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Self-Healing Functional Electronic Devices

*Yansong Gai, Hu Li, and Zhou Li**

Electronic devices with various functions bring great convenience and revolutionize the way we live. They are inevitable to degrade over time because of physical or chemical fatigue and damage during practical operation. To make these devices have the ability to autonomously heal from cracks and restore their mechanical and electrical properties, self-healing materials emerged as the time requires for constructing robust and self-healing electronic devices. Here the development of self-healing electronic devices with different functions, for example, energy harvesting, energy storage, sensing, and transmission, is reviewed. The new application scenarios and existing challenges are explored, and possible strategies and perspectives for future practical applications are discussed.

1. Introduction

With the advent of the intelligent era, various smart portable/wearable electronic devices (PWED) have become an indispensable part and played an important role in our lives,[1,2] for example, a laptop, activity tracker, or smart phone/watch/bracelet. The continuous breakthrough in materials science, information, and manufacturing technology promoted the rapid development of PWED in wide application fields, such as healthcare, sport, recreation, security, and environmental monitoring.[3–5] To date, great efforts have been devoted to improving the flexibility, lightweight, miniaturization, and multifunctionality of PWED to meet the requirements of comfort, functionality, and safety.[5–7] However, it is inevitable to cause abrasion, degradation, or mechanical damage in practical applications because of many factors, including stretching, twisting, cutting, compression, and excessive usage. Then the performance of PWED will be weakened or even broken down, thus seriously reducing the reliability and shortening the service life.[2,8–11] Sometimes, it is difficult or impossible to maintain the damaged PWED due to its high integration property.[12] Moreover, the wide application of PWED will generate enormous electronic waste, resulting in environmental pollution.[13] Therefore, PWED with self-healing ability after damage is desirably developed to tackle these problems.[2,10]

In nature, biological systems can heal themselves autonomously and restore their structure and basic function after suffering from external mechanical damage.[14,15] Inspired by the self-healing property in nature, researchers paid lots of attention to artificial self-healing systems to imitate the biological systems.[16,17] Self-healing PWED is one of the main research areas of artificial self-healing systems, which is a merger of self-healing materials and electronic devices. When developing a single electronic device or integrated functional system, self-healing polymer could be an ideal candidate material. To date, scientists have made great efforts to improve the required mechanical toughness and self-healing ability of relevant polymers. Except for these two features, their conductivity was also enhanced by mixing or doping electroconductive fillers into the polymer matrix.[18–20] It is hoped that the self-healing PWED can not only restore their structure and mechanical properties but also recover their electrical properties and functions. This will significantly enhance the durability, reliability, and safety.[21,22]

Current application scenarios of self-healing technology involve solar cells, triboelectric nanogenerators, supercapacitors, batteries, e-skins, biosensors, and some other electronic accessories (e.g., transistors and actuators) (**Figure 1**). These self-healing devices are divided into four categories according to their function: energy harvesting devices, energy storage devices, bioelectronic devices, and electronic accessories. As for these self-healing electronic devices, we summarized their recent progress and advances in terms of commonly-used self-healing materials, self-healing mechanisms, device design principles, and resultant performances. Additionally, the existing challenges possible strategies, and future perspectives are also emphasized for the future development of self-healing electronic devices with high performance and multiple functions.

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DOI: 10.1002/smll.202101383

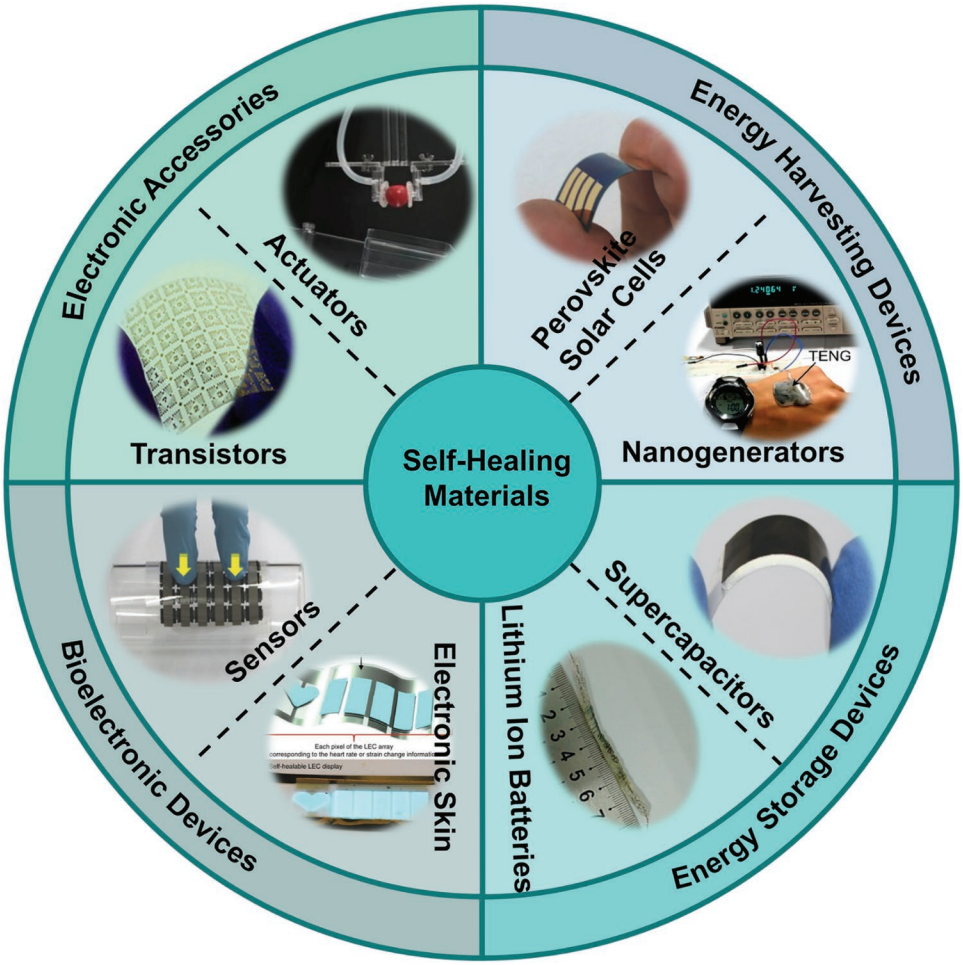

Figure 1. The classification of self-healing electronic devices with desirable functions. Perovskite Solar Cells: Reproduced with permission.[55] Copyright 2018, Wiley-VCH. Triboelectric Nanogenerators: Reproduced with permission.[70] Copyright 2019, American Chemical Society. Supercapacitors: Reproduced with permission.[71] Copyright 2014, Wiley-VCH. Lithium Ion Batteries: Reproduced with permission.[96] Copyright 2018, Elsevier. Electronic Skins: Reproduced with permission.[20] Copyright 2018, Springer Nature. Sensors: Reproduced with permission.[105] Copyright 2018, Wiley-VCH. Transistors: Reproduced with permission.[121] Copyright 2012, American Chemical Society. Actuators: Reproduced with permission.[132] Copyright 2020, Springer Nature.

2. Self-Healing Polymers (SHPs)

SHPs include autonomous and nonautonomous systems according to the difference of self-healing behaviors. A nonautonomous system requires external triggers, like light, heat, pH, or chemical reagents, to achieve self-healing purposes, while the autonomous system initiates the self-healing process upon damage without any triggers or external stimuli (**Figure 2**). Additionally, according to the self-healing principles, the SHPs can be categorized into intrinsic and extrinsic SHPs.

2.1. Extrinsic Self-Healing Mode

The extrinsic self-healing materials can heal the damage by preadded healing agents within them. The healing agents typically contain catalysts and reactive precursors within SHP. They are encapsulated in microcapsules or microvascular networks in the polymer matrix. Upon damage, the microcapsule or microvascular network render cracks and deliver the healing agents to the crack to initiate the healing process by polymerization or chemical reactions. Sometimes, an external stimulus is a necessary factor to accelerate the self-healing behavior, for example, heat or light.

White et al. reported the first SHP material through microcapsule healing agents.[23] Matrix cracks led to microcapsule rupture, releasing dicyclopentadiene (DCPD) monomers, which diffused to the crack interface by capillarity. Whereafter, DCPD monomers contacted with the embedded catalyst to initiate the ring-opening polymerization, thereby healed the cracks. The research on the microencapsulation self-healing system mainly centered on the structure design, preparation methods, and self-healing mechanisms. The preparation methods of microcapsules such as in situ/interface polymerization, melt dispersion, sol-gel reactions, miniemulsion polymerization, and pickering emulsion templating, have been mature.[14,24] Additionally, the wide selectivity of healing agents made self-healing composites have many specific characters, these agents refer to monomers, catalysis, and liquid metal alloys. Blaiszik et al. used Ga—In alloy as a liquid self-healing agent, encapsulated eutectic in microcapsules to

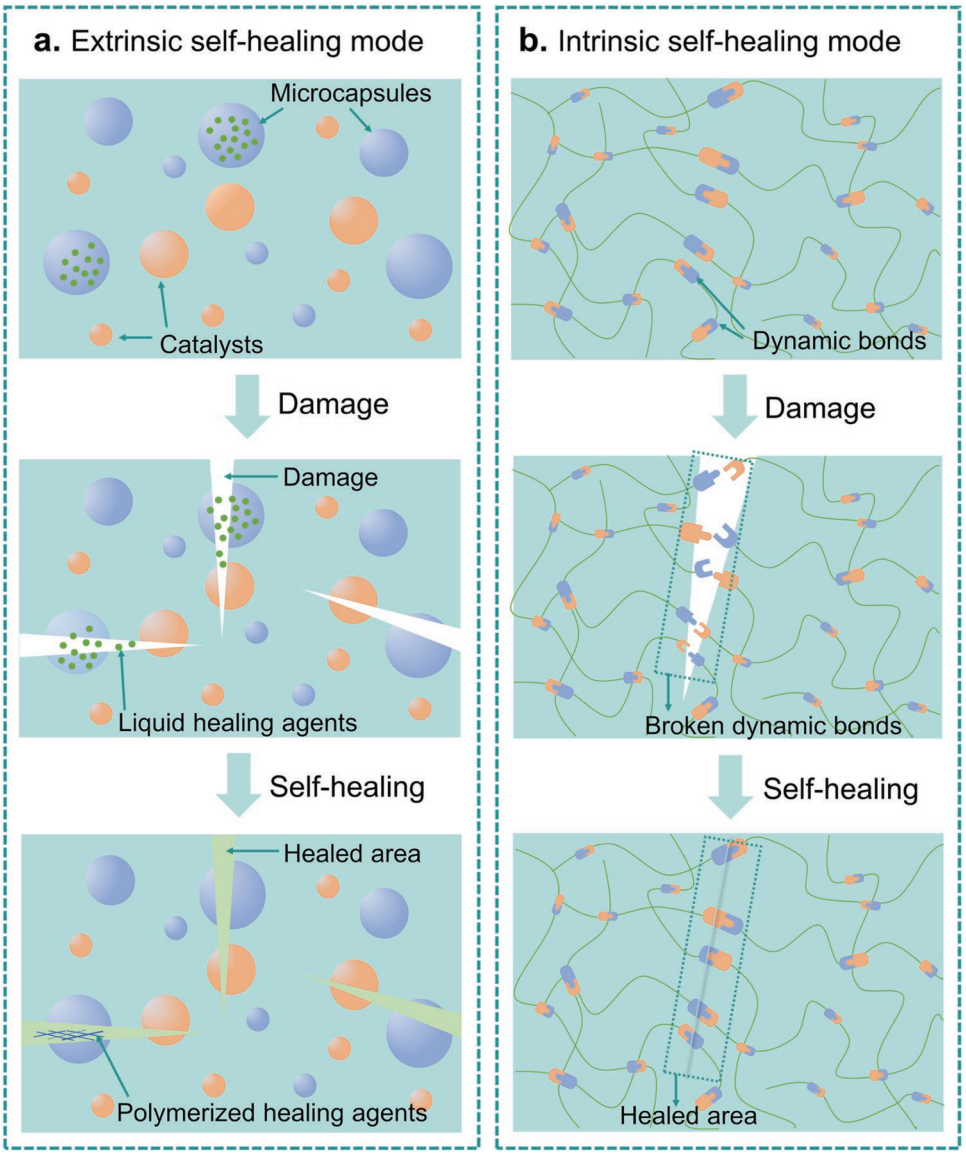

Figure 2. Extrinsic self-healing mode (a) and intrinsic self-healing mode (b).

prepare self-healing conductors.[25] When the microcapsule ruptured, the Ga—In liquid metal alloy released to the damaged area and restored the broken conductive pathway to healing conductivity. However, microencapsulated self-healing systems were difficult to achieve multiple healing at the same site due to the depletion of healing agents.

To address these limitations, White et al. developed a bionic self-healing microvascular network.[26,27] Imitating biological vascular system, a 3D hollow microtubule network was constructed in the matrix and then filled with healing agents. The self-healing mechanism of microvascular networks was similar to that of microcapsules, but the microvascular network structure can store much more healing agents and realize multiple self-healing. Later, White et al. further developed the hybrid microcapsule-microvascular self-healing system for repairing multiscale damage caused by impact puncture.[28–30] Microvascular healing system restore lost volume in the central puncture hole, while microcapsule healing system heal radiating microcracks. Although authors realized multiple self-healing targets, the fabrication processes of such self-healing systems are very complex and time-consuming.

2.2. Intrinsic Self-Healing Mode

Different from the extrinsic self-healing mode, the intrinsic self-healing mode does not require healing agents and can achieve multiple reversible healing. The intrinsic self-healing mode avoids complex problems such as encapsulation and dispersion of healing agent in the matrix and has a more stable and reliable self-healing ability compared with extrinsic self-healing mode.[22] In general, the intrinsic self-healing mode depends on recombining the intrinsic reversible dynamic covalent bonds or reconstructing non-covalent bonds between the cracking interfaces.[31] Reversible dynamic covalent bonds, such as imine bonds,[32] disulfide bonds,[33]

acylhydrazone bonds,[34] carbon–carbon double bonds,[35] urea bonds,[36] and so on, possess stronger bond energy than non-covalent bonds, which makes it possible for SHP to realize outstanding mechanical properties and stable self-healing ability. Diels–Alder reaction, disulfide exchange reaction, and transesterification are general methods to developing new materials with dynamic cross-linking property using reversible covalent bonds. However, because the formation rate of covalent bonds is slow, most of intrinsic SHP with covalent bonds need external stimulation to give rise to the healing process, for example heat, light, and pH change.[37]

Reversible dynamic non-covalent bonds including hydrogen bonds,[38] π–π stacking,[39] hydrophobic interactions,[40] host-guest interactions,[41] metal coordination bonds,[42] and others have low kinetic stability,[5,17,43] so these non-covalent bonds tend to form reversible dissociation and generation without huge amounts of energy.[44] The self-healing process depended on reversible non-covalent bonds is a typical supramolecular assembly, it realizes self-healing performance through flexibility and mobility of a polymer chain. When the supramolecular polymer is mechanically damaged, there is a great deal of dynamic supramolecular radicals on the fracture surface, and some radicals will be recombined with the movement of the polymer chain, thus repairing the cracks. By regulating the kinds of reversible non-covalent bonds, molecular association constants, and the mobility of polymer chains, not only the self-healing conditions, healing rate, and efficiency, but also the modulus, viscosity, and fluidity of corresponding polymer can be adjusted.[44,45]

3. Self-Healing Energy Harvesting Devices

3.1. Perovskite Solar Cells (PSCs)

The lead halide perovskite solar cells (PSCs), such as methyl ammonium lead iodide ($CH_3NH_3PbI_3$), exhibited great market potential for the high-power conversion efficiency (PCE) exceeding 25%, which approaches the best performance of polycrystalline silicon modules.[46–50] Although satisfied PCE has been achieved, the long-term stability issue impedes the commercial development of PSCs. The degradation of the perovskite materials in the presence of moisture, oxygen, and ultraviolet light was the main critical issue restricting the long-term stability.[51,52] To date, researchers have pay more attention to the long-term stability of PSCs under actual operational conditions. Recent progress in self-healing technology provided a promising way for PSCs to improve the durable stability.

The lead halide perovskite materials will dissolve and degrade when exposed to ambient humidity. To overcome this shortcoming, Zhao et al. fabricated a self-healing PSC architecture using polyethylene glycol (PEG) as a polymer scaffold (**Figure 3**a).[53] The enhanced stability and self-healing property of PSCs stem from the hygroscopicity of PEG molecules and their strong binding effect with CH_3NH_3I (MAI). Authors anchored PEG molecules on the perovskite grain surface by hydrogen bonding, which can effectively absorb water and form a compact moisture barrier on its surface to protect the film from water penetration. After water-spraying, perovskite crystals $MAPbI_3$ decomposed into PbI_2 and MAI. Because of the strong interaction between MAI and PEG, MAI molecules were fixed by PEG. Without water vapor, PbI_2 within the film will react with MAI molecules again and formed perovskite $MAPbI_3$ again. This self-healing effect derives from the fast decomposition–regeneration of perovskite crystals. Upon contacting water vapor, the color of the PEG scaffold perovskite film first turned from black to yellow, then reverted to black in 45 s after water vapor disappearing. On the contrary, the pure perovskite film turns yellow irreversibly. The efficiency of polymer-scaffold perovskite solar cells reached up to 16%, it has also a strong resistance to humidity and possesses a rapid self-healing behavior when staying away from water vapor.

Combining ordered crystalline semiconducting materials with amorphous self-healing materials is a great challenge for researchers. Blake P. Finkenauer et al. reported a mechanically self-healable hybrid halide perovskite semiconductor by incorporating self-healable thiourea-triethylene glycol polymer into polycrystalline perovskite using secondary-bonding interactions.[54] The thiourea-triethylene glycol polymer in hybrid halide perovskite film could facilitate the rejoining of distant perovskite grains and heal large cracks. The hybrid halide perovskite film with a polymer concentration of ≥2.1% can heal 6-µm-wide scratch after annealing at 100 °C for 1 h in a N_2 atmosphere. In addition, the PSC fabricated with hybrid halide perovskite film excited ultra-flexibility, indicating its potential applications in wearable energy harvesting devices.

The electrical recovery of device circuits after external mechanical damage is another big challenge of PSCs. Chu et al. showed a self-healing conductor using liquid metal microcapsules (LMCs) to restore the electrical properties of flexible perovskite solar cells (Figure 3b).[55] A self-healing LMC was prepared via in situ polymerization of urea-formaldehyde onto LM colloids. The synthetic capsules can be easily mixed with poly (urethane acrylate) (PUA) to form LMC/PUA composite passivation films. The self-healing LMC/PUA was utilized to passivate the gold (Au) on PSC. When Au was mechanically stimulated, such as cutting or pressing, the microcapsule ruptured and released liquid metal ($Ga_{0.61}In_{0.25}Sn_{0.13}Zn_{0.01}$) to the crack then self-repaired the electrical pathways. If without a passivation film, the conductivity between the active area and gold cannot recover well, their resistance will markedly increase to 1.73×10^{10} Ω when encountering damage. In contrast, their conductive property can well recover rapidly (<1 min) when employing passivation film; the recovered resistance was as low as 1.47 Ω (Original resistance was 0.8 Ω). A high PCE retention of about 99% can be achieved based on the electrically repaired flexible PSC.

The toxicity of lead (Pb) is a major concern in PSCs. Recently, Jiang et al. used epoxy resin (ER)-based self-healing polymers as an encapsulant to reduce Pb leakage in damaged lead halide perovskite solar modules (Figure 3c).[56] When the encapsulated PSC modules were broken by an external force (e.g., hail), the sun can trigger the self-healing process of ER films, thus the ER films can protect PSC modules from water penetration, which can greatly prevent Pb leakage.

3.2. Triboelectric Nanogenerators (TENGs)

Triboelectric nanogenerators (TENGs) can convert extensively existed low-frequent and irregular mechanical energy into electricity by utilizing the coupling effect of triboelectrification and

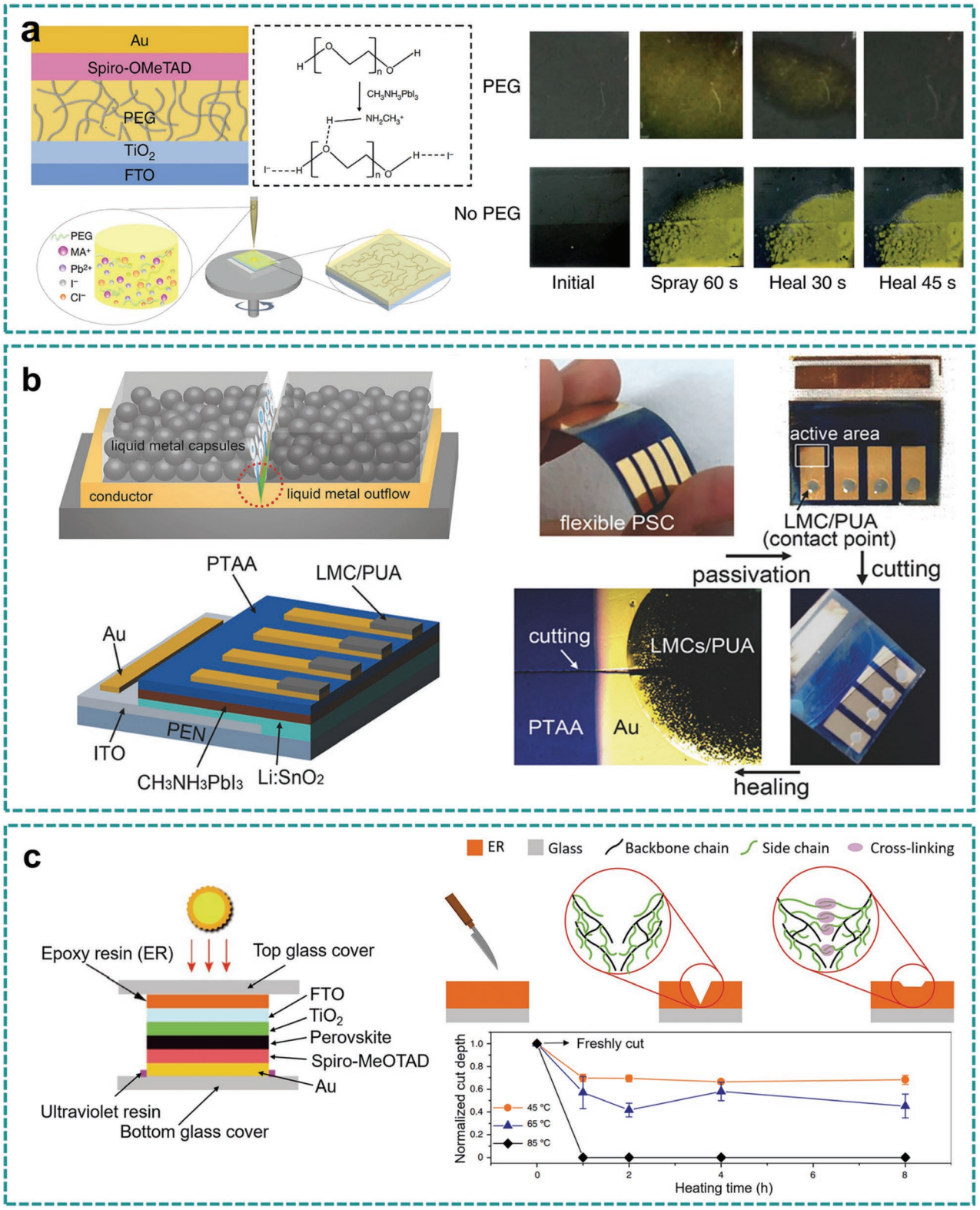

Figure 3. Self-healing PSCs. a) PEG-facilitated SHP scaffold PSC. Reproduced with permission.[53] Copyright 2016, Springer Nature. b) Self-healing conductor based on liquid metal microcapsules to restore electrical properties of PSC. Reproduced with permission.[55] Copyright 2018, Wiley-VCH. c) ER-based self-repairing polymers as encapsulant to reduce lead leakage in damaged lead halide PSC modules. Reproduced with permission.[56] Copyright 2019, Springer Nature.

electrostatic induction.[57,58] Due to its low manufacturing costs, universal availability, environmental friendliness, high conversion efficiency, and simple structures, TENG has obtained remarkable attention in many fields, such as self-powered sensing system,[59,60] biomedicine,[61–63] and flexible/wearable electronics.[64,65]

Researchers usually prepare microstructures to enlarge the triboelectric effect. However, over the lifetime of a TENG the micropatterns degrade and can be destroyed. To deal with this problem, Lee et al. showed a shape memory polymer-based self-healing TENG, it can heal and recover performance after the triboelectric layer degenerated (**Figure 4**a).[66] Polyurethane (PU) was used as a shape memory polymer and micropatterned triboelectric layer. The obtained triboelectric layer could get back to its original micro-pattern structure after 30 s above the PU glass transition temperature (T_g), thus recovering its performance. In addition, the degradation and healing process of this micropatterned triboelectric layer could be realized continuously for more than 30 times, which significantly improved the endurance and lifetime of TENG.

TENGs must be continuously triggered when harvesting mechanical energy; during this process material fracture occurred and resulted in TENG failure.[67] Xu et al. developed a fully self-healing TENG, it can recover its triboelectric performance after damage. The triboelectric layer was fabricated by coating self-healing layer of polydimethylsiloxane-polyurethane (PDMS-PU) on novel electrode consisting of small magnets (Figure 4b).[68] After TENG was damaged, the PDMS-PU could heal the mechanical properties and the magnetic-assisted electrodes could quickly heal the electrical properties. As a result, a high output voltage and current of the self-healed TENG can be restored to more than 95% of their original value after the 5th healing cycle. Parida et al. reported an extremely stretchable and healable TENG based on self-healing polyurethane acrylate (PUA). The PUA was used as a triboelectric layer and polymer matrix (Figure 4c).[69] Liquid metal and silver flakes were embedded in PUA as conductive fillers. PUA had supramolecular hydrogen bonding, which made this TENG has an excellent stretchability (2500%) and recovery ability after damage. After being healed, the mechanical performance of PUA retained 45.1%, and the conductor recovered with a high electrical healing efficiency of 96.0%.

TENGs for harvesting biomechanical energies generally difficult to adapt curvy human skin. Chen et al. fabricated a shape-adaptive and self-healing TENG, by using a viscoelastic polymer as the electrification material and matrix of CNT-putty electrodes (Figure 4d).[70] The TENG can adapt to arbitrary irregular surfaces. This viscoelastic polymer putty was fabricated by

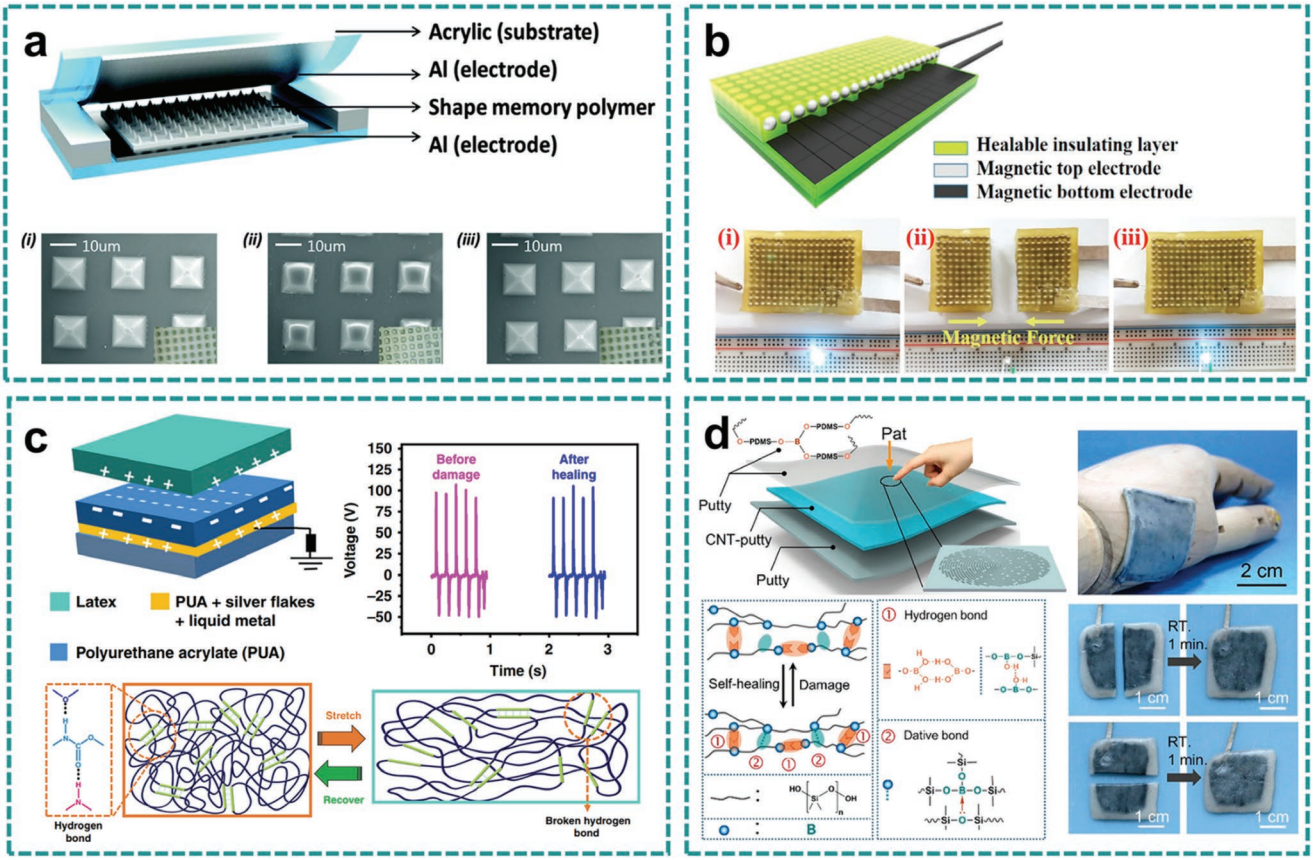

Figure 4. Self-healing TENGs. a) Shape-memory PU based self-healing TENG. Reproduced with permission.[66] Copyright 2015, The Royal Society of Chemistry. b) Magnetic-assisted self-healing TENG. Reproduced with permission.[68] Copyright 2017, Elsevier c) Thermoplastic elastomer PUA based self-healing TENG. Reproduced with permission.[69] Copyright 2019, Springer Nature. d) Viscoelastic polymer putty-based shape-adaptive and self-healable TENG. Reproduced with permission.[70] Copyright 2019, American Chemical Society.

HT-PDMS and boric acid, and its self-healing capability derived from the hydrogen bonds and dative bonds. After cutting, the TENG managed to heal automatically within 3 min at ambient temperature without any trigger, and its electrical output performances can be completely restored. This shape-adaptive and self-healing TENG provides a new strategy for the energy supply of flexible wearable electronics.

4. Self-Healing Energy Storage Devices

4.1. Supercapacitors (SCs)

The energy storage mechanism of SCs was based on electrical double layers or redox reactions. SCs usually have fast charge and discharge process, high power density, and long cycling performance.[9,71–78] Self-healing ability can greatly enhance their stability and service life during practical applications. Up to now, the main direction of the current research on self-healing SCs is the mechanical and electrical restoration. The two key factors that determine the fabrication of self-healing SCs mainly refer to their electrodes and gel electrolytes.

The purpose of a self-healing electrode is to recover electrical conductivity. The integration of self-healing material into the electrode can heal the cracks caused by mechanical damage and restore the electrical properties of the device. Wang et al. proposed the first self-healing SC, including its mechanical and electrical property (**Figure 5**a).[71] Authors spread single-walled CNT on a substrate with self-healing ability. This substrate was made up of a supramolecular network and enhanced by titanium dioxide (TiO_2) nanoparticles. Upon encountering breakdown, the separated SWCNTs can be restored and contact with each other by the sliding movement of the self-healing shell. This structure design endows SC with excellent self-healing property. The capacitance retention reaches up to 85.7% within five cutting. Yarn-based supercapacitors have great potential in wearable electronic devices. However, because the yarn electrode is very slender, it is difficult to achieve accurate docking after damage, which affects the recovery of conductivity. To solve this problem, Huang et al. fabricated a magnetic-assisted mechanically and electrically self-healable SC by using PU shell to package magnetic (Figure 5b).[79] When the yarn-based SC was subjected to mechanical damage, the broken yarn electrodes would be reconnected under the guidance of the magnetic force to restore conductivity. Meanwhile, the self-healing ability of PU could well heal the damaged areas to repair the structural integrity and mechanical property autonomically. Under the combined action of magnetic electrodes and PU shell, the SC shows a high specific capacitance retention of 71.8% and well mechanical properties within the 4th healing cycle.

The purpose of self-healing dielectric is to recover ionic conductivity. Polyelectrolytes are ideal materials for constructing self-healing electrolytes due to the advantages of high ionic conductivity, adjustable mechanical properties, and good compatibility with electrode materials. Huang et al. reported a dual crosslinked polyelectrolyte for self-healable SC (Figure 5c).[80] The polypyrrole (PPy)-deposited CNT paper was used as electrodes. The self-healing polyelectrolyte consisted of polyacrylic acid double-crosslinked hydrogen bonding and vinyl hybrid silica nanoparticles (VSNPs-PAA). The fabricated SC with this polyelectrolyte completely retained its capacitance even after 20 healing cycles. Lin et al. fabricated a new ferric improving dual physical crosslinking polyelectrolyte (Fe-DPCL), acrylic acid was served as the hydrophilic monomer, stearoyl methacrylate was served as the hydrophobic monomer.[81] The H_2SO_4 in Fe-DPCL exhibited a high ionic conductivity (>30 mS cm^{-1}), the whole hydrogel showed good self-healing efficiency as well as high stretchability. The assembled SC (Figure 5f) presented good self-healing ability and high capacitance retention about 86% even after the 7th damage.

Self-healing coating shell can heal itself after mechanical damage and thus restore device integrity and mechanical properties. In addition, self-healing coating shell can prevent corrosion or decomposition of underlying substrate materials and leakage of toxic substances by avoiding environmental exposure. Wang et al. fabricated a stretchable and healable SC via wrapping two parallel spring-like fiber electrodes with stretchable carboxylated PU as a self-healing material (Figure 5d).[82] The spring-like fiber electrode proved the stretchable property, and the carboxylated PU shell offered outstanding mechanically self-healing performance. Once the spring electrode was broken, simply aligning the electrode to the link, self-healing PU can reconnect itself and thus restore electrical properties. The specific capacitance can be to 54.2% after the third healing cycle. Yue et al. also used self-healing carboxylation PU as an outer shell to fabricate a self-healable 3D micro-supercapacitor (Figure 5e).[7] This 3D micro-supercapacitor consisted of the MXene-graphene aerogel electrode. It showed a solid mechanical performance, even when experiencing external force damage. The 3D micro-supercapacitor presented a satisfactory self-healing ability in capacitance; a high capacitance retention of about 81.7% was achieved after the 5th self-healing cycle.

4.2. Lithium Ion Batteries (LIBs)

Lithium Ion Batteries (LIBs) were dominant energy storage devices of most electronic devices due to their high volumetric energy density, gravimetric energy density, long lifespan, and environmental benignancy.[83–89] Whereas, LIBs may be damaged or even broken under deformation for example stretching and cutting, especially flexible LIBs for wearable electronics, resulting in their inability to work or even serious safety problems.[5,88] Also, the mechanical microcracks caused by the structural changes during the repetitive charge/discharge cycling process would seriously reduce the cycle stability of LIBs. Self-healing LIBs can heal external mechanical damage or microcracks inside the battery material to improve the cycle stability and lifespan.[90] To solve these problems, more studies should be made on self-healing electrodes and electrolytes.

Zhao et al. presented the first flexible self-healing LIB.[91] The electrodes were made by aligning CNT sheets on a self-healing substrate, where the CNT sheets were loaded with $LiMn_2O_4$ and $LiTi_2(PO_4)_3$. Aqueous lithium sulfate/sodium carboxymethylcellulose acted as gel electrolyte and separator (**Figure 6**a). The as-fabricated LIB could heal itself in few seconds, including its structure and electrochemical property. The capacitance decreased from 28.2 to 17.2 mAh g^{-1} at 0.5 A g^{-1}

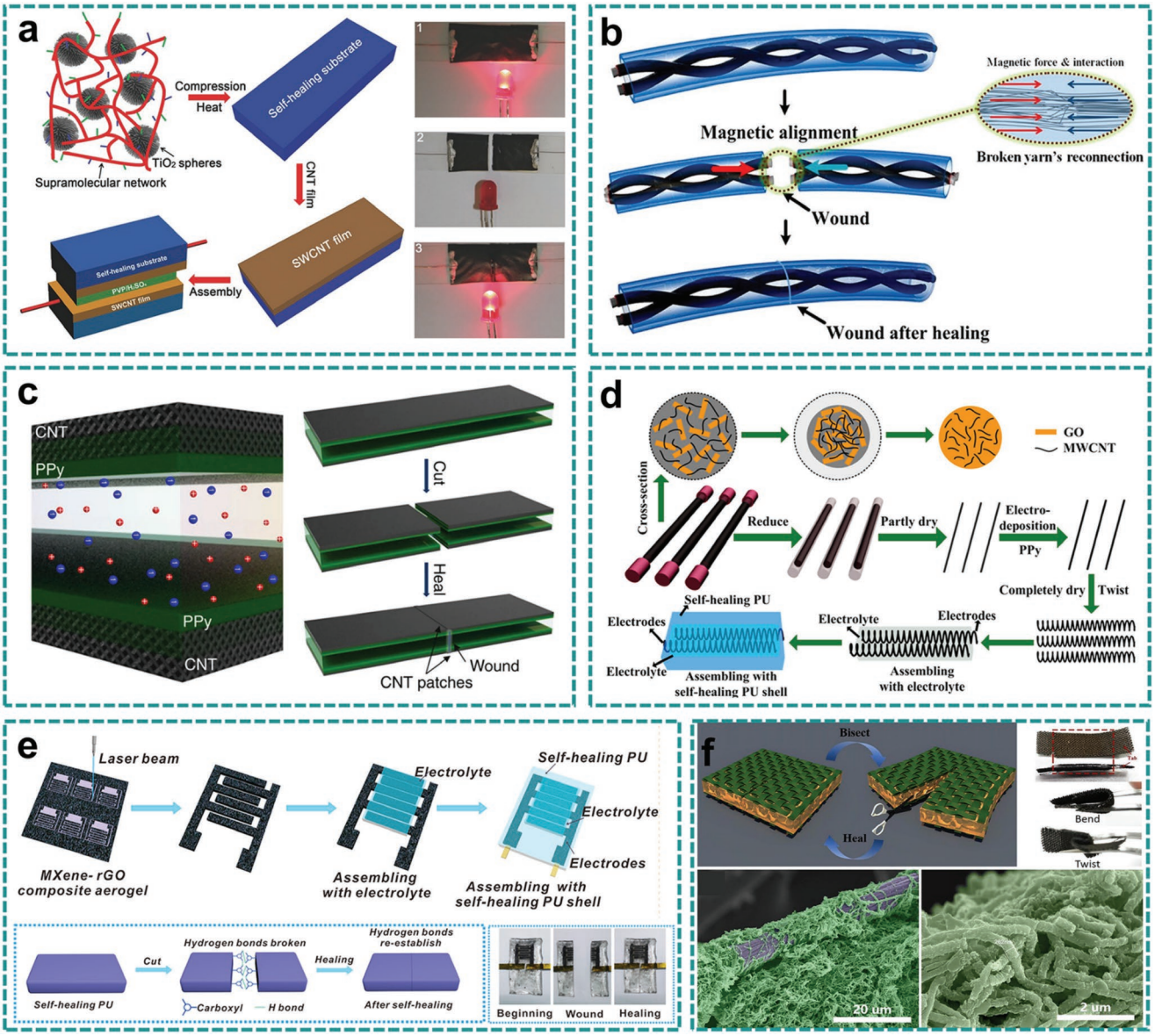

Figure 5. Self-healing SCs. a) SWCNT films spread on self-healing substrate to assemble self-healing SC. Reproduced with permission.[71] Copyright 2014, Wiley-VCH. b) Magnetic-assisted, self-healable yarn-based SC. Reproduced with permission.[79] Copyright 2015, American Chemical Society. c) Dual crosslinked polyelectrolyte based self-healable SC. Reproduced with permission.[80] Copyright 2015, Springer Nature. d) Self-healable SC with RGO based fiber springs. Reproduced with permission.[82] Copyright 2017, American Chemical Society. e) Self-healable 3D micro-supercapacitor with MXene-graphene composite aerogel. Reproduced with permission.[7] Copyright 2018, American Chemical Society. f) Ferric enhancing dual physical crosslinking polyelectrolyte based self-healing SC. Reproduced with permission.[81] Copyright 2019, Elsevier.

after the 5th cutting. Furthermore, the LIB also showed a good self-healing mechanical strength. Liquid metals and their alloys have deformability, high electronic conductivity and superior electrochemical properties, which have attracted wide attention, especially in the field of energy storage. Wu et al. reported a self-healing LIB anode using liquid metal.[92] This liquid metal was composed of Ga—Sn liquid metal alloy, it was stabilized in an RGO/CNT skeleton (Figure 6b). Sn can lower the melting point of Ga, therefore, the Ga—Sn alloy is kept as a liquid at 25 °C and capable of self-healing ability. The RGO/CNT skeleton enhanced the electrode conductivity, meanwhile, prevented Ga—Sn from aggregating or detaching during repetitive cycling. The Ga—Sn became rougher and rougher when charge and discharge were carried out. Ga—Sn showed a solid-state at full lithiation with bumps and ravines, which can be attributed to the volume expansion. After delithiation, the surface morphology recovered to smooth again. This behavior avoided expansion and contraction. Consequently, the liquid metal-based LIBs possessed excellent cycling stability during 4000 cycles. This work provides a new strategy for LIBs to achieve a long cycle life.

Coating solid electrolyte particles with self-healing polymers to produce self-healing electrolytes without interfering with the conductivity is a classical process. Whiteley et al. proposed a

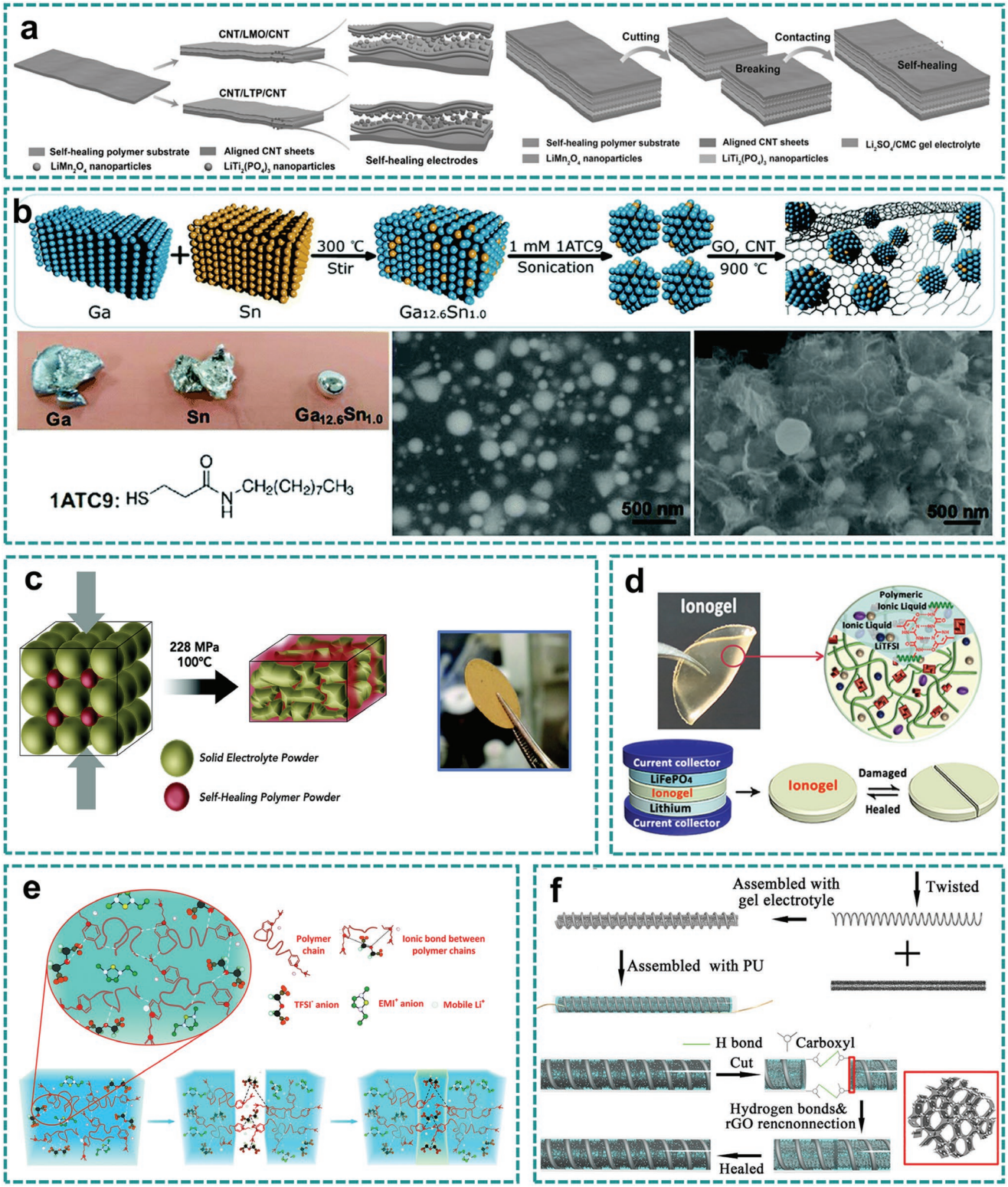

Figure 6. Self-healing LIBs. a) All-solid-state self-healing aqueous LIB. Reproduced with permission.[91] Copyright 2016, Wiley-VCH. b) RGO/CNT-supported liquid metal nanoparticles self-healing anode for LIB. Reproduced with permission.[92] Copyright 2017, The Royal Society of Chemistry. c) Self-healing polymer matrix based solid-state Li-ion electrolyte membrane. Reproduced with permission.[93] Copyright 2015, Wiley-VCH. d) Nonflammable supramolecular ionogel electrolytes for LIB. Reproduced with permission.[94] Copyright 2019, American Chemical Society. e) Ionic bonds rebuilding mechanism of the self-healing electrolytes. Reproduced with permission.[95] Copyright 2020, Elsevier. f) The fabrication procedure and self-healing mechanism of an all-fiber-based LIB. Reproduced with permission.[96] Copyright 2018, Elsevier.

self-healing Li-ion membrane.[93] The electrolyte was fabricated by filling empty voids of Li_2S-P_2S_5 with a newly malleable thermoset self-healing polyimine at a hot-pressing condition (Figure 6c). The authors developed an in-situ cross-linked network using polyimine. This process endowed samples with good mechanical robustness, meanwhile, lower its impact on electrolyte conductivity. The electrolyte membrane was only 64 µm thick, but it could provide a high solid electrolyte loading (80%). The as-fabricated LIBs achieved a good cycling performance over 200 cycles. Polymeric ionic liquids are a good choice for self-healing electrolytes due to its high ionic conductivity, electrochemical stability, and excellent processability. Guo et al. presented a healable ionogel electrolyte for LIBs based on polymeric ionic liquids.[94] Its self-repairing ability can be attributed to multiple noncovalent interactions (Figure 6d). The discharge capacity and Coulombic efficiency of the cell using the healed ionogel electrolyte membrane were quite stable during 50 charge/discharge cycles. Tian et al. developed polymer electrolytes for LIBs with outstanding self-healing ability and stretchability using ionic bonds.[95] Authors used dicationic polymerized ionic liquids as a backbone to prepare self-healing electrolyte (Figure 6e). Strong reversible ionic bonds were formed by cations and anions in the polymer matrix and ionic liquid phases. The reversible ionic bods made damaged polymer electrolytes self-repair themselves without obvious cracks within minutes. The discharge capacity and Coulombic efficiency of the as-assembled LIBs showed good stability.

Moreover, Rao et al. presented a flexible and self-healable LIB based on self-healing coating shell (Figure 6f). $LiCoO_2$ nanopartiles@RGO fiber and SnO_2 quantum dots@RGO fiber were used as cathode and anode materials, respectively.[96] The self-healing PU was used as an encapsulation layer to package batteries and provide self-repairing properties. The as-assembled LIB showed a stable capacity of about 82.6 mAh g^{-1} when experiencing deformation; the retained capacity reached up to 50.1 mAh g^{-1} even with five cuttings.

5. Self-Healing Bioelectronic Devices

5.1. Sensors

Flexible, wearable smart electronic devices show many important applications in various areas, for instance, human-machine interaction, healthcare monitoring, sports performance monitoring, and entertainment.[97–101] Sensors, that can detect and perceive external physical or chemical signals, are one of the core devices for developing flexible and wearable smart electronic equipment.[102,103] Nevertheless, sensors are unavoidably suffer from external damage, such as scratching and rupture during daily use, leading to malfunction. Sensors with high effective self-healing ability could repair themselves under hitch and restore their original structural and functional states, significantly improving their reliability and lifespan.

Huynh et al. reported a self-healing and multiparametric flexible sensing platform for monitoring pressure and temperature (**Figure 7**a).[104] The substrate, electrodes, and sensing layer were all self-healing. The self-healing ability mainly derived from the reformation of hydrogen and disulfide bonds in polyurethane derivatives. The sensor can self-heal itself in either normal or harsh conditions. Its performance can be well recovered even with cycles of cutting treatment.

The conductivity of the material has a significant effect on the performance of the sensor. Constructing intrinsically conductive materials for self-healing sensors is urgent and necessary. Wang et al. synthesized a ternary conductive polymer composite comprised of polyaniline, polyacrylic acid, and phytic acid for a strain and pressure-sensitive sensing application (Figure 7c).[105] The polymer composite exhibited excellent stretchability and conductivity. Because of the dynamic interaction between hydrogen and electrostatic binding, the electrical and mechanical properties of the polymer composites can recover about 99% efficiency within 24 hours after splitting.

Hydrogels are traditional materials for the preparation of flexible and wearable sensors. The preparation of hydrogels with both good mechanical properties, excellent self-healing properties, and high sensing sensitivity remains a difficult task. Liu et al. reported a self-healing conductive hydrogel used as a wearable strain sensor (Figure 7b).[106] This hydrogel consisted of a polymer network and cellulose nanocrystals network cross-linked by Fe^{3+} ions. Take advantage of the hierarchical network structures and reversible coordination bonds, the hydrogel exhibited many features, including physical robustness, stretchable performance, and excellent self-repairing ability. After cutting, the hydrogel can autonomously self-heal itself within 5 min without any stimuli or healing agents. Lei et al. presented the first example of a self-healing ionic skin sensor, the self-healing ability derived from a bioinspired hydrogel (Figure 7d).[107] This sensor can be applied to monitor human motion, muscle movements, and blood pressure. The bioinspired supramolecular mineral hydrogel can self-heal itself rapidly at 25 °C.

Constructing composite hydrogels is an effective strategy to expand the properties of hydrogels. Deng et al. presented a self-healing nanocomposite hydrogel using laponite nano-clay, MWCNTs, and *N*-isopropyl acrylamide.[108] Those hydrogels have 3D printability and could be used for human motion monitoring (Figure 7e). The self-healing ability of nanocomposite hydrogel can be achieved without needing external agents. The self-healing mechanism could be explained from the physical cross-linking between polymer chains caused by electrostatic interaction and intermolecular hydrogen bonding. Wang et al. prepared transparent, compliant, and adhesive skin sensors using zwitterionic nanocomposite hydrogels to detect body motion (Figure 7f).[109] The hydrogels exhibited excellent mechanical properties, compliant adhesion, a reliable self-healing property, and high strain sensitivity. The reversible physical interaction imparted the hydrogels with a rapid self-healing ability. After one day, the stretchability and stress of healed hydrogels can still reach 1700% and 0.17 MPa. The fracture strength retention was about 74%.

5.2. Electronic Skins (E-skins)

Electronic skin (E-skin) is an electronic system capable of mimicking human skin functions including stretchability, self-healing ability, and versatile sensory capability, which can turn

Figure 7. Self-healing sensors. a) Self-healing and multiparametric sensing platform. Reproduced with permission.[104] Copyright 2016, Wiley-VCH. b) Synergistic "soft and hard" hybrid networks hydrogels for strain sensors. Reproduced with permission.[106] Copyright 2017, American Chemical Society. c) Self-healable conductive polymer composite for strain and pressure sensing. Reproduced with permission.[105] Copyright 2018, Wiley-VCH. d) Bioinspired mineral hydrogel for pressure sensing. Reproduced with permission.[107] Copyright 2017, Wiley-VCH. e) Conductive self-healing nanocomposite hydrogels for human motion sensing. Reproduced with permission.[108] Copyright 2019, American Chemical Society. f) Self-healable, ionically conductive zwitterionic nanocomposite hydrogels for strain sensing. Reproduced with permission.[109] Copyright 2019, American Chemical Society.

various external stimuli into electrical signals, for instance, press, humidity, or deformation.[110–112] E-skin has many promising applications in the fields of soft robotic systems, wearable electronics, robotic prosthetics, and artificial intelligence.[113–115] To improve the stability and lifespan of e-skin, self-healing capability can be a feasible solution.

Tee et al. described a self-healing composite in electricity and mechanical property, this composite was sensitive to pressure and flexion, which make it promising for constructing e-skin.[116] The composite material was the first bulk conductive composite. It had a urea group for hydrogen networking. Nickel microparticles with nanostructure were used as a filler. This design made the composite have the self-healing ability under ambient conditions. Nickel microparticles provided an adjustable conductivity up to 40 S cm^{-1}, while also enhancing its mechanical strength. Lots of hydrogen bonds that existed in

supramolecular polymers provided the self-healing ability. The conductivity retention was about 90% after 15 s of self-healing. The recovery efficiency of mechanical properties was near to 100% within 10 min. The composite material had sensitive detection ability on tactile and flexion forces from limbs when integrated into a humanoid mannequin, showing great potential as an e-skin (**Figure 8**a).

Large-scale integration of single self-healing electronic devices into a system is a major challenge for self-healing electronic devices. So far, self-healing systems for multi-function electronic device integration have rarely been reported. By using a nanostructured conducting network, Son et al. reported the first integrated self-healable e-skin system (Figure 8b).[20] The conductive network formed by carbon nanotubes or silver nanowires was mixed with the polymer matrix. Dynamic reconstruction of polymer induced the recovery of the broken conductive network, the conduction and mechanical properties can be well repaired by themselves. In active electronic devices, this conductive composite can act as their electrodes for stretchable and self-healing electronic systems. By integrating the strain sensor, electrocardiogram sensor, and display array, authors fabricated a self-healing multi-functional e-skin system, which can collect data from the human body surface, process, and wirelessly transmit the data to the display array for visual interpretation. This work is of milestone significance, it proves the possibility of the application of self-healing components in integrated systems.

Creating materials that can self-heal underwater could greatly promote the application of aquatic robots. Cao et al. created a stretchable and self-healing e-skin for aquatic environments by adopting an amorphous and chemically compatible polymer (Figure 8c).[117] The ionic conductivity of the e-skin can be regulated to 10^{-3} S cm^{-1}. The performance of the whole device is kept normal even with a high of 2000%. The e-skin can heal itself in a dry or wet environment due to its highly reversible ion-dipole interactions. The healing efficiency of electrical conductivity was 90.7% after ten cuts. The e-skin was very sensitive to touch, pressure, and strain, demonstrating its sensory capabilities in potential applications. Real tactile perception of simulated natural skin is a major goal in the development of

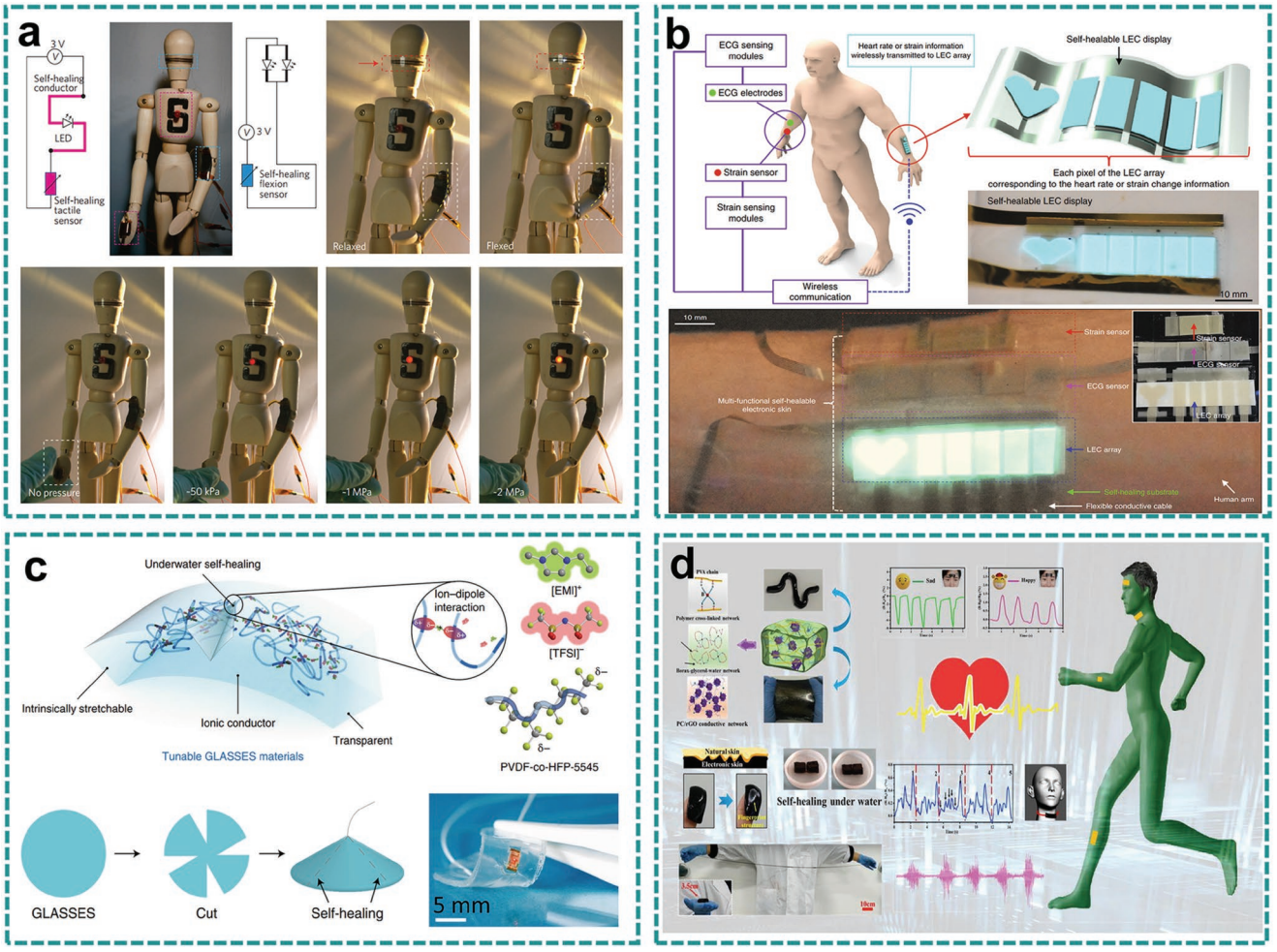

Figure 8. Self-healing e-skins. a) Room-temperature self-healing electronic sensor skin. Reproduced with permission.[116] Copyright 2012, Springer Nature. b) An integrated self-healable e-skin system. Reproduced with permission.[20] Copyright 2018, Springer Nature. c) A gel-like, aquatic, stretchable, and self-healing e-skin. Reproduced with permission.[117] Copyright 2019, Springer Nature. d) A bionic tactile plastic hydrogel-based self-healing e-skin. Reproduced with permission.[118] Copyright 2020, Elsevier.

e-skin. Pan et al. reported a bionic tactile plastic e-skin based on a composite hydrogel,[118] which possessed outstanding super-stretchability (>5000%), a rapid self-healing rate (3 s, 95.73%), and a high sensitivity when detecting strain (GF = 14.14). The hydrogel-based e-skin can not only simulate and detect some epidermal movements but also detect the human electrocardiogram and electromyography signals (Figure 8d), which has potential applications in real-time health care and prosthetics.

6. Self-Healing Electronic Accessories

6.1. Field-Effect Transistors (FETs)

Field-effect transistor (FET) is a kind of semiconductor device which uses electric field effect to control output circuit current. It is widely used in logic circuits, active matrix displays, sensor arrays, and radio frequency identification tags.[119,120] With the development of flexible, wearable, and implantable electronics, the FETs, especially organic FETs, have received great attention due to their promising applications in lightweight, large-area, low-cost, and flexible electronic components.[121,122] However, the FET with self-healing capability is rarely reported.

Gate is a crucial part of the field effect transistor. When the gate dielectric layer breaks or undergoes delamination under repeated mechanical strain, it will cause gate leakage, reduce current density, and lead to device failure. Lu et al. reported a graphene-based FET consisted of self-healing gate dielectrics (**Figure 9**a).[121] Aluminum oxide (AlO_x) has a high gate capacitance and self-healing property, it was used as both gate dielectric and spacer. After damaging the AlO_x, it can restore its initial performance when exposed to the air for several hours or by electrical annealing. Due to self-healing ability, the performance indexes of FET can almost recover to the initial state after damage, including its on/off ratio, charge mobility, and conductance. Ko et al. developed a self-healing gate insulator using a self-healing polymer dielectric (Figure 9b).[123] The self-healing polymer consisted of an ionic liquid and a copolymer; it can self-heal itself at 55 °C within 30 min. The self-healing ability came from the hydrogen bonding formed by the interaction of a catechol group and an ionic liquid. The as-fabricated self-healing FET maintained its electrical properties well even

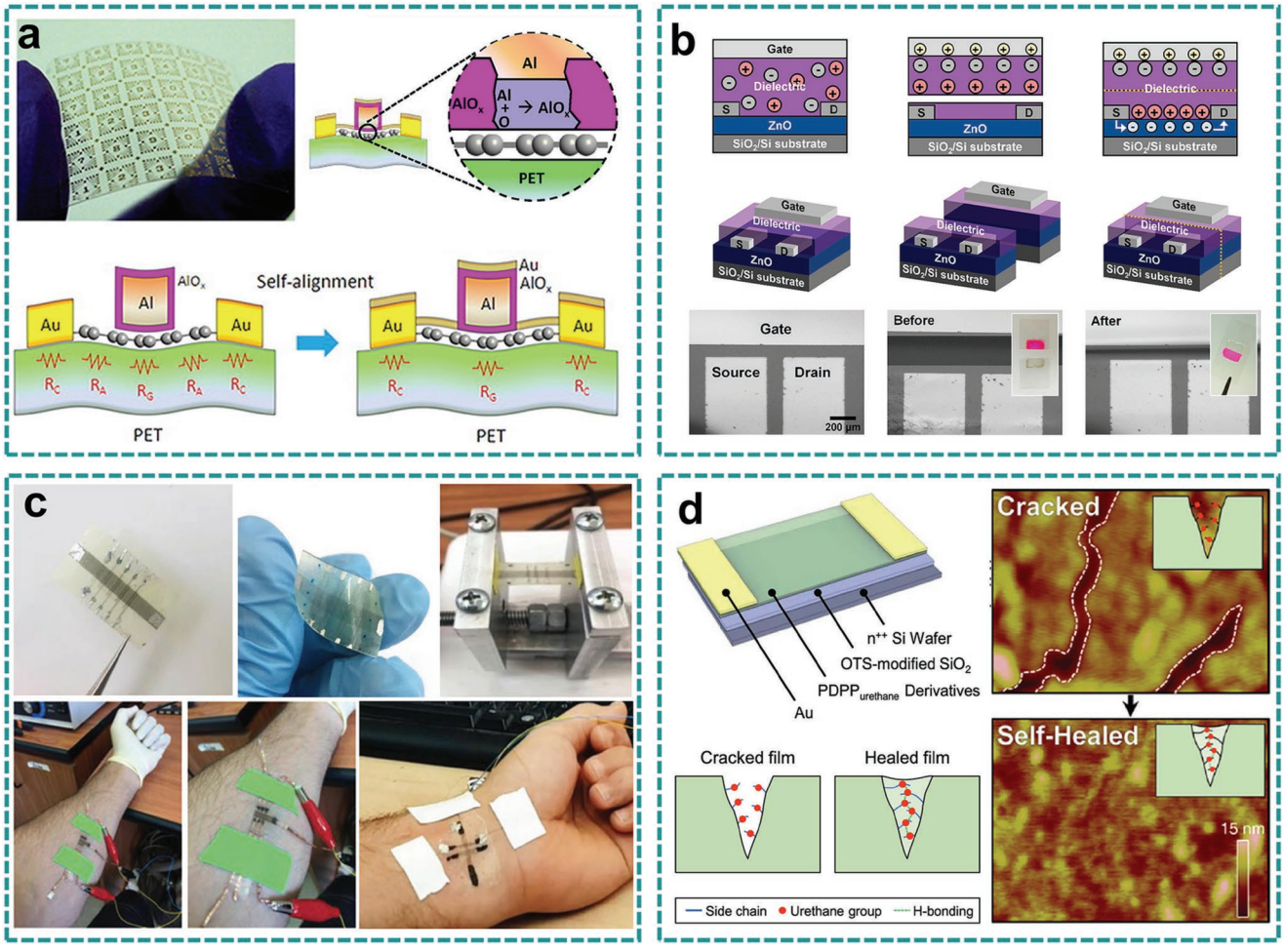

Figure 9. Self-healing transistors. a) Self-healing gate dielectrics for FETs. Reproduced with permission.[121] Copyright 2012, American Chemical Society. b) Gate insulator with self-healing polymer dielectric. Reproduced with permission.[123] Copyright 2016, American Chemical Society. c) FETs with fully self-healing property. Reproduced with permission.[6] Copyright 2019, Wiley-VCH. d) Stretchable and self-healable plastic transistor. Reproduced with permission.[124] Copyright 2020, American Chemical Society.

after repetitive self-healing mechanical breaking. The preparation of fully self-healing devices still is a great challenge. Khatib et al. fabricated a self-healable stretchable and multifunctional FET using CNTs as the filling material of self-healing disulfide-containing poly(urea-urethane) (PUU) (Figure 9c).[6] All components of the FET, including dielectric electrodes and channel, were intrinsic and had autonomic self-healing. The electrical and mechanical properties of FET could remarkably self-recover under varying degrees of damage. Moreover, the FET can sense multiple targets, for example, temperature and humidity. Lee et al. reported stretchable and self-healable diketopyrrolopyrrole-based "alternating" copolymers with urethane-containing side chains ($PDPP_{urethane}$).[124] $PDPP_{urethane}$ derivative thin films were used as active layers in plastic FETs (Figure 9d). The reversible dynamic bonding of hydrogen bonds in urethane side chains was beneficial not only to stress dissipation of the thin films under mechanical deformation but also to feature self-healing properties. After solvent vapor or/and annealing, the cracked position can repair itself and recover its electrical property.

6.2. Actuators

Actuators can respond to external stimuli and convert them into volume and shape changes, and reversible motions, which are essential for the development of soft robotics.[125,126] Due to the inherent working mode of the actuator, it is inevitable to suffer mechanical damage such as puncture and tear under long service times, which limits their longevity and performance.[127,128] Therefore, the integration of an excellent self-healing ability into a single stimulus-responsive material system will greatly facilitate and broaden the development of actuators.

Supramolecular materials can respond to external stimuli and can easily achieve self-healing, which are ideal materials for constructing self-healing actuators. Borré et al. reported a light-driven self-repairing soft actuator by supramolecular metallopolymers (**Figure 10**a).[129] The self-repairing ability of metallopolymers derived from the reversible coordination bonds within the metallopolymeric chain. Due to the photo-responsive moieties and π-conjugated emissive units in the

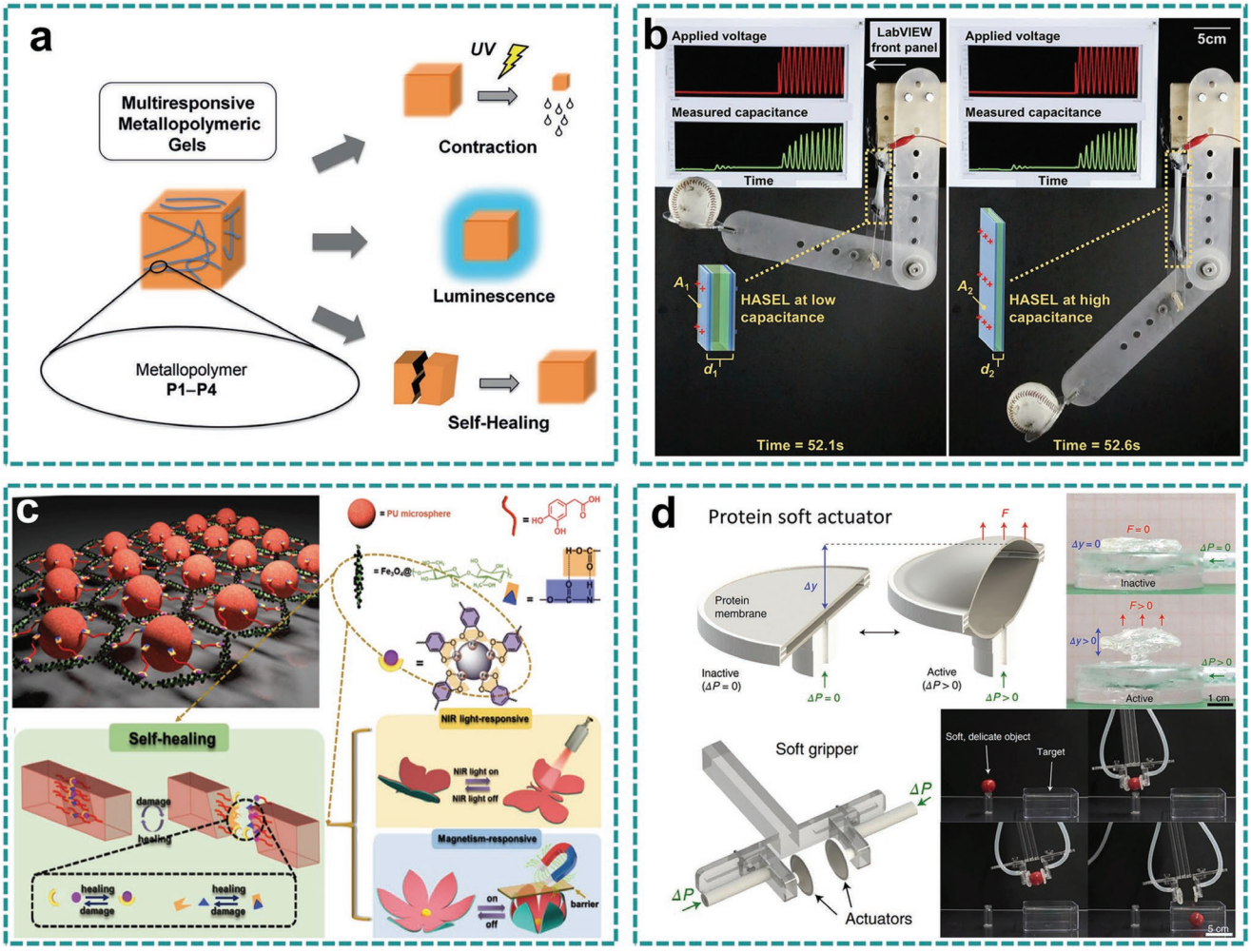

Figure 10. Self-healing actuators. a) Light-powered self-healable metallosupramolecular soft actuators. Reproduced with permission.[129] Copyright 2016, Wiley-VCH. b) Self-healing electrostatic actuators with muscle-like performance. Reproduced with permission.[131] Copyright 2018, The American Association for the Advancement of Science. c) Light- and magnetic-response self-healing actuators. Reproduced with permission.[130] Copyright 2019, Wiley-VCH. d) Self-healing protein soft actuator. Reproduced with permission.[132] Copyright 2020, Springer Nature.

polymer backbone, the metallopolymers showed mechanical actuation and luminescent properties induced by light. The metallopolymers exhibited macroscopic and light-induced orientation-related volume reduction and synergistic effects under UV light irradiation, and can be used to locally promote light-induced actuation and drug release. Wang et al. reported a rapid infrared and magnetic field response biomimetic actuator on account of a metal–ligand coordination-cross-linked supramolecular elastomer (Figure 10c).[130] The crosslinking structure of the supramolecular made the elastomer have the ability to self-heal itself under room temperature after the rupture and its healing efficiency reached 92.2%. Even after healing 20 times, the healing efficiency was still as high as 79.74%. The as-prepared actuator exhibited an ultrahigh near-infrared-light and magnetic-responsive sensitivity and repeatability.

Traditional fluid actuators, driven by gas or liquid, are multifunctional, but have a low response speed and efficiency. The dielectric elastomer actuators have the characteristics of high response efficiency and self-sensing, but it needs a high voltage electric field, which is prone to dielectric breakdown and electrical aging. To address this problem, Acome et al. developed a muscle-like actuator (Figure 10b).[131] Its elastomeric shell and electrode were made from polydimethylsiloxane (PDMS) and ionically conductive polyacrylamide (PAM) hydrogels, respectively. A vegetable-based transformer oil was used to make the actuator self-heal itself at least 50 times from dielectric breakdown. Additionally, the soft actuators were able to self-sense deformation, which have wide application prospects for future soft robots.

In recent years, the rapid development of biosynthetic materials has opened a new platform for the development of new self-healing materials. Pena-Francesch et al. reported a squid-inspired biosynthetic protein.[132] Owing to the supramolecular interactions through optimized hydrogen-bonded nanostructures and network morphology, the protein-based materials showed outstanding ability in resisting extreme damage and self-healing itself in a short time. The protein-based soft actuators can rapidly heal extreme mechanical damage (<1 min) by local heating (Figure 10d). Additionally, the protein-based actuator can be degraded on demand under pH induction.

7. Conclusion and Perspective

Self-healing technology provided an effective solution for recovering the device itself (e.g., structure and function) after damage. With the fast development of self-healing materials, structural design, and optimization of PWED, self-healing electronics have witnessed remarkable achievements in many aspects. Those successful applications refer to solar cells, triboelectric nanogenerators, supercapacitors, batteries, e-skins, biosensors, and some other electronic accessories. This general applicability further proved the importance and application potential of self-healing technology in the future world.

For the self-healing layer of PWED, the commonly-used mechanisms involve extrinsic and intrinsic self-healing modes. The extrinsic self-healing mode usually needs pre-added healing agents to repair the damaged positions. However, the healing agents are easily exhausted, so the mode is difficult to achieve for multiple healings in the same site, which limits its practical application. Compared with extrinsic self-healing mode, intrinsic self-healing mode will be the mainstream direction for self-healing technology in the future, it has a more stable and reliable self-healing ability and it can achieve multiple reversible healing by inherently reversible dynamic covalent bonds or non-covalent bonds. It is noteworthy that the construction of SHP is not limited to the reversible transformation of a single chemical bond as the fabrication of various SHP materials is with different functions. Moreover, the mechanical properties, self-healing speed, biocompatibility, or other properties required for various applications can be satisfied by different modifications of SHP materials.

For the whole PWED, its structure and function can be recovered by the self-healing layers. However, on the other hand, although scientists have made great advancements in the self-healing field, the study on self-healing electronic devices remains in its infancy. The reported self-healing efficiency of electronic devices is still not satisfactory (**Figure 11**). The precise connection between two fracture surfaces, full recovery of mechanical property, and working performance cannot be well resolved. Several challenges should be well overcome before

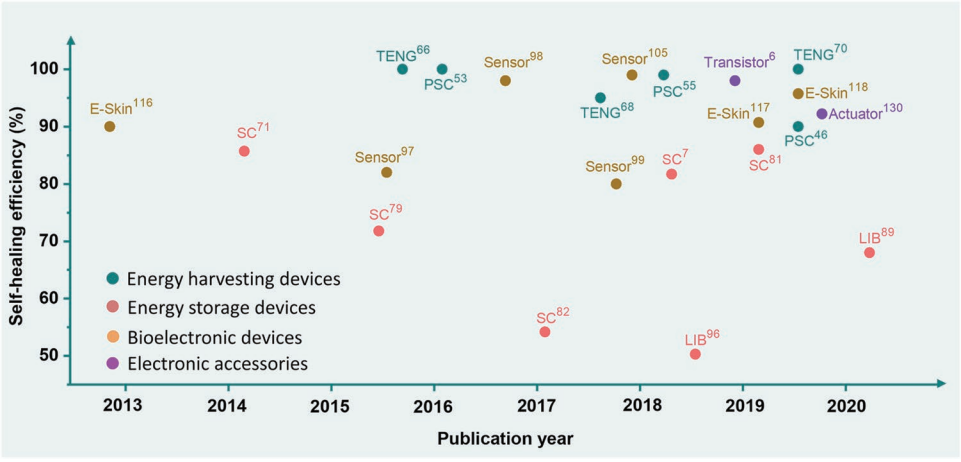

Figure 11. Reported self-healing electronic devices based on publication year and self-healing efficiency.

self-healing electronics can be used and commercialized in practical scenarios. Those existing challenges and relevant strategies are listed as follows.

i. Theory

The theoretical research on self-healing electronic devices is in the initial stage, and the self-healing behavior at the material interface has not been deeply understood and explained. Multi-scale theoretical simulation and modeling are required at the molecular level to gain insight into the healing mechanism, which may provide new theories and concepts to synthesize novel materials.

ii. Property

The physical properties, such as conductivity, sensitivity, and photochemical performance of self-healing polymers, are still inferior to non-healing materials, which limit their eventual performance and usage in devices. Therefore, the development of new self-healing materials with decent mechanical and multifunctional properties, and optimizing the nanostructure or composition will be ideal.

iii. Diagnoses

Microcracks formed in materials are undetectable in the early stages. Early damage diagnosing and timely self-healing can avoid catastrophic failure. Strategies to construct self-healing materials with self-diagnostic properties by endowing materials with visual color or fluorescence changes will be valuable.

iv. Fabrication

The integration of all self-healing components to realize completely self-healing devices remains a great challenge. Development is of new manufacturing processes and technologies, such as high-resolution 3D-printing, for small-scale self-healing devices.

v. Parasitism

In some applications, the self-healing purpose relies on healing agents or external stimuli, which may introduce parasitic effects on the substrate material or functional components of the device. Therefore, the development of materials that self-heal under ambient conditions or selectively heal on-demand at designated locations will be necessary.

At length, science advances from the multidisciplinary, such as material science and manufacturing technology, will greatly promote the progress of self-healing materials and self-healing electronic devices in practical usage. In the future, both research and commercialization of self-healing electronic devices are expected to be accelerated further. Finally, we sincerely hope this review can provide a valuable reference and bring forth new ideas for other researchers in related fields.

Acknowledgements

Y.G. and H.L. contributed equally to this work. This work was supported by the Key-Area Research and Development Program of Guangdong Province (2018B030331001), the National Natural Science Foundation of China (61875015), the Beijing Natural Science Foundation (JQ20038), and the Fundamental Research Funds for the Central Universities.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

bioelectronic devices, electronic accessories, energy harvesting, energy storage, self-healing

Received: March 8, 2021
Revised: March 24, 2021
Published online:

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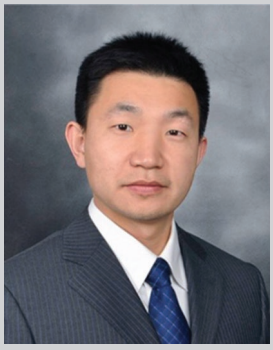

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