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Carbon nanomaterials for flexible lithium ion batteries

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ABSTRACT

With the rapid progress of wearable electronics, it is highly desirable to develop flexible power supplies, and significant progress has been thus made in making a variety of flexible batteries. Here the recent advances of flexible lithium ion batteries based on carbon nanomaterials have been carefully discussed from the viewpoint of material synthesis, structure design and property optimization. The remaining challenges and promising directions are highlighted to provide the clues for the future study in this booming field at end.

1. Introduction

The deepening energy crisis has forced people to find sustainable energy harvesting and storage systems that are low-cost, reliable and environmentally friendly [1–3]. The past three decades have witnessed the dramatic progress in developing electrochemical energy storage systems such as lithium ion batteries (LIBs) for the wide applications ranging from portable electronics, electric vehicles and spacecraft to grid-scale smart energy storage systems [4–7]. On the other hand, the emerging promising directions in electronics such as wearable electronics, smart clothes, electronic papers, electronic skins, robots and implantable medical devices are regarded as the next-generation revolution, and may open up novel application directions for future lifestyles [8–11]. To work stably in close contact with the human body, the related electronic devices above are needed to be flexible, foldable, bendable and even stretchable. As a result, the indispensable power systems should also meet these requirements.

LIBs are used as one of the most common power supplies because of their high energy density, long cycle life and high working voltage [12,13]. Conventionally, LIBs are heavy and rigid based on the currently available materials, fabrication processes and traditional configurations [14,15]. More specifically, LIBs consist of various chemical substances, including cathode materials (e.g., $LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$), anode materials (e.g., graphite, $Li_4Ti_5O_{12}$ or silicon), conductive materials (e.g., carbon black), binders, current collectors (e.g., aluminum and copper foil), separators, electrolytes and packaging materials [16–18]. The cathode and anode are prepared by coating slurry containing active material, binder and conductive material on the surfaces of aluminum and copper foils, respectively. Due to low elastic limits of metal foils, these electrodes are unable to accommodate drastic deformations. Once encountering a deformation that is beyond the critical point, a permanent change of the structure and degradation of electrochemical performance will occur. Due to the poor adhesive attraction between active materials and metal foils, the active materials are also easy to detach from metal foils and thus fail to work under deforming. In addition, conventional LIBs usually appears in bulk or cylinder structure, which may cause stress accumulation and further permanent destruction during deformation [14].

The synthesis of novel electrode materials, design of new structures, and optimization of fabrication processes are recognized as three main strategies to realize the flexibility of LIBs. Since the traditional electrode components are not deformable enough, it is highly desired to replace them by new candidates that should satisfy the following facts: (i) they should be highly electrically conductive to rapidly transfer electrons; (ii) the active materials are expected to be stably anchored on the supporting substrate with high loading capacity; (iii) they should be highly flexible and strong, and remain stable under deformations; (iv) they should exhibit high electrochemical performances.

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Carbon nanomaterials such as 1D carbon nanotube (CNT) and 2D graphene have attracted increasing interests due to their unique structures and high mechanical, electrical and electrochemical properties [19,20]. Flexible 3D sponge-like, 2D paper-like and 1D fiber-shaped LIBs and stretchable LIBs have been widely explored from the above carbon nanomaterials, and a brief chronology of the development in flexible and stretchable LIBs is shown in Fig. 1. In this review article, the advances of novel carbon nanomaterials in the aspect of synthesis, structure and property are first summarized, the application of them in flexible and stretchable LIBs is then highlighted with an emphasis on the structure control and property optimization, and the major challenges in flexible LIBs are finally discussed to provide some useful insights for the future development.

2. Carbon nanomaterials

Carbon nanomaterials composed of sp^2 conjugated carbon atoms have various allotropes with their matching microscopic architectures and assembling forms, which possess promising applications for flexible energy storage. Compared with the widely studied metallic materials, carbonaceous materials are endowed with lower mass density and higher intrinsic flexibility derived from microscopic structures (Table 1). Besides, their high chemical stability and wide potential window also avoid corrosions and benefit the cyclic reversibility. In addition, abundant reaction sites and high specific surface areas in carbonaceous nanomaterials facilitate stable loading of active materials for high electrochemical performances [28].

Among allotropes of carbon nanomaterials, CNT and graphene demonstrate significantly desirable properties and are promising in building flexible batteries. CNT, revealed as a seamless cylinder composed of carbon atoms with unique structural chirality, has been demonstrated important in modern electronics due to the expected metallic or semiconducting electronic properties and superior mechanical properties, which make it very useful for flexible energy storage devices. Graphene is a kind of honeycomb-liked 2D materials composed of monoatomic layer of carbon atoms and possesses high stiffness, electrical conductivity and thermal conductivity. Extending the afore-mentioned high properties of CNT and graphene from nanoscale to macroscopic scale remains a key while a big challenge in the construction of flexible energy storage devices. Herein, the corresponding macroscopic materials in three different dimensions composed of CNT and graphene are summarized by preparation methods, properties and applications.

2.1. 3D materials

3D architecture materials composed of CNT and graphene usually display high aspect ratios and tunable porous structures. The loosely compacted architectures and the highly tunable inner spaces endow 3D materials with great features of being lightweight and compressible, which are of importance for flexible energy storage systems.

For CNT materials, 3D architectures can be obtained mainly by wet gel-initiated method and template-directed assembling method. The former strategy is realized *via* the self-gelation behavior of CNT [36]. More specifically, CNT gels or sols are uniformly prepared in aqueous conditions as precursors, and frameworks are produced *via* the interactions among neighboring CNT bundles. Followed by freeze drying or supercritical drying process, solvents trapped among voids are removed, thus facilitating the formation of CNT materials with 3D architectures. The stabilization and enhancement of CNT skeletons are important for flexible energy storage devices [37]. The template-directed assembling methods are more facile and environmentally friendly (i.e., employing ice or cube sugar as templates) [38]. Highly orientated porous CNT materials can be obtained through the process of matching cryogen to produce high specific capacities when they were used as electrodes for batteries (Fig. 2a and b).

Graphene materials also tend to form loosely compacted 3D architectures. It is noteworthy that the inner walls need to be composed of single or several layers of graphene sheets to form 3D architectures with high aspect ratios and void ratios. Graphene oxide (GO) is widely adopted as the precursor to prepare 3D graphene materials. Apart from wet methods like CNTs, 3D graphene materials can be also obtained *via* hydrothermal methods, based on which functional components or heterogeneity atoms can be incorporated into or doped onto graphene sheets prior to hydrothermal reactions [39]. The 3D graphene foams can be also prepared by template-directed chemical vapor deposition. The obtained graphene foams consist of an interconnected network of graphene sheets with high electrical conductivity, light weight and flexibility (Fig. 2c and d) [22]. Several strategies for fabricating CNT/

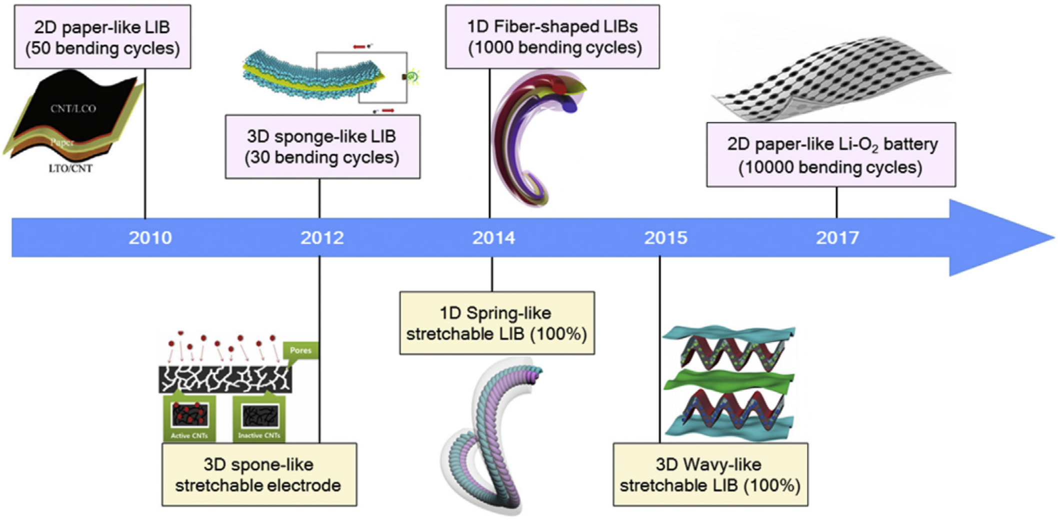

Fig. 1. A brief chronology of the development of flexible and stretchable LIBs [21–27]. (A colour version of this figure can be viewed online.)

Table 1
Physical properties of the carbon nanomaterials.

ref	material	method	Tensile strength	Young's modulus	conductivity	Specific surface area
[29]	CNT	Drawing CNT array	600 Mpa	74 GPa	10^3 S cm^{-1}	–
[29]	SWCNT	Wet-spinning	65 MPa g^{-1} cm^{-3}	12 GPa g^{-1} cm^{-3}	~140 S cm^{-1}	–
[30]	Reduced giant GO	Wet-spinning	360.1 ± 12.7 Mpa	12.8 ± 0.8 GPa	3.2×10^4 S cm^{-1}	–
[31]	RGO + AgNW	Wet-spinning	305 MPa		4.1×10^4 S cm^{-1}	–
[32]	MWCNT	slicing	–	–	Up to 10^3 S cm^{-1}	–
[33]	Graphene	Wet-spun	69 MPa	–	1.2×10^3 S m^{-1}	–
[34]	Graphene	hydrothermal	–	–	5×10^{-3} S cm^{-1}	–
[35]	CNT	Template-directed	–	–	~1 S cm^{-1}	~10^4 m^2 m^{-3}

graphene composite 3D architectures have been developed, among which GO/CNT aqueous mixtures could be directly cryodesiccated to form composite aerogel with lightweight and tunable densities [40]. In a word, 3D architecture materials composed of CNT and graphene with porous structures and high conductivity offer diversified candidates towards the construction of electrodes of flexible energy storage systems.

2.2. 2D materials

In terms of CNT films, they can be divided into randomly distributed and highly aligned structures. The CNT films based on wet methods (i.e., spray coating [41], spin coating [42] and dip coating [43]) generally share a randomly distributed structure which brings both low electrical conductivities and mechanical strengths. In contrast, the highly aligned CNT films demonstrate much enhanced electrical and mechanical properties and are thus carefully discussed in this section.

A widely explored process in the preparation of highly aligned CNT films is to draw them from spinnable aligned CNT array (Fig. 3a and b), and they can be continuously produced with low thicknesses of tens of nanometers [44]. The aligned CNT films can be also prepared by pressing CNT arrays down, and they are much thicker to be micrometers [45]. For the above two methods, the CNTs are aligned along the drawing or pressing directions. Recently, a CNT array is also demonstrated to be cut perpendicularly in relative to the CNT length direction, and the CNTs are thus perpendicular to the resulting film [46,47]. The thicknesses of such perpendicularly aligned CNT films are tuned from tens of nanometers to micrometer or even thicker.

Based on the two-dimensional atomic structure, graphene sheets are expected to easily form macroscopic 2D films. The densely compact structures endow graphene films with high mechanical, electrical and thermal properties (Fig. 3c and d) [48]. Similar to the CNT films, wet methods such as vacuum-assisted filtration [49] and spin coating are mostly explored to make 2D graphene materials. Note that, during the vacuum-assisted filtration process, functional guest components can be incorporated into graphene sheets to produce hybrid films. Besides the 2D film, 2D textiles with large specific surface areas can be modified with reduced graphene oxide (rGO) *via* dip-coating method and may offer high area energy storage capabilities when they are used as electrodes in flexible energy storage devices [50]. CNT/graphene hybrid films can be prepared by a simple drop-casting method of mixing the components into slurry, followed by coating on a substrate to produce composite films [51]. These films provided promising applications for novel electrochemical devices.

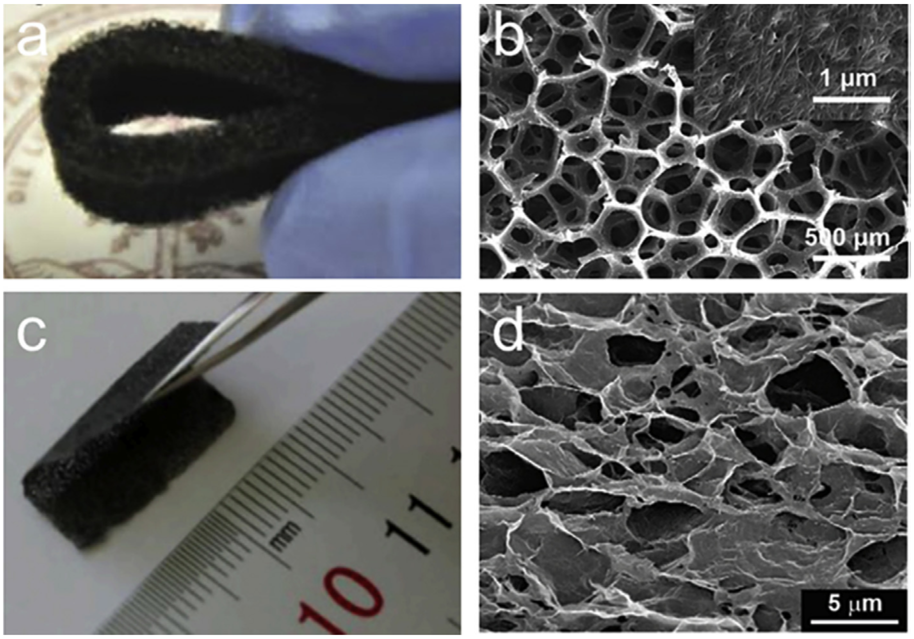

Fig. 2. **(a)** and **(b)** Photograph and scanning electron microscopy (SEM) image of 3D CNT sponge, respectively [38]. **(c)** and **(d)** photograph and SEM image of 3D graphene foam, respectively [22]. (A colour version of this figure can be viewed online.)

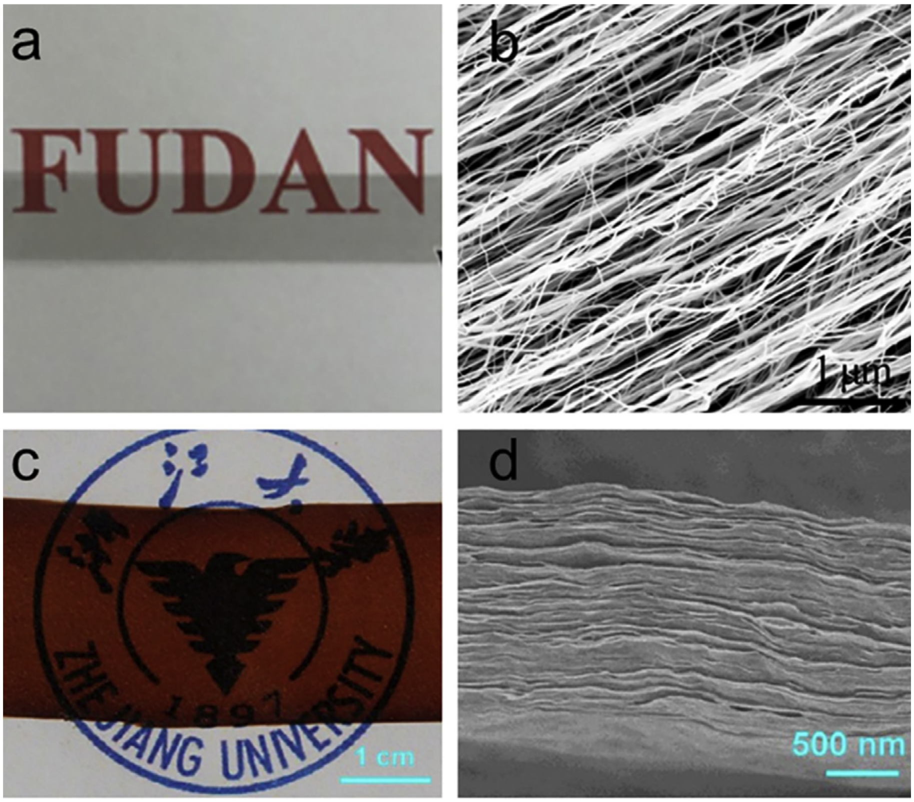

Fig. 3. (**a**) and (**b**) Photograph and SEM image of 2D aligned CNT sheet, respectively [44]. (**c**) and (**d**) photograph and SEM image of 2D graphene film, respectively [48]. (A colour version of this figure can be viewed online.)

2.3. 1D materials

The interactions among CNTs or graphene sheets play an important role during the assembly process to from macroscopic materials. They mainly include π-π stacking, van der Waal's forces, and hydrogen bonds. Due to the high aspect ratio and its one-dimensional structure, CNT tends to tangle with each other and may form a continuous structure after an appropriate design. Similar to the extensively used method in chemical fibers, macroscopic CNT fibers can be widely produced *via* wet or dry spinning methods. Wet spinning can be easily scaled up for a large-scale production. CNTs were first dispersed in a fluid, then extruded out of a spinneret, and finally coagulated into a solid fiber by extracting the dispersant [52]. The wet spinning process typically produces a randomly distributed structure of CNTs, which produces low mechanical strength and electrical conductivity. As a result, increasing interests are attracted to prepare highly aligned CNT fibers by a drying spinning process (Fig. 4a and b) [53]. The CNTs can be assembled into fibers after being drawn out of super-aligned CNT arrays [54]. During the drawing process, the interactions among neighboring CNT bundles make them form a continuous fiber with the CNTs aligned along the spinning direction. The highly aligned structure of as-prepared CNT fiber offers high mechanical strength and charge transport capability. Besides, a variety of active materials and functional components can be introduced into the fiber *via* a co-spinning strategy with high loading capacity [55]. These features are important for the construction of flexible LIBs which will be discussed later.

Different from the interactive CNTs, graphene sheets tend to stack together, and they generally form continuous fibers based on wet spinning methods [56]. More specifically, GO sheets are typically adopted as precursors because they can easily form uniform dispersions. After the formation of GO fiber, GO is reduced to rGO for graphene fibers. Due to the formation of liquid crystals in GO dispersions, GO sheets are interacted in a more compact form compared with the end-to-end structure of CNTs. Obviously, the mechanical and electrical properties of graphene fibers depended on the size of graphene layer, the interaction between two neighboring layers and the defects resulted from post processing (Fig. 4c and d). Core-sheath architectures and tunable porous structures had been also designed for flexible energy storage devices with high performances by the wet spinning method [57]. To better combine the advantages of one-dimensional CNTs and two-dimensional graphene sheets, graphene/CNT fibers had been also prepared *via* a co-spinning method. The resulting hybrid fibers were further used as electrodes to demonstrate relatively higher performances in energy storage [58].

3. Application in flexible batteries

3.1. 3D sponge-like batteries

CNTs and graphene sheets may be interconnected with each other to form sponges as substrates to support active materials and current collectors for effective charge transport. Because of the porous structure and high specific surface area, active materials can be stably incorporated into the CNT and graphene network with high loading capacity. A variety of preparation methods such as coating, hydrothermal reaction and physical mixing has been used to introduce active materials onto the sponge-like substrates. For example, nano-sized $Li_4Ti_5O_{12}$ and $LiFePO_4$ were incorporated into the graphene foam by *in situ* hydrothermal deposition to act as anode and cathode, respectively. A thin, lightweight and flexible LIB was thus obtained by assembling the two 3D bulk electrodes with a

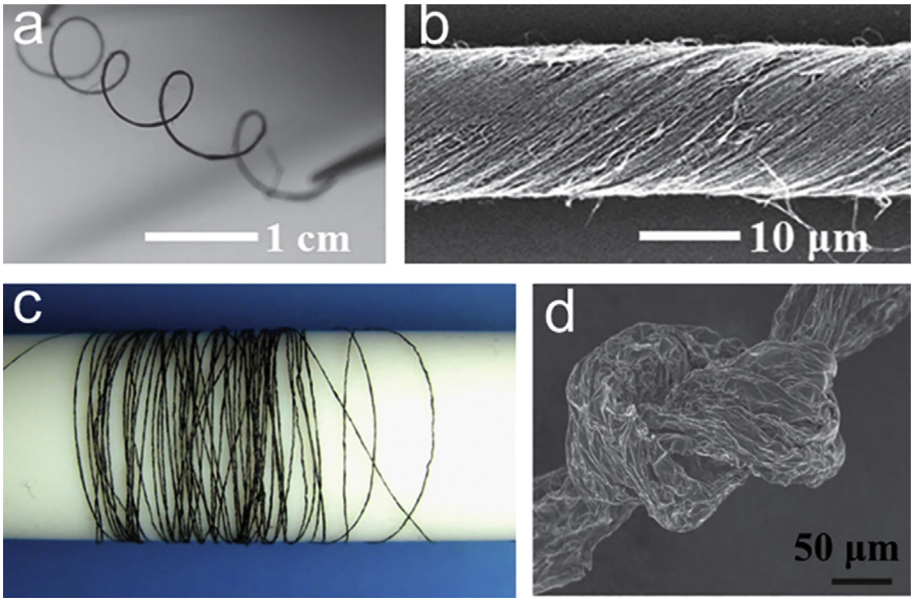

Fig. 4. (**a**) and (**b**) Photograph and SEM image of 1D aligned CNT fiber, respectively [53]. (**c**) and (**d**) photograph and SEM image of 2D graphene fiber, respectively [54]. (A colour version of this figure can be viewed online.)

separator between them (Fig. 5a) [22]. The resulting LIB showed an energy density of 110 Wh•kg^{-1}. In particular, the specific capacities were varied by less than 1% after bending to a radius of 5 mm for cycles (Fig. 5b).

Apart from the flexibility, this 3D conductive interconnected sponge architecture also favored high electrochemical performance. It provided a lot of voids and efficiently accommodated the volume change of the active material for high cycling stability, while maintaining rapid charge transport. Based on this strategy, various active materials such as Si [59], V_2O_5 [60] and SnO_2 [61] were introduced into the flexible CNT and graphene foams with enhanced rate and cycling performance. The 3D CNT/graphene/Si sponge-like composite electrode was produced by directly mixing the above three components, followed by freeze-drying and sintering [59]. The elasticity and flexibility of the sponge-like structure ensured an effective confinement of Si during volume variation and intimate contact between Si and conductive network, which enabled rapid electron transport and high cycling stability (Fig. 5c). As a result, such a composite electrode exhibited high specific capacity of 1337 mAh•g^{-1} after 100 cycles at a current density of 1.0 A g^{-1}, and good rate performance of 1000 mAh•g^{-1} at a high current density of 5.0 A g^{-1} (Fig. 5d).

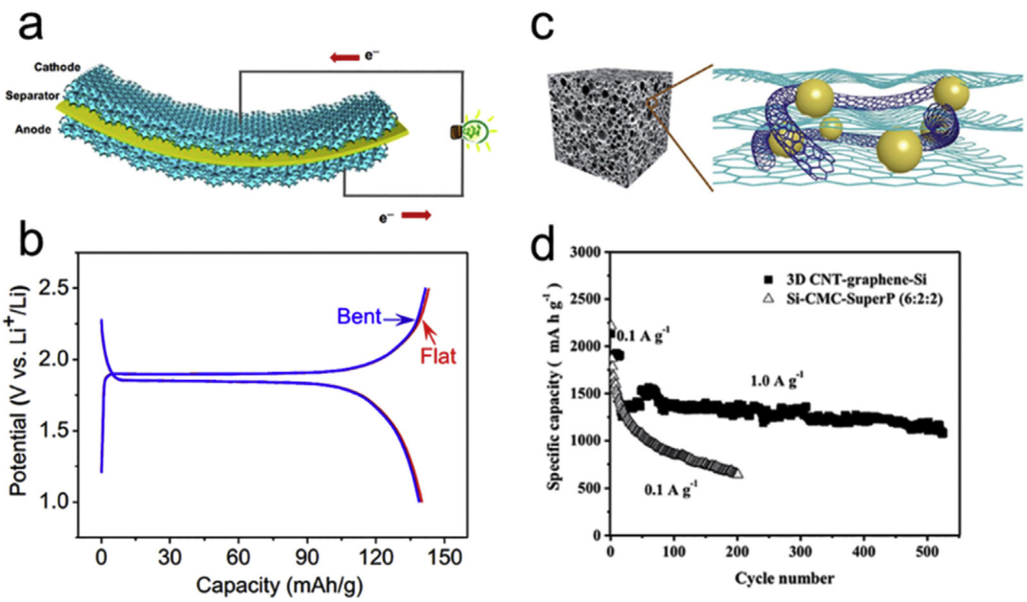

Fig. 5. (**a**) Schematic of a 3D flexible sponge-like LIB containing a cathode and an anode made from 3D interconnected graphene foam [22]. (**b**) Galvanostatic charging and discharging curves of the 3D flexible sponge-like LIB. Red and blue lines represent the as-fabricated and bent LIB after repeatedly bending to a radius of 5 mm for 20 cycles, respectively [22]. (**c**) Schematic of formation of CNT/graphene/Si composite electrode with 3D sponge-like architecture [60]. (**d**) The cycling stability of CNT/graphene/Si composite electrode [60]. (A colour version of this figure can be viewed online.)

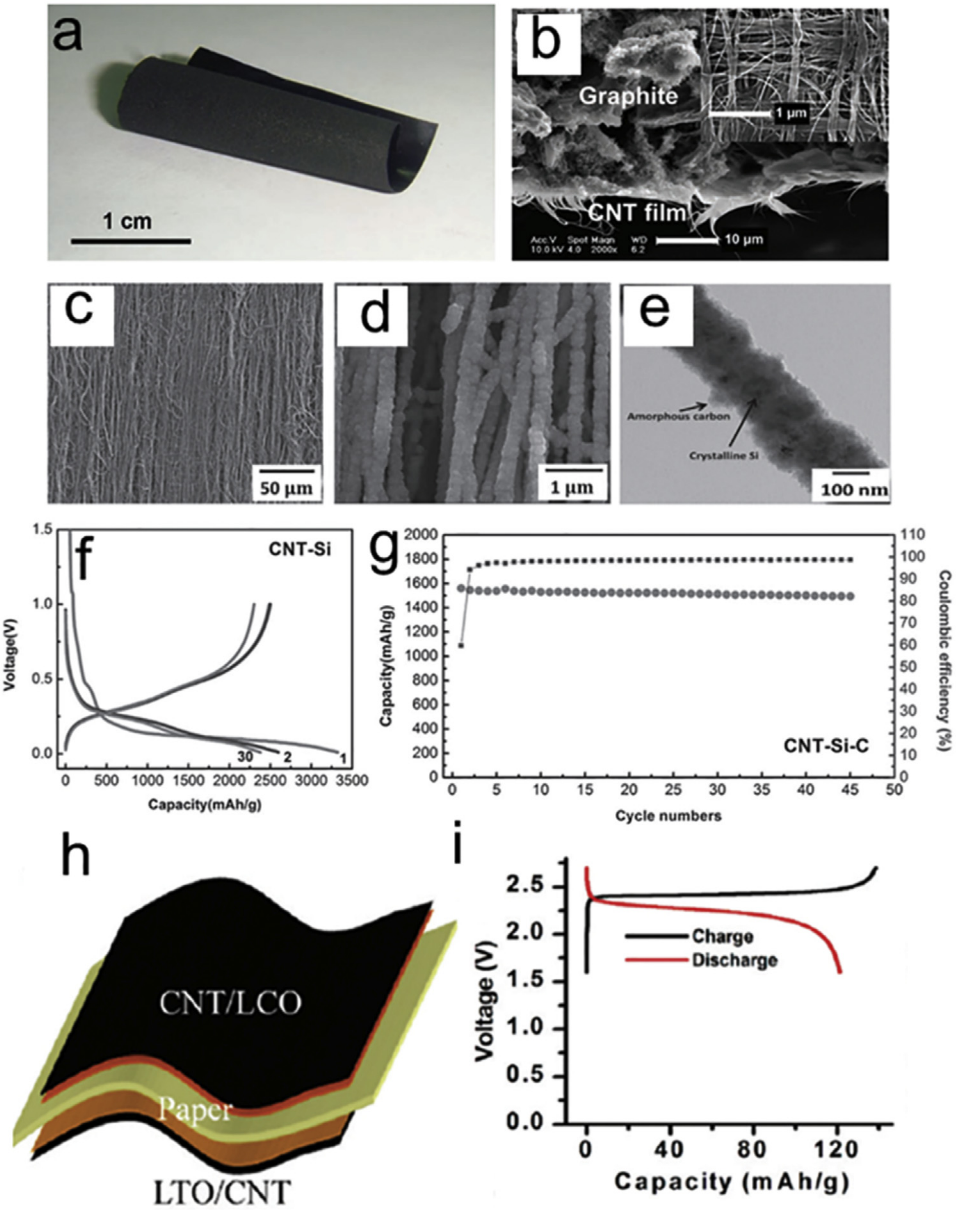

Fig. 6. (**a**) Photographs of the flexible graphite/CNT paper electrode [64]. (**b**) Cross-sectional SEM images of graphite/CNT paper electrode [64]. (**c**) and (**d**) SEM images of the CNT/Si/C sheet [65]. (**e**) TEM image of the CNT/Si/C sheet [57]. (**f**) Galvanostatic charging and discharging curves of CNT/Si/C sheet electrode *vs* Li/Li^+ [57]. (**g**) The cycling stability of CNT/Si/C sheet electrode [65]. (**h**) Schematic of the paper-like LIB [21]. (**i**) Galvanostatic charging and discharging curves of the paper-like LIB [21]. (A colour version of this figure can be viewed online.)

The 3D interconnected network can be also obtained from textiles. The flexible textile can be obtained by weaving or knotting carbon fibers. The carbon fiber textile showed high electrical conductivity and mechanical property, which served as a soft collector in replacement of the traditional metal current collector [62]. Besides, flexible conductive textile can be also prepared by coating preexisting cotton or polyester textile with various conductive carbon or active electrode materials for flexible batteries. For example, by simply coating CNT aqueous ink on a polyester textile, a flexible textile was obtained with electrical conductivity of 1300 S cm^{-1}. The conductive textile was also porous, which is an ideal candidate as substrate to support active materials. By using this 3D porous textile electrode, the obtained batteries showed high areal mass loading up to 170 mg cm^{-2} [63].

3.2. 2D paper-like batteries

A thin paper-like structure offers high flexibility for LIBs and they can be easily integrated with a variety of flexible electronic devices. Carbon nanomaterials such as CNT and graphene have been widely explored as current collectors due to their strong adhesion, mechanical durability and low contact resistance. For instance, a flexible graphite/CNT hybrid film was prepared as effective anode by coating graphite slurry onto cross-stacked CNT sheets (Fig. 6a and b) [64]. Compared with the conventional Cu current collector, it provided flexibility for higher structural integrity and lower contact resistance, which favored efficient electron transport at the graphite/CNT interface. It displayed a high cycling stability (e.g., 335 mAh·g^{-1} at 0.1 C with a capacity retention of 99.1% after 50 cycles) and rate capability (e.g., 328 mAh·g^{-1} at 2C).

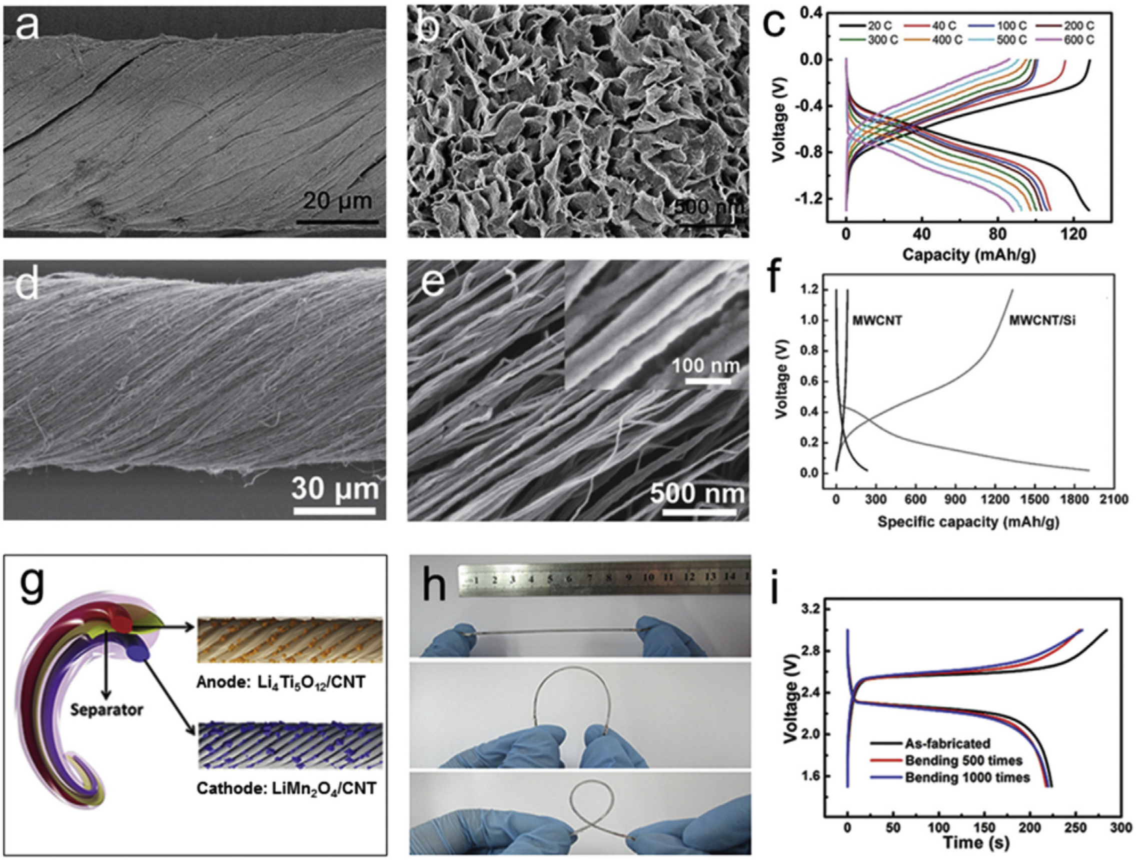

Fig. 7. (**a**) and (**b**) SEM images of the polyimide/CNT fiber electrode at low and high magnification, respectively [69]. (**c**) Galvanostatic charging and discharging curves of the polyimide/CNT fiber electrode *vs* a saturated calomel electrode [69]. (**d**) and (**e**) SEM images of the Si/CNT fiber electrode at low and high magnification, respectively [71]. (**f**) Galvanostatic charging and discharging curves of the polyimide/CNT fiber electrode *vs* Li/Li^+ [71]. (**g**) Schematic of the fiber-shaped LIB [23]. (**h**) Photographs of the fiber-shaped LIB being deformed into different shapes [23]. (**i**) Galvanostatic charging and discharging curves of the fiber-shaped LIB before and after bending [23]. (A colour version of this figure can be viewed online.)

Besides, the light weight of the CNT hybrid film increased gravimetric energy density by over 180%.

Si with the greatest lithium storage capacity was widely explored as an effective active material for high-performance flexible LIBs, but it suffered from huge volume change during cycling. To this end, CNT sheets were used as substrates to deposit Si with a stable adhesion between them (Fig. 6c–e) [65]. The aligned structure of CNTs can effectively constrain the volumetric expansion of Si. The aligned CNT/Si anode thus showed both high specific energy capacity and stable cycle performance (1494 $mAh\cdot g^{-1}$ after 45 cycles with a capacity retention of over 94%) (Fig. 6f and g). Besides current collector, carbon nanomaterial can also work as electrode itself. For instance, a flexible graphene paper electrode synthesized by mechanically pressing a graphene aerogel showed a reversible capacity of 557 $mAhg^{-1}$ at 200 mAg^{-1} [66].

Based on the flexible paper-like electrodes, 2D flexible LIBs are assembled into a sandwich structure of anode/separator/cathode. For instance, $LiMn_2O_4$/CNT and $Li_4Ti_5O_{12}$/CNT were designed as cathode and anode, respectively (Fig. 5h) [21]. The resulting LIB was packaged in polydimethylsiloxane and filled with $LiPF_6$-based electrolyte. It may bear bending for 50 cycles without failure and with high energy density of 108 $mWh\cdot g^{-1}$ (Fig. 6i).

3.3. *1D fiber-shaped batteries*

In recent years, 1D fiber-shaped LIBs have attracted more and more attentions. Compared with the planar LIBs, the fiber structure offers some unique and promising advantages. Firstly, in addition to the typical bending deformation, a fiber-shaped LIB can accommodate a variety of other deformations such as twisting, tying and stretching, which are critically important for the rapidly developing flexible electronics. Secondly, the fiber-shaped LIBs can be woven into textiles with porous structures to allow water vapor and air to transport through them, and can also effectively adapt to a variety of soft or curved substrates such as our body, which is highly desirable for wearable applications.

Developing effective fiber electrodes is the key for fiber-shaped LIBs. Recently, the main efforts were made to prepare aligned CNT fiber electrodes that can effectively work as substrates to support active materials and current collectors to transport electrons. For instance, MnO_2 nanoparticles were uniformly deposited onto the aligned CNT fiber by aqueous electrochemical deposition, and the resulting hybrid fiber did not show obvious damage in structure and electrical performance decay during use [67]. The CNT/MnO_2 fiber electrode was further paired with Li wire in 1M $LiPF_6$ electrolyte to produce specific capacity of 218 $mAh\cdot g^{-1}$. MoS_2 nanosheets were also grown onto the CNT fiber by hydrothermal method [68], and the hybrid fiber demonstrated specific capacity of 1298 $mAh\cdot g^{-1}$ at 0.2 A g^{-1}. Polyimide nanosheets were coated onto the CNT fiber after *in situ* polymerization [69]. Although polyimide was intrinsically insulating, the CNT fiber guaranteed efficient charge transports. Therefore, the CNT/polyimide fiber showed high specific capacity of 86 $mAh\cdot g^{-1}$ even at a high current rate of 600 C (Fig. 7a–c). Similarly, the other active materials such as $LiMn_2O_4$

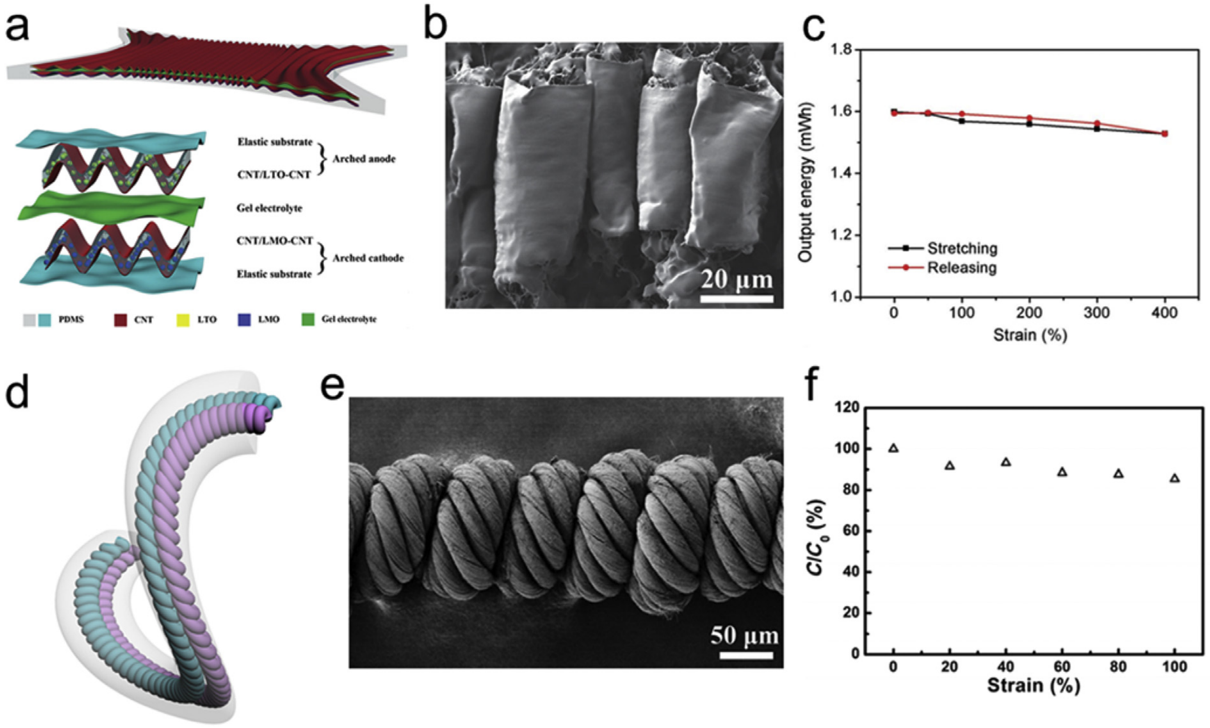

Fig. 8. (**a**) Schematic of the wavy-like stretchable LIB [27]. (**b**) SEM images of wavy-like $Li_4Ti_5O_{12}$/CNT electrode [27]. (**c**) Dependence of the output energy on strain under stretching [27]. (**d**) Schematic of the spring-like stretchable LIB [26]. (**e**) SEM image of the spring-like $Li_4Ti_5O_{12}$/CNT electrode [26]. (**f**) Dependence of specific capacity on strain under stretching [26]. (A colour version of this figure can be viewed online.)

and $Li_4Ti_5O_{12}$ nanoparticles could be also deposited into the aligned CNT fibers by co-spinning [70].

To improve the electrochemical performance, Si was also introduced as active material to prepare hybrid electrodes. Typically, Si was deposited onto the aligned CNT sheets by electron-beam evaporation, followed by scrolling into a fiber electrode [71]. The design of CNT core and Si sheath had effectively combined their advantages of high electrical conductivity and high specific capacity, respectively. No obvious damages occurred during bending, twisting and other types of deformations. After paired with a lithium wire, the resulting fiber-shaped LIB displayed a voltage plateau of 0.4 V and specific capacity of 1670 $mAh \cdot g^{-1}$ at a current density of 1 $A \cdot g^{-1}$, at the Si loading percentage of 38.1% (Fig. 7d–f).

The above two kinds of fiber electrodes were further assembled into a fiber-shaped LIB. There are mainly two typical structures for fiber-shaped LIBs, i.e., helically coaxial and parallel structures. In a helically coaxial structure, Si/CNT anode and $LiMn_2O_4$/CNT cathode fibers were wound onto a cotton fiber and separated by a layer of gel electrolyte [72]. The output voltage reached 3.4 V with specific capacity of 106 $mAh \cdot g^{-1}$. Helically coaxial structure showed a high structure integrity during use, but the related manufacturing processes were complex. Therefore, a lot of efforts had been made to fabricate fiber-shaped LIBs by assembling two electrodes in parallel, e.g., $LiMn_2O_4$/CNT anode and $Li_4Ti_5O_{12}$/CNT cathode fibers being separated by a poly (vinylidene fluoride) separator (Fig. 7g) [24]. The fiber-shaped LIB was highly flexible and could bear various deformations. The charge and discharge behaviors remained almost unchanged after bending for 1000 cycles (Fig. 7h and i).

4. Application in stretchable batteries

For many application fields such as wearable electronics, the affiliated LIBs are required to be not only flexible but also stretchable. So do the electrodes. Two methods are mostly investigated to design flexible and stretchable electrodes based on wavy-like configuration for 3D and 2D stretchable LIBs and spring-like configuration for 1D stretchable LIBs. For the former case, active materials were deposited onto a pre-stretched elastic substrate. Aligned CNT sheet and active LMO or LTO nanoparticles were attached onto poly (dimethylsiloxane) (PDMS) substrate under stretching by 450%, and the wavy-like electrodes were produced after releasing (Fig. 8a and b) [27]. The resulting LIBs exhibited stable electrochemical performance under a strain of 400% and a high stretching speed of 3 $cm\ s^{-1}$ (Fig. 8c). Note that the wavy-like LIBs showed lower electrochemical properties as the PDMS substrate did not contributed the energy storage.

The spring-like configuration can realize stretchability and also provide high electrochemical performances at the same time (Fig. 8d) [26]. The spring-like electrodes were prepared by over-twisting several aligned CNT hybrid fibers together. The uniform coiled loops brought high stretchability of over 300% (Fig. 8e). After coating a layer of elastic poly (ethylene oxide)-based gel, spring-like $LiMn_2O_4$/CNT cathode and $Li_4Ti_5O_{12}$/CNT anode fibers were twisted to fabricate the stretchable LIB. This spring-like structure avoided the use of non-capacity elastomeric polymer. Thus, the weight and volume decreased by up to 400% and 300%, respectively, which gave rise to the improvement of specific energy density. As expected, the resulting LIBs could work stably under stretching. The specific capacity was maintained by 85% after stretching by 100%, and it varied in less than 1% after stretching for 300 cycles (Fig. 8f).

5. Outlook

In this review, we have highlighted the recent advances of flexible and stretchable LIBs with a focus on material synthesis and structure design. Carbon nanomaterials including CNT, graphene and their composites act as a key component to construct flexible LIBs, where they can be either used as conductive frameworks or active materials. The strategy can be also extended to the other flexible energy storage devices. For example, CNT and graphene were widely used as flexible electrodes to construct flexible and stretchable supercapacitor [26]. Aligned CNT sheets can also worked as flexible air electrodes to enhance air diffusion and electron conduction for flexible lithium oxygen batteries [24,73]. Although great achievements are demonstrated in the past decade, there remain some challenges for practical applications.

The carbon-based nanomaterials can be easily synthesized at laboratory scale, but it is difficult to continuously produce them by the current technologies at industry. Besides, compared with the metal current collector, the electrical conductivity of carbon nanomaterials is lower for LIBs and need be further enhanced. For a fiber-shaped LIB, due to the high electrical resistance of CNT fiber electrode, it may work at centimeters and fail to effectively work at the applicable length of meters.

Safety is also a critical issue for flexible LIBs. To realize the desired flexibility and stretchability, all components including electrode, separator, electrolyte, and packaging material are required to be stable under deformations. Conventional flammable liquid electrolyte may cause leakage and short circuit during use, so developing appropriate gel or solid electrolytes with high performance is highly needed and will become a mainstream in the near future. The development of reliable packaging materials is another hot topic for the flexible LIB from a viewpoint of practical applications.

Increasing interests should be also attracted to design flexible and stretchable structures for the LIBs to simultaneously realize high energy density, power density and cycling stability. The use of flexible or elastic substrates is not favorable for LIBs. Lithium oxygen batteries and lithium sulfur batteries with much higher theoretical specific energy densities also represent promising candidates for the next-generation flexible energy storage systems. They may even replace LIBs in some fields such as wearable electronic devices, and more attentions should be paid for them.

In summary, the flexible LIBs based on carbon nanomaterials is booming in the recent years, and they may move towards a high level where intelligence and integration are underway to effectively meet the high requirements of modern electronic devices such as biocompatibility and miniaturization. To this end, their further advances need the high-quality cooperation studies from a variety of fields including chemistry, physics, biology and engineering. These novel LIBs will emerge in our daily life and change our lifestyle in the near future.

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