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A Comprehensive Review of Recent Developments in Self-Healing Electrodes Enabled by Nanomaterials

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Abstract

The development of self-healing electrodes that can repair themselves in addition to working under high electric fields is at the forefront nowadays. Beyond enhanced platform applications, the facile integration of conductive nanomaterials with these flexible electrodes has enabled new possibilities in electronic skin and sensors and energy-storage technologies for future generations by using solution-based assembly methods. Although hydrogels and polymers were previously used in self-healing electrodes, they lacked sufficient conductivity or strength to be effective long-term solutions however, nanomaterials do not share these limitations. These characteristics uses high surface area, a range of functional groups, and greater self-healing ability than many other materials which make them well-suited to the task. This review provides insight into the recent advancements of self-healing electrodes based on nanomaterials, investigating their working principles and characterization methods

Keywords: Self-healing, Nanomaterials, Sensor, Electrodes, Energy storage,

1.0 INTRODUCTION

Self-healing electrodes are electrical conductors that, like human skin, can heal internal damage on their own [1]. Electrical conductivity is what a self-healing electrode aims to restore. By incorporating self-healing material into the electrode, mechanical damage-induced cracks can be repaired, and the device's electrical characteristics can be restored. [2]. Self-healing electrodes have garnered significant interest because of their exceptional capacity to self-heal their damaged areas without the need for additional adhesives, hence regaining their original forms and qualities

[3].According to advancements and research, self-healing active metal alloys or self-healing polymers can be added to electrodes to create self-healing electrodes [4].

Flexible, lightweight, strong, and safe-to-wear electrodes have been developed in response to the growing demand for self-healing electrodes [5, 6]. The potential applications of materials with self-healing properties in electronic skins (E-skins), sensors, solar cells, supercapacitors, and other sectors have garnered significant attention [7]. Currently, self-healing electrodes with self-repairing capabilities similar to human skin are necessary to improve durability [8]. These extraordinary qualities enable the device to work with long-term performance despite damage to the electrode such as scratching, cracking, and mechanical cutting [1].

A variety of materials for self-healing have been extensively studied, including ceramics [9, 10], concrete materials,[11, 12] and metals[13].However, most of these materials require complex preparation procedures and harsh self-healing conditions (such as high temperatures or toxic solvents), and they typically only exhibit a small number of self-healing cycles. Diels–Alder reactions, Michael additions, metal–ligand interactions (such as terpyridine metal complexes), ionic contacts, π–π interactions, and hydrogen bonding are among the bonds that are accessible in these materials throughout the healing process [3].

The conductivities of earlier self-healing electrodes made of hydrogels and polymers are comparatively low (< 700 S/cm) [14, 15]. Additionally, because of the inherent mechanical characteristics of hydrogels and polymers, the majority of self-healing electrodes have relatively low strengths (< 1 MPa)[15]. The electrode may be readily distorted and constrained in everyday applications due to its weak mechanical qualities. Consequently, the need for highly conductive and potent self-healing substances that can restore damaged electrical channels and maintain their electrical properties over time has arisen. Nanomaterials unique functions and huge surface area have led to recent demonstrations of their enormous potential in promoting self-healing[16-22].The healing process is facilitated by the enormous surface area, numerous functional groups, and unique features of nanomaterials found in electrodes.

2.0 NANOMATERIALS IN SELF-HEALING ELECTRODES

Nanomaterials are fascinating because they have the potential to generate novel and inventive products in a variety of fields [23]. Freestanding nano-objects (such as nanoparticles and carbon nanotubes), materials with nano-sized holes (such as porous films), and other types of materials with a variety of different nanoscale structures (such as nanometer-thick layered structures) are all examples of nanomaterials [24].The study of matter at an extremely small scale, typically between 1 and 100 nm, is a burgeoning area in nanotechnology. Nanotechnology has the potential to usher in the next wave of scientific and engineering innovation, and the possibilities are limitless. The next generation of nanomaterials will be stronger, lighter, and longer lasting than the materials currently utilized in buildings, bridges, airplanes, and automobiles.

2.1 Nanomaterials Increase the Efficiency of External Stimuli in Self-Healing.

External stimuli like heat, light, and magnetic fields supply activation energy for the creation of covalent bonds or intermolecular interactions in non-autonomous self-healing. By converting laser irradiation to heat, the unique features of nanomaterials such as surface plasmon resonance and infrared (IR) absorption can considerably boost the efficiency of external stimuli in a self-healing process. Graphene nanosheets and silver nanowires, for example, were utilized in polyurethane to activate the Diels-Alder healing process after IR irradiation [25, 26].

2.2 Nanomaterials Promote Intramolecular Interaction in Self-Healing Electrodes.

Incorporating nanomaterials into self-healing systems results in increased interfacial surface area, improved electrical and mechanical properties, greater response to external stimuli, and increased electromagnetic energy conversion efficiency to heat [27]. Nanomaterials have a huge surface area to attach functional groups that promote self-healing via covalent bonds or intermolecular interactions. Because of its strong mechanical properties and surface functional groups (e.g. carboxylate and hydroxyl), carbon nanotubes (CNTs), graphene, and graphene derivatives such as graphene oxide (GO) have been widely studied in self-healing. CNTs and GO are often functionalized by changing carboxylic acid groups on their surfaces to more reactive acyl chloride groups using thionyl chloride.

2.3 Nanomaterial Surfaces and Interfaces Regulate Self-Healing Electrodes

Surfaces and interfaces are commonly acknowledged to dominate and influence the properties of nanomaterials as particle size decreases. The chemical and physical properties of these surfaces and interfaces, however, are frequently not measured or reported. Surface scientists have learned a lot about the behavior of surfaces during the last 40 years, including the importance of planned and accidental surface layers. Understanding and controlling the characteristics of nanoparticles and other nanomaterials requires the same rigor as understanding the chemistry of other surfaces. The electrical properties of Si nanowires, for example, are strongly reliant on the nature of the surroundings and the wire surface [28].

3.0 SELF-HEALING MECHANISM

A self-healing mechanism displays the ability to recover functioning or repair itself when damaged by utilizing resources that are typically available [29]. Several self-healing mechanisms for electrodes that have been discovered and reported can be divided into two broad groups based on the mechanism: (i) extrinsic self-healing via embedded healing agents; and (ii) internal self-healing via reversible bonds (Figure 1).

3.1 Extrinsic (Autonomous) Self-Healing

The extrinsic self-healing mechanism, also known as the autonomous healing mechanism (Figure 1b), involves the dispersion of microcontainers, such as hollow fibers, microcapsules, and microvascular networks, filled with the mending agent inside the polymer matrix. The microcontainers' shell wall ruptures upon damage, releasing the healing agent to mend the micro- and small-sized cracks at the damage site. The flow and incorporation of healing agents in micro-containers, as well as their shape, size, and distribution pattern, are examples of structural and dynamic elements that affect the materials' ability to heal and their ability to perform self-healing.

I. Capsule-Based Self-Healing

The capsule-based self-healing phenomena arises as a result of an interaction between a microencapsulated healing agent and a catalyst within an epoxy matrix [30]. If a crack forms on the electrode matrix that may be immediately damaged, the microcapsules will rupture instantly, allowing the healing agent to reach the crack via capillary action. This action will cause the healing agent disseminated in the matrix to polymerize and plug the fracture, preventing future crack growth. This healing process occurs within the structural composite electrode matrix and does not require external stimulation [31].Micro or nanocapsules have also been utilized to initiate the self-recovery process in polymers. These capsules rupture in the matrix during self-healing and heal the damaged surface or area [32].

II. Vascular Self-Healing System

Vascular self-healing works by releasing microencapsulated particles of repair resin (hardener/healing agents) into the damaged area when the material is damaged. The technique is based on a polymeric matrix with refillable channels. It appears that numerous healing cycles are getting closer thanks to these refillable conduits, which can administer resins in an additional way. This self-healing technology relies heavily on the channels, which serve as both structural reinforcement and repair resin carriers.

3.2 Intrinsic (Non-Autonomous) Self-Healing

The intrinsic self-healing technique (Figure 1c) solves the problem of repetitive healing. This is a non-autonomous technique in which reversible crosslinks are introduced into the polymer matrix, which activates the healing mechanism when exposed to environmental stimuli (such as light, heat, pH, and moisture, among others). Because of the reversible chemical connections, the same injured spot can be healed numerous times. Diels Alder (DA) reactions are thermally reversible and are widely utilized to generate a wide range of self-healing thermosetting polymers. Furan and maleimide are the two most commonly used functional groups that act as diene and dienophile in Diels Alder reactions. The formation of DA crosslinks occurs at lower temperatures because of the DA reaction.

3.3 Role of Nanomaterials in Self-Healing Mechanism

The incorporation of carbon nanotubes into nanomaterials may result in reversible hydrogen bonding interactions in electrodes [33]. As a result, the self-healing phenomena is dependent on damage repair via bond formation. Aside from physical interactions, functional carbon nanotubes may form covalent connections with electrodes[34]. Also, depending on functionalities, carbon nanotube may act as an electron donor or acceptor in relation to electrodes for the formation of covalent bonding[34].

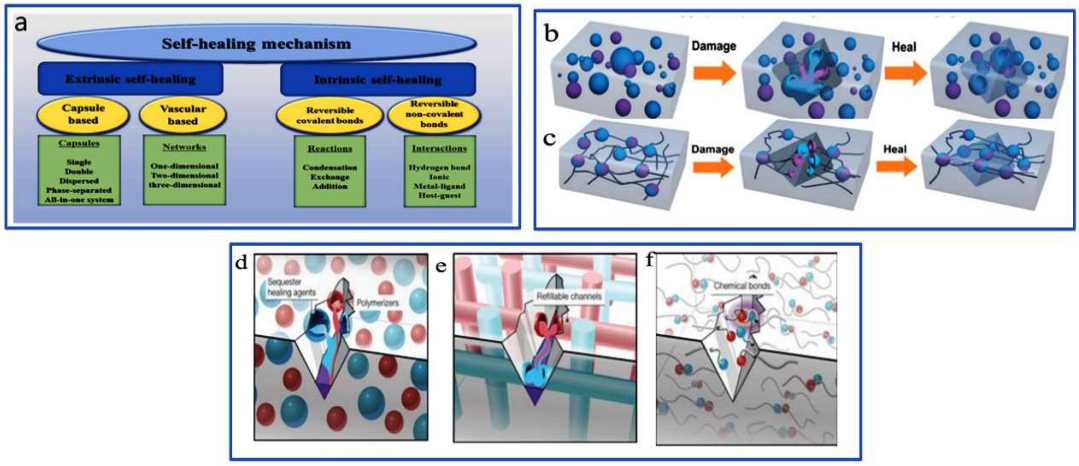


Figure 1: (a) Schematic representation of self-healing mechanisms adapted from [4]**(b)** Extrinsic self-healing mechanism **(c)** Intrinsic self-healing mechanism adapted from[35] (**d)** Capsule based self-healing agent **(e)** Vascular self-healing agent **(f)** Intrinsic self-healing agent retrieved from [30]

4.0 CHARACTERIZATION TECHNIQUES

The characterization of nanomaterials is an important step in understanding the self-healing mechanism and its applications. This section focuses on the many ways for characterizing nanomaterials used in self-healing electrodes. Because of the nanoscale size of the sample, deep structural characterization of nanomaterials is difficult; in reality, nanoparticles are made up of only a few atoms, and more conventional characterization techniques may be ineffective. As a result, new techniques for nanomaterial characterization are needed to comprehend the relationship between changes in atomic ordering, modifications, and (degradation of) performance [36].Characterization techniques, when utilized on electrodes after cycling and/or postmortem, are critical to improving battery performance. They can identify which failure mechanism is at work and provide solutions to solve it. Electrode mixtures (binder, active material, electron conductor) are frequently so complicated that a single spectrum, no matter how precise, might lead to misinterpretation.

i Field Emission Scanning Electron Microscopy (FESEM) Analysis

In this technique, an electron beam from an electron cannon is directed toward the sample holder. While the electron gun is positioned on top of the device, a vacuum is established in the chamber to direct the electron beam to the incident material. The path of the electron beam in the instrument is controlled by lenses and an electromagnetic field. When an accelerated electron beam strikes a sample, some of it is back scattered, some is passed through the sample, and some puts off secondary electrons. These dispersed and secondary electrons are tracked by the detector. Finally, the morphology of the sample can be recorded using a computer [24]

ii Auger Electron Spectroscopy

AES, as it is often defined, involves an incoming electron beam with a spatial resolution that can occasionally be utilized to collect data on individual nanomaterials. Because AES involves electron excitation, concerns of electron backscattering and transmission through a particle mean that certain additional sections of the sample may be stimulated to produce Auger electrons, limiting the true spatial resolution[37].When collecting AES data from a feature detected in a scanning electron image available in an AES instrument, analysts have a propensity to presume that the entire signal is generated simply from the area where the electron beam strikes. When an electron beam passes through a nanoparticle or other nanosized structure below or into the surrounding material, Auger signals are produced and detected from both the nanofeature and the surrounding region. When the possible difficulties are recognized, AES can be highly effective in delivering information about nanostructured materials, and it has proven especially valuable when combined with other methods [24].

iii Scanning Probe Microscopy

Unlike other surface analysis tools, scanning probe microscopy's (SPM) nano-characterization credentials are generally acknowledged, and there are several types of SPM-based methods: scanning tunneling microscopy (STM) and Atomic Force Microscopy (AFM) are the most common examples. AFM can image/visualize nanoparticles spread on a flat surface in three dimensions. It can also give qualitative and, in some situations, quantitative information on nanoparticle physical parameters such as size, shape, surface texture, and roughness. AFM-generated images can be utilized to derive particle-size distributions and even particle volumes with caution in dealing with probable tip artifacts. Although most high-value nanoparticle tests are performed on isolated particles on flat surfaces, attempts are being made to broaden the range of applicability [24].Because AFM devices are relatively

inexpensive, numerous research groups have been able to creatively expand their applicability. Individual nanomaterials (or molecules) can be measured in their interactions with a flat surface or with other nanoparticles using nanoparticles (or molecules) attached to scanning probe tips [38].

iv Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique that measures the absorption of electromagnetic radiation at wavelengths ranging from 4000 to 400cm^{-1}. It is a technique for acquiring an infrared spectrum of the absorption or emission of a solid, liquid, or gas. When a molecule absorbs IR light, its dipole moment changes, making it IR active. A recorded spectrum displays the location of bands associated with the type and strength of a bond, as well as certain functional groups, providing information about interactions and molecular structures [24].

***v*. Brunauer-Emmett-Teller (BET) Analysis**

Nitrogen is commonly utilized in BET surface area analysis since it is generally available in high purity and interacts extensively with the majority of materials. The surface is chilled with liquid nitrogen to achieve detectable levels of adsorption due to the generally poor interaction between gaseous and solid phases [24].

vi. Ultraviolet-Visible Spectroscopy Analysis

UV/Vis spectroscopy (UV/Vis) is a low-cost characterization technique that is often employed in the research of nanomaterials. It compares the intensity of light reflection from a sample to the intensity of light reflection from a reference material. The optical absorbance spectra are measured to determine the generation of NPs. UV-Vis spectroscopy offers information about the sample's transmission and absorption properties [23].

vii. X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) is a popular technique for characterizing nanomaterials. It also provides chemical information for elemental and phase analysis. X-ray diffraction (XRD) is a critical technique for evaluating a wide range of materials, including fluids, powders, and crystals [39].

viii. Transmission Electron Microscopy (TEM) Analysis

The TEM device is often used for nanomaterial analysis. Because TEM is based on the principle of electron transmission, it may provide information on bulk materials at magnifications ranging from extremely low to high. This method is used to investigate the diverse morphologies of nanomaterials..

ix. Raman Spectroscopy

Raman spectroscopy is a non-destructive, qualitative, and quantitative technique that uses vibrational modes to investigate chemical structure, phase, polymorphic, crystallinity, and molecular interactions. In this technique, accidental light from a laser source falls on sample molecules, where it interacts with chemical interactions and inelastic scattering to disclose the identification of the molecules. Each peak in a Raman spectrum corresponds to a certain vibration mode of a bond, such as C-C, C-H, C=C, N-O, and so on[40].

5.0 APPLICATIONS

Self-healing electrodes have gained extensive attention in recent decades, inspired by the independent repair of organisms following injury. Massive efforts have gone into the design and synthesis of innovative self-healing materials that satisfy the needs of varied applications. Healing agents can be stored in a variety of materials, including polymers, ceramics, concrete, and metals. This method necessitates complex healing agent encapsulation and dispersion processes [41].

Self-healing electrode nanocomposites have shown interesting properties as new sustainable, safer, and longer lasting materials for applications such as energy storage devices,[42-46] flexible electronics [47, 48], actuators [49], structural materials and corrosion protecting coatings [50].

5.1 As Energy Storage Devices

Electrochemical energy storage and conversion devices, such as batteries, fuel cells, supercapacitors, H_2O/CO_2 electrolysis, and so on, have been playing an important role in the global low/zero-carbon energy strategy for sustainable development, as well as meeting the growing usage demands across a wide range of applications, from mobility to the power sector and behind the meter applications [51, 52]. However, the performance of some devices are still insufficient in terms of their capacity, operational stability, life cycle, stability, and efficiency.

Self-healing electrochemical energy devices are made up of materials that recognize and repair some or all internal or external damages on their own. The capacity to self-heal is a feature of next-generation smart energy storage devices because to the astuteness of its functions after mechanical, thermal, or radiation damages while keeping its original integrity [53]. The development of self-healing electrode materials has been a primary focus of work to attain success.Some self-healing materials, for example, have progressed from relying on microencapsulated agents or micro-hollow fibers to intrinsic healing at the molecular level with repeated reversible healing [54].

Recently, reversible dynamic bonds such as hydrogen bonds, [48] dynamic metal–ligand interaction,[55] hydrophobic interaction,[56] and dynamic covalent boroxine bonds[57]. Despite advancements, only a few types of self-healing materials have been successfully used in ESDs. This is due to the fact that extra conditions must be met when self-healing materials are used in ESDs, such as mechanical, electrical, and self-healing characteristics, electrochemical and thermal stability, and processability [58].

5.1.1 Lithium-Ion Batteries (LIBS)

LIBs have been used to power a variety of devices, including portable gadgets, implantable medical devices, electric cars, and stationary power plants. To obtain high energy capacity and longer cycling life, further development for high-performance has emphasized the exploration of innovative materials such as silicon and its composites, as well as metallic alloys. Nonetheless, electrochemical reactions in batteries cause structural changes due to mechanical micro-cracks throughout the charge and discharge operations, resulting in insufficient cycling life [59-61].Lithium-ion batteries (LIBs) have dominated the secondary battery market due to benefits such as high energy density (150-250Wh kg^{-1}), high voltage, extended cycle life, and minimal self-discharge. They are commonly utilized in a variety of portable electronic devices (including notebook computers, mobile phones, and digital cameras) as well as electric vehicles [58].

The use of silicon (Si) for high capacity anodes of lithium-ion batteries has been hampered by the lithiation-induced volume change in the electrode caused by fragmentation and fracture, particularly during the first cycle [62, 63]. Analyzing the morphological and structural differences in Si to fully understand the self-healing process of Si-Al anodes was one way to improve capacity loss and cycle performance in Si anodes.Bhattacharya *et al*[62] used micro-Raman spectroscopy and in-situ optical microscopy to investigate self-healing Si-Al electrodes. They summarized their findings by stating that the cracks in the Si-Al interface mended at the end of the cycling process and hypothesized that a composite electrode made of Si particles embedded in a ductile phase could improve the electrochemical performance of the batteries.

5.1.2 Supercapacitor (SCS)

Supercapacitors (SCs) are another major family of electrochemical ESDs that have analogous energy storage characteristics to LIBs. They have a high specific power of more than 10,000 W kg^{-1} and a long cycle life of more than 100,000 cycles, making them suitable energy providers for rockets, lasers, and electric vehicles [64].SCs have an energy storage mechanism based on electrical double layers or redox processes. SCs are known for their quick charge and discharge processes, high power density, and long cycling performance. The capacity to self-heal can substantially improve their stability and service life during practical applications.

The aim of self-healing dielectric is to reestablish ionic conductivity. Because of their high ionic conductivity, changeable mechanical properties, and outstanding compatibility with electrode materials, polyelectrolytes are ideal materials for the construction of self-healing electrolytes. Huang *et al*. reported (Figure 2e) a dual crosslinked polyelectrolyte for self-healing SC [65]. As electrodes, polypyrrole (PPy)-deposited CNT paper was used. Polyacrylic acid double-crosslinked hydrogen bonding and vinyl hybrid silica nanoparticles (VSNPs-PAA) were used to create the self-healing polyelectrolyte. Even after 20 healing cycles, the manufactured SC using this polyelectrolyte kept 100% of its capacitance. Lin et al. created a new ferric improved dual physical crosslinking polyelectrolyte (Fe-DPCL), with acrylic acid as the hydrophilic monomer and stearoyl methacrylate as the hydrophobic monomer [66]. The H_2SO_4 in Fe-DPCL had excellent ionic conductivity (>30 mS cm^{-1}), and the entire hydrogel demonstrated good self-healing efficiency and stretchability. Even after the seventh injury, the built SC (Figure 2f) demonstrated good self-healing capabilities and capacitance retention of approximately 86%.

In another study, [46] generated a highly robust, multiresponsive healing polypyrrole-incorporated gold nanoparticle/CNT/poly(acrylamide) (PAM) (GCP@PPy) hydrogel electrode with a hierarchical honeycombed network structure by growing PPy nanoparticles in the GCP framework. The electrode, which was chemically crosslinked with gold nanoparticles, demonstrated high stretchability with an elongation of 2380% and new Au-SR bond-triggered optical and electrical healing with a 94% healing efficiency. A stretchable and real-time omni healable all-gel-state supercapacitor device was assembled as a proof-of-concept demonstration by sandwiching multifunctional GCP@PPy electrodes with a CNT-free GCP (GP) hydrogel electrolyte and then chemically soldering a layer of Ag nanowire (AgNW) film to the hydrogel electrode as the current collector via a combination of spray coating and NIR laser irradiation.

5.1.3 Capacitors

Recently, [67] has reported on the dynamic reconstruction of a nanostructured conductive network. The conductive CNT network was largely located on the top surface of the film after peeling it away from the substrate. They discovered that after the aforesaid embedding process, the resistance of the CNT-network increased 10-fold, most likely due to some inter-penetration of the insulating polymer between the CNTs. They also indicated that doping

the electrode with Au salt could increase its electrical resistance. The author used in situ monitoring to investigate the quantitative damage caused by a razor blade and then compared the effect of different forces (0.54 N) and repeated damage (20 times of a 2 N force) on the CNT electrode material at different time intervals to study the self-healing performance of a CNT electrode.

5.2 As Sensors

Previously, various materials such as metals, conducting polymers, and semiconductors, among others, were employed to fabricate sensors [68, 69]. However, most conventional strain sensors have very little stretchability. Furthermore, because it is less sensitive, it is less acceptable for usage with the human body [70].Stretchability strain sensors can be of several types, depending on aspects such as sensor type, polymer nature, conducting nature of nanomaterials utilized, and fabrication method. Polymer composite-based strain sensors typically have two components: polymer and conductive electrode [71]. By physical strain change, the conductive electrode produces a resistance or capacitance output signal, whereas the polymer provides flexibility and stretching qualities. Furthermore, the polymer component protects the sensor electrode's conducting channel from damage during strain testing. Encapsulating a strain sensor linked to the skin, in general, can aid to avoid direct exposure to bodily fluids and external conditions that could disrupt or interfere with the reception of resistive or capacitive signals [72].

Notably, several studies have been conducted that investigated various nanomaterials such as graphene, carbon black (CB), carbon nanotube (CNT), gold nanowires (AuNWs), silver nanowires (AgNWs), and silver nanoparticles (AgNPs) for the fabrication of strain sensors in order to meet the critical requirement for sensors [73, 74]. Similarly, in recent investigations, several flexible polymers such as polydimethylsiloxane (PDMS), silicone elastomer, rubber, and latex have been employed as the substrate [75].

In addition,[67] used self-healing electrodes that were manufactured as active components in devices. In particular, a wearable self-healing ECG sensor with three electrodes was fabricated (Figure 3av). The sensor was securely fastened to the human arm (Figure 3b). The recovery of real-time cardiac signal recordings (Figure 3avi) demonstrated the damage recovery of the self-healing electrode. The authors discovered that the signal might restore to its usual baseline within seconds of being damaged. They also mentioned that EMG measurements are doable with these devices. They also created a capacitive strain sensor made of PDMS-MPU0.4-IU0.6 dielectric (thickness 500 m) sandwiched between the top and bottom self-healing electrodes. They discovered that even after damaging the strain sensor (Fig. 3avii), it maintained reliable strain sensing performances within the strain range of human epidermis (25% strain)1, thanks to material homogeneity and a robust interface between the self-healing electrode and dielectric via H-bonding (Figures 3avii and 3aviii). They next inserted a notch into the strain sensor to analyze any fracture propagation that occurred as a result of stretching (Figure 3aix). Surprisingly, it could be extended to 50% strain without additional crack propagation.

One of the most promising body temperature sensing technologies is conductive materials that can sense temperature by thermoresistive behavior produced by thermal-induced charge carrier scattering or charge transport enhancement [76]. The resistance of the thermoresistive temperature sensor material should not fluctuate owing to mechanical stress since resistance changes produced by various curved surfaces and human body movements make acquiring correct signals challenging.

Again, in another study, [77] used conductive silver nanoparticles (AgNPs) on a polydimethylsiloxane (PDMS) substrate to create resistive-type strain sensors. A drop-casting process was used to create sandwich-structured-like

PDMS covered AgNPs strain sensors (Ag-PDMS) and AgNPs modified PDMS composite strain sensors (Ag@PDMS). The effect of AgNPs loading with PDMS at 0.20 wt%, 0.25 wt%, and 0.30 wt% was explored, and electromechanical performance of Ag-PDMS and Ag@PDMS composite strain sensors was compared. The gauge factor of a strain sensor manufactured with 0.25 wt% AgNPs loading in PDMS (Ag0.25@PDMS) composite revealed a gauge factor of 10.08 with a strain range of 70%, demonstrating fast time response, good stretchability, durability, and repeatability. The Ag0.25@PDMS composite strain sensor developed in this study can detect finger motion, indicating that it can be used for human body motion capture and other highly sensitive strain-sensing applications.

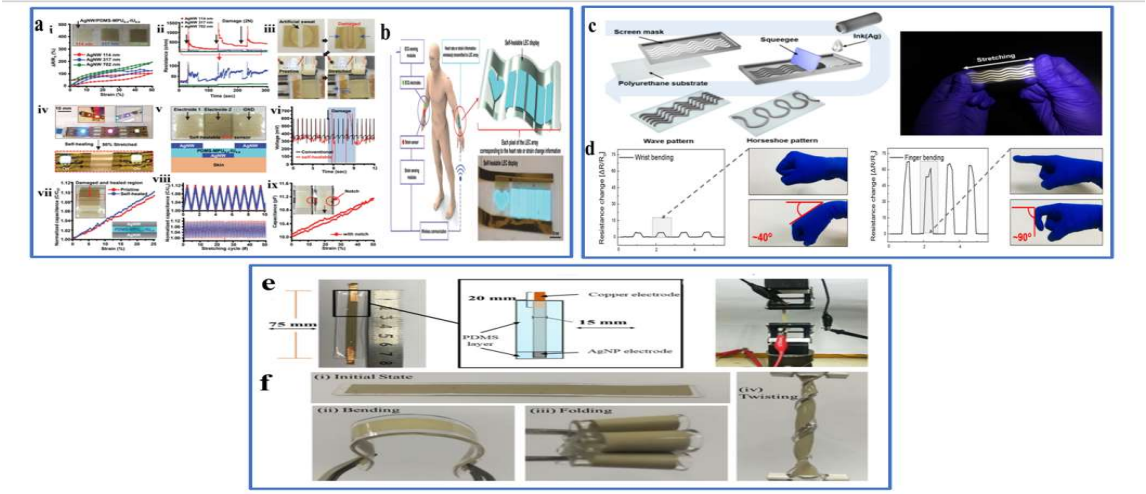


Figure 3:**illistrations of Recent self-healing electrodes used as sensors**

(a): Plot of relative resistance change of AgNW with three different thicknesses as a function of strain ii, The top frame displays a plot of resistance of a damage-resistant electrode with varying AgNW thickness as a function of time while making three successive cuts (2 N each), while the bottom frame shows a magnified low-resistance range. **(b):** Image showing attachment of the fabricated ECG sensor attached to the human arm Adapted from [67]**(c):** Schematic screen-printing process for patterning of wavy and horseshoe-shaped Ag NP electrodes on stretchable polyurethane substrate and Stretched wavy patterned Ag NP electrodes on polyurethane substrate **(d)**: Image showing the Ag NP-based strain sensor on a human wrist and human fingers which was bent about 40^0 and about 90^0which is about 20% and 40%strain respectively Adapted from [78].**(e)**: optical photograph, dimension, tensile measurement of strain sensors **(f)**: picture of strain sensors in (i) initial, (ii) bending, (iii) folding, and (iv) twisting states Adapted from [77]

5.3 Electronic Skin

Electronic skin (E-skin) is an electronic system that may replicate human skin features such as stretchability, self-healing ability, and varied sensing capability, and can convert diverse environmental inputs such as pressure, humidity, or deformation into electrical impulses [79, 80]. E-skin has a wide range of potential applications, including soft robotic systems, wearable electronics, robotic prosthetics, and artificial intelligence [81-83].Self-healing capability may be a viable method for improving the stability and lifespan of e-skin.

Cao *et al*. utilized an amorphous and chemically compatible polymer to construct a stretchy and self-healing e-skin for aquatic conditions (Figure 4a). [84]The e-skin's ionic conductivity can be adjusted to 103 S cm^{-1}. Even at a high of 2000%, the overall functioning of the gadget remains normal. Because of its extremely reversible ion-dipole interactions, e-skin can mend itself in either a dry or wet environment. After ten cuts, the healing efficiency of electrical conductivity was 90.7%. The e-skin was extremely responsive to touch, pressure, and strain, revealing its prospective applications' sensory capabilities. A primary goal in the development of e-skin is to achieve real tactile perception of emulated natural skin.

Pan *et al*. described a bionic tactile plastic e-skin based on a composite hydrogel with exceptional super-stretchability (>5000%), a fast self-healing rate (3 s, 95.73%), and great sensitivity when detecting strain (GF = 14.14). The hydrogel-based e-skin can detect human electrocardiogram and electromyography signals (Figure 4b), which has potential uses in real-time health care and prosthetics [85].

The researchers also demonstrated that the LCGO/AgNW electrode can be employed in an electronic circuit for devices like light-emitting diodes (LEDs) (figure 4c). As a result of these findings, the composite may be employed as an artificial electronic skin (figure 4d) to sense ambient factors such as compression and temperature. This self-healing artificial electronic skin has the potential to be used in human condition monitoring and robotic sensing systems electrode

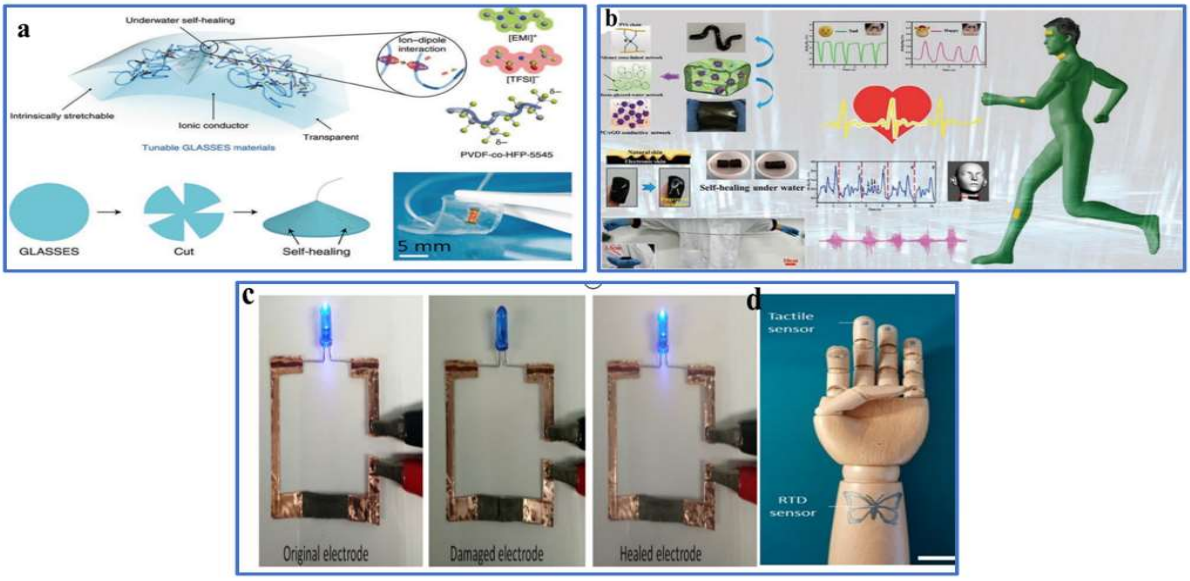


Figure 4: Representation of recent self-healing electrodes used in electronic skin

(a) A gel-like, aquatic, stretchable, and self-healing e-skin retrieved from [84]**(b)** A hydrogel-based self-healing e-skin Retrieved from [85]**(c)**Photographs of the electrode within a circuit with an LED before and after breaking and after healing **(d)** An optical image of the artificial e-skin showing e tactile sensor and resistance temperature detector were located on the fingers and wrist, respectively retrieved from [1]

5.4 Other Applications

In a recent study,[86] designed a semi-transparent polytetrafluoroethylene (PTFE)/AgPdCu (APC)-PTFE-based superlattice electrode by alternately sputtering very thin APC-PTFE hybrid layers over a polyurethane (PU) substrate at ambient temperature (figure 5a). Controlling the PTFE thickness and the number of layers of the stacked superlattice maximized the electrical and mechanical properties of the superlattice electrodes. The best PTFE/APC-PTFE/PTFE/APC-PTFE/PTFE superlattice electrode (figure 5b) has a sheet resistance of 8.5 Ohm/square and a strong conductivity even at 100% strain. The 3-dimensional conductive APC network structure in the PTFE polymer matrix is responsible for the superlattice electrode's exceptional mechanical stretchability. Furthermore, applying external strain to the superlattice electrode caused a shift in optical transmittance, which might be employed for optical switching in stretchy electronics. Stretchable electroluminescent devices, stretchable thin film heaters, and wearable temperature sensors can all be made with superlattice electrodes (figure 5c). Their successful demonstration of stretchy devices using very stretchable superlattice electrodes proved the potential of this manufacturing approach for usage in next-generation stretchable and wearable electronics.

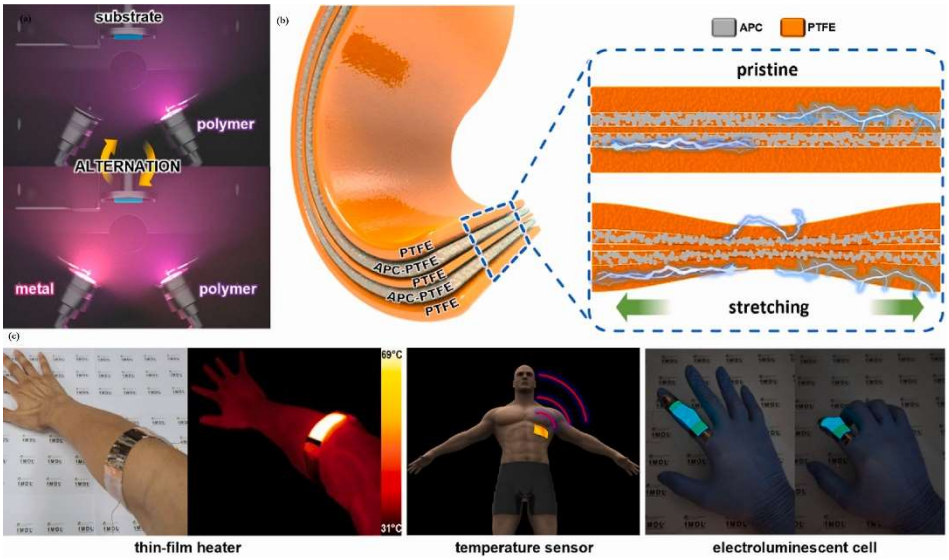


Figure 5: Structure and potential uses of superlattice electrodes.

(a) Illustration of the superlattice electrode fabrication procedure employing a multi-cathode sputtering device**. (b)**Superlattice electrode structure with PTFE/APC-PTFE/PTFE/APC-PTFE/PTFE. **(c)** Promising superlattice electrode applications include a stretchable heater, stretchable temperature sensors, and flexible electroluminescent cells Adapted from [86]

6.0 CHALLENGES AND LIMITATIONS

6.1 Characterization Challenges

Many types of nanomaterials are difficult to characterize, which frustrates researchers and engineers who want to use them for biomedical, energy, or other applications, as well as regulatory bodies that need to understand their impact on human health and the environment [87].Incomplete characterization has an impact on various elements of nanomaterials research, including the repeatability of research results, the process of scaling production to suit

industry needs, and risk assessment for human health and the environment. Despite the intrinsic intention of most research groups to do high-quality research, there are various reasons why thorough nanomaterial characterization is not realized. First, nanoparticles provide certain unique preparation and analysis challenges that are unfamiliar to several of the fields and researchers who are currently participating in nanomaterials research. Second, because the subject is multidisciplinary, not every research team has access to the variety of characterization techniques required to acquire potentially valuable information. Third, the variety of information required to comprehend nanomaterials may necessitate the use of tools and data analysis techniques that are outside the scope of the research teams' competence, resulting in less-than-optimal application of critical procedures and/or an insufficient understanding of the data provided. Nanoscience and nanotechnology are still in their infancy, and researchers are only now beginning to appreciate some of the limitations of analytical methodologies that have been effectively employed in other domains [88].

7.0 CONCLUSION

In this study, we focused on the latest developments in nanomaterial-based self-healing electrodes and their recent uses. Electrodes with self-healing properties can repair internal damage and restore electrical conductivity, much like human skin. Nanomaterials are critical to self-healing systems because of their improved mechanical and electrical properties, increased interfacial surface area, increased reactivity to external stimuli, and increased electromagnetic energy conversion efficiency. The development of nanomaterials has allowed for the creation of flexible, thin, strong, and secure electrodes. These electrodes are used in many different fields such as electronic skins, sensors, solar cells, and supercapacitors. Nanomaterials have demonstrated significant potential in promoting self-healing, enabling devices to operate at peak efficiency for prolonged periods of time even in the face of damage, owing to their unique characteristics and large surface area. Reports of self-healing nanomaterials are still few, though. Under severe circumstances, the stability of nanostructures is restricted by inadequate characterization and elevated interface-to-volume ratios.

Conflict of Interest

The authors have no known personal conflicts of interest.

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References

[1.] Sim, H.J., et al., Self-healing electrode with high electrical conductivity and mechanical strength for artificial electronic skin. ACS applied materials & interfaces, 2019. **11**(49): p. 46026-46033.

[2.] Gai, Y., H. Li, and Z. Li, Self-healing functional electronic devices. Small, 2021. **17**(41): p. 2101383.

[3.] Cheng, H., et al., Self-healing graphene oxide based functional architectures triggered by moisture. Advanced Functional Materials, 2017. **27**(42): p. 1703096.

[4.] Ezeigwe, E.R., et al., A review of self-healing electrode and electrolyte materials and their mitigating degradation of Lithium batteries. Nano Energy, 2021. **84**: p. 105907.

[5.] Kim, D.-H., et al., Epidermal electronics. science, 2011. **333**(6044): p. 838-843.

[6.] Lei, Z., et al., A bioinspired mineral hydrogel as a self-healable, mechanically adaptable ionic skin for highly sensitive pressure sensing. Advanced Materials, 2017. **29**(22): p. 1700321.

[7.] Zhang, Q., et al., Review of recent achievements in self-healing conductive materials and their applications. Journal of Materials Science, 2018. **53**(1): p. 27-46.

[8.] Wang, S., et al., Highly stretchable and self-healable supercapacitor with reduced graphene oxide based fiber springs. Acs Nano, 2017. **11**(2): p. 2066-2074.

[9.] White, S.R., et al., Autonomic healing of polymer composites. Nature, 2001. **409**(6822): p. 794-797.

[10.] Cho, S.H., S.R. White, and P.V. Braun, Self-healing polymer coatings. Advanced Materials, 2009. **21**(6): p. 645-649.

[11.] Zwaag, S., Self healing materials: an alternative approach to 20 centuries of materials science. Vol. 30. 2008: Springer Science+ Business Media BV Dordrecht, The Netherlands.

[12.] Ando, K., et al., Crack healing behaviour and high-temperature strength of mullite/SiC composite ceramics. Journal of the European Ceramic Society, 2002. **22**(8): p. 1313-1319.

[13.] Hautakangas, S., et al., Self-healing of deformation damage in underaged Al–Cu–Mg alloys. Scripta Materialia, 2008. **58**(9): p. 719-722.

[14.] Huynh, T.P. and H. Haick, Self-healing, fully functional, and multiparametric flexible sensing platform. Advanced Materials, 2016. **28**(1): p. 138-143.

[15.] Darabi, M.A., et al., Skin-inspired multifunctional autonomic-intrinsic conductive self-healing hydrogels with pressure sensitivity, stretchability, and 3D printability. Advanced Materials, 2017. **29**(31): p. 1700533.

[16.] Li, F., M. Du, and Q. Zheng, Dopamine/silica nanoparticle assembled, microscale porous structure for versatile superamphiphobic coating. Acs Nano, 2016. **10**(2): p. 2910-2921.

[17.] Qin, J., et al., Cellulose nanofiber/cationic conjugated polymer hybrid aerogel sensor for nitroaromatic vapors detection. Journal of materials science, 2017. **52**: p. 8455-8464.

[18.] Bhattacharya, S., et al., Fluorescent self-healing carbon dot/polymer gels. ACS Nano 13: 1433–1442. 2019.

19.] Shikder, M.R.A., et al., Plastic recovery and self-healing in longitudinally twinned SiGe nanowires. Nanoscale, 2019. **11**(18): p. 8959-8966.

[20.] Li, G., et al., Graphene based self-healing materials. Carbon, 2019. **146**: p. 371-387.

[21.] Kim, H.G., et al., Analysis of defect recovery in reduced graphene oxide and its application as a heater for self-healing polymers. ACS applied materials & interfaces, 2019. **11**(18): p. 16804-16814.

[22.] Xing, L., et al., Self-healable polymer nanocomposites capable of simultaneously recovering multiple functionalities. Advanced Functional Materials, 2016. **26**(20): p. 3524-3531.

[23.] Kumari, S., et al., A comprehensive review on various techniques used for synthesizing nanoparticles. Journal of Materials Research and Technology, 2023.

[24.] Baer, D.R., et al., Surface characterization of nanomaterials and nanoparticles: Important needs and challenging opportunities. Journal of Vacuum Science & Technology A, 2013. **31**(5).

[25.] Qin, H., et al., Dynamic Au-thiolate interaction induced rapid self-healing nanocomposite hydrogels with remarkable mechanical behaviors. Chem, 2017. **3**(4): p. 691-705.

[26.] Ji, S., et al., Visible-light-induced self-healing diselenide-containing polyurethane elastomer. Advanced Materials, 2015. **27**(47): p. 7740-7745.

[27.] Zhai, L., A. Narkar, and K. Ahn, Self-healing polymers with nanomaterials and nanostructures. Nano Today, 2020. **30**: p. 100826.

[28.] Jie, J., et al., Surface-Dominated Transport Properties of Silicon Nanowires. Advanced Functional Materials, 2008. **18**(20): p. 3251-3257.

[29.] Kausar, A., et al., Self-Healing Nanocomposites—Advancements and Aerospace Applications. Journal of Composites Science, 2023. **7**(4): p. 148.

[30.] Mercy, J.L. and S. Prakash, Self healing composite materials: A review. International Journal of ChemTech Research, 2016. **9**(3): p. 316-324.

[31.] JE, P.C., et al., Manufacturing challenges in self-healing technology for polymer composites—a review. Journal of Materials Research and Technology, 2020. **9**(4): p. 7370-7379.

[32.] Kopeć, M., et al., Self-healing epoxy coatings loaded with inhibitor-containing polyelectrolyte nanocapsules. Progress in Organic Coatings, 2015. **84**: p. 97-106.

[33.] Du, R., et al., Hierarchical hydrogen bonds directed multi-functional carbon nanotube-based supramolecular hydrogels. small, 2014. **10**(7): p. 1387-1393.

[34.] Punetha, V.D., et al., Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene. Progress in Polymer Science, 2017. **67**: p. 1-47.

[35.] Yue, H., Z. Wang, and Y. Zhen, Recent advances of self-healing electronic materials applied in organic field-effect transistors. ACS omega, 2022. **7**(22): p. 18197-18205.

[36.] Greco, G., Characterization of Nanomaterials in Electrochemistry. 2015: p. 1-23.

[37.] Powell, C.J., Effect of backscattered electrons on the analysis area in scanning Auger microscopy. Applied surface science, 2004. **230**(1-4): p. 327-333.

[38.] Vakarelski, I.U., et al., Nanoparticle—terminated scanning probe microscopy tips and surface samples. Advanced Powder Technology, 2007. **18**(6): p. 605-614.

[39.] Muhammad, W., et al., Optical, morphological and biological analysis of zinc oxide nanoparticles (ZnO NPs) using Papaver somniferum L. RSC advances, 2019. **9**(51): p. 29541-29548.

[40.] Paras, et al., A Review on Low-Dimensional Nanomaterials: Nanofabrication, Characterization and Applications. Nanomaterials, 2022. **13**(1): p. 160.

[41.] Zhu, D.Y., M.Z. Rong, and M.Q. Zhang, Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation. Progress in Polymer Science, 2015. **49**: p. 175-220.

[42.] Banerjee, S., et al., Photoinduced smart, self-healing polymer sealant for photovoltaics. ACS applied materials & interfaces, 2015. **7**(3): p. 2064-2072.

[43.] Zhao, Y., et al., A self-healing aqueous lithium-ion battery. Angewandte Chemie International Edition, 2016. **55**(46): p. 14384-14388.

[44.] Rao, J., et al., All-fiber-based quasi-solid-state lithium-ion battery towards wearable electronic devices with outstanding flexibility and self-healing ability. Nano Energy, 2018. **51**: p. 425-433.

[45.] Whiteley, J.M., et al., Ultra-thin solid-state Li-ion electrolyte membrane facilitated by a self-healing polymer matrix. Advanced materials, 2015. **27**(43): p. 6922-6927.

[46.] Chen, C.R., et al., A highly stretchable and real-time healable supercapacitor. Advanced materials, 2019. **31**(19): p. 1900573.

[47.] Someya, T., Z. Bao, and G.G. Malliaras, The rise of plastic bioelectronics. Nature, 2016. **540**(7633): p. 379-385.

[48.] Oh, J.Y., et al., Intrinsically stretchable and healable semiconducting polymer for organic transistors. Nature, 2016. **539**(7629): p. 411-415.

[49.] Qin, H., et al., Anisotropic and self-healing hydrogels with multi-responsive actuating capability. Nature communications, 2019. **10**(1): p. 2202.

[50.] Scheiner, M., T.J. Dickens, and O. Okoli, Progress towards self-healing polymers for composite structural applications. Polymer, 2016. **83**: p. 260-282.

[51.] Zhang, H., W. Lu, and X. Li, Progress and perspectives of flow battery technologies. Electrochemical Energy Reviews, 2019. **2**: p. 492-506.

[52.] Dunn, B., H. Kamath, and J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices. Science, 2011. **334**(6058): p. 928-935.

[53.] Ullah, H., et al., The potential of microencapsulated self-healing materials for microcracks recovery in self-healing composite systems: A review. Polymer reviews, 2016. **56**(3): p. 429-485.

[54.] Hu, R., et al., A highly stretchable, self-healing, recyclable and interfacial adhesion gel: preparation, characterization and applications. Chemical Engineering Journal, 2019. **360**: p. 334-341.

[55.] Lai, J.-C., et al., Thermodynamically stable whilst kinetically labile coordination bonds lead to strong and tough self-healing polymers. Nature communications, 2019. **10**(1): p. 1164.

[56.] Urban, M.W., et al., Key-and-lock commodity self-healing copolymers. Science, 2018. **362**(6411): p. 220-225.

[57.] Lai, J.C., et al., A stiff and healable polymer based on dynamic-covalent boroxine bonds. Advanced Materials, 2016. **28**(37): p. 8277-8282.

[58.] Mai, W., et al., Self-healing materials for energy-storage devices. Advanced Functional Materials, 2020. **30**(24): p. 1909912.

[59.] Deshpande, R.D., et al., Liquid metal alloys as self-healing negative electrodes for lithium ion batteries. Journal of the Electrochemical Society, 2011. **158**(8): p. A845.

[60.] Yi, R., et al., Micro-sized Si-C composite with interconnected nanoscale building blocks as high-performance anodes for practical application in lithium-ion batteries. Advanced Energy Materials, 2013. **3**(3): p. 295-300.

[61.] Li, W., X. Sun, and Y. Yu, Si-, Ge-, Sn-based anode materials for lithium-ion batteries: from structure design to electrochemical performance. Small Methods, 2017. **1**(3): p. 1600037.

[62.] Bhattacharya, S. and A.T. Alpas, Self-healing of cracks formed in Silicon-Aluminum anodes electrochemically cycled at high lithiation rates. Journal of Power Sources, 2016. **328**: p. 300-310.

[63.] Li, J., et al., Crack pattern formation in thin film lithium-ion battery electrodes. Journal of The Electrochemical Society, 2011. **158**(6): p. A689.

[64.] Dubal, D.P., et al., Towards flexible solid-state supercapacitors for smart and wearable electronics. Chemical Society Reviews, 2018. **47**(6): p. 2065-2129.

[65.] Huang, Y., et al., A self-healable and highly stretchable supercapacitor based on a dual crosslinked polyelectrolyte. Nature communications, 2015. **6**(1): p. 10310.

[66.] Lin, Y., et al., A physically crosslinked, self-healing hydrogel electrolyte for nano-wire PANI flexible supercapacitors. Chemical Engineering Journal, 2019. **367**: p. 139-148.

[67.] Son, D., et al., An integrated self-healable electronic skin system fabricated via dynamic reconstruction of a nanostructured conducting network. Nature nanotechnology, 2018. **13**(11): p. 1057-1065.

[68.] Chen, H., et al., Self-powered electronic skin based on the triboelectric generator. Nano energy, 2019. **56**: p. 252-268.

[69.] Wolf, M.P., G.B. Salieb-Beugelaar, and P. Hunziker, PDMS with designer functionalities—Properties, modifications strategies, and applications. Progress in Polymer Science, 2018. **83**: p. 97-134.

[70.] Lu, Y., et al., Recent developments in bio-monitoring via advanced polymer nanocomposite-based wearable strain sensors. Biosensors and bioelectronics, 2019. **123**: p. 167-177.

[71.] Xiang, D., et al., Synergistic effects of hybrid conductive nanofillers on the performance of 3D printed highly elastic strain sensors. Composites Part A: Applied Science and Manufacturing, 2020. **129**: p. 105730.

[72.] Shi, G., et al., A multifunctional wearable device with a graphene/silver nanowire nanocomposite for highly sensitive strain sensing and drug delivery. C, 2019. **5**(2): p. 17.

[73.] Ma, Y., et al., Intrinsic Raman signal of polymer matrix induced quantitative multiphase SERS analysis based on stretched PDMS film with anchored Ag nanoparticles/Au nanowires. Chemical Engineering Journal, 2020. **381**: p. 122710.

[74.] Huang, K., et al., Ultrasensitive MWCNT/PDMS composite strain sensor fabricated by laser ablation process. Composites Science and Technology, 2020. **192**: p. 108105.

[75.] Meng, Q., et al., A facile approach to fabricate highly sensitive, flexible strain sensor based on elastomeric/graphene platelet composite film. Journal of Materials Science, 2019. **54**(15): p. 10856-10870.

[76.] Yang, Y. and Z.D. Deng, Stretchable sensors for environmental monitoring. Applied Physics Reviews, 2019. **6**(1).

[77.] Soe, H.M., et al., Development and fabrication of highly flexible, stretchable, and sensitive strain sensor for long durability based on silver nanoparticles–polydimethylsiloxane composite. Journal of Materials Science: Materials in Electronics, 2020. **31**: p. 11897-11910.

[78.] Yoon, S. and H.-K. Kim, Cost-effective stretchable Ag nanoparticles electrodes fabrication by screen printing for wearable strain sensors. Surface and Coatings Technology, 2020. **384**: p. 125308.

[79.] Kang, J., et al., Tough and water-insensitive self-healing elastomer for robust electronic skin. Advanced Materials, 2018. **30**(13): p. 1706846.

[80.] Han, L., et al., Self-healable conductive nanocellulose nanocomposites for biocompatible electronic skin sensor systems. ACS applied materials & interfaces, 2019. **11**(47): p. 44642-44651.

[81.] Benight, S.J., et al., Stretchable and self-healing polymers and devices for electronic skin. Progress in Polymer Science, 2013. **38**(12): p. 1961-1977.

[82.] Ye, G., et al., Dynamic Ag–N bond enhanced stretchable conductor for transparent and self-healing electronic skin. ACS applied materials & interfaces, 2019. **12**(1): p. 1486-1494.

[83.] Peng, W., et al., A direction-aware and ultrafast self-healing dual network hydrogel for a flexible electronic skin strain sensor. Journal of Materials Chemistry A, 2020. **8**(48): p. 26109-26118.

[84.] Cao, Y., et al., Self-healing electronic skins for aquatic environments, Nat. Electron, 2019. **2**(2): p. 75-82.

[85.] Pan, X., et al., A bionic tactile plastic hydrogel-based electronic skin constructed by a nerve-like nanonetwork combining stretchable, compliant, and self-healing properties. Chemical Engineering Journal, 2020. **379**: p. 122271.

[86.] Sim, H.-M., et al., Super-stretchable polymer-AgPdCu superlattice electrodes for high-performance wearable electronics. Composites Part B: Engineering, 2022. **238**: p. 109914.

[87.] Richman, E.K. and J.E. Hutchison, The nanomaterial characterization bottleneck. 2009, ACS Publications.

[88.] Billinge, S.J. and I. Levin, The problem with determining atomic structure at the nanoscale. science, 2007. **316**(5824): p. 561-565.