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Advances and challenges for flexible energy storage and conversion devices and systems

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To meet the rapid development of flexible, portable, and wearable electronic devices, extensive efforts have been devoted to develop matchable energy storage and conversion systems as power sources, such as flexible lithium-ion batteries (LIBs), supercapacitors (SCs), solar cells, fuel cells, *etc.* Particularly, during recent years, exciting works have been done to explore more suitable and effective electrode/electrolyte materials as well as more preferable cell configuration and structural designs to develop flexible power sources with better electrochemical performance for integration into flexible electronics. An overview is given for these remarkable contributions made by the leading scientists in this important and promising research area. Some perspectives for the future and impacts of flexible energy storage and conversion systems are also proposed.

Broader context

Flexible devices are portable, lightweight, bendable and even wearable or implantable and thus have attracted extensive attention for many promising applications including roll-up displays, smart mobile devices, wearable electronics, implantable bio-sensors, *etc.* To realize fully flexible devices, flexible energy conversion and storage units with high energy storage and power density are urgently needed. During the past several years, many works have been dedicated to exploring suitable and effective electrode/electrolyte materials as well as more preferable cell configuration and structural designs. As a result, exciting progresses have been achieved in developing high performance flexible energy storage and conversion devices, *e.g.* lithium-ion batteries, supercapacitors, solar cells, *etc.* With these rapid advancements, we believe that future flexible power sources that combine both outstanding electrochemical and mechanical performance will boost the development and commercialization of next-generation flexible electronics.

1. Introduction

The advent of flexible electronics is considered as a revolutionary event which has attracted tremendous attention. Compared with conventional electronics, flexible electronics are portable, lightweight, bendable and even wearable or implantable. Those optimized and superior characteristics will facilitate the development of electronic devices with different functionalities, such as roll-up displays, smart mobile devices, implantable biosensors, *etc.* As shown in Fig. 1, there have already been some novel concept and prototype flexible electronics such as Nokia Morph Concept,[1] LG OLED (organic light-emitting diode) TV panel,[2] Philips Fluid flexible smartphone,[3] and Samsung Youm flexible display.[4] Unlike the LG OLED TV panel, which features a curved screen, a recent patent filing by Apple hints at the possibility of a smartphone with a wrap-around display.[5] In the foreseeable future, we believe there will be a big explosion in the application of flexible electronics. Consequently, the corresponding flexible energy storage and conversion systems as a new kind of power source show promising applications.

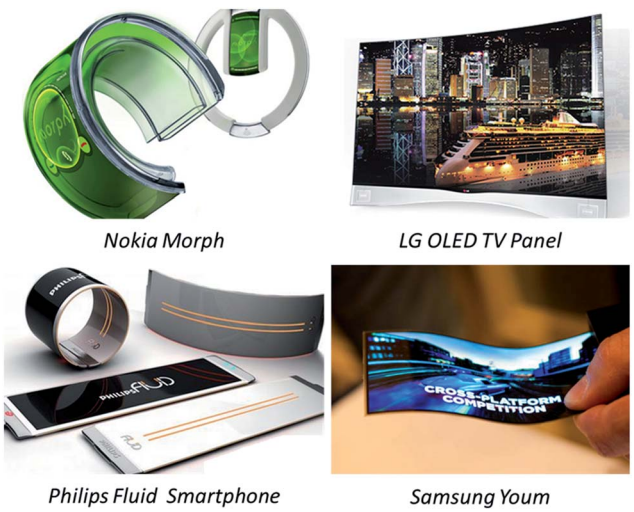

Fig. 1 Nokia Morph Concept, LG OLED TV panel, Philips Fluid flexible smartphone, and Samsung Youm flexible display.

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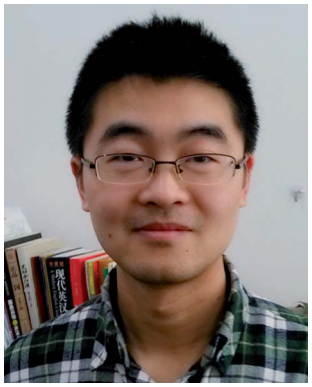
In the past few years, much progress has been made to develop high performance flexible energy storage and conversion devices, *e.g.* lithium-ion batteries (LIBs), supercapacitors (SCs), solar cells, and fuel cells. In order to achieve high energy storage and power density, long and stable cycling, and safe operation, many works have been dedicated to exploring suitable and effective electrode/electrolyte materials as well as more preferable cell configuration and structural designs. A review is given of the efforts made in this field to explore flexible power sources with better electrochemical performances. Despite the exciting progress made so far, in practice, there are still many challenges as they are still in the infancy stage of development.

Flexibility is a concept related to rigidity, which emphasizes the deformability of materials. The relationship of stress–strain can be linear elastic, anelastic, or plastic. An ideal flexible electronic device should possess such characteristics, that is, bendable, foldable (or twistable), stretchable, stable electrical performance, and safe operation. In recent years, many researchers have made great efforts to realize mechanical flexibility of batteries by making each component more flexible in order to make them more suitable for practical applications. Owing to the characteristics of flexible electronics, the corresponding power sources should be lightweight, small in size, highly efficient and stable under different mechanical deformation conditions. Unlike conventional ones, flexible energy storage and conversion devices are not limited by bulky design and configuration limitations. Planar, especially wire-shaped designs are mostly adopted by researchers, as they can be easily integrated or woven into textiles. To understand the inner mechanism and electrochemical behavior of flexible power devices under mechanical deformation, a series of studies were carried out by researchers.[6] However, given that flexible electronics is in the early stages of development, no perfect evaluation standards have been established to characterize the corresponding flexible power source devices to date. Flexibility, for example, is merely evaluated by testing the electrochemical performances under different bending conditions or bending times. Although a wire-shaped design can assure devices can be bent in any direction or even twisted into certain patterns, the



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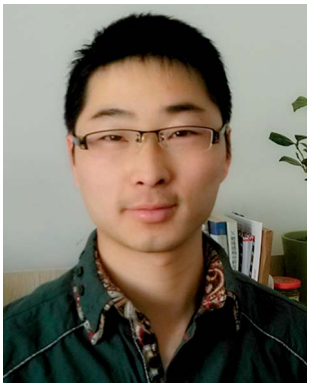

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Dr Xin-Bo Zhang (1978) joined Changchun Institute of Applied Chemistry (CIAC) as a professor of "Hundred Talents Program" of Chinese Academy of Sciences (CAS) in the spring of 2010. He received his PhD degree in inorganic chemistry from CIAC and was granted the CAS Presidential Scholarship Award in 2005. Then, during 2005–2010, he worked as a JSPS and NEDO fellow at National Institute of Advanced Industrial Science and Technology (Kansai Center), Japan. His interests mainly focus on functional inorganic materials for energy storage and conversion with fuel cells and batteries, especially lithium–air batteries.

realization of stretchability is essential when applied to particular situations.

Traditional power source designs are mainly based on brittle materials which are not suitable for use in flexible electronics. For example, in conventional LIBs, electrode active materials are usually coated on metal current collectors (mainly Al and Cu foils for positive and negative electrodes, respectively) which may easily detach form the contrast surface and would hardly restore the original shape when bent. To bring flexible power sources to practical applications, each component must use shape-conformable, highly efficient, non-flammable, non-toxic, inexpensive and scalable materials. However, most of the flexible power devices demonstrated so far do not meet these requirements. The greatest challenge facing the development of flexible power sources is the fabrication of reliable and efficient shape-conformable components. On the other hand, suitable packaging materials can prevent damage to the integrity and guarantee safe operation under various working conditions, which also plays an important role for further commercialization. Recent development in nanostructured materials has stimulated the progress in the investigation of flexible power sources. As a result, the development of flexible power sources will in turn boost the evolution of flexible electronics. However, promising as the novel flexible electronic devices are, there is still a long way to go for large-scale commercial production.

While there are many excellent reviews regarding LIBs,[7–15] SCs,[16–23] and solar cells,[24–28] there are very few focused on flexible power sources, not to mention a review that covers nearly all aspects of flexible energy storage and conversion systems in detail. Besides, most of the reviews mainly highlight the progress in materials used in electrodes. This review is organized in two main sections. In the first section, we present a comprehensive overview on the most recent advances in selection and preparation of various nanostructured flexible electrode as well as electrolyte materials, device structural designs and some representative prototypes regarding SCs, LIBs, solar cells, *etc.* In the second section of this review, some summaries are given and perspectives on the future development of flexible energy storage and conversion systems are discussed.

2. Flexible supercapacitors

Supercapacitors (SCs), also known as electrochemical capacitors or ultracapacitors, have recently attracted considerable attention due to their fast charge–discharge rates, high power density, long cycling life, and relatively simple configuration compared with lithium-ion batteries.[16,29–32] These advantages make SCs a favorable power source candidate in the field of flexible electronics.

Depending on different charge-storage mechanisms, SCs can be divided into electrical double-layer capacitors (EDLCs), where electrical energy is stored by ion absorption, and pseudocapacitors, in which electrical energy is mainly stored by fast surface redox reactions.[16,31,32] Table 1 is a brief comparison of EDLCs, pseudocapacitors, and hybrid SCs. In general, carbon-based materials are widely used as electrodes for EDLCs, while conducting polymers and transition metal oxides are used for pseudocapacitors. Owing to the two different working mechanisms, EDLCs utilizing carbon materials have excellent cycling stability and high power density but with relatively low capacitance and energy density. Pseudocapacitors, on the other hand, exhibit quite the opposite behavior. It should be noted that, since an electrode chemical reaction is involved in pseudocapacitors, irreversible components will accumulate during cycling, leading to deteriorating performance. Hybrid SCs employ both charge-storage mechanisms in EDLCs and pseudocapacitors; therefore exhibit elevated capacitance than EDLCs and better cycling stability than pseudocapacitors. At the same time, their energy density is improved without sacrificing power density.

Owing to the recent progress in nanostructured materials, tremendous research has been dedicated to the development of flexible power sources, from which SCs and lithium-ion batteries (LIBs) are under most investigation, many novel designs were proposed. For flexible SCs, materials such as graphene, carbon nanotubes (CNTs), and nanostructured transition metal oxides and electrical conducting polymers have been demonstrated as electrode materials. However, the lack of high-performance, reliable and shape-conformable materials is still a major challenge in the development of flexible power sources. Research on flexible SCs has mainly focused on developing nanostructured electroactive materials, flexible electrodes, and structural designs.

2.1 Carbon-based flexible EDLCs

Carbon materials are abundant and electrochemically stable within a wide range of operating voltage. Among them, CNTs, carbon fiber, carbide-derived carbon (CDC), and graphene are widely used as electrode materials owing to their high electrical conductivity and excellent mechanical properties, in addition to high surface area which also make them suitable for ion adsorption and charge storage.[32]

Carbon nanotubes (CNTs) have a unique one-dimensional structure with high conductivity which favors rapid charge separation and transport.[33–36] SCs based on CNT networks have been demonstrated.[35,37] Cui *et al.* reported planar flexible SCs based on conductive textiles.[38] The flexible conductive textiles were fabricated by a simple "dipping and drying" process using aqueous single-walled carbon nanotube (SWCNT) ink on cellulose cotton textile substrates (as shown in Fig. 2). A high areal capacitance of 0.48 F cm^{-2} and a remarkable cycling stability after 130 000 cycles with negligible decay in capacitance were demonstrated. Traditionally, metal foils/wires are introduced as current collectors to achieve better performances,[31,39,40] but their heavy weight and the tendency to fatigue failure under constant bending conditions largely limit their application in flexible power sources. In these works, however, the conductive CNT networks serve as 3D flexible current collectors which greatly simplified the configuration as well as lowered the total device mass.

Apart from CNT networks, CNT fibers/yarns also have outstanding properties such as high conductivity, lightweight, excellent mechanical strength and omnidirectional flexibility,

Table 1 Comparison of EDLCs, pseudocapacitors, and hybrid SCs

	Material	Capacitance	Cycling stability
EDLC	Carbon	Moderate	Excellent
Pseudocapacitor	MO_x[a], conducting polymer	High	Poor
Hybrid SC	Carbon-MO_x/conducting polymer	High	Moderate

[a] MO_x represents transition metal oxide.

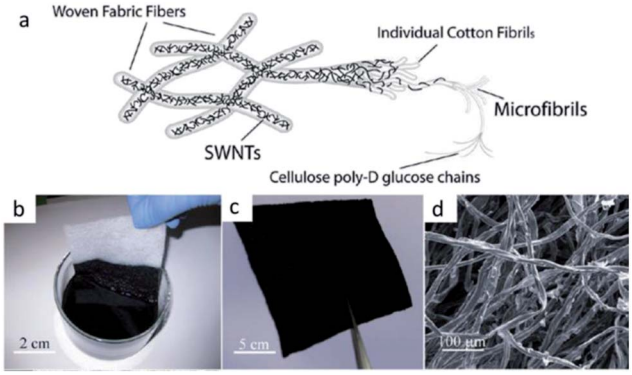

Fig. 2 (a) Schematic of SWCNTs wrapping around cellulose fibers to form a 3D porous structure. (b) Conductive textiles are fabricated by dipping textile into an aqueous SWCNT ink followed by drying. (c) A photo of SWCNT-coated cotton fabric sheet. (d) SEM image of the macroporous structure of the cotton sheet coated with SWCNTs on the cotton fiber surface. Reprinted with permission from ref. 38. Copyright 2010, American Chemical Society.

and more importantly, they can be easily woven into fabrics to fabricate electronic textiles.[41] CNT fibers can be manufactured from high concentration suspensions[42–44] or from CNT forests.[45–47] Dalton and co-workers first reported a wire-shaped supercapacitor (WSS) based on two twisted CNT fibers and demonstrated that it can be woven into textiles.[48] Very recently, Chou and co-workers reported an all-solid-state flexible and stretchable WSS consisting of two CNT fiber electrodes and H_2SO_4–PVA gel electrolyte.[49] As demonstrated in Fig. 3 the WSS was closely attached to a pre-strained spandex fiber using PDMS. After drying for 24 h, the resulting WSS device exhibited excellent stretchability which is more applicable in practical situations. Notably, when the device is at the stretched state, better performances can be achieved compared to that at the relaxed state. This may be due to the better wettability of CNT fiber electrodes with easier diffusion of ions at the kink sites of the WSS. Area-specific capacitance of 4.63–4.99 mF cm^{-2}, and long-term stability over 10 000 charge–discharge cycles were observed.

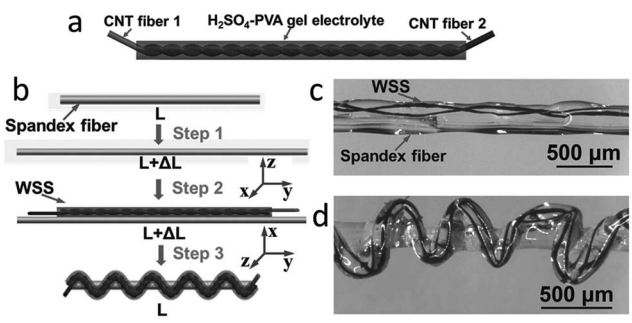

Fig. 3 (a) The structure of a CNT-based WSS and (b) schematics of the fabrication procedures for stretchable WSSs. Optical microscopy images of (c) the stretched WSS combined with pre-strained spandex fiber and (d) the buckled WSS with relaxed spandex fiber. Reprinted with permission from ref. 49. Copyright 2013, Wiley-VCH, GmbH & Co. KGaA.

As a matter of fact, the randomly dispersed CNTs in the CNT fibers can lead to a lot of boundaries among them, thus resulting in lowered conductivity, which will lower the efficiencies during charging and discharging. In addition, when CNT fibers serve not only as active materials but also as current collectors, the relatively low conductivity compared to metal current collectors will lead to larger ESR.[50] Yet, to bring flexible SCs closer to practical use, metal current collectors are not very suitable as has been noted above. To increase performances, Ren *et al.* firstly introduced MWCNT/ordered mesoporous carbon (OMC) composite fibers as electrodes for WSSs. OMC particles infiltrated in the voids among MWCNTs leading to better conductivity and larger efficient surface area for ion adsorption, which can result in enhanced energy and power density.[51] The composite fiber combined the structure and property advantages of the two components. A flexible wire-shaped EDLC was then prepared by twisting two aligned MWCNT/OMC composite fibers coated with H_3PO_4–PVA electrolyte. Recently, carbon microfibers (CMFs) were demonstrated as substitutes for metal wire current collectors.[52] MWCNTs were coated on CMFs by a simple spray-coating process. As illustrated in Fig. 4, a WSS was subsequently fabricated with the MWCNT/CMFs bundle electrodes. High capacitance and power and energy densities were achieved owing to the high conductivity of carbon microfibers and the high effective surface area. In addition, super aligned CNT (SACNT) arrays can be fabricated to high conductive films and fibers which can serve as highly conductive flexible current collectors and substrates or active materials for EDLCs. Recently, Jiang *et al.* reviewed the preparation and wide range of applications of SACNTs,[53] but the high cost of high-quality SACNT arrays will limit the commercialization of CNT-based SCs, thus prompting us to look for other substitutes.

Graphene, a two-dimensional monolayer of sp^2-bonded carbon atoms,[54–57] has many excellent properties, such as high

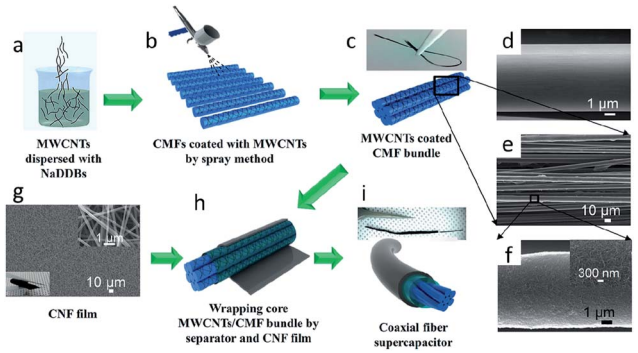

Fig. 4 Schematic of the coaxial fiber supercapacitor fabrication process. (a) MWCNTs were dispersed in a sodium dodecylbenzenesulfonate (NaDDBs) solution. (b) MWCNTs are deposited onto the CMFs by spray-coating. (c) The MWCNTs/CMFs are assembled into bundles after removing surfactant. (d and f) SEM images of single uncoated CMF and single CMF coated with MWCNTs. (e) SEM image of a MWCNTs/CMF bundle. (g) SEM image of a carbon nanofibers (CNF) film and its enlargement on the upper right (the inset is a digital photo of the bendable CNF film). (h) After soaking with polymer electrolyte, the core MWCNTs/CMF bundle was wrapped with separator and CNF film. (i) Schematic and digital photo of a coaxial fiber supercapacitor. Reprinted with permission from ref. 52. Copyright 2013, American Chemical Society.

thermal and electrical conductivity,[58,59] large surface area, superior mechanical flexibility,[60] and low fabrication cost.[61] Graphene can be cheaply obtained from graphene oxide (GO) through laser irradiation,[62] hydrothermal reaction,[63] chemical or electrochemical reduction,[64,65] *etc.* Graphene and its derivatives have attracted intense interest as promising candidates for electrode materials. Although graphene can provide a theoretical specific capacitance value of up to 550 F g^{-1},[23,66] however, the restacking of graphene films will lead to reduced effective surface area which greatly limits the specific capacitances of graphene-based SCs. As is shown in Fig. 5a, a laser reduction

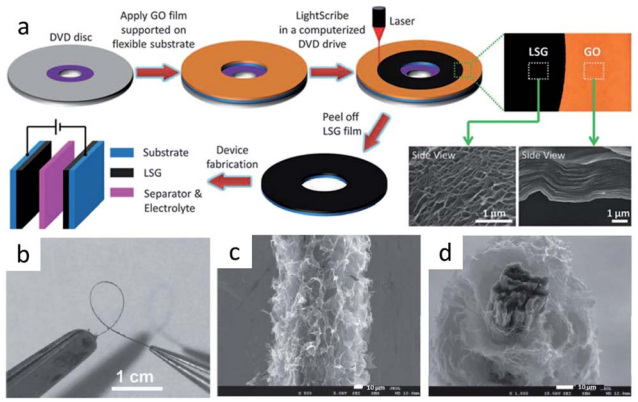

Fig. 5 (a) Schematic illustration of the fabrication of laser-scribed graphene-based SC. Reprinted with permission from ref. 62. Copyright 2012 AAAS. (b) Photo of a distorted GF@3D-G. (c and d) SEM images of a GF@3D-G. Front view (c) and cross-section view (d) of the GF@3D-G showing the core GF surrounded with vertically standing graphene sheets. Scale bars: c and d 10 μm. Reprinted with permission from ref. 74. Copyright 2013, Wiley-VCH, GmbH & Co. KGaA.

approach of GO was used to produce graphene films, this process greatly lowered the restacking of graphene films.[62] Consequently, a very high specific surface area of 1520 m^2 g^{-1} was observed for the graphene-based electrode and a high specific capacitance of 204 F g^{-1} was demonstrated for the assembled SC. Very recently, Duan and co-workers reported solid-state flexible SCs based on highly interconnected 3D structure graphene hydrogel films which was synthesized by a modified hydrothermal reduction method.[67–69] A high capacitance of 186 F g^{-1}, an areal specific capacitance of 372 mF cm^{-2} as well as a good cycling stability was demonstrated. Through chemical reduction reactions between active metal substrates and GO, Cao *et al.* reported a facial and scalable strategy to fabricate large area graphene films.[70] The thickness and patterns of the graphene film can be controlled by dipping time and patterns of metal substrates. By electrochemical reduction of GO on Au wire, Shi and co-workers prepared a solid-state WSS with high specific capacitance, rate capability and electrochemical stability.[71] Dong *et al.* produced graphene fibers (GFs) through thermal reduction of GO in glass pipelines.[72] The neat GFs can be a substitute to CNT fibers at low cost. In addition, the shape can be controlled on demand and functional components such as metal oxides can be easily integrated into the fibers to achieve better electrochemical performances. In order to improve the conductivity of graphene fibers, Xu *et al.* demonstrated Ag-doped GFs by wet-spinning of giant GO (GGO) and Ag nanowires (NWs) mixture followed by chemical reduction. The resulting GFs exhibited a high conductivity of 9.3 × 10^4 S m^{-1} and enhanced current capacity.[73] In order to increase surface area, an all-graphene flexible fiber electrode was prepared by Meng *et al.* which was composed of a GF core and a sheath of 3D graphene network (Fig. 5b–d).[74] The WSS based on the GF@3D-G electrodes showed capacitances of 1.2–1.7 mF cm^{-2}.

It should be noted that the theoretical capacitances of carbon materials are low. To further achieve better electrochemical performances, incorporating pseudocapacitance materials on carbon materials like transition metal oxides and conducting polymers is a promising approach, and this will be discussed later.

Apart from the significant progress of CNT- and graphene-based SCs, other carbon-based flexible SCs also show promising applications. Porous carbon materials have large surface area and pore volume to provide effective surface area and active sites which favors ion adsorption and charge storage.[75] Gogotsi's group reported an inexpensive and scalable way to fabricate SCs by uniformly screen printing porous carbon on cotton textiles (Fig. 6).[76] Textile SCs based on knitted carbon fiber and activate carbon with a high capacitance of 0.51 F cm^{-2} at 10 mV s^{-1} was demonstrated.[77] Micro-SCs based on onion-like carbon (OLC) with very high rate capability were demonstrated, and notably the OLC can be deposited onto flexible substrates to form flexible SCs.[78] Through selectively etching metals from metal carbides, carbide-derived carbon (CDC) with tunable microstructure such as pore size, pore volume, as well as specific surface area, can be achieved.[79] By chlorination reduction of continuous TiC nanofibers produced by electrospinning,

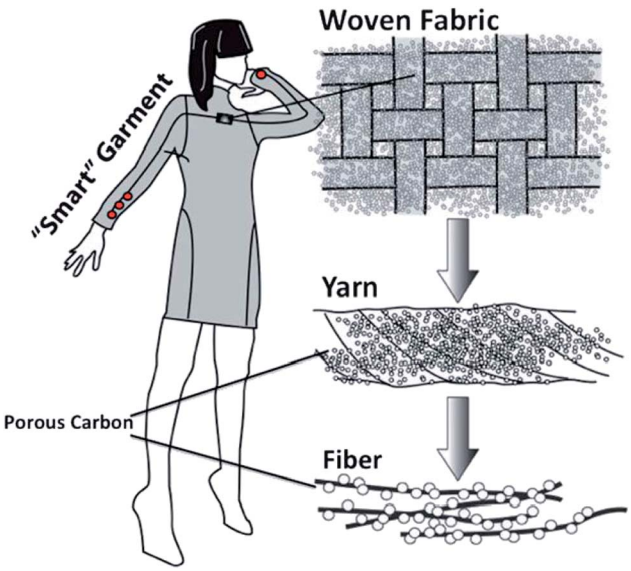

Fig. 6 Schematic of a porous textile SC integrated into a smart garment, porous carbon impregnation from the weave, to the yarn, to the fibers. Reprinted with permission from ref. 76. Copyright 2011, The Royal Society of Chemistry.

flexible electrodes based on TiC-CDC nanofelts with high specific surface area were demonstrated.[80,81]

2.2 Flexible pseudocapacitors and hybrid SCs

Despite the fact that EDLCs have fast charge–discharge rates, high power density and long cycling life, the energy stored in them is an order of magnitude lower than that of batteries.[82] Compared with EDLCs, pseudocapacitors can achieve much higher capacitance and energy density by introducing reversible redox Faradaic reactions upon charge and discharge.[83–85] Pseudocapacitance materials including transition metal oxides such as MnO_2, RuO_2, Co_3O_4, Fe_3O_4, and electrical conducting polymers like polyaniline (PANI) and polypyrrole (PPy) are widely used.[86–91] However, the poor electrical conductivity and slow response of these materials will result in low power densities and poor stability. As a solution, these materials are usually deposited on highly conductive substrates to improve conductivity as well as achieve high capacitances.

To put flexible SCs into practical applications, energy density should be increased without sacrificing power density and cycle life.[16] The well-developed EDLCs have been reported with high power density and ultra-long cycle life, while pseudocapacitors can achieve high capacitances. Hence, developing composite electrode materials by combining the advantages of EDLCs and pseudocapacitors is a feasible way to obtain higher power and energy densities. By employing both Faradaic and non-Faradaic processes, hybrid SCs were reported demonstrating better performances than EDLCs and pseudocapacitors, higher power and energy densities as well as good cycling stabilities. Lang *et al.* reported SCs based on nanoporous gold/MnO_2 composite electrodes with a very high specific capacitance of 1145 F g^{-1} (based on the mass of MnO_2).[92] The nanoporous gold acts as an EDLC as well as a current collector to enhance the pseudocapacitive behavior of MnO_2. However, the nanoporous gold/MnO_2 hybrid electrode is very difficult to fabricate; the high mass and expensive price of nanoporous gold also limit its practical application. ZnO NW arrays were grown on flexible Au-coated polymer Kevlar fiber substrates followed by deposition of MnO_2.[93] Then the electrodes were used to prepare WSSs with H_3PO_4–PVA electrolytes which exhibited a moderate 2.4 mF cm^{-2} owing to the relatively low effective surface area.

As has been discussed above, carbon nanomaterials such as CNTs and graphene have been widely investigated. Besides, highly conductive and flexible substrates like carbon cloth and carbon fiber are also suitable for the preparation of high performance flexible SCs. Pseudocapacitance materials usually suffer from low conductivity which will lower the efficiencies. Hence, the incorporation of carbon active materials with pseudocapacitance materials cast light upon the development of inexpensive and efficient hybrid capacitors. Recent reported flexible hybrid SCs with high energy and power density and long cycling stability is a notable advance in the development of flexible energy storage and conversion systems. Carbon nanomaterials like CNTs and graphene have realized scalable industrialization, which can subsequently lower the cost. The high performance pseudocapacitance material RuO_2 was widely reported in past studies, and is considered to be the best electrode material owing to its high specific capacitance;[94–97] nevertheless, the expensive cost limits its mass application.[86] Other materials such as MnO_2,[98–107] CoO_x,[97,108] Fe_2O_3,[109] PANI,[110–115] and PPy[100] are cost-effective and are promising candidates for flexible hybrid SCs.

Among these pseudocapacitance materials, MnO_2 shows many excellent properties such as high theoretical specific capacitance ($\approx$1400 F g^{-1}), low cost, low toxicity, and natural abundance. Sponges with interconnected cellulose or polymer fibers comprising hierarchical macroporous nature were used as flexible substrates to load active materials.[99] As shown in Fig. 7, a MnO_2/CNT/sponge electrode was prepared through coating CNTs by a simple and scalable "dipping and drying"

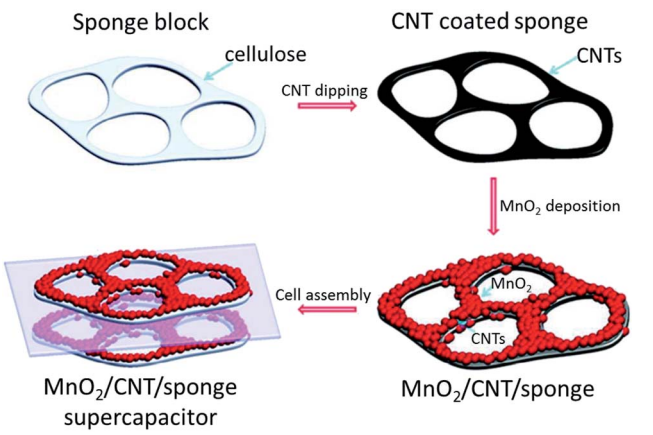

Fig. 7 Schematic illustration of the fabrication process of MnO_2/CNT/sponge supercapacitors. Reprinted with permission from ref. 99. Copyright 2011, American Chemical Society.

method, followed by electrodeposition of MnO_2. The highly conductive and porous CNT-coated sponge along with the porous electrodeposited MnO_2 resulted in more stable pseudocapacitance and double layer capacitance, a high specific capacitance of 1230 F g^{-1}, a specific power density of 63 kW kg^{-1}, a specific energy density of 31 kW h kg^{-1}, and a reliable cycling stability after 10 000 cycles with negligible decay in capacitance. Highly porous Ni foams with interconnected 3D structure were used to fabricate conductive skeletons for flexible SCs.[105] The commercially available Ni foam was firstly pressed into a ~0.2 mm thick sheet and subsequently coated with graphene by atmospheric pressure chemical vapor deposition (APCVD). A highly flexible and conductive 3D graphene network skeleton was then obtained after the removal of Ni foam (Fig. 8a). Finally, by electrochemical deposition of nanostructured MnO_2, a MnO_2/graphene composite electrode was prepared with a maximum specific capacitance of 130 F g^{-1} of the entire electrode. As shown in Fig. 8b, a flexible SC was fabricated using two pieces of 3D network MnO_2/graphene composite film, a separator, and a PET membrane outer package. Excellent and stable electrochemical performance and good flexibility was also demonstrated for the SC.

As illustrated in Fig. 9a, a poly(3,4-ethylenedioxythiophene) (PEDOT)/MWCNT nanomembrane was biscrolled into yarns by using a novel method for twist insertion,[116] then a Pt wire current collector was twisted with PEDOT/MWCNT yarn to fabricate an electrode (Fig. 9c and d). WSS based on the biscrolled yarns showed a very high power density of 40 W cm^{-3}, an energy density of 1.4 mW h cm^{-3}, and excellent rate capability.[117] Also, electrodeposition of conductive polymers like PANI on carbon materials is widely investigated. The well-defined PANI nanowire arrays provide large specific area for favorable contact with the electrolyte, leading to enhanced electrochemical performances. Meanwhile, the PANI nanowire arrays are proven to be well adapted to mechanical deformation with negligible change in capacitances. A paper-like SC comprising two slightly separated PANI/CNT nanocomposite films solidified in the H_2SO_4–PVA was prepared by Meng *et al.*,[112] the device showed stable electrochemical performances

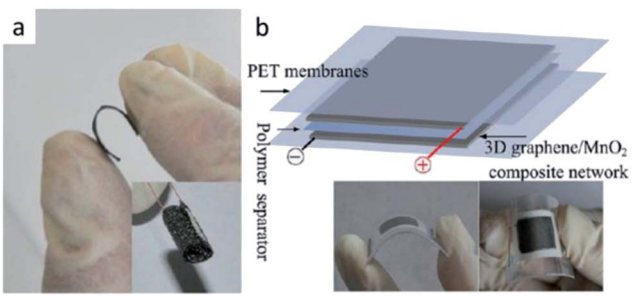

Fig. 8 (a) Digital photograph of a freestanding and flexible 3D graphene network prepared from pressed Ni foam. Inset shows the curled 3D graphene networks. (b) Schematic of the structure of the flexible SC consisting of two MnO_2/graphene composite electrodes, a polymer separator, and two PET membranes. The two digital photographs show the SC with good flexibility when bent. Reprinted with permission from ref. 105. Copyright 2013, American Chemical Society.

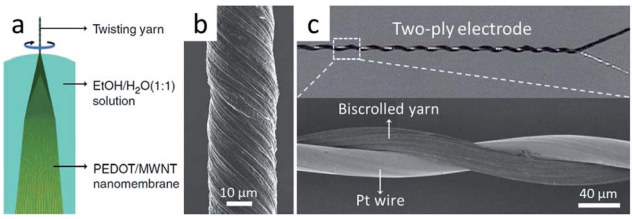

Fig. 9 (a) Schematic illustration showing the fabrication process of a biscrolled PEDOT/MWNT yarn. (b) SEM image of a biscrolled yarn. (c) Two SEM images of a PEDOT/MWNT biscrolled yarn that is plied with a Pt wire. Reprinted with permission from ref. 117. Copyright 2013, Nature Publishing Group.

under mechanical stress. A specific capacitance of as high as 31.4 F g^{-1} for the entire device was demonstrated, which is more than 6 times that of current commercial SCs.[16] Highly flexible and conductive graphene paper was fabricated by chemical reduction of GO-coated Teflon substrate.[83] Then a uniform PANI nanowire array was electrochemically grown on the graphene paper, thus constructing a PANI/graphene composite paper electrode. Consequently, the composite electrode exhibited enhanced capacitive performance of 763 F g^{-1} at 1 A g^{-1} compared with that of the graphene paper and PANI film on a Pt electrode (180 and 520 F g^{-1}, respectively). Very recently, free-standing flexible graphene films with 3D interconnected porous structure are also reported as ideal substrates to fabricate hybrid SCs.[113] First, $CaCl_2$ was added to a GO dispersion to form a uniform mixture, then with CO_2 bubbling through the mixture, $CaCO_3$ particles wrapped with GO sheets were formed. A GO/$CaCO_3$ composite film was subsequently prepared by vacuum filtration. After GO was reduced using hydrazine and $CaCO_3$ removed by dilute acid, a flexible 3D graphene skeleton film was obtained. Then PANI nanowire arrays were homogeneously grown on the outer and inner surface of the 3D graphene substrate, thus yielding a hierarchical 3D PANI/graphene composite film. Owing to the interconnected porous structure, after 5000 cycles at a current density of 5 A g^{-1}, the composite film kept 88% of its initial capacitance. SC based on the composite film also showed excellent flexibility at rate performance, highlighting the promising application in flexible SCs.

Overall, different electrode materials have their own advantages and disadvantages. Porous CNT networks with low density, good flexibility, electrical conductivity, chemical stability and high surface area, are widely used as electrode materials and support matrix in flexible EDLCs. However, it is hard to eliminate the problem of residual metallic impurities of CNTs which would affect the intrinsic properties. Compared with CNTs, graphene has similar properties to CNTs, but is easier to fabricate and has much higher surface area which can provide more electrochemical reaction sites for energy storage. In addition, graphene sheets can be easily dispersed in solution while CNTs usually suffer from entangled CNT bundles. A major disadvantage is the restacking of graphene sheets; this will result in lowered surface area and lead to reduced capacitance. Pseudocapacitance materials, as discussed above, have very

high theoretical capacitances but relative low conductivity and poor cycling stability. As a solution, hybrid SCs that combine both advantages of EDLCs and pseudocapacitors can achieve higher capacitance than EDLCs, and improved energy density than pseudocapacitors without sacrificing power density.

2.3 Prototype flexible SCs

In this section, we focus on some recent representative designs of prototype flexible SCs. Up to now, many novel flexible prototype SCs were reported with various electrode and electrolyte materials, and different assemblies. From which, electrode materials that are nontoxic and inexpensive, also with porous structure and high effective surface area, excellent conductivity, good capacitance, and stable cycling under deformation are favored. Judging from the shape of the previously reported SCs, they can be divided into two categories, planar SCs and wire-shaped SCs. Compared with planar ones, WSSs with omnidirectional flexibility can be easily integrated into textiles.

Unlike conventional bulky ones, there are many other factors that should be considered in designing flexible SCs. Safety issues are critical to flexible SCs; the use of liquid electrolytes suffers from potential leakage which would badly harm the human body and surrounding environment. In addition, the components may not be fully integrated together, and will lead to inhomogeneous distribution of electrolyte and relative movement of electrodes under mechanical stress, thus resulting in a decrease in electrochemical performances. An ideal electrolyte for flexible power sources should possess the high conductivity of liquid electrolytes, good safety and mechanical properties of solid electrolytes, excellent contact with electrodes, and flexibility.[118,119] To solve this, flexible gel polymer electrolytes (GPEs) which can function as both separators were employed as favorable substitutes. Furthermore, suitable packaging materials can protect the integrity of devices and prevent potential safety issues. As shown in Fig. 8, PET membranes served as flexible substrates and outer package of the as-prepared SC.[105] This device showed good flexibility under bending; however, some improvements are needed for further commercialization. The SC demonstrated in Fig. 3 was designed into a wire-shape which can guarantee the device can be bent in any direction.[49] Furthermore, the stretchable spandex fiber substrate realized an additional but vital function: stretchability. Stretchability is a more advanced function for the flexible power sources demonstrated so far, but is crucial for applications in various working conditions. Though further optimization is still needed, the selection of outer package material and shape design of the WSS shown in Fig. 3 is a step forward towards practical application.

Owing to the nature of flexible electronics, the corresponding power sources should be lightweight, small in size, but highly efficient, which is another factor to be considered. Polymer binding agents (binders) are intrinsically electroinsulating; the use of binders in electrode materials will lead to increased resistivity and addition of dead weight. Moreover, binders suffer from some side effects with electrolytes which are detrimental to cycling stability. Therefore, fabricating free-standing electrodes without binders will increase the overall mass capacitance and improve electrochemical performances. Metal current collectors are easy-access and can enhance the performances by providing conductive pathways for active materials. But the high density and the tendency for fatigue failure under constant bending conditions make them unsuitable to be applied in flexible SCs. Additionally, many previous studies reported flexible SCs with high mass capacitances but impractically low areal capacitances.[76,120,121] Considering the limited surface area of the human body, areal capacitance should also be an important metric to consider when designing flexible power sources for some specific application (*i.e.* wearable electronics). It has been suggested that the mass capacitance can be calculated to be very high if the mass loading is small enough.[122] High mass capacitance translates to high areal capacitance only with high mass loading per area of active materials, but too thick a layer of active materials will in turn limit the infiltration of electrolytes and lower the mass capacitances and charge–discharge rates.[112] Though many efforts have been made, the challenge of finding appropriate materials still needs to be solved.

Weng *et al.* prepared a planer SC based on graphene-cellulose paper (GCP) membranes.[123] As shown in Fig. 10, the binder-free GCP membrane electrode was developed by infiltrating graphene nanosheets (GNSs) into the cellulose structure of filter paper (as shown in Fig. 10). Polymer H_2SO_4–PVA gel electrolyte was then placed between two pieces of GCP membrane which also works as a separator. This prototype SC showed excellent mechanical strength and flexibility, good mechanical and electrochemical stability, and a maximum capacitance of 46 mF

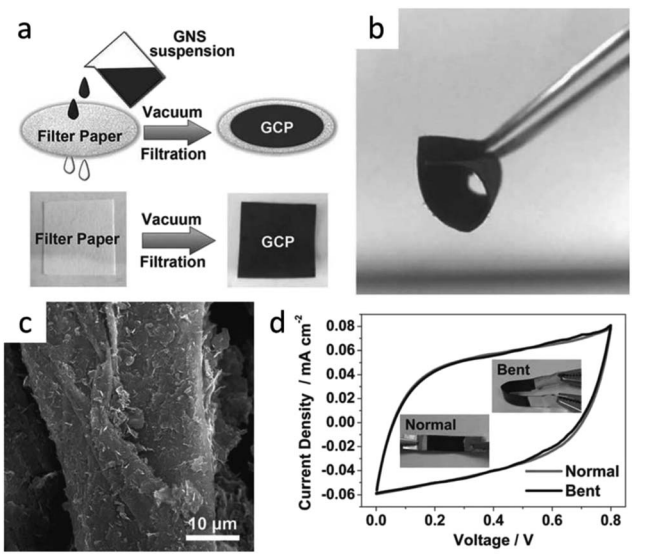

Fig. 10 (a) Schematic of the fabrication process of GCP membrane and (b) a photograph of a GCP membrane demonstrating its flexibility. (c) SEM image of a cellulose fiber in a GCP membrane. (d) Comparison of CV curves at 2 mV s^{-1} for a flexible laminated poly-SC tested as normal and bent. Reprinted with permission from ref. 123. Copyright 2011, Wiley-VCH, GmbH & Co. KGaA.

cm^{-2} was observed. To improve the specific capacitance, Xiong *et al.* used electropolymerization of aniline monomers into a nanometer-thick PANI layer that conformally coats graphitic petal (GPs) grown on conductive carbon cloth (CC) to make a CC/GPs/PANI electrode.[110] A H_2SO_4–PVA gel electrolyte was used to fabricate a solid-state SC. The SC showed negligible performance degradation even under highly bent conditions and an elevated areal capacitance of 1.5 F cm^{-2} at 1 A g^{-1} was observed. Gogotsi and co-workers demonstrated wearable SCs by screen printing activated carbon paint onto fabrics.[76,77] The device showed a comparable high areal capacitance of 0.51 F cm^{-2} at 10 mV s^{-1}. The use of nontoxic and inexpensive active materials and electrolyte, and scalable manufacturing techniques together with good performance and long-term stability highlight their potential use in flexible electronics.

Flexible on-chip micro supercapacitors (MSCs) were first introduced in 2003. Contrary to the conventional SCs with stack geometry, the electrodes are separated and placed on one plane, so separators are not needed in these devices; electrolyte ions in the narrow spaces between electrode fingers can rapidly transport to provide high power capability owing to the short ion diffusion distance.[40,87,124–127] Flexible MSCs can be potentially used in miniaturized portable electronic devices, such as microsensors, microrobots and wearable medical devices. Recently, Ajayan's group demonstrated graphene-based monolithic MSCs by direct laser reduction and patterning of hydrated GO films.[125] It was found that the water trapped in the layered GO structure can become a good ionic conductor and an electrical insulator, enabling it to serve as an electrolyte as well as an electrode separator. On this account, both planar and conventional sandwich-like SCs were prepared in a number of patterns and shapes (Fig. 11). As a result, the planar supercapacitor with a concentric circular geometry delivered an areal capacitance of ~0.51 mF cm^{-2}, almost twice that of the sandwich SC. A stretchable solid-state MSC array was reported by Kim *et al.*[40] Two-dimensional planar MSCs with SWCNT electrodes and a gel electrolyte were interconnected with long serpentine metallic conductors at the mechanical neutral state, the MSC array was encapsulated with plastic polyimide thin film to enable stretchability. Excellent and stable performances were achieved even under the maximum strain of 30% without noticeable degradation. This device shows a strong potential in application in flexible electronics as it ensures not only bendability but also stretchability.

In order to be fully integrated into textiles, wire-shaped designs possess advantages over planar ones. Well-designed WSSs are omnidirectional, flexible and even twistable, thus can be woven into any shape and become more practical. For example, textiles integrated with WSSs can be fabricated into clothes to power electronic devices, which is a great advance over planar flexible SCs. As shown in Fig. 12a and d, a flexible WSS composed of two fiber electrodes, a helical space wire, an electrolyte, and a plastic tube outer package was recently demonstrated.[32] Commercial pen ink was introduced as an active material for the first time; a uniform film with fine dispersion and strong adhesion on substrates (Fig. 12b and c) can be achieved by a simple dip-coating method and the resulting WSS exhibited a good areal capacitance of 9.5 mF cm^{-2} and a stable cycling performance over 15 000 cycles. This WSS utilized liquid electrolyte, thus a space wire is necessary to separate the two fiber electrodes. For further improvements, liquid electrolyte can be replaced with polymer electrolyte to eliminate the use of a space wire; a heat shrinkable plastic outer package can thus be introduced to tightly wrap each component and also reduce the device volume, which will ensure safe operation and enable more practical applications.

Kim and co-workers demonstrated WSSs based on two-ply electrodes with high energy densities and high rate capacities.[117] The two-ply electrode was prepared by biscrolling a PEDOT/MWCNT film into a yarn followed by plying a Pt wire current collector. The WSS utilizing H_2SO_4–PVA gel electrolyte displayed a capacitance of 73 mF cm^{-2} at a scan rate of 1 V s^{-1}. However there is still room for improvement by replacing Pt wire with other conductive fibers such as SACNT fibers and graphene fibers to lower the cost and total mass. Recently, Liu

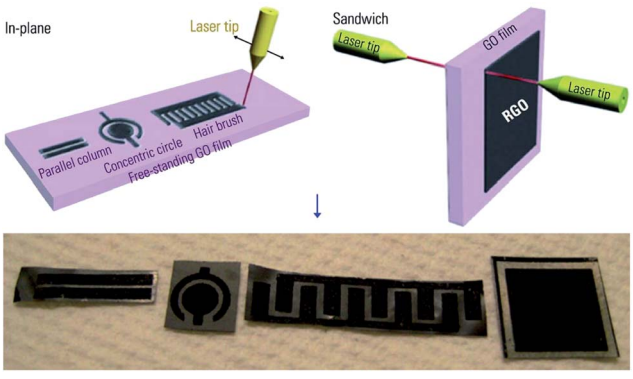

Fig. 11 Schematic of laser-patterning of hydrated GO films to fabricate RGO–GO–RGO devices with in-plane and sandwich geometries. The bottom row shows photographs of patterned films. Reprinted with permission from ref. 125. Copyright 2011, Nature Publishing Group.

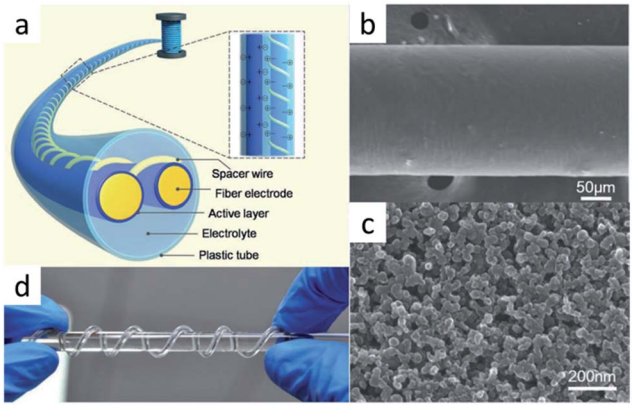

Fig. 12 (a) Architecture of the WSS and morphology of the electrode. (b) SEM image of the plastic fiber electrode coated with pen ink film. (c) SEM image of ink nanoparticles at high magnification, with a particle size of around 20 nm. (d) Photograph of a flexible WSS packaged using plastic tube. Reprinted with permission from ref. 32. Copyright 2012, Wiley-VCH, GmbH & Co. KGaA.

et al. designed a WSS based on three-dimensional PPy/MnO_2/CNT/cotton thread which showed a capacitance of 0.52 F cm^{-2} at 1 mV s^{-1}.[100] The cotton thread was coated by SWCNTs by a simple "dipping and drying" method, then MnO_2 nanostructure and PPy film were grown on SWCNT-coated cotton thread through an electrochemical deposition process. However, this device used 0.5 M Na_2SO_4 as the electrolyte, so a separator and good encapsulation is required. A WSS utilizing two PANI/CNT composite fibers and H_2SO_4–PVA gel electrolyte was recently reported by Miao and co-workers (Fig. 13a–c).[111] This device displayed a capacitance of 38 mF cm^{-2} at a current density of 0.01 mA cm^{-2} and good flexibility; textiles woven by the as-prepared WSSs with conventional yarns were also demonstrated (Fig. 13d). As is discussed in the case of the WSS demonstrated in Fig. 12, this device can be optimized by adding a heat shrinking plastic packaging to protect the integrity of the device and improve safety as flexible electrical textiles.

With future materials optimization and structure design improvements, it is believed that high performance flexible SCs will bring revolutionary advances in technology and play an important role in flexible electronics.

3. Flexible lithium-ion batteries

The continuous development of flexible electronics calls for effective corresponding power sources. From all the candidates, rechargeable lithium-ion batteries (LIBs) and SCs are leading the pack. Since they were first introduced in 1991, LIBs have been widely adapted as main power sources in the portable device market due to their high energy density, high operating voltage, low self-discharge rate, and relatively long-term cyclability. The reaction occurring in the internal LIB is associated with the lithiation and delithiation process between the positive electrode and negative electrode. Owing to the nature of flexible electronics, the corresponding power sources should be lightweight, thin and flexible. But currently, the commonly used LIBs are too heavy, rigid and bulky to meet the needs of suitable power sources for flexible electronics. Typically, a flexible LIB includes an anode and cathode, electrolyte (liquid or solid-state), separator (when liquid electrolyte is used), and a bendable (or even stretchable) plastic outer package. As has been mentioned above, the commonly used metallic current collectors and binders in conventional LIBs are also not recommended here. To further expand the practical application, many innovations of flexible LIBs have been reported mainly concentrated on selecting and developing reliable nano-engineered materials with high mechanical and electrochemical performances as well as appropriate battery structural designs. In this section, we focus on the recent progress in electrode and electrolyte material designs as well as cell configurations of flexible LIBs.

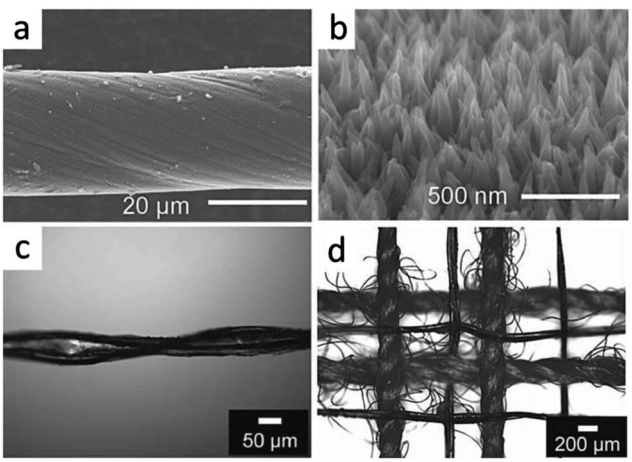

Fig. 13 (a and b) SEM images of PANI/CNT composite yarn. Ordered PANI nanowire arrays can be seen on the surface of PANI/CNT composite yarn. (c) Photograph of the WSS. (d) Photograph of a flexible electronic fabric with the WSSs co-woven with conventional cotton yarns. Reprinted with permission from ref. 111. Copyright 2013, Wiley-VCH, GmbH & Co. KGaA.

3.1 Material designs for flexible electrodes

Traditional electrodes in LIBs often consist of active materials, binders and conductive carbon additives such as graphite and carbon black.[128–133] However, these electrode materials may easily detach from flexible substrates during mechanical deformation. Hence, material designs used in conventional LIBs are not suitable for the fabrication of flexible ones. Although LIBs have high capacities, they usually suffer from low charge–discharge rates compared with SCs. Therefore, it is highly desirable to explore effective electrode materials that combine robust mechanical flexibility, superior conductivity, high capacity, and cycling stability.[134] Recently, nano-engineered materials like metal oxide nanowires and carbon materials including CNTs, carbon nanofibers and graphene have been demonstrated for use as electrode materials in flexible LIBs.

CNTs are widely used as conductive skeletons for loading active electrode materials owing to the high surface area, small diameter and excellent electrical conductivity.[135–137] A binder-free CNT film achieved by vacuum filtration was directly used as an anode for flexible LIBs.[138] By direct deposition of porous CNT networks onto a carbon fiber paper support, Chen *et al.* demonstrated a free-standing anode which can be directly used in LIBs.[139] This composite electrode showed an enhanced reversible capacity of 546 mA h g^{-1} after 50 cycles at 0.05 mA g^{-1}. Aligned CNTs grown on graphene paper (GP) were prepared as a flexible free-standing anode for LIBs.[140] The fast ion transport of the aligned CNTs and conducting GP contribute to the electrochemical performance, and a stable capacity of 290 mA h g^{-1} at 30 mA g^{-1} was achieved. However, the fabrication process is too complex and expensive to be applied to scalable production.

It should be noted that previous studies reported electrodes based on CNT delivering low capacities and possessing safety hazards with Li dendrite forming between electrode and separator, which does not meet the demands of practical application. To solve this, recent studies have reported various CNT-based composites as flexible and binder-free electrodes; these

composites can usually be achieved by CVD or vacuum filtration. Moreover, the CNTs with high conductivity can serve as current collectors which can lower the overall device mass and maximize the specific capacity. Wang *et al.* developed a lightweight, thin, and flexible CNT current collector for LIBs. Compared with metal current collectors, the CNT current collectors functioned as excellent mechanical supports and enabled efficient electron transfer and lower contact resistance at the electrode–CNT interface.[141] The performance of electrodes with CNT current collectors showed improvements in cycling stability, rate capacity, and gravimetric energy density over those with metal current collectors. In addition, the smooth surface of metal current collectors provides weak adhesion to electrode materials, whereas CNTs are much rougher and thus can facilitate interface contact.

$LiCoO_2$ is widely considered as a reliable cathode material due to its high operating potential of ~4 V and high reversible capacity.[142–145] A flexible $LiCoO_2$/SACNT composite cathode was prepared by a simple ultrasonication and co-deposition approach with $LiCoO_2$ uniformly distributed in the highly conductive super-aligned CNT network.[146] The composite was comprised of about 95 wt% of $LiCoO_2$ and only 5 wt% of CNT as a conductive and flexible skeleton network. The resilient structure of the binder-free composite is capable of enduring the volume changes on cycling and also efficiently facilitates electrolyte infiltration and faster lithium ion transport throughout the electrode, thus resulting in better cycle stability and rate capacity. Fe_2O_3 has a theoretical capacity of 1005 mA h g^{-1} and is also a promising high performance anode material.[147–150] By chemical vapor deposition of Fe on SWCNTs followed by oxidization, a flexible Fe_2O_3/SWCNT membrane was prepared with Fe_2O_3 particles tightly attached to the SWCNTs.[151] The flexible CNT network can buffer the volume change during charge and discharge and improve the conductivity of Fe_2O_3. An enhanced high reversible capacity of above 1200 mA h g^{-1} at 50 mA g^{-1} and good rate capacity was demonstrated. CNTs were also used to fabricate a V_2O_5/CNT cathode *via* a simple *in situ* hydrothermal reaction.[152] As demonstrated in Fig. 14, the interpenetrative nanocomposite of 3D V_2O_5 nanowire networks within ultra-long CNT networks created interconnected channels for effective ion transport while the CNT scaffold provides fast electron transport and mechanical robustness. Consequently, a high capacity of 340 mA h g^{-1} at 70 mA g^{-1}, a good rate capacity of 169 mA h g^{-1} at 2800 mA g^{-1} and excellent cycling stability of 87% retention in capacity after 200 cycles at 1400 mA h g^{-1} were demonstrated.

Similarly, incorporation of high capacity anode materials such as Si, Ge, Sn and transition metal oxides with CNTs will also result in better performances and have attracted considerable interest.[153–155] The main problem of these materials is pulverization and structure destruction associated with large volume change during the lithiation and delithiation process.[153–157] As a solution, the porous structure of CNTs can provide a flexible support and lithium storage matrix which allows for the volume fluctuation during cycling. Silicon has the highest lithium storage capacity per unit mass (4200 mA h g^{-1}, 10 times higher than commercial graphite) and is therefore a very promising anode material for high-performance LIBs.[158–163] A layer of nanometer-sized silicon was coated on SACNT sheets

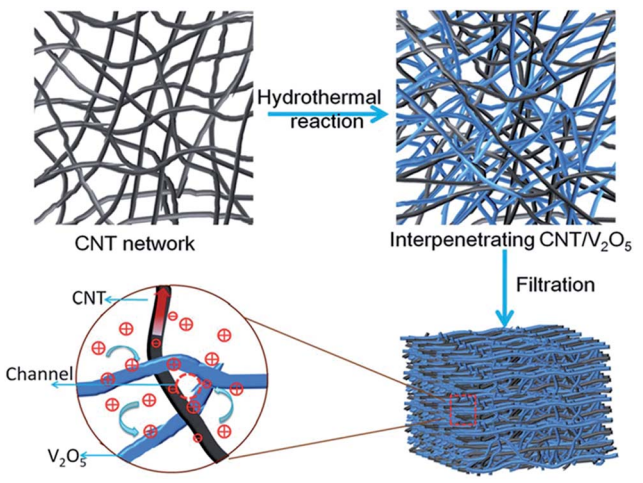

Fig. 14 Schematic of synthesis of the nanocomposites of ultra-long CNTs and V_2O_5 nanowires with an interpenetrative network structure. Reprinted with permission from ref. 152. Copyright 2012, The Royal Society of Chemistry.

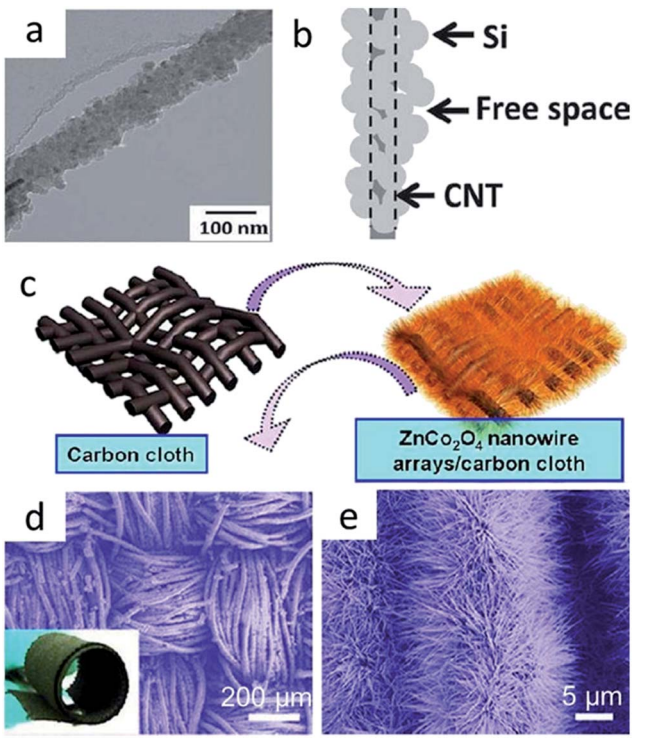

Fig. 15 TEM (a) and schematic (b) image of the Si/CNT structure. Reprinted with permission from ref. 164. Copyright 2013, Wiley-VCH, GmbH & Co. KGaA. (c) Schematic illustration of the synthesis of flexible 3D $ZnCo_2O_4$ nanowire arrays/carbon cloth. (d and e) FESEM images of the $ZnCo_2O_4$ nanowire arrays grown on carbon cloth at different magnifications. Inset in (d) is a photographic image of the rolled-up $ZnCo_2O_4$ nanowire arrays/carbon cloth composite. Reprinted with permission from ref. 167. Copyright 2012, American Chemical Society.

by CVD to form a free-standing, binder-free, and flexible anode (Fig. 15a and b).[164] The silicon coating was in an amorphous state and in accordance with previous studies exhibits better cycle performance than crystalline silicon owing to the homogenous lithium insertion, resulting in less silicon pulverization.[165,166] The SACNTs provide a high surface area and porous structure to facilitate the electrochemical kinetics between the active material Si and electrolyte. As a result, the flexible Si/CNT composite electrode showed high specific energy and stable cycling performance without dramatic capacity loss.

Another feasible solution is to modify the nanostructure of these materials and recent studies have demonstrated some carbon cloth-based flexible electrode designs. $ZnCo_2O_4$ is an attractive anode material but also suffers from poor electric conductivity and large volume change of the $ZnCo_2O_4$ nanostructures during electrochemical reaction. To solve this, by using a simple and facial hydrothermal process, hierarchical 3D $ZnCo_2O_4$ nanowire arrays were grown on carbon fiber cloth to fabricate a binder-free anode for LIBs (Fig. 15c–e).[167] The strong adhesion of 3D $ZnCo_2O_4$ nanowire arrays on carbon cloth and high conductivity of carbon cloth facilitate fast electron and ion transport and alleviate the volume change during cycling. This electrode exhibited a high reversible capacity of about 1300 mA h g^{-1}, good rate capacity, and a capacity of 1200 mA h g^{-1} after 160 cycles. The same method was used to grow $Ca_2Ge_7O_{16}$ nanowire arrays on carbon textiles to prepare a binder-free flexible anode for LIBs with excellent rate capacity and cycling stability.[168] The electrode was then paired with a commercial $LiCoO_2$/Al foil cathode to fabricate a flexible full cell. The cell was then cycled within the voltage range of 2.0–4.2 V at a current density of 200 mA g^{-1}, the cycling performance was stable and a specific capacity of about 1100 mA h g^{-1} with negligible decay was achieved after 60 cycles.

In addition, carbon nanostructured materials like graphene also attracted considerable attention as an effective material to fabricate flexible electrodes.[169–171] Owing to the layer structure of graphene, it can be easily assembled into a macroscopic membrane. However, graphene-based electrodes also suffer from large irreversible capacity and fast capacity fade, thus combining high performance active materials is necessary.[172,173] To this end, very recently, highly conductive and flexible CNT/graphene films were demonstrated as current collectors which were easily achieved by facile vacuum filtration method.[174] By using pulsed laser deposition (PLD) of V_2O_5 on graphene paper membrane, Kang and co-workers demonstrated a free-standing flexible cathode.[175] Graphene paper acted as the current collector and conducting agent, and the electrode showed good electrochemical properties and mechanical robustness. A free-standing SnO_2/graphene composite film with ordered alternating layers of nanocrystalline SnO_2 with graphene was prepared as an anode for flexible LIBs.[176] The electrode showed a high capacity of 760 mA h g^{-1} at 8 mA g^{-1} but decreased to only 225 mA h g^{-1} at 80 mA g^{-1}. A recently reported SnO_2/N-doped graphene hybrid electrode exhibited an elevated capacity of 918 mA h g^{-1} at 100 mA g^{-1} and 504 mA h g^{-1} at 5 A g^{-1} and good cycling performance.[177] This excellent performance was

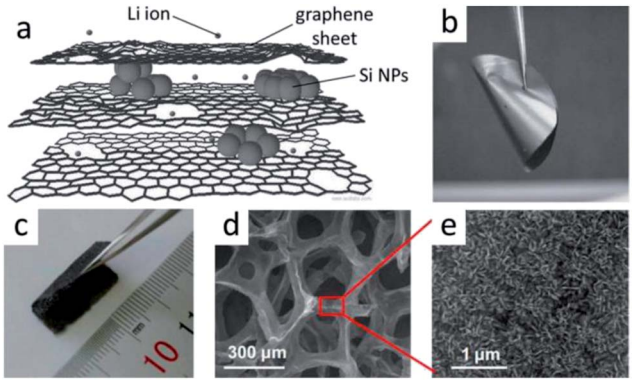

Fig. 16 (a) A schematic of a section of the Si/graphene composite electrode material constructed with a graphenic scaffold with in-plane carbon vacancy defects. (b) Photograph of the flexible Si/graphene composite paper. Reprinted with permission from ref. 178. Copyright 2011, Wiley-VCH, GmbH & Co. KGaA. (c) Photograph of the free-standing flexible LTO/GF composite electrode. (d and e) SEM images of the LTO/GF at different magnification. Reprinted with permission from ref. 191. Copyright 2011, Proceedings of the National Academy of Sciences of the United States of America.

mainly owing to the fast electrochemical kinetics and good flexibility to buffer the volume change of SnO_2. As mentioned above, Si is a potential anode material substitute for commercial graphite. Kung *et al.* introduced a planar Si/graphene composite electrode (Fig. 16a and b).[178] As demonstrated in Fig. 16a, the graphene paper was prepared by mild acid etching to produce a high density of nanometer-sized carbon vacancies in graphene sheets which greatly enhanced the ion diffusion. The incorporation of Si NPs with the 3D conducting graphene scaffold exhibited a high reversible capacity of about 3200 mA h g^{-1} at 1 A g^{-1}, a good rate capacity of 1100 mA h g^{-1} at a high rate of 8 A g^{-1}, and excellent cycling stability was also achieved. Some recent studies have demonstrated that Si NWs can accommodate the severe volume change and Si/graphene composite electrodes were reported to exhibit high capacity, excellent rate capacity and cycling stability.[179–181] Other high performance materials such as Fe_3O_4,[182–184] Co_3O_4,[185,186] TiO_2,[187,188] and Mn_3O_4 (ref. 189) incorporated with graphene sheets were also demonstrated to fabricate flexible electrodes for LIBs with excellent performances. 3D graphene foam (GF) was prepared through a template-directed CVD process[190] and was then used as a highly conductive substrate to load $Li_4Ti_5O_{12}$ (LTO) and $LiFePO_4$ (LFP) by *in situ* hydrothermal deposition to form a flexible anode and cathode.[191] The LTO/GF (Fig. 16c–e) and LFP/GF electrodes were assembled into a full battery sealed with poly(dimethyl siloxane) (PDMS). This flexible full battery showed good cycling performance with only 4% capacity loss over 100 cycles and a high rate capacity of 117 mA h g^{-1} at 10 C.

To conclude, carbon materials such as CNTs and graphene usually suffer from poor capacity and safety hazards with Li dendrites forming between the electrode and separator. Other materials such as Si, Ge, LiMO (M = Ni, Co, Mn), and $LiFePO_4$, have very high capacity but poor conductivity; furthermore, a stable structure is needed to endure the volume change during

charge and discharge. By modifying the nanostructure of these materials or incorporating them in flexible carbon scaffolds are possible solutions to fabricate desirable flexible LIB electrodes.

3.2 Flexible solid-state electrolytes

Liquid electrolytes are widely used in conventional power devices, and their high conductivity and good physical contact with electrodes ensure excellent electrochemical performances. However, as mentioned above, the use of liquid electrolytes in flexible LIBs has many drawbacks, such as safety issues, the need of separators, unstable performances under continuous mechanical deformation and different operating temperature and so on. On this account, many novel designs of shape-conformable solid-state electrolytes are proposed. Among various solid-state electrolytes, gel polymer electrolytes (GPEs) with excellent conductivity, low rates of electrolyte leakage, low flammability, and mechanical flexibility are extensively studied.[192–196]

Typically, conventional GPEs which consist of liquid electrolytes embedded in polymer frames are prepared by solvent evaporation of pre-mixed mixtures of liquid electrolytes and polymers dissolved in organic solvents. However, the initial mixture used here is fluidic with poor dimension stability, in addition, the good mechanical flexibility always comes at a price of sacrificing conductivity. Recently, Kil *et al.* introduced a flexible GPE composed of an ultraviolet (UV)-cured ethoxylated trimethylopropane triacrylate (ETPTA) polymer matrix, $LiPF_6$-based electrolyte, and Al_2O_3 NPs.[197] Here, Al_2O_3 NPs served as a functional filler to control the rheological properties of the GPE. Compared with a previous study,[198] the incorporation of Al_2O_3 NPs enabled better mechanical flexibility and good conductivity, thus more suitable for 3D electrodes with complex geometrics to maintain good interface contact. Based on this, the GPE was further introduced for use in flexible LIBs.[199] Owing to the uniformly dispersed and densely packed Al_2O_3 NPs as protective barriers, the growth of lithium dendrites was shown to be suppressed which can prevent short circuiting of the battery.

In addition, plastic crystal electrolytes (PCEs) were also reported with high ion conductivity, good flexibility, and thermal stability.[200–206] One representative example is succinonitrile (SN)/lithium salt-based PCEs, which provide a high ion conductivity of up to 10^{-3} S cm^{-1}, but the mechanical properties are poor due to the excessively plastic and liquid-like behavior.[201,202] Hence, combination of PCEs with a polymer matrix has been proposed as an effective way to overcome this drawback of SN/lithium salt-based PCEs.[203] A highly flexible and shape conformable plastic crystal composite electrolyte (PCCE) was fabricated from a UV-curable semi-interpenetrating polymer network (semi-IPN) with a PCE (1 M LiTFSI in SN) (Fig. 17a and b).[204] The PCCE exhibited excellent bendability and ion conductivity, on the other hand, a control sample without semi-IPN is too mechanically weak and broke down after only 3 bending cycles (Fig. 17c and d). Another UV-cured polymer network is also exploited with the same PCE and showed improved mechanical bendability but relatively sluggish ionic

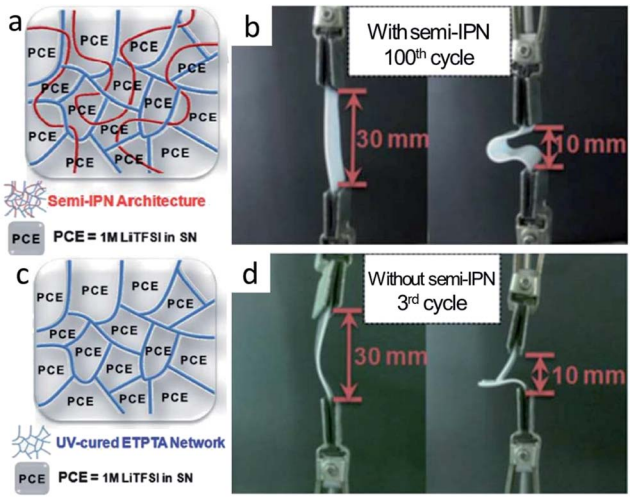

Fig. 17 (a and c) Schematic illustration of the PCCEs with and without semi-IPN, respectively. (b) PCCE with semi-IPN (after the 100th bending cycle). (d) PCCE without semi-IPN (after the 3rd bending cycle). Reprinted with permission from ref. 204. Copyright 2012, The Royal Society of Chemistry.

transport.[205] Recently, a new kind of highly thin, deformable, and safety-reinforced plastic crystal polymer electrolytes (N-PCPEs) was reported.[206] The innovative N-PCPEs were fabricated by embedding a compliant porous polyethylene terephthalate (PET) skeleton in a UV-crosslinked PCPE matrix. The PET skeleton was incorporated to enhance the mechanical properties of the N-PCPE. As a result, the N-PCPE demonstrated high flexibility and shape deformability while maintaining good ion conductivity. Moreover, a flexible LIB was prepared with the N-PCPE working as the separator and electrolyte and a LCO anode and a LTO cathode. Owing to the excellent properties of the N-PCPE, the LIB showed stable performance even under severe deformation state.

3.3 Prototype flexible LIBs

Presently, the development of flexible LIBs is at its infancy stage and many works regarding this field only demonstrated individual battery components such as electrodes, electrolytes, and current collectors. It is necessary that these components be integrated and packaged into a full cell for practical application. Recently, some novel prototype flexible LIBs have been demonstrated. Among them, planar and wire-shaped LIBs are widely investigated. This section reviews some novel and facile designs and assemblies of flexible LIBs.

Koo *et al.* prepared an all-solid-state thin-film LIB consisting of a LCO cathode, lithium phosphorous oxynitride (LIPON) electrolyte, a lithium metal anode, and a protective PDMS outer package.[207] The LIB exhibited an energy density of 2.2×10^3 μW h cm^{-3} at 46.5 μA cm^{-2}, the highest energy density ever reported for flexible LIBs. A relatively stable performance was also observed with a slight decrease in capacity and increase in polarization when the LIB was in a bent state. The high performance was also well supported by theoretical studies and finite element analysis simulation. A

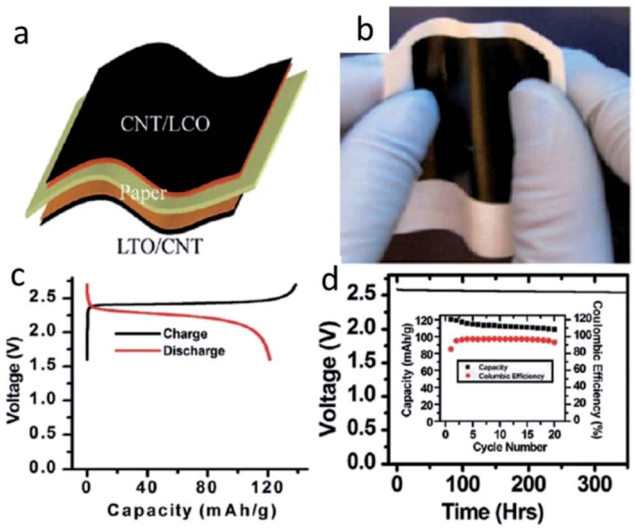

Fig. 18 (a) Schematic illustration of the flexible paper LIB structure, with both LCO/CNT and LTO/CNT laminated on both sides of the paper substrate. The paper is used as both the separator and the flexible substrate. (b) Photograph of the Li-ion paper battery before encapsulation for measurement. (c) Galvanostatic charging–discharging curves of the laminated LTO–LCO paper battery. (d) Self-discharge behavior of a full cell after being charged to 2.6 V. Inset is the cycling performance of LTO–LCO full cells. Reprinted with permission from ref. 208. Copyright 2010, American Chemical Society.

high conductivity paper serveing both as flexible substrate and current collector was prepared by coating CNT slurry on commercial paper. Then a $LiMn_2O_4$ cathode and $Li_4Ti_5O_{12}$ anode were coated on the conductive paper, a separator was further introduced between the electrodes to form a full cell.[37] Similarly, CNT ink was coated on stainless steel substrates followed by coating active materials, LTO and LCO, respectively, then the electrode films were peeled off from the substrate.[208]

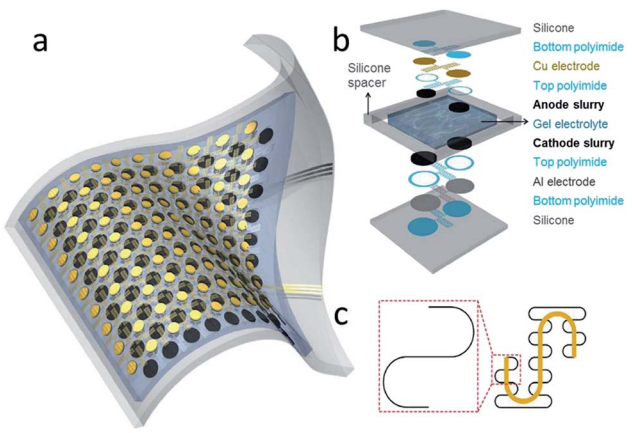

Fig. 19 (a) Schematic illustration of a completed device, in a state of stretching and bending. (b) Exploded view layout of the various layers in the battery structure. (c) Illustration of 'self-similar' serpentine geometries used for the interconnects. Reprinted with permission from ref. 209. Copyright 2013, Nature Publishing Group.

Commercial paper was inserted between the electrodes to function as both separator and mechanical support (Fig. 18a and b). The resulting LIB was very thin and had robust mechanical flexibility and was able to be bent down to <6 mm. As can be observed in Fig. 18c and d, the flexible LTO–LCO battery exhibited excellent electrochemical performances; a high energy density of 108 mW h g^{-1} (based on the total mass of the device) was also demonstrated.

By embedding the components at the neutral strain position, Xu *et al.* demonstrated a novel design of stretchable LIBs (Fig. 19).[209] The battery consisted of multi-layered LCO and LTO cells with a poly(ethylene oxide) (PEO)-based GPE, the electrochemical active parts were interconnected by a serpentine-shaped conducting wire, and a silicone elastomer outer package. As mentioned in introduction, an ideal flexible power source device should be mechanically bendable, foldable (or twistable), and stretchable. This design enables the batteries to be stretched up to 300%, or folded and twisted without noticeable degradation in performance. In addition to the novel structure design, the outer packaging material is also a key factor to ensure the excellent flexibility.

Cable-/wire-shaped designs have been recently proposed. Owing to their extreme omni-directional flexibility, they might be ideal for flexible battery technology.[210] Kim and co-workers

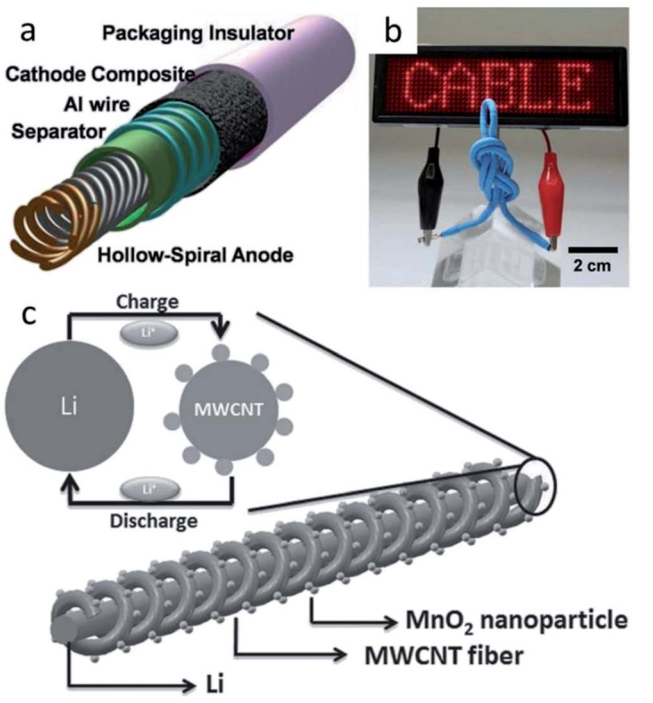

Fig. 20 (a) Schematic illustration of the cable battery with a hollow-helix anode. (b) A photograph showing the excellent mechanical flexibility of the LIB. Reprinted with permission from ref. 211. Copyright 2012, Wiley-VCH, GmbH & Co. KGaA. (c) Schematic illustration of the flexible LIB fabricated by twisting an aligned MnO_2/MWCNT composite fiber and Li wire as positive and negative electrodes, respectively. Inset in (c) is an image showing the charge–discharge process. Reprinted with permission from ref. 212. Copyright 2013, Wiley-VCH, GmbH & Co. KGaA.

demonstrated a cable-type LIB with excellent flexibility.[211] As illustrated in Fig. 20a, the battery utilized a hollow spiral Ni–Si anode with a multi-helix structure, a $LiPF_6$-based liquid electrolyte, a modified PET non-woven separator membrane, and a LCO cathode coated on an aluminum wire. A stable reversible capacity of 1 mA h cm^{-1} between 2.3 and 4.2 V was achieved. This device also showed excellent flexibility, as shown in Fig. 20b, negligible change in performance was observed when the LIB was bent or even twisted. Recently, a cable-type LIB was prepared by winding MnO_2/MWCNT composite fibers around a lithium wire as cathode and anode, a PVDF separator was placed between the electrodes, and a $LiPF_6$-based organic liquid electrolyte was used (Fig. 20c).[212] The cell demonstrated good flexibility and improved capacity with the incorporation of MnO_2. However, the lithium wire anode poses a potential safety hazard, and as such modification of anode materials is essential for making further progress toward its commercialization. In addition, the use of liquid electrolyte requires excellent outer packaging to prevent leakage. Compared with flexible WSSs, research on flexible cable-shaped LIBs is relatively rare. However, their potential in the application of portable and wearable electronics is without a doubt tremendous. Further optimization of the cell components and structure is required for the future application of cable-shaped flexible LIBs.

4. Flexible energy generators

Flexible energy generators that harvest the surrounding energy such as sunlight and human body movements and convert it to electricity are an effective approach to build low-cost, environmental friendly and self-powered flexible electronics. In this section, we focus on the recent progress concerning flexible energy generators.

4.1 Flexible solar cells

With our society becoming increasingly energy dependent and the urge to curb CO_2 emissions, we need to reduce the dependence on traditional energy industries; thus, renewable and clean solar energy is considered as a preferred and optimal solution. A solar cell is a device that can directly convert solar energy into electrical energy, which is the most effective approach for sustainable energy. Typically, solar cells can be divided into many categories, such as silicon-based solar cells, copper indium gallium diselenide (CIGS) thin film solar cells, semiconductor compound cells, dye-sensitized solar cells (DSSCs) and organic photovoltaic cells (OPVs).[25,27,213–217] Conventional solar cells are built with planar sandwich structures and rigid substrates, which restrict the application in portable and flexible electronics. Moreover, the silicon-based solar cells, for instance, though having stable performance and high photoelectric conversion efficiency (PCE), require complicated preparation processes, thus resulting in elevated manufacturing cost. CIGS solar cells were reported to achieve a very high PCE of 19.9%,[218] but the limited reserves of indium, gallium and selenium, and the difficulty to prepare high purity semiconductor materials greatly limit their development and scalable production.

Owing to the excellent characteristics such as wide applicability, non-toxicity, diverse material sources, and simple production, DSSCs have attracted considerable research interests as an alternative to solid-state silicon solar cells.[219–221] Although the performance is inferior to silicon-based solar cells, it can be offset by these advantages. Typically, DSSCs are composed of a dye-sensitized mesoporous titania electrode on a transparent conductive oxide (TCO) substrate, a platinum counter electrode, and iodine/iodide electrolyte placed between the two TCO substrates. Similarly, OPVs also have many advantages such as low-cost, abundant sources, intrinsic flexibility, and easy control of molecular structures. Recently, many novel designs of flexible solar cells have been demonstrated with high efficiency at low cost and good flexibility to be applied to flexible electronics.

Previous reported planar DSSCs based on indium tin oxide (ITO) and TiO_2 can reach a high PCE of 11.1%.[222,223] However, the flexibility of the device is limited because ITO film is brittle. In addition, as noted above, indium is a limited resource on earth, thus the use of ITO film will also increase the cost. On this account, some ITO-free solar cells have been demonstrated. Planar DSSCs composed of a ZnO nanowire array working electrode and a Pt counter electrode were prepared by Yu and co-workers (Fig. 21a and b).[224,225] The electrodes were placed between each other to form a comb-teeth architecture on PET substrates to achieve high mechanical flexibility and light transparency. DSSC counter electrodes using conducting polymers instead of TCO substrate were reported with good flexibility and a PCE of 5.08%.[226] A graphene/PEDOT counter electrode was further prepared with better conductivity and the corresponding DSSC showed a PCE of 6.26%.[227]

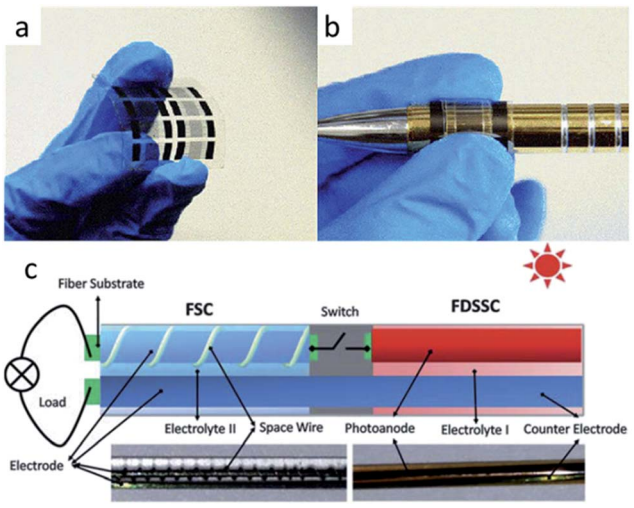

Fig. 21 (a and b) Photographs of the flexible and transparent DSSC. Reprinted with permission from ref. 224. Copyright 2013, American Chemical Society. (c) Structural schematic and photograph of an integrated power fiber consisting of a DSSC and a SC. Reprinted with permission from ref. 115. Copyright 2013, The Royal Society of Chemistry.

Compared to planar-shaped DSSCs, wire-shaped ones enable 3D light collection and better flexibility. Recently, Zou *et al.* prepared an integrated power fiber that incorporated a DSSC and a SC for energy conversion and storage (Fig. 21c).[115] A stainless steel wire coated with PANI *via* anode deposition was used as an electrode for both the DSSC and SC, a TiO_2/Ti wire as the working electrode for the DSSC, whereas a PANI/stainless steel wire twisted with a space wire was used as the other electrode for the SC. The DSSC had a PCE of up to 5.41%, which is comparable to that of Pt-based wire-shaped DSSC, the corresponding SC showed an areal capacitance of 3 mF cm^{-2} to 41 mF cm^{-2}, and the overall energy conversion of the device was up to 2.1%. By directly twisting the TiO_2/Ti anode and the Pt counter electrode, Fu *et al.* fabricated a wire-shaped DSSC with good flexibility and a high PCE of 7.02%.[228] It should be noted that the expensive Pt electrode can be replaced with other substitutes, such as carbon fibers, stainless steel, or conductive substrates sputtered or coated with Pt NPs. Replacement of the Pt wire with CNT film have been reported, but with relatively low efficiencies.[229,230] After the incorporation of Ag nanowires, the corresponding wire-shaped flexible DSSC showed an improved PCE of 2.6%.[231] Lately, a low-cost but highly efficient counter electrode was fabricated by electrodepositing Pt NPs with graphene fiber. Then a DSSC was prepared by twisting the counter electrode with a titanium wire impregnated with perpendicularly aligned titania nanotubes as the working electrode.[232] Owing to the excellent conductivity of the graphene composite fiber, a very high PCE of 8.45% was achieved.

Highly doped graphene was recently demonstrated as excellent flexible transparent electrodes for OPVs.[233] A graphene anode was deposited on polyimide (PI) substrate by CVD; the OPV with P3HT:PCBM active layer showed a maximum PCE of 3.2% which is a little lower than that with ITO electrodes (4–5%)[234,235] owing to the relatively high resistance of graphene sheets. By spin-coating a surfactant layer, glycerol monostearate (GMS), atop poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film, a highly conductive PEDOT:PSS/GMS bilayer film was prepared as the transparent anode for flexible ITO-free OPVs with a maximum PCE of 7.06%.[236] By depositing PEDOT:PSS/P3HT:PCBM on a pre-strained PDMS substrate, Bao *et al.* reported a stretchable OPV that can accommodate up to 18.5% strain.[237] A PEDOT:PSS-coated 1.4 μm-thick PET substrate was used to fabricate an ultra-thin and lightweight ITO-free flexible OPV.[238] The device showed excellent flexibility and continuous optoelectronic operation was also demonstrated even ender extreme mechanical deformation.

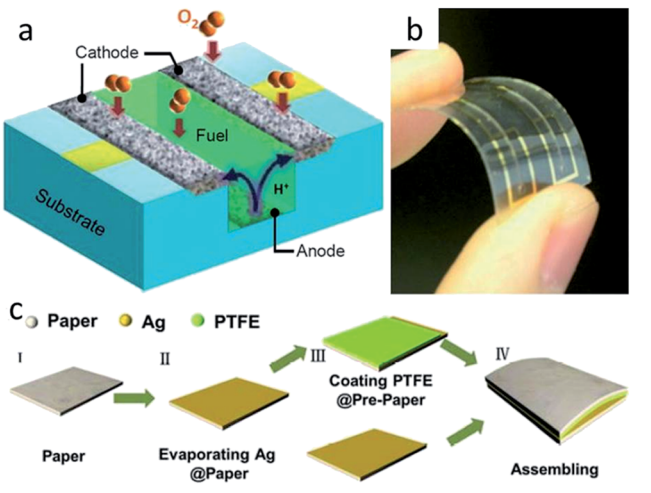

Fig. 22 (a) Schematic illustration of the on-chip fuel cell. (b) An image of the bendable on-chip fuel cell. Reprinted with permission from ref. 240. Copyright 2009, The Royal Society of Chemistry. (c) Schematic illustration of the fabrication process of the nanogenerator. Reprinted with permission from ref. 241. Copyright 2013, The Royal Society of Chemistry.

4.2 Other kind of flexible generators

Fuel cells can operate with very high electrical efficiencies approaching 60–70% which are considered as an ideal energy conversion device.[239] As shown in Fig. 22, a bendable on-chip fuel cell was fabricated on a flexible cycloolefin polymer film instead of a brittle silicon film.[240] The performance of the bendable cell was identical to that of a brittle silicon cell, this design provides an effective solution that solves the brittleness and high-cost of traditional silicon-based on-chip fuel cells.

Harvesting energy from the mechanical movement of the human body and converting it to electricity is an effective approach for building low-cost, environmental friendly, and self-powered portable devices. Recently, Zhong *et al.* demonstrated a paper-based nanogenerator for converting external mechanical energy into electricity.[241] As shown in Fig. 22c, a layer of Ag was deposited on commercially available paper by thermal evaporatoration to form Ag/paper. Then the composite paper was spin-coated with PTFE to form PTFE/Ag/paper and assembled with the Ag/paper to make the nanogenerator. This device showed a maximum output power density of ~90.6 μW cm^{-2}, and notably it can be integrated with an energy storage unit such as a SC or LIB to store the pulse energy and later supply a regulated electrical power.

5. Summary and perspective

With a focus on several aspects of flexible energy storage and conversion systems, this review highlighted the advances that have been made in recent years associated with the materials selection and construction, structural design, and cell assembly. In this review, a large part was dedicated to the recent progress in supercapacitors and lithium-ion batteries, in addition to a brief overview of flexible energy generators. These devices can be subsequently used as power sources for flexible, lightweight, or even wearable electronics. Researches on flexible power sources require each component to be mechanical robust, electrochemically stable, and highly effective. Thanks to the recent development of nano-scaled materials, structural-controllable and high-performance materials for flexible power sources were widely demonstrated. By constructing the nanostructure, one can take full advantage of the excellence of

materials; composites that introduce other materials can ameliorate their intrinsic disadvantages and enhance the overall properties. For example, high surface area can be obtained by laser reduction of GO, the stacking of graphene sheets can be largely restrained which will lead to better performance; the incorporation of PANI arrays with CNTs or graphene using a simple and controllable hydrothermal method can result in a highly conductive and capacitive electrodes for SCs. However, despite the considerable progress made so far, the constant market demand urges researchers to search for more appropriate and reliable materials that combine high performance, low-cost, non-toxicity, and shape-conformability.

Owing to the nature of flexible electronics, the corresponding power sources should be lightweight and small in size, but highly efficient. When designing flexible power sources, there are several issues that should be considered and resolved. First, binders, though widely used in traditional electrodes, are intrinsically electroinsulating which will result in increased resistivity and addition of dead weight. Fabricating free-standing electrodes is an effective way to eliminate the binders and enhance performances. Second, the high density of metal current collectors and the tendency for fatigue failure under constant bending conditions make them unsuitable to be applied in flexible power sources. In addition, the use of metal current collectors gives no contribution to the capacities; the weak adhesion to the electrode materials will also result in unstable performances and long-term degradation under continuous mechanical deformation. Recent progress in nanostructured materials, such as graphene, aligned CNTs, and conducting polymers cast light upon the fabrication of flexible and lightweight current collectors. However, their relatively low conductivity compared with metal current collectors remains as a challenge to overcome. Third, liquid electrolytes require good encapsulation to prevent leakage, and a separator is needed to avoid internal short circuiting. Non-flammable, environmentally friendly and shape-conformable solid-state electrolytes which also serve as separators were reported to replace liquid ones, but the conductivity and mechanical properties are unsatisfactory. An ideal electrolyte for flexible power sources should be highly conductive and flexible, and also have good safety and excellent contact with electrodes. The challenge in finding appropriate electrolytes is another difficulty to overcome. Fourth, cell structural design and assembly will subsequently influence the mechanical properties and overall performances of flexible power sources. For instance, wearable electronics require full integration with cloth or the human body; wire-shaped ones are more capable of guaranteeing the omnidirectional flexibility needed for constant and irregular mechanical movements than planar power sources. Also, a wire-shaped solar cell enables 3D light collection, which can effectively capture light coming from any direction. Moreover, by embedding each component at the neutral strain position, the corresponding power sources can be stretchable, which is far more applicable in future flexible electronics.

The increasing interests in flexible electronics poses great opportunities along with challenges. The fabrication of highly flexible power sources with properties such as high energy and power densities, excellent rate capacity and cycling stability, light-weight, safe operation, low-cost, and scalable production is the ultimate goal. To achieve this, material selection and construction stands as the biggest challenge concerning the investigation of electrode, electrolyte, and packaging materials. Although recent development in flexible power sources appears to be highly promising, there is still room for improvement: (1) developing reliable materials with improved electrochemical and mechanical performance for flexible electrodes, and adopting some industrial production technologies such as ink-jet and screen printing to lower the fabrication cost; (2) increasing device efficiencies by exploring new energy storage systems and improving device cycling stability to lower energy costs;[242,243] (3) improving the conductivity, mechanical properties, and safety of the current solid-state polymer electrolytes to ensure better integrity and compatibility; (4) optimizing cell structure and stabilizing packaging materials to protect the full integrity of flexible power sources under various working conditions; (5) introducing other features like stretchability, and optical transparency to flexible power sources can provide multiple functions and expand their applications.

In recent years, battery systems like lithium–air, lithium–sulfur and sodium-ion batteries (NIBs) have attracted tremendous attention. The sharp increase in interest in Li–air and Li–S batteries mostly owes to the ultra-high energy density of up to 2–3 kW h kg^{-1}, which is theoretically much higher than that of other battery systems.[244–256] Up to now, there are no reports concerning flexible Li–air and Li–S batteries. As next-generation high energy density battery systems, their application in flexible power sources will introduce some extraordinary properties and significantly improve the development of flexible electronics. Based on this, our group has carried out research on flexible Li–air batteries. The challenges mainly lie in the safety issue of the use of Li foil as the anode, and an outer package that enables air (or O_2) penetration without the leakage of battery materials. Compared to lithium, sodium is a more abundant element and exhibits similar chemical properties to Li, indicating its potential application in next generation cost-effective rechargeable batteries.[257,258] Flexible and portable devices utilizing flexible NIBs will largely lower the cost. However, considering the larger volume of Na ions, electrode materials must withstand the volume change upon Na removal or insertion;[259,260] further investigation and improvement is required for the development of flexible NIBs.

With the rapid progress in technology and materials engineering, we believe the future flexible power sources that combine both outstanding electrochemical and mechanical performance will lead to many advances in technology and boost the development and commercialization of flexible electronics.

Acknowledgements

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