



Cite this: *Chem. Commun.*, 2022, 58, 185

Recent advances in conductive polymer hydrogel composites and nanocomposites for flexible electrochemical supercapacitors

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Flexible electrochemical supercapacitors have shown great potential in the next-generation wearable and implantable energy-storage devices. Conductive polymer hydrogels usually possess unique porosity, high conductivity, and broadly tunable properties through molecular designs and structural regulations, thus holding tremendous promise as high-performance electrodes and electrolytes for flexible electrochemical supercapacitors. Numerous chemical and structural designs have provided unlimited opportunities to tune the properties of conductive polymer hydrogels to match the various practical demands. Various electrically and ionically conductive hydrogels have been developed to fabricate novel electrodes and electrolytes with satisfactory mechanical and electrochemical performance. This feature article focuses on the fabrication and applications of conductive polymer hydrogel composites and nanocomposites as respective electrodes and electrolytes for flexible electrochemical supercapacitors. First, we introduce the representative strategies to prepare electrically and ionically conductive polymer hydrogels. Second, conductive polymer hydrogel composites and nanocomposites as supercapacitor electrodes and electrolytes are presented and discussed. Finally, challenges and perspectives on conductive polymer hydrogel composites and nanocomposites for future flexible electrochemical supercapacitors are presented.

Received 30th September 2021,
Accepted 17th November 2021

DOI: 10.1039/d1cc05526g

rsc.li/chemcomm

1. Introduction

With the increasing demand for portable, flexible, and wearable electronic devices, flexible energy storage systems have received increasing attention as a key component in this emerging field.^{1–4} Owing to their indispensable role in building sustainable energy output systems, flexible energy storage systems have been touted as a key component of next-generation wearable electronics that can be bent, folded, and stretched to fit into non-planar forms for widespread applications in portable and wearable electronics, roll-up displays, electronic newspapers, paper-like mobile phones, and other easily collapsible gadgets.^{3,5,6} Supercapacitors are representative electrochemical energy storage systems that provide high power density, fast charge/discharge rate, exceptionally long cycle life compared to batteries and enhanced energy density compared to conventional capacitors.^{7–12} Currently, supercapacitors are classified into two types in terms of their charge

storage mechanism. One is electric double layer supercapacitors (EDLCs). In EDLCs, the capacitance derives from the electrostatic charge accumulated at the electrode/electrolyte interface; therefore it is strongly dependent on the surface area of electrode materials that is accessible to electrolyte ions. The other type of supercapacitors is pseudocapacitive capacitors. In these pseudocapacitors, the capacitance comes from the reversible redox reactions between the electrolyte and electroactive species on the surface of electrodes. Besides, the critical influencing factor of reversible redox reactions depends on both proton-exchanging and electron-hopping processes.¹³ The realization of flexibility in supercapacitor devices requires the integration, assembly and collaboration of different components in the device, such as the electrodes, electrolyte and current collector. However, the conventional electrodes (carbon-based materials, metal oxide/nitrides/sulfides and conducting polymers) and liquid-phase electrolytes (aqueous and organic electrolytes) for supercapacitors usually lack flexibility and are fragile. To address this challenge, abundant research has been focused on the development of intrinsically flexible conducting and electrochemically active materials for the fabrication of flexible supercapacitors.^{14,15} As electrodes and electrolytes are the key components of supercapacitors, the critical challenge in the fabrication of flexible supercapacitors

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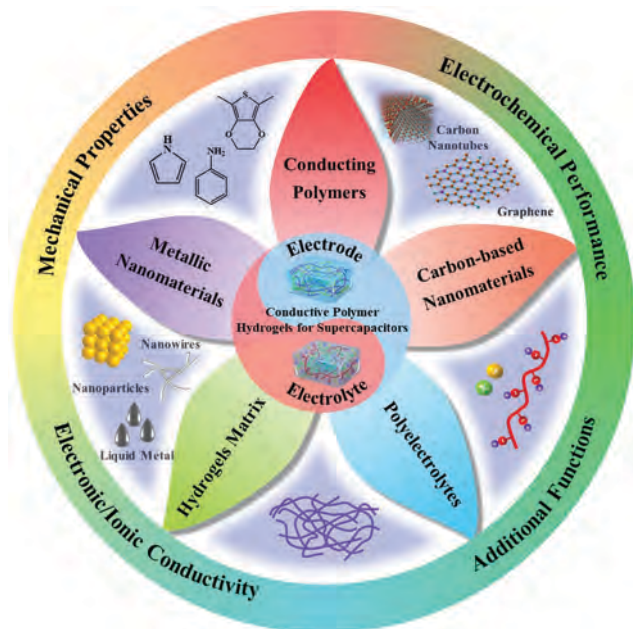


Fig. 1 Schematic illustration of the main components of conductive polymer hydrogel composites and nanocomposites as electrodes and electrolytes for flexible electrochemical supercapacitors.

lies in the exploitation of intrinsically flexible electrode and electrolyte materials.

Hydrogels are three-dimensional (3D) crosslinked polymer networks formed by either natural or synthetic materials, which could hold a lot of water due to the abundant hydrophilic groups on their backbone structure. Both chemical crosslinking (*e.g.*, covalent bonding) and physical crosslinking (*e.g.*, hydrogen bonding, ionic interaction and hydrophobic interaction) contribute to the formation of a hydrogel.¹⁶ Conductive polymer hydrogels are a new class of functional polymer hydrogels, which mainly combine a hydrophilic polymer hydrogel matrix with electrically or ionically conducting fillers, such as carbon-based materials, conducting polymers, metallic nanomaterials, polyelectrolytes, ions, *etc.* (Fig. 1). Conductive polymer hydrogels integrate the advantages of both liquid and solid, which make them promising for application in the fields of tissue engineering, strain/stress sensors, implantable electronics and flexible energy-storage devices. As for flexible electrochemical supercapacitors, conductive polymer hydrogels have the potential to be an ideal candidate for traditional electrode and electrolyte materials owing to their appropriate electrical, mechanical and chemical properties.¹⁷ Plentiful types of research studies have witnessed the remarkable performance of conductive polymer hydrogels as electrodes for flexible supercapacitors. The tunable chemical structure of the hydrophilic polymer hydrogel matrix endows conductive polymer hydrogels with extensive mechanical properties ranging from soft-and-weak to hard-and-tough, enabling devices to undergo large and complex deformations. Besides, the 3D interconnected frameworks of conductive polymer hydrogels provide continuous conducting pathways for fast electron transportation, which is essential for high-performance electrode materials. As for electrolytes, the porous microstructures

and hydrophilic characteristics of conductive polymer hydrogels endow them with the capability of swelling a large number of electrolytic ions in liquids. The electrolytic ions can be trapped and confined within the robust and 3D interconnected hydrogel frameworks. Thus, the conductive polymer hydrogels possess liquid-like ionic conductivity and solid-like structural stability, making them ideal electrolyte materials. Furthermore, the unique porous microstructure of conductive polymer hydrogels is quite favorable for the establishment of an ideal interface between the electrode and the electrolyte, thus promoting enhanced ion diffusion and efficient electrochemical reactions. More importantly, the mechanical and electrochemical performance of conductive polymer hydrogels could be easily tuned over a wide range by varying the polymer hydrogel matrix, electrically/ionically conducting fillers and their combinations.¹⁷

Based on the several reports and accumulating evidence regarding conductive polymer hydrogels in recent years, this feature article provides a review of conductive polymer hydrogels (Fig. 2). In this review, we focus on the research progress in the preparation of conductive polymer hydrogels and their applications as electrodes and electrolytes in flexible electrochemical supercapacitors. This review begins with the design and fabrication of conducting polymer hydrogel composites and nanocomposites in Section 2, which includes electrically and ionically conducting polymer hydrogels. Next, the application of conducting polymer hydrogel composites and nanocomposites as electrodes and electrolytes in flexible supercapacitors is discussed in Sections 3 and 4, respectively. Finally, we discuss the challenges and perspectives of flexible supercapacitor devices based on conductive polymer hydrogels.

2. Fabrication of conductive polymer hydrogel composites and nanocomposites

Conductive polymer hydrogels are often incorporated with functional materials such as carbon-based materials, conducting

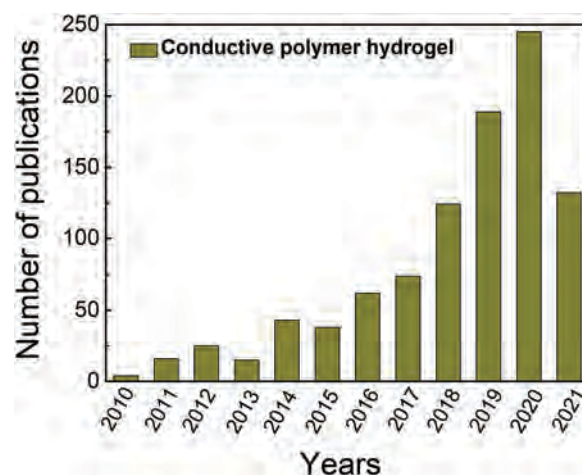


Fig. 2 Annual number of publications on "conductive polymer hydrogel" from the Web of Science until Sept. 2021.

polymers, metallic nanomaterials and ions, which endow them with electrical and ionic conductivity. Based on the different conductive mechanisms, the conductive hydrogels can be divided into two types: electrically conductive hydrogels and ionic conductive hydrogels. Within the hydrophilic hydrogel network, these incorporated functional materials establish conductive pathways to transmit either electrons or ions to yield conductive polymer hydrogels. We summarize the major strategies for the preparation of conductive polymer hydrogels in Fig. 3. Moreover, we summarize the existing methods to fabricate electrically and ionically conductive polymer hydrogels in the following.

2.1 Fabrication of electrically conductive polymer hydrogels

2.1.1 Conducting polymer-based electrically conductive polymer hydrogels.

The most widely reported conducting polymers for preparing conductive polymer hydrogels are poly(3,4-ethylene dioxythiophene) (PEDOT), polypyrrole (PPy) and polyaniline (PANI).^{18–20} These conjugated polymers share a similar mechanism in constructing an electrical pathway for mobile charge carriers.²¹ The conductivity of conducting polymers can be largely improved by simply incorporating a variety of dopants *via* simple and cost-effective synthesis routes.²² However, owing to the aromatic rings and highly conjugated structures, conducting polymers are inherently rigid and hydrophobic in nature. These features make them unsuitable for direct application in flexible electronic devices. Conducting polymer-based conductive polymer hydrogels represent a novel polymeric soft material platform that synergizes the advantages of organic conductors and hydrogels.¹⁶

There are generally three different ways to acquire conducting polymer-based conductive polymer hydrogels. The first is the direct gelation of the mixture of conducting polymers and hydrophilic polymers/monomers through the self-assembly process.^{23,24} Wu *et al.* reported a robust, highly stretchable supramolecular polymer conductive hydrogel, which was fabricated by simply

in situ doping poly(*N*-acryloyl glycinamide-*co*-2-acrylamide-2-methyl propane sulfonic) (PNAGA-PAMPS) hydrogels with poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS).²³ The as-fabricated PNAGA-PAMPS hydrogels demonstrated high mechanical performance with an ultra-high elongation at break ($\sim 1700\%$). Due to the improved conductivity by the incorporation of doped PEDOT:PSS, the fabricated supramolecular gel electrode possessed high capacitive performance. Despite some progress that has been reported in the fabrication of conducting polymer-based conductive polymer hydrogels through this method, the relatively poor solution processability of conducting polymers induced by the highly conjugated structure limits its further application.

Second, the conductive polymer hydrogels could be fabricated by *in situ* polymerization of conducting polymers within a preformed polymer hydrogel matrix. The first electrically conductive polymer hydrogel synthesized by this method was reported in 1997 by Pissis *et al.*, who polymerized PPy directly on a preformed polyacrylamide (PAM) hydrogel.²⁵ This work attracted widespread interest in the construction of conducting polymer-based electrically conductive hydrogels by a combination of various polymer hydrogel matrices and conducting polymers. With this method, Yu *et al.* reported a conductive polymer hybrid hydrogel with a double network, which was achieved by *in situ* formation of a continuous network of conductive polymer hydrogels (PANI or PPy) crosslinked by phytic acid in the poly(*N*-isopropyl acrylamide) hydrogel matrix (Fig. 4a).²⁶ The interpenetrating binary network structure provided the hybrid hydrogels with a continuous electron-transporting path, a highly porous microstructure, and strong interactions between two hydrogel networks, thus endowing the hybrid hydrogels with a unique combination of high electrical conductivity (0.8 S m^{-1}) and greatly enhanced mechanical properties. The usage of phytic acid is vital for the formation of a continuous conducting polymer network in a preformed polymer hydrogel framework, thus

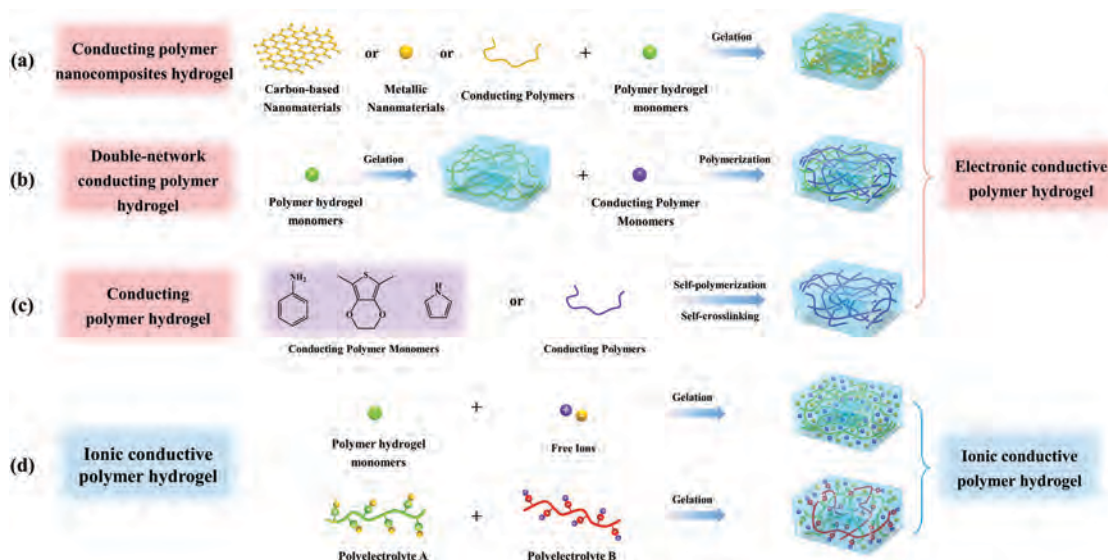


Fig. 3 Major strategies for the preparation of conductive polymer hydrogels.

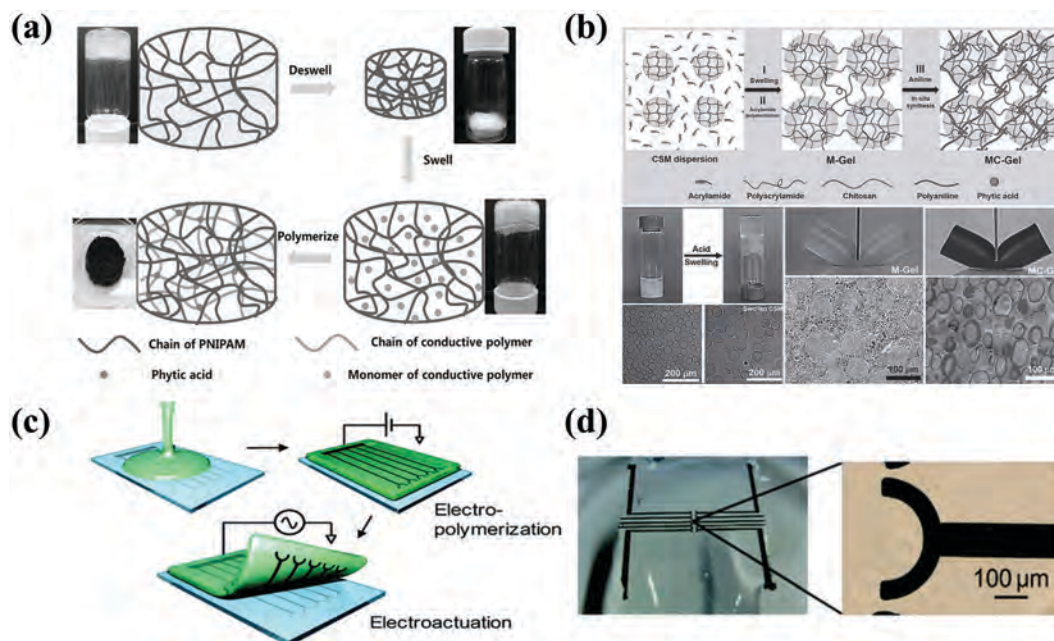


Fig. 4 Fabrication of conducting polymer-based hydrogels. (a) Schematic illustration of the synthesis process of hybrid hydrogels composed of PNIPAM and conducting polymers.²⁶ Copyright 2015, Wiley-VCH. (b) Fabrication of conductive PANI/PAM/chitosan hydrogels via *in situ* synthesizing PAM and PANI in a closely packed swollen chitosan microspheres.²⁷ Copyright 2016, Wiley-VCH. (c) Schematic illustration of the fabrication of conducting polymer/hydrogel electrodes by electro-polymerization.²⁸ Copyright 2010, American Chemical Society. (d) Photograph showing the PEDOT micro-electrode array on a gel sheet.²⁸ Copyright 2010, American Chemical Society.

leading to largely improved electronic conductivity and mechanical property. Similar research was also reported by Duan *et al.* They constructed a robust and force-sensitive hydrogel by *in situ* synthesizing PAM and PANI in closely packed swollen chitosan microspheres (Fig. 4b). The obtained conducting polymer hydrogel with multi-interpenetrating polymer networks exhibited high strength, ultra-stretchability (strain exceeding 600%) and excellent mechanical stability.²⁷ Apart from *in situ* chemical polymerization of conducting polymers, conducting polymer hydrogels were also fabricated by *in situ* electro-polymerization on a hydrogel surface to form a micropattern, which was quite important for subsequent device fabrication. Soichiro *et al.* reported the fabrication of micro-patterned conducting polymer hydrogels via electro-polymerization of PEDOT on an agarose hydrogel surface to provide a fully organic, moist, and flexible electrode.²⁸ The PEDOT/agarose electrodes were prepared via two electrochemical processes of electro-polymerization of PEDOT into hydrogels and electrochemical-actuation-assisted peeling (Fig. 4c and d). The agarose solution was poured over a Pt microelectrode on glass plates. After gelation of agarose, electro-polymerization was conducted on the gel-covered electrode in aqueous monomer solution.

The third way is to synthesize conducting polymer hydrogels through self-crosslinking or self-assembly. The above-mentioned synthetic approaches, *i.e.*, to use a non-conductive polymer hydrogel as the scaffold to support either conducting polymer filler or another conducting polymer network, always result in a conductive polymer hydrogel composite with a large proportion of non-conductive polymer matrix, which inevitably degrades the conductivity and the resulting performance of the final supercapacitor devices.¹⁷ To address this problem, extensive

attention has been paid to develop pure conducting polymer hydrogels without any insulating components.^{29–34} The first synthesized pure conducting polymer hydrogel (PANI hydrogel) was reported by Bao *et al.* in 2012. They used phytic acid as the gelator and dopants to directly form a conducting polymer network free of insulating polymers. The gelation mechanism is illustrated in Fig. 5a. Phytic acid (PA) could react with PANI by protonating the nitrogen groups on PANI. Theoretically, each phytic acid molecule could interact with six PANI chains, resulting in the formation of a mesh-like hydrogel network. With a high surface area and a 3D porous nanostructure, the fabricated PANI hydrogels demonstrated excellent electrical conductivity and electrochemical properties, which could act as high-performance supercapacitor electrodes with high specific capacitance, unprecedented rate capability and cycling stability.²⁹ This dopant cross-linking method using PA molecules is also feasible for preparing pure PPy hydrogels. Owing to the relatively poor water solubility of the pyrrole monomer, the nanostructure of PPy hydrogels was fabricated via an interfacial polymerization method. The microstructure of PPy hydrogels was tuned by altering the ratio of pyrrole and PA.³⁵ Besides PA, copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (CuPcTs) was also used as a dopant and gelator to self-assemble PPy into nanostructured hydrogels through electrostatic interactions and hydrogen bonding (Fig. 5b). The PPy hydrogels could be synthesized in bulk quantities with uniform morphology of self-assembled interconnected nanofibers. The tetra-functional dopant favored a supramolecular self-assembly mechanism to form one-dimensional PPy nanostructures. Furthermore, the CuPcTs doped and crosslinked PPy hydrogel exhibited superior

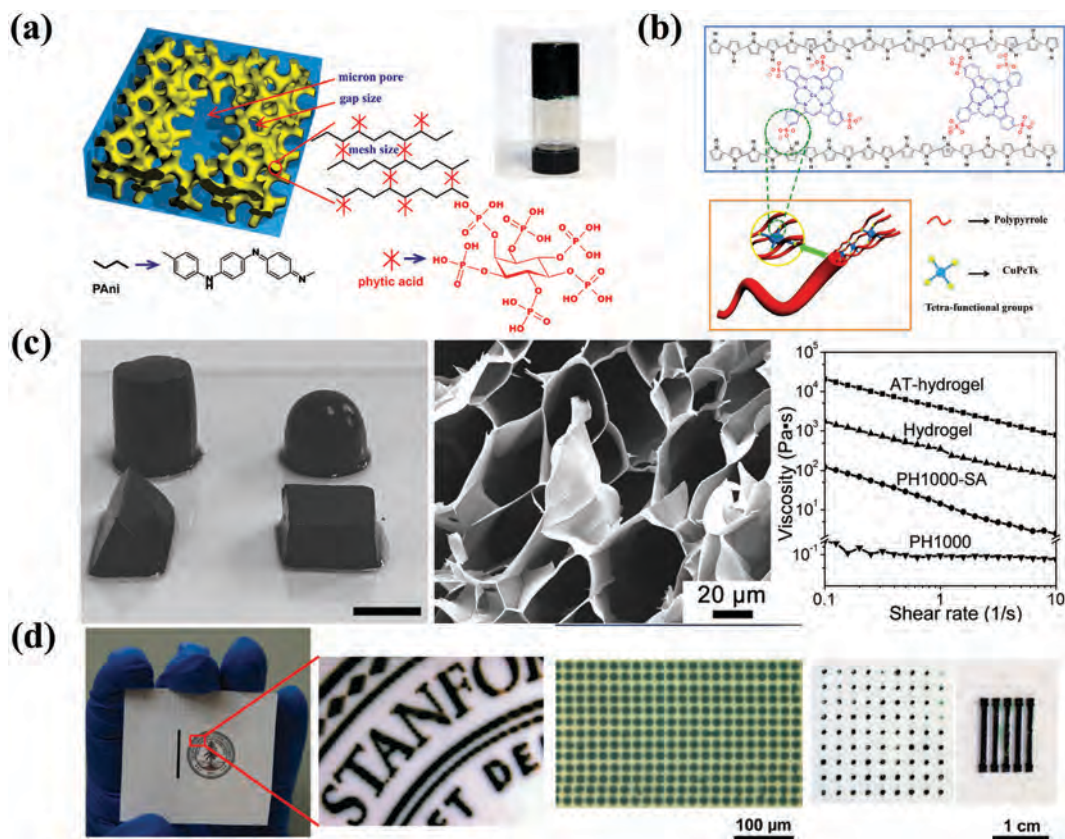


Fig. 5 Fabrication of self-crosslinked conducting polymer hydrogels. (a) PANI hydrogels crosslinked by phytic acid.²⁹ Copyright 2012, National Academy of Sciences. (b) PPy hydrogels crosslinked by CuPcTs.³² Copyright 2015, American Chemical Society. (c) Self-crosslinked PEDOT hydrogels prepared by thermal annealing in combination with concentrated sulfuric acid treatment.³⁶ Copyright 2017, Wiley-VCH. (d) Micropatterning of PANI hydrogels by ink-jet printing and spray coating.²⁹ Copyright 2012, National Academy of Sciences.

conductivity (7.8 S cm^{-1}) compared with pristine PPy (0.07 S cm^{-1}), due to the enhanced interchain charge transport through the interconnected PPy nanofibers.³²

Besides the aforementioned approaches, several distinctive controllable annealing methods have also been proposed for constructing pure conducting polymer hydrogels.^{30,31,33} As an example, a conductive PEDOT:PSS hydrogel was prepared by thermal annealing in combination with concentrated sulfuric acid treatment (Fig. 5c). The acid-induced conformational variation of PEDOT chains from a random coil to an expanded-coil structure with the assistance of heat promoted interchain interactions to form a physically crosslinked 3D network. Moreover, specific functional groups of surfactants also enabled physical entanglement with PEDOT:PSS chains and the subsequent gelation.³⁶ Guo *et al.* reported a self-crosslinked PANI hydrogel *via* an oxidative coupling reaction by using ammonium persulfate as the oxidizing agent and aniline hydrochloric salt as the precursor. This is the first case of PANI hydrogel without the use of any additional crosslinkers during polymerization. They proposed the following three reasons to explain the gelation of PANI without any crosslinkers: (1) the *ortho*-position of aniline could react with monomers to generate branched chains, and probably produced another PANI chain to obtain the network structure;

(2) π - π stacking of benzene rings could also link different chains to form mesh structures; and (3) physical entanglement of long chains could also act as crosslinking points to enhance the hydrogel network.³¹

Owing to the easy synthesis and tunable mechanical properties, the conducting polymer hydrogels showed high scalability and processability, which could be processed by scalable techniques of ink-jet printing or spray coating. Therefore, the resultant conducting polymer hydrogels showed potential in fabricating desired micropatterns for large arrays of electrochemical devices (Fig. 5d).²⁹ Ink-jet printing of polymers was often hampered by the limited solubility and high viscosity of polymer solution.¹⁸ This difficulty was overcome by separately depositing two distinct solutions containing oxidative initiators and phytic acids, and monomers for conducting polymer synthesis onto the substrate. The patterned PANI hydrogel was formed when the two solutions interacted, and the morphology of the printed hydrogels was found to be similar to that of bulk synthesized hydrogels. The conducting hydrogels were also processed by spray coating to form micropatterns of millimeter size.²⁹ Similar to ink-jet printing, two kinds of solutions were alternately deposited multiple times through poly(dimethylsiloxane) soft stencil masks onto a wide range of substrates. Through these approaches, large arrays of patterned conducting polymer hydrogels were easily fabricated, leading to

highly conductive and functional microelectrodes potentially suitable for flexible supercapacitors, lithium batteries, biosensors, chemical sensors, and other bioelectrodes.

2.1.2 Carbon-based electrically conductive polymer hydrogels. Carbon-based materials, such as carbon nanotubes (CNTs), graphene, activated carbon, carbon fibers, and porous carbon, are promising conductive materials for fabricating conductive polymer hydrogels, due to their unique properties of high electrical conductivity, excellent environmental stability and low production cost.^{16,37–39} Among the variety of carbon-based materials, CNTs and graphene have been widely explored in materials science, and have also been intensively used as conductive fillers in the fabrication of conductive polymer hydrogel nanocomposites with improved mechanical properties and electrical conductivity.^{40–44}

In a typical synthesis, graphene oxide (GO), instead of graphene, is used as a conducting filler to fabricate conducting polymer hydrogel nanocomposites owing to its significantly improved dispersion in a hydrophilic polymer hydrogel matrix.^{45,46} Besides, the functional groups of GO sheets not only make GO thoroughly exfoliated in water but also provide hydrogen-bond interactions with the polymer hydrogel matrix, further contributing to improved mechanical property of the hydrogels.^{47–49} However, GO with a high oxidation degree would exhibit a decrease in conductivity due to defects in its conjugated structures. To address this problem, a reported strategy is to reduce GO during the gel formation process. Lu *et al.* reported a conductive polydopamine (PDA) partially reduced GO (pGO)-PAM hybrid hydrogel, which simultaneously possessed high conductivity and toughness as well as self-adhesiveness and self-healing ability.⁵⁰ The synthesis

process to form the hydrogel is illustrated in Fig. 6a. First, GO was partially reduced in PDA solution, which was prepared by polymerization of dopamine under oxidative and alkaline conditions. Then, the conductive hydrogel was developed by polymerizing acrylamide monomers in the presence of pGO. The fully reduced GO (rGO) could uniformly disperse in the PAM hydrogel network and form electron-conducting pathways, providing the conductive hydrogel with good conductivity. The unreduced GO with oxygen-containing groups could interact with PAM chains *via* hydrogen bonds and electrostatic interactions. Otherwise, PDA also interacted with PAM chains by π - π stacking and hydrogen bonds. These synergistic contributions of noncovalent interactions imparted toughness and high stretchability to the conductive hydrogel. In this approach, carbon-based materials act as conductive fillers rather than crosslinking agents, and thus a stable interconnected polymer chain was necessary to provide additional structural support. Therefore, the key of this approach relies on fine dispersion of conductive fillers in sol solution and subsequently in the 3D hydrogel network.

Unlike conductive polymer-based electrically conductive polymer hydrogels where the polymer chains are typically interconnected by crosslinking, these carbon-based conductive nanofillers are isolated in polymer hydrogels, which make nanofillers difficult to form an electrically percolating network.²¹ There are two different ways to achieve connected or percolating networks in carbon-based electrically conducting polymer hydrogel nanocomposites. One is to design the morphology of nanofillers to achieve an efficient percolating network. Han *et al.* reported a type of multi-functional conducting polymer hydrogel nanocomposite with a dynamically

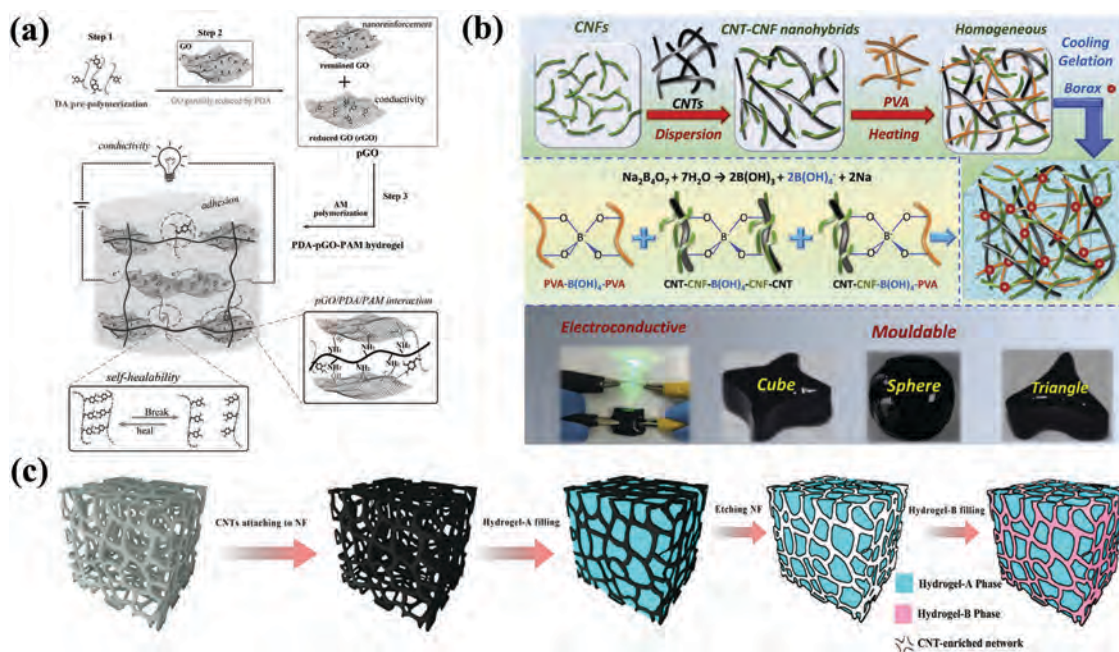


Fig. 6 (a) Schematic of the PDA-pGO-PAM hydrogel.⁵⁰ Copyright 2017, Wiley-VCH. (b) Fabrication process of CNT-CNF/PVAB composite gels and conductive CNT-CNF/PVAB hydrogels with various shapes.⁵¹ Copyright 2019, Elsevier. (c) Schematic diagram of the preparation of novel electrically conductive polymer hydrogels with double networks.⁵² Copyright 2020, Royal Society of Chemistry.

crosslinked 3D network, which was synthesized by homogeneously dispersing carbon nanotube/cellulose nanofiber (CNT–CNF) nanohybrids in a viscoelastic polyvinyl alcohol-borax (PVAB) gel matrix (Fig. 6b). The sustainable and renewable CNF acted as a bio-template and dispersant to carry CNTs to form well-dispersed CNT–CNF nanohybrids in aqueous suspensions, while borate ions served as a reversible cross-linker for the dynamic association of CNT–CNF nanohybrids and polyvinyl alcohol (PVA) chains. Based on the easy approach, the CNT–CNF nanohybrids, which not only enhanced the viscoelasticity and mechanical toughness of the hydrogel, but also endowed the CNT–CNF/PVAB hydrogel with high conductivity, flexibility and stability, were uniformly dispersed in the gel matrix to build up a hierarchically integrated conducting and reinforcing network structure.⁵¹ The other way is to build a pre-interconnected scaffold or framework before forming a hydrogel nanocomposite. For instance, Ying *et al.* reported a hydrogel with a CNT-enriched conductive network and a physical-phase-type interpenetrating network. This physical-phase-type interpenetrating network was constructed with the help of nickel foam in consideration of its unique 3D macropore network (Fig. 6c). They focused on the contribution of the CNT-enriched network to the electrical conductivity and electro-response of composite hydrogels based on poly 2-acrylamide-2-methyl-1-propane sulfonic acid-*co*-polyacrylic acid (PAMPS-*co*-PAA)-based composite hydrogels. Due to the 3D CNT-enriched conductive network, the targeted hydrogels showed outstanding electrical conductivity performance with an electrical conductivity of $1.82 \times 10^{-2} \text{ S cm}^{-1}$. The existence of the CNT-enriched network was beneficial to accelerate the electrical conductivity and response.⁵²

2.1.3 Metal-based electrically conductive polymer hydrogels.

Metals with low-dimensional nanostructures, such as nanowires, nanorods, and nanoparticles, are one of the most promising nanomaterial candidates for the fabrication of conductive polymer hydrogels owing to the advantages of high electrical conductivity, interesting optical and catalytic properties, and facile fabrication and modification processes.^{16,43,53–56} The research on metal-based conductive hydrogels is relatively rare. Recently, ionic grafting of poly(acryloyl hydrazide) (PAHz)–silver (Ag) nanocomposites was used to improve the mechanical properties and conductivity of poly(2-acrylamido-2-propane sulfonic acid) (PAMPS) hydrogels. The PAHz–Ag nanocomposites possessing different sizes of Ag nanoparticles (3–40 nm) were grafted in the PAMPS hydrogel matrix *via* ionic linkage. The resulting PAHz–Ag grafted hydrogels with a water content of 62% exhibited an ultimate tensile strength and fracture energy up to 1.14 MPa and 1600 J m^{-2} , respectively. The obtained hydrogel samples exhibited adequate conductivity and strain sensing ability, suggesting that these samples were potentially useful for various soft hydrogel electrode applications.⁵⁷ This research also implied that the metal nanoparticle grafting strategy could be a common method to improve the mechanical properties as well as the conductivity of hydrogel systems. In addition to the great efforts that have been made for fabricating metal-based conductive

hydrogels with enhanced electrical conductivity and mechanical properties, some researchers have reported the use of new metal materials (like liquid metals) to prepare novel conductive hydrogels.^{58–61} Zhang *et al.* reported PVA-stabilized liquid metal particle (PVA–LMP) hydrogels with excellent electrical conductivity and self-healing performance.⁵⁸ It was demonstrated that the hydroxyl groups of PVA stabilized the LMPs *via* hydrogen-bond interactions. Furthermore, the dynamic cross-linking bonds between hydrogels and LMPs could rupture and coalesce reversibly in the hydrogel network, endowing the hydrogels with both electrical and mechanical self-healing ability.

2.2 Fabrication of ionic conductive polymer hydrogels

With the rapid development of flexible electronic devices, ionic conductive polymer hydrogels, as a kind of flexible ionic conductor, have been used in a wide range of flexible electrochemical devices including batteries, supercapacitors and fuel cells, as well as many types of wearable sensors.^{62–66} Hydrogels provide plenty of channels for ion migration as they consist of a 3D framework structure and a continuous water phase. For ionically conductive hydrogels, the conductivity comes from the directional transportation of free ions.^{67–69} Generally, free ions are mainly derived from two components of hydrogels (polymer network and solvent). The vast majority of polyelectrolyte networks contain ionized groups (such as poly acidic monomer, acrylic acid and poly ionic liquids), which provide mobile ions arising from the hydrolyzed bonds. Polyzwitterions have both cationic and anionic charge on the same macromolecular chain, which could be used for preparing ionic conductive hydrogels because they ensure high ionic conductivity.¹⁶ Xie *et al.* reported a new kind of zwitterionic hydrogel electrolyte fabricated by free-radical polymerization of propyl sulfonate dimethylammonium propyl-methacrylamide (PDP). The fabricated hydrogel electrolyte not only had robust water retention ability from the combination of water molecules around the charged groups, but also provided ion migration channels to electrolyte ions, leading to enhanced electrochemical performance for solid-state supercapacitors.⁷⁰

Our group also reported a highly stretchable and transparent ionic conductive hydrogel (PAM-r-MVIC) from ionic liquid monomers.⁷¹ The PAM-r-MVIC hydrogel was prepared through *in situ* covalent crosslinking of 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (MVIC) and acrylamide (AM) as the comonomers. The positively charged 1-N atoms of imidazole rings in the PAM-r-MVIC hydrogel were beneficial for uniformly locking counter ions, thus contributing to an excellent ionic conductivity. According to the differences in oxygen and nitrogen electronegativity, a multi-level dense hydrogen-bonded network structure with graded response was formed between hydroxyl/amino groups and 3-N and amino groups on imidazole. The strong hydrogen-bonded network structure improved the mechanical strength as a stable crosslinking, while the weak hydrogen-bonded network structure absorbed energy through a fracture during deformation to achieve mechanical toughness enhancement and rapid stress recovery performance. As a consequence, the high-density multi-level hydrogen bonding

network structure enabled the ionic gel to gain high segmental dynamic capabilities, excellent ductility with a large fracture strain (>1000%), along with a high tensile strength of 0.47 MPa and a high toughness of 2950 kJ m^{-3} , as well as excellent fatigue resistance. Metal ions could provide both conductivity and network crosslinking.⁷²⁻⁷⁴ An anionic Fe^{3+} -coordinated polyacrylic acid network (Fe-PAA) was *in situ* formed within a confined space of the polyelectrolyte network skeleton of the cationic Fe^{3+} -coordinated chitosan network (Fe-CS) to generate an ionic conductive hydrogel (DHB-Fe/CS/PAA) with highly stretchable, fatigue-resistant and self-healing properties (Fig. 7a).⁷⁵ Interestingly, a dense hydrogen-bonded network between the Fe-PAA and Fe-CS chains within the Fe/CS/PAA hydrogel was formed by simple post-processing (salt impregnation). Benefiting from the formation of a dense hydrogen-bonded network, the resultant dense hydrogen-bonded hydrogel (DHB-Fe/CS/PAA) exhibited a high tensile strength of $\sim 0.34 \text{ MPa}$, a large stretchability of $\sim 1370\%$, excellent fatigue resistance for 1000 cycles and heat-accelerated self-healing ability. Owing to the abundant charged groups and impregnated salts, DHB-Fe/CS/PAA

demonstrated a high ionic conductivity of 0.24 S m^{-1} and excellent mechanical flexibility even under a subzero temperature of $-25 \text{ }^\circ\text{C}$.

As the most important component of hydrogels, water contained in hydrogels can dissolve ions arising from the dissociated inorganic acid, alkali, and salt, thus rendering hydrogels good ionic conductors. Hence, constructing ion channels in hydrogel networks for fast ion transportation is an effective way for the ionic conductivity improvement of this kind of ionic conductive polymer hydrogel.⁷⁷ Hu *et al.* developed a strong anisotropic wood hydrogel by combining strong and stiff aligned wood nanofibers with a weak but flexible PAM hydrogel (Fig. 7b).⁷⁶ The wood hydrogel exhibited a high tensile strength of 36 MPa along the longitudinal direction due to the strong bonding and crosslinking between the aligned cellulose nanofibers and the PAM chains. Due to the negatively charged aligned CNF, the wood hydrogel was also an excellent nanofluidic conduit with an ionic conductivity of $5 \times 10^{-4} \text{ S cm}^{-1}$ at low concentrations for highly selective ion transport.

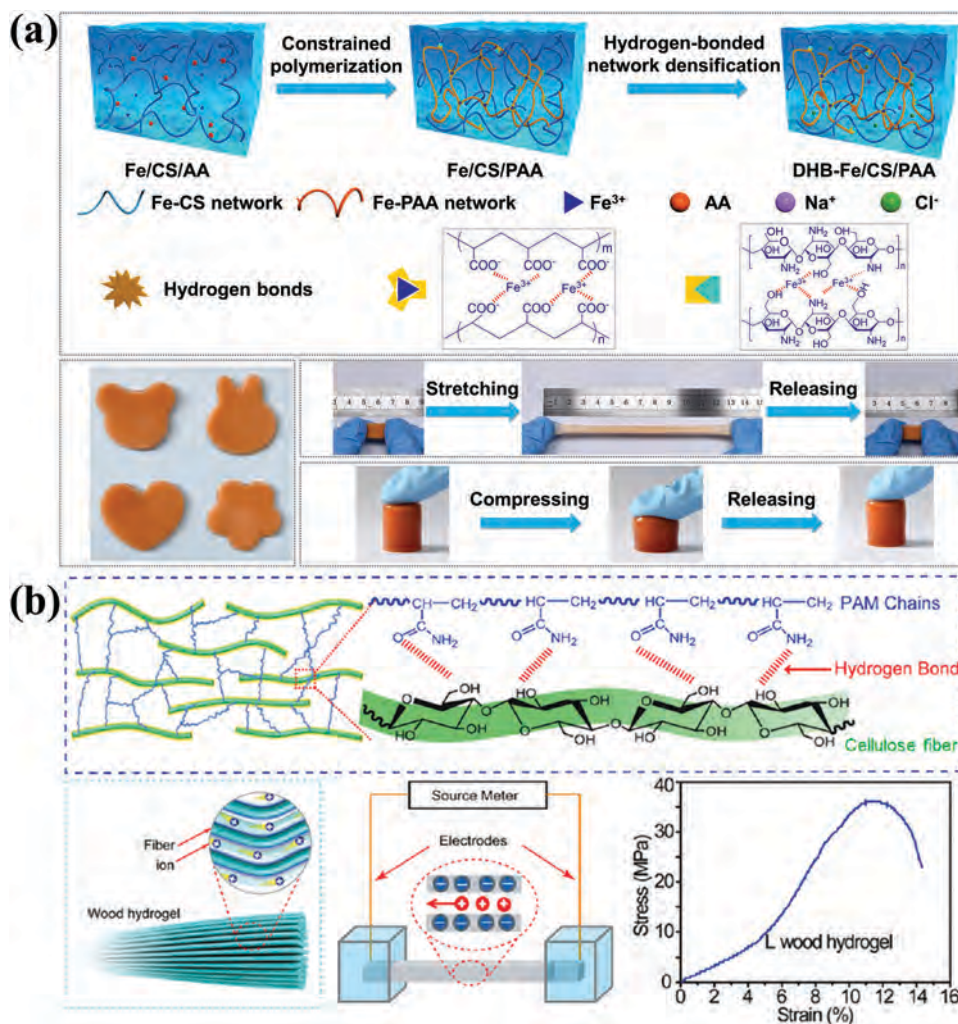


Fig. 7 (a) Preparation and schematic of the dense hydrogen-bonded Fe/CS/PAA hydrogels.⁷⁵ Copyright 2021, Elsevier. (b) Aligned cellulose fiber/PAM composite hydrogels with a low concentration of negative charges.⁷⁶ Copyright 2018, Wiley.

3. Conductive polymer hydrogel composites and nanocomposite as electrodes for flexible electrochemical supercapacitors

Conductive polymer hydrogels with a 3D hierarchical network structure have emerged as a novel class of smart flexible materials that integrate conducting materials into a highly hydrated crosslinked hydrogel matrix.⁵¹ Due to their advantageous features including hierarchically porous microstructure, inherent conductivity, high mechanical flexibility, toughness and adhesion ability, conductive polymer hydrogels are considered as a promising material platform for next-generation energy storage devices, specifically serving as soft electrode materials in flexible supercapacitors.^{78–80} First, the continuous conducting pathways in conductive polymer hydrogels can act as a conductive and monolithic framework to facilitate the transportation of electrons and ions.⁸¹ Second, the porous network structure of conductive polymer hydrogels can promote the diffusion of molecules and ions, help accommodate the stress resulting from volume change during the electrochemical reaction, and improve the interface between molecular chains and electrolyte materials for redox reactions.⁸² Last but not least, because of their unique integration of characteristics of organic conducting materials and conventional polymers, conductive polymer hydrogels could achieve enlarged and improved interfaces between the electrolyte and the electrode with high rate capability.^{35,79} Consequently, hydrogel-based electrode materials are highly promising for supercapacitors to realize mechanical flexibility, ideal electrochemical performances and additional functions. In this section, we primarily focus on the overview of three typical conducting polymer-based electrodes (*i.e.* PANI, PPy and PEDOT-based electrodes).

3.1 PANI-based hydrogel electrode

PANI has been widely investigated as a pseudocapacitive electrode material for electrochemical energy storage, as it offers fast and reversible redox reactions at the electrode surface.⁷⁹ PANI hydrogels are emerging as a promising species of electrode materials for supercapacitor applications because their 3D hierarchical nanostructure could provide (1) an excellent interface for electrolyte ions to access the electroactive surface and (2) an intrinsically electrically conducting and robust framework that promotes charge/mass transport, thus improving the electrochemical usage of active materials.

As discussed in Section 2, the first reported pure PANI hydrogel was synthesized *via* direct polymerization of aniline monomers with PA as the dopant and crosslinker. The obtained pure PANI hydrogel exhibited excellent electrical conductivity and electrochemical properties. With a high surface area and a 3D porous hierarchical nanostructure, the PANI hydrogels demonstrated potential as high-performance supercapacitor electrodes with high specific capacitance (480 F g⁻¹), unprecedented rate capability, and cycling stability (~83% capacitance retention after 10 000 cycles).²⁹ Guo *et al.* also reported a self-crosslinked PANI hydrogel, which was synthesized *via* oxidative

coupling reaction in the absence of any additional crosslinkers by using ammonium persulfate as the oxidizing agent and aniline hydrochloric salt as the precursor. The self-crosslinked PANI hydrogel electrode possessed an excellent specific capacitance of 750 F g⁻¹ at a current density of 1 A g⁻¹.³¹ Apart from the chemical oxidative polymerization to obtain bulk PANI hydrogels, the electrochemical polymerization method also provides another strategy to fabricate PANI hydrogels with desired shapes and thickness, which are ideal electrode candidates for fabricating micro-supercapacitors. Yang *et al.* reported an electrochemical polymerization method that was free of frameworks and initiators to build 3D PANI/phytic acid supramolecular hydrogels.⁸³ The as-fabricated conducting polymer hydrogels exhibited a high conductivity of 0.43 S cm⁻¹, a large areal capacitance of 561.6 mF cm⁻² and a high specific capacitance of 311.3 F g⁻¹. Due to the improved electrode interfaces between the electron and ion transporting phases, the micro-supercapacitors based on these hydrogels delivered a high areal capacitance (135.9 mF cm⁻²) and considerable cycling stability (76% capacitance retention after 10 000 cycles), which made them promising power supply candidates for future wearable electronics and on-chip integrated circuits. Despite the superior electrochemical performance, the mechanical performance of the pure PANI electrode was not satisfactory, constraining its further application in flexible portable electronics.

To enhance the mechanical performance, a compositing strategy was established to combine the conductive PANI hydrogels with other functional materials, which could not only improve the mechanical property of the hydrogel electrodes but also maintain excellent electrochemical performance. The combination with carbon nanomaterials was an efficient approach for fabricating high-performance PANI hydrogel electrodes.^{44,84–92} A typical example is a stretchable PANI/reduced graphene oxide (PANI/RGO) hydrogel fiber reported by Yu *et al.* (Fig. 8a). The stretchable fiber-shaped hydrogel electrode was manufactured *via* macromolecular self-assembly of GO and PANI hydrogels, exhibiting enhanced specific capacitance and promising mechanical strength. Specifically, PANI/GO hybrid hydrogels were formed through strong intermolecular interactions among GO, PANI, and PA, including electrostatic interactions, hydrogen bonds, and π - π stacking. The obtained PANI/RGO hydrogel fiber showed a strong tensile strength of 140 MPa with a high tensile strain of 31%, which suggested its excellent deformation-tolerance ability to overcome a large deformation with strong mechanical strength. With further gelation of the PVA-based gel electrolyte, an all-gel-state energy storage supercapacitor was developed, showing excellent energy density (8.80 mW h cm⁻³) and power density (30.77 mW cm⁻³).⁹³

Apart from carbon nanomaterials, the combination with other polymer hydrogels to construct a hybrid hydrogel is another effective strategy to simultaneously obtain desired electrochemical and mechanical performances.^{94–97} Zhang *et al.* reported a promising soft hybrid conductive hydrogel by integrating a water-soluble triblock copolymer with rigid PANI. The PANI chains served not only as a conductive network but

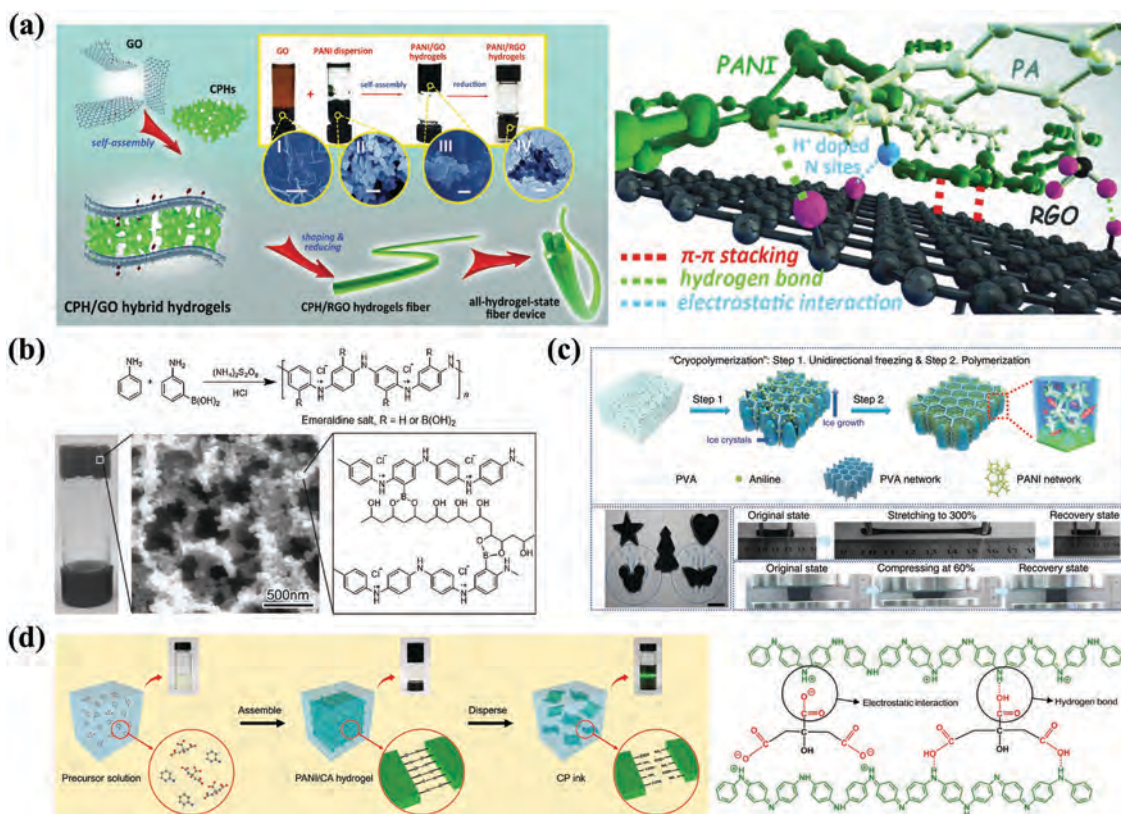


Fig. 8 (a) Schematic diagram of the CPH/RGO hydrogel fiber and the interactions between the two components.⁹³ Copyright 2018, Wiley-VCH. (b) Supramolecular strategy to prepare PANI–PVA hydrogels with dynamic bonds.¹⁰² Copyright 2016, Wiley. (c) Schematic diagram of the anisotropic PVA/PANI hybrid hydrogels with high stretchability and elasticity.¹⁰⁶ Copyright 2021, Nature Publishing Group. (d) Air-stable conductive polymer inks for printed wearable micro-supercapacitors.³⁴ Copyright 2021, Wiley-VCH.

also as a crosslinker (*via* hydrogen-bond interactions) for the gelation of the hybrid hydrogels. This hydrogel presented robust mechanical flexibility and excellent recovery ability. Electrodes based on this hydrogel exhibited superior electrochemical properties including high specific capacitance (919 F g^{-1} at 0.5 A g^{-1}), large areal capacitance (2702 mF cm^{-2} at 4 mg cm^{-2}), excellent cyclic stability, and outstanding flexibility (withstand more than 100% tensile strain). The supercapacitor assembled from these electrodes also showed superior capacitance (178 F g^{-1}), flexibility, and capacitive behavior.⁹⁸ For the hybrid hydrogels, the regulation of molecular interactions between two hydrogel networks is critical for the resultant mechanical and electrochemical performance.^{36,99–101} Ma *et al.* reported a supramolecular strategy to prepare a PANI-polyvinyl alcohol hydrogel (PPH) with excellent mechanical and electrochemical properties owing to the dynamic bonds (Fig. 8b). With a small percentage of boronic acid groups on PANI as cross-linking sites, the PANI and PVA chains could assemble to form a robust conductive hydrogel with a mesoporous structure, which facilitated fast charge transfer and mass transportation within the hydrogel. In the PPH, PANI provided fast and reversible charge storage with high specific capacitance and good chemical stability, while PVA enabled the hydrogel to obtain superior mechanical properties. Therefore, PPH retained its high capacitance despite the mechanical deformation or the repeated

swelling and shrinking during the intensive charge–discharge cyclic process. Based on this strong, robust, and active PPH material, a flexible solid-state supercapacitor was fabricated, exhibiting high specific capacitance (153 F g^{-1} at 0.25 A g^{-1}), good cyclic stability (100% capacitance retention after 1000 cycles) and mechanical durability (withstand 250% tensile strain and 90% compression strain).¹⁰²

Notably, the microstructure regulations of conductive polymer hydrogels are also meaningful for promoting the mechanical robustness and energy storage properties.^{103–105} For example, our group presented a vertical-gradient freezing and cryopolymerization strategy to design and prepare an anisotropic PANI/polyvinyl alcohol hydrogel (APPH). During the vertical-gradient freezing, PVA chains, the aniline monomer and the initiator could assemble into a 3D ordered honeycomb structure due to the oriented growth of ice dendrites. Through the subsequent cryopolymerization, the PANI nanofibrous scaffold was gradually formed due to the localized nucleation and confined polymerization of aniline within the boundaries between vertically aligned ice crystals and PVA cell walls (Fig. 8c). The as-prepared APPH showed superelastic performance with a complete recovery of 100% stretching strain, 50% compressing strain and fully bending, which was due to effective energy dissipation of the reversible deformation of the PVA scaffold network and the PANI sacrificial network, as

well as an efficient load transfer ascribed to the strong interfacial interaction between the ductile PVA and stiff PANI networks. Owing to the anisotropic porous structure with a 3D conductive PANI framework, the APPH electrode exhibited an enhanced specific capacitance and electron/ion transportation kinetics compared with the hybrid hydrogel with isotropic microstructure. This research indicates the significant importance of the microstructure (anisotropic structure) for the corresponding mechanical and electrochemical performance of conducting polymer-based hydrogels.¹⁰⁶

Printing technologies are exceedingly desirable for achieving facile, large-area, low-cost, and precision manufacture of micro-supercapacitors. Considerable effort has also been put into the field of printed hydrogels, in which the key issue lies in the exploitation of printable inks. To settle this problem, Chu *et al.* reported a low-cost, easy-fabricating and air-stable PANI hydrogel ink (Fig. 8d). The PANI chains were effectively crosslinked enabled by citric acid (CA) *via* supramolecular interactions and subsequently assembled into uniform nanosheets. These nanosheets were then interconnected to form hydrogels due to multiple active groups at the edge of nanosheets. Interestingly, the interactions among nanosheets can be easily broken through vigorous stirring or ultrasonic treatment. The PANI/CA nanosheets were thus stably distributed in water to form a stable printing ink.³⁴ Owing to the high doping level of PANI, the ink exhibited an impressive conductivity in the order of 10^{-2} S cm⁻¹ along with a remarkable specific capacitance of 386.9 F g⁻¹ at 0.5 A g⁻¹. The printable micro-supercapacitor derived from the as-prepared PANI hydrogel ink delivered a high areal capacitance of 96.6 mF cm⁻², a large volumetric capacitance of 26.0 F cm⁻³ as well as a high energy density of 2.4 mW h cm⁻³ at 238.3 mW cm⁻³, surpassing the majority of the state-of-the-art micro-supercapacitors derived from pseudocapacitive materials.

3.2 PPy-based hydrogel electrode

PPy is another conductive polymer that has been applied in the syntheses of hydrogel electrodes.³⁵ As discussed in Section 2, pure PPy hydrogels were synthesized *via* interfacial polymerization with PA as the dopant and crosslinker. The microstructure of the PPy hydrogel was tuned by adjusting the ratio of pyrrole to PA. At a high content of PA, hollow spherical structures were dominant in the corresponding hydrogel. At a low content of PA, particle-like PPy, instead of PPy hollow spheres, dominated the corresponding hydrogel. As the ratio of Py/PA was increased, the structures of the resulting PPy transformed from interconnected micro-structured hollow spheres to smaller plate-like particles, which offered a 3D porous hierarchical nanostructure, at the expense of decreasing electrical conductivity. The unique 3D porous nanostructure constructed by interconnected polymer nanospheres endowed PPy hydrogels with good mechanical properties and distinguished performance as supercapacitor electrodes with a specific capacitance of 380 F g⁻¹, excellent rate capability, and areal capacitance as high as 6.4 F cm⁻² at a mass loading of 20 mg cm⁻².³⁵ Furthermore, the microstructures of the PPy hydrogel were also determined by the molecular and geometric structures of different dopant molecules.^{32,107} A PPy gel with an interconnected fiber

structure was synthesized using CuPcTs as the crosslinker. When indigo carmine and indigo carmine dehydrate, which had molecular structures similar to one-half and one-quarter of the CuPcTs molecule, respectively, were used as crosslinkers, PPy gels with a necklace-like one-dimensional nanostructure and granular nanostructure were respectively obtained. More importantly, the electrical and electrochemical properties of PPy gels closely related to their microstructures and the dopants used during their synthesis. The synthesized PPy hydrogel exhibited high electrical conductivity (7.8 S cm⁻¹) and specific capacitance (400 F g⁻¹ at 0.2 A g⁻¹) when utilizing the CuPcTs molecule as the dopant and crosslinker.³²

Apart from high specific capacitance, the excellent deformation-tolerance ability is also crucial for conducting polymer hydrogel electrodes, especially in wearable electronics. Hybridization with a second polymer hydrogel is an effective strategy to simultaneously achieve ideal electrochemical and deformation-tolerance performance.^{108–114} However, due to the low water solubility of conductive polymers, the conductivity of the conductive polymer composite hydrogel electrode *via* direct mixing or *in situ* polymerization is low, restricting its application in flexible supercapacitors. As one of the materials rich in nature, cellulose derivatives (*i.e.*, sodium alginate, quaternary ammonium chitosan, carboxymethylcellulose sodium) have an amphiphilic structure and possess certain emulsifying effect on hydrophobic substances.^{115–117} Microcrystalline cellulose was used to fabricate a semi-interpenetrating network of PPy hydrogels.¹¹⁸ Cheng *et al.* reported a transparent PAM/carboxymethyl cellulose sodium/PPy hydrogel with high stretchability (>700%), electrical conductivity (11.07 S m⁻¹) and interfacial bonding properties.¹¹¹ Based on the emulsifying effect of carboxymethyl cellulose sodium, the PPy molecular chains were stabilized in aqueous solution, forming carboxymethyl cellulose sodium/PPy fibers. Subsequently, the PAM/carboxymethyl cellulose sodium/PPy hydrogel was obtained by *in situ* polymerization of PAM with uniformly distributed carboxymethyl cellulose sodium/PPy. As a flexible electrode, the PAM/carboxymethyl cellulose sodium/PPy hydrogel was assembled into an all-solid-state supercapacitor, which exhibited a specific capacitance of 126.38 F g⁻¹ and excellent cyclic stability (capacitance retention of 82% after 1000 cycles).

3.3 PEDOT-based hydrogel electrode

PEDOT is a widely adopted conducting polymer and pseudocapacitive electrode material for high-performance energy storage devices owing to its high electrical conductivity, good electrochemical properties, and excellent dispersion.^{119–121} In a majority of studies, commercialized PEDOT:PSS was employed as the starting material for electrode fabrication in energy storage devices.^{120,122–126} PEDOT:PSS aqueous solution is a typical micellar system, which consists of PEDOT polycations and PSS polyanions. Generally, excess PSS forms the corona of the micelle to ensure the good dispersibility of the whole system. Herein, two features should be highlighted for the PEDOT:PSS aqueous system: (1) the crystallinity of PEDOT-rich cores is relatively poor; (2) PEDOT-rich domains

are separated by PSS-rich domains (Fig. 9a). These two features are responsible for the relatively poor electrical conductivity of the PEDOT:PSS solutions.¹¹⁹ For energy storage applications, one of the most important properties of electrode materials is capacitive behavior. Generally, electrical conductivity reflects electron transport which critically depends on the availability of the electrochemical interface, which severely influences the capacitive behavior.^{119,127} Based on the above problem of the relatively low electrical conductivity of PEDOT:PSS, lots of post-treatments have been proposed to improve the electrical conductivity and the corresponding electrochemical performance. Secondary doping is an efficient method to solve this problem. Shi *et al.* reported a simple method to prepare a PEDOT:PSS hydrogel with high conductivity by simple thermal treatment of a commercial PEDOT:PSS suspension in 0.1 mol L⁻¹ sulfuric acid followed by partially removing its PSS component with concentrated sulfuric acid.³⁶ The obtained hydrogel had a low solid content of 4 wt% and an extremely high conductivity of 880 S m⁻¹. It is worth noting that sulfuric acid could be used not only to improve the conductivity but also for the gelation of PEDOT:PSS dispersion. The gelation of PEDOT:PSS was ascribed to the conformational change of PEDOT chains from a random coil to an expanded-coil structure induced by acid, thus enhancing their interchain interaction to form a 3D network with physical crosslinking. Based on this, a highly conductive and mechanically strong porous fiber was prepared by drying the PEDOT:PSS hydrogel fiber to fabricate a current-collector-free solid-state flexible supercapacitor. This fiber supercapacitor delivered a volumetric capacitance as high as 202 F cm⁻³ at 0.54 A cm⁻³ with an extraordinary high-rate performance. Apart from the sulfuric acid solution, recent research indicated that dimethyl sulfoxide (DMSO) and metal ions could also act as the secondary dopants to not only improve the conductivity but also promote the gelation of PEDOT:PSS dispersion.^{128,129} Apart from secondary doping, the increase of the crystallinity of PEDOT is another efficient strategy to obtain PEDOT-based conductive hydrogels

with high performance. Lu *et al.* reported a soft-template synthesis strategy to prepare a semicrystalline conducting polymer hybrid hydrogel by supramolecular assembly of PEDOT and PVA for making flexible supercapacitors with higher energy density and better electrochemical stability.¹³⁰ It was found that semicrystalline PEDOT nanofibers were formed by oxidative polymerization of EDOT monomers and *in situ* assembly with PVA in a water/DMSO mixture solvent. Owing to the ordered polymer chain alignments in the compact nanosheets of the hybrid hydrogel, both the energy density (24 W h kg⁻¹) and the electrochemical stability (100% capacitance retention after 15 000 cycles) of the PEDOT-based flexible supercapacitors operating at 1.4 V were far beyond those of the previously reported amorphous PEDOT-based flexible supercapacitors. This soft-template synthesis method provides an effective strategy to prepare semicrystalline PEDOT-based hybrid hydrogels with enhanced electrochemical performance for broad applications.

Hybridization with a second functional material makes it easy to synergistically utilize the mechanical strength but overcome the defects of each component, leading to improved electrical conductivity, electrochemical performance and mechanical properties of the resultant hydrogels.¹³¹⁻¹³⁸ Ion transportation generally reflects the ion accessibility and transport rate during the electrochemical process, which seriously influences the electrode's capacitive behavior. Kumar *et al.* proposed semi-interpenetrating polymer networks of a pseudocapacitive electrically conducting polymer (PEDOT) in a crosslinked ionically conducting polymer matrix (Fig. 9b). The polyethylene oxide (PEO) hydrogel network generated an ion reservoir throughout the electrode, enabling the pseudocapacitive polymer even within the bulk of the material to be accessible for charge storage reactions. This strategy increases the material utilization efficiency of the electrically conducting polymer without employing complex synthesis methods or sacrificing mechanical stability. Additionally, the flexible framework of the ionically conductive matrix could accommodate the volumetric changes associated with ion intercalation/deintercalation in the

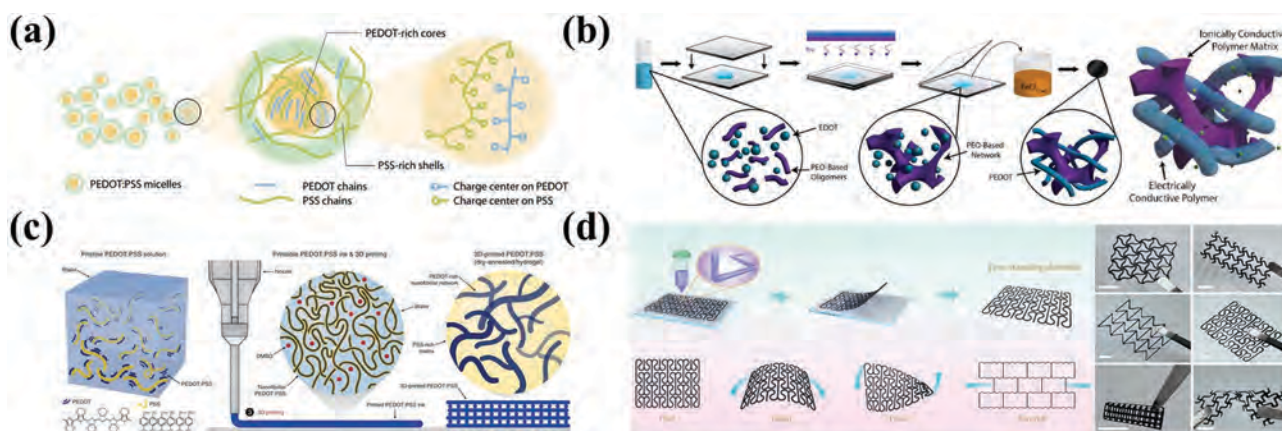


Fig. 9 (a) Structural characteristics of PEDOT:PSS.¹¹⁹ Copyright 2020, Springer. (b) Schematic of the synthesis of semi-interpenetrating polymer hydrogel networks.¹³⁹ Copyright 2017, American Chemical Society. (c) Design of 3D printable PEDOT:PSS ink.³³ Copyright 2020, Nature Publishing Group. (d) Fabrication of 3D-printed highly deformable conducting polymer electrodes with negative Poisson's ratio structures.¹⁴⁰ Copyright 2021, Royal Society of Chemistry.

pseudocapacitive polymer, minimizing mechanical stress in the electrode and yielding excellent cycling stability.¹³⁹

3D Printing technologies are extraordinarily desirable for achieving facile, large-area, low-cost, and precision manufacture of electronics. Considerable effort has also been put into the field of printed hydrogels, in which the key issue lies in the exploitation of printable inks.^{33,136,138,140} Zhao *et al.* reported a paste-like 3D printable PEDOT ink based on cryogenic freezing of aqueous PEDOT:PSS solution followed by lyophilization and controlled re-dispersion in the mixture of water and DMSO (Fig. 9c). The resultant conducting polymer ink exhibited superior 3D printability and was capable of high resolution, high aspect ratio and highly reproducible fabrication of conducting polymers. Dry-annealing of the 3D-printed PEDOT:PSS hydrogel provided highly conductive (electrical conductivity $>155 \text{ S cm}^{-1}$) and flexible 3D microstructures in the dry state.³³ Besides, electrodes with special structure designs (*i.e.*, negative Poisson's ratio structure) have been demonstrated to significantly improve the stretchability and flexibility.^{141,142} However, the electrode with a complex structure was hardly achieved through conventional fabrication techniques.¹⁴³ In this regard, ink-based 3D printing, a powerful additive manufacturing technology, has shown unparalleled advantages in the rational structure design of materials and devices with accuracy and efficiency even at micro and macroscales.⁵¹ Yang *et al.* demonstrated an economical and efficient strategy to prepare a free-standing stretchable PEDOT:PSS electrode with multi-dimensional property tunability and negative Poisson's ratio structure *via* the direct ink writing technology (Fig. 9). With the deformable pattern design, the arc-shaped microstructure was introduced into conventional negative Poisson's ratio structures, which overcame the limitations of non-tunable mechanical behaviors and broadened the narrow strain ranges of traditional supercapacitor electrodes. Apart from mechanical flexibility, the optimized electrodes also exhibited satisfactory electrochemical performance with a high areal capacitance of

990 mF cm^{-2} . Based on this, the fabricated micro-supercapacitor assembled from 3D-printed electrodes also demonstrated a promising high areal capacitance and unprecedented long-term cycling stability (74.7% retention after 14 000 cycles). The diversity of microstructures provides a wider range of effective strain and stress relief for the electrodes, showing a great degree of freedom in the design of stretchable electrodes.¹⁴⁰

In summary, conductive polymer hydrogels represent a promising material for high-performance flexible electrochemical supercapacitors because they could offer an enlarged electrode/electrolyte interface area for both electron and ion transportation, which facilitates highly efficient electrochemical reactions. Moreover, the inherent soft nature of hydrogels makes them an ideal framework for constructing high-performance electrodes with excellent mechanical performance. Table 1 summarizes and compares the performances of the above-mentioned conductive polymer hydrogel electrode-based supercapacitors, including capacitance, mechanical performance and cycling stability.

4. Conductive polymer hydrogel composites and nanocomposites as electrolytes for flexible electrochemical supercapacitors

Polymer hydrogels are tissue-like, viscoelastic, flexible and crosslinked networks of hydrophilic polymer chains swollen with tailorable volumes of solvent water, while preserving the constructional integrity under various mechanical deformations.^{95,145,146} The unique characteristics of hydrogels make them ideal candidates for soft electrolyte materials of flexible supercapacitors. First, the water-containing polymer network structure of hydrogels can dissolve ions, and numerous

Table 1 Comprehensive performance comparison of various conductive polymer hydrogel-based electrodes for flexible electrochemical supercapacitors

Hydrogel electrode	Specific capacitance	Mechanical performance	Cycling stability (retention, cycle number)
PPy ³²	400 F g ⁻¹ at 0.2 A g ⁻¹	—	85%, 1000
PPy ³⁵	155 F g ⁻¹ at 0.2 A g ⁻¹	Bend to 180°	90%, 3000
PANI/RGO ⁹³	112 F g ⁻¹ at 0.08 A g ⁻¹	—	86%, 17 000
PANI/IAOAI ⁹⁸	187 F g ⁻¹ at 0.25 A g ⁻¹	Bend to 180°	80%, 1000
PANI/PVA ¹⁰⁵	2097 mF cm ⁻² at 2 mA cm ⁻²	Stretch to 80% strain, bend to 180°	88%, 2000
Anisotropic PANI/PVA ¹⁰⁶	260 at 0.5 A g ⁻¹	Stretch to 400% strain, compress to 90% strain, bend to 180°	90%, 5000
PPy/PVA ¹⁰⁸	13.06 F g ⁻¹ at 5 mA cm ⁻³	Bend to 180°	86%, 10 000
PAAm/CMC/PPy ¹¹¹	126.38 F g ⁻¹ at 0.2 A g ⁻¹	—	82%, 1000
PVA/GO/PPy ¹¹²	258.1 F g ⁻¹ at 2 A g ⁻¹	Compress to 80% strain	83%, 2000
PEDOT:PSS/graphene ¹²⁰	82.4 F g ⁻¹ at 0.1 A g ⁻¹	Stretch to 300% strain	84%, 5000
PEDOT:PSS ³⁶	202 F cm ⁻³ at 0.54 A cm ⁻³	Bend to 180°	100%, 10 000
PEDOT/PVA ¹³⁰	181 F g ⁻¹ at 0.5 A g ⁻¹	Bend to 180°	100%, 15 000
PPy/PEDOT/rGO ¹³¹	342 F g ⁻¹ at 0.5 A g ⁻¹	—	70%, 1000
PEDOT:PSS/PVA/PMAA ¹³⁴	7.38 mF cm ⁻² at 10 mV s ⁻¹	Stretch to 100% strain	82%, 2000
Graphene/PEDOT/PVA ¹³⁷	281.2 F g ⁻¹ at 0.1 A g ⁻¹	Stretch to 500% strain	83%, 10 000
PEDOT:PSS/graphene ¹³⁸	19.3 mF cm ⁻² at 20 mV s ⁻¹	Stretch to 100% strain, bend to 90°	88.6%, 5000
PEDOT:PSS/CNT ¹⁴⁰	730 mF cm ⁻² at 1 mA cm ⁻²	Stretch to 150% strain, bend to 180°	74.7%, 14 000
PANI/PVA ¹⁴⁴	78.5 F g ⁻¹ at 1 A g ⁻¹	Stretch to 300% strain, compress to 60% strain	87%, 3000

electrolytic ions can be efficiently attracted and localized within the hydrogel network by the charged functional groups on the polymer chains. This feature endows hydrogels with desired liquid-like ionic conductivity, whereas the solid-like dimensional stability of the hydrogels can be maintained, which is hard to realize in solid-state electrolytes and thus ideal for flexible supercapacitor electrolytes.^{95,146} Second, the intrinsic viscoelasticity, flexibility and water-retention ability of quasi-solid hydrogel materials can help avoid the drawbacks of liquid electrolytes, such as volatilization and leaking over time.^{51,95} In addition, hydrogels can even serve as separators in supercapacitors, thus making it possible to fabricate ultrathin energy storage devices.^{51,95} Compared with liquid electrolytes, hydrogels can be equipped with rubbery stretchability, self-healing properties and tailorable toughness, which are ideal components in flexible energy devices. Up to now, various kinds of polymer materials, *i.e.*, PVA, PAA, PAM, and natural biopolymers, have been widely used as the candidate materials for the preparation of hydrogel electrolytes.^{118,144,147–152} In this section, we primarily concentrate on the overview of three typical synthetic polymer-based hydrogel electrolytes (*i.e.* PVA, PAA, PAM-based electrolytes) and natural biopolymer-based hydrogel electrolytes.

4.1 PVA-based hydrogel electrolyte

Compared with conventional solid or liquid electrolytes, PVA-based hydrogel electrolytes have been widely employed for constructing flexible supercapacitors because of their nontoxicity, chemical stability, universal pH applicability and relatively low cost. PVA could be crosslinked by using either physical crosslinking of hydrogen bonds or chemical crosslinking with glutaraldehyde (GA) and borax. The crosslinking renders weak PVA hydrogel films a certain degree of stretchability due to the introduction of reversible interactions. For instance, a physically crosslinked PVA hydrogel electrolyte was fabricated by mixing PVA and H₂SO₄ solution through a freezing/thawing process. The enormous dynamic hydrogen bonding provided the PVA–H₂SO₄ hydrogel electrolyte with excellent flexibility.¹⁵³ The PVA hydrogel electrolytes *via* the freezing/thawing process have demonstrated their wide application due to the simple processing, nontoxicity and chemical stability. However, several intrinsic properties of PVA indeed limited the practical applications. Although the hydroxyl groups on the side chain of PVA could attract a certain amount of water molecules, the long carbon chain and the insufficient numbers of hydrophilic side chain groups, compared with other hydrogels, would weaken the interaction between the polymer and water molecules. This potentially leads to poor water retention properties and unsatisfactory ionic conductivity that would affect the long-term stability. It was well-established that the water content was an important factor that affected the ionic conductivity of the resultant hydrogel electrolytes. Therefore, flexible supercapacitors fabricated from PVA electrolytes should be carefully sealed to minimize water evaporation. One effective way is to chemically crosslink PVA hydrogels with GA.¹⁵⁴ Multiple acetal or hemiacetal junction zones were formed because of the chemical reaction between hydroxyl groups of PVA and aldehyde groups of GA in acid conditions (Fig. 10a), resulting in an excellent

elasticity. The GA crosslinked PVA hydrogel film exhibited superior stretchability that could be sustained up to 300%. The water content of PVA hydrogels was 90%, leading to a high conductivity of 0.082 S cm⁻¹, which was close to the level of H₂SO₄ aqueous electrolyte. The 3D-connected networks of the PVA hydrogel efficiently confined water into the polymer matrix, which maintained a high ionic conductivity and kept long-term electrochemical durability for supercapacitors. Then, the two embedded PANI layers and the middle hydrogel formed an integrated prototype of a flexible supercapacitor. This supercapacitor prototype also demonstrated a large areal capacitance (488 mF cm⁻²), excellent cyclic stability (90% capacitance retention after 7000 cycles), mechanical durability and bendable properties. Most hydrogel electrolytes are prepared by solution casting, and hydrogels tend to absorb water or lose it to the surrounding environment. The environmental temperature and humidity during the preparation process are important factors that determine the water content of hydrogel electrolytes and their corresponding electrochemical/mechanical performance. Anjum *et al.* used a PVA/phosphoric acid (PVA–H₃PO₄) hydrogel electrolyte to study the influence of relative humidity (RH) on its water content, mechanical properties, and electrochemical performance (Fig. 10b).¹⁵⁵ They demonstrated that the water content in the PVA–H₃PO₄ hydrogel electrolyte was highly affected by the RH and would be saturated under a fixed RH condition. When the PVA–H₃PO₄ hydrogel electrolytes were saturated at an 80% RH and compared to 30% RH, their mechanical stiffness decreased several times, and their ionic conductivity increased by more than one order of magnitude. Besides, the measured interfacial capacitances between the PVA–H₃PO₄ hydrogel electrolyte and flat glassy carbon electrodes also increased with RH. Moreover, flexible supercapacitor prototypes using PVA–H₃PO₄ hydrogel electrolytes demonstrated that both the energy and power densities of the devices were improved when exposed to a high RH environment. Consequently, it is crucial to control and report processing humidity during the research and development of hydrogel electrolyte-based flexible supercapacitors.

Next-generation electrochemical capacitors demand the introduction of self-healing ability into hydrogel electrolytes, and therefore they could spontaneously restore their capacitance performance when they undergo physical damage and abuse of cutting off/breaking. As mentioned above, the mechanical flexibility of PVA hydrogel electrolytes could be significantly enhanced by using the chemical crosslinking method; however, the self-healing ability was usually weakened due to the strong bond strength of covalent bonds leading to inability to reform after a fracture. In this regard, a physically crosslinked PVA hydrogel electrolyte with numerous dynamic bonds is necessary to retain the self-healing ability. Peng *et al.* reported a novel self-healing hydrogel electrolyte (B-PVA/KCl/GO) that was designed and prepared through the doping of GO into a diol-borate ester bonding crosslinked PVA network (Fig. 10c).¹⁵⁶ This provided a method to solve the drawback of the conventional PVA-based electrolyte which was neither intrinsically stretchable nor healable. The B-PVA/KCl/GO hydrogel electrolyte could be easily stretched, twisted and tailored into different shapes, which provided a new strategy to construct distinct patterned

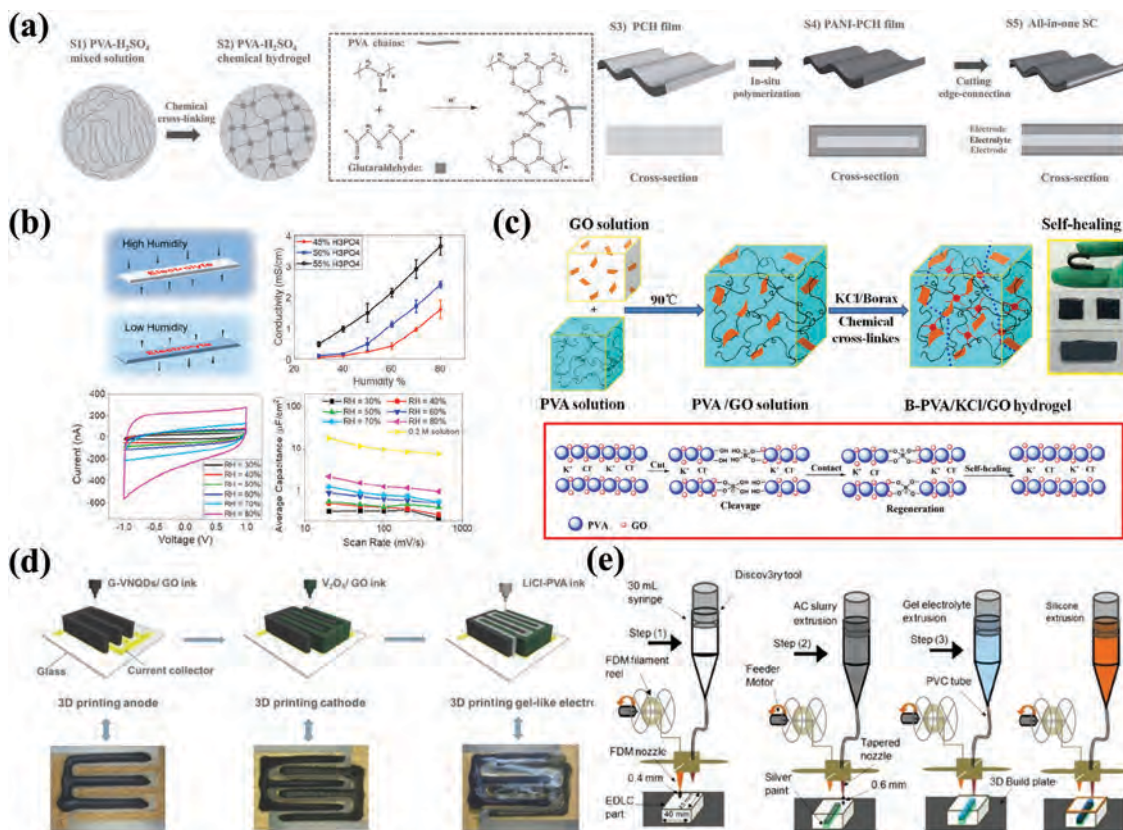


Fig. 10 (a) Schematic diagram of chemically crosslinked PVA hydrogel-based all-in-one supercapacitors.¹⁵⁴ Copyright 2015, Wiley-VCH. (b) Influence of humidity on the conductivity and electrochemical performance of hydrogel electrolytes.¹⁵⁵ Copyright 2021, Elsevier. (c) Schematic diagram of the B-PVA/KCl/GO hydrogels with stretchability and self-healing ability.¹⁵⁶ Copyright 2019, Elsevier. (d) Schematic illustration of 3D printing of micro-supercapacitors with LiCl-PVA gel ink.¹⁵⁹ Copyright 2018, Wiley-VCH. (e) Schematic illustration of the manufacturing of micro-supercapacitors with PVA gel electrolytes using a dual-nozzle system and the assembled structure.¹⁶⁰ Copyright 2017, Taylor & Francis.

supercapacitors to apply for diverse technological systems. Meanwhile, the B-PVA/KCl/GO hydrogel with excellent self-healing capability was based on not only dynamic diol-borate ester bonds, but also intermolecular hydrogen bonds between GO and polymers. It was also found that hydrogels with a moderate amount of GO had improved ionic conductivity compared with the bare B-PVA/KCl hydrogel. Moreover, the activated carbon-based supercapacitor with the B-PVA/KCl/GO hydrogel electrolyte delivered a high specific capacitance of 156 F g^{-1} at 0.3 A g^{-1} and could also restore its capacitive performance *via* 7 times healing cycles without external stimulus. This study might bring a new prospect for introducing nanomaterials into hydrogel electrolytes to not only construct numerous dynamic bonds to realize self-healing ability but also form 3D networks to facilitate ion transportation.

Traditional PVA hydrogels will unavoidably freeze and lose their original mechanical performance and electrochemical performance at low temperatures due to the existence of abundant free water molecules in the hydrogel matrix. Researchers are recently devoting tremendous efforts towards developing functional hydrogel electrolytes with excellent frost-tolerance ability. Recently, a novel supercapacitor with an extremely wide functional temperature range ($40\text{--}80 \text{ }^\circ\text{C}$) was developed by Liu *et al.*, possessing a superior specific

volumetric capacitance (295 F cm^{-3}) and still maintaining 91% of its initial capacitance after 10 000 cycles. One reason for the excellent performance of the full-temperature supercapacitor was that the montmorillonite flake/PVA hydrogel-based electrolytes reinforced by the DMSO, a nontoxic material with outstanding solubility and thermal stability, showed excellent ionic conductivity, capacitance, and low-temperature working ability, where the formation of highly conductive ionic transportation channels endowed the hydrogel with ultrahigh ionic conductivity and the hydrogen bonding between DMSO and water molecules limited the proportion of that between water molecules for lowering the freezing point.¹⁵⁷ Inspired by the nontoxic and non-freezable engine coolant, such as glycerol and ethylene glycol (EG), some research studies indicated that they could disrupt the formation of ice crystal lattices to reduce the critical point of water crystallization through making abundant alcohol groups combine with water molecules for limiting the proportion of hydrogen bonding and forming steady molecular clusters in aqueous solution. Peng *et al.* reported a facile route for the preparation of a PVA/glycerol/NaCl supramolecular gel electrolyte, which could store the PVA/glycerol/NaCl aqueous solution at room temperature without the freezing/thawing process or chemical crosslinking process. The PVA/glycerol/NaCl hydrogel was formed quickly in 2 h at

room temperature due to the abundant hydrogen bonding formation between PVA and glycerol. The specific capacitance of the flexible supercapacitor with the PVA/glycerol/NaCl hydrogel electrolyte at $-23\text{ }^{\circ}\text{C}$ reached more than 90% of its initial value. The capacitance retention could still remain at about 90.5% after 2500 cycles at low temperature.¹⁵⁸

Studies have shown that the PVA-based hydrogel electrolytes with a certain viscosity range are suitable for fabrication of micro-supercapacitors *via* 3D printing. Yang *et al.* reported a quasi-solid-state micro-supercapacitor, which was prepared by directly printing the anode inks, cathode inks, and gel electrolyte inks (LiCl-PVA) on a glass matrix (Fig. 10d).¹⁵⁹ The as-prepared micro-supercapacitors demonstrated a remarkable architecture integrity and a high working voltage of 1.6 V. Similarly, Areir *et al.* reported a novel manufacturing method to obtain a stacked printed micro-supercapacitor with printed electrodes (active carbon)/electrolyte (H_2SO_4 /PVA gel electrolyte) and frame parts by continuous direct ink writing/fused deposition modeling printing using dual-nozzle devices (Fig. 10e).¹⁶⁰ The as-prepared sandwiched micro-supercapacitors showed a specific capacitance of 38.5 mF g^{-1} with high energy density and power density (0.019 W h kg^{-1} and 165 W kg^{-1}).

4.2 PAA-based hydrogel electrolyte

PVA is the most widely used hydrogel electrolyte among the hydrogel electrolytes for flexible supercapacitors, owing to its advantages of nontoxicity, low cost and simple process. But there are some inherent shortcomings of PVA that have severely limited its widespread use. First, most of the prepared PVA-based hydrogel electrolytes hardly possess sufficient mechanical properties and additional functions (such as self-healing ability) simultaneously. Second, PVA-based hydrogel electrolytes always suffer from low water uptake and retention, which not only requires strict operating temperature and packaging technology of the device but also leads to a significant reduction in ionic conductivity and cycling stability of the resultant supercapacitors. Therefore, it is imperative to

develop novel hydrogel electrolytes with superior mechanical properties, self-healing ability and cycling stability.

PAA opens up opportunities for coordinating the control of ionic conductivity, mechanical stretchability and self-healing ability due to its distinct attributes. The superior hydrophilicity of PAA enables it to absorb a mass of water, which can dissolve various kinds of electrolyte ions, desirable for improving its conductivity. Moreover, the carboxyl groups of PAA could form abundant dynamic intra-/inter-molecular hydrogen bonds and coordination interactions with metal ions, which are favorable for enhancing mechanical stretchability and self-healing ability. For example, Wang *et al.* reported a self-healable PVA-*g*-PAA/KCl hydrogel electrolyte, which exhibited superior flexibility and high conductivity (41 mS cm^{-1}) compared with the most conventional PVA-based hydrogel electrolytes (Fig. 11a). The hydrogel electrolyte was prepared *via* converting PAA-grafted PVA into a hydrogel in the presence of KCl and borax. The grafting of PAA effectively alleviated the coagulation of PVA chains caused by the dissolved salts within the hydrogel networks, thus allowing the resulting PVA-*g*-PAA/KCl hydrogel electrolyte to exhibit enhanced mechanical performance and ion conductivity. Based on the dynamic diol-borate ester bonding, once the PVA-*g*-PAA/KCl hydrogel electrolyte was cut, it spontaneously restored its configuration, mechanical properties and ionic conductivity within 20 min.¹⁶¹ A carbon-based nano-material was also incorporated into PAA hydrogels to form composite hydrogel electrolytes with enhanced mechanical performance and self-healing ability. Qu *et al.* reported a novel methacrylate graphene oxide-PAA (MGO-PAA) hydrogel electrolyte with high ion conductivity (7.16 S m^{-1}), excellent self-healing capability and extra stretchability (up to 950% strain). The MGO-PAA hydrogel electrolyte was prepared by introducing MGO as a crosslinking mediator into the PAA matrix. The excellent self-healing capability and high stretchability of the MGO-PAA hydrogel electrolyte were ascribed to the formation of abundant hydrogen-bonded networks between PAA chains and MGO nanosheets, which also acted as crosslinking points to

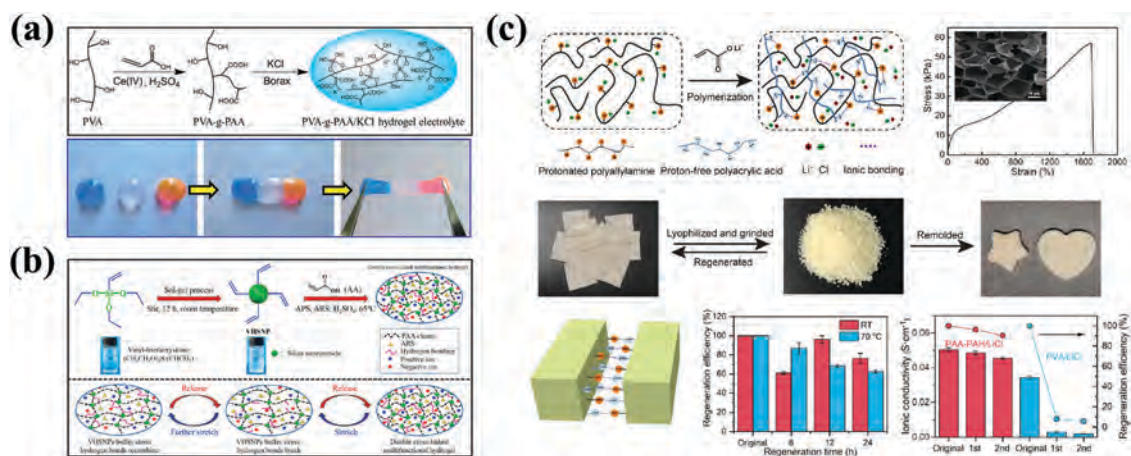


Fig. 11 (a) Schematic diagram of a self-healing hydrogel electrolyte based on PVA-*g*-PAA/KCl.¹⁶¹ Copyright 2016, Royal Society of Chemistry. (b) Schematic of the preparation process of the VHSNPs-PAA/H₂SO₄/ARS hydrogels with ultra-high stretchability.¹⁷⁵ Copyright 2020, Elsevier. (c) Preparation process and regeneration property of PAA-PAH/LiCl hydrogel electrolytes.¹⁷⁶ Copyright 2020, Elsevier.

improve the conductivity. Consequently, MGO–PAA polyelectrolytes were directly applied to build self-healing supercapacitors (80% capacitance retention after 3 cutting/self-healing cycles) and stretchable supercapacitors (300% strain with a capacitive enhancement of ~ 1.8 times) without the extra addition of other self-healing or stretchable materials.¹⁶² Apart from carbon nanomaterials, metal ions were also incorporated into PAA hydrogels and acted as a dynamic crosslinker to endow the hydrogel electrolyte with enhanced stretchability and self-healing properties. Guo *et al.* reported a novel ferric ion crosslinked PAA hydrogel electrolyte (KCl–Fe³⁺/PAA) with superior stretchability, easy-recycling properties and self-healing ability. The KCl–Fe³⁺/PAA hydrogel was stabilized by the ionic bond between Fe³⁺ and carboxylic acid ions, as well as by the intra- and intermolecular hydrogen bonding. This novel supramolecular hydrogel exhibited good conductivity (0.09 S cm^{-1}) and excellent mechanical performance (extensibility $> 700\%$, stress $> 400 \text{ kPa}$), which were ascribed to the formation of ionic bonds and hydrogen bonds. After being assembled with graphene foam-supported PPy (GF@PPy) electrodes, the supercapacitor device delivered a specific capacitance of 87.4 F g^{-1} at a current density of 0.5 A g^{-1} . The capacitance retention rate could reach 89% at a current density of 1 A g^{-1} after 5000 cycles.¹⁶³

Despite these efforts, the fabricated PAA-based hydrogel electrolyte exhibits insufficient mechanical strength (with tensile strength less than 500 kPa). Therefore, it remains a challenge to improve both mechanical property (strength and extensibility) and ionic conductivity of PAA-based electrolytes simultaneously. To address these challenges, some researchers have proposed cellulose nanofibrils (CNFs), which are derived from natural fibers, as efficient binders to improve the performance of PAA electrolytes.^{19,147,164} On the one hand, CNFs are expected to greatly enhance the mechanical strength of the polymer matrix because of the high Young's modulus and tensile strength.¹⁶⁵ Liu *et al.* reported that CNFs reinforced the mechanical performance of hydrogels by cross-linking,¹⁶⁶ and Kentaro *et al.* proposed the positive mechanical effects of CNFs on hydrogels.¹⁶⁴ On the other hand, the hydrophilic property and abundant hydroxyl groups of CNFs are beneficial to ionic conduction. For instance, to take advantage of the conducive properties of CNFs, Li *et al.* designed an alkaline gel electrolyte with PAA as the skeleton and CNFs as the reinforcing agent. The CNF/PAA electrolyte achieved improvement in both ionic conductivity and mechanical properties. It also exhibited other excellent properties such as high alkaline tolerance, superb alkaline retention, and excellent elasticity ($< 20\%$ plastic deformation after 500 stretching–releasing cycles). The incorporation of CNFs into the PAA electrolyte simultaneously improved the ionic conductivity (from 0.157 to 0.272 S cm^{-1}) and mechanical strength (from 0.656 to 1.875 MPa).¹⁶⁷ Similar research was also reported by Zhang *et al.* They added microcrystalline cellulose in an alkaline polymer matrix to obtain a composite electrolyte. With the increase of microcrystalline cellulose content, the ionic conductivity improved from 0.018 to 0.153 S cm^{-1} .¹⁶⁸

Non-covalent interactions have been introduced into the PAA-based hydrogel electrolytes with enhanced mechanical

properties, self-healing properties and ionic conductivity. But the prepared hydrogels by this approach did not significantly exhibit the desired properties. In this regard, the double crosslinked polymer hydrogels with covalent bonds and non-covalent interactions that could easily realize superior ionic conductivity, stretchability, and healable properties represented promising candidates for use as electrolytes of multifunctional supercapacitors. Huang *et al.* prepared a double crosslinked VSNPs–PAA polyelectrolyte based on vinyl hybrid silica nanoparticles (VSNPs) and hydrogen bonds, which possessed a remarkable stretchable strain of 3700% . Meanwhile, the specific capacitance of the VSNPs–PAA polyelectrolyte-based supercapacitor was well-maintained after 20 breaking/healing cycles.⁶⁴ Xu *et al.* developed a novel zwitterionic hydrogel electrolyte (DMAP-S-PAA/H₂SO₄) by combining covalent bonds and non-covalent interactions (hydrogen bonds and ionic associations), which displayed an extraordinary self-healing ability within 5 min and an outstanding stretchability of 2900% strain. Additionally, the recently demonstrated supercapacitors based on stretchable and healable hydrogel electrolytes usually suffer from relatively poor electrode specific capacitance, thus limiting their practical applications.¹⁶⁹ The previous studies showed that the introduction of redox mediators into the hydrogel electrolytes could immensely improve the total energy density and specific capacitance of the supercapacitor devices because of the electron transfer redox reaction of active molecules at the electrolyte/electrode interface contributing additional pseudocapacitance.^{170–174} Feng *et al.* developed a multifunctional VHSNPs–PAA/H₂SO₄/ARS hydrogel supercapacitor with extremely excellent stretchability and favorable self-healing ability.¹⁷⁵ The VHSNPs–PAA/H₂SO₄/ARS hydrogel polyelectrolyte copolymerized through VHSNPs and extensive hydrogen bonding was prepared by stirring the vinyl triethoxysilane solution for acquiring the vinyl hybrid silica nanoparticle (VHSNP) suspension and copolymerizing acrylic acid (AA), the alizarin red S (ARS) redox mediator, and ammonium persulfate (APS), following by the infiltration process of immersing the resultant product in H₂SO₄ solution. As shown in Fig. 11b, the functional VHSNPs as stress buffer and the excellently resilient scaffold of the PAA electrolyte that possessed a myriad of dynamic hydrogen bonding endowed the dual-crosslinking multifunctional hydrogel with outstanding self-healing ability (92% capacitance retention after 10 damaging/self-healing cycles) and stretchability (up to 2400% strain). Additionally, the ARS redox mediator made the prepared hydrogel show superior ionic conductivity (up to 33 mS cm^{-1}) and extra pseudocapacitance.

Easy renewability of core components of supercapacitors such as the electrolyte is highly required in advanced electrochemical devices. To introduce great renewability into hydrogel electrolytes, a high density of non-covalent bonds between polymers was highly demanded. Liu *et al.* reported a reliable, regenerable, and stretchable hydrogel electrolyte based on ionic bonds between polyacrylic acid (PAA) and polyallylamine (PAH).¹⁷⁶ The high density of ionic bonds along the polymer backbone endows the hydrogel with great renewability; on the other hand, the high density of ionic bonds between PAA and

PAH can significantly enhance the mechanical property of the hydrogel (Fig. 11c). The ionic bonded PAA and PAH hydrogel electrolyte mixed with 1.0 M LiCl (PAA–PAH/LiCl) demonstrated great ionic conductivity (0.050 S cm^{-1}), excellent mechanical properties (strain at fracture of 1688%, stress at fracture of 57.0 kPa) and renewability (96% and 90% of the original ionic conductivity after the first and second regeneration, respectively). Supercapacitors based on this gel electrolyte delivered ultrahigh cycling stability (nearly 100% capacitance retention after 5000 cycles), great flexibility (nearly 100% capacitance retention at the crimping and stretching states), and excellent renewability (97.6% capacitance retention for the completely regenerated device).

4.3 PAM-based hydrogel electrolyte

The PAM-based hydrogels have also been applied as electrolyte materials for flexible supercapacitors due to their high ionic conductivity, high water content, and easy fabrication as well as good tolerance under different pH conditions. On account of the functional group difference between amide and hydroxyl, carboxyl groups, PAM usually shows relatively weak intermolecular hydrogen bonding compared with the PAA and PVA. Thus, it is generally difficult to achieve remarkable stretchability for pure PAM hydrogels.

Various strategies have been proposed to enhance the mechanical properties of PAM-based hydrogel electrolytes. The first strategy is to introduce more crosslinking points to toughen the hydrogel electrolytes. Zhi *et al.* reported a super stretchable hydrogel electrolyte comprising proton-incorporated PAM crosslinked by vinyl hybrid silica nanoparticles (VSNPs).⁹⁵ Vinyl hybrid silica nanoparticle cross-linkers were introduced into PAM hydrogel backbones to promote dynamic cross-linking of the polymer networks (Fig. 12a). These cross-linkers served as stress buffers to dissipate energy when strain was applied, providing a solution to the intrinsically low stretchability and compressibility

shortcomings of conventional covalent crosslinked PAM hydrogels. The prepared PAM electrolyte possessed all the advantages of tunable ionic conductivity, super-stretchability, and high compressibility. As a result, the supercapacitor containing PAM electrolytes exhibited high capacitance, intrinsic super-stretchability (unprecedented 1000% stretching with a 2.6-fold capacitance enhancement), and intrinsic high compressibility (50% compression with 99.4% retained capacitance and holding 257-fold its weight).

Another strategy is to construct a double-network structure for performance enhancement of the corresponding hydrogel electrolytes. For example, Suo *et al.* developed a novel type of hierarchical dual network crosslinking hydrogel that possessed the first network composed of rigid covalent PAM polymeric chains and the second network formed by reversible weak Ca^{2+} ion-bonding of alginate, which exhibited several exceptional advantages including satisfactory water retention (contains almost 90% water), extremely excellent stretchability of up to 2000% strain, and high fracture energy (up to 9000 J m^{-2}). The first-network matrix with rigid covalent PAM polymeric chains played a crucial role in dissipating enormous mechanical energy. The second network frame with abundant reversible ion-bonding restored the stretched hydrogel to the initial state. This was regarded as a promising super-stretchable hydrogel configuration.¹⁷⁷ Besides, the covalent and noncovalent interactions (ionic bonding, hydrogen bonding) within and between the double networks are also crucial for the regulation of the corresponding hydrogel electrolytes. In general, strong and irreversible interactions of covalent bonds provide the pristine soft hydrogel with solid dimension stability and rigid performance; furthermore, weak and reversible interactions of ionic bonds and hydrogen bonding confer elasticity and recovery ability after deformation to the hydrogel, dissipating enormous mechanical and thermal energy generated by deformation.¹⁷⁸ The appropriate combination of the two kinds of interactions endows the crosslinked hydrogels with high

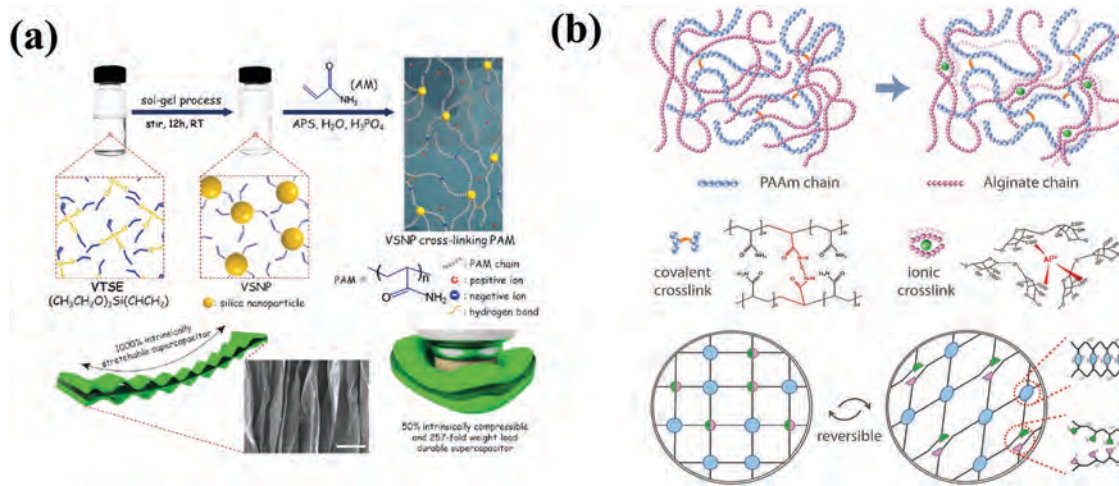


Fig. 12 (a) Preparation of VSNPs from VTSE followed by the fabrication of the VSNPs–PAM electrolytes and schematic of the intrinsically stretchable and compressible supercapacitors.⁹⁵ Copyright 2017, Wiley-VCH. (b) Schematics of the structure and energy-dissipation mechanism of Al–alginate/PAM hydrogels.¹⁷⁹ Copyright 2012, Nature Publishing Group.

stretchability and decent mechanical properties. Therefore, the crosslinked hydrogels are relatively soft (low strength, toughness and high stretchability) during insufficient crosslinking, whereas they are relatively rigid (high strength, toughness and low stretchability) during an excessive degree of crosslinking.¹⁷⁷ Based on the strategy of dual-network cross-linked hydrogel electrolytes with various interactions, Zhi *et al.* proposed an Al³⁺ reinforced alginate/PAM hydrogel, which exhibited extremely excellent stretchability/compressibility and robustness to buffer the electrode and collector components from extremely harsh external mechanical stress and impact effectively, where the Al³⁺-alginate ionic crosslinks as a sacrificial and reversible second-network dissipated massive energy through breaking ionic crosslinks and recovering the deformed hydrogel to the original state by rebuilding ionic crosslinks (Fig. 12b).¹⁷⁹ The designed damage-resistant supercapacitor was composed of the Al³⁺-reinforced alginate/PAM hydrogel electrolyte and PPy electrodeposited carbon-nanotube paper electrodes, which had the potential to withstand severe deformation and catastrophic impact damage. Besides, a multiply crosslinked PAM-alginate hydrogel showed extremely excellent stretchability (21 times that of the pristine hydrogel), which was achieved through bonding the carboxyl groups of the alginate and amine groups of the PAM covalently and making the alginate interpenetrate in the long-chain PAM by Ca²⁺ gelation.^{180,181}

In addition, to endure significant distortions, the integrated wearability electronics are also required to withstand the multifarious working strain and serious mechanical breakage or even restore primordial electrochemical and mechanical properties including the initial conductivity, strength, and elongation. Self-healing ability is essential for supercapacitors to improve their reliability and lifespan when powering electronics. Most of the reported healable supercapacitors have been fabricated by either employing an extra self-healing polymer layer to wrap/support the electrode or using an additional electrode patch combined with the self-recovered electrolyte.⁶⁴ These non-intrinsically self-healing configurations between two electrodes sandwiched with an indispensable electrolyte layer lead to low healing efficiency and low energy density. Therefore, it is of great practical significance to realize and maintain the integrated current collector–electrode–electrolyte–electrode–current collector configuration during the device fabrication and after mechanical fractures. Faced with these challenges, the creation of effective healing motifs for the design and construction of an Omni-healable supercapacitor is highly desirable and important. Yu *et al.* reported a kind of magnetic Fe₃O₄@Au/PAM (MFP) hydrogel, which was fabricated by chemically crosslinking disulfide bond-functionalized Fe₃O₄@Au nanocomposites into a polymeric network.¹⁸² Owing to the effective energy dissipation mechanism from the homogeneously interconnected network structure, the MFP hydrogel demonstrated tough mechanical performance with a large stretchability of 2250% of its initial length and strong notch-insensitivity. Additionally, notable photothermal and magneto-thermal properties of the hydrogel enabled the fabricated hydrogel with fast optical and remotely controllable magnetic healability relying on high-density dynamic Au–SR coordination bonds. By

incorporating PPy nanoparticles into the MFP network as the electrode, a supercapacitor prototype was assembled by sandwiching two MFP–PPy electrodes with an MFP hydrogel electrolyte and spray-coating silver nanowire (AgNW) films as current collectors. The synergistic effects of Au–SR, Ag–SR bonds allowed the assembled supercapacitor with an integrated configuration to exhibit the largest areal capacitance up to 1264 mF cm⁻² and a record-breaking device-level stretchability of 1200%, confirming it as one of the best performers among the flexible and healable supercapacitors. Impressively, this supercapacitor possessed intrinsically multi-responsive healing capability with ~90% of capacitance restored over 10 optical, electrical, and magnetic healing cycles, respectively.

4.4 Natural biopolymer-based hydrogel electrolyte

Natural biopolymer-based conductive hydrogels, which combine the inherent renewable, nontoxic features, biocompatibility and biodegradability of biopolymers and the excellent flexibility and conductivity of conductive hydrogels, exhibit great potential for application in flexible and stretchable hydrogel electrolytes. Different from traditional synthetic polymers, biopolymers that are extracted from a bioresource with intrinsic biocompatibility and biodegradability are commonly considered as appropriate candidates for constructing wearable devices. For example, biopolymers, such as cellulose and chitosan, are usually chosen as promising candidates to construct conductive hydrogels, endowing the hydrogels with enhanced mechanical properties and remarkable biocompatibility.^{183–188} Chen *et al.* fabricated a PVA/nanofibrillated cellulose (NFC) hydrogel electrolyte with a large fracture elongation of 604.5%, a moderate tensile/compressive strength of 23.1/26.2 kPa, superb viscoelasticity, and great adhesive property.¹⁸⁷ Importantly, the hydrogel electrolyte could self-heal in a very short time without any stimuli or healing agents and possessed a large ionic conductivity of 18.1 mS cm⁻¹. A flexible quasi-solid-state zinc-ion hybrid supercapacitor (ZHS) was assembled utilizing the PVA/NFC hydrogel electrolyte, the active carbon paper cathode, and the zinc foil anode. The ZHS achieved a high specific capacity of 504.9 mF cm⁻² at 0.5 mA cm⁻² with a high working voltage of 1.8 V. Besides, the ZHS exhibited an extraordinary capacitance retention (95.3% after 5000 cycles), high tolerance to mechanical deformation and excellent self-healing ability. Yang *et al.* fabricated a flexible, transparent, and eco-friendly polymer hydrogel electrolyte film based on a biodegradable polymer of carboxylated chitosan *via* phase separation of a carboxylated chitosan hydrogel in hydrochloric acid.¹⁸⁴ The obtained carboxylated chitosan hydrogel film with excellent flexibility exhibited a high electrolyte uptake rate of 742.0 wt% and a high ionic conductivity of 8.69 × 10⁻² S cm⁻¹. All-solid-state supercapacitors using a carbon cloth and two activated carbon films as the current collector and electrodes, respectively, and carboxylated chitosan hydrogel film as the gel polymer electrolyte showed a high specific capacitance of 45.9 F g⁻¹ at 0.5 A g⁻¹ and a maximum energy density of 5.2 W h kg⁻¹ at a power density of 226.6 W kg⁻¹. This recent progress indicated that the natural biopolymer hydrogel as a new gel polymer electrolyte material has great potential in

Table 2 Comprehensive performance comparison of various conductive polymer hydrogel-based electrolytes for flexible electrochemical supercapacitors

Hydrogel electrolyte	Conductivity ($S\ m^{-1}$)	Mechanical performance	Cycling stability (retention, cycle number)
PVA-H ₂ SO ₄ ¹⁵³	13.64	380% stretching	80%, 2400
PVA-GA ¹⁵⁴	8.2	300% stretching	90%, 7000
PVA-H ₃ PO ₄ ¹⁵⁵	0.36	Elastic modulus: 33.6 MPa	99.3%, 10 000
B-PVA/KCl/GO ⁴¹	4.75	273.3% stretching, 180° twisting	90%, 3000
Montmorillonite/PVA ¹⁵⁷	0.342	Tensile strength: 10 MPa	91%, 10 000
PVA/NaCl/glycerol ¹⁵⁸	9.25	575% stretching	90.5%, 2500
PVA-g-PAA/KCl ¹⁶¹	4.1	—	—
MGO-PAA ¹⁶²	7.16	950% stretching	80%, 3 healing cycles
KCl-Fe ³⁺ /PAA ¹⁶³	9.0	700% stretching	89%, 5000
CNF/PAA ¹⁶⁷	27.2	<20% plastic deformation in 500 cycles	—
VSNPs-PAA ⁶⁴	—	3700% stretching	~100%, 20 healing cycles
VHSNPs-PAA/H ₂ SO ₄ /ARS ¹⁷⁵	3.3	2400% stretching	92%, 10 healing cycles
PAA-PAH/LiCl ¹⁷⁶	5.0	1600% stretching	~100%, 5000
VSNPs-PAM ⁹⁵	—	1000% stretching	99.4%, 50% compression
Alginate-Ca ²⁺ -PAM ¹⁷⁷	—	2000% stretching	—
Fe ₃ O ₄ @Au/PAM ¹⁸²	—	2250% stretching	90%, 10 healing cycles
PVA/NFC ¹⁸⁷	1.81	604.5% stretching	95.3%, 5000

practical applications of all-solid-state, flexible, and portable energy storage devices.

In conclusion, the multifunctional conductive polymer hydrogel electrolytes with outstanding energy storage and mechanical performance are reviewed, introduced and discussed. Table 2 compares the performances of the above-mentioned conductive polymer hydrogel electrolyte-based supercapacitors. Generally speaking, the most common advantages of conductive polymer hydrogels are that the designable nanostructured porous network could be generated through crosslinking polymerization, which serves as an adhesive framework of the electrolyte and ionic transportation channels. Besides, the conductive polymer hydrogel electrolyte combines the characteristics of both solid and liquid, showing higher security than liquid electrolytes and higher electrical conductivity than the solid electrolytes, which makes it an ideal candidate for constructing the emerging smart energy storage devices.

5. Conclusion and outlook

Due to the urgent demand for next-generation wearable electronics, supercapacitors that integrate high energy storage and excellent mechanical flexibility are the most promising energy storage devices to be realized shortly. Considering the merits of conductive polymer hydrogels including high conductivity, flexibility and mechanical performance, these kinds of hydrogels have become perfect candidates for electrodes and electrolytes of next-generation supercapacitor devices. In this review, we first present the descriptions of various approaches to realize the synthesis of multiple kinds of conductive polymer hydrogels and their composites/nanocomposites, including electrically and (or) ionically conductive polymer hydrogels and their composites and nanocomposites. Those conductive polymer hydrogels are developed by incorporating various single material components across an expansive area covering conducting polymers, carbon-based nanomaterials, metallic nanomaterials,

polyelectrolytes and ions. Based on their excellent electrochemical performance, tunable conductivity and superior mechanical properties, we present the applications of typical electrically and ionically conductive polymer hydrogels as electrodes and electrolytes for flexible electrochemical supercapacitors, respectively. The mechanical properties, electrochemical performance, electrical/ionic conductivity and additional functions (*e.g.*, self-healing ability) are discussed in detail. Despite efforts in this field, several aspects still need to be considered in the design of conductive polymer hydrogel-based electrodes and electrolytes for flexible supercapacitors in the future.

(1) Previous studies reported conductive polymer hydrogels to exhibit impressive electrochemical performance and mechanical properties. However, to bring them into practical applications, mechanical properties, including fracture strength, flexibility, and stretchability, should be improved without sacrificing electrochemical properties and ionic/electrical conductivity. For instance, the double-networked gel strategy could improve the mechanical strength without sacrificing the ionic conductivity, but it might result in the deterioration of electrical conductivity due to the introduction of insulated polymers as an energy-dissipation network. It is challenging to fabricate high-performance conductive polymer hydrogels simultaneously possessing excellent mechanical and electrochemical performance.

(2) Given strong interactions with water molecules, hydrogel materials have shown promising ion reservoir effects in aqueous electrolytes, offering desired high ionic conductivity and charge transportability. However, the use of an aqueous medium as the solvent limits the operating temperature and durability of the energy devices. A possible solution is, but not limited to, constructing interpenetrating networks or integrating functional additives to tune the phase-transition behaviors of the contained water.

(3) A more in-depth understanding of ion and electron transportation in conductive polymer hydrogels is essential. Such an understanding not only allows improvement of the charge transport properties in hydrogel materials but also inspires the optimized design of integrated supercapacitor

devices. For example, the studies of ion and electron transportation on the electrolyte–electrode interfaces are also crucial for the final performance of supercapacitor devices.

(4) 3D printing technologies are favorable for scalable preparation of conducting polymer hydrogel-based electrodes/electrolytes and the whole integrated supercapacitor devices. Developing conducting polymer hydrogels with ideal viscosity, rheological property and gelation rate that are compatible with the printing technology is another future development direction, which is essential for the precise processing and mass production of conducting polymer hydrogel materials for the subsequently assembled supercapacitors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21875033, 52003107), the China Postdoctoral Science Foundation (Grant No. 2021M691266), and the Jiangsu Province Postdoctoral Science Foundation (Grant No. 2021K168B).

References

- 1 T. Chen and L. M. Dai, *J. Mater. Chem. A*, 2014, **2**, 10756–10775.
- 2 H. Zhang, Y. Cao, M. O. L. Chee, P. Dong, M. Ye and J. Shen, *Nanoscale*, 2019, **11**, 5807–5821.
- 3 K. Keum, J. W. Kim, S. Y. Hong, J. G. Son, S. S. Lee and J. S. Ha, *Adv. Mater.*, 2020, **32**, 2002180.
- 4 Y. Q. Wang, Y. Ding, X. L. Guo and G. H. Yu, *Nano Res.*, 2019, **12**, 1978–1987.
- 5 C. Wang, C. Wang, Z. Huang and S. Xu, *Adv. Mater.*, 2018, **30**, 1801368.
- 6 L. Li, J. Zhou, C. Zhang and T. X. Liu, *Compos. Commun.*, 2019, **15**, 162–167.
- 7 A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. van Schalkwijk, *Nat. Mater.*, 2005, **4**, 366–377.
- 8 J. K. Lee, K. B. Smith, C. M. Hayner and H. H. Kung, *Chem. Commun.*, 2010, **46**, 2025–2027.
- 9 D. W. Wang, F. Li, M. Liu, G. Q. Lu and H. M. Cheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 373–376.
- 10 G. M. Zhou, F. Li and H. M. Cheng, *Energy Environ. Sci.*, 2014, **7**, 1307–1338.
- 11 Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H. M. Cheng, *Nat. Mater.*, 2011, **10**, 424–428.
- 12 H. Gwon, H. S. Kim, K. U. Lee, D. H. Seo, Y. C. Park, Y. S. Lee, B. T. Ahn and K. Kang, *Energy Environ. Sci.*, 2011, **4**, 1277–1283.
- 13 A. Eftekhari, L. Li and Y. Yang, *J. Power Sources*, 2017, **347**, 86–107.
- 14 X. F. Zhang, J. Q. Zhao, T. Xia, Q. Y. Li, C. H. Ao, Q. H. Wang, W. Zhang, C. H. Lu and Y. L. Deng, *Energy Storage Mater.*, 2020, **31**, 135–145.
- 15 Z. P. Wang, J. L. Cheng, Q. Guan, H. Huang, Y. C. Li, J. W. Zhou, W. Ni, B. Wang, S. S. He and H. S. Peng, *Nano Energy*, 2018, **45**, 210–219.
- 16 Q. Rong, W. Lei and M. Liu, *Chemistry*, 2018, **24**, 16930–16943.
- 17 T. Cheng, Y. Z. Zhang, S. Wang, Y. L. Chen, S. Y. Gao, F. Wang, W. Y. Lai and W. Huang, *Adv. Funct. Mater.*, 2021, **31**, 2101303.
- 18 Y. Zhao, B. R. Liu, L. J. Pan and G. H. Yu, *Energy Environ. Sci.*, 2013, **6**, 2856–2870.
- 19 L. Li, K. Wang, Z. Q. Huang, C. Zhang and T. X. Liu, *Nano Res.*, 2016, **9**, 2938–2949.
- 20 Z. Q. Huang, L. Li, Y. F. Wang, C. Zhang and T. X. Liu, *Compos. Commun.*, 2018, **8**, 83–91.
- 21 Y. Guo, J. Bae, Z. Fang, P. Li, F. Zhao and G. Yu, *Chem. Rev.*, 2020, **120**, 7642–7707.
- 22 T. Nezakati, A. Seifalian, A. Tan and A. M. Seifalian, *Chem. Rev.*, 2018, **118**, 6766–6843.
- 23 Q. Wu, J. Wei, B. Xu, X. Liu, H. Wang, W. Wang, Q. Wang and W. Liu, *Sci. Rep.*, 2017, **7**, 41566.
- 24 Y. Y. Lee, H. Y. Kang, S. H. Gwon, G. M. Choi, S. M. Lim, J. Y. Sun and Y. C. Joo, *Adv. Mater.*, 2016, **28**, 1636–1643.
- 25 P. Pissis and A. Kyritsis, *Solid State Ionics*, 1997, **97**, 105–113.
- 26 Y. Shi, C. B. Ma, L. L. Peng and G. H. Yu, *Adv. Funct. Mater.*, 2015, **25**, 1219–1225.
- 27 J. Duan, X. Liang, J. Guo, K. Zhu and L. Zhang, *Adv. Mater.*, 2016, **28**, 8037–8044.
- 28 S. Sekine, Y. Ido, T. Miyake, K. Nagamine and M. Nishizawa, *J. Am. Chem. Soc.*, 2010, **132**, 13174–13175.
- 29 L. Pan, G. Yu, D. Zhai, H. R. Lee, W. Zhao, N. Liu, H. Wang, B. C. Tee, Y. Shi, Y. Cui and Z. Bao, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 9287–9292.
- 30 Y. Lu, W. He, T. Cao, H. Guo, Y. Zhang, Q. Li, Z. Shao, Y. Cui and X. Zhang, *Sci. Rep.*, 2014, **4**, 5792.
- 31 H. T. Guo, W. N. He, Y. Lu and X. T. Zhang, *Carbon*, 2015, **92**, 133–141.
- 32 Y. Wang, Y. Shi, L. Pan, Y. Ding, Y. Zhao, Y. Li, Y. Shi and G. Yu, *Nano Lett.*, 2015, **15**, 7736–7741.
- 33 H. Yuk, B. Lu, S. Lin, K. Qu, J. Xu, J. Luo and X. Zhao, *Nat. Commun.*, 2020, **11**, 1604.
- 34 X. Chu, G. Chen, X. Xiao, Z. Wang, T. Yang, Z. Xu, H. Huang, Y. Wang, C. Yan, N. Chen, H. Zhang, W. Yang and J. Chen, *Small*, 2021, **17**, 2100956.
- 35 Y. Shi, L. J. Pan, B. R. Liu, Y. Q. Wang, Y. Cui, Z. A. Bao and G. H. Yu, *J. Mater. Chem. A*, 2014, **2**, 6086–6091.
- 36 B. Yao, H. Wang, Q. Zhou, M. Wu, M. Zhang, C. Li and G. Shi, *Adv. Mater.*, 2017, **29**, 1700974.
- 37 H. Joo, H. Han and S. Cho, *Polymers*, 2020, **12**, 928.
- 38 A. Alam and M. Moussa, *Polym. Compos.*, 2020, **41**, 809–816.
- 39 A. Gupta, S. Sardana, J. Dalal, S. Lather, A. S. Maan, R. Tripathi, R. Punia, K. Singh and A. Ohlan, *ACS Appl. Energy Mater.*, 2020, **3**, 6434–6446.
- 40 A. R. Karimi and A. Khodadadi, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27254–27263.
- 41 B. G. Li, C. Wu, C. Y. Wang, Z. Y. Luo and J. P. Cao, *J. Appl. Polym. Sci.*, 2020, **137**, 48781.
- 42 D. Ren, Y. J. Chen, H. Li, H. U. Rehman, Y. L. Cai and H. Z. Liu, *Colloids Surf., A*, 2019, **580**, 123731.
- 43 F. L. Yi, F. C. Meng, Y. Q. Li, P. Huang, N. Hu, K. Liao and S. Y. Fu, *Composites, Part B*, 2020, **198**, 108246.
- 44 Y. B. Zou, Z. C. Zhang, W. B. Zhong and W. T. Yang, *J. Mater. Chem. A*, 2018, **6**, 9245–9256.
- 45 J. Liu, C. Chen, C. He, J. Zhao, X. Yang and H. Wang, *ACS Nano*, 2012, **6**, 8194–8202.
- 46 Y. Xu, Q. Wu, Y. Sun, H. Bai and G. Shi, *ACS Nano*, 2010, **4**, 7358–7362.
- 47 L. Li, L. Xu, W. Ding, H. Y. Lu, C. Zhang and T. X. Liu, *Composites, Part B*, 2019, **177**, 107381.
- 48 X. Jing, H. Y. Mi, X. F. Peng and L. S. Turng, *Carbon*, 2018, **136**, 63–72.
- 49 L. Zhang, Z. P. Wang, C. Xu, Y. Li, J. P. Gao, W. Wang and Y. Liu, *J. Mater. Chem.*, 2011, **21**, 10399–10406.
- 50 L. Han, X. Lu, M. Wang, D. Gan, W. Deng, K. Wang, L. Fang, K. Liu, C. W. Chan, Y. Tang, L. T. Weng and H. Yuan, *Small*, 2017, **13**, 1601916.
- 51 J. Q. Han, H. X. Wang, Y. Y. Yue, C. T. Mei, J. Z. Chen, C. B. Huang, Q. L. Wu and X. W. Xu, *Carbon*, 2019, **149**, 1–18.
- 52 Z. R. Ying, Q. Wang, J. Xie, B. Li, X. M. Lin and S. J. Hui, *J. Mater. Chem. C*, 2020, **8**, 4192–4205.
- 53 J. Q. Cai, X. Zhang, W. F. Liu, J. H. Huang and X. Q. Qiu, *Polymer*, 2020, **202**, 122643.
- 54 N. S. El-Sayed, M. A. Moussa, S. Kamel and G. Turkey, *Synth. Met.*, 2019, **250**, 104–114.
- 55 M. Gniadek, S. Malinowska, K. Kaniewska, M. Karbarz, Z. Stojek and M. Donten, *J. Electroanal. Chem.*, 2018, **812**, 273–281.
- 56 X. He, C. Zhang, M. Wang, Y. Zhang, L. Liu and W. Yang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 11134–11143.

- 57 S. Mandal, A. Seth, V. Yadav, S. Kumari, M. Kumar and U. Ojha, *ACS Appl. Polym. Mater.*, 2019, **2**, 618–625.
- 58 M. Liao, H. Liao, J. Ye, P. Wan and L. Zhang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 47358–47364.
- 59 J. E. Park, H. S. Kang, J. Baek, T. H. Park, S. Oh, H. Lee, M. Koo and C. Park, *ACS Nano*, 2019, **13**, 9122–9130.
- 60 Z. X. Zhang, L. Tang, C. Chen, H. T. Yu, H. H. Bai, L. Wang, M. M. Qin, Y. Y. Feng and W. Feng, *J. Mater. Chem. A*, 2021, **9**, 875–883.
- 61 X. P. Hao, C. Y. Li, C. W. Zhang, M. Du, Z. M. Ying, Q. Zheng and Z. L. Wu, *Adv. Funct. Mater.*, 2021, **31**, 2105481.
- 62 J. Le Bideau, L. Viau and A. Vioux, *Chem. Soc. Rev.*, 2011, **40**, 907–925.
- 63 C. Keplinger, J. Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides and Z. Suo, *Science*, 2013, **341**, 984–987.
- 64 Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie and C. Zhi, *Nat. Commun.*, 2015, **6**, 10310.
- 65 A. Wang, Y. F. Wang, B. Zhang, K. N. Wan, J. X. Zhu, J. S. Xu, C. Zhang and T. X. Liu, *Chem. Eng. J.*, 2021, **411**, 128506.
- 66 K. W. Xu, Y. F. Wang, B. Zhang, C. Zhang and T. X. Liu, *Compos. Commun.*, 2021, **24**, 100677.
- 67 A. Keller, J. Pham, H. Warren and M. In Het Panhuis, *J. Mater. Chem. B*, 2017, **5**, 5318–5328.
- 68 L. Guan, S. Yan, X. Liu, X. Li and G. Gao, *J. Mater. Chem. B*, 2019, **7**, 5230–5236.
- 69 X. Y. Yin, Y. Zhang, X. B. Cai, Q. Q. Guo, J. Yang and Z. L. Wang, *Mater. Horiz.*, 2019, **6**, 767–780.
- 70 X. Peng, H. Liu, Q. Yin, J. Wu, P. Chen, G. Zhang, G. Liu, C. Wu and Y. Xie, *Nat. Commun.*, 2016, **7**, 11782.
- 71 B. Zhang, X. Zhang, K. Wan, J. Zhu, J. Xu, C. Zhang and T. Liu, *Research*, 2021, **2021**, 9761625.
- 72 Y. F. Wang, M. Tebyeterkerwa, Y. Liu, M. Wang, J. X. Zhu, J. S. Xu, C. Zhang and T. X. Liu, *Chem. Eng. J.*, 2021, **420**, 127637.
- 73 M. X. Wang, Y. M. Chen, Y. Gao, C. Hu, J. Hu, L. Tan and Z. Yang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 26610–26617.
- 74 C. Shao, M. Wang, L. Meng, H. Chang, B. Wang, F. Xu, J. Yang and P. Wan, *Chem. Mater.*, 2018, **30**, 3110–3121.
- 75 H. Song, Y. L. Sun, J. X. Zhu, J. S. Xu, C. Zhang and T. X. Liu, *Composites, Part B*, 2021, **217**, 108901.
- 76 W. Kong, C. Wang, C. Jia, Y. Kuang, G. Pastel, C. Chen, G. Chen, S. He, H. Huang, J. Zhang, S. Wang and L. Hu, *Adv. Mater.*, 2018, **30**, 1801934.
- 77 X. D. Li, H. Charaya, G. M. Bernard, J. A. W. Elliott, V. K. Michaelis, B. Lee and H. J. Chung, *Macromolecules*, 2018, **51**, 2723–2731.
- 78 Y. Shi, J. Zhang, L. J. Pan, Y. Shi and G. H. Yu, *Nano Today*, 2016, **11**, 738–762.
- 79 Y. Shi, L. Peng and G. Yu, *Nanoscale*, 2015, **7**, 12796–12806.
- 80 F. Zhao, Y. Shi, L. Pan and G. Yu, *Acc. Chem. Res.*, 2017, **50**, 1734–1743.
- 81 Q. Ding, X. Xu, Y. Yue, C. Mei, C. Huang, S. Jiang, Q. Wu and J. Han, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27987–28002.
- 82 Y. Shi and G. H. Yu, *Chem. Mater.*, 2016, **28**, 2466–2477.
- 83 X. Chu, H. C. Huang, H. T. Zhang, H. P. Zhang, B. N. Gu, H. Su, F. Y. Liu, Y. Han, Z. X. Wang, N. J. Chen, C. Yan, W. Deng, W. L. Deng and W. Q. Yang, *Electrochim. Acta*, 2019, **301**, 136–144.
- 84 P. Y. Chen, N. M. D. Courchesne, M. N. Hyder, J. F. Qi, A. M. Belcher and P. T. Hammond, *RSC Adv.*, 2015, **5**, 37970–37977.
- 85 W. Chen, S. Jiang, H. Xiao, X. Zhou, X. Xu, J. Yang, A. H. Siddique and Z. Liu, *ChemSusChem*, 2021, **14**, 938–945.
- 86 P. Dou, Z. Liu, Z. Z. Cao, J. Zheng, C. Wang and X. H. Xu, *J. Mater. Sci.*, 2016, **51**, 4274–4282.
- 87 G. Z. Guo, Y. Y. Sun, Y. B. Ma, Y. Y. Zhou, Z. Y. Xiong and Y. Q. Liu, *Int. J. Electrochem. Sci.*, 2019, **14**, 5899–5912.
- 88 N. Hu, L. Zhang, C. Yang, J. Zhao, Z. Yang, H. Wei, H. Liao, Z. Feng, A. Fisher, Y. Zhang and Z. J. Xu, *Sci. Rep.*, 2016, **6**, 19777.
- 89 Q. Q. Liu, Z. Y. Bai, J. B. Fan, Z. P. Sun, H. Y. Mi, Q. Zhang and J. S. Qiu, *Appl. Surf. Sci.*, 2018, **436**, 189–197.
- 90 M. Moussa, M. F. El-Kady, D. Dubal, T. T. Tung, M. J. Nine, N. Mohamed, R. B. Kaner and D. Losic, *ACS Appl. Energy Mater.*, 2019, **3**, 923–932.
- 91 Z. X. Tai, X. B. Yan and Q. J. Xue, *J. Electrochem. Soc.*, 2012, **159**, A1702–A1709.
- 92 D. Wu and W. B. Zhong, *J. Mater. Chem. A*, 2019, **7**, 5819–5830.
- 93 P. Li, Z. Jin, L. Peng, F. Zhao, D. Xiao, Y. Jin and G. Yu, *Adv. Mater.*, 2018, **30**, 1800124.
- 94 R. F. Hu, J. Zhao, R. Y. Jiang and J. P. Zheng, *J. Mater. Sci.: Mater. Electron.*, 2017, **28**, 14568–14574.
- 95 Y. Huang, M. Zhong, F. Shi, X. Liu, Z. Tang, Y. Wang, Y. Huang, H. Hou, X. Xie and C. Zhi, *Angew. Chem., Int. Ed.*, 2017, **56**, 9141–9145.
- 96 R. Jia, H. Du, X. D. Zhang, Z. J. Chen and D. Chen, *J. Electrochem. Soc.*, 2018, **165**, A3792–A3798.
- 97 F. L. Lai, Z. M. Fang, L. Cao, W. Li, Z. D. Lin and P. Zhang, *Ionics*, 2020, **26**, 3015–3025.
- 98 G. Zhang, Y. Chen, Y. Deng and C. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36301–36310.
- 99 Z. K. Liu, J. S. Chen, Y. Zhan, B. Liu, C. X. Xiong, Q. L. Yang and G. H. Hu, *ACS Sustainable Chem. Eng.*, 2019, **7**, 17653–17660.
- 100 Z. K. Yang, J. Ma, B. R. Bai, A. D. Qiu, D. Losic, D. J. Shi and M. Q. Chen, *Electrochim. Acta*, 2019, **322**, 134769.
- 101 L. Cao, S. Y. Huang, F. L. Lai, Z. M. Fang, J. Cui, X. S. Du, W. Li, Z. D. Lin, P. Zhang and Z. R. Huang, *Ionics*, 2021, **27**, 3431–3441.
- 102 W. Li, F. Gao, X. Wang, N. Zhang and M. Ma, *Angew. Chem., Int. Ed.*, 2016, **55**, 9196–9201.
- 103 W. Li, X. F. Li, X. T. Zhang, J. Wu, X. H. Tian, M. J. Zeng, J. Qu and Z. Y. Yu, *ACS Appl. Energy Mater.*, 2020, **3**, 9408–9416.
- 104 J. Yang, X. Yu, X. Sun, Q. Kang, L. Zhu, G. Qin, A. Zhou, G. Sun and Q. Chen, *ACS Appl. Mater. Interfaces*, 2020, **12**, 9736–9745.
- 105 Y. S. Zhao, B. Z. Zhang, B. W. Yao, Y. Qiu, Z. H. Peng, Y. C. Zhang, Y. Alsaïd, I. Frenkel, K. Youssef, Q. B. Pei and X. M. He, *Mater.*, 2020, **3**, 1196–1210.
- 106 L. Li, Y. Zhang, H. Lu, Y. Wang, J. Xu, J. Zhu, C. Zhang and T. Liu, *Nat. Commun.*, 2020, **11**, 62.
- 107 C. Yang, P. Zhang, A. Nautiyal, S. Li, N. Liu, J. Yin, K. Deng and X. Zhang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 4258–4267.
- 108 L. Zang, Q. Liu, J. Qiu, C. Yang, C. Wei, C. Liu and L. Lao, *ACS Appl. Mater. Interfaces*, 2017, **9**, 33941–33947.
- 109 Z. Y. Peng, C. Z. Wang, Z. C. Zhang and W. B. Zhong, *Adv. Mater. Interfaces*, 2019, **6**, 1901393.
- 110 S. Brahim and A. Guiseppi-Elie, *Electroanalysis*, 2005, **17**, 556–570.
- 111 Y. Cheng, X. Y. Ren, L. J. Duan and G. H. Gao, *J. Mater. Chem. C*, 2020, **8**, 8234–8242.
- 112 D. L. Wei, J. Q. Zhu, L. C. Luo, H. B. Huang, L. Li and X. H. Yu, *J. Mater. Sci.*, 2020, **55**, 11779–11791.
- 113 Y. Q. Li, H. Zhang, S. Z. Ni and H. N. Xiao, *Mater. Lett.*, 2018, **232**, 175–178.
- 114 Y. Huang, H. F. Li, Z. F. Wang, M. S. Zhu, Z. X. Pei, Q. Xue, Y. Huang and C. Y. Zhi, *Nano Energy*, 2016, **22**, 422–438.
- 115 X. H. Zhang, N. N. Sheng, L. A. Wang, Y. Q. Tan, C. Z. Liu, Y. Z. Xia, Z. H. Nie and K. Y. Sui, *Mater. Horiz.*, 2019, **6**, 326–333.
- 116 A. M. Youssef, M. E. Abdel-Aziz, E. S. A. El-Sayed, M. S. Abdel-Aziz, A. A. Abd El-Hakim, S. Kamel and G. Turkey, *Carbohydr. Polym.*, 2018, **196**, 483–493.
- 117 X. W. Shi, L. Zhang, J. Cai, G. Z. Cheng, H. M. Zhang, J. Li and X. H. Wang, *Macromolecules*, 2011, **44**, 4565–4568.
- 118 X. T. Liang, B. Qu, J. R. Li, H. N. Xiao, B. H. He and L. Y. Qian, *React. Funct. Polym.*, 2015, **86**, 1–6.
- 119 H.-W. Chen and C. Li, *Chin. J. Polym. Sci.*, 2019, **38**, 435–448.
- 120 I. K. Moon, B. Ki and J. Oh, *Chem. Eng. J.*, 2020, **392**, 123794.
- 121 J. Zhang, X. Fan, X. Meng, J. Zhou, M. Wang, S. Chen, Y. Cao, Y. Chen, C. W. Bielawski and J. Geng, *ACS Nano*, 2021, **15**, 8870–8882.
- 122 C. Qian, T. Higashigaki, T. A. Asoh and H. Uyama, *ACS Appl. Mater. Interfaces*, 2020, **12**, 27518–27525.
- 123 H. Shi, C. C. Liu, Q. L. Jiang and J. K. Xu, *Adv. Electron. Mater.*, 2015, **1**, 1500017.
- 124 L. Manjakkal, A. Pullanchiyodan, N. Yogeswaran, E. S. Hosseini and R. Dahiya, *Adv. Mater.*, 2020, **32**, 1907254.
- 125 Z. Li, G. Ma, R. Ge, F. Qin, X. Dong, W. Meng, T. Liu, J. Tong, F. Jiang, Y. Zhou, K. Li, X. Min, K. Huo and Y. Zhou, *Angew. Chem., Int. Ed.*, 2016, **55**, 979–982.
- 126 Z. Yang, D. Shi, W. Dong and M. Chen, *Chemistry*, 2020, **26**, 1846–1855.
- 127 Y. Gogotsi and P. Simon, *Science*, 2011, **334**, 917–918.
- 128 V. R. Feig, H. Tran, M. Lee, K. Liu, Z. Huang, L. Beker, D. G. Mackanic and Z. Bao, *Adv. Mater.*, 2019, **31**, 1902869.
- 129 B. Lu, H. Yuk, S. Lin, N. Jian, K. Qu, J. Xu and X. Zhao, *Nat. Commun.*, 2019, **10**, 1043.
- 130 H. Lu, Y. H. Li, Q. Chen, L. L. Chen, N. Zhang and M. M. Ma, *ACS Appl. Energy Mater.*, 2019, **2**, 8163–8172.

- 131 P. Pattananuwat and D. Aht-Ong, *Mater. Lett.*, 2016, **184**, 60–64.
- 132 L. T. Duy and H. Seo, *Appl. Surf. Sci.*, 2020, **521**, 146467.
- 133 Y. Q. Han, M. X. Shen, Y. Wu, J. J. Zhu, B. Ding, H. Tong and X. G. Zhang, *Synth. Met.*, 2013, **172**, 21–27.
- 134 C. C. Shih, Y. C. Lin, M. Y. Gao, M. Wu, H. C. Hsieh, N. L. Wu and W. C. Chen, *J. Power Sources*, 2019, **426**, 205–215.
- 135 W. L. Teng, Q. Q. Zhou, X. K. Wang, H. B. Che, P. Hu, H. Y. Li and J. S. Wang, *Chem. Eng. J.*, 2020, **390**, 124569.
- 136 H. Wei, M. Lei, P. Zhang, J. Leng, Z. Zheng and Y. Yu, *Nat. Commun.*, 2021, **12**, 2082.
- 137 T. Xu, D. Z. Yang, S. Y. Zhang, T. Y. Zhao, M. Zhang and Z. Z. Yu, *Carbon*, 2021, **171**, 201–210.
- 138 W. R. Yan, J. H. Li, G. P. Zhang, L. Wang and D. Ho, *J. Mater. Chem. A*, 2020, **8**, 554–564.
- 139 K. D. Fong, T. Wang, H. K. Kim, R. V. Kumar and S. K. Smoukov, *ACS Energy Lett.*, 2017, **2**, 2014–2020.
- 140 J. Y. Yang, Q. H. Cao, X. W. Tang, J. J. Du, T. Yu, X. Xu, D. M. Cai, C. Guan and W. Huang, *J. Mater. Chem. A*, 2021, **9**, 19649–19658.
- 141 L. Weng, C. J. Xu, B. B. Chen, J. Q. Zhou, R. Cai and Y. T. Shi, *Mech. Mater.*, 2020, **150**, 103567.
- 142 C. Huang and L. Chen, *Adv. Mater.*, 2016, **28**, 8079–8096.
- 143 Y. H. Yan, X. Y. Liu, J. Yan, C. Guan and J. Wang, *Energy Environ. Mater.*, 2021, **4**, 502–521.
- 144 Y. L. Zou, C. Chen, Y. J. Sun, S. C. Gan, L. B. Dong, J. H. Zhao and J. H. Rong, *Chem. Eng. J.*, 2021, **418**, 128616.
- 145 Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara and T. Aida, *Nature*, 2010, **463**, 339–343.
- 146 C. C. Kim, H. H. Lee, K. H. Oh and J. Y. Sun, *Science*, 2016, **353**, 682–687.
- 147 D. W. Zhao, C. J. Chen, Q. Zhang, W. S. Chen, S. X. Liu, Q. W. Wang, Y. X. Liu, J. Li and H. P. Yu, *Adv. Energy Mater.*, 2017, **7**, 1700739.
- 148 J. Hou, M. S. Liu, H. C. Zhang, Y. L. Song, X. C. Jiang, A. B. Yu, L. Jiang and B. Su, *J. Mater. Chem. A*, 2017, **5**, 13138–13144.
- 149 E. M. Ahmed, *J. Adv. Res.*, 2015, **6**, 105–121.
- 150 Y. S. Ji, N. Liang, J. Xu, R. Qu, D. Z. Chen and H. W. Zhang, *Electrochim. Acta*, 2018, **283**, 97–103.
- 151 N. Lu, X. Zhang, R. Na, W. Ma, C. Zhang, Y. Luo, Y. Mu, S. Zhang and G. Wang, *J. Colloid Interface Sci.*, 2019, **534**, 672–682.
- 152 J. L. Hao, Q. Z. Xiao, G. T. Lei, Z. H. Li and L. J. Wu, *Electrochim. Acta*, 2014, **125**, 450–456.
- 153 Y. Guo, K. Zheng and P. Wan, *Small*, 2018, **14**, 1704497.
- 154 K. Wang, X. Zhang, C. Li, X. Sun, Q. Meng, Y. Ma and Z. Wei, *Adv. Mater.*, 2015, **27**, 7451–7457.
- 155 N. Anjum, N. Joyal, J. Iroegbu, D. P. Li and C. W. Shen, *J. Power Sources*, 2021, **499**, 229962.
- 156 H. Peng, Y. Y. Lv, G. G. Wei, J. Z. Zhou, X. J. Gao, K. J. Sun, G. F. Ma and Z. Q. Lei, *J. Power Sources*, 2019, **431**, 210–219.
- 157 Q. Liu, A. R. Zhao, X. X. He, Q. Li, J. Sun, Z. B. Lei and Z. H. Liu, *Adv. Funct. Mater.*, 2021, **31**, 2010944.
- 158 S. J. Peng, S. X. Liu, Y. J. Sun, N. P. Xiang, X. C. Jiang and L. X. Hou, *Eur. Polym. J.*, 2018, **106**, 206–213.
- 159 K. Shen, J. W. Ding and S. B. Yang, *Adv. Energy Mater.*, 2018, **8**, 1800408.
- 160 M. Areir, Y. M. Xu, D. Harrison, J. Fyson and R. R. Zhang, *Mater. Manuf. Processes*, 2018, **33**, 905–911.
- 161 Z. K. Wang, F. Tao and Q. M. Pan, *J. Mater. Chem. A*, 2016, **4**, 17732–17739.
- 162 X. T. Jin, G. Q. Sun, H. S. Yang, G. F. Zhang, Y. K. Xiao, J. Gao, Z. P. Zhang and L. T. Qu, *J. Mater. Chem. A*, 2018, **6**, 19463–19469.
- 163 Y. Z. Guo, X. Zhou, Q. Q. Tang, H. Bao, G. C. Wang and P. Saha, *J. Mater. Chem. A*, 2016, **4**, 8769–8776.
- 164 K. Abe and H. Yano, *Cellulose*, 2012, **19**, 1907–1912.
- 165 K. Oksman, A. P. Mathew, D. Bondeson and I. Kvien, *Compos. Sci. Technol.*, 2006, **66**, 2776–2784.
- 166 L. Liu, L. Li, Y. Qing, N. Yan, Y. Q. Wu, X. J. Li and C. H. Tian, *Polym. Chem.*, 2016, **7**, 7142–7151.
- 167 L. Li, L. Liu, Y. Qing, Z. Zhang, N. Yan, Y. Q. Wu and C. H. Tian, *Electrochim. Acta*, 2018, **270**, 302–309.
- 168 Y. S. Zhang, C. Li, X. X. Cai, J. S. Yao, M. Li, X. Zhang and Q. Z. Liu, *Electrochim. Acta*, 2016, **220**, 635–642.
- 169 Y. Shi, Y. Zhang, L. Jia, Q. Zhang and X. Xu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 36028–36036.
- 170 H. Y. Yu, J. H. Wu, L. Q. Fan, K. Q. Xu, X. Zhong, Y. Z. Lin and J. M. Lin, *Electrochim. Acta*, 2011, **56**, 6881–6886.
- 171 S. T. Senthilkumar, R. K. Selvan, J. S. Melo and C. Sanjeeviraja, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10541–10550.
- 172 L. Q. Fan, J. Zhong, J. H. Wu, J. M. Lin and Y. F. Huang, *J. Mater. Chem. A*, 2014, **2**, 9011–9014.
- 173 B. C. Nath, B. Gogoi, M. Boruah, S. Sharma, M. Khannam, G. A. Ahmed and S. K. Dolui, *Electrochim. Acta*, 2014, **146**, 106–111.
- 174 G. F. Ma, E. K. Feng, K. J. Sun, H. Peng, J. J. Li and Z. Q. Lei, *Electrochim. Acta*, 2014, **135**, 461–466.
- 175 E. K. Feng, W. Gao, Z. Yan, J. J. Li, Z. L. Li, X. X. Ma, L. H. Ma and Z. M. Yang, *J. Power Sources*, 2020, **479**, 229100.
- 176 G. Zhou, L. Yang, W. Li, C. Chen and Q. Liu, *iScience*, 2020, **23**, 101502.
- 177 J. Y. Sun, X. Zhao, W. R. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. Suo, *Nature*, 2012, **489**, 133–136.
- 178 X. G. Cao, C. M. Jiang, N. Sun, D. C. Tan, Q. K. Li, S. Bi and J. H. Song, *J. Sci.-Adv. Mater. Rev.*, 2021, **6**, 338–350.
- 179 Z. X. Liu, G. J. Liang, Y. X. Zhan, H. F. Li, Z. F. Wang, L. T. Ma, Y. K. Wang, X. R. Niu and C. Y. Zhi, *Nano Energy*, 2019, **58**, 732–742.
- 180 J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv. Mater.*, 2003, **15**, 1155–1158.
- 181 T. L. Sun, T. Kurokawa, S. Kuroda, A. B. Ihsan, T. Akasaki, K. Sato, M. A. Haque, T. Nakajima and J. P. Gong, *Nat. Mater.*, 2013, **12**, 932–937.
- 182 H. Qin, P. Liu, C. Chen, H. P. Cong and S. H. Yu, *Nat. Commun.*, 2021, **12**, 4297.
- 183 L. Cao, M. Yang, D. Wu, F. Lyu, Z. Sun, X. Zhong, H. Pan, H. Liu and Z. Lu, *Chem. Commun.*, 2017, **53**, 1615–1618.
- 184 H. Z. Yang, Y. Liu, L. B. Kong, L. Kang and F. Ran, *J. Power Sources*, 2019, **426**, 47–54.
- 185 W. J. Ge, S. Cao, Y. Yang, O. J. Rojas and X. H. Wang, *Chem. Eng. J.*, 2021, **408**, 127306.
- 186 J. J. Xu, R. N. Jin, X. Y. Ren and G. H. Gao, *Chem. Eng. J.*, 2021, **413**, 127446.
- 187 M. F. Chen, J. Z. Chen, W. J. Zhou, J. L. Xu and C. P. Wong, *J. Mater. Chem. A*, 2019, **7**, 26524–26532.
- 188 L. Y. Yang, L. Song, Y. Feng, M. J. Cao, P. C. Zhang, X. F. Zhang and J. F. Yao, *J. Mater. Chem. A*, 2020, **8**, 12314–12318.