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Recent progress of fiber-shaped asymmetric supercapacitors

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ABSTRACT

Fiber-shaped supercapacitors have attracted widely attention for their great potential application in future portable and wearable electronics compared with traditional 2D planar structured super-capacitors, which is associated to their high flexibility, tiny volume and good deformability. Asymmetric designed supercapacitors usually couple two different electrodes with a Faradaic or battery-type electrode as the energy source role and a non-faradaic (or electric double-layer) electrode as the power source in one configuration, and thus can operate in much wider potential windows than that of the symmetrical design, thus potentially leading to a substantial increase in the energy density. Here, we focused on the recent progresses and advances of fiber-shaped asymmetric supercapacitors (FASCs) with respect to their electrode materials, design and configuration. Firstly, capacitive and pseudocapacitive materials, such as carbon materials, conductive polymers and metal oxides/sulfides/nitrides, are comprehensively discussed with the scope of their working potential ranges, proper electrolytes and working principles. Then the progresses to date on the FASCs including the device design, electrode fabrication and electrochemical performance of the FASCs are summarized. Finally, a short conclusion is made, combining with the future perspectives in this rapid developing area.

1 Introduction

The developments of efficient renewable energy technologies become more and more significant due to the rapidly depletion of fossil fuels and climate change now. Energy storage systems with the merits of cost-effective, maintenance-free, highly efficient, and environment-friendly are becoming increasingly demanding and make rapid development. Supercapacitors, also called electro- chemical capacitors, present the attractive advantage of bridging the energy density gap between traditional capacitors and batteries (Fig. 1) [1-4]. This is due to that they can provide a higher power density than batteries, and higher energy density than conventional capacitors, while offering long cycle lifetimes [5]. Significant efforts have been made to achieve high energy density supercapacitors without sacrificing their power density in the past decades, however further breakthrough for supercapacitors toward practical utilization is also full of challenges [6].

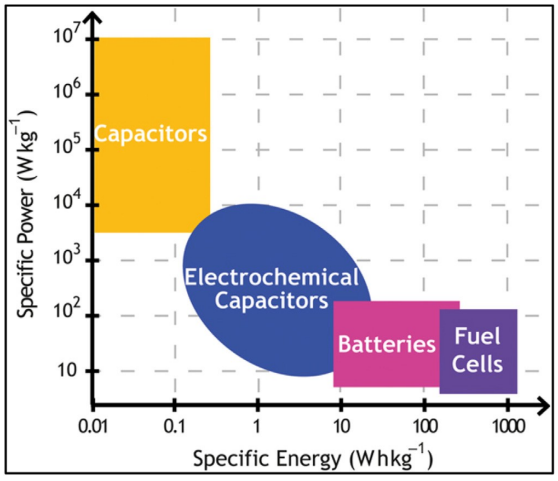

Fig. 1. Specific power versus specific energy plot comparing common electrical energy storage devices. Reproduced with permission [3]. Copyright 2011, Cambridge Core.

Recently, wearable electronic devices, including displays, sensors, transistors, etc. have attracted extensively attention for their applications in various fields, such as medical treatment, military, outdoor sports. These advanced wearable electronic devices require the miniaturized size of electronic components and more importantly incorporating them into clothes or other accessories (watch, eyeglass, etc.) [7]. Flexible solid-state supercapacitors, which have been considered to be the promising candidates to power portable and flexible electronic devices, have also been extensively studied. Compared with the 2D traditional planar structured supercapacitors, fiber-shaped supercapacitors have exhibited great potential in portable and wearable electronics due to their tiny volume, higher flexibility, and excellent deformability [8,9]. Recently, fiber-shaped supercapacitors have made consider- able progress [10-12]. However, most of the fiber-shaped super- capacitors are based on the symmetrical design with two identical electrodes in aqueous based gel electrolyte. In this content, the symmetric-type cell has a limited operating working potential less than 1 V, and thus displays relatively low energy density according to the equation of E $1/2CV^2$ [13-15]. Most reported fiber-shaped symmetric supercapacitors possess an energy density in a range 10^{4} to 10^{2} m Wh cm ^{2}, which cannot meet the requirement from the practical applications [16-18]. Asymmetric supercapacitors usually consist of two different electrodes with a Faradaic or battery type electrode as the energy source and a non-faradaic (electric double-layer) electrode as the power source, can work in much wider potential windows and achieve a substantial increase in the energy density [19-21]. Therefore, asymmetric strategy may be one of the most effective way to overcome the energy-density limit compared with symmetric design. Fig. 2 shows the schematic illustration of asymmetric supercapacitors.

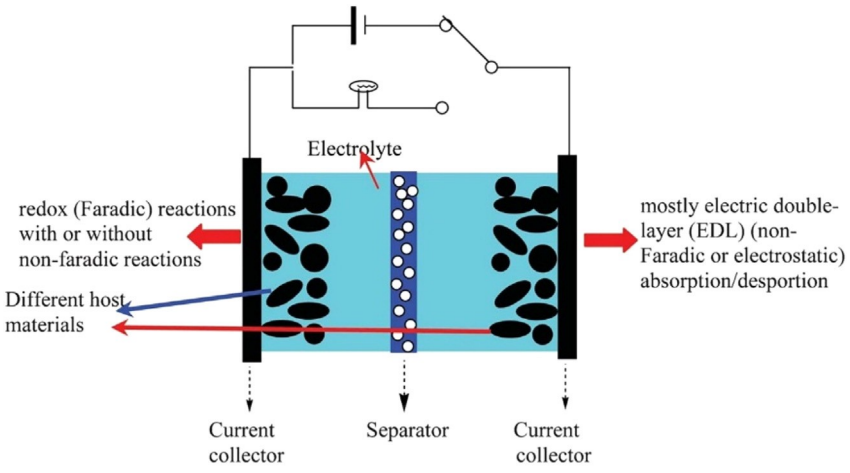

Fig. 2. Schematic illustration of asymmetric supercapacitors. Reproduced with permission [1]. Copyright 2013, The Royal Society of Chemistry.

Here, we will focus on the recent progress and advances of fiber- shaped asymmetric supercapacitors (FASCs). We first review the advantages of FASCs. Fiber-shaped supercapacitors are a promising energy storage device for wearable electronics due to their unique features such as high flexibility, knittability, small size and light weight. In addition, a proper asymmetric design combining two materials with different potential windows in the same electrolyte can largely increase the operating voltage, thus achieving higher energy density. Then, we summarize the capacitive performance of various electrode materials and evaluate their possibility of utilization in FASCs. One important factor for fabricating a high performance FASC is how to choose the electrode materials. In this section, capacitive or pseudocapacitive materials such as carbon materials, conductive polymers and metal oxides/sulfides/nitrides are discussed in detail, as well as their proper electrolytes and working potentials. Thirdly, we focus on the progress to date on the FASCs. In this part, the device design, electrode fabrication and electrochemical performance of the FASCs are summarized. Many reported studies show that electrodes are usually fabricated using metal wires (Au, Cu, Ni, Ti, etc.) or carbon-based fibers (carbon fibers, CNT fibers and graphene fibers (GF), etc.) as the current col- lectors. Most metal wires or carbon fibers have excellent properties in conductivity, and flexibility, thus providing conveniences in fabricating various high-performance FASCs as expected. Moreover, in order to meet the requirements from wearable electrodes, several FASCs with unique functionalities, such as stretchable, self- healable, shape-memory and electro-chromism are developed and are also summarized in this review. Lastly, a short conclusion combining with the future perspectives in this fast developing field is given. Overall, further improvements in energy and power performance are still needed including proper design of positive and negative materials electrode, gel electrolyte with high ion conductivity, large voltage window and safety. Moreover, it is highly desirable to develop FASCs with multiple functionalities with the high energy density, making them even more attractive for the customers. This review aims to give a comprehensive illustration of the FASCs, as well as a summary of selected contributions which we consider to be the representative ones. Through this review, we can have better understanding of the FASCs and their potential applications in wearable electronics.

2 Device configurations of FASCs

2. 1 Types of device configurations

Most FASCs can be classed to three types of device configurations that are parallel-like type, twisted type, and coaxial type [12]. In general, a parallel-like FASC device is composed of two parallel fiber-shaped electrodes with a gel-electrolyte as a separator. Twisted type FASCs are fabricated by twisting two fiber-shaped electrodes, while the coaxial type FASCs are assembled by wrapping the gel electrolyte coated core fiber-shaped electrode with an outer electrode layer. The fiber-shaped devices, with the advantages of light weight and good flexibility, could be easier to woven into electronic clothes. In addition, the coaxial type structure can provide larger and more efficient areas, thus decrease the contact resistance between the two electrodes. However, for all types of FASCs, it is crucial to balance the charges and avoid short circuit of the positive and negative electrodes.

2.2 Electrolytes of FASCs

Supercapacitors are typically composed by three parts: electrodes, electrolyte and separator. Electrolytes play a very important role on the performance of supercapacitors. For fiber-shaped energy storage devices, gel electrolytes are the most attractive because of their good mechanical strength under various deformity and ionic conductivity [12]. Among various polymer electrolytes, PVA based gel electrolytes, such as PVA/H_2SO_4, PVA/H_3PO_4, PVA/ KOH, and PVA/LiCL, have been mostly used in FASCs [16]. Other polymers, such as poly(ethylene oxide) (PEO), poly(methyl meth- acrylate) (PMMA), polyacrylate (PAA) and so on, have also been investigated for their using in gel electrolytes. Recently, organic liquid and ionic liquid electrolyte have been attracted extensive interesting for their high operating potential window [22-24]. However, only very few of fiber-shaped supercapacitors have been fabricated using organic liquid or ionic liquid electrolyte, due to their disadvantages of high cost and difficult to package. Even so, this providing us a potential avenue to fabricate FASCs with high working potential, thus achieving high energy densities.

2.3 Electrode materials of FASCs

Electrode materials are the most critical component as they determine the performance of an energy storage device to a certain extent. Carbon based micro/nano materials, conductive polymers and transition metal oxides are often used as the electrode mate- rials and have been investigated extensively. In this part, we mainly discussed the electrode materials for aqueous asymmetric super-capacitors and their proper electrolyte and working potential, as summarized in Fig. 3.

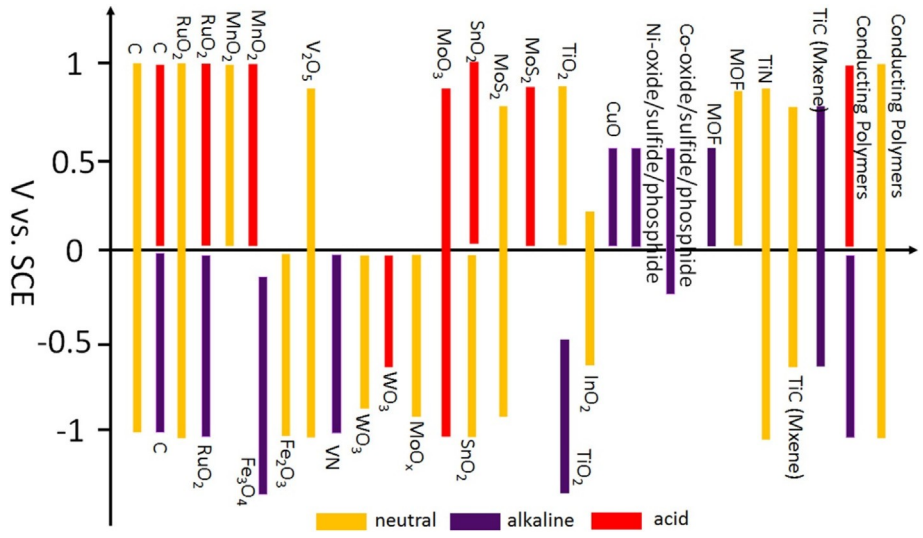

Fig. 3. Electrode materials for aqueous asymmetric supercapacitors. Refs. 25-63.

2.3.1 Carbon materials

Carbon materials with good conductivity and high specific sur- face area, show the typical double-layer capacitive characteristics, which are always considered as the optimal electrode materials for supercapacitor. Carbon materials include activated carbon, carbon nanotubes (CNTs), graphene and so on, have been widely investigated and can be used as both the positive and negative electrode materials, as shown in Fig. 3. Activated carbon, usually produced by carbonizing of biomaterials or polymer precursors, is the most widely used electrode material for commercial supercapacitors. The specific capacitance of activated carbon is determined by sur- face area, pore size and electronic conductivity, as well as the functional groups (such as N, O, S functionalities) with pseudocapacitive properties on the surface. CNTs with high electrical conductivity, a narrow pore size distribution, and excellent mechanical properties also attracted widely attention as the electrode mate- rials for supercapacitor [25]. Niu et al. first reported the capacitive properties of HNO_3-treated CNTs in a 38% H_2SO_4 electrolyte, which displayed a high specific capacitance [25]. In spired by this, various works on CNTs using as the supercapacitor electrode have been reported. Hata et al. used the aligned densely packed bulk form of single-walled CNTs as the electrode for supercapacitor [26]. The single-walled CNTs bulk displayed an ultra-high energy density of 69.4 Wh Kg^{-1}. In addition, extensive studies found that the hetero- atoms (N, O, S et al.) make great influence on the capacitive performance of CNTs by reversible Faradic reaction in the framework or as functional groups on the surface [27,28]. Above all, CNTs with its unique properties in 1D structure, good conductivity, and malleability play a very important role in fiber-shaped wearable electronic devices, which will be discussed detailed in this review. Graphene, a well-known 2D monolayer composed of sp^2-bonded carbon, has attracted increasing attention for their applications in electronics, transistors, photonics and energy storage [29-31]. Ruoff and co-workers first reported the chemically modified graphene as electrode materials with the high specific capacitances of 135 and 99 F g^{1} in both aqueous and organic electrolytes [32]. Zhu et al. synthesized a porous carbon through activation of graphene [33]. This obtained activated carbon exhibits a higher BET surface area up to 3200 m^2 g^{1}, high electrical conductivity and a low O and H content, showing the excellent capacitive performance in ionic liquids. Nitrogen-doped graphene developed by Kang and co-workers through a plasma doping process displayed the large increase in capacitance as compared to that of pristine graphene [34]. A lot of researches have been successfully demonstrated showing that

graphene can be a good candidate as electrode materials for supercapacitors, yet, their performance still needs to be improved to meet the requirements from practical application.

2.3.2 Conducting polymers

Conducting polymers, discovered in 1976, have the advantages of reversible Faradaic redox nature, good electric conductivity and convenience for preparation (typically formed through chemical oxidation or electrochemical oxidation of the monomers), showing great potential as the electrode materials for supercapacitors [35-38]. The mostly used conducting polymers for supercapacitors are polyaniline (PANI), polypyrrole (PPy), poly (3, 4-ethylenedioxythiophene) (PEDOT) and their derivatives. An all-solid-state PANI based flexible supercapacitor with a 40 mm PVA/ H_3PO_4 membrane as both the electrolyte and separator was fabricated by Yuan and co-workers, which displayed an energy density of around 0.01 Wh cm^{-3} at a power density of 3 W cm^{3} [39]. PPy- coated CNT paper via electrochemical polymerization method had been reported to be used as the electrode to assemble stretchable and self-healable supercapacitors, which can be stretched up to 600% strain with enhanced capacitive performance and retaining of the original capacitance even after 20 times of breaking/healing [40]. The specific capacitance of the PEDOT electrode is usually inferior than that of PANI or PPy, but the major advantage is that PEDOT can work in a comparatively higher potential window (~1.2 V), which will facilitate to fabricate asymmetric type super- capacitor device with a high working potential [41,42]. Further- more, conducting polymers often show better flexibility than other electrode materials due to their inherent elastic polymeric nature. Overall, conducting polymers have made remarkable contribution to the development of advanced energy storage devices toward the future flexible electronics.

2.3.3 Metal oxides/nitrides/sulfides

Transition metal oxides, mainly including RuO_2, MnO_2, V_2O_5, FeO_x, MoO_3, et al., can provide much higher specific capacitance than that of conventional electrostatic carbon materials. This is due to their pseudo-capacitance arises from the faradic redox reactions on surface [43,44]. RuO_2, with the advantages of high proton conductivity, high specific capacitance, wide potential window (Fig. 3), stability in various electrolytes, long cycle life and high rate capability, is the best optimal candidate as the electrode materials for supercapacitors [45-48]. However, the high cost and environ- mentally hazardous of Ru-based electrode materials hinder their widespread use in supercapacitors. Accordingly, cheaper and environmental friendly electrode materials are in urgent need to be developed. MnO_2, with the merits of low cost, environment safety and high theoretical specific capacitance of 1380 F g^{1}, has attracted extensive attention in energy storage area [49,50]. MnO_2 can be widely used as the positive material in fiber-shaped super-capacitors due to its simple preparation and good electrochemical performance in neutral aqueous electrolytes. Extensive works on MnO_2 based materials for supercapacitors now includes various synthetic methods, MnO_2 polymorphs (amorphous to highly crystalline), and nanostructures (thin films, powder composites, advanced 3D architectures), leading to a wide range of metrics in electrochemical performance. V_2O_5 also exhibits typical pseudo- capacitive characteristics in neutral aqueous electrolytes. V_2O_5 can be used as both positive and negative electrode for asymmetric configuration [51,52]. Various methods were investigated to pre- pare V_2O_5 electrodes, such as sol-gel process, quenching, hydro- thermal method, and electrodeposition [53,54]. Recently, Ni or Co- based oxides and hydroxides have also attracted extensive attention in fiber-shaped supercapacitors due to their easy syn- thesis and high theoretical capacity in alkaline electrolytes [55-57]. However, the safety issue, caused by the strong basicity electrolyte, possibly hinders their practical application in future wearable electronics. Many other metal oxide materials, such as MoO_3, FeO_x, WO_3, SnO_2, and InO_2, have also been explored as electrode materials for supercapacitors [58-62]. However, these metal oxide materials suffer from one problem or

another, for example, poor conductivity, instability or sluggish kinetics. Accordingly, their electrochemical properties are needed to be enhanced. Overall, their applications in FASCs have not been extensively studied yet.

In recent years, transition metal sulfides (FeS, CuS, NiS, CoS, MoS_2) have attracted more and more attention as electrode mate- rials for supercapacitors. Their unique physical and chemical properties in relatively higher electrical conductivity, mechanical and thermal stability than those of their corresponding metal ox- ides contribute to their high specific capacitances. In addition, metal nitrides also show much improved sustainability and better electrical conductivity (4000e55000 S cm^{-1}) than the corresponding metal oxides [63,64], and thus become attractive as electrode materials for supercapacitors. However, strict operation condition in the synthesizing of metal nitrides is not compatible with the wearable electronics, especially for the supercapacitors based on textiles. Recently, some new energy storage materials, such as Mxenes, metal organic frameworks (MOFs), some lithium/ sodium ion containing metal oxides are also investigated and exhibit potential application in supercapacitors. All in all, to realize the widespread industrial applications further, mild reaction, low cost, and less demanding synthetic approaches for achieving the large-scale production of metal nitrides are needed.

3 Electrode design of FASCs

FASCs with unique 1D structure gained widespread attention in applications for future portable and wearable electronics. Recently, efforts have been extensively devoted to fabricate fiber-shaped supercapacitors with high energy performance and robust mechanical properties (such as flexibility and stretchability). Besides from proper paring with two positive and negative active materials, suitable fiber-shaped substrate is the most important factor for the fabrication of FASCs. Various fiber electrodes have been wildly investigated, such as metal wires, carbon based fibers (CNT fibers, graphene fibers (GF)), and composite fibers.

3.2 Metal fiber supported electrodes

Metal wires, such as Au, Ni, and Ti, exhibit excellent conductivity, good mechanical strength and flexibility. Thus, metal wires can be served as both physical support for active materials and current collectors in fiber supercapacitor design. Xia and co- workers reported a flexible, wire-shaped solid-state asymmetric supercapacitor, which was fabricated by twisting a $Ni(OH)_2$-nano- wire coated Ni-fiber electrode and an ordered mesoporous carbon coated Ni-fiber electrode together with a PVA/KOH gel as electrolyte and separator [65]. Fig. 4a-d shows the SEM images of $Ni(OH)_2$ nanowire coated Ni-fiber electrode in different magnifications. This FASC exhibits a high operating voltage up to 1.5 V and a high specific capacitance up to 6.67 mF cm^{-1} (or 35.67 mF cm^{-2}), while the capacitance retention is 70% over 10 000 cycles. This work show that high performance flexible energy storage devices can be realized via optimizing nanostructure of active electrode materials and choosing of proper electrodes couple. Likewise, previous researches fabricated Ni_3S_2 nanorod and $NiO/Ni(OH)_2$/PEDOT composite coated Ni-wire as fiber electrode [66,67]. These fiber electrodes were paired with ordered mesoporous carbon (CMK-3) and pen ink as counter electrodes, respectively, to assemble asymmetric supercapacitors. Fig. 4e shows the schematic illustration of the Ni_3S_2//pen ink fiber-shaped supercapacitor. The Ni_3S_2// pen ink device works with an operating voltage window of 1.4 V and thus delivers a maximum specific capacitance of 87.25 F cm^{-1} with an energy density of 0.81 m Wh cm^{-3} at a power density of 21.12 mW cm^{-3}. Chen et al. designed a fiber electrode by depositing Co_3O_4 nanowires on Ni-fiber via a solvothermal method [68]. Fig. 4f-i shows the XRD and SEM images of Co_3O_4 nanowires grown on Ni-fiber. The Co_3O_4 coated Ni-fiber

electrode showed a specific capacitance up to 560 F cm^{-3} with an alkaline electrolyte in a three- electrode configuration. Such superior pseudocapacitive performance is associated to the increased electrochemical active surface of the porous nanostructures and the shortened electronic trans- port and ion diffusion paths. In view of that the Ni-fiber is too heavy to be used in light-weight electronic devices, the authors also developed supercapacitors using Co_3O_4 nanowires grown on Ti- wire as positive electrode. With an operating potential of 1.5 V, this fiber-shaped asymmetric supercapacitor presented largely improved energy and power delivery as well as superior flexibility. More importantly, this work successfully integrated this FSAS with photodetector to realize a new flexible device with multi-functionalities.

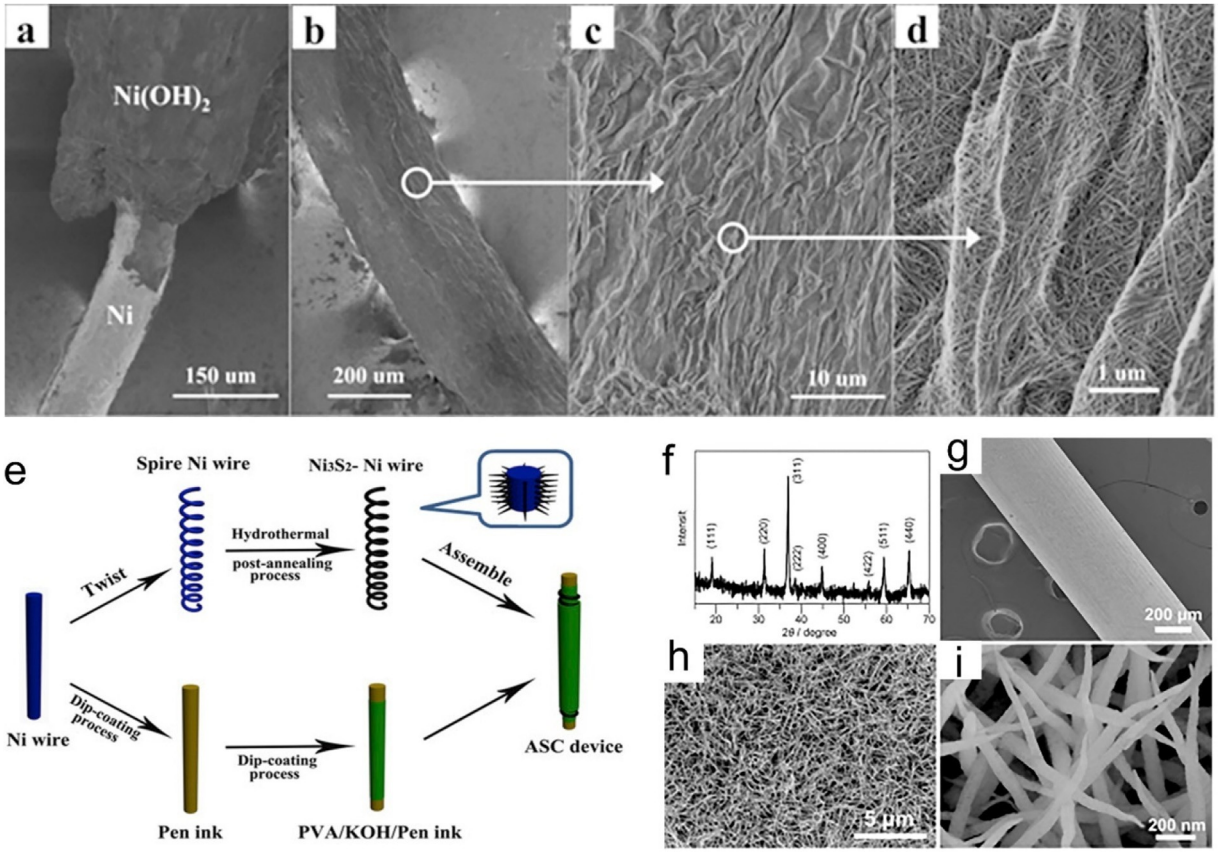

Fig. 4. (a-d) Microscopy measurements of $Ni(OH)_2$-nanowire fiber-electrode SEM images with different magnifications. Reproduced with permission [65]. Copyright 2014, Wiley- VCH. (e) Schematic illustration of the flexible fiber-type solid-state ASC device. Reproduced with permission [66]. Copyright 2016, Elsevier. (f) XRD pattern of Co_3O_4 scraped off a nickel fiber. (g-i) SEM images of the as-synthesized Co_3O_4 nanowires on a nickel fiber. Reproduced with permission [68]. Copyright 2014, Wiley-VCH.

Beside from Ni-wire based fiber electrode, Au, Cu, and stainless steel yarn have also been investigated for the fabrication of flexible FASCs [69-72]. Xu et al. developed a coaxial-type fiber asymmetric supercapacitor with a working voltage of 1.8 V by wrapping a MnO_2-modified nano-porous gold wire (NPG@MnO_2) with a conducting carbon paper and using the PVA/LiCl gel as the electrolyte (Fig. 5a) [73]. This modified NPG wire served as an excellent support for MnO_2 exhibiting large tensile strength,

good flexibility and excellent electronic conductivity. A high energy density of 5.4 m Wh cm $^{-2}$ was obtained with a good cycling performance (90% after 2000 cycles). Recently, Zhi et al. presented a high energy- performance and flexible fiber-shaped supercapacitor by electro- depositing PEDOT@MnO_2 and C@Fe_3O_4 composites on stainless steel wire as the positive and negative electrodes, respectively [72]. As-fabricated fiber-shaped supercapacitor with a high working voltage of 2 V displays a high areal specific capacitance of 60 mF cm ^{2} and a large energy density of 0.0335 mW h cm $^{-2}$. This fiber-shaped supercapacitor also exhibits good flexibility and can be deformed without obviously capacitance decay. Moreover, this fiber-shaped supercapacitor can be woven into a textile in series which can successfully power a LED, showing its promising practical application in wearable electronics. Wang and co-workers used a copper wire (CW) as substrate to be wrapped with 3D porous graphene hydrogel (GH) through directly immersing the CW in aqueous GO suspension, resulting in a 3D structured porous GH/CW electrode [74]. The optical and SEM images with different magnifications of GH/CW electrode are presented in Fig. 5b-h. This GH/CW electrode can be used to match up with MnO_2/RGO/carbon fiber electrode to fabricate flexible all-solid-state asymmetric supercapacitor. Due to the synergistic effects from different com- ponents and advantages of nano-porous structured fiber electrodes, the resultant fiber asymmetric supercapacitor device can be reversibly charged/discharged with a wide voltage range from 0 to 1.6 V, delivering a high areal energy density of 18.1 m Wh cm^{-2} and volumetric energy density of 0.9 m Wh cm $^{-3}$. Furthermore, this fiber-shaped flexible supercapacitor also shows the advantages in flexibility, rate capability, and cycling stability.

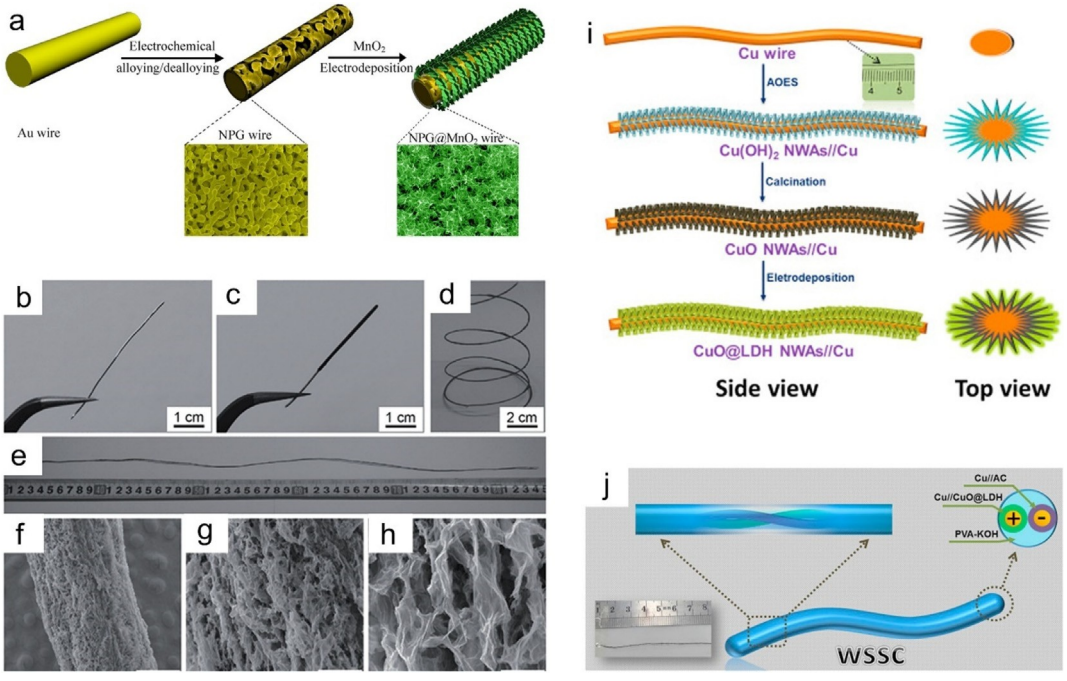

Fig. 5. (a) Schematic illustration of the synthesis and morphology of the (Nanoporous gold) NPG@MnO_2 electrode, Reproduced with permission [73]. Copyright 2015, Springer. Optical images of (b) CW, (c) GH/CW electrode, (d) standing GH/CW spring and (e) dry GH/CW with a length of about 22 inches. (feh) SEM images of the GH/CW composite at different magnifications. Reproduced with permission [74]. Copyright 2015, The Royal Society of Chemistry. (i) Schematic illustration for the

fabrication of hierarchical CuO@CoFe- LDH coreeshell NWAs supported on the copper wire. (j) Schematic representation of the flexible asymmetric wire shaped all-solid-state supercapacitor based on CuO@CoFe-LDH, active carbon electrode, and PVA/KOH electrolyte (the inset shows the photograph of the as-prepared WSSC). Reproduced with permission [69]. Copyright 2016, Elsevier.

Recent studies demonstrated that 1D nanowire can enhance the electrochemical performance due to their high interfacial area and short ion diffusion path [75,76]. 1D nanowire arrays with core-shell architecture were demonstrated as good choice for fabricating fiber-shaped energy storage device. Shao and co-workers presented the design and fabrication of well-aligned CuO@CoFe-LDH core-shell nanowire arrays on a copper wire substrate as shown in Fig. 5i [69]. Due to the synergetic effect between core and shell, the as-obtained electrode shows high electrochemical performance in specific capacitance and rate capability. Fig. 5j shows the schematic and optical image of the flexible asymmetric wire shaped all-solid- state supercapacitor based on CuO@CoFe-LDH, active carbon electrode, and PVA/KOH electrolyte. This can deliver a high energy density of 93.75 m Wh cm^{-2} and long-term cycle stability.

3.3 Carbon materials based fiber supported electrodes

Fiber-shaped asymmetric supercapacitors based on metal wires current collectors shows attractive performance for wearable electronics. However, metal wires occupied a considerable portion of total weight of the assembled devices, which unavoidably reduced the gravimetric energy/power density of the full device. Carbon based fibers, such as carbon fibers bundles, CNTs fibers, and GF have the advantages of low densities, slender structure, and good flexibility. They can serve as both flexible current collector and capacitive materials to replace the metal wires for fabricating excellent wearable energy storage materials [77-81].

3.3.1 Carbon fiber bundle

Shen and co-workers fabricated fiber-shaped asymmetric supercapacitor with length of longer than 1 m, using $CoNiO_2$ nanowires@carbon fibers and active carbon (AC)@carbon fibers as positive and negative electrode, respectively [82]. Fig. 6a shows the schematic of the fabrication process of the fiber-shaped asymmetric supercapacitor. The fiber-shaped positive and negative electrodes were spirally twisted together around a poly-methylmethacrylate (PMMA) fiber with KOH/PVA gel as electrolyte and a PDMS layer as shell. As obtained device delivered the high specific capacitance of 1.68 mF cm^{-1} at a current density of 0.05 mA cm^{-1}. Furthermore, the corresponding device also showed excellent mechanical properties, flexibility, and stability during weaving as a textile, watchband, and Chinese knot and can be integrated with our daily dress to power LED and a MP3 as shown in Fig. 6b-d.

He et al. explored tough and flexible carbon fibers for fiber-shaped micro-supercapacitors [83]. This micro-carbon fibers with diameters of ~50 mm, were mechanically extracted from commercial carbon fibers, demonstrating excellent strength, flexibility, and light weight. WO_3 nanowires were chemical-vapor-deposited on carbon fibers as a scaffold for PPy and V_2O_5 growth, yielding the hierarchical WO_3/PPy negative and WO_3/V_2O_5 positive electrodes, respectively. Fig. 7a-c shows the photographs of the commercial flexible and scalable carbon fibers, mechanically extracted micro-carbon fibers, and the bending micro-carbon fibers grown with WO_3 (diameter ~70 mm), respectively. SEM image in Fig. 7d exhibits the vertical WO_3 nanowire arrays with a length of ~20 mm. Furthermore, the assembled fiber-shaped micro-supercapacitor, with a high operating voltage of 2.0 V, exhibited an energy density of 31.3 m Wh cm^{-3} and excellent stability as well as good bending performance. In addition, the micro-supercapacitors can be integrated in series or in parallel to meet the high power and energy requirements

from various practical applications, such as powering LEDs (Fig. 7e-g). The performance of the device demonstrated that this type micro-supercapacitor can bridge the energy density gap between micro-batteries and micro-supercapacitors for the application in miniaturized portable electronics. This work represented a promising strategy towards exploring new flexible micro- energy devices with the high density. Zhu's group employed the ultrathin MnO_2 nanosheet/carbon fiber composite electrode to fabricate a fiber-shaped asymmetric supercapacitor [84]. In this electrode, MnO_2 nanosheet arrays can be directivity deposited on conductive carbon fibers tightly, which shows a high specific capacitance up to 634.5 F g^{-1}. The as-fabricated FSAS displays a high specific capacitance of 87.1 F g^{-1} and an exceptional energy density of 27.2 Wh kg^{-1}. This device shows the exceptional flexibility and mechanical stability and the electrochemical performance of this device has no decay even under severely bending states. In addition, this fiber device could successfully power a CdS nanowires based photodetector without applying any external bias voltage. Thus, this work provides a new strategy for the development of wearable and self-powered nano-devices. Kim et al. reported the fabrication of a new high voltage fiber-shaped asymmetric super-capacitor with porous carbon coated carbon fibers as the negative electrode and copper hexacyanoferrate coated carbon fibers (CuHCF@CFs) as the positive electrode as shown Fig. 7h-i [85]. The as-fabricated supercapacitor can be cycled reversibly in the range from 0 to 2 V and showed excellent electrochemical performance with a specific capacitance of 19.2 F g^{-1} and an energy density of 10.6 W h kg^{-1}. Impressively, this novel fiber-shaped supercapacitor can be well knitted into a cloth, suggesting good wearability and bendability (Fig. 7j-k).

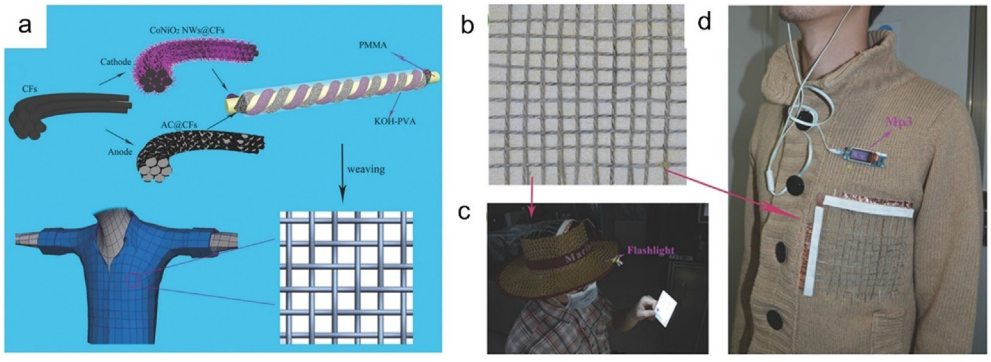

Fig. 6. (a) Schematic illustration of the fabrication process of the asymmetric wire-supercapacitors (AWSs). (b) The AWSs can be weaved as a textile to be integrated with our daily dresses to power a MP3 and LED flash light, respectively. Reproduced with permission [82]. Copyright 2016, Wiley-VCH.

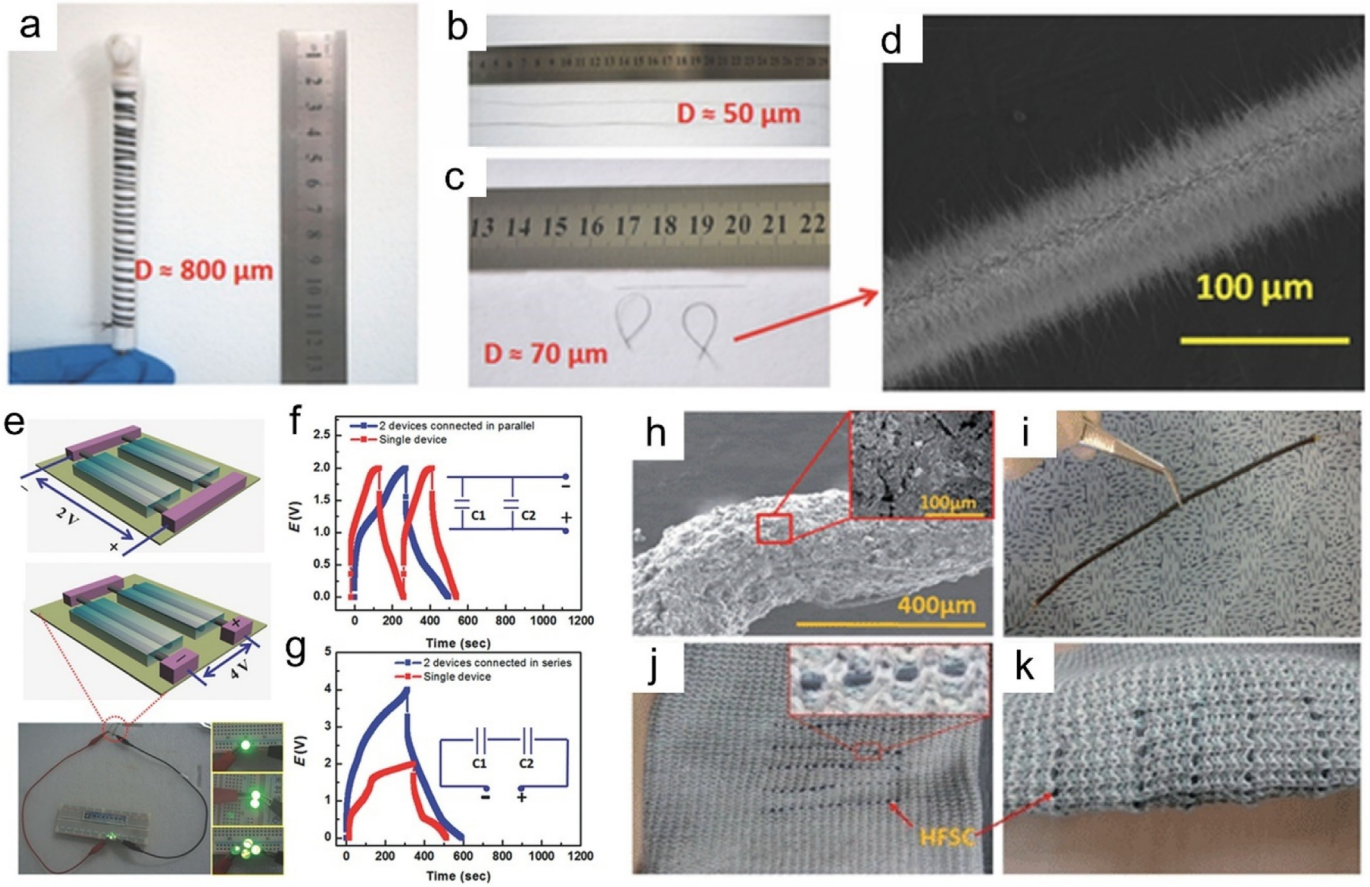

Fig. 7. Synthesis and microstructures of the different microfibers. (a) The commercial flexible and scalable carbon fibers with the diameter of 800 mm. (b) Mechanically extracted micro-CFs with the diameter of 50 mm from the commercial CFs. (c) The bending micro-CFs grown WO3 NWs (diameter ~70 mm). (d) SEM image of the micro-CFs with uniform WO3 NWs on the surface. (e) Schematic of integrated micro-SCs and optical pictures the LEDs lighted by a micro-supercapacitors assembly in series. (f-g) Galvanostatic charge and discharge (GCD) curves of the device in parallel and in series, respectively. Reproduced with permission [83]. Copyright 2015, Wiley-VCH. (h) CuHCF@CFs electrode (inset: high resolution SEM image). (f) Photo image of the fabricated HFSC and its (g) wearable and (h) flexible nature. Reproduced with permission [85]. Copyright 2016, Royal Society of Chemistry.

3.3.2 CNT fibers

CNT fibers have many advanced properties, such as high mechanical strength, high electrical and thermal conductivities, extraordinary structure flexibility and high surface area, which make them a promising candidate for next generation wearable devices [86-88]. The CNT fiber can be simply prepared through spinning a CNT homogeneous dispersion into a polyvinyl alcohol(PVA) coagulation bath [89]. To date, four main methods had been developed to produce CNT fibers: spinning from CNT solution [90,91], spinning from a vertically aligned CNT array previously grown on a substrate [92-94], spinning from a CNT aerogel formed in a chemical vapor deposition (CVD) reactor [95], and twisting/ rolling from a CNT film [96]. CNTs fibers is relatively expensive and needs the complicated synthesis. However, CNT fibers have been extensively investigated for their use in fiber-shaped super- capacitors due to their uniquely

physical or mechanical properties [97-99].

Zhang's group developed a fiber-shaped asymmetric super- capacitor using CNT@ZnO-NWs@MnO_2 fiber as positive electrode and CNT fiber as negative electrode, respectively [99]. The as-assembled supercapacitor could be cycled reversibly in the voltage region of 0e1.8 V, and displayed a maximum specific capacitance of 31.15 mF cm^{-2} at a current density of 10 mA, corresponding to a high energy density of 13.25 m Wh cm^{-2}. Fig. 8a and b shows the optical photos of the obtained fiber-shaped super-capacitors integrated into a textile and exhibiting good flexibility. The schematics of FASCs connected in serial and parallel is shown in Fig. 8c. Moreover, electrochemical characterizations were performed on three devices in serial or parallel (Fig. 8d and e), showing their good electrochemical performance. Peng's lab developed a novel fiber-shaped asymmetric supercapacitor with the high- volumetric energy density using CNT fibers as flexible and conductive substrate [100]. Fig. 8f shows the schematic of fabrication process of the fiber-shaped asymmetric supercapacitor. In this FASC, a ternary hybrid fiber was employed as a positive electrode by growing MnO_2 nanosheets onto a PEDOT:PSS coated CNT fiber and an ordered microporous carbon/CNT fiber was used as a negative electrode. SEM images in Fig. 8g and h at the low and high magnifications show the preparation of the bare CNT fibers by rolling stacked ten layers of aligned CNT sheets via a rotating motor. This fiber supercapacitor can operate with a high operating voltage of 1.8 V, producing an energy density as high as 11.3 m Wh cm^{3} which is highly compared with the thin-film lithium-ion batteries. Due to the conductive, lightweight, and flexible CNT fibers, this FASC can be woven or knitted into flexible power textiles with the distinguished mechanical stability. Another example is the asymmetric two-ply yarn supercapacitor fabricated in which an as-spun CNT yarn was used as the negative electrode and a CNT yarn coated with MnO_2/polymer composite was employed as the positive electrode [102]. This asymmetric design shows significantly higher energy density than the above stated AC//MnO_2 bulk asymmetric supercapacitor and symmetric supercapacitors constructed from CNT yarn coated with MnO_2 composite. Furthermore, the obtained device shows high cycle stability and flexibility, which may meet the requirements from wearable electronic applications.

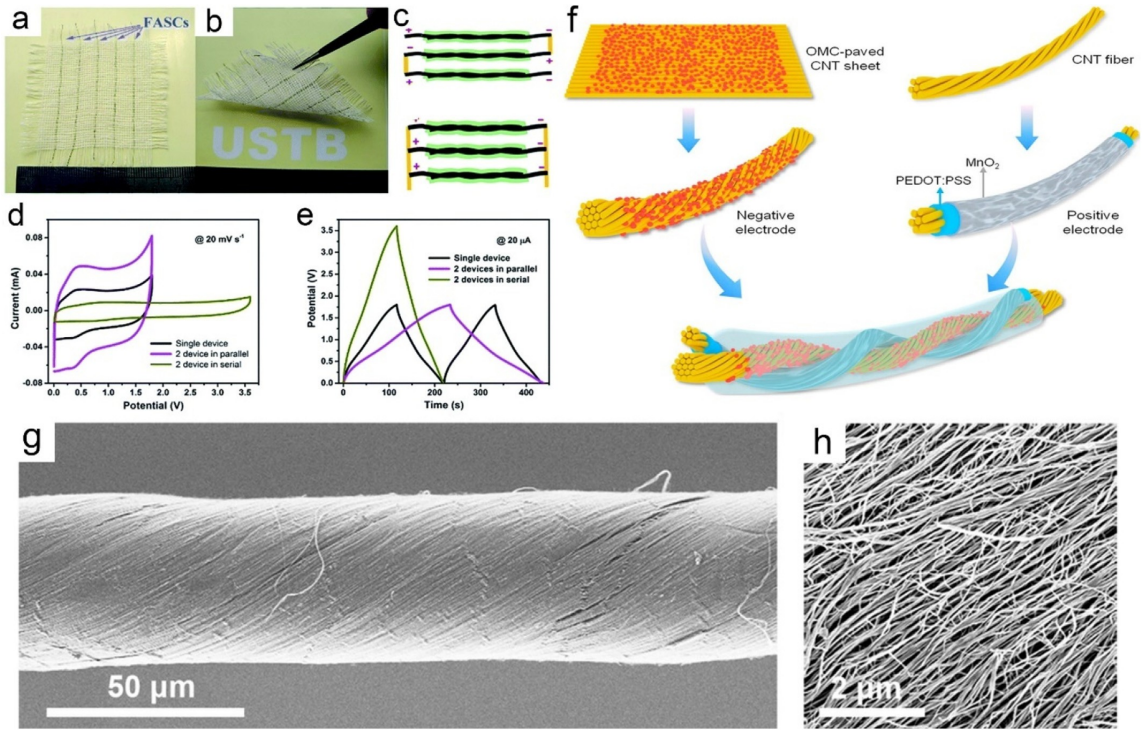

Fig. 8. (a, b) Photos of the textile embedded with FASCs devices; (c) Schematics of FASCs connected in serial and parallel; (d) CV curves and (e) GCD curves for two FASCs connected in serial and parallel. Reproduced with permission [99]. Copyright 2016, Royal Society of Chemistry. (f) Schematic illustration to the fabrication of fiber-shaped asymmetric supercapacitor (FAS). (g, h) Bare CNT yarn at low and high magnifications, respectively. Reproduced with permission [100]. Copyright 2016, American Chemical Society.

Extensive attention has been received for MoS_2 as energy storage materials. MoS_2 can efficiently store charges through pseudo- capacitance within a wide potential window due to the faradaic charge-transfer process on the Mo center (slower process) or the formation of a double-layer at the electrode/electrolyte interface due to the adsorption of protons or other cations on the MoS_2 monolayers (faster process) [103]. Thus, MoS_2 can be considered as an attractive electrode material for asymmetric supercapacitors. Chen and co-workers firstly incorporated MoS_2 with reduced graphene oxide into a well-aligned multi-walled carbon nanotube (MWCNT) sheet to fabricate MoS_2-rGO/MWCNT and rGO/MWCNT fibers (Fig. 9a) [104]. Such nearly perfect alignment structure of individual MWCNTs sheet (Fig. 9b) preserved the good electrical conductivity and mechanical strength of the hybrid fibers obtained by twisting (Fig. 9c-d). Thus, an novel FASC is fabricated by using MoS_2-rGO/MWCNT and rGO/MWCNT as positive and negative electrode, respectively, displaying a high capacitance of 5.2 F cm^{-3}, good rate capability and cycling stability. The above works demonstrate the merits of CNT fibers when they used in future wearable electronics. The fabrication of these fiber-shaped super-capacitors however generally is high cost and requires complex processes, which make them difficult production in large scale for the commercialization.

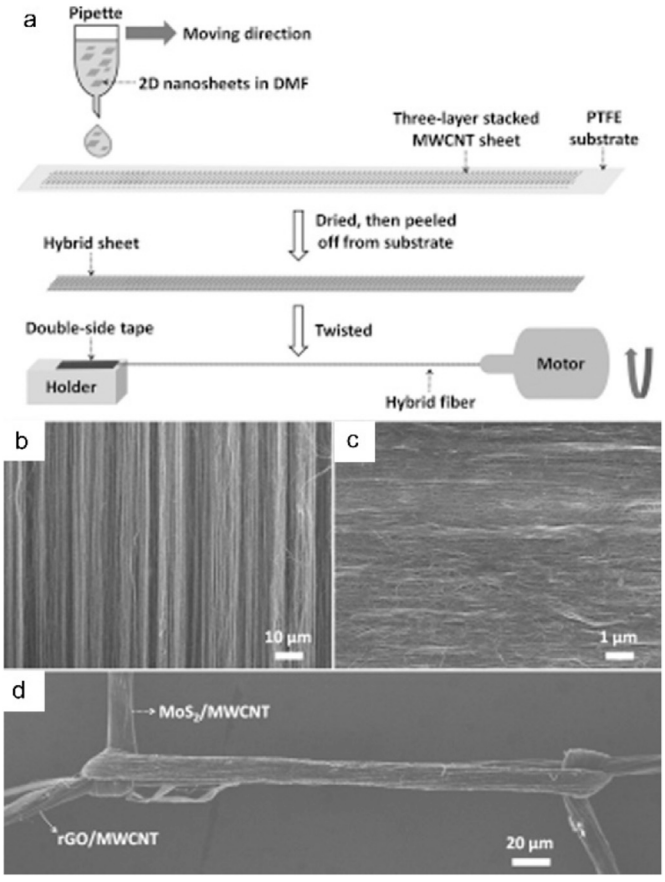

Fig. 9. (a) Schematic illustration of fabrication of the hybrid fiber. SEM images of (b) well-aligned MWCNT sheet, (c) MWCNT sheet incorporating MoS_2 nanosheets, and (d) tightly knotted MoS_2/MWCNT and rGO/MWCNT fibers. Reproduced with permission [103]. Copyright 2015, Wiley-VCH.

3.3.3 Graphene fiber (GF)

GF represent a new type of fiber for practical importance. This is due to the following properties: electrical and thermal conductivities, high strength, and good flexibility. Over the past few years, GF based supercapacitors have obtained significant attention. Recently, various methods have been developed to fabricate 1D graphene-based macro-scaled architectures, including wet- spinning methods, laser-reduction technique and hydrothermal strategy [105-107]. It should be pointed out that supercapacitors based on bare GF generally display a low capacitance, which restricts their potentially wide applications to some extent.

Zhu and co-workers fabricated hierarchically structured MnO_2 nanowire/graphene hybrid fibers through a simple, scalable wet-spinning method using a mixture suspension of MnO_2 nanowire and GO [108]. Fig. 10a-c shows that hundreds of meters long MnO_2/ GO hybrid fibers can be obtained by this method. This strategy presented in this work shows the great potential to the rational design of other nanomaterials/graphene hybrid fibers for the next generation flexible energy storage devices. Fiber-based micro-supercapacitors have increasingly attracted the attention of re searchers because of their flexibility and wovenability. The main challenge of fiber-based micro-supercapacitors is how to improve their energy density while maintaining high power density. Gao et al. assembled a type of fiber-based asymmetric

micro- supercapacitors with two different graphene fiber-based electrodes [109]. MnO_2/graphene hybrid fibers were fabricated by depositing a flower-like MnO_2 sheath on the wet-spinning GF. Fig. 10d-i shows that the core-sheath morphology of the hybrid fibers. Asymmetric micro-supercapacitor was assembled using MnO_2/graphene hybrid fibers as positive electrode and CNT/graphene as negative electrode, which can operate a potential window of 1.6 V with an area energy density of 11.9 mWh cm^{-2} and volume energy density of 11.9 mW h cm^{-3}. Moreover, this micro-supercapacitor exhibited a good cycling performance with 92.7% of initial capacitance retention after constant 8000 cycles. Cai and co-workers reported that the GF can be fabricated by wet spinning using a silicone tubing as reactor [110]. After being coated with $NiCo_2S_4$ nanoparticles via the solvothermal deposition method, the obtained GF/$NiCo_2S_4$ hybrid fiber exhibited a high tensile strength of 226 MPa and a high conductivity of 39 S cm^{-1}. The GF/$NiCo_2S_4$ electrode displayed a high volumetric capacitance up to 388 F cm^{3} in a three-electrode cell at 2 mV s^{-1}. Fig. 10j show the fabrication process of the asymmetric fiber supercapacitor. Moreover, the as- fabricated device achieved a high energy density of 12.3 m Wh cm^{-3} and a maximum power density of 1600 mW cm^{-3}, as well as good cycle stability exceeding 2000 cycles. Furthermore, the fabricated device shows the good flexibility as it tested under different bending angles ranging from 0 to 180^0 or even under water with no decay in electrochemical performance. To demonstrate the potential use in wearable applications, a fabricated supercapacitor ring was woven into a textile and three fabricated supercapacitors connected in series can power a light-emitting diode (LED). The volumetric energy density of the fabricated supercapacitor based on GF/$NiCo_2S_4$ is extremely high, which is among the highest performance reported for fiber-shaped wearable supercapacitors. Thus, these FASCs design based on GF can be considered as the promising candidate for the next generation flexible and wearable electronic devices.

3.4 Functional FASCs

In order to meet the requirements of future smart wearable devices, multifunctional supercapacitors that are incorporated with novel features such as stretchability, self-healability, shape-memory, and electro-chromism have been attracted widely attention. For example, a stretchable FASC was fabricated using MnO_2/CNT hybrid fiber positive electrode, pristine CNT fiber negative electrode and KOH-PVA gel as electrolyte and separator [111]. A remarkable stretchability of up to 100% tensile strain can be achieved. Yu and co-authors fabricated a core-sheath FASC through wrapping gel electrolyte coated CNT@MnO_2 core fiber with CNT@PPy composite film. Then the FASC was over-twisting to form a stretchable helical structure. The obtained FASC presented stable performance during mechanical stretching to 20% strain, and exhibited a capacitance retention of 88% after 200 stretching cycles [112]. Recently, Zhi et al. realized a modularized approach to fabricate functional fiber- shaped supercapacitors via using a NiTi shape memory alloy wire [113]. Among the resultant devices, fiber-shaped WO_3//PPy asymmetric supercapacitor with a high working voltage of 1.3 V exhibited decent areal and volumetric capacitance as well as outstanding mechanical flexibility and shape memory recovery ability. Except for these, a number of functional supercapacitors also have been developed, such as poly[4,7-bis(3,6-dihexyloxy-thieno[3,2-b]thiophen-2-yl)]-benzo[c][1,2,5]thiadiazole (PBOTT- BTD) electrode based asymmetric supercapacitor which displays a dual energy storage/electrochromic functionality, self-healable supercapacitors using PAA hydrogel electrolyte which is both self- healable and electrochemically active, and a FASC composed of titanium wire/Co_3O_4 nanowires and carbon fibers/graphene electrodes which displays a dual energy storage/photodetection functionality [114-116]. Although abundant smart materials with single or multi-functionalities have been developed, only a few have been successfully utilized in the FASCs. Thus, the investigation of functional FASCs with high energy storage performance is still in the primary stage. Further exploration of advanced functional FASCs is still urgently needed.

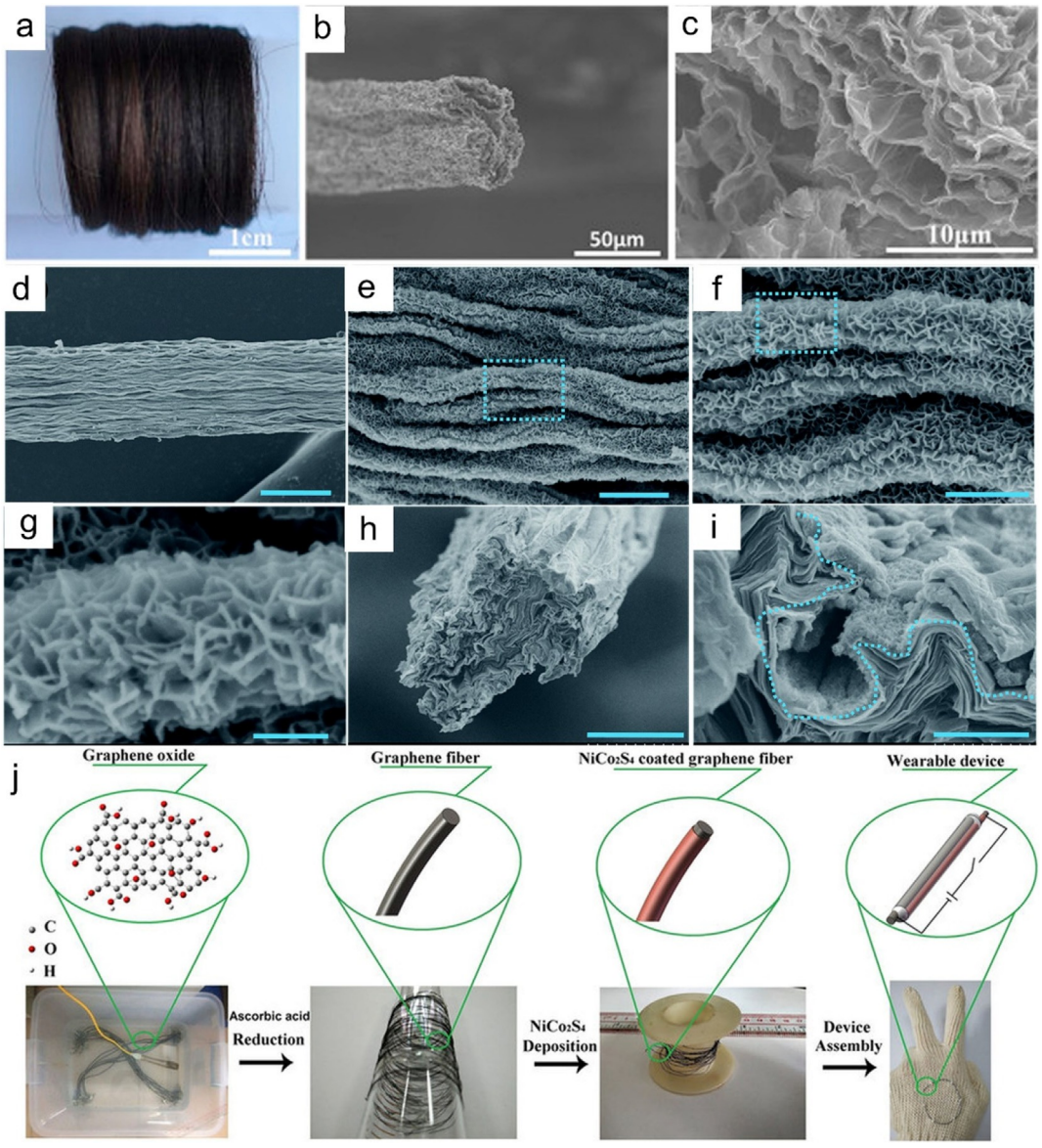

Fig. 10. (a) Photograph of the MnO_2/GO fiber collected onto a bobbin; (b-c) Cross-sectional SEM images at different magnifications of the MnO_2/GO fiber. Reproduced with permission [107]. Copyright 2016, Elsevier. (d-g) SEM images of the MnO_2-coated core-sheath graphene fiber in different magnifications. (h) Cross sectional image of MnO_2/ graphene hybrid fibers observed by SEM. (i) Magnified picture of (h), and the boundary between MnO_2 and graphene is marked as a blue dotted line. Scale bars are 10 mm, 1 mm, 500 nm, 150 nm, 10 mm and 1 mm, respectively. Reproduced with permission [108]. Copyright 2014, Royal Society of Chemistry. (j) Schematic illustration of the fabrication process of wearable FASC. Reproduced with permission [109]. Copyright 2016, Nature Publishing Group. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The representative researches of FASCs were discussed in the above part. For easy comparison, we

marked the main types andkey performances of the supercapacitors in Table 1.

Table 1 Design and performance of the FASCs.

Electrode		Electrolyte	Cell voltage	Capacitance	Energy density	Power density	Cycle life	Ref
Positive	Negative							
$Ni/Ni(OH)_2$ nanowires	Ni/ordered mesoporous carbons	PVA-KOH	1.5 V	6.67 mF cm^{-1} 35.67 mF cm^{-2}	0.01 m Wh cm^{-2} 2.16 m Wh cm^{-3}		70% 10 000	[65]
Ni/Ni_3S_2	Ni/pen ink	PVA-KOH	1.4 V	87.25 F cm^{-1}	0.81 m Wh cm^{-3}	21.12 mW cm^{-3}	93.1% 3000	[66]
$Ni/NiO/Ni(OH)_2$/PEDOT	Ni/CMK-3	PVA-KOH	1.45 V	31.6 mF cm^{-2} 3.16 F cm^{-3}	0.011 m Wh cm^{-2}	0.33 mW cm^{-2}	1400	[67]
Ni/Co_3O_4	CF/graphene	PVA-KOH	1.5 V	2.1 F cm^{-3}	0.62 m Wh cm^{-3}	1.47 W cm^{-3}	84% 1000	[68]
Cu/CuO@CoFe-LDH	Cu/AC	PVA-KOH	1.2 V	9.38 F cm^{-3}	93.75 m Wh cm^{-2} 1.857 m Wh cm^{-3}	45 720 mW cm^{-2} 914.5 mW cm^{-3}	99.5% 2000	[69]
$Cu/CuO@AuPd@MnO_2$	$CF/Fe_2O_3@C$	PVA-LiCl	1.6 V	2.46 F cm^{-3}	0.85 m Wh cm^{-3}	0.10 W cm^{-3}	93% 4000	[71]
ss/PEDOT@MnO_2	ss/C@Fe_3O_4	PVA-LiCl	2.0 V	60 mF cm^{-2} 7.2 F cm^{-3}	0.0335 m Wh cm^{-2} 4.02 m Wh cm^{-3}	0.6 mW cm^{-2} 72 mW cm^{-3}	80% 800	[72]
Au/MnO_2	CNT/carbon paper	PVA-LiCl	1.8 V	12 mF cm^{-2}	5.4 m Wh cm^{-2}	284 mW cm^{-2}	90% 2000	[73]
CF/RGO@MnO_2	Cu/graphene hydrogel	PAAK-KCl	1.6 V	2.54 F cm^{-3} 50.8 mF cm^{-2}	18.1 m Wh cm^{-2} 0.9 m Wh cm^{-3}		90% 10 000	[74]
CF/MnO_2	CF/graphene	PVA-LiCl	1.5 V	87.1 F g^{-1}	27.2 Wh kg^{-1}	979.7 W kg^{-1}	95.2% 3000	[84]
CF/CuHCF	CF/porous carbon	PVA-KCl	2.0 V	19.2 F g^{-1} 68.2 mF cm^{-2} 3.1 F cm^{-3}	10.6 Wh kg^{-1} 180.85 m Wh cm^{-2} 8.11 m Wh cm^{-3}	50.6 W kg^{-1} 180.85 m Wh cm^{-2} 8.11 m Wh cm^{-3}	84% 3000	[85]
$CF/WO_3/V_2O_5$	CF/WO_3/PPy	PVA-LiCl	2.0 V	56 F cm^{-3}	31.1 m Wh cm^{-3}	280 mW cm^{-3}	93% 3000	[83]
$CF/CoNiO_2$ nanowires	CF/AC	PVA-KOH	1.8 V	1.68 mF cm^{-1}	0.95 m Wh cm^{-3}	1.14 mW cm^{-3}	97% 5000	[82]
CF/TiN@GNS	CF/Fe_2N@GNS	PVA-LiCl	1.6 V	58 F g^{-1}	15.4 Wh kg^{-1} 0.51 m Wh cm^{-3}	6.4 kW kg^{-1} 211.4 mW cm^{-3}	98% 20 000	[21]
$CF/CNTeNiCo(OH)_x$	CF/AC	PVA-KOH	1.6 V		33.0 mW h cm^{-2} 0.84 mW h cm^{-3}	0.75 mW cm^{-2} 19.1 mW cm^{-3}	100% 8000	[19]
CF/NiP_x	CF/Ni@RGO	PVA-KOH	1.6 V	33 F cm^{-3}	8.97 mW h cm^{-3}	3.51 W cm^{-3}	93.7% 5000	[79]
CF/MnO_2@TiN	CF/N-MoO_{3-x}	PVA-LiCl	2.0 V	10.3 mF cm^{-1} 4.1 F cm^{-3}	2.29 m Wh cm^{-3}	1.64 W cm^{-3}	80.3% 5000	[113]
CNT/ZnO-NWs@MnO_2	CNT	PVA-H_2SO_4	1.8 V	31.15 mF cm^{-2}	13.25 m Wh cm^{-2}	210 mW cm^{-2}	96.7% 1000	[100]
CNT/MnO_2/PEDOT:PSS	CNT/ordered microporous carbon	CMC-Na_2SO_4	1.8 V	23.4 F cm^{-3}	11.3 m Wh cm^{-3}	0.03 W cm^{-3}	85% 10 000	[101]
MoS_2-rGO/MWCNT	rGO/MWCNT	PVA-H_2SO_4	1.4 V	5.2 F cm^{-3}	~1.5 m Wh cm^{-3}	~0.04 W cm^{-3}	100% 7000	[104]
CNT/MnO_2	CNT	KOH-PVA	1.5 V	157.53 mF cm^{-1} 16.87 mF cm^{-2} 21.21 F cm^{-3}	39.85 m Wh cm^{-1}	15.03 mW cm^{-1}	99% 10 000	[111]
$GF/NiCo_2S_4$	GF	PVA-KOH	1.5 V	39.4 F cm^{-3}	12.3 m Wh cm^{-3}	1.6 W cm^{-3}	92% 2000	[110]
GF/MnO_2	GF/MWCNT	PVA-LiCl	1.6 V	33.6 mF cm^{-2}	11.9 m Wh cm^{-2} 11.9 m Wh cm^{-3}		92.7% 8000	[109]
CNT@MnO_2	CNT@PPy	PVA-KOH	1.5 V	60.435 mF cm^{-2}	18.88 m Wh cm^{-2}		80%	[11

				[2]				[2]
					2.98 m Wh cm^{-3}		5000	
MnO_2/rGO/CNT	N-rGO/CNT	PVA-$NaSO_4$	1.8 V	11.1 F cm^{-3}	5 m Wh cm^{-3}		87%	[117]
							1000	
NiCo-DHs/CNT	Pen ink/CNT	PVA-KOH	1.55 V		9.57 m Wh cm^{-2}	492.17 mW cm^{-2}	86%	[118]
							5000	
MnO_2/GO	MoO_3/GO	PVA-H_3PO_4	1.6 V	53.5 F cm^{-3}	18.2 m Wh cm^{-3}	76.4 mW cm^{-3}	96.8%	[119]
							3000	

4 Conclusion and outlook

In this review, we have focused on the recent progresses and advances of FASCs with respect to their electrode materials, design and configuration. Fiber-shaped supercapacitor, is a promising energy storage device for wearable electronics by virtue of its unique features in high flexibility, knittability, small size and light weight. In addition, a proper asymmetric design combining two materials with different potential window in the same electrolyte can boost the working voltage range, thus achieving higher energy density. Electrode materials play a critical role to the performance of supercapacitors. Capacitive or pseudocapacitive materials such as carbon materials, conductive polymers and metal oxides/sulfides/nitrides are carefully discussed including their proper electrolyte and working potential. Then the progresses to date on the FASCs including the device design, electrode fabrication and electrochemical performance of the FASCs are summarized. Finally, a short conclusion is given, combining with the future perspectives in this fast developing field. Overall, more strategies to further improvements in power and energy performance are still needed, such as proper design of positive and negative materials electrode, gel electrolyte with high ion conductivity, large voltage window and safety.

Although significant advancements in FASCs have been developed, most of the reported prototypes are just at the initial stage. Many problems still need to be solved to realize their bright future. First, further improvement in the performance of FASCs, for example, achieving high energy density without sacrificing their power density and cycle life too much, is still a challenging topic. A potential problem solving method is the proper design of the prototype including the choice of active materials, electrolytes, and optimization of charge ratio of the positive and negative electrode which is very important for the fabrication of asymmetric super- capacitors. In addition, new electrode materials (MOFs, Mxenes) should be promising candidates. Second, most of the FASCs developed so far used H_2SO_4, H_2PO_4 or KOH based gel electrolyte, which is high risky for wearable electronics. Mild neutral electrolyte, ionic liquid and organic based electrolyte may be the promising alter- native choices. Organic electrolytes or liquid Ionics can increase the cell voltage, which will be in favor of energy performance enhancement of the devices. It should be noted that harsh working environments for example water-free and oxygen-free conditions are needed, which may potentially increase the difficulties in fabricating the FASCs using the organic electrolytes or liquid Ionics [120,121]. Thus, this is an effective but challenging avenue to fabricate FASCs with high working potential, thus achieving high energy densities. Third, high conductive, light weight, and high flexible fiber substrates are very essential for wearable electronics, because metal wires are always heavy and carbon-based fibers usually have the relatively low conductivity and need fussy fabrication. Zheng et al. fabricated Ni-coated cotton yarns by an electro- less deposition method for supercapacitors, offering us a potential avenue to fabricate good performance fiber-shaped substrates[122]. Fourth, while the emerging FASCs have been demonstrated as promising energy storage devices to be implemented in smart textiles, challenges still exist in achieving the combination of both high mechanical flexibility, stretchability and excellent electro- chemical performance. Moreover, multifunctional FASCs,

that can be responsive to changes in configurational integrity, voltage, mechanical deformation, light, and temperature, called self-healability, electro-chromism, shape memory, photodetection, and thermal response, are in their infancy and will boost in the future, in view of potential application in consumer products. Fifth, to realize large scale applications of the FASCs, low cost and scalable methods should be exploited for fiber electrode synthesis, asymmetric supercapacitors assembling, and integration with other electronic components. Actually, some better properties are dependent on expensive raw materials or complicated processes, therefore, the comprehensive improvement of FASCs, especially in cost and electrochemical performances, should be concerned. Finally, The self-discharge and leak current problems of the FASCs should also be investigated systematically. This is due to that the rapid self-discharge process is one of the biggest challenges remaining for various supercapacitors, directly leading to poor energy retention. FASCs systems with various configurations of electrodes and electrolytes may display different self-discharge mechanisms which are still blank till now. It is therefore necessary to understand the fundamentals of self-discharge mechanisms in FASCs with different electrode/electrolyte systems in better controlling and tailoring the self-discharge process to meet the requirements from practical applications.

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