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Soft materials for wearable supercapacitors

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Abstract

Along with the rapid progress of wearable and portable electronic devices including electrical sensors, flexible displays, and health monitors, there is an ever-growing demand for wearable power sources. Supercapacitors, as a new kind of energy storage device, have received considerable attention for decades due to their high power density, excellent cycling stability, and easy fabrication. To fulfill the demand of wearable power sources, wearable supercapacitors are also further developed and studied. New electrode materials that play a significant role in determining both the wearability and electrochemical performance of wearable supercapacitors are also extensively explored. Herein, the recent progress on wearable soft electrode/electrolyte materials and the structure design strategies for developing wearable supercapacitors are summarized. Additionally, the existing challenges in current technologies and research are highlighted and discussed with the hope of inspiring future studies.

Keywords: Soft materials, electrodes, electrolytes, structure design, wearable supercapacitors

INTRODUCTION

Nowadays, along with the rapid growth of the electronic industry, portable/wearable electronics including health monitors, electronic sensors, and human healthcare equipments are becoming a noticeable technological trend that has experienced rapid growth[1,2]. In this regard, wearable energy storage devices are obviously indispensable parts for portable/wearable electronics[3-5]. The design and fabrication of the power

supply systems with high flexibility and high energy and power densities is needed in current rechargeable energy storage markets. The most applied, Li-ion batteries are not very suitable for portable/wearable electronics due to the issues of rigid and bulky electrode and the toxic Li^+ electrolyte[2]. Additionally, studies also indicated that the heat generated from the commercially available Li-ion batteries would affect biologic tissues and limit their application in portable/wearable electronics[6,7].

In this context, high-performance and functional supercapacitors (SCs), as a kind of newly developed energy storage device, have already been extensively applied to meet the pressing demand for future wearable electronics due to their long-term stability, rapid charge - discharge capability, and temperature tolerance[8,9]. To further fulfill the specific energy demands of the aforementioned external and *in vivo* portable electronics, wearable supercapacitors (WSCs) that can be stretched, compressed, bent, twisted, and deformed into arbitrary shapes provide a promising alternative. However, on the one hand, most commercial SCs are fully or partially composed of planar and rigid materials, which require the use of obtrusive, hard supports and easily cause discomfort and instable power output. On the other hand, the electrolytes for commercial SCs are most commonly aqueous electrolytes including salt, acid, and alkaline solutions, which are toxic when used in external or *in vivo* wearable electronics[10,11]. Thus, the replacement of the bulky, rigid, and toxic materials is needed. The enhancement of the wearability and functionality of SCs is also significant to accelerate the investigation and design of WSCs.

WSCs for external or *in vivo* wearable electronics should provide user comfort, compliant mechanics, soft integration, multifunctionality, and, especially, the stable and intimate contact to the soft human tissues without adding any mechanical and thermal loading or causing tissue breakdown. Therefore, advanced soft materials that are designed or fabricated for the utilization of electrodes and electrolytes of WSCs are extremely desirable and significant. Tremendous research efforts have been directed at the design of advanced soft electrode materials and electrolytes for WSCs that could partly address the aforementioned functions of WSCs.

This review summarizes the recent progress in WSCs with flexible, stretchable, and textile characteristics. We discuss the most widely applied electrode materials (graphene, carbon nanotubes, conductive polymers, metal compounds, *etc*.) for WSCs, the newly developed electrode materials (hydrogels, MOFs, and MXenes), and solid-state electrolytes for WSCs with an emphasis on the configuration, design principles, and electrochemical performance [Figure 1][12-17]. Additionally, the prospects and challenges for the development of WSCs for wearable and implantable electronic devices are highlighted and discussed, with the aim of inspiring further research and development in the field of bioelectronics.

STRUCTURAL CHARACTERISTICS AND ENERGY STORAGE PRINCIPLES OF SCS

SCs have attracted notable scientific attention in the past decades due to their potential of clean energy, easy assembly, and high performance. The advantageous characteristics of SCs have also contributed to the rapid growth of low-power electronics, including wearable and portable electronic devices[18,19]. Figure 2A schematically illustrates the structure and energy storage mechanisms of supercapacitors: (1) Electrochemical double layer capacitance (EDLC) presents the immediate formation of an electrical double layer on the surface of the electrodes [Figure 2B]. EDLCs exhibit higher energy densities than conventional capacitors with their high effective surface space and minimal charge separation distances. (2) Pseudocapacitance presents fast reversible redox reactions or reversible intercalation on the surface of the active electrode materials. Reversible redox chemical reactions combine with dynamic equilibrium oxidation, the adsorption and desorption of ions on the surface of electrochemical active materials [Figure 2C], while the reversible intercalation and exfoliation processes move ions in the electrolyte between

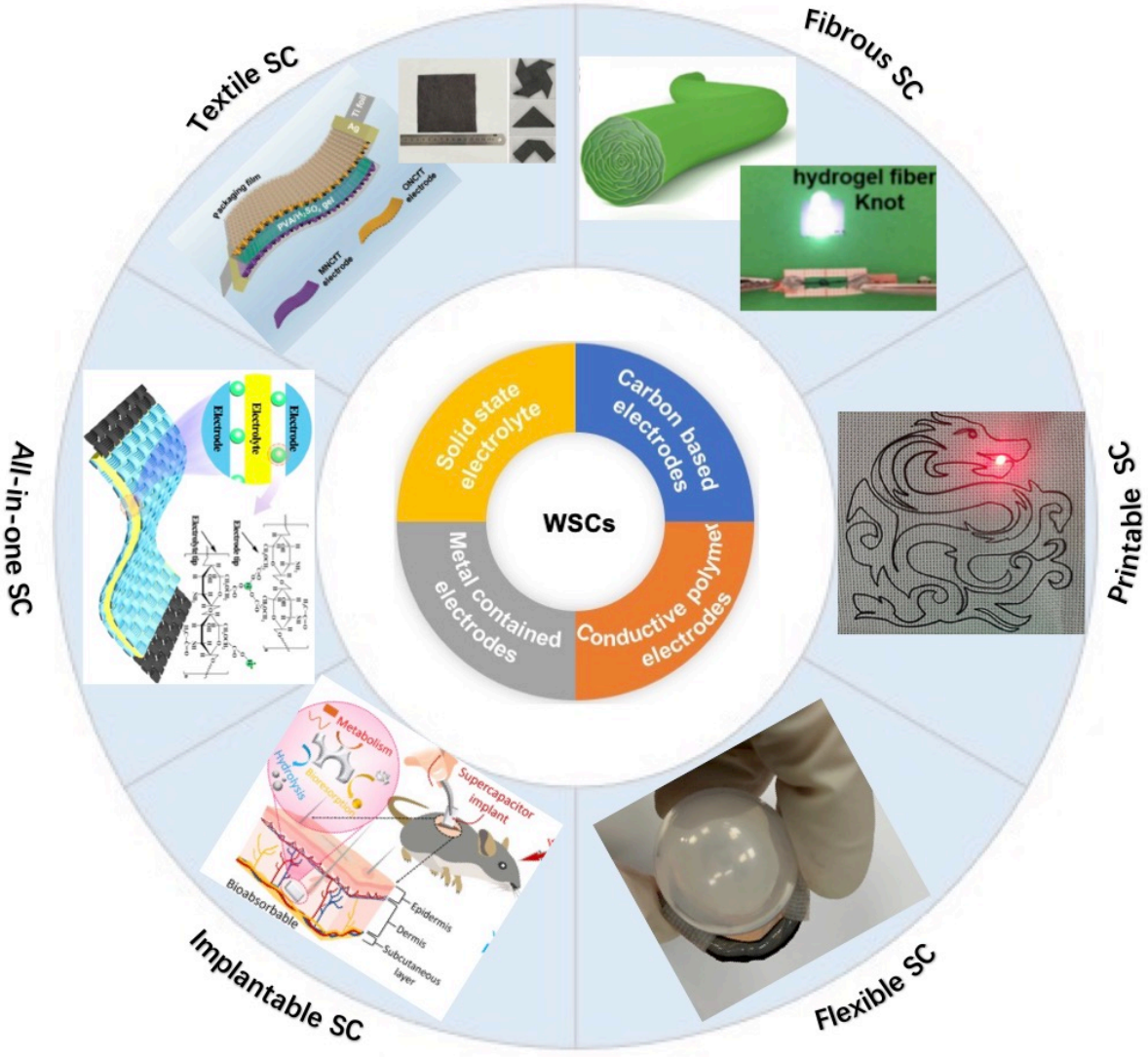

Figure 1. A graphic overview of this review. Section 2 introduces the structural characteristics and energy storage principles of SCs. Section 3 discusses the required properties of soft materials for WSCs. Section 4 presents soft electrode materials for wearable supercapacitors. Section 5 introduces studies on solid-state electrolytes for WSCs. Section 6 introduces recent studies on all-in-one wearable supercapacitor devices. The photographs on top are reproduced with permission[12-17]. WSCs: Wearable supercapacitors; SCs: supercapacitors.

the electrodes during the electrochemical energy storage process[20-22] [Figure 2D].

According to the above-mentioned energy storage mechanisms, the performance of SCs is primarily dependent on the electrode materials and the interactions between the electrode and the electrolyte. The electrochemical properties, conductivity, and specific surface areas of the electrode materials, as well as the ion conductivity of the electrolyte, are all key factors that determine the electrochemical performance of SCs, which is usually reflected by capacitance, energy density, and power density. For capacitance, including gravimetric specific capacitance (F g^{-1}), area capacitance (F cm^{-2}), and volume capacitance (F cm^{-3}), which are chosen depending on the shape or structure of the SCs, can be calculated from the cyclic voltammetry (CV) or the galvanostatic charge-discharge data. For energy density and power density of SCs, their units depend on the unit of capacitance. Equations (1)-(3) are taken as examples to calculate the gravimetric

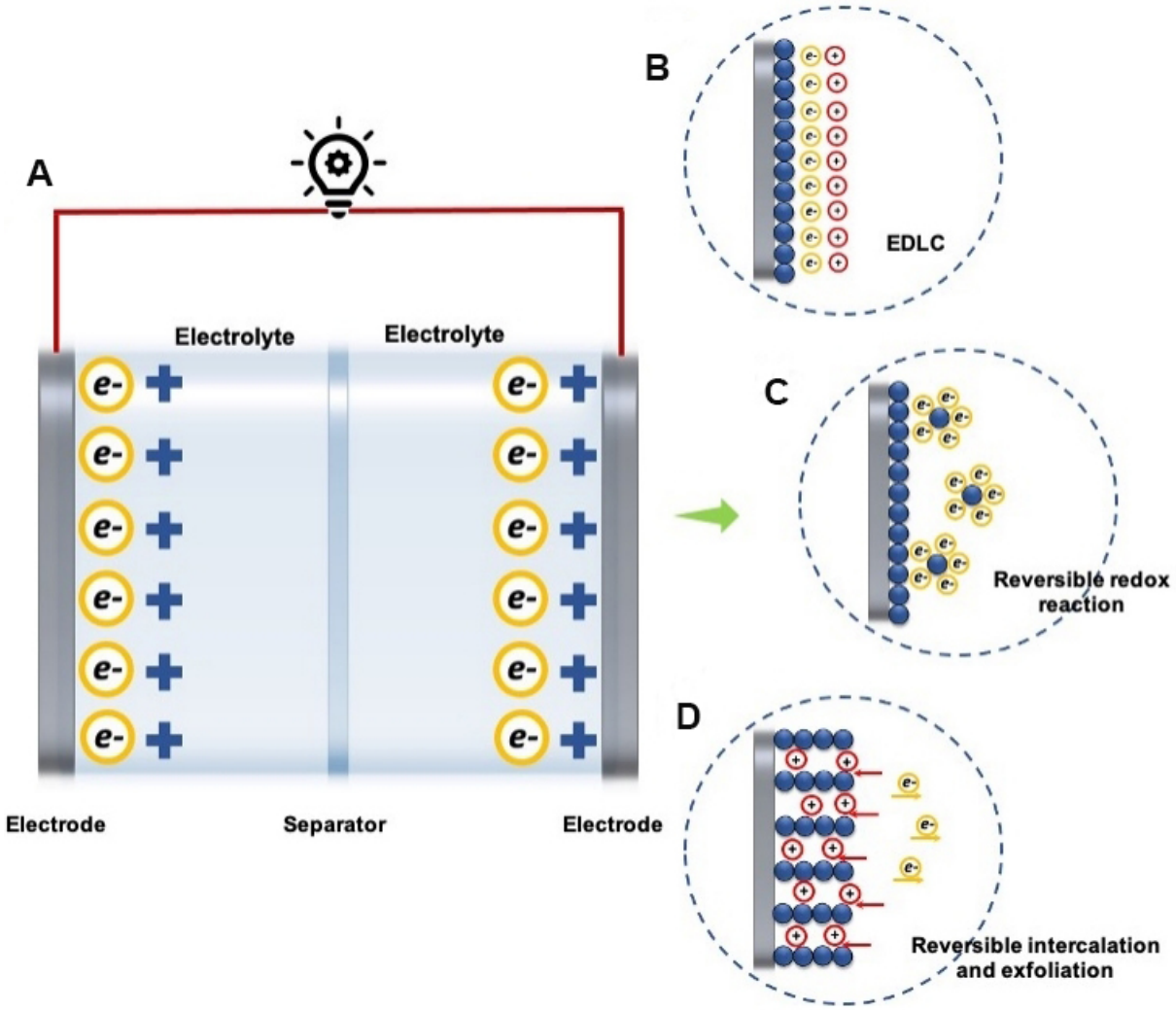

Figure 2. (A) Schematic structure of a supercapacitor. Energy storage mechanisms illustration: (B) EDLC; (C) reversible redox reaction; and (D) reversible intercalation and exfoliation process. EDLC: Electrochemical double layer capacitance.

specific capacitance [C_s, Equation (1)], energy density [E_s, Equation (2)], and power density [P_s, Equation (3)] based on CV data.

$$C_s = \frac{\int Idv}{vm\Delta V} \tag{1}$$

$$E_s = \frac{1}{m}\int IV(t)\,dt \tag{2}$$

$$P_s = \frac{E_s}{t} \tag{3}$$

where I is the constant current, m is the total mass of the active materials, v is the scan rate, and ΔV is the width of the voltage window[17].

Numerous attempts have been made to improve the electrochemical performance of SCs through these aspects[23-28]. Moreover, considering the structural characteristics of SCs, achieving advanced multifunctional WSCs depend on the specific characteristics of the electrode materials. Meanwhile, replacing the aqueous electrolytes in conventional SCs is also significant for preparing WSCs for wearable and portable electronics.

REQUIRED PROPERTIES OF SOFT MATERIALS FOR WSCS

To further meet the requirements of external/*in vivo* WSCs, both the electrode materials and electrolyte materials need to be deformed into arbitrary shapes to adapt to the human physiological and musculoskeletal environment. Conventional brittle and rigid electrode materials could result in fractures when accommodating a small amount of imposed strain, which is inappropriate for fully stretchable devices. Thus, some special properties, different from those of traditional bulk and rigid materials, are highly needed for SCs.

Table 1 summarizes the required properties of electrode materials for WSCs. Young's modulus is a mechanical property that measures the tensile stiffness of a solid material. It quantifies the relationship between tensile stress and strain [(proportional deformation) in the linear elastic reign of a material Figure 3A][29,30]. Corresponding to the Young's modulus value of the skin or other human soft tissues, a small value (10^1-10^6 kP) in a broad stress range is required for WSCs[31], However, the most used electrode materials including carbon and metal oxides exhibit higher Young's modulus values, as shown in Figure 3B. To address this issue, downscaling the electrically active materials and embedding them in or onto soft materials that have lower Young's modulus values is one of the most popular strategies to fabricate WSCs[32,33]. Stretchability is also significant for WSCs because biological tissues are capable of enduring high dynamic and mechanical stress. For example, the skin, muscles, and peripheral nerves can experience 30% tensile strain and displacement during exercise in conventional postures[34,35]. Thus, high stretchability is needed for soft materials for WSCs which could be deformed into arbitrary shapes. Similar to the case of Young's modulus performance, the normally used electrode materials for SCs possess low stretchability [Figure 3C], which could also be improved by downscaling the dimension of active materials or embedding them in or onto soft materials with higher stretchability[36-39]. Conductivity is also an essential property, which determines the electrochemical performance of SCs, especially the cycle stability and rate performance. As shown in Figure 3D, active materials with low Young's modulus and high stretchability usually possess low conductivity. Therefore, many studies have been committed to improving the conductivity through doping or combining materials with high conductivity[17,40-43]. In addition, due to the direct contact with human skin, active materials with high biocompatibility are also desired, especially for implantable SCs[44-46]. According to these requirements, the following sections summarize conventional "soft" electrode materials and recently developed "soft" electrode materials for WSCs, from the aspects of material properties and preparation strategies.

SOFT ELECTRODE MATERIALS FOR WEARABLE SUPERCAPACITORS

According to the storage mechanism of SCs discussed above, the most significant part that determines the electrochemical property of SCs is the electrode material, which is also the key part to meet the demands of wearable electronics. In the following, conventional electrode materials including carbon-based electrodes, polymer-based soft electrodes, and metal-containing soft composites and their specific preparation strategies are summarized and discussed. Moreover, some newly developed soft electrode materials are also highlighted.

Table 1. Necessary mechanical and physicochemical properties for WSCs

Properties	Description	Typical strategies	Proper values	Ref.
Young's modulus	Proper value is required for direct contact with human skin or implantable SCs	Embedding inorganics in/onto the organic substrate/hydrogels	10^{1}-10^{6} kP	[32,33]
Stretchability	Essential when being deformed into arbitrary shapes	Downscaling the dimension of active materials/electrode materials (0D, 1D, 2D)		[36-39]
		Being printed onto plastic substrates	Higher than 10^{0}	
		Strain-tolerant electrode/collector		
Conductivity	High conductivity is required for high cycle stability and rate performance	Carbon-based composite materials		[17,40-43]
		Bimetal oxides		
		Metal compounds (metal nitrides, metal sulfides, *etc.*) Conductive metal-organic frameworks (MOFs) MXene	Higher than 10^{-2} (S m^{-1})	
Biocompatibility	Low toxicity or nontoxicity is required for long-term retention of WSCs on human skin or in the human body	Encapsulation or compositing with biocompatible materials	No toxicity to cells or tissues	[44-46]
		Adopting natural or intrinsically nontoxic polymers and metal oxides		
		Biodegradable materials		

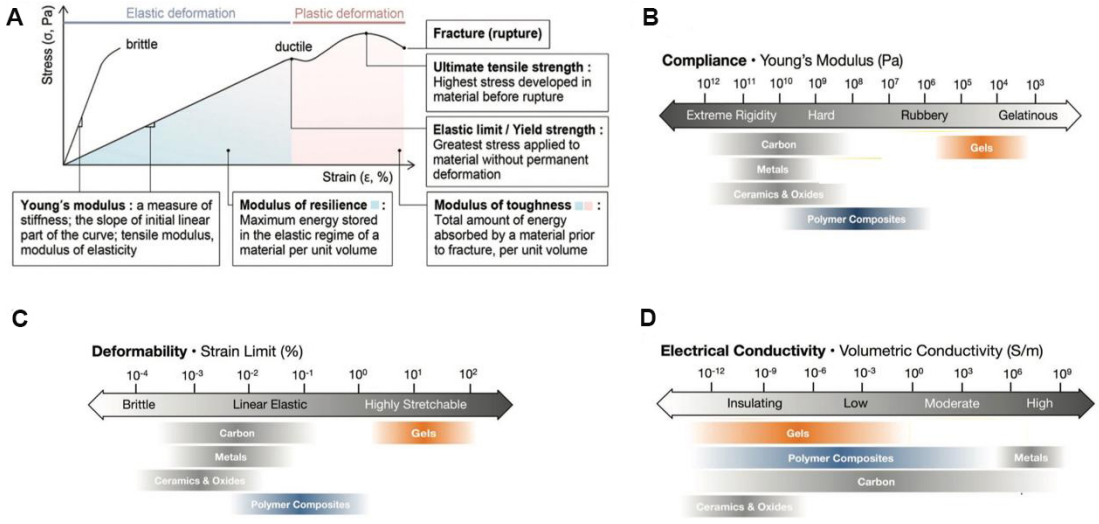

Figure 3. Summarized required properties for WSCs. (A) Stress-strain profiles of brittle and ductile materials and the description of important material properties[29]. (B-D) The compliance, deformability, and electrical conductivity of widely used materials for WSCs, respectively[30]. WSCs: Wearable supercapacitors.

Carbon-based soft electrodes for wearable supercapacitors

As the most developed electrode materials, carbon-based materials with EDLC behavior have attracted huge attention as electrode materials for SCs. The mostly widely used are active carbons or porous carbons derived from natural mass (e.g., wood[47], coal[48], nutshell[49], loofah[50], *etc.*) by physical or chemical process, which are not available for WSCs due to their bulkiness and brittleness. Thus, according to Figure 3 and Table 1, to further adapt them to the development of WSCs, down scaling the dimension, embedding them on or into organic substrates/hydrogels, and specific structures would endow them with the appropriate material properties (low Young's modulus, high deformability, and high conductivity) as soft electrodes for WSCs.

Graphene-based electrodes for WSCs

Graphene has already been widely studied as an electrode for SCs due to its excellent electrical, mechanical, and capacitance properties[51,52]. Furthermore, its easy assembling onto different soft substrates property makes it a promising candidate electrode for WSCs. In this section, recent advanced research on graphene-based soft electrode for WSCs is reviewed.

1. Flexible and free-standing graphene-based electrodes

Graphene can be easily assembled into mechanically strong films due to its two-dimensional (2D) structure and stacking trend[53]. Thus, flexible and free-standing graphene-based electrodes have been wildly prepared as electrodes for flexible SCs. Reduced graphene oxide (rGO) produced by chemical redox process is the most widely used electrodes for SCs due to its lower production cost, and it can be easily modified and assembled into strong films or onto different flexible substrates[54,55].

Vacuum filtrating and chemical reduction process were first used to prepared rGO papers, which possess a Young's modulus of 41.8 GPa, a tensile strength of 293.3 MPa, and an electrical conductivity of 118 S cm^{-1}[56]. This study showed the feasibility of rGO to be applied as a free-standing and flexible electrode for SCs. Freeze-drying processes were also applied to prepare free-standing and flexible rGO papers[57]. The obtained rGO electrode also possessed good conductivity of 18 S cm^{-1} and capacitance of 172 F g^{-1} at current density of 1 A g^{-1} capacitance. These results prove the potential application of rGO paper-like electrode materials for WSCs. To further improve their electrochemical performance, strategies also focus on improving the conductivity of these rGO papers when used as electrodes for WSCs[58]. However, the tightly stacked nature of free-standing rGO films lowers the electrolyte accessible surface area and blocks the formation of electrical double layers, leading to lower electrochemical capacitance performance.

To address this issue, the most common strategy is to introduce a porous structure into rGO layers, which can effectively increase the electrolyte accessible surface area and improve the electrochemical performance of flexible and free-standing paper-like graphene electrodes. One typical porous structure is graphene hydrogels/aerogels[59-62]. These studies proved that this interconnected porous structure could improve the electrochemical performance of graphene-based electrodes by lower rGO sheet stacking, more accessible specific surface area, and rapid ion diffusion and electron transport throughout the entire interconnected porous network. Moreover, according to the energy storage principle (EDLC and pseudocapacitance) of SCs, the introduction of pseudocapacitive components into rGO sheets during the preparation process can not only hinder the re-stacking of rGO sheets but also further improve either the mechanical or electrochemical properties of as-prepared free-standing and flexible electrodes for WSCs[63-67]. Our groups prepared ternary composite free-standing and flexible rGO-based films. The vaporing process was carried out to firstly produce free-standing and flexible rGO-TiO_2 films. TiO_2 nanoparticles were introduced to hinder the stacking of rGO sheets and contribute their pseudocapacitance. To further improve the capacitance performance while still keeping the flexibility of rGO films, conductive polymers (CPs) were deposited on the surface of rGO-TiO_2 films to form ternary free-standing and flexible rGO-TiO_2-CPs composite films. The results indicate not only the synergistic effects of materials with different capacitance behavior in improving the electrochemical performance of rGO-TiO_2-CPs composite electrodes but also their functional retention after combining with different materials[21,68]. These results indicate the synergistic effects EDLC and pseudocapacitance, as well as the universal strategy to prepare flexible and free-standing graphene-based electrodes for WSCs. However, the mechanism property of flexible graphene-based supercapacitors is also an important factor that determines their application in flexible and wearable devices.

2. Flexible and elastic substrates supported graphene-based electrodes

Although these above flexible and free-standing graphene-based films have already been applied as electrode materials for WSCs, the fabrication of fully flexible electronics with both satisfactory electrochemical performance and mechanical stretchability remains a significant technological hurdle for graphene-based SCs. Thus, some flexible and stretchable substrates such as elastic substrates and textiles provide proper strategies to fabricate flexible and stretchable graphene-based electrodes for WSCs[69,70]. El-Kady *et al.*[71] produced rGO films (reduced by laser-scribe) on a polyethylene terephthalate and nitrocellulose membrane (with 0.4 um pore size). The as-prepared films exhibit excellent specific surface area (~1520 $m^2 g^{-1}$) and conductivity (~1738 S m^{-1}), which contributed to the high electrochemical performance when used as electrodes for SCs. In addition to the plastic substrates, new strategies are also developed to directly coat graphene-based SCs on textiles to obtain WSCs. Afroj *et al.*[72] produced highly conductive, ultra-flexible, and machine-washable graphene-based wearable e-textile electrodes by a simple and scalable pad-dry-cure method [Figure 4A and B]. The as-prepared graphene-based e-textile has a very low sheet resistance (11.9 W sq^{-1}) even after 10 home washing cycles. The assembled wearable supercapacitor also possessed good electrochemical performance (2.7 mF cm^{-2} at 0.1 mA cm^{-2}) and stable cycle stability (98% capacitance retained after 15,000 cycles).

Printing technology is also an attractive way to manufacture WSCs being low-cost, time-saving, versatile, and environmentally-friendly[73]. During this process, inkjet printing[74], screen printing[75], and 3D printing[76,77] are usually applied to print the desirable structure on different elastic substrates (papers[78,79], plastic substrates, textiles[80], *etc.*) to fabricated WSCs. Graphene and graphene-based composite ink was widely used to fabricate WSCs through this method. Figure 4C displays a printed supercapacitor on flexible glass. Seven printed layers of graphene flakes acted as electrodes and PVA-H_3PO_4 gel acted as electrolyte. The device has small capacitance decay upon bending conditions (from 8.7 to 8.1 mF cm^{-2} at a curvature radius of 2.75 cm and a scan rate of 50 mV s^{-1})[81]. To further improve the restack tendency of graphene flakes, Pham *et al.*[82] added a chemical leavening agent in rGO ink to suppress this restacking during the printing process [Figure 4D and E). Hyun *et al.*[83] processed a scalable, self-aligned inkjet printing process to manufacture flexible graphene SCs in a high-throughput manner. This strategy offers a promising process and desirable operation metrics including high areal specific capacitance (268 μF cm^{-2}), excellent lateral spatial resolution (20 μm minimum feature size), small footprint (< 1 mm^2 active device area), and outstanding reliability (44 devices with 100% yield) [Figure 4F]. However, the utilization of electrode materials and the plastic substrates, the breathability, and comfort of the aforementioned studies are not good enough when integrated in wearable devices, especially for skin-touching devices. Therefore, further efforts need to be put into improving these properties. Additionally, strategies from the material point of view including the stretchable, washable, and wear-resistant electroactive materials, stretchable and robust solid-state electrolyte, and proper packaging materials are also extensively needed.

3. Graphene-based textile fiber electrodes

Graphene-based fiber electrodes have also been widely applied in WSCs, due to their mechanical flexibility for textiles, light weight, and especially the improved breathability and comfort[84,85]. Meng *et al.*[86] designed a unique all graphene core-sheath fiber, in which a core of graphene fiber is covered with a sheath of three-dimensional (3D) porous graphene network [Figure 5A-C]. High conductivity and greater electrolyte accessible surface area were provided by this hierarchical hybrid structure. The as-prepared flexible all-solid-state fiber supercapacitor was assembled by intertwining two as-prepared graphene fibers with H_2SO_4-PVA (polyvinyl alcohol) gel as polyelectrolyte [Figure 5D]. The flexibility is shown in Figure 5F.

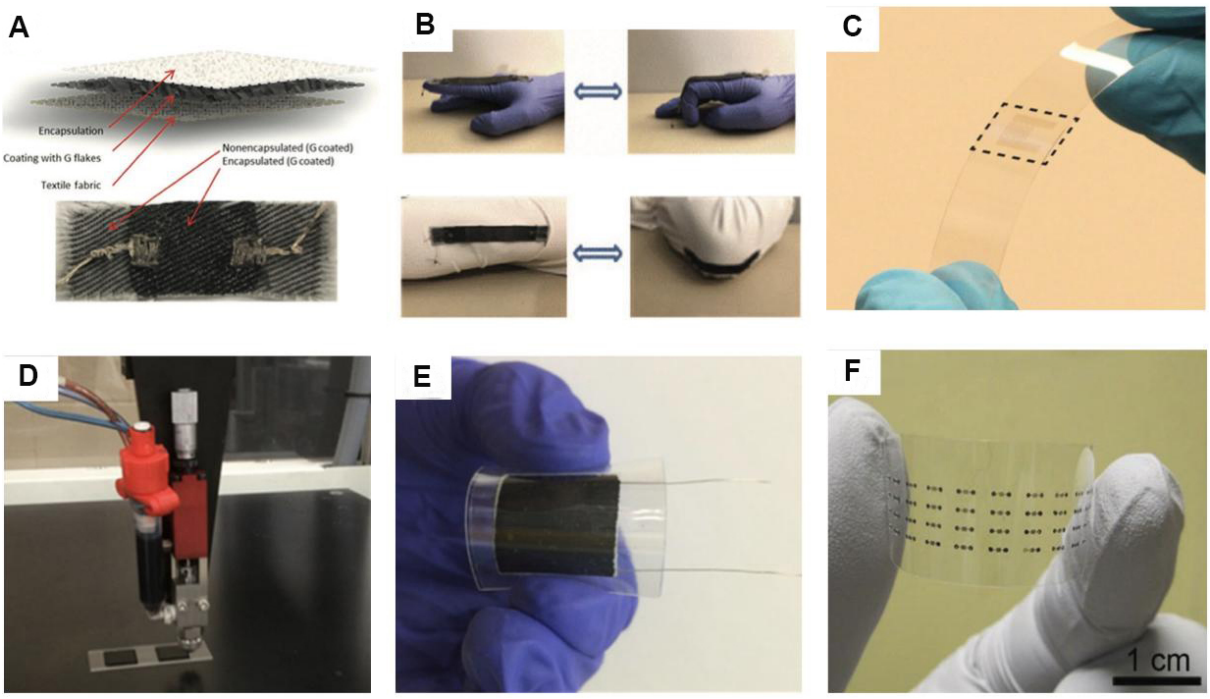

Figure 4. (A) Schematic cross-sectional view of graphene coated, compressed, and encapsulated fabric (top) and a real sample after 10 washing cycles (bottom). (B) Finger joint motion detection, wrist joint detection, and elbow joint motion detection by compressed and encapsulated graphene textile[72]. Flexible transparent micro-supercapacitor before electrolyte deposition[81]. (B) A snapshot of the GO ink printing on a glass slide. (C) Assembled reduced graphene oxide (rGO) supercapacitor on flexible PET substrate[82]. (D) Photograph of a 4 × 11 array of graphene MSCs printed on a flexible PET film. (E) Schematic circuit diagram (top) and optical image (bottom) of three devices in a series connection. (F) Galvanostatic charge-discharge (GCD) profiles for the three devices connected in series and parallel, respectively, in comparison with the GCD profiles for a single device. The GCD profiles were acquired at a current of 0.21 μA[83].

Additionally, Figure 5G and H presents the woven textile and further demonstrates the use of the fiber supercapacitor in electronic textile or clothing integrated devices.

To further improve the capacitance performance of graphene fiber electrodes, specific structures and materials with pseudocapacitance behavior were combined[87,88]. Qu *et al.*[89] produced hollow rGO-conductive polymer composite fibers. The high electrical conductivity (4700 S m^{-1}) determines their excellent electrochemical performance (fiber shape supercapacitor device with the capacitance and energy density of 304 mF cm^{-2} and 6.8 μW h cm^{-2}, respectively). Moreover, the as-prepared SC can also be tied into knots, rolled up, and woven into textiles owing to the high flexibility. Although graphene-based fibers have been widely investigated and possess good flexibility and comfort, their stretchability is rarely studied, especially in different temperature conditions. Moreover, the washability of the as-integrated wearable textiles also needs to be further proved, and, to fabricate a proper textile electrode, more textile technologies also need to be developed.

4. Graphene-based hydrogel electrodes for WSCs

Graphene-based hydrogels - a kind of porous graphene matrix that can endow electron transfer along the graphene chains, while ions can conduct through the aqueous part within the graphene hydrogels - have attracted lots of attention in the research on WSCs because of their high specific surface area, suitable nano - to micropores and pore network, high conductivity, and multidimensional electron transport

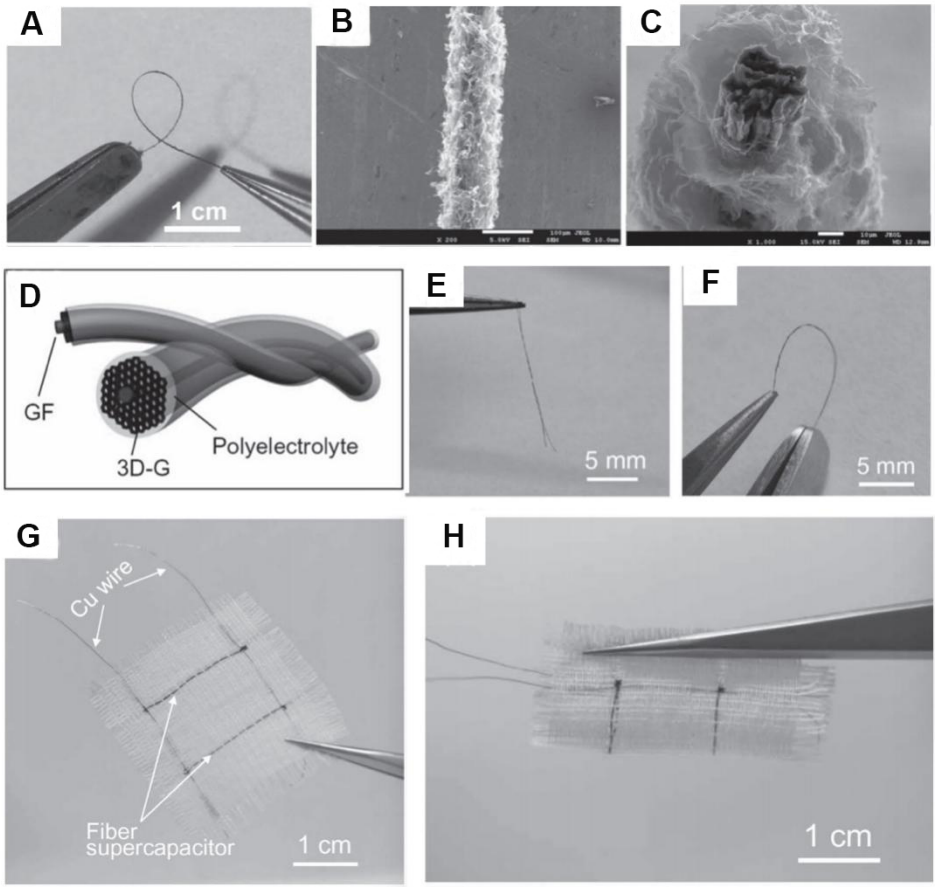

Figure 5. (A) A photograph of a distorted graphene fiber. (B) SEM images of as-prepared graphene fiber. (C) Cross-section view of a graphene fiber showing the core graphene network surrounded by standing graphene sheets. (D) Schematic illustration of a wire-shaped supercapacitor fabricated from two twined graphene fibers with a polyelectrolyte. (E, F) Photographs of fiber supercapacitor in free and bending states. (G, H) Photographs of the textile embedded with two graphene fiber supercapacitors in flat and bending states, respectively[86].

pathways[90,91]. Figure 6 displays a graphene hydrogel film electrode for WSCs, fabricated by a facile hydrothermal process. The as-prepared graphene hydrogel-based flexible all-solid-state supercapacitor presented good electrochemical performance due to the highly interconnected 3D network structure of graphene hydrogels[59,61]. Important advances have also been made to further improve the electrochemical performance and multifunctionality of graphene hydrogel electrodes, including graphene hydrogels composed with 1D or 2D metal-compound[92-94] and graphene hydrogels combined with conductive polymers[95-97]. Although graphene-based hydrogels have been widely investigated and possess good flexibility and compressivity, their other mechanical properties are still unsatisfactory, especially the poor stretchability, which is caused by the weak π-π stacking and hydrogen bonding within the reduced graphene oxide matrix that formed during the hydrothermal process.

For decades, although impressive progresses on flexible graphene SCs have already been obtained, the functionality of supercapacitors has always been gained by sacrificing electrochemical performance. Thus, it is still a big challenge to gain flexibility or other functions while still retaining or even improving the capacitance performance of graphene-based electrodes.

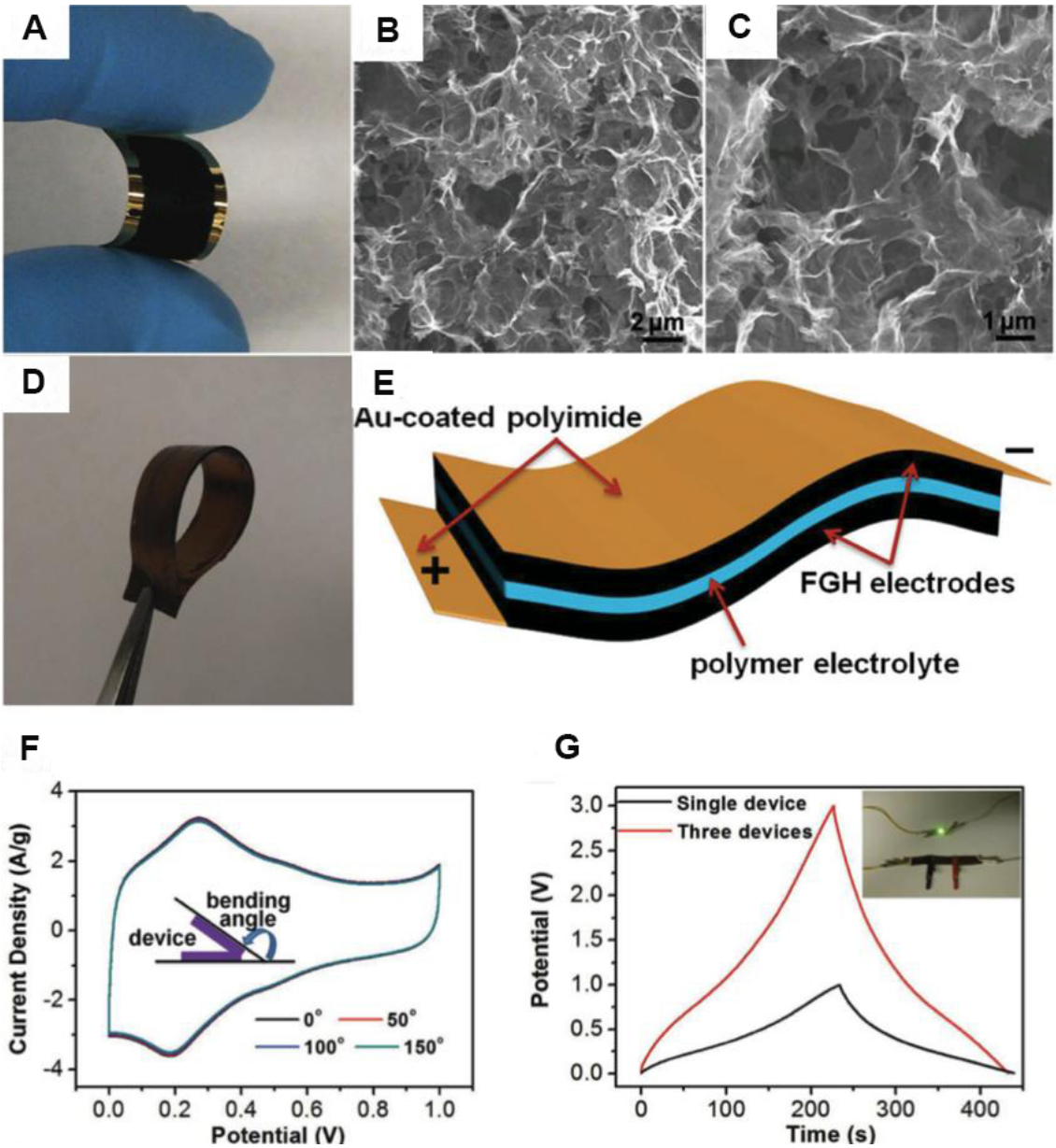

Figure 6. (A) Digital photograph of a flexible FGH thin film electrode. (B) low- and (C) high- magnification SEM images of interior microstructures of the FGH film. (D) Digital photograph of an FGH-based flexible solid-state supercapacitor. (E) A schematic diagram of the solid-state device with H_2SO_4-PVA polymer gel as the electrolyte and separator. (F) Cyclic voltammetry (CV) curves at 10 mV s^{-1} of the FGH-based flexible solid-state supercapacitor at different bending angles. (G) One cycle of galvanostatic charge-discharge (GCD) curves at 1 A g^{-1} of a three-supercapacitor in-series group. The inset shows a photograph of a green LED turned on by the tandem device[61].

Carbon nanotube electrodes for WSCs

Carbon nanotubes (CNTs) are another wieldy developed carbon-based electrode material for WSCs and have attracted lots of attention during the preparation of supercapacitors owing to their unique pore and fiber structure, superior electronical properties, and good mechanical and thermal stability[98,99]. Tremendous studies have explored CNT-based fiber SCs corresponding to the fibrous structure nature of CNTs[100,101]. Other electroactive materials have also been exploited to combine with CNTs to fabricate fibrous structures for textile SCs and improve the electrochemical performance[102-104].

Similar to graphene, combining CNTs with elastomer substrates is the most common strategy to fabricate flexible or stretchable electrodes for WSCs by transferring[105,106] or coating[107-109] methods. Recently, seamlessly connected graphene/carbon nanotube hybrids with covalent interconnections were developed by growing vertically aligned CNTs on graphene layers. This special 3D structure could efficiently prevent the aggregation and possess large surface area and excellent electrical properties. A free-standing tubular structure of seamless graphene/CNTs textile structure was obtained by etching off the original nickel textile. After being deposited with polyaniline (PANi), this as-prepared electrode material exhibited a high area specific capacitance of 164 mF cm^{-2}. Due to the unique textile-like structure, the assembled supercapacitor exhibited not only excellent flexibility but also high stretchability of 200%[110].

Printing technology is also a popular way to fabricate CNT-based electrodes for WSCs. Lee *et al.*[80] assembled printed SCs composed of multiwalled carbon nanotube electrodes and ionic liquid/thiolene polymer network skeleton/SiO_2 nanoparticle-based gel electrolytes on a T-shirt by printing-assisted aesthetic clothing designs [Figure 7]. This simple and scalable printing process, combined with the properly designed electrodes and electrolytes, make the printed WSCs possess excellent form factors, mechanical flexibility, and thermal stability. Furthermore, the printed T-shirts maintain their electrochemical activity even upon exposure to laundering, wringing, ironing, and folding, which are common activities for clothing, demonstrating their potential in wearable electronics. This study provided a useful strategy to produce washable and comfortable WSCs, however, the wearable demand in the everyday-use level still has not been investigated and efforts still need to be done to realize the commercial WSCs.

Polymer-based electrodes for WSCs

Conductive polymer-based electrodes for WSCs

Conductive polymers, such as polypyrrole (PPy), PANi, polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT), are another kind of electrode materials that have been widely applied in supercapacitors owing to their pseudocapacitance behaviors[111-113]. As shown in Figure 3, the Young's modulus, deformability, and conductivity of conductive polymers is more suitable than those of carbon- or metal oxide-based materials for WSCs. Especially the conductivity can reach up to 10^4 S cm^{-1} by different doping levels or dopants[112].

However, the poor stability of conductive polymers, which comes from their backbone shrink and deterioration during the electrochemical process, will decline the power density and energy density of the whole devices and hinder their further applications[1,21,112]. Thus, fabricating conductive polymers on a designed surface structure or combined with other electroactive materials such as carbon-based ones or metal compounds are the most popular strategies to utilize the advantages of each material and achieve high electrochemical performances. For WSCs, the above-mentioned method is applicable and achievable by using elastic substates. Vertical PPy nanotube arrays and carbon nano-onions grown on spandex fabric to fabricate a flexible and stretchable electrode for WSCs are shown in Figure 8A. The assembled stretchable supercapacitors exhibit 64 F g^{-1}, and they also present capacitance retention of 99% at a strain of 50% after 500 cycles. This as-prepared stretchable supercapacitor device can provide a stable energy supply under different bending conditions for practical applications [Figure 8E-G][114].

Printing technology is also applied in fabricating conductive polymer-based electrodes for WSCs. Recently, a low-cost, easy-to-fabricate, and air-stable PANi ink was developed through a facile assemble-disperse strategy. The printable SC derived from as-prepared CP ink, as shown in Figure 9A, delivers high areal capacitance of 96.6 mF cm^{-2}, large volumetric capacitance of 26.0 F cm^{-3}, and considerable energy density of 2.4 mWh cm^{-3} at 238.3 mW cm^{-3} [Figure 9][115].

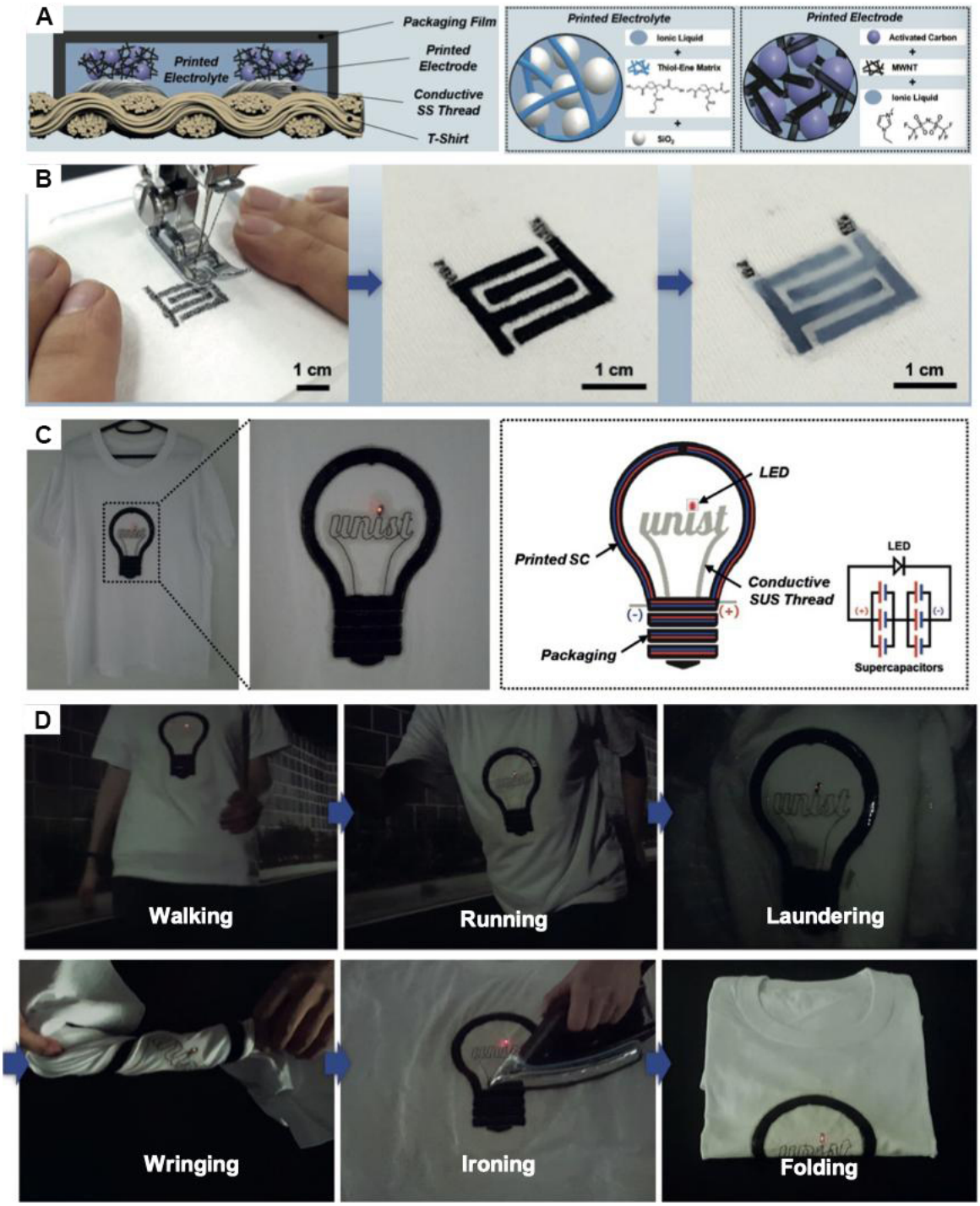

Figure 7. (A) Schematic representation illustrating an SC-printed T-shirt and its major components [SS thread current collector, printed electrode (AC/MWCNT/ionic liquid), printed gel electrolyte (ionic liquid/thiolene polymer network skeleton/SiO_2 nanoparticles), and packaging film]. (B) Schematic representation depicting the printing-based, stepwise fabrication procedure of the SC-printed T-shirt. Application of a SC-printed T-shirt as a potential electronic garment. (C) Photographs and a conceptual illustration of the bulb-shaped SC (3.0 V/15 mF cm^{-2}, scan rate = 2.0 mV s^{-1}) that powered an LED lamp. The SC was directly printed on a white T-shirt and connected to the LED lamp using conductive SS thread. (D) Photographs of the SC-printed T-shirt upon exposure to various wearable test modes (walking, running, laundering, wringing, ironing, and folding) encountered in the daily wear of garments[80].

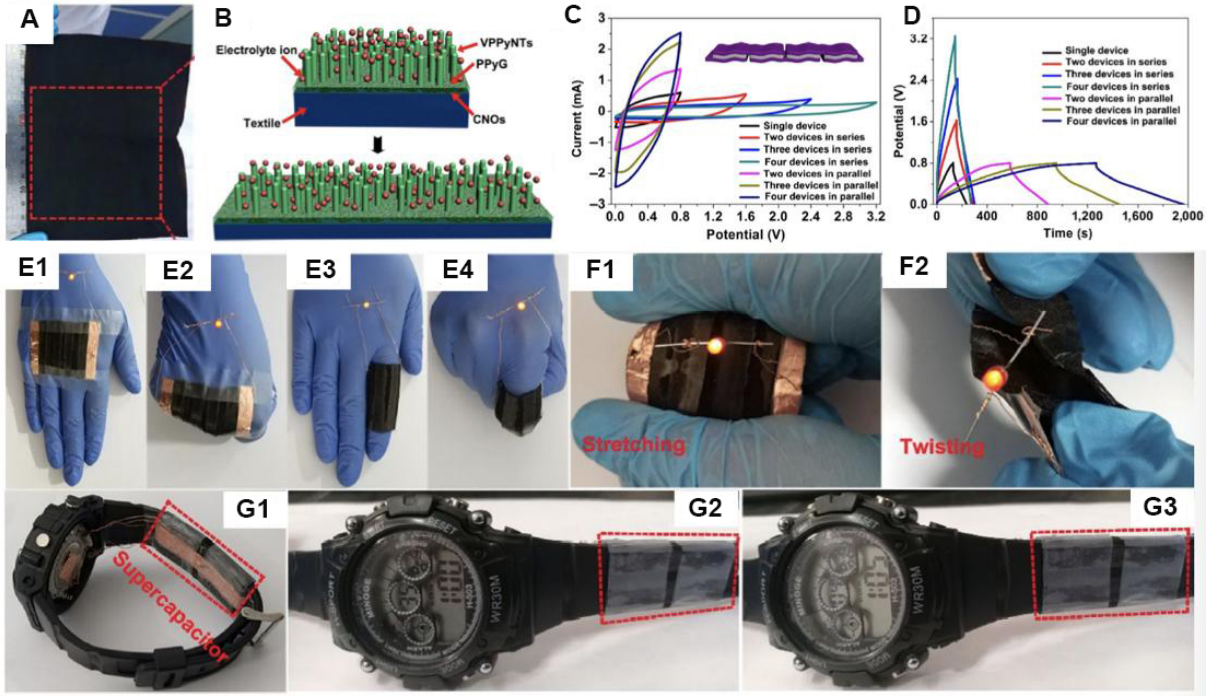

Figure 8. (A) Photograph of a large-area piece of spandex fabric after the growth of the PPy structure. (B) Schematic illustration of the conductivity retaining mechanism of the stretchable WSC based on a textile electrode during stretching. (C) CV and (D) GCD curves of the stretchable SC composed of multiple devices in series and parallel under scan rate of 10 mV s^{-1} and current density of 0.2 A g^{-1}. The inset is the cartoon of a stretchable SC device composed by four single devices in series. (E1-E4) Photographs of a red LED lit up by the stretchable SC as a wearable power supply attached on the human hand and finger under the original and stretchable states. (F1, F2) Photographs of a red LED bubble lit up by the as-prepared SC under stretch and twist condition. (G) Photographs of an electronic watch powered by a stretchable supercapacitor[114].

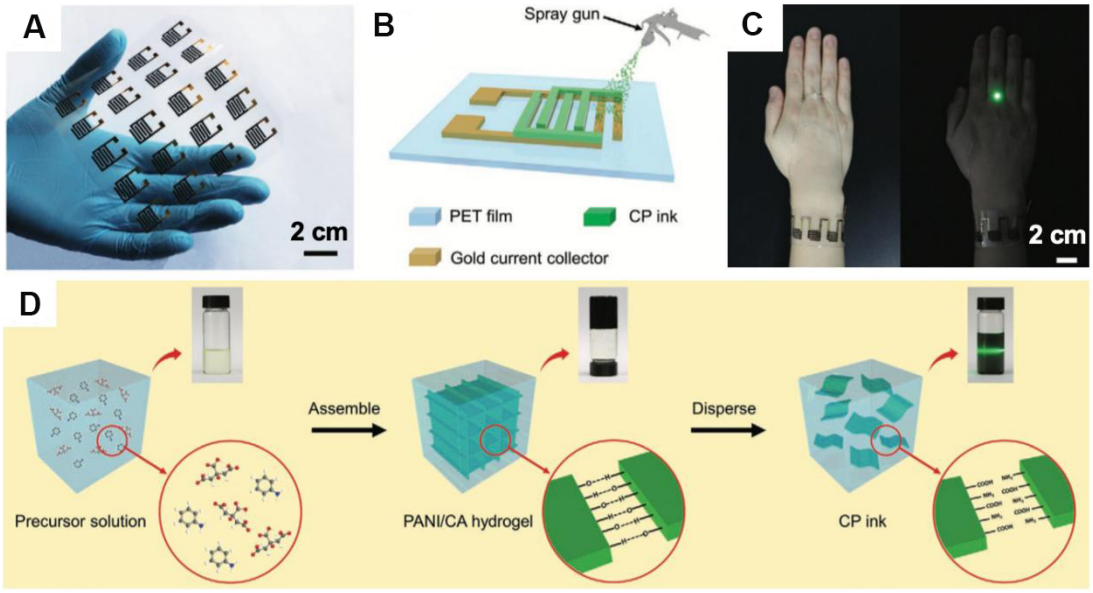

Figure 9. (A) Flexible WSC array derived from air stable conductive polymer ink. (B) Schematic illustration for the fabrication of printed WSCs with a mask-assisted spray-coating method. (C) Integrated circuit of a WSC wristband that can successfully power a green LED bulb. (D) Air-stable conductive CP ink can be easily prepared through a facile assemble-disperse strategy, in which PANi and citric acid assemble into hydrogel in the assemble stage and sequentially disperse well in water to form CP ink in the disperse stage[115]. PET: Polyethylene terephthalate; CP: conductive polymer.

Although the deposition of conductive polymers on stretchable elastic substrates, such as polyurethane, polydimethylsiloxane, and thermoplastic copolyester, is the most common strategy to obtain flexible and stretchable electrodes for WSCs, these conventional stretchable electrodes are limited by the deformability of the substrate during the stretching or deformation process[116,117]. Recently, Yang *et al.*[118] developed an additive-free, free-standing stretchable electrodes by a 3D printing process based on poly(3,4ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) ink. Figure 10A displays the schematic illustration of the fabrication process of the conducting polymer electrode. Different 3D patterns were firstly prepared on a glass substrate; after being pulled off, different free-standing stretchable electrodes were obtained [Figure 10B]. These well-designed arc-shaped microstructures provided a uniform stress area and reduced the peak strain in the electrode, which led to excellent flexibility and extreme stretchability (maximum elongation of 150%; Figure 10C). The quasi-solid-state symmetric supercapacitor, further assembled by hybrid polymer/CNT electrode, exhibited a high energy density of 0.065 mW h cm^{-2} and maintained excellent capacitance after 14,000 cycles. However, the mass loading of the ink during the printing process still hinders their development. Furthermore, the comfort also needs to be further considered.

Conductive polymer-based hydrogels for WSCs

The intrinsic soft/wet properties of hydrogels provide an excellent interface between the electronic transporting phase (electrode) and the ionic transporting phase (electrolyte), between biological and synthetic systems, and between soft and hard materials[29,88]. Moreover, according to the mechanical properties of gels [Figure 3], hydrogels are very promising electrode materials for WSCs. Therefore, hydrogel electrodes are recently widely explored. However, most hydrogels with unconducive polymer backbones cannot fulfill the demands of SCs. To resolve this issue, the most common strategy is using conductive polymers, e.g., PTh, PEDOT, PANi, and PPy, as backbones to fabricate hydrogels with unique structural and electronic properties (conductivity and pseudocapacitance behavior)[119-122]. PANi matrix hydrogels [Figure 11A and B] were first reported by using phytic acid as the gelator dopant. These as-prepared PANi hydrogels show excellent conductivity of about 0.11 S cm^{-1} and high capacitance as electrode for supercapacitors (480 F g^{-1} and 83% capacitance retention after 10,000 cycles)[123,124]. Similar studies using acid-linked conductive polymer-based hybrid hydrogels can also combine functional particles to form functional hydrogel electrodes for WSCs, For example, Ag nanoparticles were introduced into a folic acid cross-linked PANi hydrogel to improve the conductivity and energy storage property of the as-prepared hydrogels[125]. To further improve the electrical property of conductive polymer based hydrogels, multivalent metal ions (Fe^{3+}, Mg^{2+}, and Cu^{2+}) were also used to cross-link the conductive polymer chains as the gelator dopant to form conductive polymer-based electrode hydrogels free of insulating components[122,126,127].

In conductive polymer-based hydrogels, the conjugated structures of polymers are inherently rigid and fragile, which impairs the mechanical properties that are also significant factors for WSCs. New double network and low temperature strategies were applied to prepare great stretchable conductive polymer-based hydrogels with a hierarchical micro-/nanostructure[128]. The as-prepared hydrogels possess good toughness (29-fold enhancement) and electrochemical performance (specific and areal capacitance is 888 F g^{-1} and 2097 mF cm^{2}, respectively) while slightly sacrificing the conductivity (5.99 mS cm^{-1}; after adding phytic acid, the conductivity is 91 mS cm^{-1}). However, it is still a challenge for researchers to prepare conductive polymer-based hydrogels with high stretchability and high conductivity simultaneously. Other functions, such as biocompatibility, can be realized by introducing biomolecules into conductive polymer-based hydrogels[129]. Few works have applied such hydrogel electrodes in biocompatible or implantable supercapacitors. Hence, it is also important to further modify the conductive polymer hydrogels or combine other electroactive materials to endow more unconventional functions or specific properties for conductive

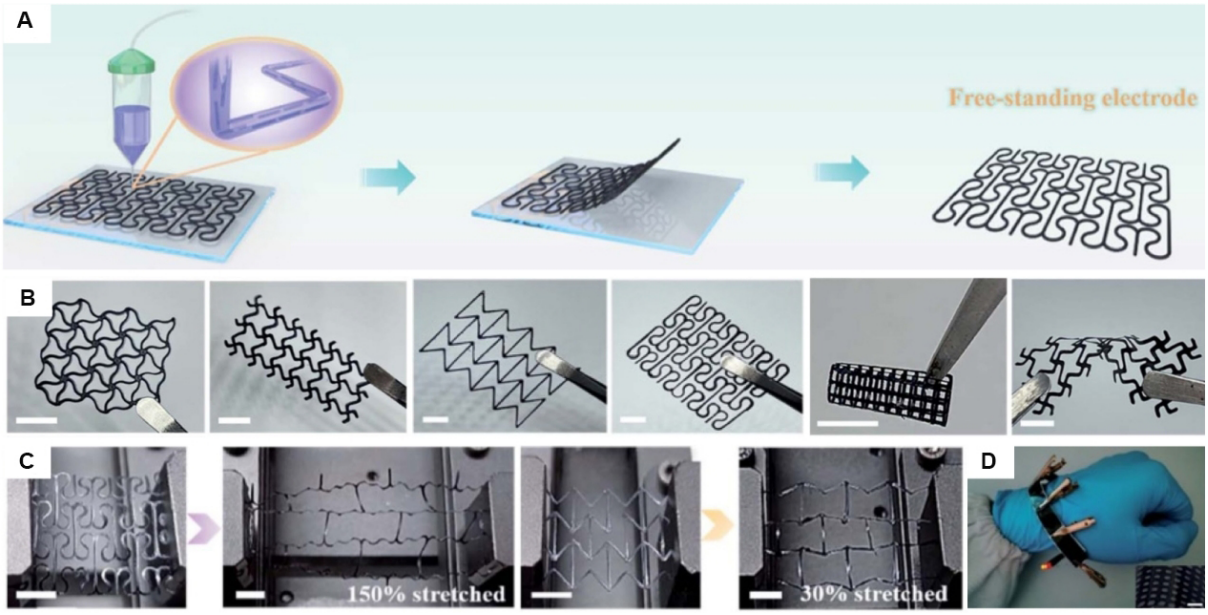

Figure 10. (A) Schematic illustration of the fabrication process of the conducting polymer electrode. (B) Images of as-printed electrodes with di erent structures. Scale bars: 5 mm. (C) S-hinged and re-entrant structure electrodes in the maximum stretch state. Scale bars: 6 mm. (D) Photographs of the wearable PEDOT:PSS/CNT quasi-solid-state symmetric supercapacitor lighting up a red LED bubble. The inset shows magnified optical image of the electrode. The scale bar is 1 mm[118].

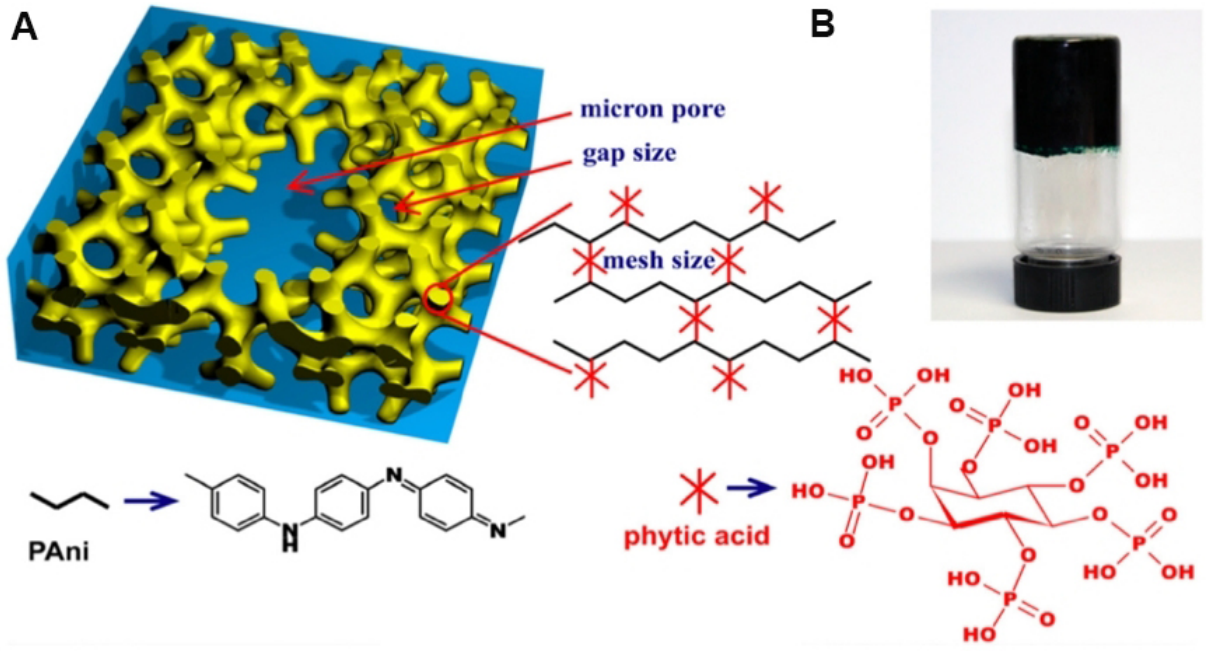

Figure 11. (A) Schematic illustrations of the 3D hierarchical microstructure of the gelated PANi hydrogel where phytic acid plays a role as a dopant and a crosslinker. The three-level hierarchical porosity of angstrom, nanometer, and micron size pores is highlighted by red arrows. (B) A photograph of the PANi hydrogel inside a glass vial[123]. PANi: Polyaniline.

polymer-based hydrogel electrodes for WSCs.

Metal-containing electrodes for WSCs

Metal compound electrodes for WSCs

Tremendous efforts have been made in the investigation of metal compound electrode materials for SCs, including meta oxides, metal nitrides, metal sulfides, and metal carbides[26]. According to the energy storage mechanism of supercapacitors, metal-based electrodes which possess pseudocapacitance behavior could obtain higher electrochemical performance compared with carbon-based electrodes, which present EDLC behavior. However, the deformability and Young's modulus of bulk and rigid metal compounds cannot meet the demands of electrodes for WSCs. Down scaling is the most common strategy to improve the properties of metal compounds for WSCs. Nano/microstructure metal compounds are the most popular candidate electrodes, but they have to face the decline of conductivity. Thus, metal compounds composed with carbon-based or conductive polymers are the most popular strategy, which not only improves the conductivity of the whole electrode for WSCs but also enhances the electrochemical performance by the synergistic effect of both pseudocapacitance behavior and EDLC behavior. In our previous work, metal oxides (nano-TiO_2 and Co_3O_4) composed with graphene and conductive polymers (PPy, PANi, and PTh) were applied as free-standing, flexible electrodes for WSCs [Figure 12A-C][21,130,131]. To further improve the conductivity and electrochemical properties of the metal oxides, series of metal compound electrodes consisting of metal oxides, bimetal oxides, and metal nitrides ($NiCoO_2$ @Co_3O_4@Co_2N, $NiMoO_4$ @MoO_3 @Mo_2N, and $NiFe_2O_4$ @Fe_3O_4@Fe_2N) were also combined with rGO to produce electrodes for flexible all-solid-state supercapacitors [Figure 12D-F]. These studies not only proved the synergistic effects of different capacitance behaviors but also proved a universal designed strategy to produce hybrid materials for high-performance functional WSCs[17,132].

In addition to the free-standing, flexible, and paper-like metal compound-containing hybrid electrodes for WSCs, fiber-shaped hybrid electrodes have been developed[133,134]. Salman *et al.*[135] integrated tungsten with rGO to fabricate hybrid fiber supercapacitors with high electrochemical performance (16.29 F cm^{-3} at 0.05 A cm^{-3}, energy density of 1.448 mW h cm^{-3}, and 84.7% capacitance retention after 10,000 cycles). To further improve the stretchability of metal compound-based electrodes, printing technology and elastic substrates have also been applied[136,137]. Recently, an implantable and biodegradable printed micro-supercapacitor was prepared by a facile super-assembly manufacturing and screen-printing strategy. The produced and optimized implantable and biodegradable supercapacitor which was super-assembled by a patterned Zn@PPy electrode and NaCl/agarose electrolyte exhibits energy density of 0.394 mW h cm^{-2} and can be fully degraded *in vivo* in 30 days without any adverse effects in the host organism[46]. This work gives us inspiration to study transient electronics for further implantable electronics. However, the design and choice of electrodes and electrolytes of implantable SCs is still the most challenging part. The materials must possess high biocompatibility, be soft (compatible with soft organs and tissues), and have no toxicity. For electrolytes, NaCl or phosphate-buffered saline could be proper since they already exist in the human body. Additionally, to further adapt to the unique physiological environment of the human body, implantable SCs with the ability to be stretched, compressed, bent, twisted, and deformed into arbitrary shapes must be further studied and developed.

Metal-organic frameworks based electrodes for WSCs

Metal-organic frameworks (MOFs) have attracted significant interests since the studies conducted by Hoskins and Robson[138,139]. These structures are defined by their assembly from metal/cluster-ligand coordination with multimodal ligands to fabricate extended, different dimensional porous networks with characteristics of high surface area, permeability to foreign entities, and structural tailorability[140-143]. MOFs as an important family of metal-containing materials have also been well studied as electroactive materials for SCs due to their porous structure and active sites, which could contribute both EDLC behavior and pseudocapacitance behavior.

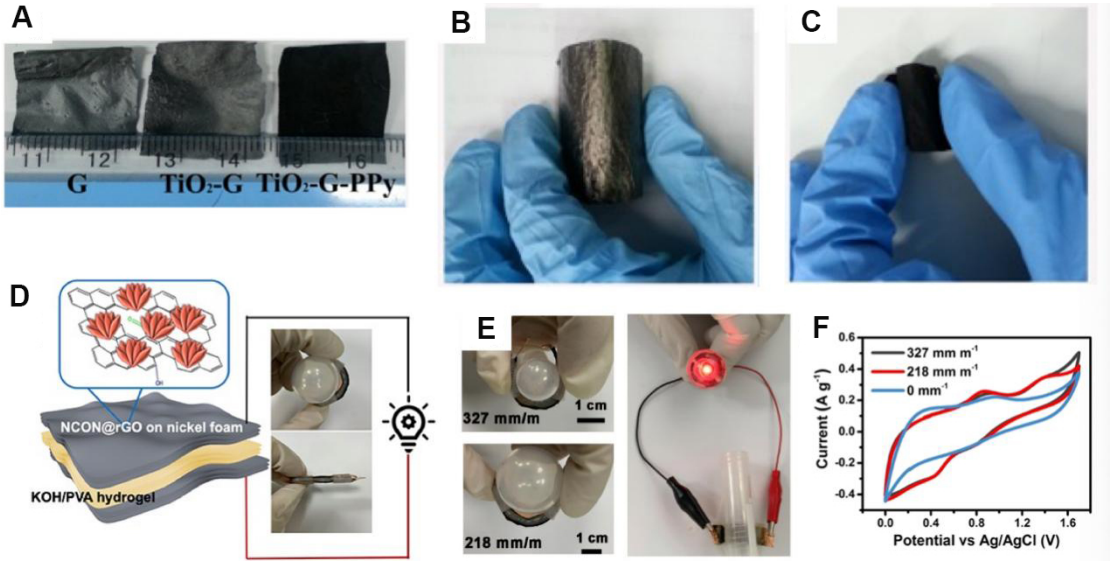

Figure 12. (A) Photographs of rGO and rGO-based composite films including free-standing and flexible rGO films (denoted as G), TiO_2-rGO film, and TiO_2-rGO-PPy film. (B) Bent flexible TiO_2-rGO film. (C) Bent flexible TiO_2-rGO-PPy film[130]. (D) Schematic illustration of the as-assembled hybrid high-performance, flexible, and all-solid-state supercapacitor. (E) CV curves of FSS at different curvatures. (F) Photographs of FSS under different bending conditions and an LED light bulb lit up by FSS at the curvature of δ = 327 mm m^{-1}[17]. rGO: Reduced graphene oxide; PPy: polypyrrole.

The utilization of MOFs include two aspects: On the one hand, MOFs are utilized as novel templates for preparing porous metal compounds or carbons. They can be applied as electrode materials for WSCs engaging with wearable substrates due to the nano/microscale nature of MOFs. Zhou *et al.*[144] directly grew MIL-88-Fe MOF-derived spindle-like Fe_2O_3@C on oxidized CNT fibers to produced fiber-shaped electrodes for WSCs. The assembled wearable asymmetric supercapacitor possessed high specific capacitance of 201.4 mF cm^{-2}, energy density of 135.3 μWh cm^{-2}, and good stability (97.1% retains after 4000 cycles). Zhou *et al.*[145] prepared PPy-coated conductive bacterial cellulose (BC) membranes via a ZIF-67 sacrificing polymerization process. This flexible and binder-free electrode exhibits high electrochemical performance due to the recovered electrolyte accessible channels afforded by the well-ordered PPy alignments along the BC nanofibers [Figure 13A]. However, in these studies, most MOFs only serve as the sacrificial templates/precursors with facile structural collapse and loss of intrinsically large surface area and pore volume.

On the other hand, MOFs with pseudocapacitive redox centers can be directly used as electrode materials[146-149]. Although the specific structure of MOFs can be kept, the poor intrinsic conductivity of pristine MOFs is also a challenging issue that needs to be resolved. To solve this issue, an extensively studied strategy is combining with other electronically conducting materials including conductive polymers and carbon-based materials which possess both good electronic conductivity and excellent redox or EDLC characteristics[150-152]. Another effective strategy is exploring novel MOFs with intrinsic conductivity[153]. Figure 13B and C shows intrinsically conductive Cu-MOF nanowire arrays on a free-standing PPy membrane electrode. The conductive Cu-MOFs nanowire arrays endowed the electrode with high conductivity and high surface area for the accessibility of electrolyte, whereas the PPy membrane provided flexibility, efficient charge transfer skeleton, and extra capacitance. The assembled flexible supercapacitors possessed exceptional electrochemical performance (areal capacitance of 252.1 mF cm^{-2}, energy density of 22.4 μWh cm^{-2} , power density of 1.1 mW cm^{-2} , and 90% capacitance retention after 8000 cycles)[154]. Additionally, to further improve the stretchability of MOF-based electrodes for WSCs, printing strategies

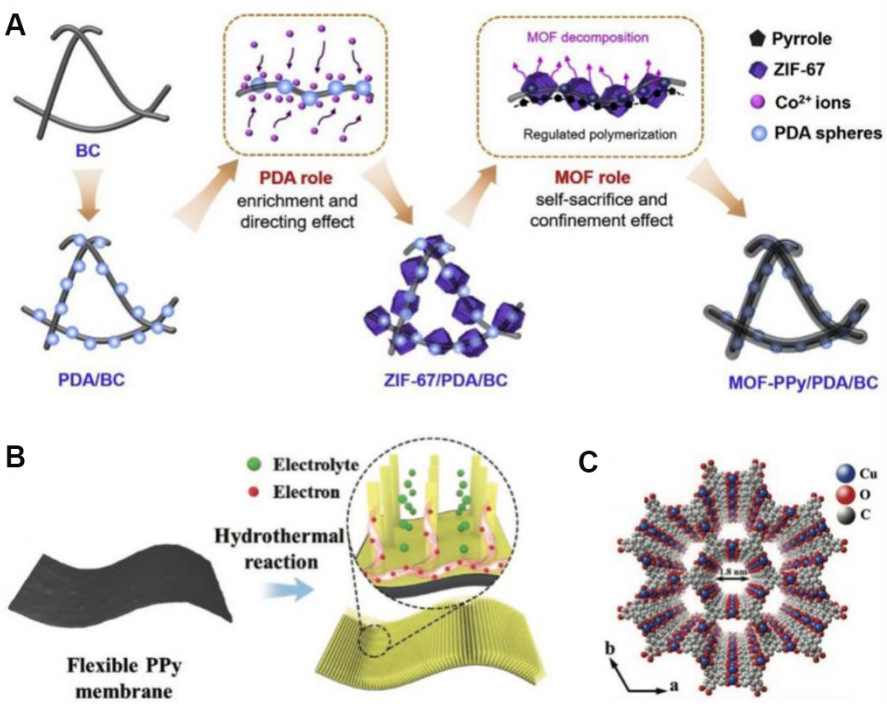

Figure 13. (A) Illustration of PPy-coated conductive bacterial cellulose (BC) membranes via a ZIF-67 sacrificing polymerization process[145]. (B) Illustration of the preparation of Cu-MOF nanowire arrays on free-standing PPy membrane electrode. (C) Simulated crystal structure of Cu-MOF[154]. PPy: Polypyrrole.

have also been applied to print MOF hybrids on elastic substrates[152,155].

MXene-based electrodes for WSCs

Since the first discovery of MXene in 2011[156] (a family of 2D transition metal carbides or nitrides), it has been intensively investigated, resulting in the discovery of more than 30 compositions including Ti_2CT_x, Nb_2CT_x, V_2CT_x, $Ti_3C_2T_x$, $Mo_2TiC_2T_x$, $Mo_2Ti_2C_3$, $Ti_yNb_{2-y}CT_x$, and $Nb_yV_{2-y}CT_x$, along with dozens more explored by computational methods[157,158]. The general formula of MXene is $M_{n+1}X_nT_x$(n = 1-4), where M represents transition metals, A is an element of Groups 13-15 in the periodic table, X is carbon or nitrogen, and T_x is surface functional groups (OH, O, Cl, and F)[159,160]. Owing to the above unique structure and components, MXenes possess specific physical and chemical merits such as great miscibility, high surface area to volume ratio, accessible active sites, surface charge state and electron-rich density, and absorption of electromagnetic waves, indicating their potential in electrochemical energy storage and conversion, electromagnetic shielding, wearable sensors, and personal thermotherapy[161,162]. Moreover, the presence of surface termination groups is responsible for the hydrophilicity and excellent reactivity of MXene, which also facilitates stable colloidal solution preparation in aqueous medium and different solvents[163-165]. Similar to the above-mentioned metal compounds and MOFs, MXenes have also been integrated into various elastic substrates for WSCs via coating[166,167], chemical and physical vapor deposition[168,169], and printing[170-173].

For instance, Wang *et al.*[13] developed a tailorable and foldable solid-state asymmetric supercapacitor through one-step scalable chemical oxidization and $Ti_3C_2T_x$ MXene ink painting of N-doped carbon fiber textile (NCFT) substrate. By regulating the oxidization time and MXene loading, the active layer of MXene-decorated NCFT (MNCFT) and O-functionalized NCFT (ONCFT) electrodes analogously presented tight

skin structure, avoiding the risk of active materials detaching from the support during mechanical deformation. The as-prepared MNCFT/ONCFT supercapacitor possessed high electrochemical performance (extended voltage window of 1.6 V, high areal energy density of 277.3 μWh cm^{-2}, and 90% capacitance retention after 30,000 cycles) and could be tailored into suitable size or shape for conformable integration without impairing its performance [Figure 14A-G]. However, to ensure the electrochemical properties of the as-prepared MXene-carbon fiber textile electrodes, the textile had to be coated with a large amount of MXenes. Therefore, it remains challenging to convert the electrical insulative textiles into highly conductive textiles at low MXene loading. Some studies tried to resolve this issue by combining MXenes with conductive polymer[174,175] or carbon-based materials[176-178]. Zheng *et al.*[179] reported a novel and facile vapor-phase polymerization and spray-coating strategy to produce PEDOT/MXene-decorated cotton fabrics (PMF). The condensed PEDOT contributed continuous electron pathways and pseudocapacitance to improve both the electrical conductivity and electrochemical performance of textiles [Figure 14H and I]. Additionally, in addition to combining with conductivity polymer and carbon-based materials, the aforementioned metal compounds and MOFs were integrated to further improve the electrochemical performance of MXene-based electrodes of WSCs[180-182]. Although the above studies of flexible textiles make metal-based materials a promising electrode for WSCs, it remains a big challenge to fabricate soft electrodes with the ability to deform into arbitrary shapes with the human body under the moving condition and without sacrificing the electrochemical performance of WSCs. Novel strategies for producing low-cost, environment-friendly, and soft composite materials also need to be further developed.

SOLID-STATE ELECTROLYTES FOR WSCS

Aqueous electrolytes such as salt, acid, and alkaline solutions are still the most commonly used electrolytes for commercial SCs[10,11]. However, these aqueous electrolytes are unable to adapt to WSCs because of the leakage of toxic component when dynamically deformed or implanted into the human body. Thus, solid electrolytes have attracted lots of attention[11,183-185]. Hydrogel-based electrolytes are the most studied solid electrolytes as both electrolytes and separators for all-solid-state SCs. Their typical swollen porous structure with absorbed aqueous endows them with high ionic conductivity and less electrolyte leakage possibility. In addition to their highly flexible and stretchable nature, hydrogel-based electrolytes are becoming the most indispensable unit for the rapid development of portable/wearable electrical devices.

PVA is the most widely used solid electrolyte due to its high structural integrity and good mechanical properties[186-191]. Moreover, the easy gelation process and the large water content absorbed in the PVA polymer matrix also helps it offer proper ionic conductivity, which makes it widely used in WSCs[192-194] and stretchable SCs[195,196]. In addition to PVA hydrogel electrolytes, polyacrylic acid (PAA)[197-199] and natural polymers, such as gelatin[200-202], lignin[203,204], and cellulose[205,206], were also developed to further improve the high retention of water in the polymer matrix to make sure the ionic conductivity[183,207]. For example, cross-linked networks of lignin-based hydrogel electrolytes showing high ionic conductivity (10.4 mS cm^{-1} at room temperature) and mechanical integrity (swelling capability of 532% water) were prepared for free-standing, flexible SCs[203]. Additionally, these biopolymer-based electrolytes could also be applied in implantable devices, because of their unique merits such as good compactivity, biodegradability, naturel abundance, and sustainability[46,208].

Recently, along with the appearance of smart SCs, self-healable electrolytes are also being investigated to fulfill the demands of self-healable SCs. A smart ionic conductive and self-healable sodium alginate/polymethylacrylic acid hydrogel electrolyte (SPMA-Zn: $ZnSO_4$) was developed for flexible hybrid supercapacitors. The as-prepared SPMA-Zn exhibits an excellent self-healing ability and can recover its electrochemical performance after multiple mechanical damages. The assembled supercapacitor displays

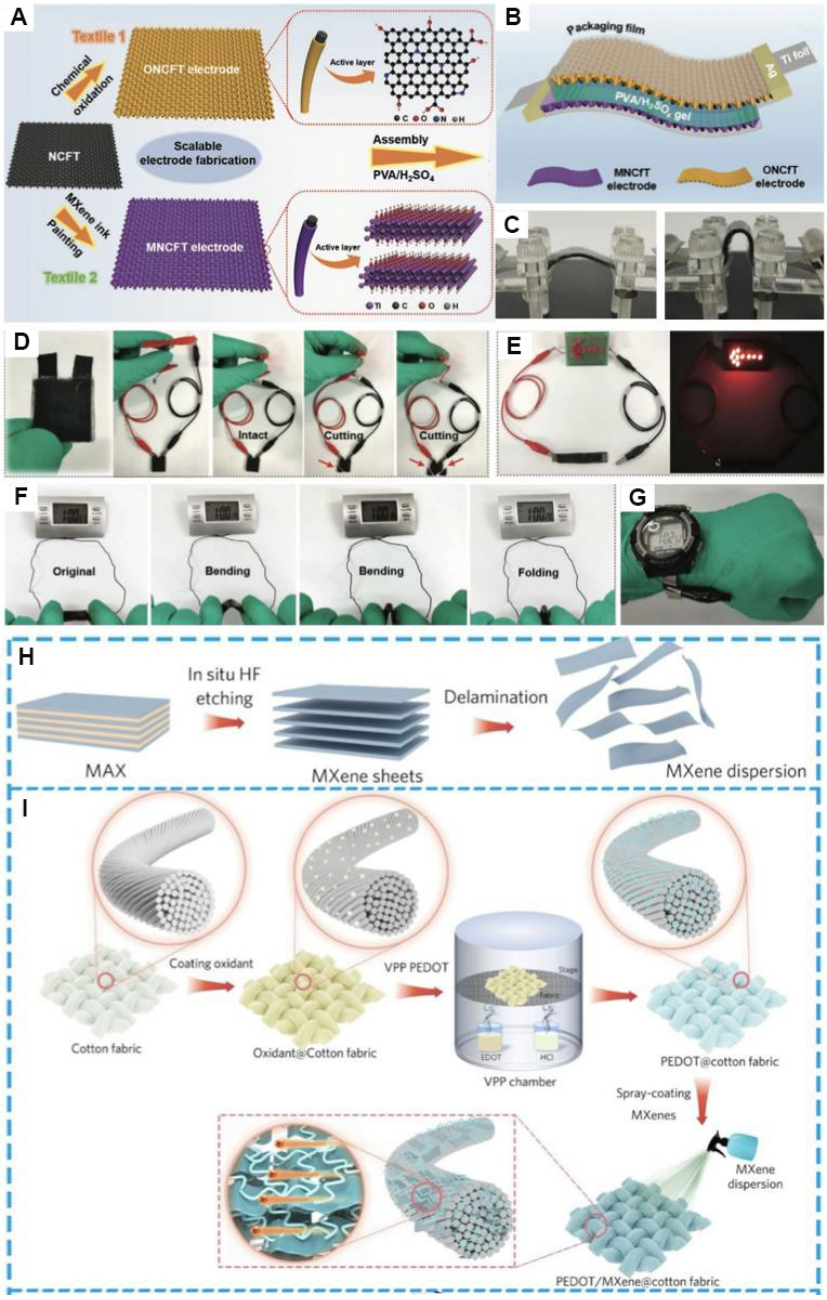

Figure 14. (A) Schematic illustration of the scalable synthesis protocol of the positive ONCFT electrode and negative MNCFT electrode. (B) The assembled MNCFT/ONCFT ASC. (C) Photographs of an MNCFT/ONCFT ASC at different bending angles of 45 and 180. (D) A square MNCFT/ONCFT ASC (2 cm × 2 cm) normally powers a fan under different damage states. (E) Photograph of two MNCFT/ONCFT ASCs connected in series which can drive an indicating arrow containing 10 red LED lights. (F) Images of an MNCFT/ONCFT ASC driving an electronic watch at different deformable status. (G) Wearable exhibition of an energy storage watchband[13]. (H) Schematic illustration of the fabrication of $Ti_3C_2T_x$ MXene. (I) Fabrication of PMFs[179]. MNCFT: MXene-decorated N-doped carbon fiber textile; ONCFT: O-functionalized N-doped carbon fiber textile.

excellent electrochemical performance with a wide and stable working voltage range of 0-2.2 V, high energy density of 164.13 Wh kg^{-1} at the power density of 1283.44 Wh kg^{-1}, and good stability with a capacity retention of 95.3% after 5000 charge-discharge cycles at 10 A g^{-1}[209]. However, self-healable is a passive process that requires meticulous manual alignment of electrodes and electrolytes, and sometimes even

requires external stimuli to ensure more effective healing. The mechanical strength is usually greatly deteriorated and thus brings the risks of performance decay and device failure. This is still a big challenge that needs to be overcome to be further applied in smart WSCs.

Thermal stability of hydrogel electrolytes is also a research challenge because of the polymer/monomer nature and the aqueous electrolyte contained within the hydrogels. Recently, all-temperature hydrogel electrolytes have also been developed to further adapt to harsh environments, especially in severe cold and hot regions, in which WSCs need to work[192,208,210-213]. Peng *et al.*[214] prepared a phosphoric acid/chitosan/PAA (CS-PAAm) hydrogel electrolyte. The as-prepared CS-PAAm hydrogels possess extremely high ionic conductivity and wide range of temperature tolerance from -60 to 100 °C. Additionally, this electrolyte also possesses good adhesiveness, toughness and flexibility, which is also important to further apply it for WSCs. The realization of all temperature self-healing hydrogel electrolytes could promote the development of existing WSCs.

ALL-IN-ONE WEARABLE SUPERCAPACITOR DEVICES

The most common way to fabricate all-in-one WSCs, whose structure is different from the traditional sandwich structure, is to deposit or *in situ* grow conductive polymers[212,215,216]/active materials[217,218] on both the upper and lower side of a multifunctional hydrogel electrolyte. For example, Wang *et al.*[219] produced an all-in-one supercapacitor by *in situ* growing PANi on high-strength PVA hydrogels [Figure 15A-D]. The as-prepared all-in-one SC also had high electrochemical properties (the highest volumetric capacitance is 2220 mF cm^{-3} at an aniline concentration of 0.5 mol L^{-1}, the capacitance remains 90% after 7000 cycles, and energy density and areal power density are 42 μWh cm^{-2} and 160 μW cm^{-2}, respectively). Furthermore, the mechanical properties including flexibility, toughness, and stretchability are all dependent on the hydrogel electrolyte.

Hence, based on such investigation, all-in-one SCs with specific functions were also developed along with the development of hydrogel electrolytes. Self-healing, fatigue-resistant, and self-recovering all-in-one supercapacitors were produced through PANi-decorated supramolecular PVA/poly(N-hydroxyethyl acrylamide) (PVA/PHEA) hydrogel electrolyte[212]. The multiple hydrogen bonding between PVA and PHEA and the ionic interaction among PANi not only endow excellent mechanical properties (tensile strength of 1.07 MPa and tearing energy of 2492 J m^{-2}) but also facilitate the transfer of charge and ions, which enhances the good electrochemical performance of the as-prepared all-in-one SC (98 mF cm^{-2} at current density of 0.2 mA cm^{-2}). Inspired by the temperature-tolerance hydrogel electrolytes, anti-freezing all-in-one SCs were also developed by one-step *in situ* growth of PANi onto a hydrogel electrolyte from cross-linked PAM networks soaked in ethylene glycol/water/H_2SO_4[220]. The as-prepared supercapacitors possess high mechanical (stretchability of 200% at -30 °C and can be repeatedly stretched for 100 cycles without significant capacitance loss) and electrochemical properties (91.7% capacitance retention after 100,000 cycles at -30 °C).

To further increase the skin-friendliness and safety of all-in-one SCs, moderate acids and biodegradable or natural polymers were applied in the investigation of all-in-one supercapacitors. All-in-one configured flexible and autonomously self-healable supercapacitors were prepared by *in situ* polymerizing and depositing rGO and PANi onto both sides of the tannic acid-treated gelatin mathacrylate and cellulose hydrogels[221]. The as-prepared all-in-one supercapacitor not only has good electrochemical performance (the volume capacitance, energy density, and power density of the as-prepared SC reached 1861 mF cm^{-3}, 20.65 mW cm^{-3}, and 595.59 mWh cm^{-3}, respectively) and mechanical properties but also give inspiration to the further study of biocompatible or implantable SCs. However, the stretchability, especially the

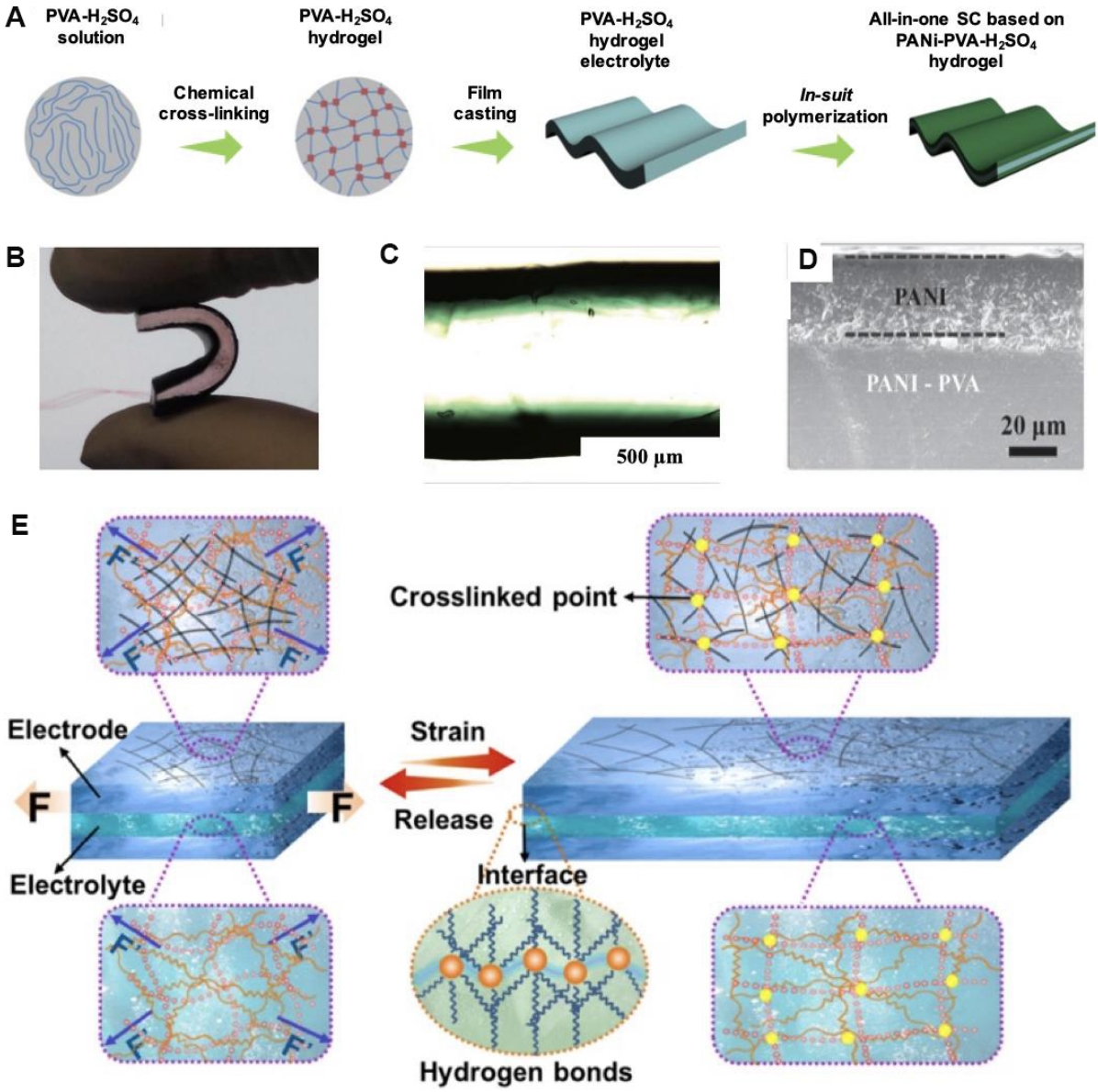

Figure 15. (A) Schematic of the device preparation process of SCs based on a single hydrogel electrolyte. (B) Image of a PANi-PVA SC. (C) Optical microscopy cross-section image of a PANi-PVA SC. (D) Cross-sectional SEM image of a PANi SC[219].(E) Schematic illustration of the stable network structure of an integrated all-hydrogel supercapacitor during the stress-strain process (F: force). (B-G) Electrochemical stability of an all-hydrogel supercapacitor under variant deformations[222].

compressibility, of the aforementioned assembled all-in-one supercapacitors is still limited because of the different mechanical properties of the non-hydrogel electrode and hydrogel electrolytes. Moreover, the energy density and power density still need to be further improved.

To overcome the mismatch of the mechanical properties of the different electrodes and electrolytes in all-in-one supercapacitors, all hydrogel-based all-in-one supercapacitors were recently reported. This supercapacitor consisted of hydrogel electrode (polyacrylamide/sodium alginate dual-network hydrogel with additional CNT and PEDOT:PSS) and the same hydrogel electrolyte (polyacrylamide/sodium alginate dual-network hydrogel with salt/redox couple) [Figure 15E][222]. Because of this specific structure and the

same hydrogel matrix for both electrode and electrolyte, the as-prepared supercapacitor possesses high stretchability and compressibility, strong self-adhesion, and good electrochemical performance (maintain areal capacitance of 128 mF cm^{-2} at 1 mA cm^{-2}, energy density of 3.6 μWh cm^{-2}, and stable energy output). This study, combining the traditional sandwich structure of SCs and the newly developed functional hydrogel electrodes, inspires a new strategy to develop WSCs, which can inherent the multiple functions of hydrogels to match the demands of wearable or implantable bioelectronics.

CHALLENGES AND FUTURE PROSPECTS

In this report, we discuss the up-to-date advancements in soft electrode materials and their synthesis approaches for WSCs, focusing on the importance of, as well as challenges involved in, endowing supercapacitors with multifunctional properties for wearable electronics. Heretofore, the development of soft materials for supercapacitors that can be deformed into arbitrary shapes and adapt to random musculoskeletal deformations in the human body is still a considerable challenge. The few operational multifunctional SCs that have been reported to date remain largely limited in terms of accommodating external wearable electronics. The development of some kinds of functional SCs such as hydrogel- and degradable material-based SCs satisfying the requirements for next-generation smart wearable or implantable bioelectronics, e.g., tactile sensors, implantable nervous sensors, electrophysiology sensors, and feedback stimulators, remains an arduous task, owing to the complicated physiological environment of the human body.

The electrochemical performance and advantageous characteristics of WSCs, including their areal, volume, and mass capacitance, cycle stability, rate capability, energy density, and power density, are usually determined by their behavior under normal, bent, twisted, or compressed shape conditions. The majority of WSCs that have been developed to date possess multifunctionality features, albeit sacrificing their electrochemical performance to some extent. More importantly, the stable energy output of these devices can hardly be guaranteed under dynamic deformation conditions; furthermore, the majority of studies to date have tested their electrochemical performance under static conditions. Therefore, ensuring the high electrochemical performance of WSCs, especially in terms of energy/power density, while preserving their multifunctionality features under physiological conditions, is probably the most significant challenge. Moreover, washable, breathable, wear-resistant, and comfortable properties, as well as a robust and nontoxic solid-state electrolyte, for WSCs are also needed to be seriously considered to fulfill the demand of everyday use. The stable electrochemical performance of WSCs after repeated washing is also the main limitation in the commercial devices.

Using existing electrode materials and flexible substrate as a starting point for satisfying their energy demand, the development of WSCs exhibits a promising future. Various pathways to design novel materials and device structures still need to reach the desired electrochemical performance and functionality of WSCs. Herein, we discuss the possible future directions for the development of WSCs for wearable and implantable bioelectronics.

Hydrogel electrodes combining conductive fillers

Embedding conductive fillers which perform EDLC or pseudocapacitance behavior in an existing non-conductive hydrogel matrix is also an effective strategy for fabricating conductive soft hydrogels, which could also be potential soft electrodes for WSCs. Han *et al.*[223] prepared a dual-network structure multifunctional polyvinyl alcohol (PVA)/CNT-cellulose composite hydrogel electrode for WSCs. The as-prepared solid-state supercapacitor obtains 117.1 F g^{-1} and capacitance retention of 96.4% after 1000 cycles. PVA has excellent hydrophilicity, solubility, biocompatibility, and non-toxicity properties[224]. Therefore,

PVA-based conductive hybrid hydrogels could inherit the mechanical properties of the PVA matrix and present special features, such as compressivity, toughness, and thermal stability, which are also desired for further intelligent WSCs[225,226]. To date, except PVA-based hydrogel electrodes for SCs, few works focus on the other polymer-based hydrogel electrodes for WSCs; thus, our group designed a series of self-adhesive, tough, and conductive polyacrylamide hydrogels[227-231] which could be further applied as soft electrodes for WSCs. In these previous studies, polydopamine (PDA) was combined with the hydrogels, which endowed the hydrogels with good self-adhesiveness inspired by the mussel[232]. Self-adhesiveness makes hydrogels guarantee comfortable wear experience, reliable and comfortable contact with tissue, and reduced interface resistance for the stable signal detection when applied in bioelectronics[233,234]. Furthermore, PDA, as a quinone-rich polymer, has already been applied in energy storage materials due to the redox behavior of quinone[235-237]. rGO has also been extensively applied as electrodes for SCs[238,239]. Based on the designed component of PDA and rGO, these conductive and self-adhesive hydrogels could also be potential candidates for functional WSCs. Other materials with pseudocapacitance behavior such as conductive polymers (PEDOT, PANi, and PPy), MOFs, and metal compounds have also been applied, which not only improve their electrochemical performance but also endow the electrodes with repeatable, long-term mussel-inspired self-adhesiveness[231]. These results also inspired our following study on multifunctional hydrogel electrodes for future intelligent multifunctional SCs in wearable and implantable bioelectronics.

Multifunctional soft electrodes for supercapacitors

One of the primary aspects of modern supercapacitor development is to accommodate the power needs of the soft bioelectronic devices used to monitor human health conditions. To successfully adapt to this unique physiological environment, soft electrodes with the ability to be stretched, compressed, bent, twisted, and deformed into arbitrary shapes must be further studied and developed.

Self-adhesion reduces the interfacial resistance between the electrode and the electrolyte, while further guaranteeing the stable, accurate, and simultaneous sensing of multiple stimuli by allowing the direct and robust adhesion of WSCs to human skin or other tissues under tensile, compressive, or twisting stress conditions[240-242]. In a dynamic/random motion environment, flexible, stretchable, tough, and self-adhesive bioelectronics are highly desired to ensure the conformal contact between the device and the biological tissue, a factor which critically affects their performance. Hence, soft materials such as hydrogel-based electrodes with self-adhesive properties are highly desirable for matching these advanced bioelectronics.

Implantable or biodegradable *in vivo* WSCs

Implantable or biodegradable WSCs are completely or partially embedded into the human or animal body and remain inside to match or power other bioelectronics and complete special tasks. The development of implantable SCs is an arduous task that must address multiple issues, such as the aspects of biocompatibility and biostability. For the long-term implantation of SCs, power output stability is another important factor that needs to be considered. At the same time, several important material properties, such as mechanical strength and conductivity, are significantly compromised by the swelling of materials under the water-rich human physiological solutions. Thus, materials with superior biocompatibility and long-term biostability must be designed to obtain functional electrode materials. To achieve power output stability, certain techniques that rely on harvesting energy from movement, chemical reactions, and ion-related changes in the human body also provide inspiration for the design of sophisticated implantable SCs[68,243,244]. Furthermore, some types of SCs consisting of environmentally and biologically degradable byproducts can completely dissolve *in vivo* after performing their special functions[46]. Therefore, biodegradable hydrogels need to be designed for functional biodegradable SCs.

Environmentally tolerant WSCs

Environmental tolerance is of great significance for WSCs, especially for applications in harsh environments. Conventional supercapacitors can operate in the temperature range from -40 to 200 °C[245,246]. The temperature tolerance of the devices is mainly dependent on the temperature tolerance of the electrode materials and hydrogel electrolytes. Thus, improving the temperature tolerance and stability of electrodes without compromising their other functionalities also constitutes a considerable challenge in designing WSCs with excellent durability and adaptability to harsh and complex environments.

DECLARATIONS

Author's contributions

Designed and wrote the manuscript: Jiang L
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All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

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