PSS-based 3D hydrogel lattice simultaneously linearizes the electrical transduction and mechanical behaviors of iontronic tactile sensors by independently designing interfacial contact and compressive deformation [166].

As an emerging interdisciplinary field, 3D printing of PEDOTs is still at the laboratory stage, where opportunities and challenges remain. Future development will enable the synchronous implementation of printability and property-tunability. Thus, high-performance PEDOTs-based materials could be printed into precise yet complex geometries for integrated intelligent functions without sacrificing reliability and customizability.

Current and future challenges

Although dependent on material portfolios, the common fabrication instability precipitates line breaking-up, pattern spreading-out, and structural collapse, hindering PEDOTs from high-resolution 3D architectures. The competition effect among material components further limits technical strategies by compromising material properties or structural characteristics.

High-resolution features are still the pursuit of current research on 3D-printed PEDOTs. Despite recent advances in precise instrumentation, there is still a challenge to realize voxel or sub-voxel resolution. For example, die-swelling expands the extruded filaments before deposition. Near-field optical proximity effect and light scattering also inhibit high-resolution features. These issues impede the printing resolution scaling down to the voxel size.

Three-dimensional geometries are generally defined as freestanding architectures with overhanging, thin-walled, or hollow features against structural collapse. Despite computer-controlled ink deposition, one consequent obstacle is how to timely construct and stably maintain structural rigidity throughout the fabrication process. Temporary polymer frameworks are one of the promising and generalized routes but still time-consuming to completely remove the sacrificial material.

Shape fidelity describes the agreement between desired models and printed structures. Notably, current characterizations still focus on the spreading distortion of 2D patterns by imaging analysis for printed grids and sharp angles. A variety of dimension-raising characterizations, such as ultra-deep-field 3D microscopes and computed tomography, would provide more comprehensive evaluations but still lack widespread usage.

Finally, consistency and yield rate required for high-throughput fabrication need further enhancements to fulfill mass manufacturing of 3D printed PEDOTs. Long-term stability (at least days) requires rational ink designs for sufficient fabrication

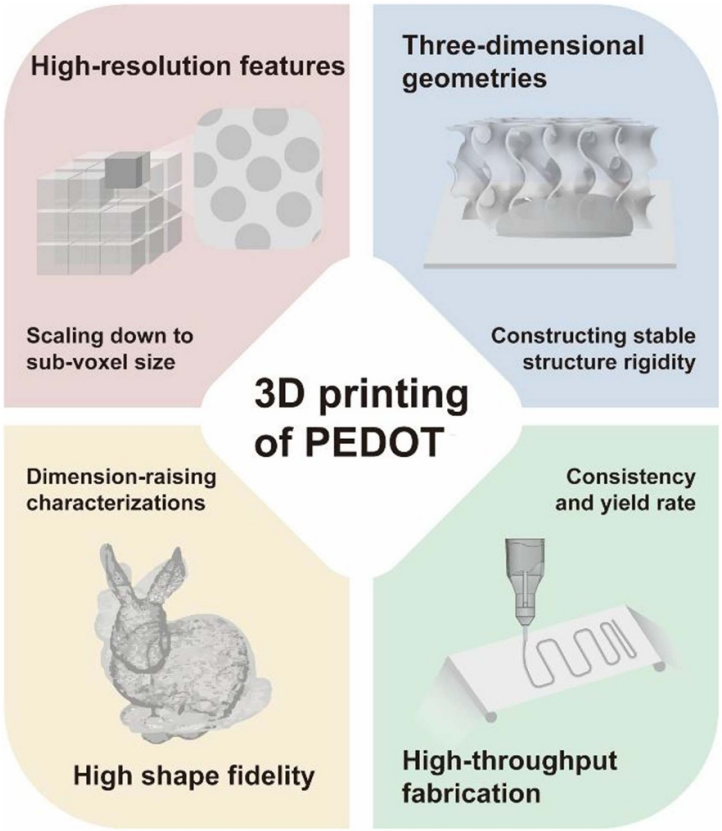

Figure 20. Overview of existing challenges in 3D printing of PEDOTs.

time-window against sedimentation, hydrolysis, and spontaneous chain-folding.

Advances in science and technology to meet challenges

To address the above issues, recent efforts have been devoted to both material designs and technical developments.

Cross-scale material designs enable 3D-printable PEDOTs-based inks by synthesis, compositing, or regulation. In the early stage of this field, nozzle-based printing has attracted wide attention due to its low cost and material compatibility. This technique usually relies on the sol-gel transition induced by the shear-yielding properties of precursor inks to construct structures after deposition. Doping printable materials as the ink matrix is one of the most straightforward methods but usually compromises PEDOTs for their low solid content. A milestone work is that Yuk *et al* proposed a lyophilization-redispersion strategy to prepare PEDOT:PSS nanofibril inks [167]. By adjusting the solid content, the controllable ink directly facilitates high-resolution (30 μm) and high-throughput fabrication of conducting polymers. To inhibit the components' competition effect, another promising route uses secondary dopants to tune the intermolecular interactions inside PEDOTs-based inks. For example, by incorporating ionic liquid colloids into PEDOT:PSS, the enhanced hydrogen bonding between PEDOT chains induces PEDOT:PSS colloidal stacking, and thus shear-yielding behaviors for printing [168]. All these chain conformational changes of PEDOT:PSS achieve a more controllable and scalable rheological regulation. Despite recent advances in rheology regulation, the low-density polymer network nature still limits shear yield stress to commonly less than 1 kPa, one order of magnitude lower than typical printable polymers. Photopolymerizations have been widely used in 3D-printed polymers, but are still impeded by the absorption competition between PEDOT-based materials and photoinitiators at the near-ultraviolet wavelengths. Hence, optimizing the ratio of PEDOTs to photo-sensitive dopants is one of the hot topics in this field. Notably, 3,4-ethylenedioxythiophene (EDOT) with ease of stable dispersion could be ingeniously used as the photosensitive core. For example, EDOT can react with photocatalysts via a double hydrogen-atom transfer process to trigger its dehydrogenation and photopolymerization, facilitating 3D PEDOT:PSS conductive structures with high resolution (220 nm) [169].

Advanced printing techniques introduce field assistance for enhancing forming performance. For example, embedded 3D printing utilizes a bath matrix to trap and provide a buoyancy field to support deposited PEDOTs-based architectures in space [170]. The supporting bath replaces the surroundings of printed inks (typically the air and substrates)

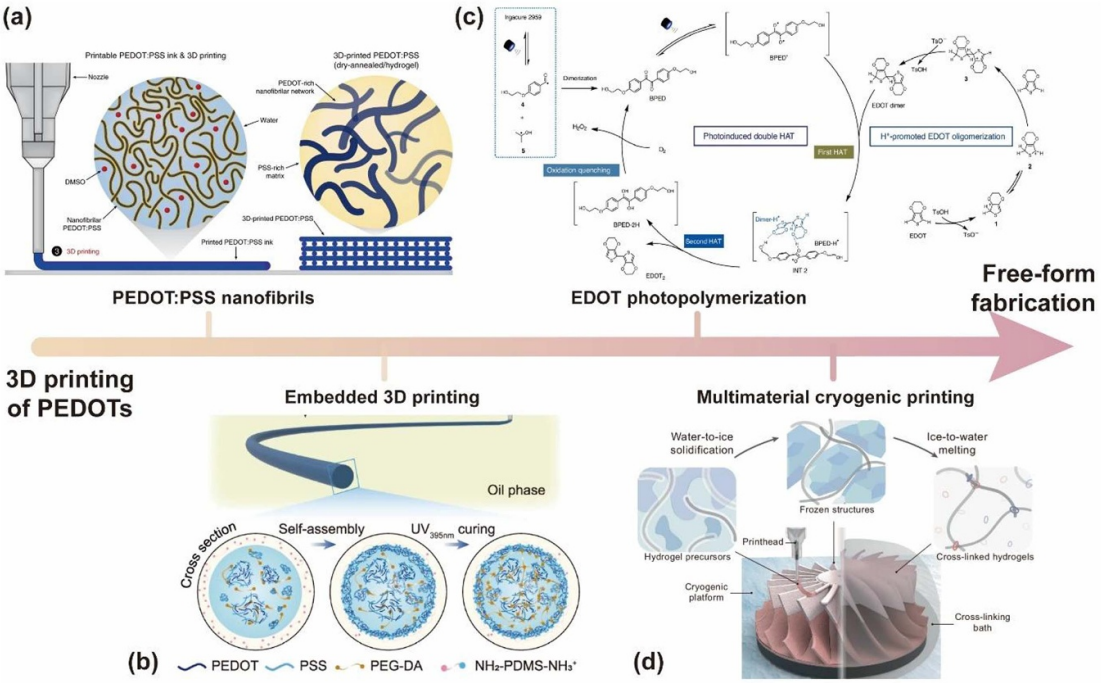

Figure 21. Designed strategies for 3D printing of PEDOTs. (a) Rheology regulation with varying PEDOT:PSS nanofibril concentrations. Reproduced from [167]. CC BY 4.0. (b) Embedded 3D printing of PEDOT:PSS colloidal particles with irradiation assistance. Reproduced from [170]. CC BY 4.0. (c) Photoinduced polymerization of EDOT. Reproduced with permission from [169]. CC BY-NC 4.0. (d) Multimaterial cryogenic printing of 3D hydrogel-based machines. Reproduced from [171]. CC BY 4.0.

and weakens the capillary-driven instability in precise structures. External physical fields like cryogenic temperature can facilitate rapid yet reversible solidification of printed structures to trade off shape fidelity and mechanical robustness. By harnessing all-in-cryogenic solvent phase transition, multimaterial cryogenic printing enables generalized fabrication for 3D hydrogel machines with material diversity and geometrical complexity [171].

This progress in 3D-printability also enables the introduction of diverse components for sophisticated functions [172]. A good example is that the introduction of mechanical phases enables remarkably improved toughness and stretchability [17]. Composing adhesive hydrogel matrix provides PEDOTs-based devices with reliable conformability.

Concluding remarks

3D-printed PEDOTs have already made significant progress in customizing high-resolution 3D structures. This fabrication capability facilitates diverse PEDOT:PSS-based machines and robots for implantable stimulating, wearable sensing, and responsive actuating. However, this technique is still at the laboratory stage, where engineered systems require in-depth investigations on multimaterial compatibility and consistency in high-throughput fabrication. Further developments will advance with both polymer science and precise manufacturing toward the free-form fabrication of high-performance PEDOTs.

Acknowledgments

We acknowledge the National Natural Science Foundation of China (Grant Nos T2293725, 52473179, 5237318, 524B2047), Science and Technology Commission of Shanghai Municipality under Grant 24511103400, and New Cornerstone Science Foundation through the XPLORER PRIZE.

13. PEDOT-based organic electrochemical transistors

*Meijing Wang, Chi-hyeong Kim, Jiaxin Fan**
Department of Chemical Engineering, Polytechnique Montreal, Québec, Canada

*Email: jiaxin.fan@etud.polymtl.ca

Status

PEDOT-based transistors play a key role in driving the advancements of flexible, stretchable, and sustainable bioelectronics [173]. By leveraging the unique properties of PEDOT-based materials as organic mixed ionic–electronic conductors (OMIECs), including high conductivity, mixed ionic-electronic transport, biocompatibility, stability in aqueous environment, and compatibility with low-cost scalable fabrication techniques, these transistors expand into a wide range of applications, ranging from biosensing, neural interfacing, and wearable electronics to neuromorphic computing, demonstrating the potential to revolutionize health monitoring, disease diagnosis, and AI hardware [174].

PEDOT-based materials have been explored in different transistor configurations; OECTs stand out as the most widely studied due to their suitability in bioelectronic applications. OECT operation relies on the reversible electrochemical doping/dedoping of the channel, a process that occurs across the entire film thickness. During gating, ions from the electrolyte penetrate the OMIEC channel and modulate its doping state, resulting in changes in the channel conductivity. This distinguishes OECTs from field-effect transistors, where charge modulation occurs primarily at the semiconductor/dielectric or semiconductor/electrolyte interface. The volumetric gating in OECTs enables high transconductance (g_m, 0.1–100 mS), supporting efficient signal amplification with high signal-to-noise ratios. In addition, low operating voltages (<1 V) due to electrolyte gating and the mixed ionic-electronic conduction of PEDOT-based materials are well suited for interacting with biological environments, allowing efficient transduction of ion-based biological signals into electrical outputs. To evaluate the OECT performance independently of device geometries, the figure of merit (μC^*) was introduced, which is defined as the product of the channel volumetric capacitance (C^*) and the charge carrier mobility (μ) within the channel [175].

Recent progress in PEDOT-based OECT research has focused on improving device performance for diverse applications through device architecture engineering, material design, and novel fabrication strategies for flexible and stretchable bioelectronics. Innovative device structures, such as the vertical device architecture (figures 22(a) and (b)), have been shown to improve device properties, enabling fast switching speed (<1 ms) [176–178]. As the demand for soft electronics increases, methods such as pre-stretching (figure 22(c)) [179] have been investigated to achieve fully flexible and stretchable OECTs. Pre-stretching creates buckled or wavy structures that relieve mechanical strain and preserve electrical conduction during deformation. To meet these mechanical and functionality requirements, PEDOT-based materials have been blended with various additives and/or tailored through functionalization to enhance their mechanical and electrical properties for high performance OECTs. In addition, gel electrolytes were investigated to achieve fully stretchable PEDOT-based OECTs [176, 180]. The fabrication of soft OECTs has been demonstrated by rapid and cost-effective additive manufacturing techniques [181]. 3D printing, in particular, has several advantages, including fast prototyping, easy customization with digital pattern design, and a wide range of material selection. Despite these advances, some key challenges remain in understanding the device operation, addressing limitations in depletion-mode device performance, and developing sustainable device materials, which are discuss in the following section.

Current and future challenges

The challenges are discussed from multiple perspectives, including mechanistic understanding of device operation, performance limitations due to depletion mode operation, challenges in soft electronics, and requirements for sustainable development.

The operation of OECTs is governed by interactions between OMIECs and electrolytes, involving electronic transport, ionic transport, and ionic-electronic coupling. Such mixed transport leads to complex working mechanisms in PEDOT-based OECTs that remain insufficiently understood, particularly in different PEDOT systems interfaced with diverse electrolytes [182]. In PEDOT:PSS, mixed conduction has been demonstrated to depend on material composition and microstructure. Electronic transport is facilitated by π-stacked crystallites, and ionic transport primarily occurs within the amorphous regions. Therefore, achieving an optimal balance between the two types of transport is essential for tailoring device performance for specific applications. However, establishing a comprehensive framework that correlates material composition, microstructure, and properties, especially under device operation, remains challenging. The inherent structural heterogeneity of PEDOT-based materials makes it difficult to elucidate and resolve localized structure-property relationships. A major obstacle is that the current operando characterization techniques have limited spatial resolution for mapping localized ionic and electronic processes during device operation.

Other significant challenges for further improvement of PEDOT-based transistors involve reducing their power consumption. Most PEDOT-based

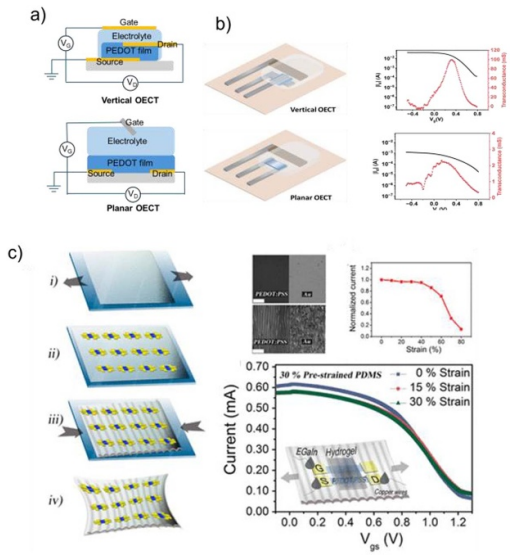

Figure 22. (a) Cross-sectional schematics of vertical and planar OECTs. (b) Schematics of vertical and planar OECTs and their corresponding transfer and transconductance curves. Reproduced from [176]. CC BY 4.0. (b) Stretchable OECTs fabricated on pre-stretched PDMS substrate via parylene transfer. Transfer curves of the stretchable OECTs under different strains. Reprinted with permission from [179]. Copyright (2017) American Chemical Society.

OECTs work in depletion mode (normally ON), which causes relatively high power consumption and limits their application in certain integrated circuits. Additionally, PEDOT-based transistors typically have high OFF currents, limiting their capability of achieving high ON/OFF ratios. For instance, PEDOT:PSS OECTs commonly exhibit ON/OFF ratios in the range of 10^3–10^4 and switching times on the order of milliseconds, depending on device structure, channel dimensions, and material compositions. Reported figure of merit μC^* values typically range from tens to hundreds of F cm^{-1} V^{-1} s^{-1}, depending on composition and microstructure of the channel material.

Mechanical flexibility and stretchability pose another critical challenge for achieving high-performance PEDOT-based transistors in wearable and conformal electronics. Blending soft insulative additives into PEDOT-based OMIECs to improve stretchability requires a careful selection of materials since it may degrade their EC and/or OECT performance. Additionally, while improvements in mechanical stretchability have been demonstrated for PEDOT-based materials, achieving consistent device performance under repeated mechanical strain over long terms remains challenging. Improving the mechanical durability of PEDOT-based transistors is essential for realizing their applications for long-term wearable health monitoring and electronic skin.

Lastly, with the global trend shifting toward more sustainable and greener technology approaches, it is important to take sustainability into consideration for electronic device design. Despite the improved sustainability for certain PEDOT formulations, achieving transistors that are biodegradable or recyclable without compromising their device performance is crucial for their adoption in sustainable electronics to address pressing concerns for electronic waste.

Advances in science and technology to meet challenges

Recent advances in PEDOT-based OECT technologies align with the challenges discussed in the previous section. In particular, developments in device structure, characterization techniques, material design, and fabrication approaches aim to address key limitations, such as low ionic transport kinetics, high power consumption, mechanical durability in flexible devices, and the need for sustainable electronic materials.

To address the limited mechanistic understanding of mixed ionic-electronic transport in PEDOT-based OECTs, the advancement of operando and *in situ* characterization techniques has greatly deepened our understanding of device operation (figure 23(a)) [37]. Techniques such as EQCM and x-ray fluorescence have been utilized to monitor ionic transport both qualitatively and quantitatively [183]. To establish microstructure-property relationships in PEDOT systems, which are characterized by intrinsic heterogeneity, the development and application of scanning probe techniques are essential. Scanning electrochemical cell microscopy presents significant potential for investigating localized electrochemical properties. Integrating these complementary techniques will enable simultaneous probing of electronic, ionic (including solvent-related), structural, and electrochemical properties, providing a comprehensive understanding of the complex mechanisms in the operation of PEDOT OECTs. Computational modeling at the molecular and atomic levels can provide further insights into device operation by elucidating ion-polymer interactions, charge transport pathways, and the coupling between ionic and electronic processes in OMIECs [37]. To draw comprehensive conclusions across different PEDOT systems, it is important to study them systematically to summarize both general trends and case-specific behaviors, which is critical for designing and optimizing PEDOT-based devices.

To overcome the performance limitations associated with the depletion-mode operation and high power consumption, strategies in device and material engineering have been proven to be effective in further improving the performance of PEDOT transistors. Tailoring PEDOT formulations through chemical treatment is being explored to realize accumulation-mode transistors. For example, introducing aliphatic amines, such as polyethyleneimine, diethylenetriamine, and 1,8-diazabicyclo[5.4.0]undec-7-ene, into PEDOT:PSS

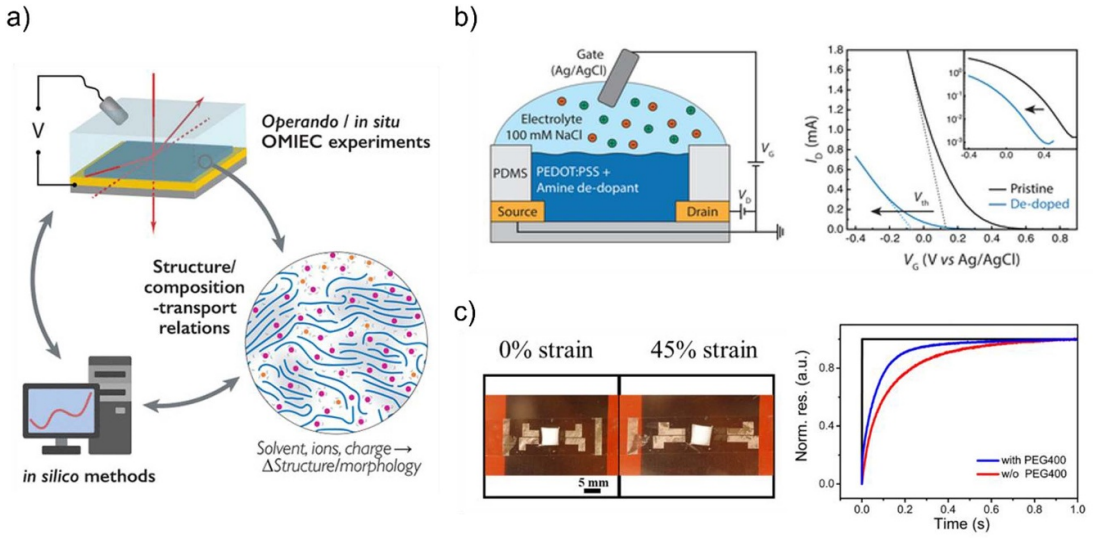

Figure 23. (a) Operando characterizations reveal the structure-property relationships of OMIEC. Reproduced with permission from [37]. CC BY-NC-ND 4.0. (b) Enhancement-mode OECT using amine as de-dopant and their corresponding transfer characteristics. Reproduced from [184]. CC BY 4.0. (c) Stretchable OECTs with PEDOT:PSS/PEG channel under different strains and the normalized time response of I_{ds} during de-doping for channels with and without PEG400. Reproduced from [185].

films as de-dopants, has been shown to enable accumulation mode operation (figure 23(b)), reducing the drain current by a factor of 15–20x at zero gate potential [184]. Modification of the device geometries and materials, such as introducing additional dielectric layers to suppress leakage current and utilizing non-aqueous electrolytes, allows for improved performance. The additional dielectric layer can effectively reduce the parasitic leakage pathways and improve device gating. Non-aqueous electrolytes have a wider electrochemical stability window, supporting efficient ionic transport in the device. Developing OECTs with reduced OFF current and operating in accumulation mode would greatly reduce power consumption and enhance sensitivity, which helps to broaden their applications further.

To address challenges associated with mechanical durability for soft electronics, PEDOT-based materials have been combined with elastomers and plasticizers to achieve higher mechanical stretchability while maintaining electrical performance during deformation. For instance, PEG was incorporated into PEDOT:PSS to enhance EC and mechanical stretchability. In this case, PEG also acts as an ionic conductor that further helps ion transport, leading to faster device response speed (figure 23(c)) [185]. To obtain improved PEDOT composites as OMIECs for high performance OECTs, when designing additive materials, various properties and the microstructure of the resulting OMIECs should be considered.

Finally, to meet the increasing demand for sustainable electronics, recent research has explored self-healing PEDOT formulations in transistors to extend device lifetime for long-term wearable applications. Self-healing materials can recover electrical and/or mechanical functionality after mechanical damage through polymer interactions, improving device durability during repeated deformation. Additionally, research efforts are aimed toward developing biodegradable and recyclable PEDOT derivatives, along with utilizing solution-based and energy-efficient manufacturing techniques. These advancements would boost PEDOT-based transistors toward green electronics, reducing environmental impact while expanding their potential applications. These developments highlight how continued innovation in PEDOT-based materials, device architectures, and characterization techniques can contribute to the advancement of bioelectronics, including neural interfaces, wearable monitoring platforms, and integrated healthcare systems.

Concluding remarks

PEDOT-based transistors are key technology platforms for advancing biosensing and bioelectronic applications, particularly for interfacing with soft biological systems. Promising research opportunities exist for PEDOT-based transistors, especially in understanding operation mechanisms, optimizing material and device designs, and improving sustainability. Continued research and development will push boundaries for the applications of PEDOT-based transistors, shaping the future of flexible, intelligent, and green electronics.

Acknowledgments

M W acknowledges Fonds de recherchedu Québec (FRQNT) for a Doctoral Research Scholarship. J F acknowledges support from the Natural Science and Engineering Council Canada (NSERC) Postdoctoral Fellowship.

14. Advancing bioelectronics with PEDOT: neuromodulation, stretchable devices, and neuromorphic computing

*Daniel T Simon**, *Klas Tybrandt and Simone Fabiano*
Laboratory of Organic Electronics, ITN, Linköping University, Norrköping, Sweden

*Email: daniel.simon@liu.se

Status

PEDOT has emerged as one of the most widely studied conducting polymers for bioelectronics—and bio-inspired—applications over the past two decades, with the PEDOT:PSS formulation playing a pivotal role in enabling stable and high-performance devices. By the late 1990s, conducting polymers such as polypyrrole were already being explored for neuroscience applications to stimulate cell growth morphologies. With the rise of PEDOT:PSS in the late 1990s, studies demonstrating its favorable combination of high conductivity, mechanical flexibility, electrochemical stability, and aqueous dispersibility made it a strong contender for neural interfaces and biosensors. Early work by Inganäs *et al* and Marfn *et al* demonstrated PEDOT:PSS coatings that lowered impedance and improved charge injection capacity [186] and the first PEDOT:PSS biosensors [107]. These breakthroughs fostered continued refinement for biocompatibility and durability, ensuring devices remain functional in reactive, body-temperature, and protein-rich environments.

Today, PEDOT-based technologies are widely pursued for stimulation and recording in clinical and research settings (figure 24(a)). Achieving low-impedance, high-capacitance electrode surfaces that interface seamlessly with tissue remains a central goal in neural implants (e.g. cochlear implants, deep-brain stimulators, and emerging platforms like Neuralink). Further advances, such as new coatings to improve water stability and biofunctionalization, and strategies for *in situ* polymerization [187], promise to enhance how PEDOT:PSS systems integrate with the body, unlocking more sophisticated neuromodulation and biosensing capabilities.

Despite PEDOT's tendency to be somewhat brittle, a large variety of flexible thin-film devices have been made possible by leveraging its stability and versatility. Moving beyond flexible toward truly deformable devices requires softer and more stretchable formulations [35]. Two main approaches have recently been pursued: plasticized PEDOT composites [188] and PEDOT-based conductive hydrogels [189] (figure 24(b)). Plasticizers such as glycerol, PEG, ionic liquids, and surfactants can reduce the Young's modulus of PEDOT:PSS from about 500 MPa to <50 MPa and greatly increase fracture strain, although plastic deformation often remains an issue. In parallel, conductive hydrogels that incorporate a large fraction of water and hydrogel-forming polymers can achieve Young's moduli well below 100 kPa [189], making them attractive for emerging bioelectronic applications where mechanical matching with son tissues is crucial. Ongoing developments in material processing, stability, and performance are laying the groundwork for transitioning these stretchable PEDOT formulations from research prototypes to viable medical devices.

In neuromorphic electronics, a bio-inspired field that emulates the structure and function of the nervous system in hardware to enable devices that learn and adapt in ways reminiscent of the brain, PEDOT:PSS has become a cornerstone material due to its mixed ionic-electronic conductivity, low operating voltages, and biocompatibility. These characteristics allow it to replicate synaptic functions such as short- and long-term plasticity, spike-timing-dependent plasticity, and adaptation, making it suitable for artificial synapses and neuromorphic computing [190]. Advanced PEDOT:PSS devices can support over 500 discrete conductance states and consume as little as 10 pJ per switching event, enabling energy-efficient neural computation [191]. PEDOT:PSS has also demonstrated real-time neurotransmitter-mediated synaptic plasticity [192] and can closely mimic the structural plasticity of biological systems [193] (figure 24(c)). These attributes highlight its potential for brain–machine interfaces and adaptive prosthetics, potentially enabling seamless integration between biological and artificial networks.

Current and future challenges

Despite remarkable progress, several obstacles must be overcome to ensure the long-term viability and broader adoption of PEDOT-based devices and technologies. In neuromodulation and neuro-recording, one major challenge is maintaining performance in complex, reactive, and dynamic biological settings, where mechanical stress, biofouling, and immune responses can degrade device integrity over time. For chronic implants, delamination or degradation of PEDOT:PSS coatings can lead to increased impedance and lower signal quality. Repeated stimulation at high charge density regimes or near hydrolysis voltages can further exacerbate performance degradation [194], underscoring the need for stable electrode chemistries over repeated cycles.

Controlling dopant and additive distributions in PEDOT remains an additional hurdle, as there is often a trade-off between achieving high conductivity and maintaining high electrochemical capacitance. Although *in situ* polymerization methods [187] show promise in addressing these trade-offs, scalability and reproducibility remain open questions. In stretchable PEDOT materials, a key challenge is achieving high conductivity alongside softness and reversible

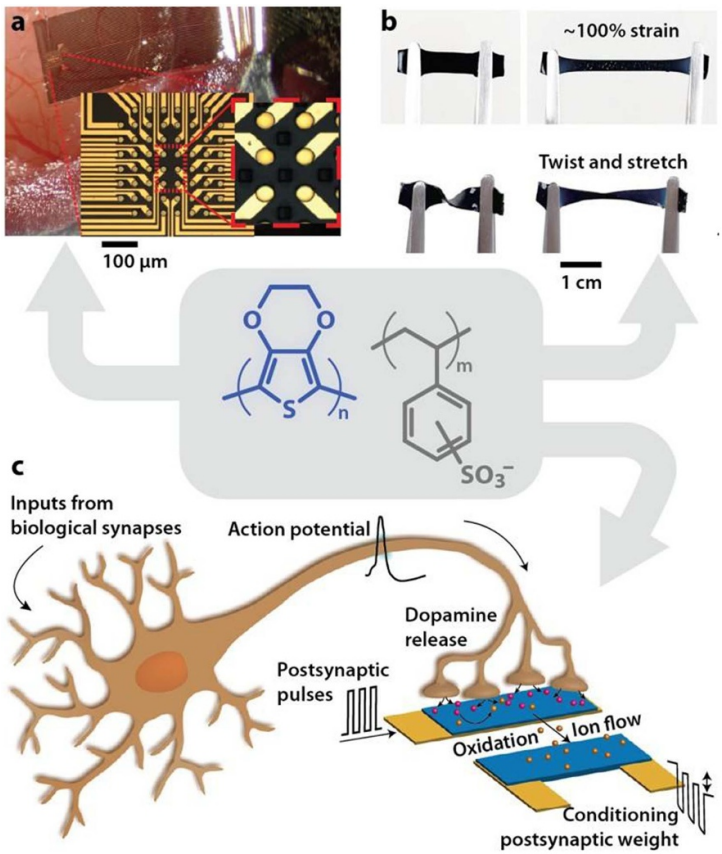

Figure 24. Versatility and utility of PEDOT:PSS in bioelectronics. (a) PEDOT:PSS-coated electrodes for effective stimulation and recording of neural signals from mouse cortex. (b) PEDOT:PSS + poly(vinyl alcohol) 'double network' hydrogel under stretching, twisting, and twisted stretching, showing that the hydrogel can survive at large strains. (c) Integration of biological neurons with PEDOT:PSS-based neuromorphic transistor. (a) Reproduced with permission from Uguz and Shepard, *Science Advances* (2022). CC BY-NC 4.0. (b) [189] John Wiley & Sons. © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Reproduced from [192], with permission from Springer Nature.

mechanical properties. While hydrogels can be very son, they often lack sufficient conductivity, and more conductive gels tend to be relatively stiff. Processing methods for PEDOT-based hydrogels can also be restrictive, limiting film thicknesses and device architectures. Similarly, plasticized PEDOT often exhibits stiffness in the MPa range or faces possible toxicity and leakage of plasticizers. Combining ultra-softness, high conductivity, and good processability is vital for the future of stretchable bioelectronics.

In neuromorphic systems, ensuring long-term stability is particularly pressing. Ion diffusion, material degradation, and environmental factors such as humidity and oxygen can compromise the retenfon of conductance states over prolonged operation. Encapsulation and solid-state electrolytes can help but may add cost, complexity, and limit the device's direct interaction with its surroundings. Scaling PEDOT:PSS devices to sub-micron dimensions for high-density arrays also introduces challenges in reproducibility, uniformity, and retention of analogue-like conductance levels. Access devices (secondary circuit elements) can improve state retention but reduce overall network density, a limitation for large-scale artificial neural networks. Finally, most current research involves planar (2D) device architectures, which are inherently limited in emulating the complexity and interconnectivity of the nervous system. Realizing more 3D designs is essential for advanced neuromorphic networks.

Advances in science and technology to meet challenges

Addressing these challenges calls for coordinated efforts in material design, device architecture, and fabrication strategies. In neuromodulation and neural recording, the development of new PEDOT formulations and processing methods that integrate seamlessly with tissue is a priority. Approaches that incorporate 3D electrode geometries, porous scaffolds, or hydrogel architectures can increase surface area, improve cell infiltration, and reduce tissue damage [195, 196]. Functionalization of PEDOT:PSS coatings with biomolecules, growth factors, or antifouling layers can further enhance biocompatibility, open opportunities for localized drug delivery, and offer controlled release of signaling molecules. Strengthening the mechanical resilience and electrical stability of PEDOT-based electrodes paves the

way toward more reliable long-term interfaces for implantable neuromodulation.

For stretchable PEDOT systems, a crucial strategy is designing morphologies that allow for robust electrical conduction without mechanically 'locking' the network, thereby preserving softness. Inspiration can be drawn from composites of inorganic nanomaterials where sliding networks of nanoparticles, nanosheets, or nanowires maintain electrical contact even under strain. PEDOT's molecular tunability—from backbone structure to doping—provides an expansive toolbox for realizing sliding or transiently bonded networks. Achieving truly reversible liquid-to-solid transitions without compromising electrical properties would enable even more advanced bioelectronic modalities that can adapt and conform to changing tissues.

In neuromorphic computing, innovations in material formulations—such as blending PEDOT:PSS with stabilizing agents or using crosslinking strategies—can mitigate ion diffusion and improve long-term reliability. Achieving high-resolution device arrays requires fabrication methods with sub-micron precision, possibly leveraging additive manufacturing or other printing-based techniques that balance miniaturization with energy efficiency. Advanced device architectures, including in-operando polymerization, allow dynamic control of PEDOT channel growth for extended memory retention and reduced reliance on external circuits. This approach can be further extended to 3D designs, moving away from planar arrays toward volumetric networks that better emulate the complex connectivity of the brain. Collectively, these advancements in materials, processing, and device design will help unlock the full potential of PEDOT:PSS in scalable, energy-efficient, and biologically integrated neuromorphic hardware.

Concluding remarks

PEDOT has evolved from an emerging conducting polymer to a sophisticated platform underpinning modern bioelectronic applications in neuromodulation, stretchable devices, and neuromorphic computing. Building on its exceptional chemical, mechanical, and electrochemical properties, researchers are now engineering PEDOT-based interfaces that seamlessly integrate with biological systems for more effective implantable therapies, son and wearable devices, and highly efficient neural-inspired computing architectures. While key challenges remain in ensuring long-term stability, scalability, and biocompatibility, the continuing development of novel formulations, architectures, and processing methods ensures that PEDOT—and, more broadly, organic bioelectronics—will play a defining role in shaping the future of healthcare and advanced computing. By tackling these challenges head-on, the field stands poised to deliver transformative innovations in patient care and bioelectronic technologies.

Acknowledgments

We gratefully acknowledge support by the Knut and Alice Wallenberg Foundation, the Swedish Research Council, the Swedish Foundation for Strategic Research, and the European Research Council (Grants 834677, 101089075).

Data availability statement

No data to report.

ORCID iDs

Fabio Cicoira 0000-0002-0047-608X
Erica Colaprico 0000-0003-0600-3408
Simone Fabiano 0000-0001-7016-6514
Jiaxin Fan 0000-0001-6033-174X
Guoying Gu 0000-0002-0923-4319
Amali G Guruge 0000-0002-2202-9061
Laure V Kayser 0000-0001-7143-2677
Jeonghun Kwak 0000-0002-4037-8687
Junghyun Lee 0000-0001-7369-2384
Jinhao Li 0009-0001-1535-3664
George G Malliaras 0000-0002-4582-8501
David C Martin 0000-0003-1195-3838
Alexandra Sandéhn 0009-0004-1403-1868
Daniel T Simon 0000-0002-2799-3490
Jeong Han Song 0009-0000-5628-7635
Alessandro Troisi 0000-0002-5447-5648
Klas Tybrandt 0000-0002-9845-446X
Qingshuo Wei 0000-0002-2181-4877
Shun Watanabe 0000-0001-7377-6043
Yuhang Wu 0000-0001-8043-8181
Igor Zozoulenko 0000-0002-6078-3006

References

[1] Tian Y, Wei Y, Wang M, Wang J, Li X, Qin X and Zhang L 2025 Ultra-stretchable, tough, and self-healing polyurethane with tunable microphase separation for flexible wearable electronics *Nano Energy* **139** 110908
[2] Yang X, Chen W, Fan Q, Chen J, Chen Y, Lai F and Liu H 2024 Electronic skin for health monitoring systems: properties, functions, and applications *Adv. Mater.* **36** 2402542
[3] Park J, Lee Y, Cho S, Choe A, Yeom J, Ro Y G, Kim J, Kang D-H, Lee S and Ko H 2024 Soft sensors and actuators for wearable human–machine interfaces *Chem. Rev.* **124** 1464–534
[4] Jahandar M, Kim S and Lim D C 2024 Transforming wearable technology with advanced ultra-flexible energy harvesting and storage solutions *Nat. Commun.* **15** 8149
[5] Guo H S *et al* 2020 Universally autonomous self-healing elastomer with high stretchability *Nat. Commun.* **11** 2037
[6] Li Y *et al* 2022 Recent progress on self-healable conducting polymers *Adv. Mater.* **34** 2108932

[7] Wang Y *et al* 2017 A highly stretchable, transparent, and conductive polymer *Sci. Adv.* **3** e1602076
[8] Zhang S and Cicoira F 2017 Water-enabled healing of conducting polymer films *Adv. Mater.* **29** 1703098
[9] Li Y, Li X, Zhang S, Liu L, Hamad N, Bobbara S R, Pasini D and Cicoira F 2020 Autonomic self-healing of PEDOT: PSS achieved via polyethylene glycol addition *Adv. Funct. Mater.* **30** 2002853
[10] Oh J Y, Kim S, Baik H-K and Jeong U 2016 Conducting polymer dough for deformable electronics *Adv. Mater.* **28** 4455–61
[11] Zhou X *et al* 2024 Conducting polymer films and bioelectrodes combining high adhesion and electro-mechanical self-healing *J. Mater. Chem.* C **12** 5708–17
[12] Li Y, Zhang S, Hamad N, Kim K, Liu L, Lerond M and Cicoira F 2020 Tailoring the self-healing properties of conducting polymer films *Macromol. Biosci.* **20** 2000146
[13] Lin H-W, Wu C-T, Chang C-W, Lo T-Y, Chen H-R and Chen J-T 2024 Enhancing conductivity and self-healing in PEDOT: PSS/poly (ionic liquid) elastomers for sensor applications *ACS Appl. Polym. Mater.* **6** 14740–8
[14] Alehosseini M, Kadumudi F B, Revesz S, Karimi Reikandeh P, Henriksen J R, Zsurzsan T-G, Spangenberg J and Dolatshahi-pirouz A 2025 Self-maintainable electronic materials with skin-like characteristics enabled by Graphene-PEDOT: PSS fillers *Adv. Sci.* **12** 2410539
[15] Kim J, Fan J, Petrossian G, Zhou X, Kateb P, Gagnon-lafrenais N and Cicoira F 2024 Self-healing, stretchable and recyclable polyurethane-PEDOT:PSS conductive blends *Mater. Horiz.* **11** 3548–60
[16] Zhou X, Rajeev A, Subramanian A, Li Y, Rossetti N, Natale G, Lodygensky G A and Cicoira F 2022 Self-healing, stretchable, and highly adhesive hydrogels for epidermal patch electrodes *Acta Biomater.* **139** 296–306
[17] Zhou T *et al* 2023 3D printable high-performance conducting polymer hydrogel for all-hydrogel bioelectronic interfaces *Nat. Mater.* **22** 895–902
[18] Farmer E E, Gao Y Q, Lenzoni G, Wolfender J L and Wu Q 2020 Wound- and mechanostimulated electrical signals control hormone responses *New Phytol.* **227** 1037–50
[19] Diacci C, Abedi T, Lee J W, Gabrielsson E O, Berggren M, Simon D T, Niittylä T and Stavrinidou E 2021 Diurnal *in vivo* xylem sap glucose and sucrose monitoring using implantable organic electrochemical transistor sensors *iScience* **24** 101966
[20] Bihar E *et al* 2023 Self-healable stretchable printed electronic cryogels for *in-vivo* plant monitoring *npj Flex. Electron.* **7** 48
[21] Armada-moreira A, Dar A M, Zhao Z, Cea C, Gelinas J, Berggren M, Costa A, Khodagholy D and Stavrinidou E 2023 Plant electrophysiology with conformable organic electronics: deciphering the propagation of Venus flytrap action potentials *Sci. Adv.* **9** adh4443
[22] Meder F, Saar S, Taccola S, Filippeschi C, Mattoli V and Mazzolai B 2021 Ultraconformable, self-adhering surface electrodes for measuring electrical signals in plants *Adv. Mater. Technol.* **6** 2001182
[23] Yang Y, He T, Ravindran P, Wen F, Krishnamurthy P, Wang L, Zhang Z, Kumar P P, Chae E and Lee C 2024 All-organic transparent plant e-skin for noninvasive phenotyping *Sci. Adv.* **10** adk7488
[24] Armiento S, Bernacka-wojcik I, Dar A M, Meder F, Stavrinidou E and Mazzolai B 2025 Powering a molecular delivery system by harvesting energy from the leaf motion in wind *Bioinsp. Biomim.* **20** 016023
[25] Oikonomou V K *et al* 2024 eSoil: a low-power bioelectronic growth scaffold that enhances crop seedling growth *Proc. Natl Acad. Sci. USA* **121** e2304135120
[26] Strand E J, Palizzi M J, Crichton C A, Renny M N, Bihar E, McLeod R R and Whiting G L 2023 Multimodal operation of printed electrochemical transistors for sensing in controlled environment agriculture *Sens. Actuators* B **387** 133763
[27] Mousavi S A R, Chauvin A, Pascaud F, Kellenberger S and Farmer E E 2013 2013 Glutamate receptor-like genes mediate leaf-to-leaf wound signalling *Nature* **500** 422–6
[28] Kim J J, Allison L K and Andrew T L 2019 Vapor-printed polymer electrodes for long-term, on-demand health monitoring *Sci. Adv.* **5** eaaw0463
[29] Kim J J, Fan R, Allison L K and Andrew T L 2020 On-site identification of ozone damage in fruiting plants using vapor-deposited conducting polymer tattoos *Sci. Adv.* **6** abc3296
[30] Janni M, Cocozza C, Brilli F, Pignattelli S, Vurro F, Coppede N, Bettelli M, Calestani D, Loreto F and Zappettini A 2021 Real-time monitoring of Arundo donax response to saline stress through the application of *in vivo* sensing technology *Sci. Rep.* **11** 18598
[31] Han S, Pasquini D, Sorieul M, Boratto M H, Gatecliff L, Dickson A, Jang S, Davy S, Malliaras G G and Chen Y 2025 Implantable ion-selective organic electrochemical transistors enable continuous, long-term, and *in vivo* plant monitoring *Adv. Sci.* **12** e04283
[32] Wang S *et al* 2024 Highly stretchable, robust, and resilient wearable electronics for remote, autonomous plant growth monitoring *Device* **2** 100322
[33] Miyake T, Haneda K, Nagai N, Yatagawa Y, Onami H, Yoshino S, Abe T and Nishizawa M 2011 Enzymatic biofuel cells designed for direct power generation from biofluids in living organisms *Energy Environ. Sci.* **4** 5008–12
[34] Groenendaal L, Jonas F, Freitag D, Pielartzik H and Reynolds J R 2000 Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future *Adv. Mater.* **12** 481–94
[35] Kayser L V and Lipomi D J 2019 Stretchable conductive polymers and composites based on PEDOT and PEDOT:PSS *Adv. Mater.* **31** 1806133
[36] Boehler C, Aqrawe Z and Asplund M 2019 Applications of PEDOT in bioelectronic medicine *Bioelectron. Med.* **2** 89–99
[37] Wu R, Matta M, Paulsen B D and Rivnay J 2022 Operando characterization of organic mixed ionic/electronic conducting materials *Chem. Rev.* **122** 4493–551
[38] Modarresi M and Zozoulenko I 2022 Why does solvent treatment increase the conductivity of PEDOT:PSS? Insight from molecular dynamics simulations *Phys. Chem. Chem. Phys.* **24** 22073–82
[39] Shi H, Liu C, Jiang Q and Xu J 2015 Effective approaches to improve the electrical conductivity of PEDOT:PSS: a review *Adv. Electron. Mater.* **1** 1500017
[40] Strakosas X, Wei B, Martin D C and Owens R M 2016 Biofunctionalization of polydioxythiophene derivatives for biomedical applications *J. Mater. Chem.* B **4** 4952–68
[41] Ajjan F N, Casado N, Rębiś T, Elfwing A, Solin N, Mecerreyes D and Inganäs O 2016 High performance PEDOT/lignin biopolymer composites for electrochemical supercapacitors *J. Mater. Chem. A* **4** 1838–47
[42] Lo C-Y *et al* 2024 Imidazolium-based sulfonating agent to control the degree of sulfonation of aromatic polymers and enable plastics-to-electronics upgrading *JACS Au* **4** 2596–605
[43] Uva A, Michailovich S, Hsu N S Y and Tran H 2024 Degradable π-conjugated polymers *J. Am. Chem. Soc.* **146** 12271–87
[44] Zahabi N, Petsagkourakis I, Rolland N, Beikmohammadi A, Liu X, Fahlman M, Pavlopoulou E and Zozoulenko I 2025 Deciphering conductivity in PEDOT guided by machine learning: from solvent baths to charge paths *Phys. Rev. Mater.* **9** 105402
[45] Zozoulenko I, Franco-Gonzalez J F, Gueskine V, Mehandzhiyski A, Modarresi M, Rolland N and Tybrandt K 2021 Electronic, optical, morphological, transport, and electrochemical properties of PEDOT: a theoretical perspective *Macromolecules* **54** 5915–34

[46] Yue B et al 2022 Photoexcitation-based supramolecular access to full-scale phase-diagram structures through in situ phase-volume ratio phototuning Angew. Chem., Int. Ed. 61 e202209777
[47] Tran V C, Mastantuoni G, Garemark J, Dreimol C H, Wang X, Berggren M, Zhou Q, Kroon R and Engquist I 2024 Interconnecting EDOT-based polymers with native lignin toward enhanced charge storage in conductive wood ACS Appl. Mater. Interfaces 16 68416–25
[48] Kuang C, Chen S, Liao M, Rahmanudin A, Banerjee D, Edberg J, Tybrandt K, Zhao D and Jonsson M P 2024 Electrically tunable infrared optics enabled by flexible ion-permeable conducting polymer-cellulose paper npj Flex. Electron. 8 55
[49] Karst J, Floess M, Ubl M, Dingler C, Malacrida C, Steinle T, Ludwigs S, Hentschel M and Giessen H 2021 Electrically switchable metallic polymer nanoantennas Science 374 612–6
[50] Chen S et al 2020 Conductive polymer nanoantennas for dynamic organic plasmonics Nat. Nanotechnol. 15 35–40
[51] Duan Y, Chen S and Jonsson M P 2025 Broadband chiroptics with twist-stacked hyperbolic conducting polymer thin films Adv. Mater. 37 2417024
[52] Rajesh M, Manikandan R, Kim B C, Becuwe M, Yu K H and Raj C J 2020 Electrochemical polymerization of chloride doped PEDOT hierarchical porous nanostructure on graphite as a potential electrode for high performance supercapacitor Electrochim. Acta 354 136669
[53] Khan Z et al 2022 Water-in-polymer salt electrolyte for slow self-discharge in organic batteries Adv. Energy Sustain. Res. 3 2100165
[54] Li Y, Wen R, Li P and Fan X 2022 Metallic and low-work-function PEDOT:PSS cathodes for flexible organic solar cells exhibiting over 15% efficiency and high stability ACS Appl. Energy Mater. 5 7692–700
[55] Reza K M, Mabrouk S and Qiao Q 2018 A review on tailoring PEDOT:PSS layer for improved performance of perovskite solar cells Proc. Nat. Res. Soc. 2 02004
[56] Åkerlund L, Emanuelsson R, Hernández G, Ruipérez F, Casado N, Brandell D, Strømme M, Mecerreyes D and Sjödin M 2019 In situ investigations of a proton trap material: a PEDOT-based copolymer with hydroquinone and pyridine side groups having robust cyclability in organic electrolytes and ionic liquids ACS Appl. Energy Mater. 2 4486–95
[57] Lim J-E, Lee S-M, Kim S-S, Kim T-W, Koo H-W and Kim H-K 2017 Brush-paintable and highly stretchable Ag nanowire and PEDOT:PSS hybrid electrodes Sci. Rep. 7 14685
[58] Ge Y, Duan X, Zhang M, Mei L, Hu J, Hu W and Duan X 2018 Direct room temperature welding and chemical protection of silver nanowire thin films for high performance transparent conductors J. Am. Chem. Soc. 140 193–9
[59] Makki H and Troisi A 2022 Morphology of conducting polymer blends at the interface of conducting and insulating phases: insight from PEDOT:PSS atomistic simulations J. Mater. Chem. C 10 16126–37
[60] De Izarra A, Park S, Lee J, Lansac Y and Jang Y H 2018 Ionic liquid designed for PEDOT:PSS conductivity enhancement J. Am. Chem. Soc. 140 5375–84
[61] Keene S T et al 2022 Efficient electronic tunneling governs transport in conducting polymer-insulator blends J. Am. Chem. Soc. 144 10368–76
[62] Modarresi M, Franco-Gonzalez J F and Zozoulenko I 2019 Computational microscopy study of the granular structure and pH dependence of PEDOT:PSS Phys. Chem. Chem. Phys. 21 6699–711
[63] Modarresi M, Mehandzhiyski A, Fahlman M, Tybrandt K and Zozoulenko I 2020 Microscopic understanding of the granular structure and the swelling of PEDOT:PSS Macromolecules 53 6267–78
[64] Modarresi M, Franco-Gonzalez J F and Zozoulenko I 2018 Morphology and ion diffusion in PEDOT:Tos. A coarse grained molecular dynamics simulation Phys. Chem. Chem. Phys. 20 17188–98
[65] Franco-Gonzalez J F and Zozoulenko I V 2017 Molecular dynamics study of morphology of doped PEDOT: from solution to dry phase J. Phys. Chem. A 121 4299–307
[66] Guruge A G, Makki H and Troisi A 2024 Structural properties of conductive polymer blends interfaced with water: computational insights from PEDOT: PSS J. Mater. Chem. C 12 19245–57
[67] Kim D, Franco-Gonzalez J F and Zozoulenko I 2021 How long are polymer chains in Poly(3,4-ethylenedioxythiophene):Tosylate films? An insight from molecular dynamics simulations J. Phys. Chem. A 125 10324–34
[68] Guruge A G, Makki H and Troisi A 2026 Morphological changes in PEDOT:PSS under electrolytes, dopamine, and PEG-400 exposure: a molecular simulation perspective Macromolecules 59 1752–62
[69] Giordani M, Sensi M, Berto M, Di Lauro M, Bortolotti C A, Gomes H L, Zoli M, Zerbetto F, Fadiga L and Biscarini F 2020 Neuromorphic organic devices that specifically discriminate dopamine from its metabolites by nonspecific interactions Adv. Funct. Mater. 30 2002141
[70] Marrink S J and Tieleman D P 2013 Perspective on the Martini model Chem. Soc. Rev. 42 6801–22
[71] Landi A, Reisjalali M, Elliott J D, Matta M, Carbone P and Troisi A 2023 Simulation of polymeric mixed ionic and electronic conductors with a combined classical and quantum mechanical model J. Mater. Chem. C 11 8062–73
[72] Shaw D E et al 2021 Anton 3: twenty microseconds of molecular dynamics simulation before lunch Proc. Int. Conf. for High Performance Computing, Networking, Storage and Analysis pp 1–11
[73] Yang J, Wang Y and Chen Y 2007 GPU accelerated molecular dynamics simulation of thermal conductivities J. Comput. Phys. 221 799–804
[74] Raghuram E, Padmarajan R and Kalpathy S K 2022 Hydrogen bond induced solvent ordering in aqueous poly (sodium p-styrenesulfonate) Polymer 262 125380
[75] Dong B X, Nowak C, Onorato J W, Strzalka J, Escobedo F A, Luscombe C K, Nealey P F and Patel S N 2019 Influence of side-chain chemistry on structure and ionic conduction characteristics of polythiophene derivatives: a computational and experimental study Chem. Mater. 31 1418–29
[76] Prodhan S, Manurung R and Troisi A 2023 From monomer sequence to charge mobility in semiconductor polymers via model reduction Adv. Funct. Mater. 33 2303234
[77] Khodagholy D, Gelinas J N, Thesen T, Doyle W, Devinsky O, Malliaras G G and Buzsáki G 2014 NeuroGrid: recording action potentials from the surface of the brain Nat. Neurosci. 18 310–5
[78] Khodagholy D et al 2013 In vivo recordings of brain activity using organic transistors Nat. Commun. 4 1–7
[79] Jiang Y et al 2022 Topological supramolecular network enabled high-conductivity, stretchable organic bioelectronics Science 375 1411–7
[80] Liu Y et al 2019 Soft and elastic hydrogel-based microelectronics for localized low-voltage neuromodulation Nat. Biomed. Eng. 3 58–68
[81] Lu B, Yuk H, Lin S, Jian N, Qu K, Xu J and Zhao X 2019 Pure PEDOT:PSS hydrogels Nat. Commun. 10 1–10
[82] Zhou W et al 2023 Soft and stretchable organic bioelectronics for continuous intraoperative neurophysiological monitoring during microsurgery Nat. Biomed. Eng. 7 1270–81
[83] O'neill S J K, Huang Z, Li J, Mccune J A, Scherman O A, Ahmed M H, Velasco-bosom S, Malliaras G G, Boys A J and Owens R M 2023 Tissue-mimetic supramolecular polymer networks for bioelectronics Adv. Mater. 35 2207634

[84] Yano H, Kudo K, Marumo K and Okuzaki H 2019 Fully soluble self-doped poly(3,4-ethylenedioxythiophene) with an electrical conductivity greater than 1000 S cm^{-1} *Sci. Adv.* **5** 9492–504
[85] Hagler J, Yeu J, Zhou X, Ducharme G, Amilhon B and Cicoira F 2022 Electrodeposited PEDOT:BF4 coatings improve impedance of chronic neural stimulating probes *in vivo Adv. Mater. Interfaces* **9** 2201066
[86] Horii T, Li Y, Mori Y and Okuzaki H 2015 Correlation between the hierarchical structure and electrical conductivity of PEDOT/PSS *Polym. J.* **47** 695–9
[87] Ouyang L, Musumeci C, Jafari M and Ederth T 2015 Imaging the phase separation between PEDOT and polyelectrolytes during processing of highly conductive PEDOT:PSS films *ACS Appl. Mater. Interfaces* **7** 19764–73
[88] Rivnay J, Inal S, Collins B, Sessolo M, Stavrinidou E, Strakosas X, Tassone C, Delongchamp D and Malliaras G 2016 Structural control of mixed ionic and electronic transport in conducting polymers *Nat. Commun.* **7** 11287
[89] Ouyang J, Xu Q, Chu C, Yang Y, Li G and Shinar J 2004 On the mechanism of conductivity enhancement in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment *Polymer* **45** 8443–50
[90] Kim Y H, Sachse C, MacHala M, May C, Müller-meskamp L and Leo K 2011 Highly conductive PEDOT:PSS electrode with optimized solvent and thermal post-treatment for ITO-free organic solar cells *Adv. Funct. Mater.* **21** 1076–81
[91] Tounakti C, Decorse P and Kouki F 2023 Relationship between enhancement of PEDOT:PSS conductivity by solvent treatment and PSS chain reorganization *J. Polym. Sci.* **61** 582–603
[92] Kumar S, Kurra N and Alshareef H 2016 Enhanced high temperature thermoelectric response of sulphuric acid treated conducting polymer thin films *J. Mater. Chem. C* **4** 215–21
[93] Kim N, Kee S, Lee S, Lee B, Kahng Y, Jo Y, Kim B and Lee K 2014 Highly conductive PEDOT:PSS nanofibrils induced by solution-processed crystallization *Adv. Mater.* **26** 2268–72
[94] He S, Mukaida M, Kirihara K, Lyu L and Wei Q 2018 Reversible protonic doping in poly(3,4-ethylenedioxythiophene) *Polymers* **10** 1065
[95] Guo Z *et al* 2024 Band transport evidence in PEDOT:PSS films using broadband optical spectroscopy from terahertz to ultraviolet region *Commun. Mater.* **5** 26
[96] Yi H T, Gartstein Y N and Podzorov V 2016 Charge carrier coherence and Hall effect in organic semiconductors *Sci. Rep.* **6** 23650
[97] Kang K *et al* 2016 2D coherent charge transport in highly ordered conducting polymers doped by solid state diffusion *Nat. Mater.* **15** 896–902
[98] Yamashita M, Otani C, Shimizu M and Okuzaki H 2011 Effect of solvent on carrier transport in poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) studied by terahertz and infrared-ultraviolet spectroscopy *Appl. Phys. Lett.* **99** 143307
[99] Smith N V 2001 Classical generalization of the Drude formula for the optical conductivity *Phys. Rev. B* **64** 155106
[100] Kim N, Lee B, Choi D, Kim G, Kim H, Kim J, Lee J, Kahng Y and Lee K 2012 Role of interchain coupling in the metallic state of conducting polymers *Phys. Rev. Lett.* **109** 106405
[101] Zotti G, Zecchin S, Schiavon G, Louwet W, Groenendaal L, Crispin X, Osikowicz W, Salaneck W and Fahlman M 2003 Electrochemical and XPS studies toward the role of monomeric and polymeric sulfonate counterions in the synthesis, composition, and properties of poly(3,4-ethylenedioxythiophene) *Macromolecules* **36** 3337–44
[102] Kim D and Zozoulenko I 2019 Why is pristine PEDOT oxidized to 33%? A density functional theory study of oxidative polymerization mechanism *J. Phys. Chem.* B **123** 5160–7
[103] Lang U, Muller E, Naujoks N and Dual J 2009 Microscopical investigations of PEDOT:PSS thin films *Adv. Funct. Mater.* **19** 1215–20
[104] Dauzon E, Mansour A E, Niazi M R, Munir R, Smilgies D M, Sallenave X, Plesse C, Goubard F and Amassian A 2019 Conducting and stretchable PEDOT:PSS electrodes: role of additives on self-assembly, morphology, and transport *ACS Appl. Mater. Interfaces* **11** 17570–82
[105] Yamato H, Ohwa M and Wernet W 1995 Stability of polypyrrole and poly(3,4-ethylenedioxythiophene) for biosensor application *J. Electroanal. Chem.* **397** 163–70
[106] Kirchmeyer S and Reuter K 2005 Scientific importance, properties, and growing applications of poly(3,4-ethylenedioxythiophene) *J. Mater. Chem.* **15** 2077–88
[107] Cui X and Martin D C 2003 Electrochemical deposition and characterization of poly(3,4-ethylenedioxythiophene) on neural microelectrode arrays *Sens. Actuators* B **89** 92–102
[108] Thomas C A, Zong K, Schottland P and Reynolds J R 2000 Poly(3,4-alkylenedioxypyrrole)s as highly stable aqueous-compatible conducting polymers with biomedical implications *Adv. Mater.* **12** 222–5
[109] Tallman D E, Vang C, Wallace G G and Bierwagen G P 2002 Direct electrodeposition of polypyrrole on aluminum and aluminum alloy by electron transfer mediation *J. Electrochem. Soc.* **149** C173–C179
[110] Lee J, Chhatre S, Sitarik P, Wu Y, Baugh Q and Martin D C 2022 Electrochemical fabrication and characterization of organic electrochemical transistors using poly(3,4-ethylenedioxythiophene) with various counterions *ACS Appl. Mater. Interfaces* **14** 42289–97
[111] Bert Groenendaal L, Zotti G, Aubert P-H, Waybright S M and Reynolds J R 2003 Electrochemistry of Poly(3,4-alkylenedioxythiophene) derivatives *Adv. Mater.* **15** 855–79
[112] Mantione D, Casado N, Sanchez-sanchez A, Sardon H and Mecerreyes D 2017 Easy-to-make carboxylic acid dioxythiophene monomer (ProDOT-COOH) and functional conductive polymers *J. Polym. Sci.* A **55** 2721–4
[113] Povlich L K, Cho J C, Leach M K, Kim J, Corey J M and Martin D C 2012 Synthesis, copolymerization, and peptide-modification of carboxylic acid-functionalized 3,4-ethylenedioxythiophene (EDOTacid) for neural electrode interfaces *Biochim. Biophys. Acta* **1830** 4288–93
[114] Sitarik P, Nagane S S, Chhatre S, Wu Y, Baugh Q and Martin D C 2022 Synthesis and characterization of maleimide functionalized poly(3,4-ethylenedioxythiophene) (PEDOT) polymers *Mater. Adv.* **3** 6037–49
[115] Wei B, Liu J, Ouyang L, Kuo C-C and Martin D C 2015 Significant enhancement of PEDOT thin film adhesion to inorganic substrates with EDOT-acid *ACS Appl. Mater. Interfaces* **7** 15388–94
[116] Kim M, Iezzi R J, Shim B S and Martin D C 2019 Impedimetric biosensors for detecting vascular endothelial growth factor (VEGF) based on poly(3,4-ethylene dioxythiophene) (PEDOT)/gold nanoparticle (Au NP) composites *Front. Chem.* **7** 234
[117] Fenoy G E, Azzaroni O, Knoll W and Marmisollé W A 2021 Functionalization strategies of PEDOT and PEDOT:PSS films for organic bioelectronics applications *Chemosensors* **9** 8
[118] Nagane S, Sitarik P, Wu Y, Baugh Q, Chhatre S, Lee J and Martin D C 2020 Functionalized polythiophene copolymers for electronic biomedical devices *MRS Adv.* **5** 943–56
[119] Ouyang L, Kuo C-C, Farrell B, Pathak S, Wei B, Qu J and Martin D C 2015 Poly[3,4-ethylene dioxythiophene (EDOT) -co- 1,3,5-tri[2-(3,4-ethylene dioxythienyl)]-benzene (EPh)] copolymers (PEDOT-co-EPH): optical, electrochemical and mechanical properties *J. Mater. Chem.* B **3** 5010–20

[120] Cocuk N, Wu Y, Lee J, Baugh Q and Martin D C 2025 Influence of boron-containing dopants on the structure and electrochemical properties of poly(3,4-ethylene dioxythiophene) (PEDOT) *J. Mater. Sci.* **60** 18946–67
[121] Subramanian V and Martin D C 2021 Direct observation of liquid-to-solid phase transformations during the electrochemical deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) by liquid-phase transmission electron microscopy (LPTEM) *Macromolecules* **54** 6956–67
[122] Narayan S, Stoica L, Liess A and Reisinger A 2021 Amplicoat®—conductive polymer coating with enhanced durability and performance for chronic implants *2021 Design of Medical Devices Conf., American Society of Mechanical Engineers Digital Collection* (https://doi.org/10.1115/DMD2021-1082)
[123] Zhang P, Zhu B, Du P and Travas-Sejdic J 2024 Electrochemical and electrical biosensors for wearable and implantable electronics based on conducting polymers and carbon-based materials *Chem. Rev.* **124** 722–67
[124] Zhang P and Travas-Sejdic J 2021 Fabrication of conducting polymer microelectrodes and microstructures for bioelectronics *J. Mater. Chem.* C **9** 9730–60
[125] Burtscher B, Diacci C, Makhinia A, Savvakis M, Gabrielsson E O, Veith L, Liu X, Strakosas X and Simon D T 2024 Functionalization of PEDOT:PSS for aptamer-based sensing of IL6 using organic electrochemical transistors *npj Biosensing* **1** 7
[126] Aerathupalathu Janardhanan J and Yu H-H 2024 Recent advances in PEDOT/PProDOT-derived nano biosensors: engineering nano assemblies for fostering advanced detection platforms for biomolecule detection *Nanoscale* **16** 17202–29
[127] Fu X, Cheng W, Wan G, Yang Z and Tee B C K 2024 Toward an AI era: advances in electronic skins *Chem. Rev.* **124** 9899–948
[128] Cui F, Yue Y, Zhang Y, Zhang Z and Zhou H S 2020 Advancing biosensors with machine learning *ACS Sens.* **5** 3346–64
[129] Wang J, Wang D and Hui N 2020 A low fouling electrochemical biosensor based on the zwitterionic polypeptide doped conducting polymer PEDOT for breast cancer marker BRCA1 detection *Bioelectrochemistry* **136** 107595
[130] Meng L, Turner A P F and Mak W C 2020 Tunable 3D nanofibrous and bio-functionalised PEDOT network explored as a conducting polymer-based biosensor *Biosens. Bioelectron.* **159** 112181
[131] Ma L, Jayachandran S, Li Z, Song Z, Wang W and Luo X 2019 Antifouling and conducting PEDOT derivative grafted with polyglycerol for highly sensitive electrochemical protein detection in complex biological media *J. Electroanal. Chem.* **840** 272–8
[132] Zhu B, Bryant D T, Akbarinejad A, Travas-Sejdic J and Pilkington L I 2022 A novel electrochemical conducting polymer sensor for the rapid, selective and sensitive detection of biothiols *Polym. Chem.* **13** 508–16
[133] Ghazal M *et al* 2023 Electropolymerization processing of side-chain engineered EDOT for high performance microelectrode arrays *Biosens. Bioelectron.* **237** 115538
[134] Wu Q *et al* 2023 Flexible 3D printed microwires and 3D microelectrodes for heart-on-a-chip engineering *Biofabrication* **15** 035023
[135] Chan E W C, Sun X and Travas-Sejdic J 2023 Recent progress and future prospects in transient polymer electronics *Macromolecules* **56** 3755–73
[136] Kang S D and Snyder G J 2017 Charge-transport model for conducting polymers *Nat. Mater.* **16** 252–7
[137] Alam J, Xu X, Adu P C O, Meng Q, Zuber K, Afshar S, Kuan H-C and Ma J 2024 Enhancing thermoelectric performance of PEDOT: PSS: a review of treatment and nanocomposite strategies *Adv. Nanocomposites* **1** 16–18
[138] Song J H, Jeong J, Choi Y, Cho S, Imae I and Kwak J 2025 Recent advances in engineering electronic and thermal properties of PEDOT:PSS for efficient thermoelectric energy conversion *J. Mater. Chem.* C **13** 14144–67
[139] Li C A, Shan C, Luo D, Gu X, Le Q, Kyaw A K K, Dong Z, Sun K and Ouyang J 2024 Great enhancement in the seebeck coefficient of PEDOT:PSS by polaron level splitting via π-π overlapping with nonpolar small aromatic molecules *Adv. Funct. Mater.* **34** 2311578
[140] Petsagkourakis I *et al* 2023 Improved performance of organic thermoelectric generators through interfacial energetics *Adv. Sci.* **10** 2206954
[141] Wang X W, Feng Y, Sun K, Chai N, Mai B, Li S, Chen X, Zhao W and Zhang Q 2024 Ultrafast laser-induced excellent thermoelectric performance of PEDOT:PSS films *Energy Environ. Mater.* **7** e12650
[142] Du F P, Zhang H, Yao J-A, Chen S-Y, Xiao J-K, Fu P and Zhang Y-F 2022 Enhanced thermoelectric performance by constructing PEDOT:PSS/graphene quantum dots/single-walled carbon nanotube multilayer films *J. Alloys Compd.* **911** 164998
[143] Park J, Jang J G, Kang K H, Kim S H and Kwak J 2024 High thermoelectric performance in solution-processed semicrystalline PEDOT:PSS films by strong acid-base treatment: limitations and potential *Adv. Sci.* **11** 2308368
[144] Song J H, Park J, Kim S H and Kwak J 2023 Vitamin C-induced enhanced performance of PEDOT:PSS thin films for eco-friendly transient thermoelectrics *ACS Appl. Mater. Interfaces* **15** 2852–60
[145] Song J, Jeong J, Park J, Park G, Imae I and Kwak J 2024 Enhanced performance and stability of PEDOT:PSS thin-film thermoelectrics by de-doping with nitrogen-doped graphene quantum dots *ACS Appl. Electron. Mater.* **6** 6313–21
[146] Chiang K C, Fincher C R Jr, Park Y W, Heeger A J, Shirakawa H, Louis E J, Gau S C and MacDiarmid A G 1977 Electrical conductivity in doped polyacetylene *Phys. Rev. Lett.* **39** 1098
[147] Evans D 2018 A bird's eye view of the synthesis and practical application of conducting polymers *Polym. Int.* **67** 351–5
[148] Im S G and Gleason K K 2007 Systematic control of the electrical conductivity of poly (3, 4-ethylenedioxythiophene) via oxidative chemical vapor deposition *Macromolecules* **40** 6552–6
[149] Mohammadi A, Hasan M A, Liedberg B, Lundström I and Salaneck W R 1986 Chemical vapour deposition (CVD) of conducting polymers: polypyrrole *Synth. Met.* **14** 189–97
[150] Brooke R, Cottis P, Talemi P, Fabretto M, Murphy P and Evans D 2017 Recent advances in the synthesis of conducting polymers from the vapour phase *Prog. Mater. Sci.* **86** 127–46
[151] Bubnova O *et al* 2014 Semi-metallic polymers *Nat. Mater.* **13** 190–4
[152] Winther-Jensen B and West K 2004 Vapor-phase polymerization of 3, 4-ethylenedioxythiophene: a route to highly conducting polymer surface layers *Macromolecules* **37** 4538–43
[153] Winther-Jensen B, Breiby D W and West K 2005 Base inhibited oxidative polymerization of 3, 4-ethylenedioxythiophene with iron (III) tosylate *Synth. Met.* **152** 1–4
[154] Fabretto M V, Evans D R, Mueller M, Zuber K, Hojati-talemi P, Short R D, Wallace G G and Murphy P J 2012 Polymeric material with metal-like conductivity for next generation organic electronic devices *Chem. Mater.* **24** 3998–4003
[155] Cho B, Park K S, Baek J, Oh H S, Koo Lee Y-E and Sung M M 2014 Single-crystal poly(3,4-ethylenedioxythiophene) nanowires with ultrahigh conductivity *Nano Lett.* **14** 3321–7
[156] Gueye M N *et al* 2016 Structure and dopant engineering in PEDOT thin films: practical tools for a dramatic conductivity enhancement *Chem. Mater.* **28** 3462–8

[157] Petsagkourakis I, Kim D, Modarresi M, Rudd S, Rudd R, Zozoulenko I and Evans D 2023 A nuanced understanding of the doping of poly (3, 4-ethylenedioxythiophene) with tosylate *Discov. Mater.* **3** 10
[158] Ali M A, Wu K H, McEwan J and Lee J 2018 Translated structural morphology of conductive polymer nanofilms synthesized by vapor phase polymerization *Synth. Met.* **244** 113–9
[159] Sharma A, Andersson G, Rivnay J, Alvino J F, Metha G F, Andersson M R, Zuber K and Fabretto M 2018 Insights into the oxidant/polymer interfacial growth of vapor phase polymerized PEDOT thin films *Adv. Mater. Interfaces* **5** e1800594
[160] Chen S *et al* 2020 Unraveling vertical inhomogeneity in vapour phase polymerized PEDOT:Tos films *J. Mater. Chem. A* **8** 18726–34
[161] Chang S-C, Liu J, Bharathan J, Yang Y, Onohara J and Kido J 1999 Multicolor organic light-emitting diodes processed by hybrid inkjet printing *Adv. Mater.* **11** 734–7
[162] Li H *et al* 2024 PEDOTs-based conductive hydrogels: design, fabrications, and applications *Adv. Mater.* **37** 2415151
[163] Chen S *et al* 2025 PEDOT:PSS-based electronic materials: preparation, performance tuning, processing, applications, and future prospect *Prog. Polym. Sci.* **167** 101990
[164] Zhang P, Zhu B, Luo Y and Travas-sejdic J 2022 Micropipette-based fabrication of free-standing, conducting polymer bilayer actuators *Adv. Mater. Technol.* **7** 2200686
[165] Tomaskovic-crook E *et al* 2019 Human neural tissues from neural stem cells using conductive biogel and printed polymer microelectrode arrays for 3D electrical stimulation *Adv. Healthcare Mater.* **8** 1900425
[166] Li J, Yu Q, Shen Z, Wang D and Gu G 2025 Soft 3D lattice iontronic tactile sensor *SmartBot* **1** e70002
[167] Yuk H, Lu B, Lin S, Qu K, Xu J, Luo J and Zhao X 2020 3D printing of conducting polymers *Nat. Commun.* **11** 1604
[168] Oh B *et al* 2024 3D printable and biocompatible PEDOT:PSS-ionic liquid colloids with high conductivity for rapid on-demand fabrication of 3D bioelectronics *Nat. Commun.* **15** 5839
[169] Zhou X, Fang S, Hu Y, Du X, Ding H, Chai R, Han J, Xie J and Gu Z 2024 Photoinduced double hydrogen-atom transfer for polymerization and 3D printing of conductive polymer *Nat. Synth.* **3** 1145–57
[170] Xie X, Xu Z, Yu X, Jiang H, Li H and Feng W 2023 Liquid-in-liquid printing of 3D and mechanically tunable conductive hydrogels *Nat. Commun.* **14** 4289
[171] Li J *et al* 2025 Multimaterial cryogenic printing of three-dimensional soft hydrogel machines *Nat. Commun.* **16** 185
[172] Li J, Cao J, Lu B and Gu G 2023 3D-printed PEDOT:PSS for soft robotics *Nat. Rev. Mater.* **8** 604–22
[173] Yao Y, Huang W, Chen J, Liu X, Bai L, Chen W, Cheng Y, Ping J, Marks T J and Facchetti A 2023 Flexible and stretchable organic electrochemical transistors for physiological sensing devices *Adv. Mater.* **35** e2209906
[174] Rivnay J, Inal S, Salleo A, Owens R M, Berggren M and Malliaras G G 2018 Organic electrochemical transistors *Nat. Rev. Mater.* **3** 17086
[175] Inal S, Malliaras G G and Rivnay J 2017 Benchmarking organic mixed conductors for transistors *Nat. Commun.* **8** 1767
[176] Azimi M, Kim C H, Fan J and Cicoira F 2023 Effect of ionic conductivity of electrolyte on printed planar and vertical organic electrochemical transistors *Faraday Discuss.* **246** 540–55
[177] Brodsky J, Gablech I, Migliaccio L, Havlicek M, Donahue M J and Glowacki E D 2023 Downsizing the channel length of vertical organic electrochemical transistors *ACS Appl. Mater. Interfaces* **15** 27002–9
[178] Galeana Perez Negron A, Schander A, Skowrons M, Barbosa H F P and Lussem B 2024 Approaching the intrinsic limits of short channel vertical organic electrochemical transistors *ACS Appl. Mater. Interfaces* **16** 45234–41
[179] Zhang S, Hubis E, Tomasello G, Soliveri G, Kumar P and Cicoira F 2017 Patterning of stretchable organic electrochemical transistors *Chem. Mater.* **29** 3126–32
[180] Kim C-H, Azimi M, Fan J, Nagarajan H, Wang M and Cicoira F 2023 All-printed and stretchable organic electrochemical transistors using a hydrogel electrolyte *Nanoscale* **15** 3263–72
[181] Massetti M *et al* 2023 Fully 3D-printed organic electrochemical transistors *npj Flex. Electron.* **7** 11
[182] Wang M, Fan J, Bilodeau-Calame M, Kim C, Chiang C L, Segura A F, Vurro V, Bargigia I, Mauzeroll J and Cicoira F 2025 Robust and flexible organic electrochemical transistors enabled by electropolymerized PEDOT *npj Flexible Electron.* **9** 74
[183] Wu R, Paulsen B D, Ma Q, McCulloch I and Rivnay J 2023 Quantitative composition and mesoscale ion distribution in p-type organic mixed ionic-electronic conductors *ACS Appl. Mater. Interfaces* **15** 30553–66
[184] Keene S T, van der Pol T P A, Zakhidov D, Weijtens C H L, Janssen R A J, Salleo A and van de Burgt Y 2020 Enhancement-mode PEDOT:PSS organic electrochemical transistors using molecular de-doping *Adv. Mater.* **32** e2000270
[185] Li Y, Zhang S, Li X, Unnava V R N and Cicoira F 2019 Highly stretchable PEDOT:PSS organic electrochemical transistors achieved via polyethylene glycol addition *Flex. Print. Electron.* **4** 044004
[186] Åsberg D P and Inganäs O 2003 PEDOT/PSS hydrogel networks as 3-D enzyme electrodes *Synth. Met.* **137** 1403–4
[187] Strakosas X *et al* 2023 Metabolite-induced in vivo fabrication of substrate-free organic bioelectronics *Science* **379** 795–802
[188] Kim N *et al* 2020 Elastic conducting polymer composites in thermoelectric modules *Nat. Commun.* **11** 1424
[189] Li G, Huang K, Deng J, Guo M, Cai M, Zhang Y and Guo C F 2022 Highly conducting and stretchable double-network hydrogel for sor bioelectronics *Adv. Mater.* **34** 2200261
[190] Gkoupidenis P, Schaefer N, Garlan B and Malliaras G G 2015 Neuromorphic functions in PEDOT:PSS organic electrochemical transistors *Adv. Mater.* **27** 7176–80
[191] van de Burgt Y, Lubberman E, Fuller E J, Keene S T, Faria G C, Agarwal S, Marinella M J, Alec talin A and Salleo A 2017 A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing *Nat. Mater.* **16** 414–8
[192] Keene S T *et al* 2020 A biohybrid synapse with neurotransmitter-mediated plasticity *Nat. Mater.* **19** 969–73
[193] Janzakova K, Balafrej I, Kumar A, Garg N, Scholaert C, Rouat J, Drouin D, Coffinier Y, Pecqueur S and Alibart F 2023 Structural plasticity for neuromorphic networks with electropolymerized dendritic PEDOT connections *Nat. Commun.* **14** 8143
[194] Maner L, Abdullaeva O S, Shaner S, Leal J and Asplund M 2024 Bioelectronic direct current stimulation at the transition between reversible and irreversible charge transfer *Adv. Sci.* **11** 2306244
[195] Feig V R, Tran H, Lee M and Bao Z 2018 Mechanically tunable conductive interpenetrating network hydrogels that mimic the elastic moduli of biological tissue *Nat. Commun.* **9** 2740
[196] Aggas J R, Abasi S, Phipps J F, Podstawczyk D A and Guiseppi-elie A 2020 Microfabricated and 3-D printed electroconductive hydrogels of PEDOT:PSS and their application in bioelectronics *Biosens. Bioelectron.* **168** 112568