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Conductive polymers for stretchable supercapacitors

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ABSTRACT

Stretchable energy storage devices, maintaining the capability of steady operation under large mechanical strain, have become increasing more important with the development of stretchable electronic devices. Stretchable supercapacitors (SSCs), with high power density, modest energy density, and superior mechanical properties are regarded as one of the most promising power supplies to stretchable electronic devices. Conductive polymers, such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and poly(3,4-ehtylenedioxythiophene) (PEDOT), are among the well-studied electroactive materials for the construction of SSCs because of their high specific theoretical capacity, excellent electrochemical activity, light weight, and high flexibility. Much effort has been devoted to developing stretchable, conductive polymer-based SSCs with different device structures, such as sandwich-type and fiber-shaped type SSCs. This review summarizes the material and structural design for conductive polymer-based SSCs and discusses the challenge and important directions in this emerging field.

KEYWORDS

conductive polymer, stretchable, supercapacitor, pseudocapacitive, energy storage

1 Introduction

Thriving studies on electronic sensors, flexible robots, and wearable implantable sensors have recently composed a noticeable technology trend towards wearable electronic devices [1–7]. To enable electronics with reliable flexibility and stretchability, the corresponding energy storage devices, such as stretchable supercapacitors and batteries, should be featured with small volume, lightweight, and high energy/power density [8, 9]. Supercapacitors (SC) (also called electrochemical capacitor or ultracapacitor) show high power density, fast charge/discharge rate, and long cycle life, representing one of the most promising energy storage devices. Moreover, all-solid-state supercapacitor could fulfill superior stretchability, via packaged into sandwich-type by sandwiching gel electrolytes between two active electrodes, or twisted into fiber type with hydrogel-electrolyte-wrapped electrode materials [10–17]. So far, fibrous and thin-film all-solid-state SSCs have been reported, in which conductive polymer composite materials are often used as active electrode materials [1, 3, 16, 18–22].

Conductive polymers (CPs), which store chemical energy through redox reaction, are promising candidates as stretchable supercapacitor electrode materials owing to high capacitance [23], good flexibility, excellent conductivity [1], light weight, and low cost [24, 25]. However, the longevity of devices was severely restricted by the collapse of polymer structures upon cycling considering the swelling and shrinking during doping and dedoping processes. The most common strategies are the employment of composites with other robust substrates, such as cellulosic and carbon materials [10, 26–31]. To further fabricate SSCs with CPs, the mechanical property should be considered as one of the most important characteristics. Other properties, such as conductivity and specific surface area, dominating the capacity and rate performance also need to be taken into consideration.

Several recent reviews for CP-based SSCs have been reported, however, there are more challenges that should be considered and tackled in the future. In this review, we focus on the design of electrode materials and device structures based on conductive polymers, and their further applications in SSCs are covered as well. According to the design of electrode materials, CP-based electrode materials have been divided into two classes: conductive polymers and their composites. The former uses CP as the active material without other materials added, and the latter adopts CP composites with other electrode materials, such as transition metal oxides and carbon materials. According to the design of device structures, SSCs can be classified into two types: fiber-shaped and sandwich-type. To achieve stretchability, the helical structure was used in fiber-shaped SSCs and the wavy structure was introduced into sandwich SSCs. Strategies to achieve high stretchability, high rate performance, and stabile cycles based on the properties of the basic building blocks will be discussed along with the challenges and perspectives in this emerging field.

2 Material design for stretchable supercapacitor (SSC)

In SSCs, the substrate, current collector, electrolyte, and electrode material should all be taken into account to demonstrate the stretchability. At present, the most widely used stretchable substrates are elastic polymers with intrinsic stretchability, for example: polydimethysiloxane (PDMS) [16], silicone rubber (Ecoflex®) [13], polyurethane (PU) [32], and acrylate rubber [22]. Textiles and cellulose [33] that are less stretchable or non-stretchable can also be applied as substrates after structural modification.

Metals are the preferred materials as the current collector, such as gold, silver, and copper et al. [34, 35]. These metallic materials

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have high conductivity which is particularly useful for high rate performance. However, the intrinsic rigidity of bulk metal materials leads to deteriorated conductivity under low strain, which limits their application in stretchable devices. Some wavy structure has been designed and some nanostructured metals have been developed to improve the stretchable property [36]. And carbon materials such as carbon nanotube (CNT) and graphene have been introduced into stretchable supercapacitor as current collectors, thanks to their high conductivity and flexibility [37].

As for electrolytes, polyvinyl alcohol (PVA) is the most commonly used electrolyte for stretchable supercapacitors, while the capability of deformation is limited to minor strain. Other electrolytes such as polyacrylamide hydrogel [38] have been designed to accommodate large strain. And the promising electrode materials, considered as the core of stretchable supercapacitor, include conductive polymer, transition metal oxide, and carbon materials. Most of them are intrinsically low stretchable or non-stretchable at all, requiring specific structural designs to achieve stretchability.

Conductive polymers are one typical class of pseudo-capacitive materials that can engage in electrochemical doping or redox reaction with anions and cations. Many CPs (Fig. 1(a)) such as polyaniline (PANI), polypyrrole (PPy) and derivatives of polythiophene (PTh) have been widely applied in supercapacitors in light of their large capacitances, good flexibility, and high conductivity.

The mechanism of CP storing charges can be described by the following two formulas, i.e., p-doping upon oxidization and n-doping upon reduction,

$$\mathrm{CP} \rightarrow \mathrm{CP}^{n+}(\mathrm{A}^-)_n + ne^- \text{ (p-doping)} \quad (1)$$

$$\mathrm{CP} + ne^- \rightarrow (\mathrm{C}^+)_n\mathrm{CP}^{n-} \text{ (n-doping)} \quad (2)$$

where A^- and C^+ represent the anion and cation in the electrolyte. The most CPs work as p-doped state, such as PANI [39] and PPy [40], and only PTh materials [41] can be n-doped in commonly used CPs. During the reversible doping and dedoping, the counter ions with opposite charges will be entrapped or released from the polymer matrix (Fig. 1(b)).

2.1 Conductive polymer for stretchable supercapacitor

According to the mechanism of CPs storing charges, the structure will change back and forth between swelling and shrinking with anion and cation moving between electrode and electrolyte. Therefore, cycling performance of SSCs was severely restricted by the collapse of their structures during the doping and dedoping. To improve the cycle performance of SSCs, substrates with excellent mechanical property and high conductivity play a key role in the stability of conductive polymers.

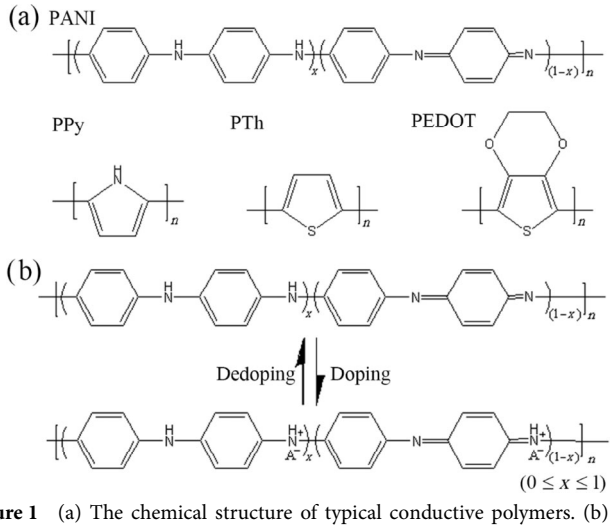

Figure 1 (a) The chemical structure of typical conductive polymers. (b) The mechanism of the doping/dedoping process of PANI.

Conductive polymers that could be easily deposited on the flexible/stretchable substrate by chemical or electrochemical oxidation, are promising candidates as stretchable supercapacitor electrode materials [13, 19, 30, 32, 42–44]. Different substrates have been explored to obtain stretchable properties, such as PDMS and elastic fibers, etc. Most substrates are insulators, therefore some conductive stretchable substrates are introduced into the SSCs (Fig. 2(a)). For example, Zhi et al. use stretchable stainless-steel mesh as substrate while the stretchable supercapacitor shows good rate performance under 20% strains due to the good electric conductive mesh [45], while this kind of supercapacitors can only work under small stretch range because of the low stretchability of substrates. Another design of CP electrode relies on the remarkable processability of it, by depositing CPs on some flexible/stretchable electrolytes (Fig. 2(b)), and provides another method to achieve stretchable supercapacitors. Wan et al. used PANI and physically crosslinked PVA hydrogel to construct an all-in-one configuration supercapacitor, which shows good flexibility, good cycling stability and robust self-healing capability [17].

The mechanical property is crucial for stretchable supercapacitors. Powder-like conductive polymers have relatively poor mechanical properties, therefore, some interconnected nanostructures have been designed to stabilize the structure of conductive polymers [46–48]. Bao and co-workers synthesized interconnected three-dimensional (3D) PANI nanofiber, showing capacitance retention ~ 91% over 5,000 cycles and ~ 83% retention over 10,000 cycles at a high current density of 5 $A \cdot g^{-1}$ (Fig. 2(c)). The cycling performance confirms the highly porous interconnected nanostructures can accommodate the swelling and shrinking of the polymer network during intensive cycling processes [49].

2.2 Conductive polymer composite materials for stretchable supercapacitor

The most common design of conductive polymers in stretchable supercapacitor is synthetic composite with other materials, which include carbon materials and transition metal oxides/hydroxides. Among them, carbon materials have high conductivity and good mechanical property, while their specific theoretical capacitance is relatively lower. In addition, transition metal oxide/hydroxide materials possess good electrochemical activity, high specific theoretical capacitance, but low conductivity in the meantime. Composite materials consist of the combination of two or more materials, in which each individual component exhibit its unique chemical, mechanical and physical properties [50–53]. Therefore, with the adoption of composite-based electrode materials, the performance of stretchable supercapacitor can be improved by integrating the advantages of several materials.

2.2.1 *Composite with carbon materials*

Carbon materials were the most commonly used composite materials due to their high conductivity and good mechanical property. For example, carbon nanotube, graphene, graphene oxide (GO) and carbon nanofiber have been used as composite components to maintain the specific capacitance and rate performance of the CP-based stretchable supercapacitors [54–56]. For example, Peng et al. deposited PANI on CNT with pre-stretched elastic substrate, and then developed a stretchable fiber-shaped SC, which can maintain 79.4 $F \cdot g^{-1}$ after stretching with a strain of 300% for 5,000 cycles (Fig. 3(a)). In this SSC, PANI shows high specific capacitance and excellent stretchability combined with aligned CNT and elastic Ecoflex [57].

Most commonly, a stretchable substrate was used as support for SSC to ensure its mechanical properties. However, the specific

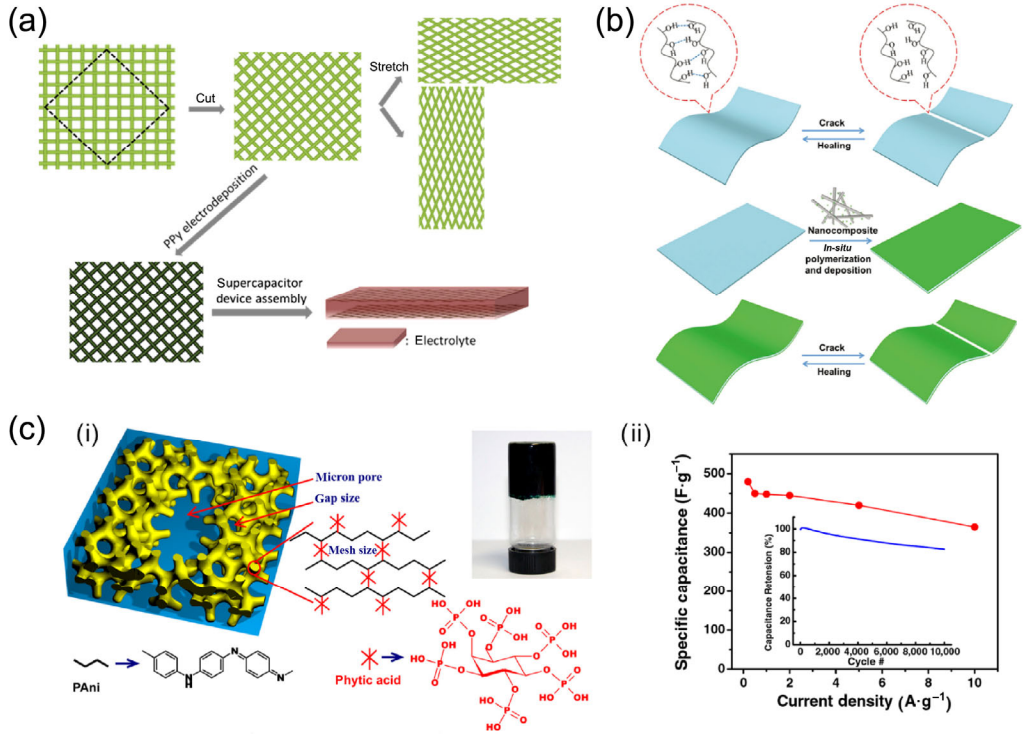

Figure 2 (a) Schematic illustration of fabrication of stretchable steel mesh with PPy electrodeposition (reproduced with permission from Ref. [45], © Elsevier 2015). (b) Schematic illustration of preparing the flexible healable all-in-one configured supercapacitor from the *in-situ* polymerization (reproduced with permission from Ref. [17], © Wiley 2018). (c) (i) Schematic illustration of fabrication of 3D hierarchical microstructure of the gelated PANI hydrogel; (ii) the rate and cycle performance of the microstructured PANI (reproduced with permission from Ref. [49], © Proceedings of the National Academy of Science of the United States of America 2017).

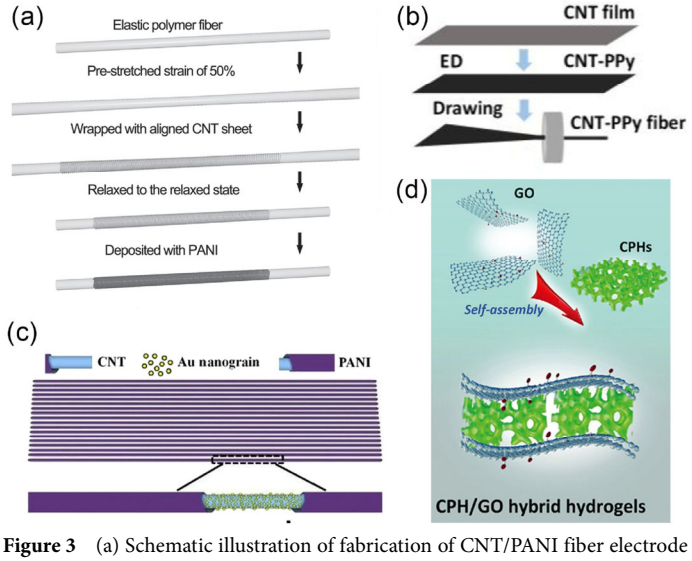

Figure 3 (a) Schematic illustration of fabrication of CNT/PANI fiber electrode (reproduced with permission from Ref. [57], © Wiley 2014). (b) Schematic illustration of preparing the CNT-PPy composite fiber (reproduced with permission from Ref. [19], © Royal society of chemistry 2016). (c) Schematic illustration of fabrication of PANI@Au@CNT sheet (reproduced with permission from Ref. [44], © Elsevier 2017). (d) Schematic illustration of CPH/GO hybrid hydrogels formation (reproduced with permission from Ref. [30], © Wiley 2018).

capacitance will be deteriorated because substrate itself occupies the device weight without providing capacity. Therefore, a lot of researchers have focused on self-supporting electrode in order to increase the specific capacity. Carbon-based materials have been widely used for constructing free-standing electrode in SCs due to their unique electrical and mechanical properties. Wei and co-workers prepared CNT-PPy fibers from porous macroscopic CNT-PPy composite film by drawing through several diamond wire-drawing dies (Fig. 3(b)), which exhibit high specific capacitance of 302 $F \cdot g^{-1}$ in the liquid electrolyte. Nevertheless, the fiber-shaped stretchable supercapacitor can only work at low strain about 10% [19].

Conductivity is one of most important roles for SC electrodes, especially for stretchable supercapacitors, because in usual cases conductivity decreases when the strain increases. To improve the axial electron transport, Baughman et al. use Au nanograin decorated with aligned multiwall carbon nanotube sheets, followed by incorporation of polyaniline [44] (Fig. 3(c)). In such an electrode, the embedded Au nanograins result in fast axial electron transport in the liner electrode. Three-dimensional continuous nanostructure can help electron transmission and ion transport. Yu and co-workers reported interconnected, self-standing 3D nanostructured conductive polymer hydrogel (CPH)/GO composite hydrogel fiber-shaped electrode (Fig. 3(d)), showing enhanced specific capacitance and good mechanical strength [30]. Other key properties such as rate performance, cycle life and power density can be improved by further optimizing the morphology and structure of electrode materials.

2.2.2 *Composite with transition metal oxide materials*

Transition metal oxides are also promising candidate electrode materials for stretchable supercapacitor due to their high theoretical capacitance, while the low conductivity restricts their performances. The most commonly adopted solution is combining metal oxides with carbon materials and conductive polymers. Conductive polymers and their transition metal oxide composites are well-recognized positive electrode materials [27, 58–60]. And carbon materials are first employed as negative electrode for CP-based SSC due to their good conductivity, high specific surface area and stable electrochemical property. Chou and co-workers prepared asymmetric SSC fiber with CNT@MnO_2 core and CNT@PPy coating (Fig. 4(a)) [58]. The resulted stretchable asymmetric SC exhibits a specific capacitance of 60.435 $mF \cdot cm^{-2}$.

As we all known, the energy density E can be calculated by the equations as follows: $E = C\Delta V^2/2$, where C is the capacitance of

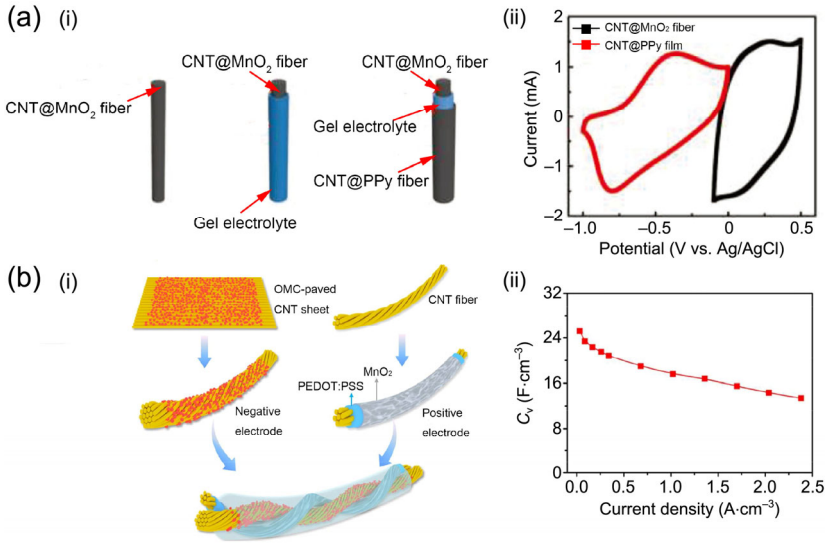

Figure 4 (a) (i) Schematic of asymmetric coaxial fiber supercapacitor fabrication process; (ii) the cyclic voltammetry (CV) curves of CNT@MnO_2 fiber and CNT@PPy film electrode, in which operating potential window can be increased to 1.5 V (reproduced with permission from Ref. [58], © Wiley 2016). (b) (i) Schematic illustration of fabrication of ordered microporous CNT and MnO_2@PEDOT:PSS coated CNT fiber asymmetric supercapacitor; (ii) the specific volumetric capacitance of the supercapacitor (reproduced with permission from Ref. [61], © American Chemical Society 2016).

the electrode, ΔV is the voltage window during the discharge process. Peng et al. developed a solid-state asymmetric fiber-shaped supercapacitor made of ordered microporous CNT negative electrode and MnO_2@poly(3,4-ethylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS) coated CNT fiber positive electrode (Fig. 4(b)), which shows high operating voltage 1.8 V, high volumetric energy density and high flexibility [61]. Other materials were also developed as composite materials, such as MoS_2 [59], $Ti_3C_2T_x$, V_2O_5 [31], nickel-cobalt layered double hydroxide [62] and so on.

3 Structural design of SSCs

Good mechanical durability, in terms of stretching or twisting reliability, is the key component for designing and fabricating wearable energy storage devices with high capacity, energy density, power density, stability, and safety. For SC, there are three strategies to fabricate stretchable supercapacitor: 1) obtaining stretchability through wavy, helical [63] or pre-stretched structures (depositing electrode materials onto a stretchable substrate); 2) connecting rigid active device islands with stretchable linkers (such as micro-supercapacitor); 3) assembling devices with all intrinsically stretchable components [64]. In the methods above, the first strategy was the most commonly used.

For SSCs, the capacitance can be calculated following the formula

$$C = I\Delta t/\Delta V \quad (3)$$

where C is the capacitance of the electrode, I is the discharge current, Δt is the discharge time, ΔV is the voltage window during the discharge process. The gravimetric specific capacitance is $C_m = C/m$, the areal specific capacitance $C_A = C/A$, the volumetric specific capacitance $C_V = C/V$, where m is weight of the electrode, L is the length of the electrode, A is the surface area of the fiber electrode ($A = \pi dL$), d is the diameter of the fiber, V is the volume of the fiber electrode ($V = \pi d^2 L/4$). The energy density E and power density P can be calculated by the equations as follows: $E = C\Delta V^2/2$, $P = E/\Delta t$. According to these formulas, the performance of SSCs is closely associated to C and ΔV, which is influenced by the characteristics of electrode material, such as conductivity, porosity, chemical property, morphology and so on. Thus, improving these features of the electrode materials will be the priority during the fabrication of SSCs.

For conductive polymer-based SC, designers need to take full account of synergism of every part of electrode materials: 1) the composition percentage of CP on electrode: The specific capacitance and energy density can increase with the raise of weight percent of active materials (PANI, PPy or PEDOT:PSS), while the stability will be negatively affected; 2) the area of contact with the current collector: Large effective area in contact with current collector ensures the rate performance. Based on these considerations, two kinds of SSCs were designed: fiber-shaped stretchable supercapacitor and sandwich-type stretchable supercapacitor.

3.1 Fiber-shaped stretchable supercapacitors (FSSCs)

Fiber-shaped stretchable supercapacitors exhibit lightweight, small volume and large flexibility, which render them easily weaved, twisted or stretched, and facilitate their integration into devices [54, 65–69]. To optimize the performance of FSSCs, some properties should be improved specially during stretching or twisting, which include: specific capacitance ($F\cdot g^{-1}$, $mF\cdot cm^{-2}$, or $mF\cdot cm^{-3}$), energy density ($Wh\cdot kg^{-1}$, $\mu Wh\cdot cm^{-2}$, or $\mu Wh\cdot cm^{-3}$), power density ($kW\cdot kg^{-1}$, $mW\cdot cm^{-2}$, or $mW\cdot cm^{-3}$), rate performance, cycle life, and so on.

The FSSCs can be divided into coaxial (core/shell structured) and non-coaxial according to their structures, as shown in Fig. 5, the former uses an elastic or carbon material fiber as core, layer by layer coated with a layer of active material, a layer of electrolyte and another layer of active material; the latter has two intertwined fibers coated with electrode materials. The core/shell structure of FSSCs makes the active materials of two electrodes in close contact, while the loading weight cannot be very high. And non-coaxial FSSCs, however, is the opposite.

In order to fulfill stretchability, the elastic polymer is employed as the core fiber wrapped with electrode materials. For example, Peng and co-workers demonstrated two aligned electrodes prepared using pre-stretched Ecoflex® coated with CNT and PANI [57] (Fig. 6(a)). The CNT sheets ensure the fast electron transport. In addition, polyaniline provides high pseudocapacitance for the fiber-shaped supercapacitor (FSC) and the elastic polymer supports the structural stability. Due to the pre-stretched core, the fiber-shaped SC can be stretched up to a high strain of 500%.

Textiles, whose structures can accommodate deformation due to body movement, have been developed as electrode substrates. Self-powered garments can be created by combining them with piezoelectric, or thermoelectric devices to capture energy from body

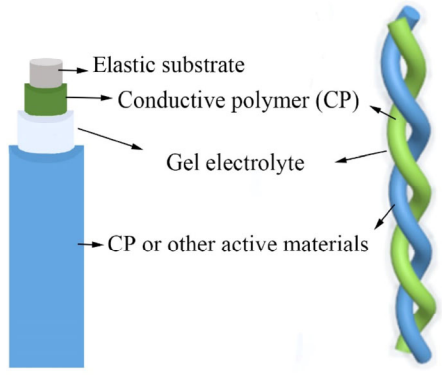

Figure 5 Schematic illustration of conductive polymer-based fiber-shaped stretchable supercapacitor (left is coaxial structure and right is non-coaxial structure).

movement or heat respectively. Zhu et al. used urethane elastic fiber and cotton fiber as substrate, CNT as a dyestuff and polypyrrole as active material to prepare stretchable yarn supercapacitor (Fig. 6(b)), which delivered high capacitance at 80% stain [42].

To increase the weight percentage of active materials, a useful method is proposed to fabricate self-supporting fiber electrode. By combining carbon materials with conductive polymer, the additional substrate weight and volume can be lower, and the performance of the devices can consequently increase. In Fig. 6(d), Wei and co-workers prepared carbon nanotube-polypyrrole fiber-shaped supercapacitor, obtained flexible fibers by transforming composite film, achieving the power density and energy density up to 3.8 $kW \cdot kg^{-1}$ and 3.6 $Wh \cdot kg^{-1}$, respectively. Without elastic substrate, the fibers were not stretchable, therefore, the helical structure was designed to achieve stretchability [19].

Most free-standing electrodes with simply mixed active materials and carbon materials have reduced flexibility. In this regard, Yu and co-workers developed a universal and facile strategy to construct highly efficient and robust self-standing CPH/GO hydrogel (Fig. 6(e)). The FSSC based on this hydrogel shows uniform interconnectivity and enhanced mechanical properties, delivering high volumetric energy density of 8.8 $mWh \cdot cm^{-3}$ and can maintain 86% of the initial capacitance after 17,000 cycles.

Other designs of electrode structures and active materials have been reported to realize different properties, such as self-healing [32, 70], transparent [71–73], or self-charging [14]. Jiang and co-workers reported a stretchable and self-healable supercapacitor

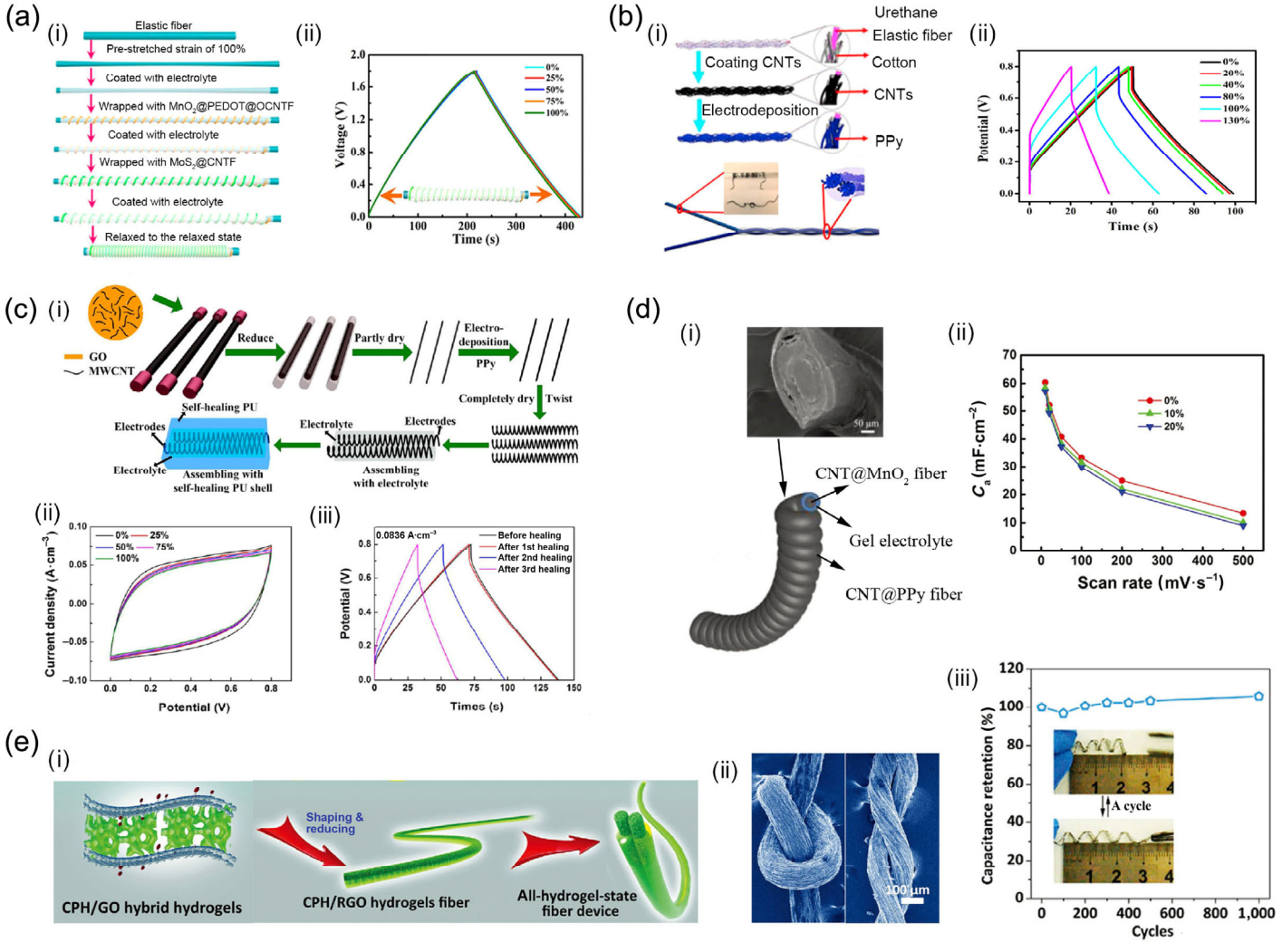

Figure 6 (a) Schematic illustration of fabrication of MnO_2@PEDOT:PSS@CNT fiber electrode and its performance under different stretching states (reproduced with permission from Ref. [59], © Elseriver 2017). (b) Schematic illustration of all-solid-state yarn supercapacitor by coating CNT@PPy on urethane elastic fiber and its performance under different stretching states (reproduced with permission from Ref. [43], © Elseriver 2016). (c) Schematic diagrams of stretchable and self-healable PPy@RGO@MWCNT electrodes and its performance under different stretching and after self-healing (reproduced with permission from Ref. [32], © American Chemical Society 2017). (d) Schematic of helical CNT@PPy fiber supercapacitor and its performance under different stretching (reproduced with permission from Ref. [58], © Wiley 2016). (e) Schematic illustration of CPH@GO hybrid all-hydrogel-state fiber device and the elasticity of the spring-like full cell (reproduced with permission from Ref. [30], © Wiley 2018).

by wrapping fibrous springs with a self-healing polymer outer shell [32]. The supercapacitor has 54.2% capacitance retention after third healing (Fig. 6(c)).

3.2 Sandwich-type stretchable supercapacitors (SSSCs)

Compared to fiber-shaped supercapacitor, sandwich structure supplies more contact area between active materials and current collectors, which helps the electron collection. While owing to the larger area of loading tensile force, thin film-configured supercapacitors are more likely to be damaged than fibrous ones when applied with large tensile strain [16]. To realize the stretchability of sandwich-type supercapacitors, elastic substrates have been used, such as PDMS [16, 28], Ecoflex rubber film [13], acrylate rubber [22] and nylon lycra fabric [42].

Thin-film structure cannot be easily spiraled to approach stretchability, therefore it shows high dependence on substrate in terms of extensibility. PDMS is often used as substrate for SSSCs. Wei et al. prepared graphene woven fabric (GWF) and polyaniline sandwich-type stretchable supercapacitor by pre-stretching PDMS (Fig. 7(a)). The SSC works well during dynamic stretching process due to the shape of grid. Combining with carbon nanotube, the stretchable supercapacitor reported by Kim et al. showed 77 $F \cdot g^{-1}$ and 6.87 $Wh \cdot kg^{-1}$ at biaxial strain of 600% thanks to the biaxial pre-strain (Fig. 7(b)).

A lot of researchers focused on high stretchability of sandwich-type supercapacitor [74], Chen and co-workers developed highly stretchable thin-film electrodes by compositing aligned compact CNT and silver-doped PEDOT:PSS (Fig. 7(c)). Their all-solid-state supercapacitors could achieve a stretchability of 480% with 98% performance retention considering that the aligned compact CNTs are bundled tightly by the chains of PEDOT:PSS and can maintain good contact with each other [16]. Honeycomb-lantern-inspired 3D stretchable supercapacitors designed by Chen and co-workers can maintain a capacitance ratio of 95% even under the reversible strain of 2,000% after 10,000 stretch-and-release cycles [75].

Intrinsically stretchable electrode possessing good mechanical performance and high electronic conductivity can improve specific capacitance and rate capability compared to insulating elastic substrate. Wang and co-workers developed intrinsically stretchable electrodes composed of acrylate rubber (ACM)/multiwall carbon nanotube (MWCNT) composite film, supported poly(1,5-diaminoanthraquinone) (PDAA) and PANI. A high energy density of 2.14 $mWh \cdot cm^{-3}$ at a power density 0.021 $W \cdot cm^{-3}$ has been obtained by an asymmetric organic stretchable supercapacitor [22].

3.3 Stretchable micro-supercapacitors (SMSCs)

Micro-supercapacitors (MSCs), as the indispensable component of energy harvesting and storage systems, being possibly scaled down in dimensions to fit on-chip geometry of integrated circuits, have gained great research interests. For stretchable micro-supercapacitors, electrode materials were usually deposited on stretchable substrate, such as PDMS [20, 76], polypropylene (PP) film, stretchable textile [34] and so on. The output voltage of MSC can be further improved by arraying through photolithography, etching or 3D printing methods [77]. To obtain SMSC array, the usual method is connecting several single devices together or designing an MSC array mold, and then transferring it to stretchable substrate. For example, Ha and co-workers directly connected several MSCs together to form arrays and then embed them into PDMS to build integrated MSSCs [78].

Good stretchability and stable electrochemical performance can be coordinated by introducing some structural designs, such as wavy electrodes. For example, Shen and co-workers fabricated highly stretchable micro-supercapacitors and designed wavy hybrid multiwalled carbon nanotubes/polyaniline electrodes (Fig. 8(a)), which are almost invariable under different stretching stations ranging from 5%–40% [77].

Connection structure can also be designed to approach stretchable, for example, Komvopoulos et al. design a honeycomb PDMS substrate for stretchable micro-supercapacitor arrays (Fig. 8(b)).

These structures can accommodate a large deformation without producing excessive strain in the MSCs and interconnects [20].

Recent papers about SSCs with conductive polymers were summarized in Table 1, and we conclude that: The conductive

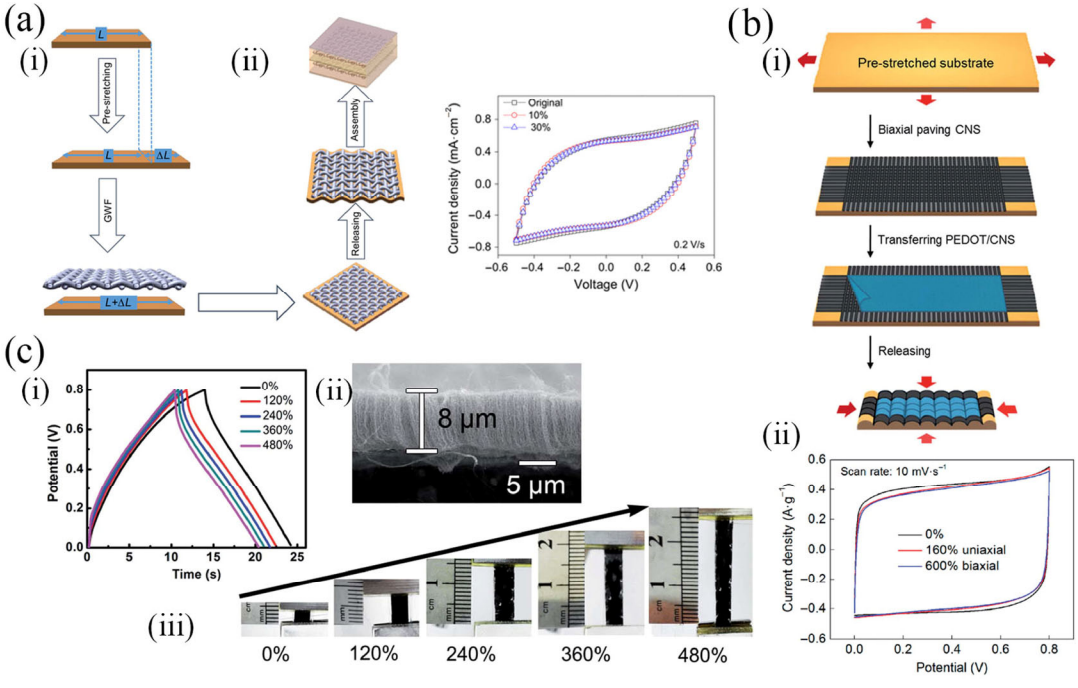

Figure 7 (a) Schematic illustration of stretchable GWF-based supercapacitor and its performance under different stretching states (reproduced with permission from Ref. [28], © Elseriver 2015). (b) Schematic digram of the fabrication process of stretchable PEDOT@PSS hybrid nanomembrane and its performance under different stretching states (reproduced with permission from Ref. [13], © Roayal society of chemistry 2016). (c) (i) Stretchable properties of supercapacitors-based Ag-doped PEDOT:PSS/CNT; (ii) SEM image of as-transferred CNT film on PDMS substrate; (iii) the photographs of electrode and supercapacitor during stretching from 0%–480% (reproduced with permission from Ref. [16], © Roayal society of chemistry 2018).

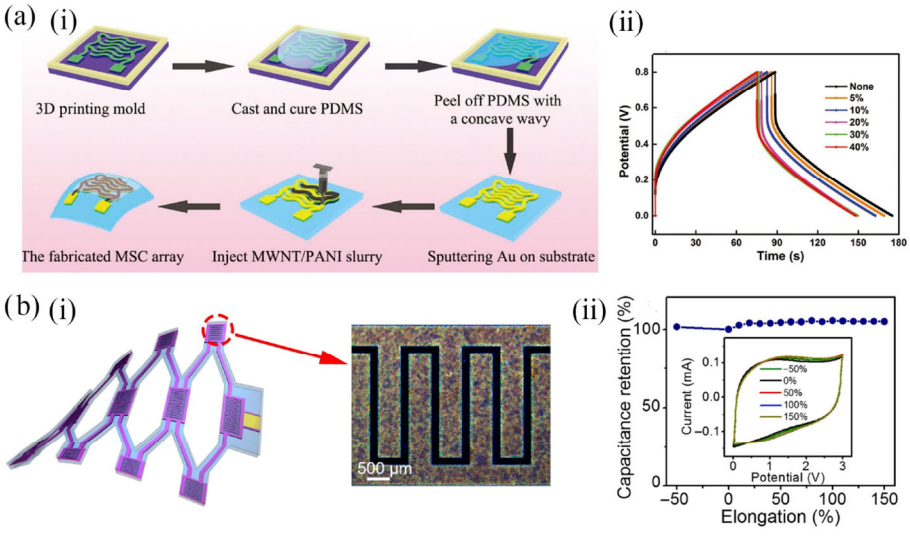

Figure 8 (a) Schematic illustration of the fabrication of stretchable micro-supercapacitor and its performance under different stretching states (reproduced with permission from Ref. [77], © Wiley 2017). (b) Schematic diagram of fabrication honeycomb structure MSC array device and its performance under different stretching states (reproduced with permission from Ref. [20], © American Chemical Society 2016).

Table 1 Comparison of conductive polymer based SSCs

Electrode	Substrate	Electrolyte	Specific capacitance ($F·g^{-1}$)	Areal capacitance ($mF·cm^{-2}$)	Power density ($mW·cm^{-3}$)	Energy density ($mWh·cm^{-3}$)	V (V)	Stretchability	Ref.
PPy/CNT	—	PVA/H_3PO_4	69	74.1	9.9 ($kW·kg^{-1}$)	3.6 ($Wh·kg^{-1}$)	0.8	10% strain	[19]
PPy/CNT & MnO_2/CNT	—	PVA/KOH	—	60.435	1.6 ($mW·cm^{-2}$)	0.18 ($mWh·cm^{-2}$)	1.5	20% strain	[58]
PANI/CNT/Au	—	PVA/H_3PO_4	—	0.2 ($F·cm^{-3}$)	—	—	0.75	400% strain	[44]
PEDOT:PSS/MnO_2/OCNTF & MoS_2/OCNTF	Elastic fiber	PVA/LiCl	—	278.6	—	125.37 ($\mu Wh·cm^{-2}$)	1.8	100% strain	[59]
PANI/CNT	Elastic polymer fiber	PVA/H_3PO_4	111.6	3.08	—	—	1.0	400% strain	[57]
PANI/CFT & functionalized CFT	—	PVA/H_3PO_4	—	4.5 ($F·cm^{-3}$)	6.57	2	1.6	100% strain	[27]
PPy/CNT	Urethane elastic fiber	PVA/H_3PO_4	—	69	10.8	0.4678	0.8	80% strain	[43]
PPy/rGO/MWCNT	—	PVA/H_3PO_4	—	25.9 ($F·cm^{-3}$)	7.3	0.94	0.8	100% strain	[32]
PANI/GO	—	PVA/H_2SO_4	112	—	30.77	8.8	0.8	40% strain	[30]
PANI/CNT	Elastic cord	PVA/H_2SO_4	394	15.4	—	—	0.6	100% strain	[54]
PEDOT/CNT/MnO_2	—	PVA@LiCl	—	11.88	—	—	1.0	74% (1,000 cycles at 200% strain)	[12]
PPy/RGO	Fabric nylon lycra	Li_2SO_4 aqueous	114	—	—	2.53 ($Wh·kg^{-1}$)	0.8	50% strain	[42]
PEDOT/CNS	Ecoflex rubber film	PVA/LiCl	82	11	—	7.28 ($Wh·kg^{-1}$)	0.8	600% strain	[13]
PANI/GWF	PDMS	PVA/H_3PO_4	—	8	—	—	0.5	30% strain	[28]
PPy	Steel mesh	PVA/H_3PO_4	214	—	—	—	0.6	20% strain	[45]
PEDOT/SWCNT	PDMS	PVA/H_3PO_4	215	1.6	19.2 ($kW·kg^{-1}$)	6 ($Wh·kg^{-1}$)	0.9	100% strain	[18]
Ag-PEDOT/CNT	PDMS	PVA/H_3PO_4	85.3	64	—	—	0.8	480% strain	[16]
PANI /MWCNT	PDMS	PMMA-PC-$LiClO_4$	—	44.13	0.07 ($mW·cm^{-2}$)	0.004 ($mWh·cm^{-2}$)	0.8	40% strain	[77]
PANI/MWCNT	Acrylate rubber	ACM/Et_4NBF_4-AN quasi-solid-state	—	17.2 ($F·cm^{-3}$)	—	2.14	2.7	50% strain	[22]
PANI/GO & GO	PDMS	PVA/LiCl	576	—	—	77.8 ($Wh·kg^{-1}$)	1.9	100% strain	[56]
PPy/CNT	—	VSNPs-PAA	—	—	—	—	0.6	600% strain	[70]
PANI	—	Porous PVA/H_2SO_4	—	300.9	—	—	0.8	75% strain	[79]
PPy/CNT	—	VSNP-PAM/H_3PO_4	—	—	—	—	0.6	1,000% strain	[38]
PPy/CNT & MnO_2/CNT	—	KCl–CH_2=CH–SiO_2/PAAM	—	2.2 ($F·cm^{-3}$)	4	0.31	2.0	100% strain	[80]

polymer-based electrodes are mostly composed of carbon materials or integrated with electrolyte for enhanced stability; sandwich-type SSCs show higher energy density than fiber-shaped ones because of the higher weight loading, while maintaining less stretchability; the voltage window of conductive polymer-based SSCs can be widened by employing asymmetric electrode materials; stretchable electrolytes play a key role in building SSCs, therefore it is important to develop novel electrolytes with high stretchability.

4 Stretchable electrolyte

The electrolyte plays an important role in stretchable supercapacitor. Most stretchable supercapacitors use PVA-based electrolyte, and all-solid-state SSCs can be assembled by composite H_2SO_4, H_3PO_4 or KOH with PVA gel. Adopting intrinsically stretchable electrolytes without substrate will be a good solution to improve the specific capacitance of SSSCs. Zheng et al. prepared porous PVA/PANI composite supercapacitor (Fig. 9(a)), which shows high areal capacitance of 300.9 mF·cm^{-2} due to *in situ* polymerization PANI on PVA [79].

An appropriate electrolyte for stretchable supercapacitor needs high stretchability and compressibility, thus electrolyte molecules and structures should be well designed [80, 81]. Hu et al. fabricated a high strain 3D porous PVA by using sodium dodecyl sulfonate (SDS) as template, and this kind of electrolyte makes the SSC retain 78% capacitance with 75% strain [79]. Moreover, the mechanical strength of hydrogel electrolyte needs to be improved while maintaining a high level of stretchability and electrolyte adsorption ratio. Other electrolytes have been designed to obtain better mechanical property. For example, Zhi and co-workers showed an innovative stretchable electrolyte: introducing vinyl hybrid silica nanoparticle cross-linkers into polyacrylamide hydrogel backbones to promote dynamic cross-linking of polymer networks (Fig. 9(b)), and the electrolyte can be stretched up to 1,000% strain [38]. They further obtained self-healable and highly stretchable supercapacitor by designing intrinsically self-healable and high-stretchability electrolyte (Fig. 9(c)), making the SSC retain capacitance even after 20 breaking/healing cycles or with up to 600% strain [75].

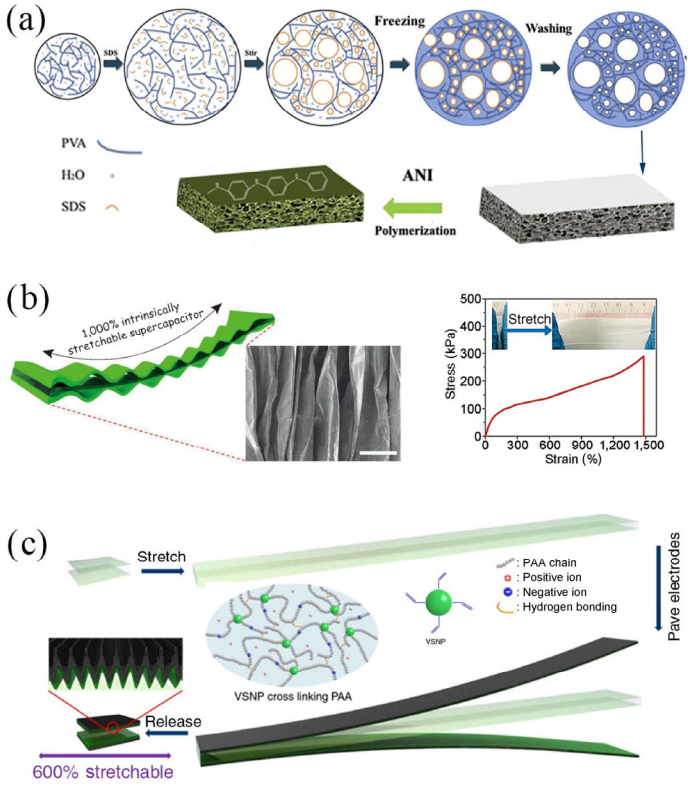

Figure 9 (a) Schematic of stretchable electrolyte and its strain property (reproduced with permission from Ref. [79], © Wiley 2017). (b) Schematic illustration of porous PVA electrolyte and PVA/PANI composite supercapacitor (reproduced with permission from Ref. [38], © Elsevier 2017). (c) Schematic illustration of preparation of polyelectrolyte by using VSNPs crosslinker and fabrication of stretchable supercapacitor (reproduced with permission from Ref. [70], © Nature 2015).

5 Conclusion and prospect

Stretchable supercapacitors are of great importance in wearable, on-skin and/or implantable soft electronic systems. In this review, we focus on material and structural design to realize the high-performance stretchable power devices in terms of electroactivity and stretchability. We first discuss the electrode materials of stretchable supercapacitors from conductive polymers to their composites, and then summarize the structural design strategies, which include fiber-shaped SSC, sandwich-type SSC and micro SSC. It is noteworthy that the electrolyte is also a significant component in building stretchable supercapacitors. For conductive polymer based stretchable supercapacitors, to approach high capacity, energy and power density, stability, accompanied with good mechanical durability in terms of stretching or twisting reliability, two main designs should be considered: 1) material design: i) improving stability and conductivity by compositing CP with other high conductive materials; ii) accelerating ion transport and electric transfer by designing 3D porous nanostructure. 2) structural design: i) obtaining stretchability through wavy or helical structure; ii) connecting rigid active device islands with stretchable linkers; iii) assembling electrodes by pre-stretching substrate.

Other key components should also be considered in stretchable supercapacitor, such as substrate, current collector, and electrolyte. Undoubtedly, existing conductive polymer-based SSCs electrodes are mostly composites with carbon materials to improve stability and conductivity. Nevertheless, simple mixing can lead to the aggregation of electrode components and further influence the mechanical performance of SSCs. Thus, universal and facile strategies should be designed to synthesize composites with conductive polymer and carbon materials. Combining 3D nanostructure morphology, micro-porous structure, high conductivity and good mechanical property, innovative conductive polymer electrode materials should be designed. PVA-based gel electrolyte is the most commonly used electrolyte, while being limited by poor stretchability and narrow voltage window. Some novel electrolytes with broad potential range and excellent stretchability need to be paid more attention. Finally, main efforts should be focused on practical considerations, such as *in situ* characterization of performance and/or realizing long-term stability and durability.

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