

Design principles for π -conjugated hydrogel semiconductors

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Hao Huang ^{1,2,6}, Jing Bai ^{1,6}, Silan Zhang ^{3,4,5}, Binbin Cui¹, Xiaonan Chen¹, Shilei Dai ¹, Xiang Meng ¹, Ngai Wong ¹, George G. Malliaras ³ & Shiming Zhang ^{1,2} ✉

Hydrogels are widely used in biomedical and bioelectronic applications owing to their tissue-like properties, including biocompatibility, softness and three-dimensional architecture. In recent years, semiconducting behaviour was demonstrated in hydrogels through the network design of π -conjugated polymers, extending their potential to advanced electronic applications such as transistors. In this Review, we provide an overview of the design, fabrication, characterization and benchmarking standards of π -conjugated hydrogel semiconductors, a rapidly evolving field requiring interdisciplinary knowledge across organic electronics, electrochemistry and soft materials. We demonstrate how to understand and regulate ion and electron transport, as well as their interactions, both thermodynamically and kinetically, in these π -conjugated supramolecular systems. Finally, we envision the potential of these materials to advance spatiotemporal biological research, wearable healthcare, implantable medicine and beyond.

Semiconductors are materials with electrical conductivity between that of conductors and insulators¹. Their conductivity can be precisely tailored through the introduction of dopants or the application of external stimuli such as voltage. This tunability endows them with unique capabilities for fabricating integrated circuits, sensors and advanced micro-electronic devices, thereby driving progress in computing, energy and communications. As the demand for higher integration density, greater computing power and continued scaling in accordance with Moore's law intensifies, the semiconductor industry is continually advancing device architectures and exploring novel materials to enable next-generation functional devices².

In parallel, the advancement of bioelectronic technologies, such as wearable and implantable devices, demands biosensors and biocomputing architectures with improved tissue compatibility to address the mechanical, biological and dimensional mismatches with living systems³. Traditional silicon or organic semiconductor materials face challenges for this purpose owing to their rigidity and two-dimensional

(2D) planar form, fundamentally mismatched with the soft, irregular and three-dimensional (3D) nature of biological systems⁴.

Efforts have been dedicated to tailoring the mechanical properties of semiconductors (Supplementary Table 1). While these strategies enhance mechanical compatibility by gaining stretchability, their Young's modulus remains in the megapascal to gigapascal range, higher than the kilopascal-scale modulus of biological tissues⁵. Given that mechanical conformability is fundamentally determined by modulus, semiconductors with tissue-level softness are being pursued beyond mere stretchability.

Hydrogels have long been used in biomedical applications such as medical bandages⁶, cell culture⁷ and in vivo drug delivery⁸, because of their tissue-like properties, including biocompatibility, 3D structure and tissue-level softness^{6,7}. Recent advances in multi-networked supramolecular hydrogels have led to the development of conducting hydrogels with controllable mechanical properties^{9–12}. However, the absence of semiconducting property confines them to passive

¹Department of Electrical and Computer Engineering, The University of Hong Kong, Hong Kong SAR, China. ²School of Biomedical Engineering, The University of Hong Kong, Hong Kong SAR, China. ³Department of Engineering, Electrical Engineering Division, The University of Cambridge, Cambridge, UK. ⁴Cavendish Laboratory, University of Cambridge, Cambridge, UK. ⁵Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, Sweden. ⁶These authors contributed equally: Hao Huang, Jing Bai. ✉ e-mail: beszhang@hku.hk

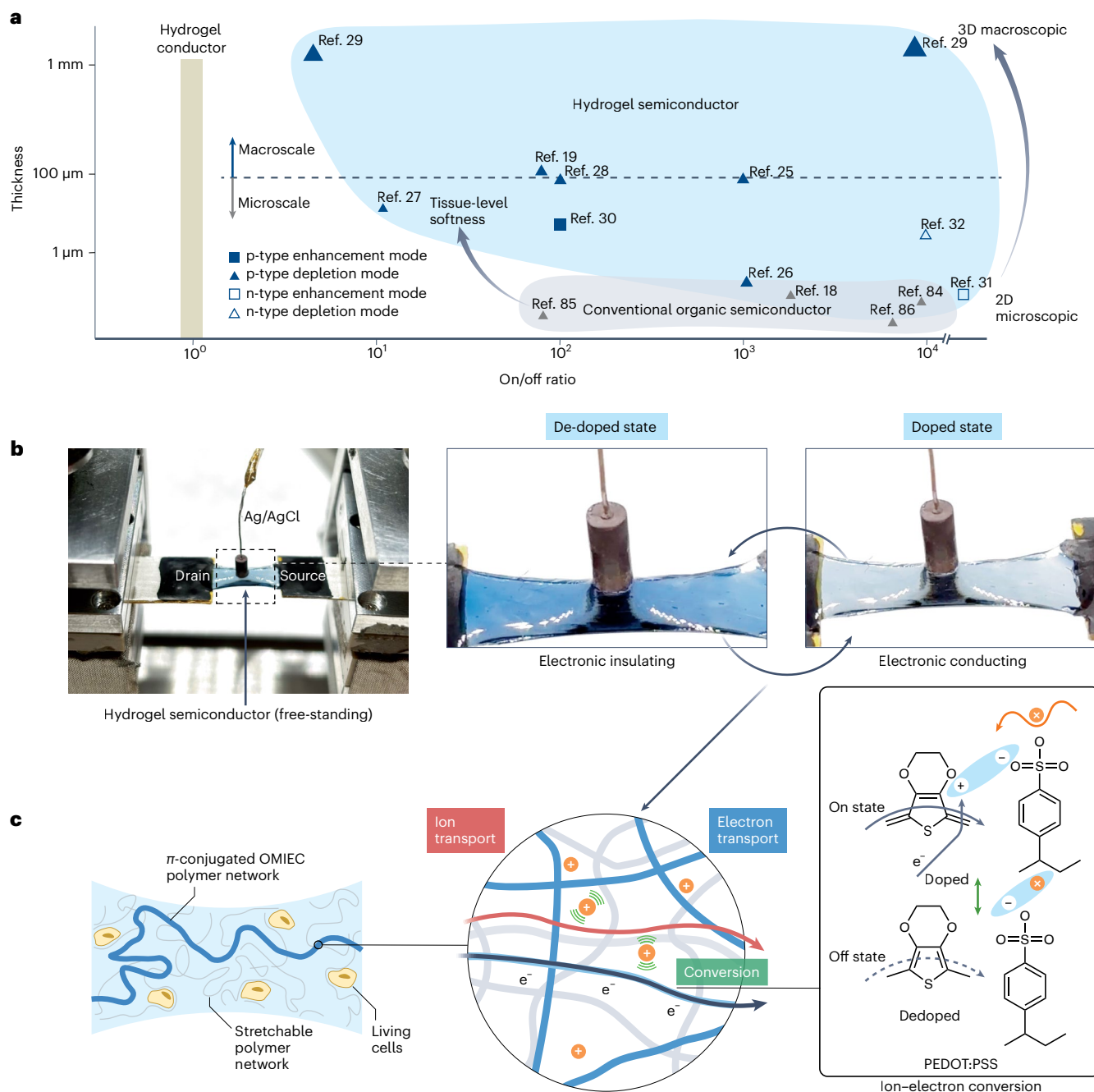


Fig. 1 | The rise of hydrogel semiconductors, integrating ion transport, electron transport and ion–electron conversion within living soft matter.

a, Comparison between hydrogel semiconductors, hydrogel conductors and conventional organic semiconductors. Conventional organic semiconductors achieve high on/off ratios but are rigid and confined to microscale thicknesses (100 μm , the boundary between micro- and macroscale⁸³). Hydrogel conductors enable macroscale thickness and softness but exhibit no semiconducting behaviour (switching ability, quantifiable with on/off ratios). Hydrogel semiconductors solve this dilemma, combining macroscale thickness and softness with switching ability through bulk modulation. The symbols

correspond to n-type enhancement mode³¹, n-type depletion mode³², p-type enhancement mode³⁰, p-type depletion mode^{19,25–29} and conventional organic semiconductors operating with bulk modulation^{18,84–86}; the thickness refers to the bulk modulation thickness of the semiconductor. **b**, Optical images depicting the colorimetric behaviour of a stretchable ion–electron transistor based on a free-standing hydrogel semiconductor. **c**, Ion transport, electron transport and ion–electron conversion in a hydrogel semiconductor are crucial for the electrical conductivity switching behaviour for two-way cell–transistor interactions. Panel **b** adapted from ref. 87 under a Creative Commons licence CC BY 4.0.

conductors only. This limits their use for advanced bioelectronics such as bio-signal amplifiers, biologic integrated circuits and programmable biohybrid systems (Fig. 1a).

Hydrogel semiconductors have recently emerged, originating from efforts to enhance the mechanical properties of a representative organic bioelectronic device, the organic electrochemical transistor (OECT)^{13–19}. OECTs are mixed ion–electron transistors using

π -conjugated organic mixed ionic–electronic conductors (OMIECs) as channel materials^{13,15}, whose electronic conductivity can be modulated through the insertion of ions, which is challenging with conventional semiconductors (Fig. 1b,c). Their high sensitivity and analogies to biological neurons make them ideal for applications such as tissue-interfaced biosensing¹⁶ and neuromorphic computing¹⁷. However, despite progress in improving the stretchability of OECTs,

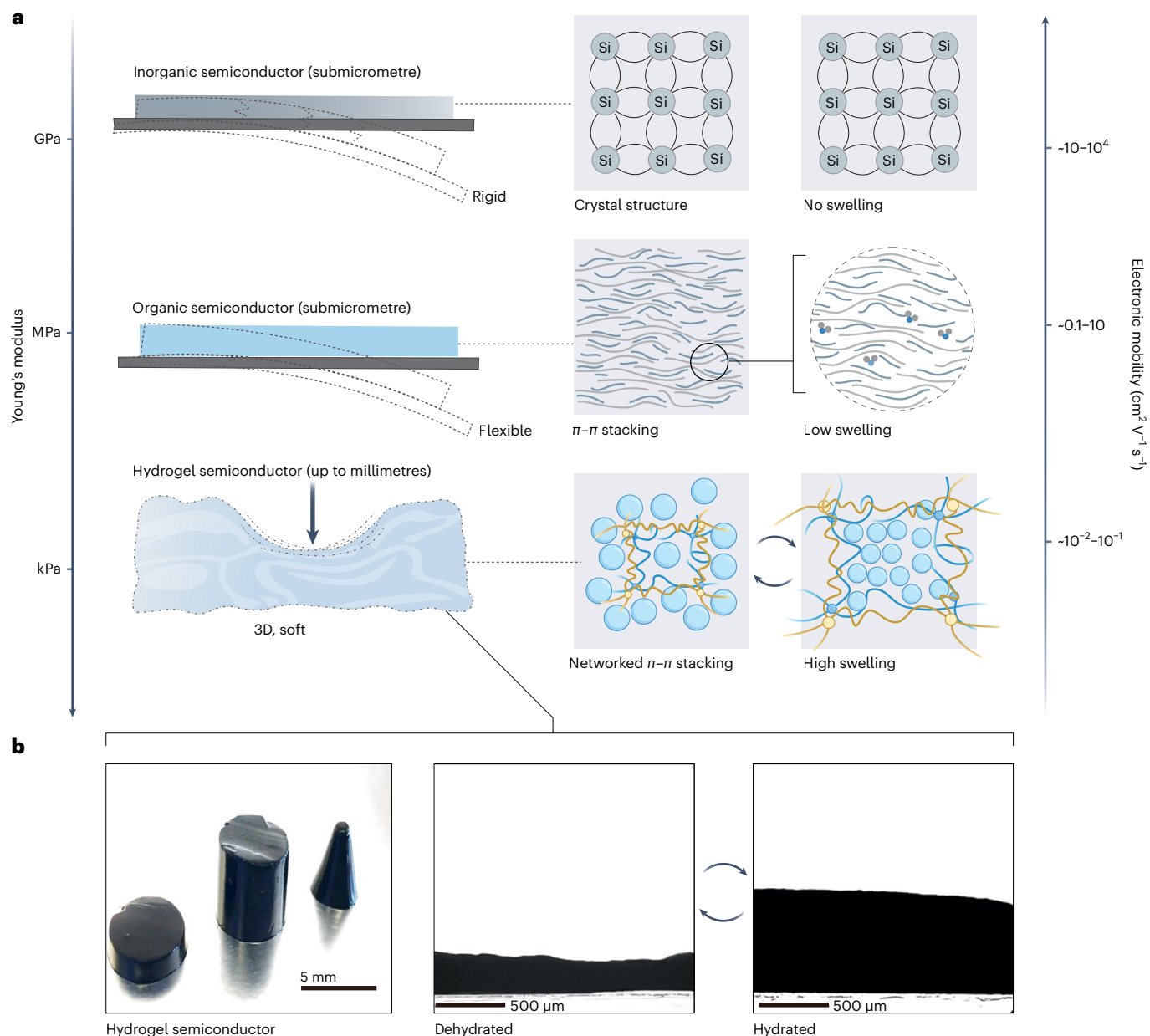


Fig. 2 | Comparison of inorganic, organic and hydrogel semiconductors. a, Inorganic semiconductors such as silicon exhibit high Young's modulus on the gigapascal scale owing to highly crystalline covalent bonds and electron delocalization. Their rigid, non-porous lattice prevents accommodation of solvent molecules (for example, water), prohibiting swelling. Organic semiconductors, while containing soft polymer chains, still exhibit high crystallization levels, resulting in a modulus in the megapascal to gigapascal range. They offer flexibility with limited swelling ability⁸⁸. Hydrogel

semiconductors achieve a tissue-level modulus in the kilopascal range, owing to intentionally designed multi-network structures and microscale topologies. In addition, they can be highly stretchable and, with increased porosity, can reversibly swell up to 500% while maintaining excellent semiconducting properties. **b,** Image of hydrogel semiconductors formed at room-temperature¹⁹ (left) and a demonstration of a hydrogel semiconductor showing reversible swelling behaviour²⁹ (middle and right). Panel **b** reproduced with permission from: left, ref. 19, Wiley; right, ref. 29, AAAS.

Young's modulus of OMIECs remains in the megapascal to gigapascal range, which fundamentally limits their compatibility with soft biological tissues¹⁸ (Fig. 2a).

Hydrogel semiconductors were initially proposed to reduce Young's modulus of OMIEC channels in OECTs by retaining water content during the processing of OMIECs through a direct water-to-gel phase transition^{15,19}, rather than conventional thermal processing, which removes water. In addition, it was hypothesized that retained water content could decouple ion transport from the polymer backbone by forming parallel, continuous liquid pathways, thus reducing the material design hurdle of OMIECs^{20,21}. However, constructing hydrogel-like structures in OMIECs to enhance ion transport while

preserving long-range electron transport has been a major materials design challenge²⁰⁻²².

This dilemma was addressed by designing a supramolecular double-network hydrogel system that blends a typical water-stable and commercially available OMIEC, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), with non-conducting polyacrylamide (PAAm) under aqueous conditions¹⁹. Both PEDOT:PSS suspensions and acrylamide (AAM) monomers can form hydrogels under controlled processing conditions, thus enabling the creation of a composite hydrogel that can maintain efficient ion transport while preserving long-range π - π conjugation for efficient electronic transport. Specifically, PEDOT:PSS suspensions can form hydrogels by

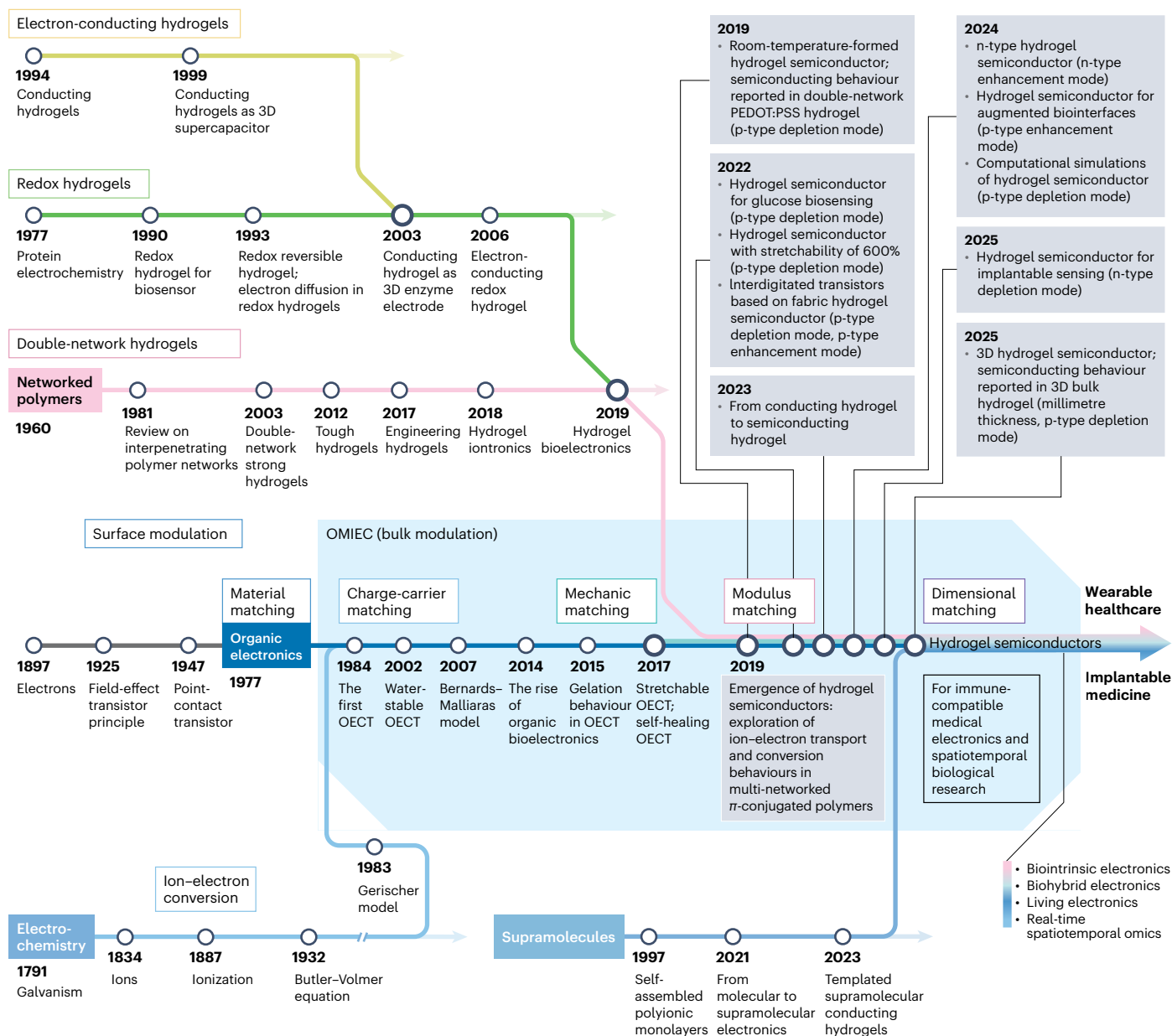
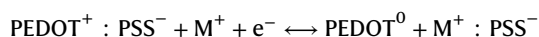


Fig. 3 | The roadmap for developing hydrogel semiconductors. The emergence of hydrogel semiconductors represents a convergent, cross-disciplinary research effort encompassing organic electronics, soft matter, electrochemistry and supramolecules. The goal is to minimize the electronic–biological mismatch to enable seamless bioelectronics applications at soft–wet interfaces, including but not limited to, soft and living electronics, wearable healthcare devices, and implantable medical technologies. Key dates and references are: 1925 (ref. 89),

1947 (ref. 90), 1983 (ref. 70), 1984 (ref. 91), 1993 (refs. 92,93), 1997 (ref. 41), 1999 (ref. 94), 2002 (ref. 24), 2003 (refs. 11,95), 2006 (ref. 96), 2007 (ref. 59), 2012 (ref. 10), 2014 (ref. 4), 2015 (ref. 15), 2017 (refs. 6,14,97), 2018 (ref. 53), 2019 (refs. 12,19), 2021 (ref. 22), 2022 (refs. 25,26,28), 2023 (refs. 40,98,99), 2024 (refs. 27,30,31), 2025 (refs. 29,32). A comprehensive list of references for each section is provided in Supplementary Table 2.

increasing the ionic strength of the mixture^{19,23}, which separates PEDOT⁺ and PSS⁻, facilitating the formation of a continuous PEDOT⁺–PEDOT⁺ conjugated network through π – π interactions. Meanwhile, the AAm monomers can form a stretchable PAAM hydrogel in the presence of chemical crosslinkers. Consequently, a double-network interpenetrated OMIEC hydrogel with tissue-level modulus of 1–100 kPa was achieved¹⁹ (Fig. 2b). Semiconducting properties were observed by recording an ~100 on/off ratio in the assembled OEET, enabled by the preserved reversible redox activity of the PEDOT:PSS OMIEC hydrogel, as described by the following reaction²⁴:



where PEDOT⁺ and PEDOT⁰ are doped and de-doped states of the PEDOT:PSS, and M⁺ denotes cations from the electrolyte¹⁹.

In the past 5 years, substantial efforts have been subsequently dedicated to broaden the understanding of PEDOT:PSS OMIEC hydrogel semiconductors from various perspectives (Fig. 3). For instance, using a double-network approach, Tseng and Sakata revealed that PEDOT:PSS/PAAM hydrogel semiconductors can reach a higher on/off ratio up to 1,000 at microscale thicknesses²⁵. Su et al. demonstrated that hydrogel transistors can attain extreme stretchability of up to 600% by blending PEDOT:PSS with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA) hydrogel²⁶. Gregorio et al. revealed that the ion transport behaviour in hydrogel semiconductors differs from that in conventional thin-film semiconductors²⁷.

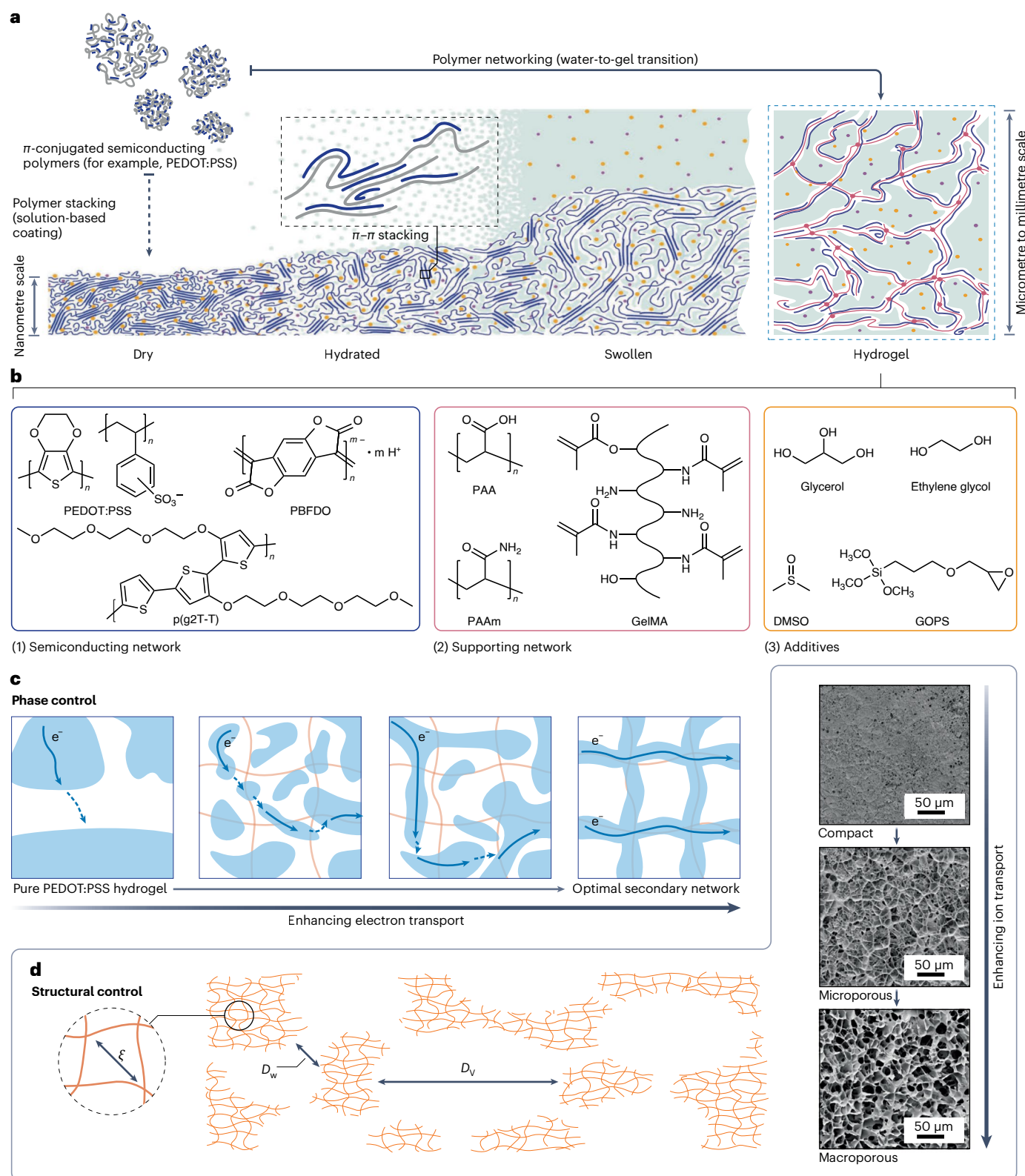


Fig. 4 | Material strategy for constructing hydrogel semiconductors.

a, Illustration of the differences between processing a conventional semiconducting polymer film (dry, hydrated and electrolyte-swollen states) and processing a hydrogel semiconductor. The former uses thermal processing to form conductive dry films by removing solvents in the solution, whereas the latter uses a direct water-to-gel transition to retain water in the solution for ion transport by forming 3D porous networks, followed by post-processing to refine the network. **b**, Material components of hydrogel semiconductors,

including semiconducting network, supporting network and doping agent.

c, Phase engineering to promote electron transport. **d**, Mesosstructural engineering to promote ion transport. Balancing ion and electron transport optimizes the semiconductor properties by maximizing ion–electron conversion efficiency; D_p is the pore size, D_w is the size of the interconnection between pores and ξ is the mesh size of the crosslink network. GelMA, gelatin methacryloyl; DMSO, dimethyl sulfoxide; GOPS, (3-glycidioxypropyl)trimethoxysilane. Panels adapted with permission from: **a**, ref. 21, Annual Reviews; **c,d**, ref. 29, AAAS.

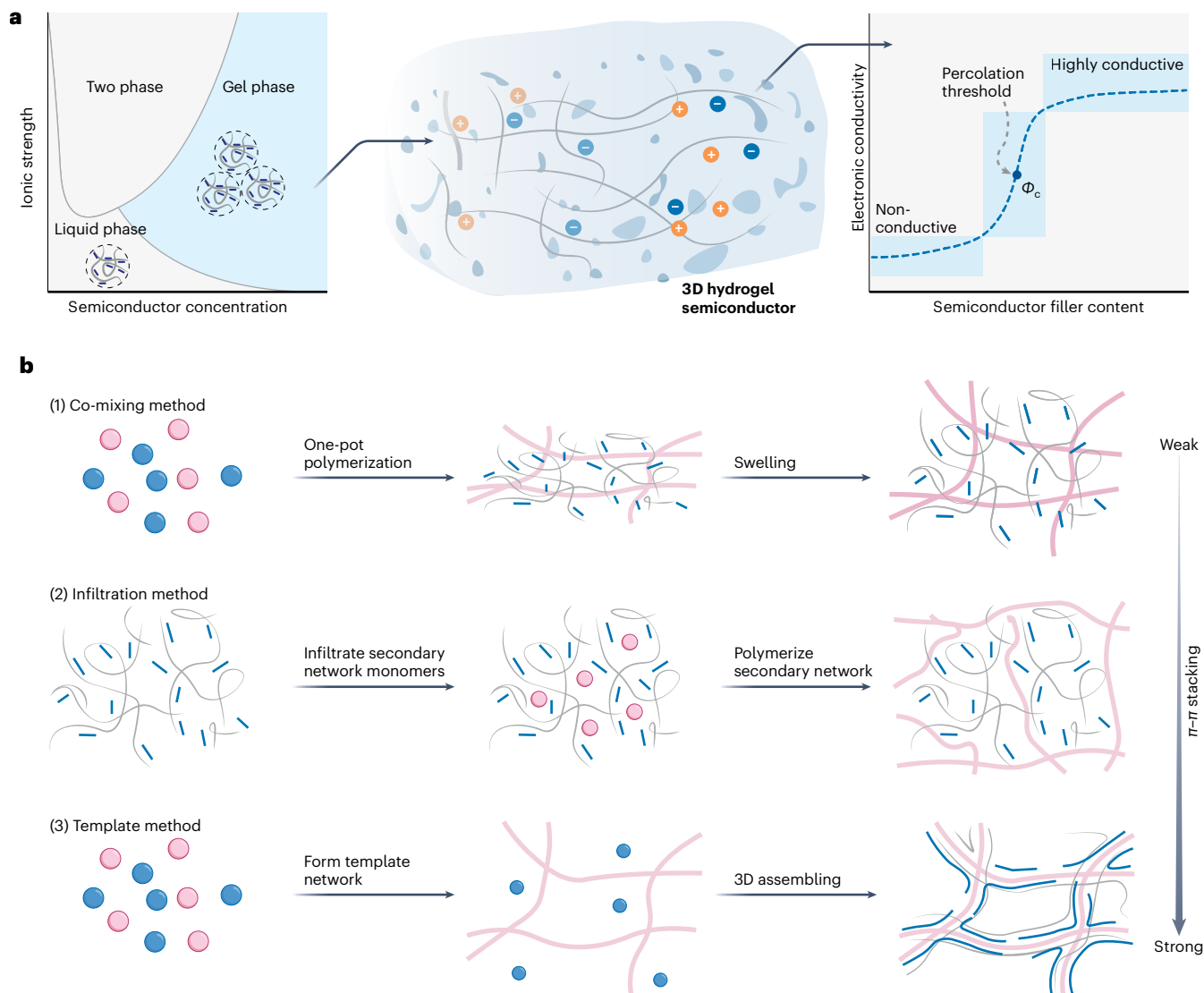


Fig. 5 | Network design and processing of hydrogel semiconductors.

a, Left: schematic phase diagram of PEDOT:PSS hydrogels, showing a two-phase regime, pure liquid phase and pure gel phase. The phase transition thresholds are determined by both polymer concentration and ionic strength²³. Middle: hydrogel semiconductors are 3D OMIECs that transport both ions and electrons within a highly water-swollen polymer network. Right: electronic conductivity

versus semiconductor content in hydrogel semiconductors follows percolation theory, where a critical content volume (ϕ_c) triggers a sharp transition to conductivity as continuous electron pathways form⁴³. **b**, Existing network processing approaches for constructing hydrogels: (1) co-mixing method, (2) infiltration method and (3) template method.

Jo et al. demonstrated that high-transconductance OECTs can be achieved through fibrillary gelation of hydrogel semiconductors using biocompatible ionic liquids²⁸. Recently, macroscopic semiconducting behaviour has been demonstrated in 3D hydrogel semiconductors with channel thicknesses reaching the millimetre scale, achieved through a templated network design method, wherein π -conjugated polymers self-assemble into 3D porous structures with continuous phases in water²⁹. This method can help to simultaneously overcome the modulus and thickness limitations of conventional thin-film semiconductors, which are restricted to nano- and microscale thicknesses.

In addition to PEDOT:PSS, other types of π -conjugated OMIEC hydrogel semiconductor have been explored with the customized double-network design approach. In this regard, Dai et al. reported a double-network hydrogel semiconductor using the p-type, but enhancement-mode, polymer poly(2-(3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thiophene) (p(g2T-T)), blended with polyacrylic acid (PAA). It achieved a tissue-like modulus of 81 kPa

and stretchability of up to 150%. Sensors fabricated with the hydrogel semiconductor demonstrated a limit of detection of 500 nM, orders of magnitude lower than the reference device³⁰. Li et al. reported a hydrogel semiconductor using an n-type, enhancement-mode polymer poly(pyridinium-vinylene) (P(PyV)). The resulting n-type semiconducting hydrogel sensors exhibited high water stability, allowing in vivo applications for electrooculography and electrocardiography recordings with a signal-to-noise ratio 50 times greater than that of traditional gold electrodes³¹. Liang et al. reported a hydrogel semiconductor based on an n-type depletion-mode polymer, poly(benzodifurandione) (PBFDO), within a PAAm network. The resulting hydrogel transistors exhibited high transconductance (43 mS), robust mechanical properties and excellent biocompatibility, making them suitable for both in vitro and in vivo biosensing applications³².

Despite the above joint efforts on hydrogel semiconductors, research in this rapidly evolving field remains in its infancy, with design principles and standardized benchmarks yet to be established. In this Review, we discuss the design principles, fabrication strategies and

BOX 1

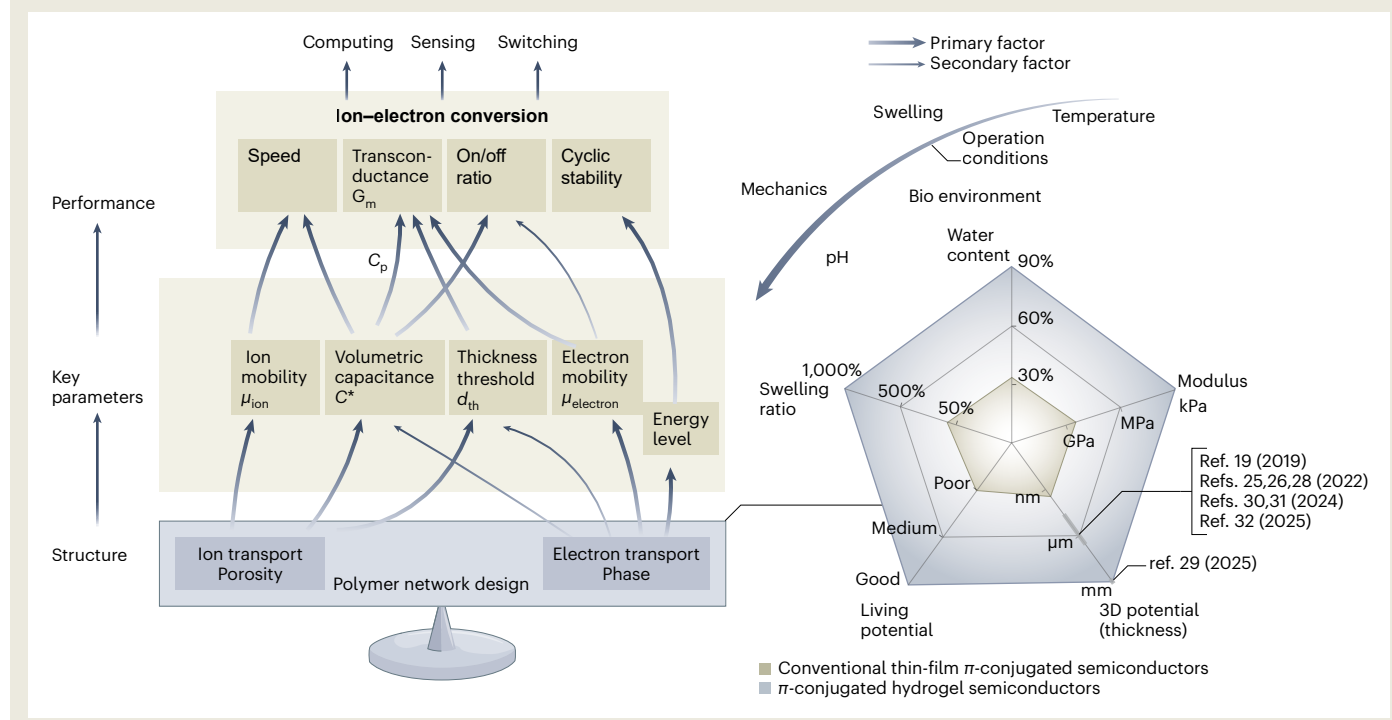
Design considerations of hydrogel semiconductors

High-performance hydrogel semiconductors rely on a balance between ion transport and electron transport, as described by the hierarchical structure–parameter–performance framework. Device performance (response speed, transconductance, on/off ratio and long-term aqueous stability) is governed by three interconnected processes: ion transport, electron transport and ion–electron conversion.

Ion transport is primarily regulated by the hydrogel's structural features, particularly porosity and mesh size²⁷. These structural attributes directly influence key parameters such as ion mobility (μ_{ion}), volumetric capacitance (C^*) and thickness threshold (d_{th} , the maximum thickness at which the linear capacitance–thickness relationship holds²⁹). At the performance level, response speed, transconductance and on/off ratio are affected. If ion mass transport limits the electrochemical doping/de-doping process, it will restrict ion–electron conversion efficiency and response speed. For steady-state metrics such as transconductance and on/off ratio, sufficient ion accessibility to redox-active sites is essential for complete, reversible doping and maximal charge-carrier density^{61,72}.

Electron transport relies on the phase continuity and percolation of the π -conjugated semiconducting polymer network within the hydrogel, providing uninterrupted pathways for charge carriers. This continuity primarily dictates electron mobility (μ_{electron}), the primary metric of electronic performance. Furthermore, frontier molecular orbital energy levels have a critical role in reflecting electron transport. An optimal energy-level position facilitates efficient charge injection and hopping while minimizing parasitic redox reactions with dissolved O_2 and H_2O . Inappropriate energy-level positioning can increase trap states or reduce carrier density, thereby limiting μ_{electron} even in well-percolated networks¹⁰⁰.

Balancing ion and electron transport is the key to high-performance hydrogel semiconductors, especially for high-transconductance sensor application^{20,62,88}. These represent a fundamental trade-off: electron transport benefits from ordered, rigid structures, whereas efficient ion transport requires hydrated, porous structures²⁹. Maximizing transconductance and $\mu_{\text{electron}}C^*$ therefore demands balanced structural control to ensure that hydrated ions can access the largest possible fraction of the percolating semiconducting polymer network.



key performance metrics of hydrogel semiconductors. We outline how ion–electron transport and coupling in π -conjugated supramolecular hydrogel systems can be understood and tuned—thermodynamically and kinetically—via integrated electrical, electrochemical and optical characterization. Finally, we highlight their potential in advancing 3D tissue-integratable bioelectronics, essential for real-time spatiotemporal biological research, wearable healthcare and implantable medicine.

Water-to-gel transition of hydrogel semiconductors

The fabrication of OMIEC hydrogel semiconductors differs fundamentally from that of conventional organic semiconductors, primarily in

terms of the processing methods (Fig. 4). Organic semiconductors, including OMIECs, are typically fabricated via solution-based coating followed by an annealing process to remove solvents, yielding conductive dry films. In contrast, hydrogel semiconductors can be fabricated through a direct water-to-gel transition that retains water, followed by post-processing steps to refine the supramolecular structure¹⁹ (Fig. 5a,b).

For spontaneous water-to-gel transition, the processing method must be thermodynamically favourable, meaning that the overall change in Gibbs free energy (ΔG) must be negative. The free energy change comprises an enthalpy contribution (ΔH) and entropy contribution ($T\Delta S$):

$$\Delta G = \Delta H - T\Delta S$$

where T is the absolute temperature. Below, we introduce and discuss the mechanism of several water-to-gel transition strategies that can be used to fabricate OMIEC hydrogel semiconductors.

The first strategy involves precise control of the OMIEC concentration in solution. Flory–Huggins theory provides a quantitative framework to describe the thermodynamics of mixing, which governs phase behaviour and gelation. The Gibbs free energy of mixing is expressed as³³:

$$\Delta G_{\text{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}]$$

where n_1 and n_2 are mole numbers of solvent and polymer, ϕ_1 and ϕ_2 are their respective volume fractions, and χ_{12} is the interaction parameter that quantifies the energetic compatibility between the polymer and solvent. R is the gas constant. At elevated temperatures, the entropic contributions ($n_1 \ln \phi_1 + n_2 \ln \phi_2$) dominate and favour polymer–solvent mixing. In contrast, at lower temperatures or under poor solvent conditions (that is, high χ_{12}), the enthalpic term ($n_1 \phi_2 \chi_{12}$) becomes dominant, potentially leading to phase separation or aggregation (that is, $\Delta G_{\text{mix}} > 0$)³⁴. Taking PEDOT:PSS for example, this enthalpy contribution arises from the release of electrostatic energy between PEDOT⁺ and PSS[−] chains and the formation of π – π stacking interactions, which promote 3D self-assembly of PEDOT⁺ chains and their long-range ordering. By precisely controlling the gelation process, the energetic and conformational disorders can be minimized at long-range, leading to improved charge transport.

The second strategy leverages hydrodynamic effects to facilitate the water-to-gel transition. OMIECs are typically hydrophobic, and to make them dispersible in water, hydrophilic counterions are commonly used. These counterions facilitate the formation of coiled colloidal structures, which stabilize OMIECs in aqueous environments. Electrostatic repulsion between these colloidal particles prevents direct π – π stacking of the semiconducting polymer backbones—an interaction that is critical for gelation. To understand and control this gelation process, Debye–Hückel theory provides a theoretical framework. Specifically, the Debye screening length (κ^{-1}) quantifies the range over which electrostatic interactions act in an ionic environment. It relates to the ionic strength (I) of the solvent²³:

$$\kappa^{-1} = (\epsilon_r \epsilon_0 k_B T / 2 N_A e^2 I)^{1/2}$$

where ϵ_r is the relative permittivity of the medium, ϵ_0 is the vacuum permittivity, k_B is the Boltzmann constant, N_A is Avogadro's number and e is the elementary charge. As κ^{-1} becomes comparable to or smaller than the hydrodynamic radius (R_h) of the colloidal particles—that is, when $\kappa^{-1} \lesssim R_h$, the frequency of colloidal collisions increases owing to the reduction of long-range electrostatic repulsion. At a critical ionic concentration threshold^{19,23}, this diminished electrostatic stabilization allows short-range attractive forces, such as π – π stacking between conjugated polymer backbones, to become dominant^{19,28}. These interactions promote the formation of a percolated gel network characterized by long-range structural order and spatial uniformity. This transition represents the onset of hydrodynamically assisted gelation, where the interplay between electrostatic screening and hydrodynamic confinement governs the self-assembly and macroscopic phase behaviour of the system.

Network design of hydrogel semiconductors

Hydrogel semiconductors consist of a semiconducting network, often complemented by a secondary soft hydrogel network to form supramolecular systems to regulate tissue-like properties^{19,30}. This secondary network can be a soft polymer network for enhanced mechanical properties or a doping network for enhanced electrical properties (Fig. 4b). Optimal semiconducting properties require precise control

of material concentration and controlled processing conditions to ensure proper phase formation of the semiconducting network within the multi-networked hydrogel and finely tuned hydrogel porosity, enabling efficient ion–electron transport and coupling²¹. Below, we introduce key networking approaches for constructing hydrogel semiconductors (Fig. 5b).

Co-mixing method: in this approach, polymers that form the multi-network hydrogel are simply co-mixed, followed by simultaneous gelation³⁵. By tuning processing parameters including initiator concentration, temperature, pH and solvent composition, this approach enables the fabrication of interpenetrating polymer networks, in which the constituent chains diffusively entangled without covalent grafting, thereby enhancing mechanical synergy and structural homogeneity³⁶. As a paradigmatic one-pot synthesis, it offers pronounced cost-effectiveness and scalability compared with sequential polymerization methods, minimizing procedural complexity³⁷. However, achieving optimal interpenetration often necessitates the addition of surfactants or compatibilizers to avert phase separation and filler aggregation, which can compromise network continuity. Such additives may introduce cytotoxicity or compromise biocompatibility, particularly for biomedical applications, highlighting the need for biocompatible alternatives or post-synthesis purification strategies³⁸.

Infiltration method^{9,19}: in this method, one network is formed first, followed by infiltration of another network. For example, a PEDOT:PSS-based hydrogel semiconductor can be formed by sequentially creating a primary PEDOT:PSS-based semiconducting network via ionic strength modulation^{23,39}, followed by infiltration and *in situ* polymerization of secondary precursors such as AAm to yield an interpenetrating PAAm network, thereby sustaining high conductivity while enhancing stretchability through dissipative secondary bonds. This approach outperforms the co-mixing method in initial percolation and biocompatibility by avoiding harsh solvents¹⁹. However, it faces the challenge of incomplete interpenetration, as the first-formed network may create diffusion barriers for the secondary precursors, fostering microscale voids, heterogeneous filler distribution and aggregation that induces structural non-uniformity and inhibits 3D charge transport³⁷.

Template method^{29,40}: this approach involves forming a template network to confine and guide the 3D supramolecular self-assembly of the semiconducting network. For instance, a porous PAA network can template the growth of a semiconducting phase through dynamic ionic interactions, such as the hydrogen bonds between the carboxylate groups of PAA and the PSS shell of PEDOT:PSS, resulting in an ultrathin, fibrous PEDOT:PSS coating that adheres uniformly along the template chains⁴¹. This approach improves network homogeneity, continuity and volumetric electron transport, yielding ultrahigh conductivity while fostering a tunable porous architecture⁴⁰. Relative to co-mixing and infiltration techniques, this approach excels in percolation efficiency and structural uniformity, effectively suppressing filler aggregation and microscale voids, and promoting efficient ion diffusion to support efficient ion–electron conversion processes in intrinsically 3D structures²⁹. Nevertheless, the reliance on reversible supramolecular bonds requires strict material pairing to enhance and ensure the system's stability. In addition, fabrication demands stringent processing controls and is relatively complex.

Phase design of hydrogel semiconductors

In a hydrogel, three phases can exist: water, gel and a water–gel mixture²³ (Fig. 5a). For hydrogel semiconductors, achieving a pure gel phase is critical to ensure stability. Rheology tests can help assess the phase composition. An increase in reduced viscosity, or when the storage modulus largely exceeds the loss modulus, indicates gel formation⁴².

Alongside achieving a pure gel phase, it is equally important to establish a continuous semiconducting phase and long-range π -conjugation within the hydrogel semiconductor^{29,30} (Fig. 4c). For

instance, in a pure PEDOT:PSS hydrogel semiconductor, the PEDOT⁺ semiconducting phase often lacks continuity owing to blockage by the non-conducting PSS[−] counterion chains, resulting in limited semiconducting properties^{39,40}. The continuity of the semiconducting phase can be improved by introducing secondary hydrogel networks. For example, combining the PEDOT:PSS network with secondary networks such as polyethylene glycol diacrylate, polyvinyl alcohol, PAAm and PAA can increase the conductivity, indicating enhanced semiconducting phase continuity²⁹.

Percolation theory can provide guidance to evaluate the continuity of the semiconducting phase. The relationship between electrical conductivity and the content of conductive fillers in a composite material typically follows power-law equation⁴³:

$$\sigma_{\text{electron}} = \sigma_0(\phi - \phi_c)^t \text{ if } (\phi > \phi_c)$$

where σ_{electron} is the electrical conductivity, σ_0 is a scaling factor, ϕ is the volume fraction of the conductive filler, ϕ_c is the percolation threshold, and t is the critical exponent that depends on the dimensionality and structure of the system. Once the volume fraction of the conductive filler, ϕ , reaches a critical value, ϕ_c , an abrupt transition from a non-conductive state to a conductive state occurs, corresponding to the formation of a continuous pathway for electron transport. Identifying the percolation threshold, ϕ_c , is crucial for understanding the semiconducting behaviour of composite hydrogels. A smaller ϕ_c may indicate better phase continuity, which is beneficial for efficient electron transport⁴⁴.

Structural design of hydrogel semiconductors

The structural design of hydrogel semiconductors involves regulating the porosity of the hydrogel, which can be defined by three key parameters: average pore size (D_p), interconnections size between pores (D_w) and mesh size (ξ) of the crosslinked networks⁴⁵ (Fig. 4d). Controlling these parameters facilitates ion transport in hydrogels, which is essential for regulating their semiconducting properties²⁹.

The porosity of hydrogels can be tuned using various strategies, such as kinetic or templating approaches⁴⁵. Common kinetic methods include bubble generation from reactions⁴⁶, gas injection⁴⁷ and freeze-drying⁴⁸. In these methods, the microstructure of the system evolves dynamically until it is fixed. In contrast, templating methods create porous polymers as replicas of the original template. These techniques can produce hydrogels with pore sizes up to 1,000 μm (using bubble-generation methods) and porosity as high as 90% (using emulsion-templating methods)²⁹.

Increasing the porosity of hydrogels enhances their ionic conductivity⁴⁹. For example, increasing the porosity of a PEDOT:PSS hydrogel semiconductor from 5% to 90% enhances ionic conductivity by over one order of magnitude²⁹. Increasing the porosity of the p(g2T-T)-based hydrogel semiconductor was also found to be beneficial for enhancing charge transport³⁰.

Increased porosity directly correlates with a higher swelling ratio, which is an indicator of ion storage capacity. For instance, as the porosity of a PEDOT:PSS-based hydrogel semiconductor increases from 5% to 10% and then to 90%, the swelling ratio rises from 5% to 100% and ultimately to 500% (ref. 29). These swelling processes are reversible, demonstrating the stability and robustness of the microporous structure, which is critical for maintaining the reversible functionality of hydrogel semiconductors. The sufficient degree of hydration produces a mobile solvation shell of water, facilitating vehicle transport²¹.

Ion–electron transport in hydrogel semiconductors

In OMIEC hydrogel semiconductors, ion and electron transport occur simultaneously. The porous, hydrated and 3D network provides continuous pathways that support ion transport. Meanwhile, the π -conjugated

polymer backbones embedded within this hydrated network enable electron transport along percolative pathways. These two processes are inherently coupled, often exhibiting trade-offs (Box 1). For instance, optimizing porosity for faster ion transport may compromise electron percolation pathways^{29,50}.

In this section, we discuss the key metrics for evaluating and benchmarking ion and electron transport in hydrogel semiconductors. The discussion draws on established knowledge in OMIECs^{21,51}, OECTs¹³ and conducting hydrogels⁵².

Ion transport in hydrogel semiconductors is promoted by their high water content and porous structure. In contrast to dry-state polymer electrolytes where ion mobility is intrinsically coupled to the segmental dynamics of the polymer backbone, hydrogel semiconductors provide continuous aqueous pathways that decouple ion transport from polymer chain dynamics⁵³.

Several metrics can be used to evaluate ion transport efficiency and capacity. These include: ionic conductivity (σ_{ion}), which quantifies overall charge flux; ionic mobility (μ_{ion})⁵⁴, reflecting the drift velocity of ions under an electrical field; ionic diffusivity (D_{ion})⁵⁵, capturing diffusion behaviour; and transference numbers (t^+ or t^-)⁵⁶, denoting the fractional contribution of cations or anions to total ionic current. Among these, σ_{ion} is most widely used and is often measured via electrochemical impedance spectroscopy⁵⁷. This approach yields reproducible values, typically spanning 1–100 mS cm^{-1} (ref. 50). As σ_{ion} is influenced by factors such as swelling degree, ionic species, solvation shells and ionic concentration, it should be reported alongside ion transport metrics to facilitate cross-study comparability.

Electron transport in hydrogel semiconductors relies on continuous percolation pathways⁴⁴, which are highly susceptible to disruption from hydration and ionic transport³⁰. In this context, in addition to the electronic conductivity (σ_{electron}), which is widely used for benchmarking passive hydrogel conductors, electronic mobility (μ_{electron}) is another key metric, offering an intrinsic gauge of transport efficiency that disentangles it from the carrier concentration.

Accurately characterizing μ_{electron} in hydrogel semiconductors presents substantial experimental challenges. Ionic conduction pathways often obscure electronic contributions in impedance-based measurements, necessitating ion-blocking contacts and advanced analytical methods to isolate the electronic component from mixed ion–electron transport⁵⁸. These difficulties are further complicated by transient swelling behaviours and ion sorption dynamics, which reduce measurement reproducibility and data fidelity⁵⁰. As a result, extracting reliable values of μ_{electron} typically necessitates specialized approaches, such as time-of-flight measurements⁵⁹ and small signal analysis performed within the OECT configuration⁶⁰.

Ion–electron conversion in hydrogel semiconductors

In hydrogel semiconductors, the ion–electron conversion process is governed by volumetric electrochemical doping, where ionic influx modulates electron transport throughout the 3D semiconducting network^{29,30}. OECTs are now widely used as a testbed for benchmarking ion–electron conversion efficiency¹³. However, methods commonly used in conventional thin-film OECTs have not been fully validated for hydrogel semiconductors⁶⁰, where challenges such as elevated contact resistance, swelling dynamics and interfacial instability necessitate further refinement.

The steady-state ion–electron conversion limit in hydrogel semiconductors can be evaluated by the on/off ratio of the assembled hydrogel OECTs (hydrogel transistor)⁶¹. Current hydrogel semiconductors mostly achieve on/off ratios in the range of 10^2 to 10^4 (refs. 29–31). Further enhancing the on/off ratio remains a challenge for hydrogel semiconductors, potentially owing to the aqueous operating environment that causes inevitable ion leakage currents. In contrast, poor on/off ratios often reflect incomplete doping/de-doping owing to

restricted ion transport in porous networks or inadequate electronic percolation, which compromise ion–electron conversion and result in poor switching performance²⁹.

The ion–electron conversion efficiency can be evaluated by the figure of merit of OEET, $\mu_{\text{electron}} C^*$ where C^* , the volumetric capacitance, reflects the material's ability to store charge per unit volume⁶². The metric, $\mu_{\text{electron}} C^*$, directly determines the transconductance, which quantifies the signal amplification ability of ionic signals into electronic signals, and thus the sensitivity of the hydrogel transistors⁵⁹. However, this metric can be unreliable when extracted directly from OEET models, as it is highly sensitive to device-level artefacts including swelling or dehydration⁶³, which may be more pronounced in hydrogel transistors. Independent measurements of μ_{electron} and C^* can effectively avoid these measurement artefacts.

The ratio of pseudo-capacitance to volumetric capacitance (C_p/C^*) can be another key material metric for evaluating ion–electron conversion efficiency. Solely using C^* to describe the charging behaviour fails to capture the complex electrochemical behaviour observed experimentally in both conjugated polymer thin-film and hydrogel semiconductors^{25,29,60}. C^* arises from two primary contributions: (1) the non-faradaic (double-layer) capacitance (C_{dl}) at the polymer/electrolyte interface, and (2) the pseudo-capacitance (C_p) originating from reversible faradaic redox processes. Both components inherently reflect the coupled transport of ions and electrons throughout the bulk of the hydrogel. To distinguish non-faradaic and pseudocapacitive currents, the cyclic voltammetry of the hydrogel semiconductor is fitted to the empirical model proposed by Dunn⁶⁴:

$$i(V) = k_1 v + k_2 v^{1/2}$$

where i is the current at a given potential V , v is the potential scan rate, $k_1 v$ represents the capacitive process and $k_2 v^{1/2}$ corresponds to redox processes. The coefficients k_1 and k_2 can be extracted, enabling a clear distinction between the two processes^{65,66}. Studies have shown that a large C_p indicates the presence of numerous redox-active sites that are readily accessible, which facilitate charge transfer in redox reactions⁶⁷. Hydrogel semiconductors rely on fast switching between two redox states. Consequently, the C_p/C^* ratio should be adopted as another key material metric for evaluating ion–electron conversion efficiency. Unlike $\mu_{\text{electron}} C^*$, C_p/C^* can be determined directly from device-independent electrochemical measurements (for example, cyclic voltammetry or electrochemical impedance spectroscopy), thereby providing an intrinsic material metric for assessing ion–electron conversion efficiency in hydrogel semiconductors^{64–66}.

Beyond $\mu_{\text{electron}} C^*$ and C_p/C^* , threshold thickness (d_{th}) should be treated as a key material metric for hydrogel semiconductors³. The d_{th} value represents a thickness threshold beyond which the capacitance fails to increase linearly with the thickness owing to thickness-limited ion diffusion⁶⁸. Hydrogel semiconductors, compared with their thin-film counterparts, can show a higher d_{th} up to millimetre scales owing to their 3D porous networks²⁹.

To advance the understanding and benchmarking of ion–electron conversion in hydrogel semiconductors, a unified charge-transfer model is urgently needed to capture the coupled kinetics of both ions and electrons. Traditionally, ion and electron transfer in electrochemical systems can be described using classical frameworks such as transition-state theory, including the Arrhenius equation and Eyring theory (which links the kinetic process with thermodynamic process), and the derived phenomenological Butler–Volmer equation. Marcus then recognized that conventional transition-state theory cannot be directly applied to electron-transfer reactions and thus introduced a vibrational model that incorporates the reorganization energy (λ), which quantifies the nuclear and solvent reorganization required before electron transfer⁶⁹. Gerischer subsequently defined the Fermi level of the electrolyte, and established correlations between

electrochemical potentials and energy levels, leading to the development of Marcus–Gerischer theory, which provides a powerful tool for analysing charge transfer and redox stability at semiconductor–electrolyte interfaces⁷⁰ (Supplementary Fig. 1). These classical models assume that either ion transfer or electron transfer is the rate-limiting step, but both processes occur simultaneously in hydrogel semiconductors. In this regard, the recently proposed coupled ion–electron transfer theory by Bazant⁷¹ provides a promising framework capable of capturing the interdependent dynamics of ion and electron transfer in hydrogel semiconductors.

Stability and reliability of hydrogel semiconductors

Stability and reliability of hydrogel semiconductors are essential for practical applications yet remain underexplored. Their high water content and viscoelastic nature render them highly sensitive to hydration levels, mechanical stress and environmental conditions (for example, temperature, pH, ionic strength). For example, insufficient hydration can reduce stretchability from 50% to 10% (ref. 30). Besides, the wet nature of hydrogel semiconductors poses additional challenges in establishing robust electrical contact with electrodes^{9,29,50}. To address these issues, it is crucial to establish a standardized process for the synthesis, fabrication and characterization⁵⁰ of hydrogel semiconductors. For example, Swagelok-type electrochemical cells can help establish reliable soft–rigid contacts for studying ion and electron transport of hydrogel semiconductors, while device architectures based on all soft materials may enhance interfacial robustness.

Furthermore, understanding the stability of hydrogel semiconductors requires operando characterization to enable real-time monitoring of multimodal material properties under complex, biomimetic conditions⁷². Unlike conventional semiconductors, which can be evaluated using steady-state characterization methods, hydrogel semiconductors demand specialized operando platforms to study how their structure, properties and performance evolve in real time when subjected to factors such as strain, temperature and humidity. Recent advances have focused on creating such platforms to explore charge-carrier transport and ion–electron coupling in hydrogels under multiple simultaneous stimuli, including electrical, electrochemical, mechanical and biological inputs⁷².

Another aspect is the study of the thermodynamic and hydrodynamic properties of hydrogel semiconductors. The overall performance of hydrogel semiconductors is determined by the interplay between these two properties, and their synergy and balance are crucial for optimizing and stabilizing the structure, environmental adaptability and semiconductor characteristics. Thermodynamic properties primarily influence network interactions⁷³, phase transition behaviours⁷⁴ and the activation energy of electrochemical reactions, thereby affecting the structural stability and environmental responsiveness. For multi-network hydrogel semiconductors, energy minimization is necessary to maintain the balance between networks and to prevent undesired phase separation or internal damage. In addition, thermodynamic behaviour influences the degree of disorder in the electron transport network and the stability of interfacial properties⁴⁰. Hydrodynamic properties, in contrast, impact the charge transport kinetics, internal fluid flow and permeability, which in turn affect dynamic characteristics, charge transport and conversion behaviours⁷⁵. A balance between these two properties is the key to ensuring the stable performance of hydrogel semiconductors in dynamic environments.

Discussion and perspectives

In summary, we have provided an overview and design guidelines for hydrogel semiconductors, which uniquely combine the electrical properties of semiconductors with the tissue-like properties of hydrogels. By addressing multimodal mismatches between semiconductors and living systems at soft–wet interfaces, hydrogel semiconductors

offer unprecedented opportunities for next-generation bioelectronics—including biohybrid, biointrinsic, living and symbiotic electronics—essential for advancing 3D soft electronics, real-time spatiotemporal biological research, wearable healthcare, implantable medicine and beyond.

At the material level, hydrogel semiconductors can immediately help to address the mechanical limitations of conventional OMIECs. Simultaneously, they also enhance ion transport in OMIECs by decoupling ion transport from the semiconducting polymer backbone through the formation of continuous liquid pathways, thereby simplifying OMIEC materials design^{21,53}.

At the device level, hydrogel semiconductors overcome the thickness limitations of traditional OMIECs, achieving complete volumetric doping/de-doping even at millimetre-scale thicknesses²⁹. This enables the exclusive fabrication of macroscopic 3D OMIEC devices that mimic biological systems across different length scales. Their large feature sizes and tissue-like softness simplify fabrication, making it possible to create 3D logic devices using accessible low-resolution techniques such as printing and textile manufacturing.

The transition from conventional 2D rigid semiconductors to 3D soft hydrogel semiconductors provides opportunities for developing advanced bioelectronic systems, particularly in three key areas.

Real-time spatiotemporal biological research: despite a century of progress, the study of biology remains constrained by a fundamental mismatch—biological processes are dynamic, but our tools are static⁷⁶. Activities such as protein folding, neuronal firing, metabolite flux and disease progression unfold continuously across space and time, yet conventional analysis requires halting them through tissue extraction, sectioning, fixation or freezing. Even recent spatiotemporal omics, which maps biomolecules across locations and time points, still relies on non-living samples. As a result, we observe biological processes much like reconstructing a film from a few still images, piecing together continuous dynamics from disconnected snapshots⁷⁶. Hydrogel semiconductors offer a way past this limitation by enabling direct, continuous observation of biological processes within living tissue. Their tissue-like softness, 3D conformability and volumetric ion–electron coupling make it possible to build bioelectronic tools that sense, record and analyse biological activity in real time and in vivo^{29–32}. Such tools could reshape our understanding of biological processes, expanding fragmented snapshots into an end-to-end view of how they truly unfold.

Wearable healthcare: since the introduction of the pacemaker in the 1950s, wearable healthcare has continuously advanced towards soft, tissue-like electronics. Hydrogel semiconductors, by uniting the softness of hydrogels with the signal amplification capability of semiconductors, can substantially improve electrode technologies. They enable the transition from classic 2D rigid, poorly conformal electrodes to 3D soft interfaces. These improvements can enhance signal quality, reduce motion artefacts and immune responses, and ultimately support precise, reliable and long-term monitoring or therapeutic use^{30,77}.

Implantable medicine: hydrogel semiconductors, leveraging their intrinsically 3D, tissue-compatible properties, enable intimate integration with cells across scales—from the microscale to the organ level. This capability supports programmable tissue engineering⁷⁸ and controlled drug delivery⁸. For example, bioactive drugs can be loaded into an implantable hydrogel-based electronic device, with release actively regulated and programmed by electronic or biological cues⁷⁹. In addition, therapeutic cells (such as cardiomyocytes) can replace drug cargos to repair damaged tissues, offering pathways towards regenerative medicine⁸⁰.

We further envision a research direction that hydrogel semiconductors can enable—biointrinsic electronics. Biointrinsic electronics can be defined as electronic systems whose intrinsic material properties—mechanical modulus, hydration state, signal transduction modality, dimensional architecture, chemical composition and temporal

dynamics—simultaneously converge with those of living biological systems, not through extrinsic engineering strategies but through the fundamental molecular and structural design of the constituent materials themselves. What sets biointrinsic electronics apart from bioinspired electronics is the shift from solving one mismatch at a time—mechanics, hydration or dimensionality—to resolving all of them at once within a single material system. This is a scientific challenge that has not yet been systematically defined, let alone conquered, providing opportunities for those aiming to develop advanced bioelectronic healthcare systems at wet and soft interfaces.

Beyond the field of bioelectronics, hydrogel semiconductors also hold potential in other emerging fields such as soft robotics⁸¹ and environmental sensing⁸². Their inherent softness and in-sensor computing capabilities make them excellent for developing sensitive artificial muscles in robotics. Their ability to work in water makes them highly suitable for environmental and ocean sensors. The ability to control ion–electron behaviour further allows for the creation of next-generation programmable supercapacitors and batteries with enhanced efficiency and tunability. Furthermore, their unique colorimetric properties offer opportunities to develop cost-effective soft displays for use in water environments.

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Author contributions

Shiming Zhang conceived of the review, acquired funding and supervised this work. Shiming Zhang and H.H. designed the structure of this review. H.H. and J.B. prepared the schematics and figures. H.H., X.M., Silan Zhang, J.B., B.C., X.C., N.W. and G.G.M. contributed to the content discussions. Shiming Zhang drafted the paper, with assistance from H.H. and X.M. All authors contributed to the review and revision of the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Shiming Zhang.

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