

# Autonomous Chemistry Enabling Environment-Adaptive Electrochemical Energy Storage Devices

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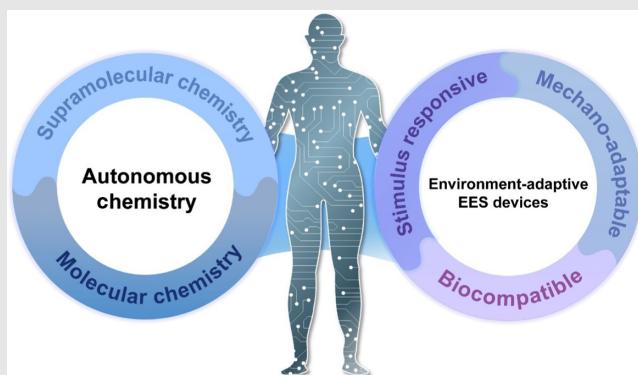
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Cite this: CCS Chem. 2023, 5, 11–29

DOI: [10.31635/ccschem.022.202202153](https://doi.org/10.31635/ccschem.022.202202153)

Next-generation electronics that are fused into the human body can play a key role in future intelligent communication, smart healthcare, and human enhancement applications. As a promising energy supply component for smart biointegrated electronics, environment-adaptive electrochemical energy storage (EES) devices with complementary adaptability and functions have garnered huge interest in the past decade. Owing to the advancements in autonomous chemistry, which regulate the constitutional dynamic networks in materials, EES devices have witnessed higher freedom of autonomous adaptability in terms of mechano-adaptable, biocompatibility, and stimuli-response properties for biointegrated and smart applications. In this mini-review, we summarize the recent progress in emerging environment-adaptive EES devices enabled by the constitutional dynamic network of mechanical adaptable materials, biocompatible materials, and stimuli-responsive

supramolecular polymer materials. Finally, the challenges and perspectives of autonomous chemistry on the environment-adaptive EES devices are discussed.



Keywords: autonomous chemistry, biointegrated electronics, environmental adaption, electrochemical energy storage devices

## Introduction

Advancements made in the merging of human consciousness and machine capabilities have driven the emergence of smart electronics.<sup>1–6</sup> The fusion of electronics into human beings to form biointegrated systems has motivated the development of electronics with a higher

degree of adaptability in ever-changing environments. To intimately integrate electronics with the human body, electronics are becoming more flexible and stretchable to accommodate the arbitrary shapes of the human body and mechanical deformation during human motion. Alongside mechanical adaptability, biointegrated electronics are also required to be biocompatible so as to

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Link to VoR: <https://doi.org/10.31635/ccschem.022.202202153>

operate in physiological environments, such as near-body, on-skin, and *in vivo* environments. Moreover, by combining with other smart functions, such as biometric sensing and stimuli-responsive actuating, smart biointegrated electronics can allow humans to share their senses and engage in collaborative work with machines to extend the limitation of the human body and machines. Progress in such adaptability of electronics and emerging symbiosis between humans and machines has unlocked exciting opportunities in fabricating biointegrated electronics for smart healthcare and human enhancement applications.

To seamlessly power the emerging environment-adaptive electronics, in the last decade, the indispensable electrochemical energy storage (EES) devices, mainly supercapacitors and batteries, have witnessed complementary changes in mechanical adaptability, biocompatibility, and smart functionalities for biointegrated applications.<sup>7–9</sup> The environment-adaptive transformations in the EES devices would not be realized without the participation of autonomous chemistry. Autonomous chemistry is an adaptive and self-evolved chemical system that manipulates the covalent and non-covalent constitutional dynamic networks to autonomously adapt and respond to internal and external stimuli, such as light, temperature, pH, and biological enzymes (Figure 1). The molecular chemistry governing the dynamic covalent bonds (Figure 1a) and supramolecular chemistry implementing the intermolecular interactions (Figure 1b) create building blocks of constitutional dynamic chemistry networks.<sup>10–14</sup> These dynamic chemistry networks extend and combine with molecules of various sizes to allow for variation and adaptation through autonomous component selection and response to internal and external environmental stimuli (Figure 1c). The introduction of autonomous chemistry into materials science opens up new perspectives on self-adaptive materials. These autonomously adaptive materials integrated with device technologies provide great opportunities for the development of environment-adaptive EES devices.

Autonomous chemistry allows for regulating the functions of environment-adaptive EES devices. By using autonomously adaptive materials, autonomously operating chemical systems in devices can adapt and respond to environmental changes (Figure 2a–f, h). Since the first transformation from the original rigid prototype into flexible devices in 2007, environment-adaptive EES devices have ushered in a new era.<sup>7,15</sup> With enhanced flexibility of electrode materials via flexible and stretchable molecular and supramolecular design, intrinsically flexible and stretchable electrodes can endow the mechano-adaptable EES devices with adaptability to arbitrary shapes of the human body.<sup>16–22</sup> Accompanying the enhanced mechanical adaptability, the molecular designs of biodegradable and bioresorbable materials

enable EES devices to be autonomously biocompatible with the human body for skin-mounted, ingestible, and implantable applications.<sup>23–26</sup> Furthermore, the incorporation of stimuli-responsive alloys and supramolecular polymers has spurred EES devices towards smart transformations (e.g., self-healing, shape memory, thermal protection, and electrochromism), providing environment-adaptive EES devices with self-responsive and self-protective functions under external mechanical, thermal, and/or electrical stimuli.<sup>27–30</sup> The design and synthesis of autonomous molecular and supramolecular networks with autonomous operation in mechano-adaptable materials, biocompatible materials, and stimuli-responsive supramolecular polymer materials have enabled the development of EES devices with programmable environment-adaptive functions, offering new opportunities to power the next-generation smart and biointegrated electronics.<sup>31,32</sup>

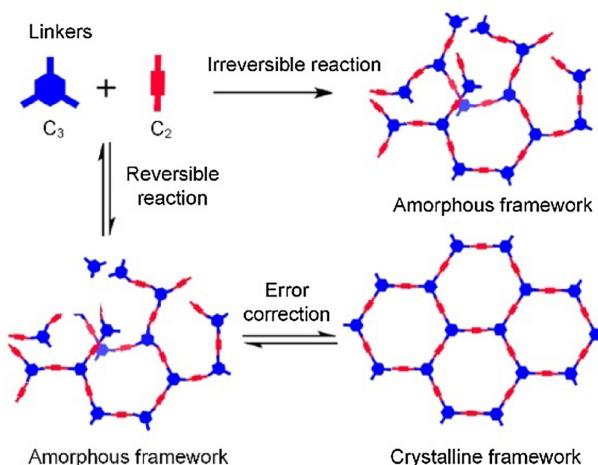
Herein, we review recent important advances in environment-adaptive EES devices that are enabled by autonomous chemistry. Specifically, electrodes, electrolytes, and devices associated with constitutional dynamic networks of mechano-adaptable materials, biocompatible materials, and stimuli-responsive supramolecular polymers will be discussed. The emerging mechano-adaptable, biocompatible, and smart EES devices for environment-adaptive applications will also be emphasized. Finally, this review concludes with an outlook on the challenges and opportunities in this fast-developing field.

## Constitutional Dynamic Networks for Mechano-Adaptable EES Devices

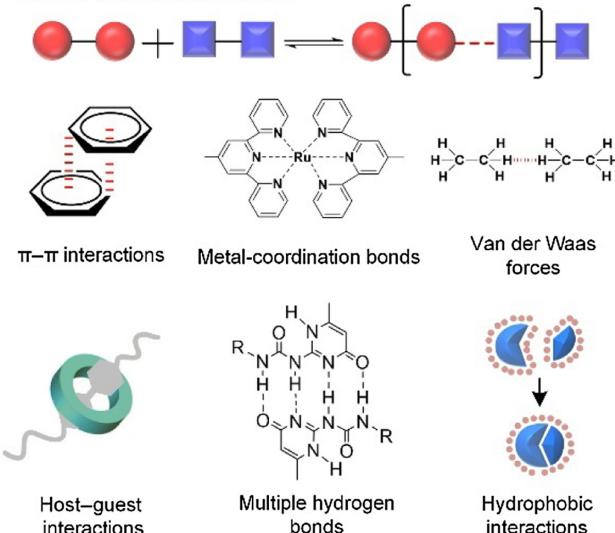
The basic mechanical deformations of EES devices involve bending and stretching to cover the curved surface of human skin and soft tissues. Conventional EES devices with packaging consist of two electrodes separated by an electrically insulating separator immersed in a liquid electrolyte (Figure 2g). However, the maximum elastic strains these components in conventional EES devices, including electrodes, separators, and packaging, are typically less than 1%, which cannot match the stretchability (>50%) required for biointegrated applications.<sup>33,34</sup> Clearly, improving the tensile strains of these components is essential to designing mechano-adaptable EES devices.

To make the components in EES devices stretchable, two strategies have been exploited, including directly replacing inelastic materials with elastic alternatives and constructing structural nanomaterial networks for stretchable electrodes. The inextensible components—electrolytes, separators, and packaging—can be directly replaced by their stretchable alternatives. For example, silicone rubbers such as polydimethylsiloxane and Ecoflex are frequently adopted as stretchable packaging

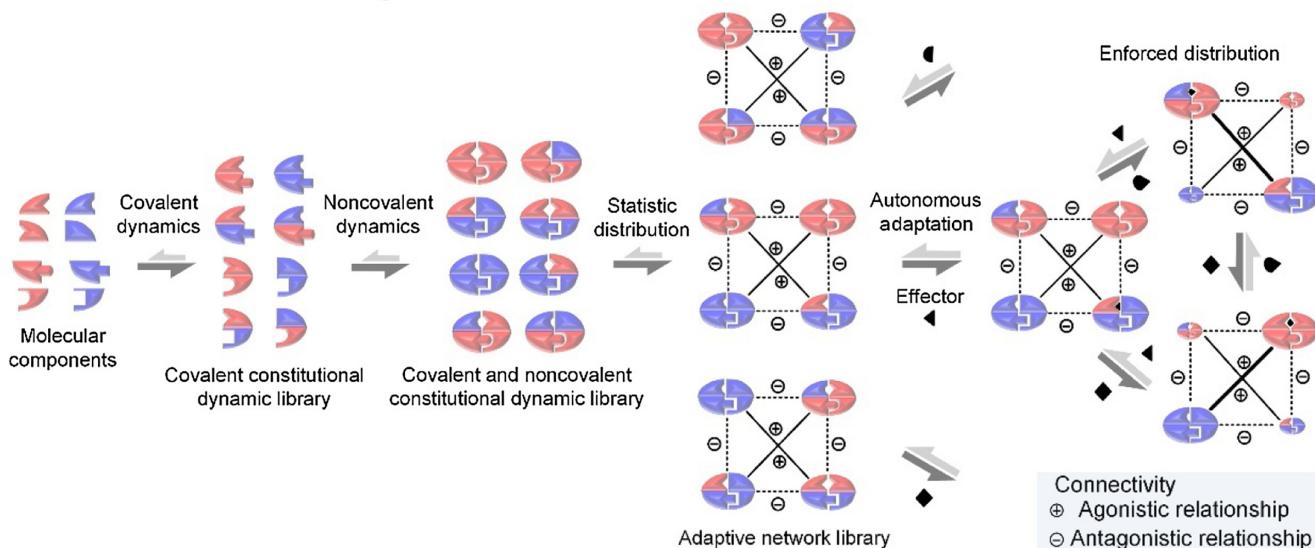
## (a) Covalent bonds



## (b) Noncovalent bonds



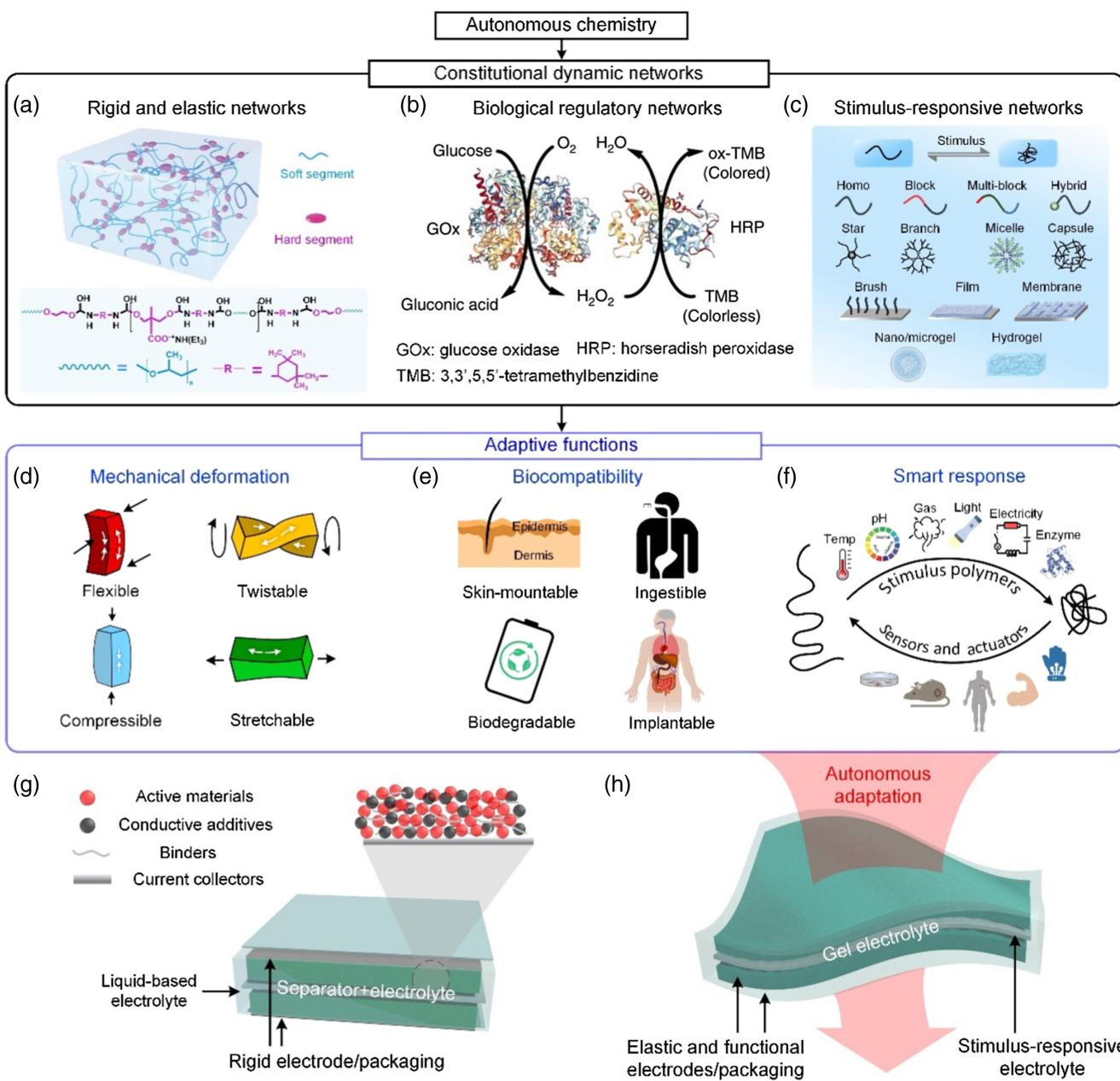
## (c) Autonomous chemistry



**Figure 1 |** The emergence of autonomous chemistry toward adaptive and self-evolved chemical systems. (a) Schematic representation of the dynamic reversible and irreversible molecular interactions for the formation of the crystalline and amorphous covalent organic framework. Adapted with permission from ref 14. Copyright 2019 American Chemical Society. (b) Schematic representation of the noncovalent constitutional dynamic network for supramolecular interactions. (c) Autonomous chemistry with covalent and noncovalent constitutional dynamic networks to construct adaptive and self-evolved chemical systems.

materials, and gel electrolytes with stretchable molecular design can serve as both electrolytes and stretchable separators to eliminate the necessity of poorly elastic separators and possible leakage of liquid electrolyte. As for electrodes, the available inelastic materials can be reinforced with conductive nanomaterials (e.g., graphene, carbon nanotubes (CNTs), and conductive polymers) that have higher tensile strains. However, the tensile strain of composite electrodes is still less than 10%.<sup>35,36</sup> In this regard, directly replacing electrode

materials with elastic alternatives is not enough. As a complementary method, a stretchable structural design has been developed to improve the stretchability of the electrode. Based on thin and porous nanomaterials, more bendable electrodes cooperate with elastic polymer substrates and proper electrode layouts, such as wave-like wrinkled structures, coiled and braided structures, and kirigami structures, which are highly stretchable and can accommodate tensile strain greater than 100%.<sup>16,20,37-42</sup>



**Figure 2 |** The transformation of traditional EES devices into environment-adaptive EES devices enabled by autonomous chemistry. Autonomous chemistry modulates the constitutional dynamic (a) rigid and elastic networks, (b) biological regulatory networks, and (c) the stimulus-response networks for environment-adaptive EES with (d-f) desired functionalities. (a) Chemical structure and illustration of stretchable and adhesive water-dispersible PUs with both soft and hard segments. Reproduced with permission from ref 22. Copyright 2021 Wiley-VCH. (b) Colorimetric detection of glucose using cascade enzyme reaction systems with glucose oxidase and horseradish peroxidase. Adaptable with permission from ref 26. Copyright 2019 Springer Nature Limited. (c) Stimuli-responsive polymers designed with different kinds of topological structures and morphologies. (d) The representative mechanical deformations. (e) The biofriendly interfaces with the human body that require biocompatible properties. (f) The stimulus-responsive smart functions. (g) Schematic device structure of conventional EES devices. (h) The schematic device structure of the environment-adaptive EES devices.

Instead of using structural designs, the molecular design of intrinsically stretchable polymers is an effective way to realize flexible and stretchable electrodes and electrolytes

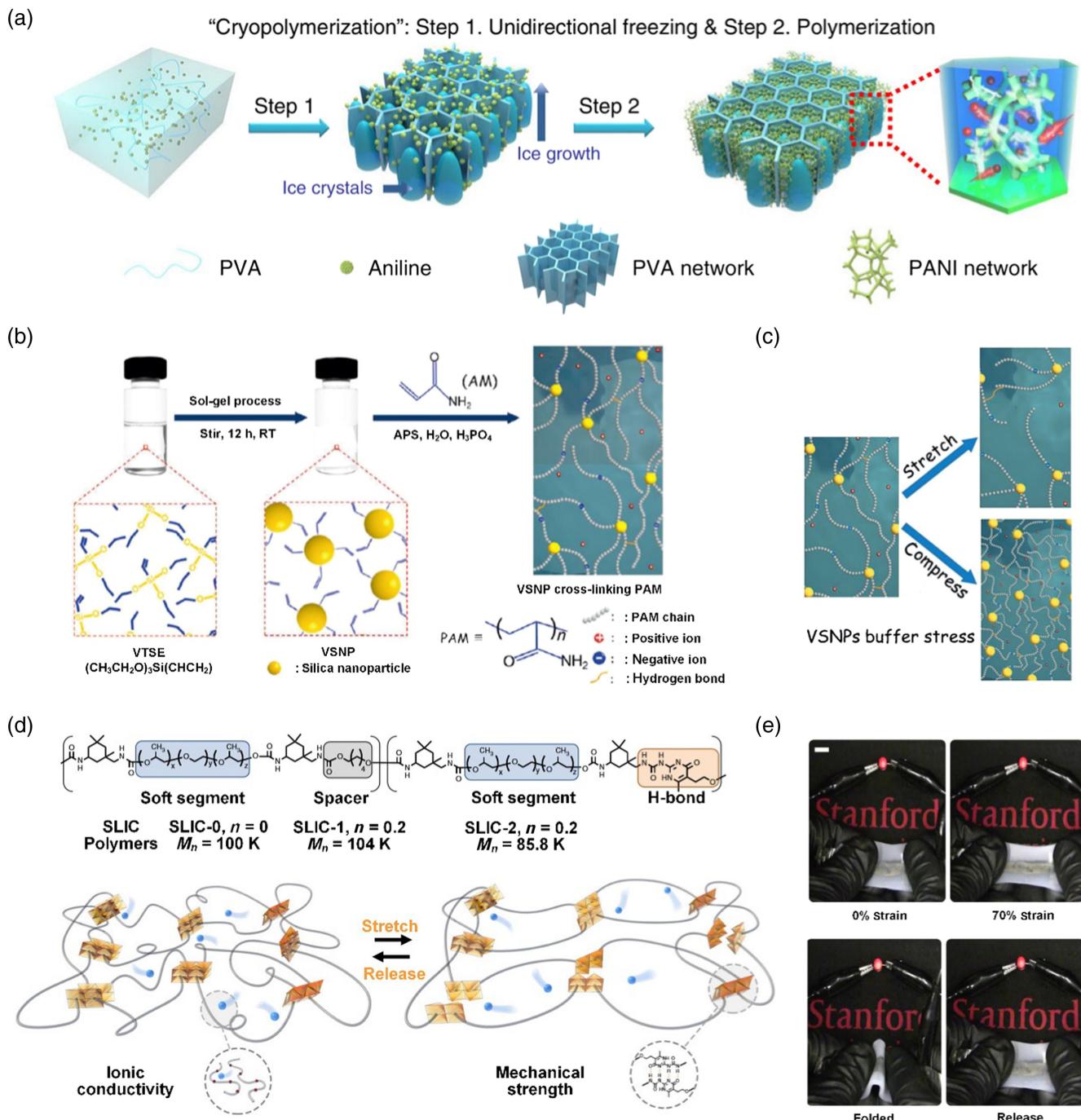
for mechano-adaptable EES devices. Common conjugated polymers, including polypyrrole (PPy), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT),

when doped into a conducting state, are promising pseudocapacitive materials for flexible supercapacitors.<sup>21,43,44</sup> However, the doped conductive polymers usually possess a close-packed and laminated structure that is not capable of releasing mechanical stresses induced by ion exchange in the charging/discharging process and mechanical deformation. This leads to the deterioration of both electrochemical and mechanical performances of as-fabricated devices during mechanical deformation.<sup>21</sup> To address this issue, partially doping anion into a conductive polymer matrix has been applied to prevent the overstacking of polymer chains. Taking the electropolymerization of PPy as an example, a porous PPy/black phosphorus oxide (BPO) composite electrode was prepared through a two-step electropolymerization method by utilizing partially oxidized black phosphorus (BP) as dopant.<sup>21</sup> The BPO surface was partially doped into the PPy matrix, while the unoxidized BP surface helped to form micropores during the deposition of PPy/BPO composites on the CNT films. As a comparison, the doped PPy composite electrode showed densely packed structures when the anion dopants ( $\text{SO}_4^{2-}$  and graphene oxides (GO)) with fully covered oxygen functional groups were employed for the electropolymerization process. Owing to the porous structures to buffer the strain under deformation, the as-prepared stretchable supercapacitors with the porous PPy/BPO-CNT electrode exhibited 97% capacitance retention when being stretched to 2400%, which is superior to that of dense stacking PPy/ $\text{SO}_4^{2-}$  and PPy/GO electrode-enabled stretchable supercapacitors (78% and 87% respectively).

Besides tuning the dopant in conductive polymers, the additional template and solvent precursors also affect the polymerization process, thus affecting the resultant morphology and stretchability of the conductive polymer-based electrodes. With the template of ice crystals, anisotropic polyvinyl alcohol (PVA)/PANI hybrid hydrogels were synthesized through a cryopolymerization strategy (Figure 3a).<sup>43</sup> During the freezing process, the 3D-ordered honeycomb structure of PVA was formed along the growing direction of vertically aligned ice crystals. Followed by cryopolymerization, the polymerization of PANI nanofiber was confined within the boundaries between PVA cell walls and ice crystals. The honeycomb structures with the PVA and PANI interpenetrating networks enabled isotropic PVA/PANI hybrid hydrogels with maximum elongation up to 416%. The as-fabricated supercapacitors delivered 85% capacitance under 200% tensile strain, demonstrating an exciting avenue to synthesize conductive polymer hybrid hydrogels as intrinsically stretchable electrodes for mechano-adaptable EES devices. Additionally, adding dimethyl sulfoxide (DMSO) into an aqueous PEDOT:polystyrene sulfonate (PSS) solution for dry annealing and rehydration processes can lead to a well-controlled

phase separation to form interconnected networks of PEDOT:PSS nanofibrils in the as-prepared pure PEDOT:PSS hydrogels. In contrast, fragmented PEDOT:PSS microgel was obtained from the PEDOT:PSS aqueous solution without DMSO due to the separation between the soft PSS-rich domain and the rigid PEDOT-rich domain under the same drying and swelling process.<sup>44</sup> The pure PEDOT:PSS hydrogels (20 vol % DMSO in the preparation) can be used as intrinsically stretchable electrodes for supercapacitors and reach a maximum stretchability up to 35% in phosphate-buffered saline (PBS) solution, which closely matches the stretchability of biological tissues (~20% for neural tissues and ~50% for skin).<sup>35</sup>

Apart from the stretchable electrodes, the molecular design of supramolecular dynamic polymers with both mechanically robust and ionically conductive segments is also used to fabricate intrinsically stretchable electrolytes for mechano-adaptable EES devices.<sup>45</sup> Pure polyacrylamide (PAM) hydrogels with weak hydrogen bonds are hard to make ultrastretchable, which limits their applications as stretchable electrolytes for stretchable supercapacitors. To enhance the toughness and stretchability of the PAM hydrogel, the hydrogel skeleton was reinforced by the strong covalent bonding between the PAM chains and vinyl hybrid silica nanoparticles (VSNPs) (Figure 3b).<sup>45</sup> The VSNPs-PAM hydrogels with ionically conductive PAM polyelectrolyte matrix and stress-buffering of VSNP cross-linkers enabled stretchable supercapacitors to possess intrinsic superstretchability (up to 1000% strain) and compressibility (up to 50% strain) without degradation of their initial capacitance (Figure 3c).<sup>45</sup> Similarly, the crosslinking of hairy nanoparticles helped strengthen the stretchable hydrogel electrolytes. The stretchable supramolecular lithium-ion conductor with mechanically reinforced hydrogen bonds was designed to serve as the polymer electrolyte for stretchable lithium-ion batteries (LIBs) (Figure 3d).<sup>46</sup> To decouple mechanical robustness from ionic conductivity in low- $T_g$  (the glass transition temperature) polymer electrolytes, a copolymer was created by introducing a dynamic bonded ureido-pyrimidinone (UPy) backbone into low- $T_g$  polyether backbone, wherein the low- $T_g$  polyether backbone provided the polymer electrolyte with high ionic conductivity ( $1.2 \pm 0.21 \times 10^{-4} \text{ S cm}^{-1}$ ), and the Upy group enhanced the mechanical toughness of the polymer electrolyte ( $29.3 \pm 0.21 \times 10^{-4} \text{ MJ m}^{-3}$ , three times higher than reported polymer electrolytes) by dynamic hydrogen bonds. The as-prepared polymer electrolyte-based stretchable LIBs, with a capacity density of  $1.1 \text{ mAh cm}^{-2}$  function well to power light-emitting diodes even when stretched up to 70%, suggesting the promising application of tough ion-conducting polymers for conformable EES devices (Figure 3e).



**Figure 3 | Molecular design of flexible and stretchable polymers for mechano-adaptable EES devices.** (a) The fabrication of the anisotropic hybrid porous PVA/PANI hydrogels for stretchable supercapacitors with diverse shapes under stretching and compression. Reproduced with permission from ref 43. Copyright 2019 Springer Nature Limited. (b) The synthesis process of VSNPs-PAM electrolytes for stretchable and compressible supercapacitors by cross-linking the VSNPs from vinyltriethoxysilane with acrylamide monomers at the presence of the ammonium persulfate initiator and phosphoric acid. Reproduced with permission from ref 45. Copyright 2017 Wiley-VCH. (c) Illustration of the VSNPs cross-linking PAM network for superstretchability and high compressibility. Reproduced with permission from ref 45. Copyright 2017 Wiley-VCH. (d) The chemical structure of the lithium-ion conductor (LIC) and diagram showing the LIC polymer electrolyte upon stretching. The orange squares represent hydrogen-bonding UPy moieties, black wires are poly(propylene glycol)-pol(ethylene glycol)-poly(propylene glycol) (PPG-PEG-PPG) chains, and the blue circles are lithium ions. Reproduced with permission from ref 46. Copyright 2019 Springer Nature Limited. (e) The application of the supramolecular LIC for stretchable LIBs. Reproduced with permission from ref 46. Copyright 2019 Springer Nature Limited.

## Constitutional Dynamic Networks for Biocompatible EES Devices

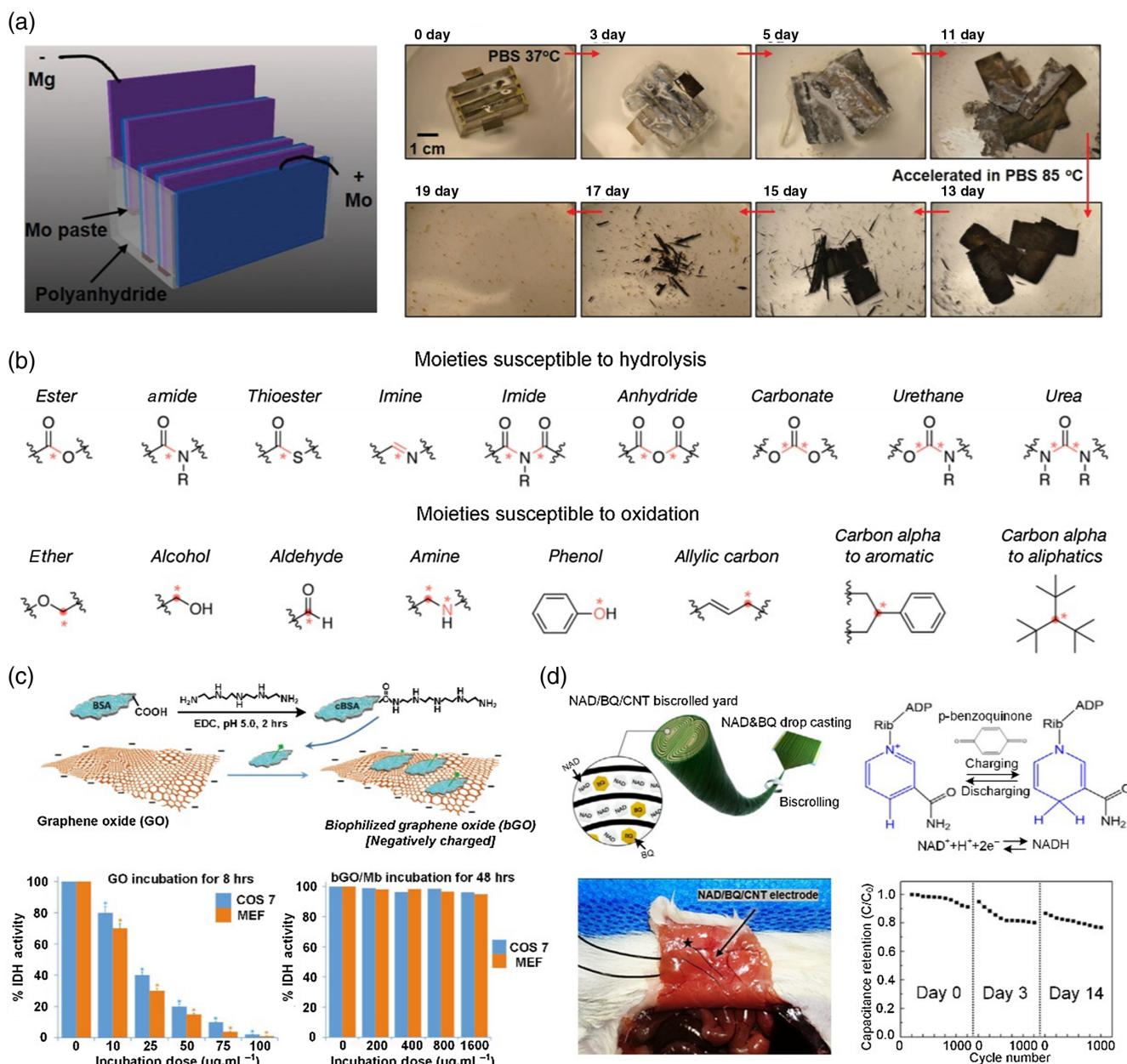
The boom in environment-adaptive electronics for real-time *in vivo* health monitoring and diagnosis has stimulated the development of EES devices with not only mechano-adaptability but also biocompatibility, so as to adapt to biological environments and intimately integrate onto/into essential organs of the human body.<sup>47</sup> However, developing biocompatible EES devices that avoid the likelihood of infection remains a great challenge, especially in the exploration of nontoxic and biodegradable devices. To safely use biocompatible EES devices for *in vivo* applications, the original corrosive and toxic materials in EES devices should be replaced with nontoxic and biodegradable alternatives that can be autonomously dissolved and resorbed or disposed of by the body through biochemical processes like metabolism and bioabsorption.

Such biodegradable materials include inorganic materials and organic polymers. Inorganic metals (e.g., Mg, Mo, and Li) that can react and dissolve in aqueous solutions are suitable materials to fabricate biodegradable electrodes for EES devices. Likewise, biodegradable polymers that can undergo chemical or enzymatical hydrolysis and/or oxidation are suitable as well.<sup>48–52</sup> A representative biodegradable battery system is shown in Figure 4a, wherein the primary Mg–Mo battery is packaged with polyanhydride materials to provide a constant current density of  $0.1 \text{ mA cm}^{-2}$  at a voltage of 1.6 V for around 6 h.<sup>49</sup> Because all the constituent materials in the battery are water-soluble, the Mg–Mo battery is fully degradable after 11 days in PBS at 37 °C followed by another 8 days in PBS at 85 °C. The biodegradation of polyanhydride in the Mg–Mo battery stems from the fact that its ester bonds are susceptible to hydrolysis. Other hydrolytically degradable moieties as shown in Figure 4b, like the amide, thioester, and imine, can serve as the synthetic polymer backbone for eco-friendly degradation.<sup>48</sup> Complementary to hydrolysis, oxidation is another way to biologically degrade polymers. Polymers designed with oxidizable moieties, such as ethers, alcohols, and phenols, are susceptible to oxidative cleavage (Figure 4b).<sup>53</sup> Currently, previous reports about the degradation of biocompatible EES devices are mainly limited to hydrolysis of electrode materials in physiological conditions, and the mechanism for the oxidation of polymers in biodegradable EES devices has yet to be thoroughly explored.

As the EES devices become incorporated into the digestive system, biocompatible EES devices that can be ingested by individuals also emerge, with emphasis on biodegradable, bioresorbable, and noncytotoxic characteristics of the devices. Conventional active materials, such as MnO<sub>2</sub>, which is a constituent material of

supercapacitors, pose a threat to the human body (causing abdominal pain and nausea) when ingested. Moreover, the toxicity of many nanomaterials is still unknown.<sup>24,54</sup> In this case, naturally derived materials (e.g., biochar, cellulose, silk, and collagen) provide alternatives to fabricate biocompatible and edible devices due to their intrinsic nontoxicity and enzymatic degradability.<sup>48,55</sup> Edible supercapacitors with naturally-derived food materials, including active charcoal as the electrode material, egg whites as the edible binder, and high-purity gold leaf as the current collector, can be connected in series to power a red LED and dissolved in the simulated gastric environment. This suggests that naturally derived materials are promising nontoxic materials to build biocompatible EES devices.<sup>24</sup>

As for the implantable EES devices, most of the literature related to degradable devices has only investigated degradation in deionized water or stimulated biofluids such as PBS solution.<sup>47,49,50</sup> We note that the behavior of *in vivo* degradation is different from that of *in vitro* degradation due to the interaction between electrode materials and complex biological components (e.g., proteins and cells). To improve the biophilic properties and reduce the cytotoxicity for implantable applications, the commonly used active materials for supercapacitors, such as CNT and GO, have been modified with oxygen-containing functional groups, proteins, and conductive polymers.<sup>56,57</sup> A biocompatible supercapacitor with hydrophilic aligned CNTs treated by oxygen plasma was able to operate in biological fluids, such as PBS, serum, and blood.<sup>56</sup> The cytotoxicity test has proved that the synthesized hydrophilic CNTs with oxygen species, including hydroxyl, carbonyl, and carboxylic groups, show better biocompatibility and interaction for cell attachment and growth than hydrophobic CNTs. Another study utilized protein-modified biophilicized reduced graphene oxide (brGO) as the electrode for nontoxic supercapacitors (Figure 4c).<sup>57</sup> No toxicity of myoglobin (Mb)-modified brGO materials (up to high doses of  $1600 \mu\text{g mL}^{-1}$ ) to mouse embryo fibroblasts (MEFs) and COS-7 cell cultures was observed in the biocompatible test. The maximum nontoxic concentration was 160 times higher than that of unmodified GO electrodes. Besides surface treatment and protein modification, the conductive polymer-modified composites also show good biocompatibility for implantation. A fiber-shaped supercapacitor, consisting of PEDOT:PSS/Ferritin-multiwalled CNT yard electrodes, was implanted into the abdominal cavity of a mouse.<sup>25</sup> No infection was observed during the 4-week implantation. Moreover, the implantable supercapacitor maintained 90% capacitance retention after 8 days of implantation. In living cells, cellular energy transduction involves the natural redox biomolecule, like the nicotinamide adenine dinucleotide (NAD), to produce the energy storage molecule adenosine triphosphate. Inspired by this cellular redox



**Figure 4 | Biodegradable and biocompatible materials for biocompatible EES devices.** (a) The dissolution of the biodegradable Mg-Mo battery with degradable inorganic metallic electrodes and an organic polyanhydride spacer. Reproduced with permission from ref 49. Copyright 2014 Wiley-VCH. (b) The chemical structures of moieties tend to be hydrolyzed and oxidized, and the red marks indicate the hydrolyzation and oxidation sites. Images adapted with permission from ref 48. Copyright 2018 American Chemical Society. (c) The biophilized graphene oxide (bGO)-Mb electrode for biocompatible supercapacitors. Upper: the synthesis of bGO with the negative charge by absorbing cationized bovine serum albumin (cBSA) ion of cBSA onto GO sheet. Down: dose-dependent toxicity in (COS-7) and MEF cells coincubated with GO and bGO/Mb as measured by the intracellular dehydrogenases activity. Reproduced with permission from ref 56. Copyright 2017 Wiley-VCH. (d) An implantable NAD/BQ/CNT yarn supercapacitor. Top: Fabrication scheme of NAD/BQ/CNT yarn electrode and the reversible redox reaction of NAD with the assistance of BQs (oxidized and reduced forms of NAD abbreviated as  $NAD^+$  and reduced nicotinamide adenine dinucleotide [ $NADH$ ], respectively). Down: Implantation of the yarn supercapacitors into the abdominal cavity of a mouse and the capacitance retention of the implantable supercapacitors on the day of surgery, 3 and 14 days after implantation. Reproduced with permission from ref 58. Copyright 2021 Wiley-VCH.

system, an implantable CNT yarn supercapacitor was fabricated by employing twisted CNT electrodes with electrochemically deposited NAD and benzoquinone (BQ; Figure 4d).<sup>58</sup> The biocompatible NAD/BQ/CNT yarn electrodes implanted into the abdominal cavity of a rat exhibited the stable *in vivo* electrical performance of a supercapacitor even after 14 days implantation (Figure 4d).

## Constitutional Dynamic Networks for Smart EES Devices

With the scope of electronics research further expanded into biomimetics, soft robotics, and artificial intelligence (AI), smart EES devices with self-adaptation and self-protection to respond to external stimuli have emerged as a new class of biontegrated devices. In particular, four main kinds of smart EES devices have been developed, including self-healing, shape-memory, thermal protective, and electrochromic EES devices. These emerging smart EES devices cannot be realized without the assistance of stimuli-responsive supramolecular materials. The dynamic bonds designed in supramolecular materials can be autonomously reconstructed when they are exposed to external mechanical, thermal, and electric stimuli, endowing the EES devices with environmental adaptability for smart applications.<sup>59,60</sup>

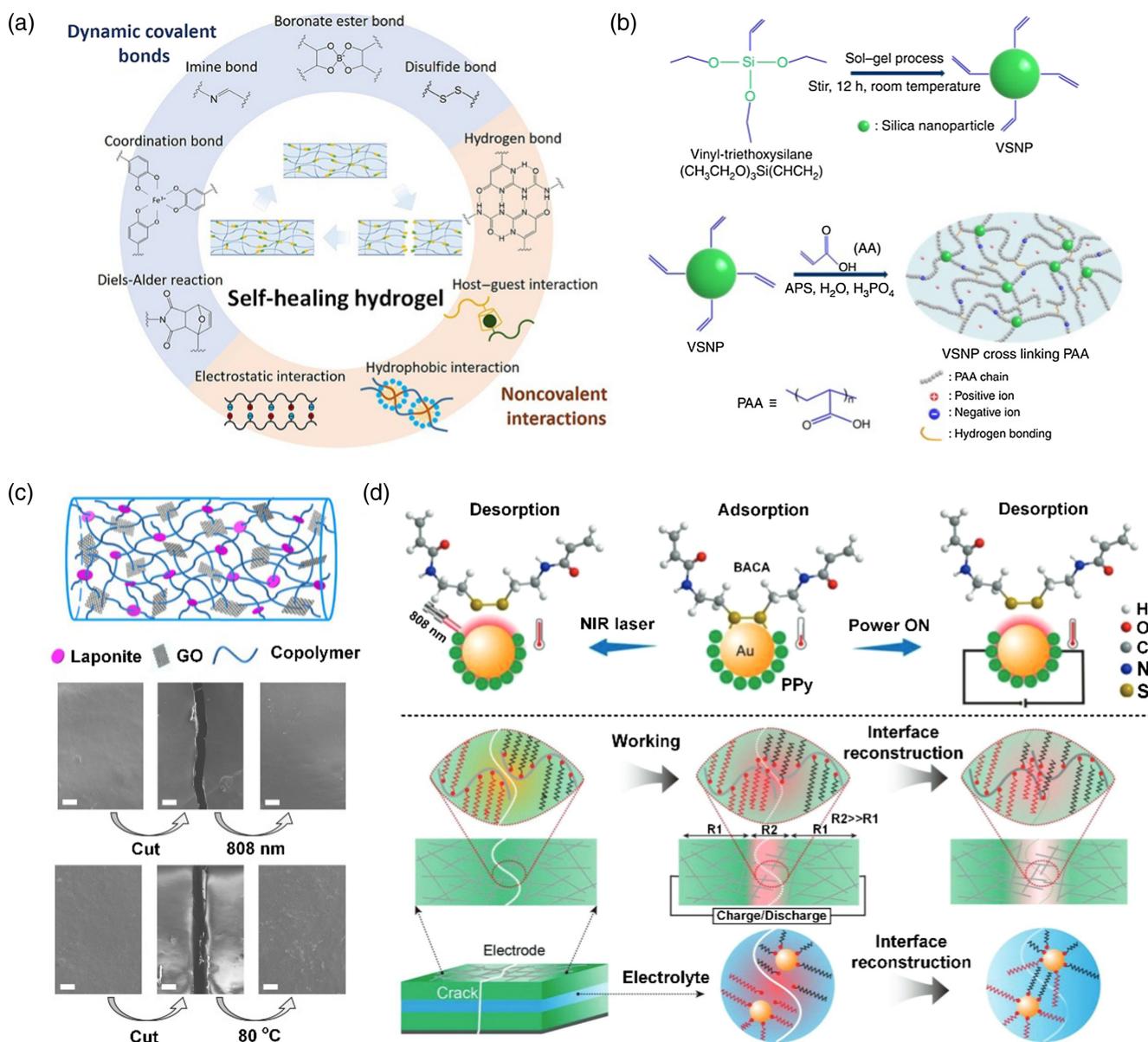
### Self-healing dynamic networks for self-healing EES devices

Irreversible mechanical damage is inevitable in EES devices during repeated mechanical deformation. Mechanical damage of EES devices can lead to the shutdown of electronics and increased costs of operation. Inspired by the human skin that can self-heal its wounds, self-healing properties have been imparted into EES devices to self-repair mechanical damage. Self-healing polymer materials with superior mechanical deformability and dynamic bonds play a key role in the fabrication of self-healing EES devices.<sup>61,62</sup> According to this mechanism, three main routes have been used to construct self-healing polymer materials—microencapsulation, molecular interdiffusion, and reversible covalent and non-covalent cross-linking.<sup>59,63–65</sup>

The microencapsulation approach involves microencapsulated healing agents (e.g., dicyclopentadiene and epoxy) and catalysts dispersed within the polymer matrix. When damage to polymers occurs, the healing monomer is released into cracks and then polymerized by the catalyst in the polymer matrix to cure and prevent crack propagation.<sup>63,66</sup> Molecular interdiffusion is another self-healing process, which is often associated with thermoset materials such as polyurethane (PU) networks and thermoplastic materials like poly(methyl methacrylate). This category of self-healing process involves crack

surface rearrangement and wetting of the cracked surfaces to ensure high chain mobility, which is then followed by the interdiffusion of the polymer chains to remove the crack interfaces.<sup>67</sup> Another main mechanism for self-healing relies on reversible covalent and noncovalent networks to heal the crack of polymers with or without a stimulus such as light or heat. Some of such representative dynamic covalent reactions include the Diels-Alder reaction, reduction of thiol/disulfide linkages into two thiol groups, and cleavage of allyl sulfide linkages into thiyl radicals. Reversible noncovalent reactions include metal bonding, ionomers, and hydrogen bonding (Figure 5a).<sup>28,68–72</sup> So far, the self-healing polymers with reversible covalent and noncovalent networks have been utilized mostly in self-healing EES devices due to the facile integration of these polymers as the self-healing substrate or electrolyte.<sup>28,68–71,73</sup>

The first self-healing supercapacitor was pioneered by Chen et al.,<sup>28</sup> where the self-healing substrate was prepared by the modified Leibler method. The supramolecular network cross-linked with TiO<sub>2</sub> nanoparticles provided large amounts of reversible hydrogen bonds for self-healing at room temperature. Due to its reversible hydrogen bonds, the supercapacitor with CNT film electrodes on the self-healing substrate could light LED again after being cut and healed. After sandwiching the PVP/H<sub>2</sub>SO<sub>4</sub> gel electrolyte with two self-healing electrodes, the as-prepared self-healing supercapacitor only retained 82.3% initial capacitance after the fifth healing. Considering that the additionally added electrochemically inactive self-healing materials will decrease in their self-healing efficiency and specific volumetric/mass capacitance, another effective way to integrate self-healing properties into supercapacitors is to directly synthesize self-healing polyelectrolyte.<sup>68</sup> In this regard, an intrinsically stretchable and self-healing polyelectrolyte was developed to dually cross-link polyacrylic acid (PAA) by VSNNPs and hydrogen bonding (Figure 5b). Similarly, self-healing and electroconductive hydrogels were also developed as both electrolyte and active electrodes for self-healing supercapacitors through dynamically cross-linking CNT/CNF (cellulose nanofibers) nanohybrids, PVA, and borax.<sup>69</sup> In addition to the conventional planar supercapacitors, it is highly desirable for the reconstruction of broken yarn-shaped devices.<sup>70</sup> With the assistance of magnetic field and hydrogen bonding, yarn-based supercapacitors with a self-healing PU shell can recover 71.8% of initial capacitance after four breaking/healing cycles. Furthermore, on-demand and healable supercapacitors that can respond to light and heat were reported that used a hydrogel comprising dual linkers of Laponite and GO (Figure 5c), as well as poly(acrylamide) hydrogel with dynamic metal-thiolate bonds (Figure 5d).<sup>71</sup> Supercapacitors equipped with these hydrogels can achieve repeated and real-time healability under light, heat, or



**Figure 5 | Self-healing supercapacitors.** (a) Summary of the representative noncovalent interactions and dynamic covalent bonds for self-healing hydrogels. Reproduced with permission from ref 72. Copyright 2018 Frontiers Media S. A. (b) Synthesis of PAA polyelectrolyte with VSNPs crosslinker for stretchable and self-healing supercapacitors. Reproduced with permission from ref 68. Copyright 2015 Springer Nature Limited. (c) A hydrogen of a copolymer cross-linked by double linkers of Laponite (synthetic hectorite-type clay) and GO for ultrastretchable and self-healing supercapacitors. Up: Schematic illustration of poly(2-acrylamido-2methylpropane sulfonic acid-co-N, N-dimethylacrylamide) Laponite/GO composite hydrogels with GO and Laponite acted as the crosslinkers. Down: SEM images of the self-healing process of composite hydrogels stimulated by 808 nm infrared light for 20 min (middle) and 80° for 60 min (down). All the scale bars are 100  $\mu$ m. Reproduced with permission from ref 73. Copyright 2019 Springer Nature Limited. (d) Highly stretchable and real-time healable supercapacitor based on dynamic metal-thiolate bonds. Up: schematic showing the self-healing mechanism of PPy-incorporated gold nanoparticle/CNT/poly(acrylamide) (GCP@PPy) composite hydrogel relying on dynamic Au-thiolate (Au-SR) bonds induced by near-infrared laser and electricity. Down: Schematics of the healing process of GCP@PPy-based supercapacitors by electrical-resistance-triggered temperature increase during the charging/discharging process. Reproduced with permission from ref 71. Copyright 2019 Wiley-VCH.

electrical treatment. Besides the aforementioned self-healing supercapacitors, batteries based on carboxylated PU with dynamic hydrogen bonds<sup>74</sup> and UPy-based poly(ethylene glycol) with intermolecular quadruple hydrogen-bonding interactions<sup>75</sup> have also been explored for self-healing applications.

### Shape-memory dynamic networks for shape-memory EES devices

Shape-memory properties, referring to automatically adapting shapes to external stimuli, have also been imparted to biointegrated EES devices to allow for promising applications in biomimetics, drug delivery, and soft robots.<sup>30,76–79</sup> Alloys (e.g., TiN, CuAlNi, and FeMnSi), polymers (e.g., polynorbornene, styrene-butadiene copolymer, segmented PU, etc.) and ceramics (e.g., ZrO<sub>2</sub>) are three major categories of shape-memory materials.<sup>63</sup> Because of their better mechanical properties and facile processability, shape-memory alloys and polymers have been intensively investigated for use in shape-memory EES devices.<sup>29,76</sup> The shape-memory behaviors of alloys rely on the phase change between martensite and austenite. Cooling down the alloy at a temperature between the transition temperatures of martensite start (M<sub>s</sub>) and martensite finish (M<sub>f</sub>) will lead to the transformation from austenite in shape-memory alloys into martensite with a soft twin crystalline structure. On the other hand, heating between transition temperatures of austenite start (A<sub>s</sub>) and austenite finish (A<sub>f</sub>) results in the restoration of the original shape due to the transformation from martensite to austenite with a harder crystalline structure.<sup>80</sup> Based on the TiNi-based electrode, a watchband-like shape-memory supercapacitor was also realized by using a negative electrode with graphene on a TiNi alloy current collector, a positive electrode with ultrathin MnO<sub>2</sub>/Ni film, and a gel electrolyte separator. The supercapacitor automatically recovered its shape to a bending state by contact with a human wrist.<sup>76</sup>

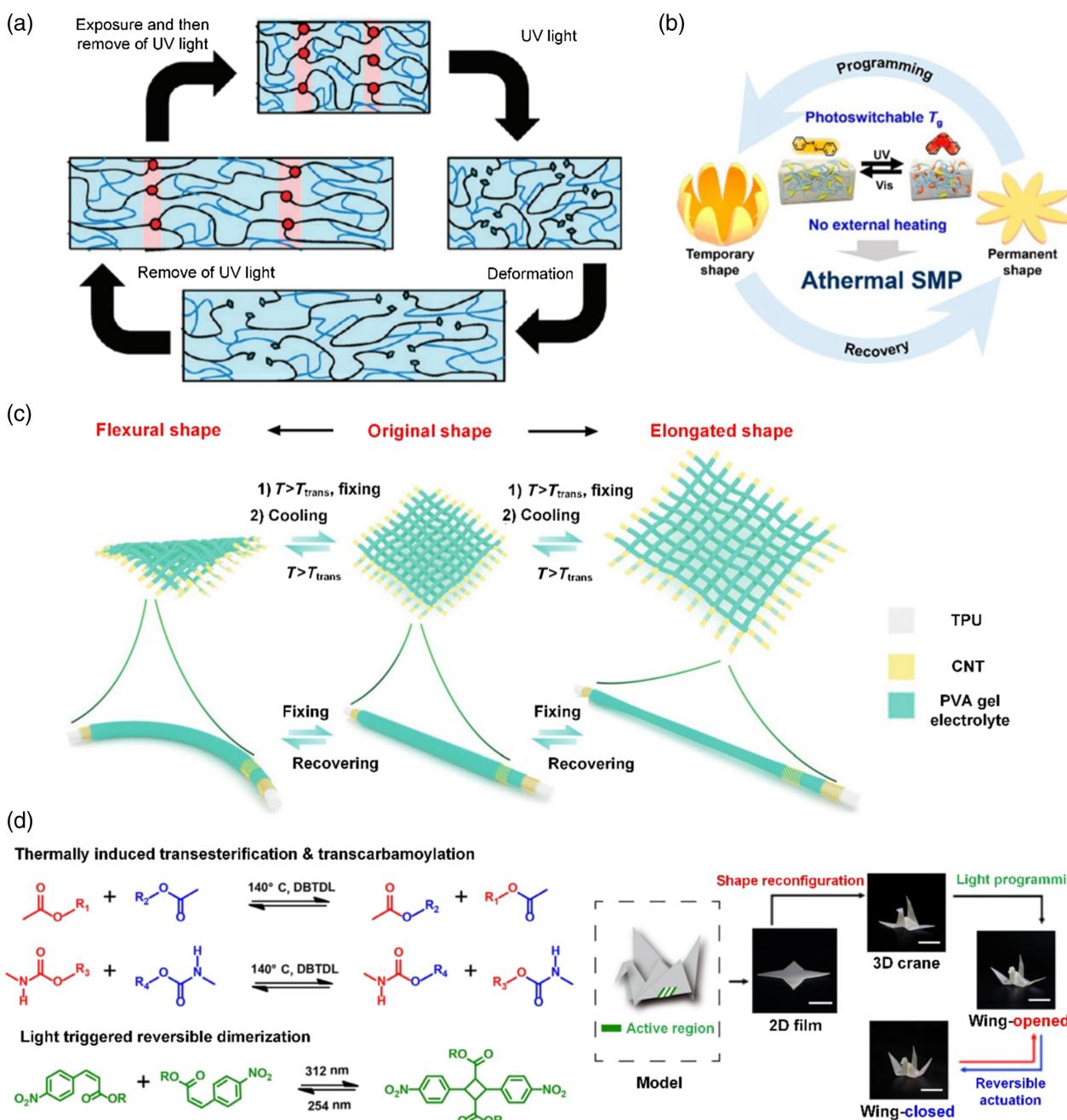
Shape-memory polymers usually comprise a stable network and a reversible switching segment (Figure 6a).<sup>81</sup> The stable network with physical or chemical cross-linking determines the original shape, and the reversible switching segments are responsible for the shape-memory process of polymers under external photo and thermal stimulus (Figure 6a,b).<sup>78,82,83</sup> For the sake of discussion, take temperature as an example: when the temperature is above the phase-transition temperature, shape-memory polymers like PU substrate are soft and can be deformed into various shapes. After cooling, they become stiff and can maintain the predesigned shapes. Subsequently, reheating the shape-memory polymers above the phase-transition temperature results in the recovery of the original shape. Supercapacitors based on

coaxial CNT fibers and shape-memory PU electrodes can reversibly transform into elongated and flexural shapes and return them to original shapes under heat treatment (Figure 6c).<sup>29</sup> Instead of a single stimulus for one-time recovery of shapes, the combination of thermal and photo stimuli provides the shape-memory polymers with dynamic reversible actuation. By simultaneously introducing the thermal reversible ester, urethane bonds, and photoreversible cinnamate bonds into one component, a programmable crystalline shape-memory polymer transforms complex 3D objects with reversible actuation into a single-component robot (Figure 6d).<sup>84</sup> The above shape-memory materials and supercapacitors maintain stable capacitance during the shape recovery process, suggesting promising applications in smart textiles and electronics.

### Thermoresponsive dynamic networks for thermoprotective EES devices

Thermoresponsive EES devices feature reversible thermoswitchable energy storage to avoid overheating.<sup>85,86</sup> The smart response of the thermoresponsive EES devices is based on the drastic change in the aqueous solubility of thermoresponsive polymers (mainly as the additives of separator or electrolyte), which results in the reversible sol-gel transition at a critical solution temperature. Detailed mechanisms and types of thermoresponsive polymers for the protection of EES devices have been fully discussed previously (Figure 7a).<sup>86</sup>

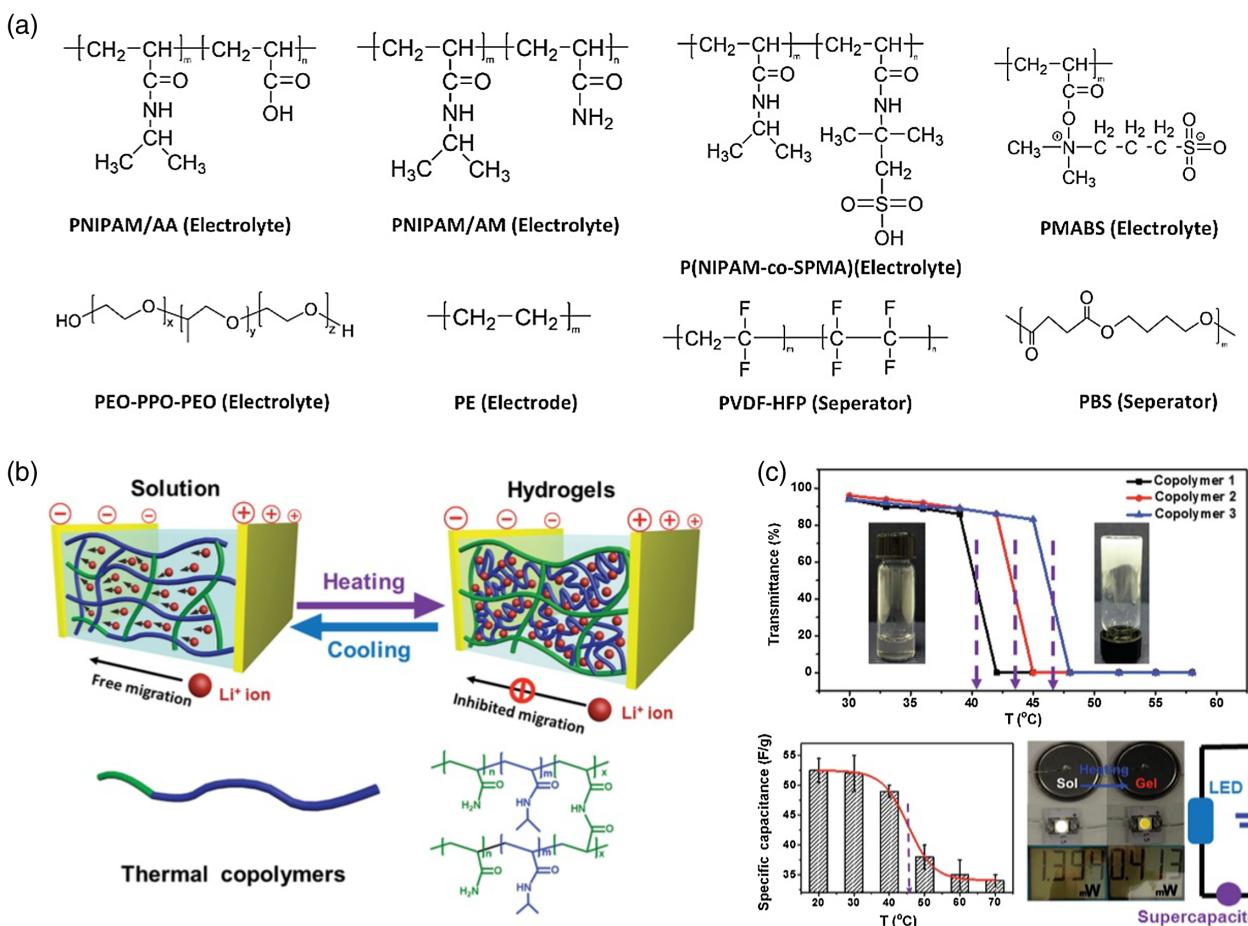
To achieve self-protective function, the Chen group reported a smart EES device with a reversible sol-gel electrolyte that can efficiently prevent the devices from thermal runaway.<sup>30</sup> The synthesized copolymer poly(*N*-isopropyl acrylamide-co-acrylamide) (PNIPAM/AM) was added to the LiOH electrolyte and served as the thermo-responsive agent. Once the temperature has increased up to the phase-transition temperature, the hydrophilic state of thermal-responsive copolymer PNIPAM/AM changed into the hydrophobic state due to the bond rupture between water and *N*-isopropyl groups. The hydrophobic association of thermal-responsive copolymer enabled the formation of the hydrogel, which hindered the movability of ions between electrodes and thus decrease the capacitance of supercapacitors (Figure 7b). It is worth noting that the transition reaction and electrochemical performance of the electrolyte were reversible when the temperature was cooled down. The tunable sol-gel transition temperature ranging from 40 to 47 °C could be obtained by changing the molar ratio between AM and NIPAM (Figure 7c). With a molar ratio of NIPAM to AM at 8:3, the transition temperature for the sol-gel system was 47 °C. Upon increasing the temperature from 20 to 70 °C, the fabricated supercapacitors with CNT film electrodes and the thermoresponsive electrolyte showed a



**Figure 6 | Shape-memory materials for shape-memory EES devices.** (a) The mechanism of shape-memory behavior in metal-ligand complexes induced by UV light. Reproduced with permission from ref 82. Copyright 2016 American Chemical Society. (b) Athermal shape-memory effect triggered by Photoswitchable Glass Transition Temperature from the reversible trans-cis isomerization. Reproduced with permission from ref 83. Copyright 2016 American Chemical Society. (c) Schematic showing the shape memory, fiber-shaped supercapacitors based on TPU woven into the textile with reversible states from flexural state and elongated state to the original state. Reproduced with permission from ref 29. Copyright 2015 Wiley-VCH. (d) Thermally induced reversible ester and urethane bonds and photoreversible dimerization of nitro-cinnamate. Application of the shape-memory polymer for reversible actuation in complex 3D objects. Reproduced with permission from ref 84. Copyright 2018 AAAS.

decrease of 35.3% capacitance from 52.5 to 34.0 Fg<sup>-1</sup>, and the energy storage capacity could be reversed by cooling the electrolyte, suggesting that this approach is a novel

strategy in smart thermal self-protection. Following this work, other researchers have also explored microsuper-capacitors with an enhanced “switched on-and-off”



**Figure 7 | (a)** Summary of the chemical structure of the thermal-responsive polymers and their roles in protecting EES devices from thermal runaway. Reproduced with permission from ref 86. Copyright 2018 Wiley-VCH. **(b)** Schematic of the transformation of electrolyte from solution to hydrogel via hydrophobic association induced by the increased temperature. The sol-gel transformation inhibits the ionic transport between two electrodes. Reproduced with permission from ref 30. Copyright 2015 Wiley-VCH. **(c)** The thermal-responsive polymer electrolyte and supercapacitors. Up: the change in transmittance of the self-protective copolymer PNIPAM/AM solution ( $0.2 \text{ g mL}^{-1}$ ) with a different molar ratio of PNIPAM to AM under the temperature from 33 to 58 °C. Down: the specific capacitance of supercapacitors with copolymer PNIPAM/AM electrolyte at different temperatures and the demonstration of the thermal self-protective supercapacitor during a sol-gel transition showing a reduction of power at 60 °C. Reproduced with permission from ref 30. Copyright 2015 Wiley-VCH.

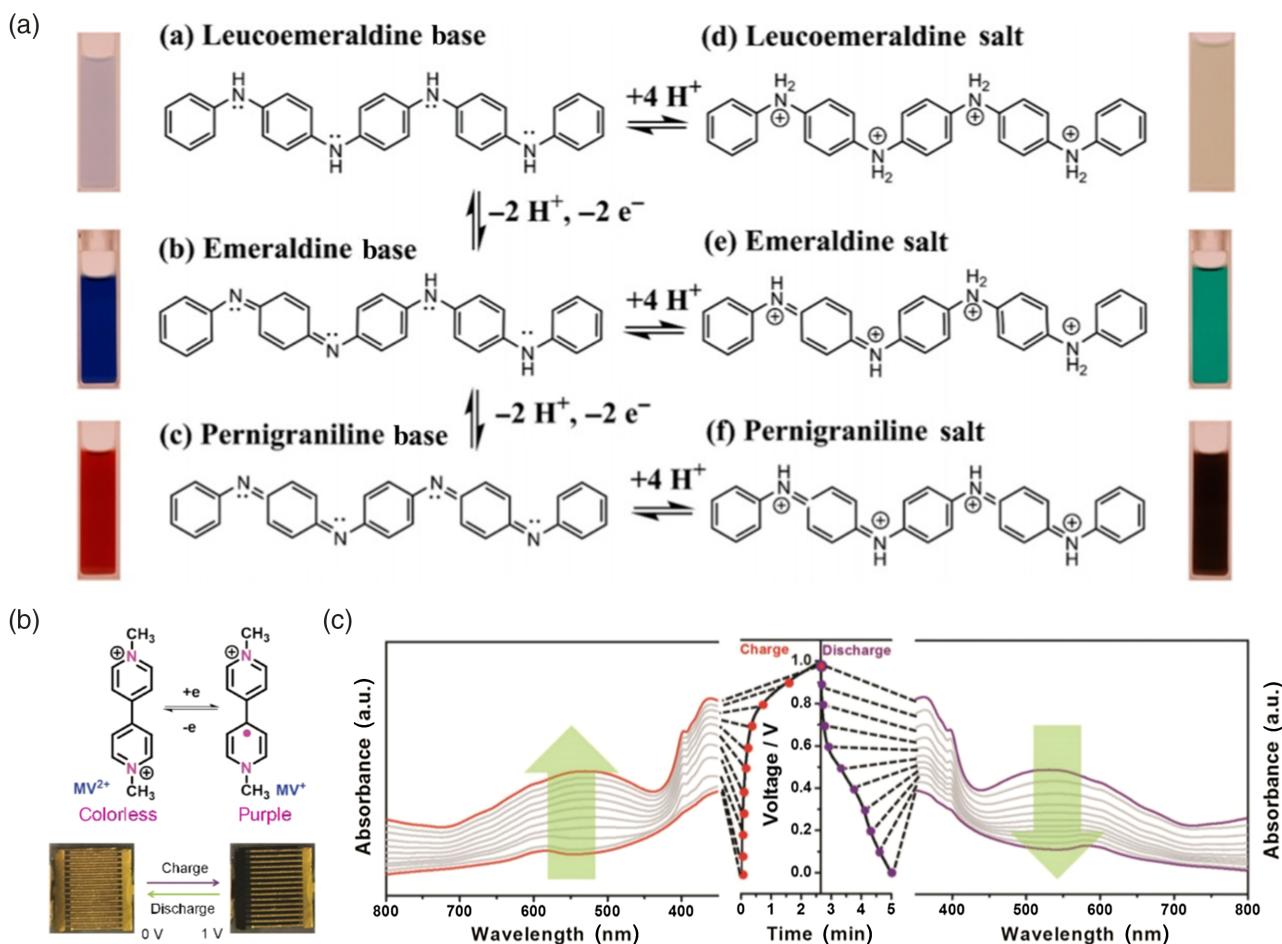
temperature of up to 80 °C, by utilizing the thermoresponsive poly(3,4-ethylene dioxythiophene).<sup>85</sup>

### Color-changing dynamic networks for electrochromic EES devices

Inspired by the remarkable color-changing capability of the chameleon skin, electrochromic materials with color-changing functions have been developed for EES devices.<sup>87,88</sup> Electrochromism is the phenomenon in which materials reversibly change their colors or opacities by electrical field-induced reduction/oxidation reactions or by ion insertion/extraction. The electrochromic materials mainly include inorganic oxides, polymers (e.g., PANI, poly(3-hexylthiophene-2,5-diyl), poly[1-amine bis

(furfuryl glycidyl ether)-N,N-bis(4-nitrophenyl)benzene-4,4'-dimaleimidophenylmethane]imide, and organic compounds (e.g., Prussian blue and viologen).<sup>87,88</sup>

Tungsten oxide ( $\text{WO}_3$ ) is the representative inorganic electrochromic and supercapacitor material in which the ion insertion/extraction contributes to its tunable color property. Mai et al. designed an electrochromic supercapacitor by depositing the  $\text{WO}_3$  film on the fluorine-doped tin oxide glass. The capacitance of the  $\text{WO}_3$  electrode reached  $639.8 \text{ F g}^{-1}$ , and its optical transmittance at a wavelength of 633 nm changed from 91.3% to 15.1% under a voltage of  $-0.6 \text{ V}$ .<sup>89</sup> Similar ion insertion/extraction mechanisms were also found for  $\text{Ni(OH)}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_x$ , and so on.<sup>27,90,91</sup> Owing to the superiority of their mechanical properties to the inorganic oxides,



**Figure 8 | Constitutional dynamic color-change network for electrochromic EES devices.** (a) Chemical structure and color change of phenyl-capped anile tetramer during the protonic doping process. Reproduced with permission from ref 94. Copyright 2016 American Chemical Society. (b) The electrochromic the viologen-based electrolyte and microsupercapacitors. Upper: The electrochromic mechanism of viologen as the additive in electrolytes of a flexible microsupercapacitor. Down: photos of the reversible electrochromic properties of the flexible microsupercapacitors based on the EG/V<sub>2</sub>O<sub>5</sub> microelectrodes and electrochromic LiCl/PVA-viologen electrolytes. Reproduced with permission from ref 77. Copyright 2017 Wiley-VCH. (c) The UV-vis spectra of flexible microsupercapacitors operated under different voltages between 0 to 1 V during one charge-discharge cycle. Reproduced with permission from ref 77. Copyright 2017 Wiley-VCH.

conductive polymers and organic complexes are attractive alternative candidates for the fabrication of flexible and stretchable electrochromic supercapacitors for smart applications.<sup>92,93</sup> As for the electrochromic conductive polymer PANI-based supercapacitors, different colors stem from three structures of PANI under different voltages: that is, leucoemeraldine at a fully reduced state exhibits a yellow color at a voltage below  $-0.5$  V; emeraldine at the partially oxidized state (0 V) exhibits a slightly green color; and pernigraniline at a voltage higher than 0.5 V appears blue in color (Figure 8a).<sup>93,94</sup> Through a combination of patternable W<sub>18</sub>O<sub>49</sub> with PANI for an integrated electrode, the smart supercapacitors can be operated in a wide and different voltage window to recognize the patterned color schemes (Figure 8b).<sup>92</sup>

Apart from the conductive polymers serving as electrode materials, electrochromic viologen ( $MV^{2+}$ ) has also been added into PVA/LiCl to serve as the electrolyte of flexible microsupercapacitors with exfoliated graphene (EG)/V<sub>2</sub>O<sub>5</sub>. Utilization of the reversible reaction from colorless  $MV^{2+}$  into purple  $MV^+$  resulted in a visible electrochromic change during the charging/discharging process (Figure 8c).<sup>77</sup>

## Conclusion and Outlook

Innovative chemistry and processing techniques have enabled a wide range of constitutionally dynamic networks to be used as the components of environment-

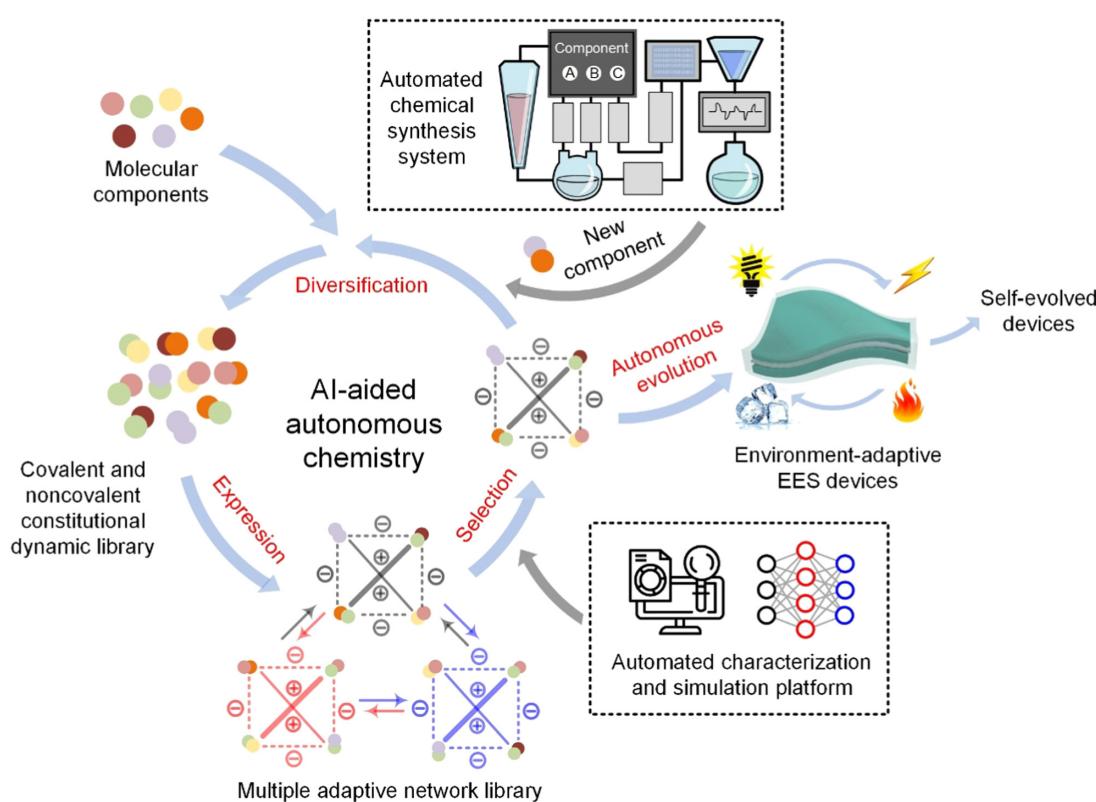
adaptive EES devices. In this review, we have summarized environment-adaptive EES devices developed in recent years that have used autonomous chemistry in the design of constitutionally dynamic networks of electrode materials and hydrogel electrolyte, to achieve autonomous functions including mechanical adaptability, biocompatibility, and smart functions. With increasing development in this field, numerous new environment-adaptive EES devices with extraordinary performance and functionalities have been developed. Meanwhile, emerging challenges pertaining to autonomous chemistry in the next generation of environment-adaptive EES devices remain to be addressed (Figure 9).

Because the primary function of EES devices is to store energy, new active materials that can store more energy at a faster rate are desirable. In recent years, various new topological materials such as metal-organic frameworks, covalent organic frameworks, and various two-dimensional materials and their heterostructures have been developed as active materials with interesting properties.<sup>14,95–99</sup> Further development of new constitutional dynamic networks based newly emergent molecular components and their extensions is urgent for developing EES devices with higher energy/power density and new functions. Moreover, recent developments in automated robotic platforms combined with machine learning will

accelerate the synthesis, discovery, and prediction of high-energy and functional molecular components for environment-adaptive EES devices.<sup>7,100,101</sup>

With various new materials and designs to be developed, a fundamental understanding of the working mechanisms underlying the new materials/designs is necessary to drive further development. In this regard, automated advanced characterization and simulation techniques should be applied to the newly developed adaptive materials to facilitate multiple dynamic network designs.<sup>102,103</sup> Moreover, *in situ* characterization of the environment-adaptive EES devices working under various extreme conditions (high/low temperature, pressure, etc.), different physiological environments within the body, and under external stimulus fields (force, magnetic, light, etc.) should be explored to gain a better understanding of the influence of external stimulations on the operation of environment-adaptive EES devices. This will promote the further development of material and chemical designs that fit the specific working conditions better.

As more and more new materials and designs are involved, the complexity of the fabrication processes will also increase, making newly developed environment-adaptive EES devices incompatible with the industrial protocol. This can limit the product yield, quality, and



**Figure 9 |** Future AI-aided autonomous chemistry that combines automated chemical synthesis systems, characterization, and simulation platform towards autonomous evolved environment-adaptive EES devices.

DOI: 10.31635/ccschem.022.202202153

Citation: CCS Chem. 2023, 5, 11–29

Link to VoR: <https://doi.org/10.31635/ccschem.022.202202153>

thus the commercialization of the environment-adaptive EES devices. As such, reliable, large-scale, low-cost fabrication and printing processes, such as multimaterial, multinozzle 3D printing, are highly desirable to drive customizable biointegrated EES devices into the next stage of development.<sup>104,105</sup> In addition to the functions introduced above, environment-adaptive EES need to be integrated with other kinds of autonomous constitutional dynamic networks to achieve more functions/adaptability, such as wireless charging, freezing tolerance, and fire tolerance. Energy harvesting devices (solar cells, biofuel cells, triboelectric nanogenerators, etc.), and other electronic components (transistors, actuators, sensors, etc.) are also expected to generate an all-in-one and fully self-adaptable device.<sup>106–111</sup> Moving forward, we believe that synergy between novel chemical designs and advanced device fabrication processes will allow the next generation of autonomously operating chemical systems to be incorporated into EES devices for applications in wearable, biointegrated, and smart devices.

## Conflict of Interest

There is no conflict of interest to report.

## Acknowledgments

This work was financially supported by the Agency for Science, Technology and Research (A\*STAR) under its AME Programmatic Funding Scheme of Cyber-Physiochemical Interfaces Programme (Project No. A18A1b0045).

## References

1. Qi, D.; Liu, Z.; Liu, Y.; Jiang, Y.; Leow, W. R.; Pal, M.; Pan, S.; Yang, H.; Wang, Y.; Zhang, X. Highly Stretchable, Compliant, Polymeric Microelectrode Arrays for in Vivo Electrophysiological Interfacing. *Adv. Mater.* **2017**, *29*, 1702800.
2. Lee, H.; Choi, T. K.; Lee, Y. B.; Cho, H. R.; Ghaffari, R.; Wang, L.; Choi, H. J.; Chung, T. D.; Lu, N.; Hyeon, T. A Graphene-Based Electrochemical Device with Thermoresponsive Microneedles for Diabetes Monitoring and Therapy. *Nat. Nanotech.* **2016**, *11*, 566–572.
3. Liu, Z.; Qi, D.; Hu, G.; Wang, H.; Jiang, Y.; Chen, G.; Luo, Y.; Loh, X. J.; Liedberg, B.; Chen, X. Surface Strain Redistribution on Structured Microfibers to Enhance Sensitivity of Fiber-Shaped Stretchable Strain Sensors. *Adv. Mater.* **2018**, *30*, 1704229.
4. Wallin, T.; Pikul, J.; Shepherd, R. 3D Printing of Soft Robotic Systems. *Nat. Rev. Mater.* **2018**, *3*, 84–100.
5. Wan, C.; Chen, G.; Fu, Y.; Wang, M.; Matsuhisa, N.; Pan, S.; Pan, L.; Yang, H.; Wan, Q.; Zhu, L. An Artificial Sensory Neuron with Tactile Perceptual Learning. *Adv. Mater.* **2018**, *30*, 1801291.
6. Umrao, S.; Tabassian, R.; Kim, J.; Zhou, Q.; Nam, S.; Oh, I.-K. MXene Artificial Muscles Based on Ionically Cross-Linked Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> Electrode for Kinetic Soft Robotics. *Sci. Robot.* **2019**, *4*, eaaw7797.
7. Lv, Z.; Li, W.; Yang, L.; Loh, X. J.; Chen, X. Custom-Made Electrochemical Energy Storage Devices. *ACS Energy Lett.* **2019**, *4*, 606–614.
8. Zhang, P.; Wang, F.; Yu, M.; Zhuang, X.; Feng, X. Two-Dimensional Materials for Miniaturized Energy Storage Devices: From Individual Devices to Smart Integrated Systems. *Chem. Soc. Rev.* **2018**, *47*, 7426–7451.
9. Wang, F.; Zhang, P.; Wang, G.; Nia, A. S.; Yu, M.; Feng, X. Functional Electrolytes: Game Changers for Smart Electrochemical Energy Storage Devices. *Small Sci.* **2022**, *2*, 2100080.
10. Lehn, J. M. Perspectives in Chemistry—Aspects of Adaptive Chemistry and Materials. *Angew. Chem. Int. Ed.* **2015**, *54*, 3276–3289.
11. Sun, P.; Qin, B.; Xu, J.-F.; Zhang, X. Supramonomers for Controllable Supramolecular Polymerization and Renewable Supramolecular Polymeric Materials. *Prog. Polym. Sci.* **2022**, *124*, 101486.
12. Wang, H.; Wu, H.; Yi, Y.; Xue, K.-F.; Xu, J.-F.; Wang, H.; Zhao, Y.; Zhang, X. Self-Motivated Supramolecular Combination Chemotherapy for Overcoming Drug Resistance Based on Acid-Activated Competition of Host-Guest Interactions. *CCS Chem.* **2021**, *3*, 1413–1425.
13. Kwon, T.-W.; Choi, J. W.; Coskun, A. Prospect for Supramolecular Chemistry in High-Energy-Density Rechargeable Batteries. *Joule* **2019**, *3*, 662–682.
14. Kandambeth, S., Dey, K., Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. *J. Am. Chem. Soc.* **2019**, *141*, 1807–1822.
15. Pushparaj, V. L.; Shaijumon, M. M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R. J.; Nalamasu, O.; Ajayan, P. M. Flexible Energy Storage Devices Based on Nanocomposite Paper. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 13574–13577.
16. Yu, C.; Masarapu, C.; Rong, J.; Wei, B.; Jiang, H. Stretchable Supercapacitors Based on Buckled Single-Walled Carbon-Nanotube Macrofilms. *Adv. Mater.* **2009**, *21*, 4793–4797.
17. Hu, L.; Pasta, M.; Mantia, F. L.; Cui, L.; Jeong, S.; Deshazer, H. D.; Choi, J. W.; Han, S. M.; Cui, Y. Stretchable, Porous, and Conductive Energy Textiles. *Nano Lett.* **2010**, *10*, 708–714.
18. Chmiola, J.; Largeot, C.; Taberna, P.-L.; Simon, P.; Gogotsi, Y. Monolithic Carbide-Derived Carbon Films for Micro-Supercapacitors. *Science* **2010**, *328*, 480–483.
19. Fu, Y.; Cai, X.; Wu, H.; Lv, Z.; Hou, S.; Peng, M.; Yu, X.; Zou, D. Fiber Supercapacitors Utilizing Pen Ink for Flexible/Wearable Energy Storage. *Adv. Mater.* **2012**, *24*, 5713–5718.
20. Lv, Z.; Luo, Y.; Tang, Y.; Wei, J.; Zhu, Z.; Zhou, X.; Li, W.; Zeng, Y.; Zhang, W.; Zhang, Y.; Qi, D.; Pan, S.; Loh, X. J.; Chen, X. Editable Supercapacitors with Customizable Stretchability Based on Mechanically Strengthened Ultralong MnO<sub>2</sub> Nanowire Composite. *Adv. Mater.* **2018**, *30*, 1704531.
21. Lv, Z.; Tang, Y.; Zhu, Z.; Wei, J.; Li, W.; Xia, H.; Jiang, Y.; Liu, Z.; Luo, Y.; Ge, X. Honeycomb-Lantern-Inspired 3D Stretchable Supercapacitors with Enhanced Specific Areal Capacitance. *Adv. Mater.* **2018**, *30*, 1805468.
22. Wang, S.; Fang, Y.; He, H.; Zhang, L.; Li, C. a.; Ouyang, J. Wearable Stretchable Dry and Self-Adhesive Strain Sensors

- with Conformal Contact to Skin for High-Quality Motion Monitoring. *Adv. Funct. Mater.* **2021**, *31*, 2007495.
23. Luan, P.; Zhang, N.; Zhou, W.; Niu, Z.; Zhang, Q.; Cai, L.; Zhang, X.; Yang, F.; Fan, Q.; Zhou, W. Epidermal Supercapacitor with High Performance. *Adv. Funct. Mater.* **2016**, *26*, 8178–8184.
24. Wang, X.; Xu, W.; Chatterjee, P.; Lv, C.; Popovich, J.; Song, Z.; Dai, L.; Kalani, M. Y. S.; Haydel, S. E.; Jiang, H. Food-Materials-Based Edible Supercapacitors. *Adv. Mater. Technol.* **2016**, *1*, 1600059.
25. Sim, H. J.; Choi, C.; Lee, D. Y.; Kim, H.; Yun, J.-H.; Kim, J. M.; Kang, T. M.; Ovalle, R.; Baughman, R. H.; Kee, C. W. Biomolecule Based Fiber Supercapacitor for Implantable Device. *Nano Energy* **2018**, *47*, 385–392.
26. Zhang, P.; Sun, D.; Cho, A.; Weon, S.; Lee, S.; Lee, J.; Han, J. W.; Kim, D.-P.; Choi, W. Modified Carbon Nitride Nanozyme as Bifunctional Glucose Oxidase-Peroxidase for Metal-Free Bioinspired Cascade Photocatalysis. *Nat. Commun.* **2019**, *10*, 940.
27. Wei, D.; Scherer, M. R.; Bower, C.; Andrew, P.; Ryhänen, T.; Steiner, U. A Nanostructured Electrochromic Supercapacitor. *Nano Lett.* **2012**, *12*, 1857–1862.
28. Wang, H.; Zhu, B.; Jiang, W.; Yang, Y.; Leow, W. R.; Wang, H.; Chen, X. A Mechanically and Electrically Self-Healing Supercapacitor. *Adv. Mater.* **2014**, *26*, 3638–3643.
29. Deng, J.; Zhang, Y.; Zhao, Y.; Chen, P.; Cheng, X.; Peng, H. A Shape-Memory Supercapacitor Fiber. *Angew. Chem. Int. Ed.* **2015**, *54*, 15419–15423.
30. Yang, H.; Liu, Z.; Chandran, B. K.; Deng, J.; Yu, J.; Qi, D.; Li, W.; Tang, Y.; Zhang, C.; Chen, X. Self-Protection of Electrochemical Storage Devices via a Thermal Reversible Sol-Gel Transition. *Adv. Mater.* **2015**, *27*, 5593–5598.
31. Oh, J. Y.; Rondeau-Gagné, S.; Chiu, Y.-C.; Chortos, A.; Lissel, F.; Wang, G.-J. N.; Schroeder, B. C.; Kurosawa, T.; Lopez, J.; Katsumata, T. Intrinsically Stretchable and Heatable Semiconducting Polymer for Organic Transistors. *Nature* **2016**, *539*, 411–415.
32. Hu, L.; Zhang, Q.; Li, X.; Serpe, M. J. Stimuli-Responsive Polymers for Sensing and Actuation. *Mater. Horizons* **2019**, *6*, 1774–1793.
33. Wang, B.; Facchetti, A. Mechanically Flexible Conductors for Stretchable and Wearable E-Skin and E-Textile Devices. *Adv. Mater.* **2019**, *31*, 1901408.
34. Wen, L.; Li, F.; Cheng, H. M. Carbon Nanotubes and Graphene for Flexible Electrochemical Energy Storage: from Materials to Devices. *Adv. Mater.* **2016**, *28*, 4306–4337.
35. Chen, X. Making Electrodes Stretchable. *Small Methods* **2017**, *1*, 1600029.
36. Bao, Z.; Chen, X. Flexible and Stretchable Devices. *Adv. Mater.* **2016**, *28*, 4177–4179.
37. Niu, Z.; Dong, H.; Zhu, B.; Li, J.; Hng, H. H.; Zhou, W.; Chen, X.; Xie, S. Highly Stretchable, Integrated Supercapacitors Based on Single-Walled Carbon Nanotube Films with Continuous Reticulate Architecture. *Adv. Mater.* **2013**, *25*, 1058–1064.
38. Choi, C.; Kim, S. H.; Sim, H. J.; Lee, J. A.; Choi, A. Y.; Kim, Y. T.; Lepró, X.; Spinks, G. M.; Baughman, R. H.; Kim, S. J. Stretchable, Weavable Coiled Carbon Nanotube/MnO<sub>2</sub>/Polymer Fiber Solid-State Supercapacitors. *Sci. Rep.* **2015**, *5*, 9387.
39. Kim, D.; Shin, G.; Kang, Y. J.; Kim, W.; Ha, J. S. Fabrication of a Stretchable Solid-State Micro-Supercapacitor Array. *ACS Nano* **2013**, *7*, 7975–7982.
40. Gong, X.; Yang, Q.; Zhi, C.; Lee, P. S. Stretchable Energy Storage Devices: From Materials and Structural Design to Device Assembly. *Adv. Energy Mater.* **2021**, *11*, 2003308.
41. Wang, H.; Wang, C.; Jian, M.; Wang, Q.; Xia, K.; Yin, Z.; Zhang, M.; Liang, X.; Zhang, Y. Superelastic Wire-Shaped Supercapacitor Sustaining 850% Tensile Strain Based on Carbon Nanotube@Graphene Fiber. *Nano Res.* **2018**, *11*, 2347–2356.
42. Lv, Z.; Wang, C.; Wan, C.; Wang, R.; Dai, X.; Wei, J.; Xia, H.; Li, W.; Zhang, W.; Cao, S. Strain-Driven Auto-Detachable Patterning of Flexible Electrodes. *Adv. Mater.* **2022**, *34*, 2202877.
43. Li, L.; Zhang, Y.; Lu, H.; Wang, Y.; Xu, J.; Zhu, J.; Zhang, C.; Liu, T. Cryopolymerization Enables Anisotropic Polyaniline Hybrid Hydrogels with Superelasticity and Highly deformation-Tolerant Electrochemical Energy Storage. *Nat. Commun.* **2020**, *11*, 62.
44. Lu, B.; Yuk, H.; Lin, S.; Jian, N.; Qu, K.; Xu, J.; Zhao, X. Pure PEDOT:PSS Hydrogels. *Nat. Commun.* **2019**, *10*, 1043.
45. Huang, Y.; Zhong, M.; Shi, F.; Liu, X.; Tang, Z.; Wang, Y.; Huang, Y.; Hou, H.; Xie, X.; Zhi, C. An Intrinsically Stretchable and Compressible Supercapacitor Containing a Polyacrylamide Hydrogel Electrolyte. *Angew. Chem. Int. Ed.* **2017**, *56*, 9141–9145.
46. Mackanic, D. G.; Yan, X.; Zhang, Q.; Matsuhisa, N.; Yu, Z.; Jiang, Y.; Manika, T.; Lopez, J.; Yan, H.; Liu, K. Decoupling of Mechanical Properties and Ionic Conductivity in Supramolecular Lithium Ion Conductors. *Nat. Commun.* **2019**, *10*, 5384.
47. Chae, J. S.; Park, S. K.; Roh, K. C.; Park, H. S. Electrode Materials for Biomedical Patchable and Implantable Energy Storage Devices. *Energy Stor. Mater.* **2019**, *24*, 113–128.
48. Feig, V. R.; Tran, H.; Bao, Z. Biodegradable Polymeric Materials in Degradable Electronic Devices. *ACS Cent. Sci.* **2018**, *4*, 337–348.
49. Yin, L.; Huang, X.; Xu, H.; Zhang, Y.; Lam, J.; Cheng, J.; Rogers, J. A. Materials, Designs, and Operational Characteristics for Fully Biodegradable Primary Batteries. *Adv. Mater.* **2014**, *26*, 3879–3884.
50. Fu, K.; Liu, Z.; Yao, Y.; Wang, Z.; Zhao, B.; Luo, W.; Dai, J.; Lacey, S. D.; Zhou, L.; Shen, F. Transient Rechargeable Batteries Triggered by Cascade Reactions. *Nano Lett.* **2015**, *15*, 4664–4671.
51. Aguilar, M. R.; San Román, J. *Smart Polymers and Their Applications*; Woodhead Publishing: Cambridge, United Kingdom, **2019**.
52. Kocak, G.; Tuncer, C.; Bütün, V. pH-Responsive Polymers. *Polym. Chem.* **2017**, *8*, 144–176.
53. Buchanan, F. *Degradation Rate of Bioresorbable Materials: Prediction and Evaluation*; Woodhead Publishing: Cambridge, United Kingdom, **2008**.

54. Stauss, S.; Honma, I. Biocompatible Batteries—Materials and Chemistry, Fabrication, Applications, and Future Prospects. *Bull. Chem. Soc. Jpn.* **2018**, *91*, 492–505.
55. Esquivel, J. P.; Alday, P.; Ibrahim, O. A.; Fernández, B.; Kjeang, E.; Sabaté, N. A Metal-Free and Biotically Degradable Battery for Portable Single-Use Applications. *Adv. Energy Mater.* **2017**, *7*, 1700275.
56. Mosa, I. M.; Pattammattel, A.; Kadimisetty, K.; Pande, P.; El-Kady, M. F.; Bishop, G. W.; Novak, M.; Kaner, R. B.; Basu, A. K.; Kumar, C. V.; Rusling, J. F. Ultrathin Graphene-Protein Supercapacitors for Miniaturized Bioelectronics. *Adv. Energy Mater.* **2017**, *7*, 1700358.
57. He, S.; Hu, Y.; Wan, J.; Gao, Q.; Wang, Y.; Xie, S.; Qiu, L.; Wang, C.; Zheng, G.; Wang, B. Biocompatible Carbon Nanotube Fibers for Implantable Supercapacitors. *Carbon* **2017**, *122*, 162–167.
58. Jang, Y.; Park, T.; Kim, E.; Park, J. W.; Lee, D. Y.; Kim, S. J. Implantable Biosupercapacitor Inspired by the Cellular Redox System. *Angew. Chem. Int. Ed.* **2021**, *60*, 10563–10567.
59. Liu, K.; Jiang, Y.; Bao, Z.; Yan, X. Skin-Inspired Electronics Enabled by Supramolecular Polymeric Materials. *CCS Chem.* **2019**, *1*, 431–447.
60. Qin, B.; Yin, Z.; Tang, X.; Zhang, S.; Wu, Y.; Xu, J.-F.; Zhang, X. Supramolecular Polymer Chemistry: From Structural Control to Functional Assembly. *Prog. Polym. Sci.* **2020**, *100*, 101167.
61. Cheng, D.; Li, B.; Sun, S.; Zhu, L.-J.; Li, Y.; Wu, X.-L.; Zang, H.-Y. Proton-Conducting Polyoxometalates as Redox Electrolytes Synergistically Boosting the Performance of Self-Healing Solid-State Supercapacitors with Polyaniline. *CCS Chem.* **2021**, *3*, 1649–1658.
62. Li, S.; Li, Y.; Wang, Y.; Pan, H.; Sun, J. Highly Stretchable, Elastic, Healable, and Ultra-Durable Polyvinyl Alcohol-Based Ionic Conductors Capable of Safe Disposal. *CCS Chem.* **2021**, *30*, 3360–3370.
63. Huang, Y.; Zhu, M.; Huang, Y.; Pei, Z.; Li, H.; Wang, Z.; Xue, Q.; Zhi, C. Multifunctional Energy Storage and Conversion Devices. *Adv. Mater.* **2016**, *28*, 8344–8364.
64. Sinawang, G.; Osaki, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. Supramolecular Self-Healing Materials from Non-Covalent Cross-Linking Host-Guest Interactions. *Chem. Commun.* **2020**, *56*, 4381–4395.
65. Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions Beyond Chemical Recycling and Self-Healing. *Chem. Rev.* **2021**, *121*, 1716–1745.
66. White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S.; Brown, E.; Viswanathan, S. Autonomic Healing of Polymer Composites. *Nature* **2001**, *409*, 794–797.
67. Ghosh, S. K. *Self-Healing Materials: Fundamentals, Design Strategies, and Applications*; Wiley-VCH: Weinheim, **2009**.
68. Huang, Y.; Zhong, M.; Huang, Y.; Zhu, M.; Pei, Z.; Wang, Z.; Xue, Q.; Xie, X.; Zhi, C. A Self-Healable and Highly Stretchable Supercapacitor Based on a Dual Crosslinked Polyelectrolyte. *Nat. Commun.* **2015**, *6*, 10310.
69. Han, J.; Wang, H.; Yue, Y.; Mei, C.; Chen, J.; Huang, C.; Wu, Q.; Xu, X. A Self-Healable and Highly Flexible Supercapacitor Integrated by Dynamically Cross-Linked Electro-Conductive Hydrogels Based on Nanocellulose-Templated Carbon Nanotubes Embedded in a Viscoelastic Polymer Network. *Carbon* **2019**, *149*, 1–18.
70. Huang, Y.; Huang, Y.; Zhu, M.; Meng, W.; Pei, Z.; Liu, C.; Hu, H.; Zhi, C. Magnetic-Assisted, Self-Healable, Yarn-Based Supercapacitor. *ACS Nano* **2015**, *9*, 6242–6251.
71. Chen, C. R.; Qin, H.; Cong, H. P.; Yu, S. H. A Highly Stretchable and Real-Time Healable Supercapacitor. *Adv. Mater.* **2019**, *31*, 1900573.
72. Liu, Y.; Hsu, S.-H. Synthesis and Biomedical Applications of Self-Healing Hydrogels. *Front. Chem.* **2018**, *6*, 449.
73. Li, H.; Lv, T.; Sun, H.; Qian, G.; Li, N.; Yao, Y.; Chen, T. Ultrastretchable and Superior Healable Supercapacitors Based on a Double Cross-Linked Hydrogel Electrolyte. *Nat. Commun.* **2019**, *10*, 536.
74. Park, S.; Thangavel, G.; Parida, K.; Li, S.; Lee, P. S. A Stretchable and Self-Healing Energy Storage Device Based on Mechanically and Electrically Restorative Liquid-Metal Particles and Carboxylated Polyurethane Composites. *Adv. Mater.* **2019**, *31*, 1805536.
75. Zhou, B.; He, D.; Hu, J.; Ye, Y.; Peng, H.; Zhou, X.; Xie, X.; Xue, Z. A Flexible, Self-Healing and Highly Stretchable Polymer Electrolyte via Quadruple Hydrogen Bonding for Lithium-Ion Batteries. *J. Mater. Chem. A* **2018**, *6*, 11725–11733.
76. Liu, L.; Shen, B.; Jiang, D.; Guo, R.; Kong, L.; Yan, X. Watchband-like Supercapacitors with Body Temperature Inducible Shape Memory Ability. *Adv. Energy Mater.* **2016**, *6*, 1600763.
77. Zhang, P.; Zhu, F.; Wang, F.; Wang, J.; Dong, R.; Zhuang, X.; Schmidt, O. G.; Feng, X. Stimulus-Responsive Micro-Supercapacitors with Ultrahigh Energy Density and Reversible Electrochromic Window. *Adv. Mater.* **2017**, *29*, 1604491.
78. Yang, H.; Leow, W. R.; Wang, T.; Wang, J.; Yu, J.; He, K.; Qi, D.; Wan, C.; Chen, X. 3D Printed Photoresponsive Devices Based on Shape Memory Composites. *Adv. Mater.* **2017**, *29*, 1701627.
79. Xia, Y.; He, Y.; Zhang, F.; Liu, Y.; Leng, J. A Review of Shape Memory Polymers and Composites: Mechanisms, Materials, and Applications. *Adv. Mater.* **2021**, *33*, 2000713.
80. Huang, Y.; Zhu, M.; Pei, Z.; Xue, Q.; Huang, Y.; Zhi, C. A Shape Memory Supercapacitor and Its Application in Smart Energy Storage Textiles. *J. Mater. Chem. A* **2016**, *4*, 1290–1297.
81. Meng, H.; Li, G. A Review of Stimuli-Responsive Shape Memory Polymer Composites. *Polymer* **2013**, *54*, 2199–2221.
82. Kumpfer, J. R.; Rowan, S. J. Thermo-, Photo-, and Chemo-Responsive Shape-Memory Properties from Photo-Cross-Linked Metallo-Supramolecular Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 12866–12874.
83. Zhang, X.; Zhu, C.; Xu, B.; Qin, L.; Wei, J.; Yu, Y. Rapid, Localized, and Athermal Shape Memory Performance Triggered by Photoswitchable Glass Transition Temperature. *ACS Appl. Mater. Interfaces* **2019**, *11*, 46212–46218.

84. Jin, B.; Song, H.; Jiang, R.; Song, J.; Zhao, Q.; Xie, T. Programming a Crystalline Shape Memory Polymer Network with Thermo- and Photo-Reversible Bonds toward a Single-Component Soft Robot. *Sci. Adv.* **2018**, *4*, eaao3865.
85. Zhang, P.; Wang, J.; Sheng, W.; Wang, F.; Zhang, J.; Zhu, F.; Zhuang, X.; Jordan, R.; Schmidt, O. G.; Feng, X. Thermo-switchable On-Chip Microsupercapacitors: One Potential Self-Protection Solution for Electronic Devices. *Energy Environ. Sci.* **2018**, *11*, 1717–1722.
86. Yang, H.; Leow, W. R.; Chen, X. Thermal-Responsive Polymers for Enhancing Safety of Electrochemical Storage Devices. *Adv. Mater.* **2018**, *30*, 1704347.
87. Chou, H.-H.; Nguyen, A.; Chortos, A.; To, J. W.; Lu, C.; Mei, J.; Kurosawa, T.; Bae, W.-G.; Tok, J. B.-H.; Bao, Z. A Chameleon-Inspired Stretchable Electronic Skin with Interactive Colour Changing Controlled by Tactile Sensing. *Nat. Commun.* **2015**, *6*, 8011.
88. Zheng, R.; Wang, Y.; Jia, C.; Wan, Z.; Luo, J.; Malik, H. A.; Weng, X.; Xie, J.; Deng, L. Intelligent Biomimetic Chameleon Skin with Excellent Self-Healing and Electrochromic Properties. *ACS Appl. Mater. Interfaces* **2018**, *10*, 35533–35538.
89. Yang, P.; Sun, P.; Chai, Z.; Huang, L.; Cai, X.; Tan, S.; Song, J.; Mai, W. Large-Scale Fabrication of Pseudocapacitive Glass Windows that Combine Electrochromism and Energy Storage. *Angew. Chem. Int. Ed.* **2014**, *53*, 11935–11939.
90. Grote, F.; Yu, Z. Y.; Wang, J. L.; Yu, S. H.; Lei, Y. Self-Stacked Reduced Graphene Oxide Nanosheets Coated with Cobalt–Nickel Hydroxide by One-Step Electrochemical Deposition toward Flexible Electrochromic Supercapacitors. *Small* **2015**, *11*, 4666–4672.
91. Chen, W.; Rakhi, R.; Hu, L.; Xie, X.; Cui, Y.; Alshareef, H. N. High-Performance Nanostructured Supercapacitors on a Sponge. *Nano Lett.* **2011**, *11*, 5165–5172.
92. Tian, Y.; Cong, S.; Su, W.; Chen, H.; Li, Q.; Geng, F.; Zhao, Z. Synergy of  $W_{18}O_{49}$  and Polyaniline for Smart Supercapacitor Electrode Integrated with Energy Level Indicating Functionality. *Nano Lett.* **2014**, *14*, 2150–2156.
93. Chen, X.; Lin, H.; Chen, P.; Guan, G.; Deng, J.; Peng, H. Smart, Stretchable Supercapacitors. *Adv. Mater.* **2014**, *26*, 4444–4449.
94. Mohtasebi, A.; Chowdhury, T.; Hsu, L. H.; Biesinger, M. C.; Kruse, P. Interfacial Charge Transfer between Phenyl-Capped Aniline Tetramer Films and Iron Oxide Surfaces. *J. Phys. Chem. C* **2016**, *120*, 29248–29263.
95. Halder, A.; Ghosh, M.; Khayum, M. A.; Bera, S.; Addicoat, M.; Sasmal, H. S.; Karak, S.; Kurungot, S.; Banerjee, R. Interlayer Hydrogen-Bonded Covalent Organic Frameworks as High-Performance Supercapacitors. *J. Am. Chem. Soc.* **2018**, *140*, 10941–10945.
96. Xiao, H.; Wu, Z.-S.; Chen, L.; Zhou, F.; Zheng, S.; Ren, W.; Cheng, H.-M.; Bao, X. One-Step Device Fabrication of Phosphorene and Graphene Interdigital Micro-Supercapacitors with High Energy Density. *ACS Nano* **2017**, *11*, 7284–7292.
97. Deng, Y.; Shang, T.; Wu, Z.; Tao, Y.; Luo, C.; Liang, J.; Han, D.; Lyu, R.; Qi, C.; Lv, W. Fast Gelation of  $Ti_3C_2T_x$  MXene Initiated by Metal Ions. *Adv. Mater.* **2019**, *31*, 1902432.
98. Yu, F.; Liu, W.; Ke, S.-W.; Kurmoo, M.; Zuo, J.-L.; Zhang, Q. Electrochromic Two-Dimensional Covalent Organic Framework with a Reversible Dark-to-Transparent Switch. *Nat. Commun.* **2020**, *11*, 5534.
99. Zhang, P.; Ouyang, Y.; Sohn, Y. S.; Nechushtai, R.; Pikarsky, E.; Fan, C.; Willner, I. pH- and miRNA-Responsive DNA-Tetrahedra/Metal-Organic Framework Conjugates: Functional Sense-and-Treat Carriers. *ACS Nano* **2021**, *15*, 6645–6657.
100. Wang, M.; Wang, T.; Cai, P.; Chen, X. Nanomaterials Discovery and Design through Machine Learning. *Small Methods* **2019**, *3*, 1900025.
101. May, M. A DIY Approach to Automating Your Lab. *Nature* **2019**, *569*, 587–589.
102. Wei, J.; Zhong, L.; Xia, H.; Lv, Z.; Diao, C.; Zhang, W.; Li, X.; Du, Y.; Xi, S.; Salanne, M. Metal-Ion Oligomerization Inside Electrified Carbon Micropores and Its Effect on Capacitive Charge Storage. *Adv. Mater.* **2022**, *34*, 2107439.
103. Tang, Y.; Zhang, Y.; Malyi, O. I.; Bucher, N.; Xia, H.; Xi, S.; Zhu, Z.; Lv, Z.; Li, W.; Wei, J. Identifying the Origin and Contribution of Surface Storage in  $TiO_2$  (B) Nanotube Electrode by *in Situ* Dynamic Valence State Monitoring. *Adv. Mater.* **2018**, *30*, 1802200.
104. Skylar-Scott, M. A.; Mueller, J.; Visser, C. W.; Lewis, J. A. Voxelated Soft Matter via Multimaterial Multinozzle 3D Printing. *Nature* **2019**, *575*, 330–335.
105. Zhang, Y.-Z.; Wang, Y.; Cheng, T.; Yao, L.-Q.; Li, X.; Lai, W.-Y.; Huang, W. Printed Supercapacitors: Materials, Printing and Applications. *Chem. Soc. Rev.* **2019**, *48*, 3229–3264.
106. Pan, S.; Ren, J.; Fang, X.; Peng, H. Integration: An Effective Strategy to Develop Multifunctional Energy Storage Devices. *Adv. Energy Mater.* **2016**, *6*, 1501867.
107. Xia, H.; Lv, Z.; Zhang, W.; Wei, J.; Liu, L.; Cao, S.; Zhu, Z.; Tang, Y.; Chen, X. Hygroscopic Chemistry Enables Fire-Tolerant Supercapacitors with a Self-Healable “Solute-in-Air” Electrolyte. *Adv. Mater.* **2022**, *34*, 2109857.
108. Yin, L.; Kim, K. N.; Trifonov, A.; Podhajny, T.; Wang, J. Designing Wearable Microgrids: Towards Autonomous Sustainable on-body Energy Management. *Energy Environ. Sci.* **2022**, *15*, 82–101.
109. Zhang, W.; Xia, H.; Zhu, Z.; Lv, Z.; Cao, S.; Wei, J.; Luo, Y.; Xiao, Y.; Liu, L.; Chen, X. Decimal Solvent-Based High-Entropy Electrolyte Enabling the Extended Survival Temperature of Lithium-Ion Batteries to  $-130$  °C. *CCS Chem.* **2021**, *3*, 1245–1255.
110. Qin, J.; Chu, K.; Huang, Y.; Zhu, X.; Hofkens, J.; He, G.; Parkin, I. P.; Lai, F.; Liu, T. The Bionic Sunflower: A Bio-Inspired Autonomous Light Tracking Photocatalytic System. *Energy Environ. Sci.* **2021**, *14*, 3931–3937.
111. Wang, J.; Wang, C.; Cai, P.; Luo, Y.; Cui, Z.; Loh, X. J.; Chen, X. Artificial Sense Technology: Emulating and Extending Biological Senses. *ACS Nano* **2021**, *15*, 18671–18678.