Review Article
The Carbon Nanotube Fibers for Optoelectric Conversion and Energy Storage

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This review summarizes recent studies on carbon nanotube (CNT) fibers for weavable device of optoelectric conversion and energy storage. The intrinsic properties of individual CNTs make the CNT fibers ideal candidates for optoelectric conversion and energy storage. Many potential applications such as solar cell, supercapacitor, and lithium ion battery have been envisaged. The recent advancement in CNT fibers for optoelectric conversion and energy storage and the current challenge including low energy conversion efficiency and low stability and future direction of the energy fiber have been finally summarized in this paper.

1. Introduction

Flexible and portable electronic devices have been extensively studied for a wide range of applications in solar cell [1–21], lithium ion battery [22, 23], supercapacitor [24–29], sensors [30], and their integrated device [31–36]. Weavable electronic devices usually require corresponding fiber materials to fabricate them. There is an increasing interest in flexible solar cells and researchers have been investigating weavable fiber solar cells based on metal wires, glass fibers, or polymer fibers [37–42]. Unfortunately, the low efficiencies of these fiber-based solar cells greatly limit their promising applications.

Carbon nanotubes have been widely introduced to fabricate high-efficiency organic solar cells because of their extremely high surface area (e.g., ca. 1600 m²/g for single-walled nanotubes) and superior electrical properties [43]. However, nanotubes are used in electrode materials. For example, the incorporation of nanotubes onto titania nanoparticle films has been shown to increase the roughness factor and decrease the charge recombination of electron/hole pairs [44], and the replacement of platinum with nanotubes as counter electrode catalyzed the reduction of triiodide to improve the cell performance. The distribution of nanotubes within the photoactive layer improved the short circuit current density and fill factor owing to rapid charge separation at the nanotube/electron donor interface and efficient electron transport through nanotubes [45]. However, the degrees of improvement are far from what is expected for nanotubes, mainly because of random aggregation of nanotubes in the cells. For a random nanotube network, the electrons have to cross many more boundaries. Therefore, alignment of nanotubes will further greatly improve cell performance as charge transport is more efficient. To improve the practical application of CNTs, scientists are exploring various nanomaterials to improve charge separation and transport in these fiber-based photovoltaic devices. Researchers aligned continuous multiwalled CNT sheets and fibers to produce materials with high mechanical strength and electrical conductivity; it is critically important to extend their physical properties from the nanoscale to the macroscopic scale. The excellent mechanical and electrical performance of individual CNTs make the CNT fibers ideal candidates for optoelectric conversion and energy storage.

CNT fibers can be fabricated directly from chemical vapor deposition (CVD) [50] or can be spun from high-quality aligned CNT arrays [1, 2, 51–53]; Li and coauthors [50] spun fibers and ribbons of CNTs directly from CVD synthesis zone of a furnace using a liquid source of carbon and an iron nanocatalyst. This process was realized through the appropriate choice of reactants, control of the reaction conditions, and continuous withdrawal of the product with a rotating spindle used in various geometries. This direct
spinning from a CVD reaction zone is extendable to other types of fiber and to the spin coating of rotating objects in general. But these CNT fibers contained 5 to 10 wt% iron and a large number of defects. To produce desired high-quality CNT fibers [1, 2], the high-quality nanotube arrays are firstly synthesized by a typical chemical vapor deposition method. This provided an important clue to the use of multiwalled CNTs at macroscopic scale, and researchers have made multiple efforts to optimize this aligned structure and improve the properties of CNT fibers [54–61] to many applications; for example, Chen et al. [2] and Luo et al. [3] use flexible, light-weight, ultrastrong, and semiconductive CNT fibers to develop a novel solar cell. The high alignment of building nanotubes in the fiber allows charges to separate and transport along the fibers efficiently, which provides a fiber solar cell with high performance.

In this review, we briefly highlight the fabrication of CNT fibers and its applications for solar cell, lithium ion battery, supercapacitor, and their integrated device.

2. Fabrication of High-Quality Carbon Nanotube Fibers

High-quality CNT fibers are obtained by dry spinning from highly aligned CNT arrays (see Figure 1). The synthetic details of the CNT arrays are summarized as follows: Fe/Al₂O₃ was used as the catalyst, ethylene served as the carbon source, and Ar with 6% H₂ was used to carry the precursor to a tube furnace, where the growth took place. The reaction temperature was controlled at 750°C and the reaction time was typically between 10 and 20 min. CNT fibers were directly spun from the high-quality aligned CNT array, and the fiber diameter was controlled from 6 to 20 μm by varying the initial ribbon, a bunch of nanotubes pulled out from the array at the beginning of the spinning. The CNT fibers can be spun with lengths of tens of meters or even longer, and the fiber is uniform in diameter. The density of the nanotube fiber was calculated to be on the order of 1 g·cm⁻³, and its linear density was on the order of 10 μg·m⁻¹, relative to 10 mg·m⁻¹ and 20–100 mg·m⁻¹ for cotton and wool yarns, respectively [1, 62]. As shown in Figure 1(c), the CNT fibers are flexible and will not break after being bent, folded, or even tied many times. High-resolution transmission electron microscopy (see Figure 1(d)) indicates a multiwalled structure for the building nanotubes with diameter of approximately 8.5 nm in the fiber. The high degree of alignment of the component nanotubes gives the fiber excellent mechanical and electrical properties.

3. The Applications of Carbon Nanotube Fibers

3.1. Dye-Sensitized Solar Cells (DSC) Based on Carbon Nanotube Fibers

A DSC, a low-cost solar cell, is based on...
a semiconductor formed between a photosensitized anode and an electrolyte, a photoelectrochemical system. The DSC can convert solar energy to electric energy, which is a promising technology to use renewable energies, and have typically been fabricated from rigid plates [63]. Solar cells are unfavorable for many applications, especially in the fields of portable and highly integrated equipment. As a result, flexible devices have become the subject of active research as a good solution [64]. In particular, weavable fiber devices are very promising and have attracted increasing attention in recent years. The CNT fibers in fiber-shaped photovoltaic devices have been widely incorporated into active layers to improve charge separation and transport or directly used as electrodes, for example, as counter electrode in replacement of conventional platinum in a planar DSC to catalyze the reduction of triiodide. For random CNT networks, the charges have to cross a lot of contacting points, so the charge transport in the random CNT networks is much slower than that in the CNT fibers. Fiber solar cells based on metal wires, glass fibers, or polymer fibers have been investigated [37–42]. Metal wires and glass fibers have bad flexibility, and conductive performance of polymer fibers is not good. So Chen et al. [2] and Luo et al. [3] developed a novel solar cell based on flexible, light-weight, ultrastrong, and semiconductive CNT fibers (Figure 2). They used CNT/N719 composite fibers to fabricate the organic solar cells on fluorine-doped tin oxide, and the power conversion efficiencies can reach 2.6%; the high alignment of CNTs arrays in the fiber allows charges to separate and transport along the fibers efficiently, which provides a fiber solar cell with high performance. The efficiency of the above fiber device may be further improved through the increase of the open-circuit photovoltaic value by shifting the Fermi level of nanotubes more negatively, increasing fill factor by improving the electric contact between the fiber and the charge collector and increasing the short-circuit photocurrent value by enhancing the dye loading of the nanotube fiber. This discovery expands the scope of materials and architectures available for photovoltaic devices.

To take advantage of the CNT fibers, Cai and his coauthors [5] designed and fabricated an all CNT fibers dye-sensitized solar cell; CNT/N719 and CNT/PVDF fibers in Figure 3 were used as working and counter electrodes in replacement of metal wire electrode, respectively. The power conversion efficiency of this kind of photovoltaic wires was greatly improved through modification at the working electrode, for example, incorporation of titanium dioxide nanomaterials. But a short circuit was produced in this device. So the researchers [6] developed a fiber-shaped DSC based on flexible, ultralight, and ultrastrong CNT fibers as both working and counter electrodes (Figure 5), and the conversion efficiency is up to 2.94%. This fiber solar cell may be easily scaled up for a practical application, as the power conversion efficiency is independent of both the cell length and the incident light. And Chen and his coauthors [9] have studied the performance of a fiber dye-sensitized solar cell by using a CNT fiber as the counter electrode and a titanium wire modified with perpendicularly aligned TiO₂ nanotubes as the working electrode (Figure 4(c)). This novel interface design provides the photovoltaic wire with a high efficiency of 4.6%. The photovoltaic wires can be easily integrated into various flexible devices by a convenient weaving technology, which remains challenging to conventional planar solar cells.

On this basis, Yang and his coauthors [17] have developed fiber-shaped photovoltaic devices based on graphene/Pt composite fibers (Figure 6). The high flexibility, mechanical strength, and electrical conductivity of graphene fibers resulted in a certified maximum energy conversion efficiency of 8.45%, which is much higher than that of the aforementioned fiber-shaped photovoltaic devices. These flexible fiber solar cells can act as woven fabrics to make textiles by a conventional weaving technology, which enables a wide variety of applications in portable devices, for example, power regeneration for space aircraft and clothing integrated photovoltaics. These discoveries also provide a paradigm to develop new materials for high-performance solar cells.

Pan et al. [46] developed an organic thiolate/disulfide redox couple with low absorption in the visible region for use in fabricating fiber dye-sensitized solar cells (see Figure 7(a)). These flexible wire devices achieved high energy conversion efficiencies with a maximal value of 7.33%. This work also opens a new avenue in the development of highly efficient optoelectronic and electronic devices by designing matchable materials in different parts and making effective structures. At the same time, a coaxial DSC fiber [14] has been fabricated with a highly aligned multiwalled CNT sheet as the counter electrode (see Figure 7(b)), and energy conversion efficiency of 4.10% is achieved. The coaxial DSC fiber also shows a
Figure 3: (a) Schematic illustration of a photovoltaic wire with two twined CNT fibers as working and counter electrodes, respectively. (b) The working principle of the CNT fiber-based sensitized photovoltaic wire, in which CB represents conduction band of CNT [5].

Figure 4: (a) Schematic illustration of side view of a fiber solar cell, (b) a polymer fiber solar cell from top view [8], and (c) a fiber-shaped dye-sensitized solar cell by top view [9]. Here an aligned TiO$_2$ nanotube-modified titanium wire as the working electrode is twined with one CNT fiber as the counter electrode to produce the fiber solar cell.
high flexibility and stability. Although a fiber-shaped DSC has been demonstrated in this work, the aligned multiwalled CNT sheet can be also used as an electrode material to fabricate coaxial, fiber-shaped polymer solar cells and other various optoelectronic and electronic devices.

The above fiber solar cells need liquid electrolyte, which is volatile, so device performance is not stable. In order to overcome this problem, Sun et al. [19] developed a quasi-solid-state, coaxial DSC fiber (see Figure 8), which has a high performance including a high thermal stability and flexibility that offer particularly promising applications for flexible devices at high temperatures. This fiber DSC has also established some foundations for future photovoltaics and electronics with an ongoing push towards smaller and faster devices that are still confined to the planar silicon wafer.

3.2. Supercapacitor Based on Carbon Nanotube Fibers. Supercapacitor, formerly electric double-layer capacitor or pseudocapacitor, is one important electrochemical energy storage device that has been extensively developed for many applications. The energy storage capability, power delivery capability, and cycle life of supercapacitor are highly desired to satisfy the increasing performance demands. CNT fibers have been explored as both electrode materials and electrode additives for developing high-performance supercapacitors which based on CNT fibers recently attracted more attention. Cai et al. [24] synthesized highly aligned multiwalled CNT-polyaniline composite fibers with excellent mechanical, electrical, and electrochemical properties through an easy electrodeposition process. They were further twisted to fabricate a fiber-shaped supercapacitor (see Figure 9) with high specific capacitances up to 263 mF cm$^{-1}$. The light weight, high flexibility, high strength, and good weavability provide them with promising applications in various fields. This work also presents a fabrication paradigm for the development of high performance energy storage devices based on the use of new electrode nanomaterials. A flexible and wearable electric double-layer capacitor wire by twisting two aligned multiwalled CNT/ordered mesoporous carbon composite fibers as electrodes has been developed.

Figure 5: Schematic illustration of a wire-shaped DSC fabricated from two CNT fibers. (a) Two CNT fibers twined into a cell. (b) Top view of a cell. (c) Working mechanism [6].
As the ordered mesoporous carbon is incorporated into the axially aligned multiwalled CNT skeleton to combine the structure and property advantages of the two components in the composite fiber electrode, the electric double-layer capacitor wire exhibits high specific capacitance and long life stability. Compared with the conventional planar structure, the capacitor wire is also lightweight and can be integrated into various textile structures that are particularly promising for portable and wearable electronic devices.

And then Chen et al. [25] developed coaxial electric double-layer capacitor fibers from the CNT fibers (see Figure 10), which functioned as two electrodes with a polymer gel sandwiched between them. The unique coaxial structure had decreased the contact resistance between the two electrodes with a maximum discharge capacitance of $59 \, \text{F g}^{-1}$ ($32.09 \, \text{F cm}^{-3}$ or $29 \, \mu\text{F cm}^{-1}$ or $8.66 \, \text{mF cm}^{-2}$), much higher than $4.5 \, \text{F g}^{-1}$ of the electric double-layer capacitor by twisting two CNT fibers together. These electric double-layer...
capacitor fibers exhibit energy densities up to 1.88 Wh kg\(^{-1}\) and power densities up to 755.9 W kg\(^{-1}\). In addition, they are flexible and stretchable and can be easily scaled up with high efficiency and low cost. These electric double-layer capacitor fibers also represent the first demonstration of stretchable energy devices in a fiber format, which is critically important for the practical application in the flexible equipment such as various electronic textiles. This work further provides a general and effective strategy in the development of highly efficient electronic devices.

Yang et al. [47] and Xu et al. [65] developed highly stretchable, fiber-shaped, high-performance supercapacitors (see Figure 11). Aligned CNT sheets that are sequentially wrapped on an elastic fiber serve as two electrodes (see Figure 11(a)). The use of aligned CNT sheets offers combined remarkable properties including high flexibility, tensile strength, electrical conductivity, and mechanical and thermal stability. As a result, the fiber-shaped supercapacitor maintains a high specific capacitance of approximately 18 F/g after stretch by 75% for 100 cycles. The high stretchability and specific capacitance have been simultaneously achieved by designing a coaxial structure that favors high contact areas between the electrode and electrolyte besides the combined remarkable properties enabled by the aligned CNTs.
3.3. Lithium Ion Battery Based on Carbon Nanotube Fibers.

Lithium ion batteries are receiving considerable attention in applications, ranging from portable electronics to electric vehicles, due to their superior energy density over other rechargeable battery technologies. However, lighter, thinner, and higher capacity lithium ion batteries necessitate ongoing research for novel materials with improved properties. Researchers require a concerted development of both electrodes and electrolyte to improve battery capacity, cycle life, and charge-discharge rates while maintaining the highest degree of safety available. CNT fibers are a candidate material for use in lithium ion batteries. A fiber device can be easily woven into textiles or other structures to exhibit unique and promising applications. CNT fibers as a conductive additive at a lower weight loading than conventional carbons, like carbon black and graphite, present a more effective strategy to establish an electrical percolation network. Ren et al. [22] used twisted CNT fibers and composite fibers to produce both fiber-shaped lithium ion batteries with high capacitive performances (see Figure 12). The microsupercapacitor fiber was fabricated by twisting two CNT fibers and showed a mass specific capacitance of 13.31 F/g, area specific capacitance of 3.01 mF/cm², or length specific capacitance of 0.015 mF/cm at 2 × 10⁻³ mA (1.67 A/g). The fiber-shaped battery was produced by twisting a CNT fiber and a lithium wire which functioned as positive and negative electrodes, respectively. The specific capacity was calculated as 94.37 mAh/cm³ or 174.40 mAh/g at 2 × 10⁻³ mA. The energy and power densities in both supercapacitors and batteries could be further greatly improved by incorporation of MnO₂ nanoparticles into CNT fibers. For instance, the charge and discharge energy densities achieved 92.84 and 35.74 mWh/cm³ while the charge and discharge power densities were 3.87 and 2.43 W/cm³ at 2 × 10⁻³ mA in the fiber-shaped microbattery. The combined flexible fiber structure and high tensile strength also enable promising applications in various fields; for example, these fibers can be easily integrated into electronic textiles by a conventional weaving technique. This work further presented a fabrication paradigm in the development of novel storage devices by using strong and conductive nanostructured fibers as effective electrodes.

And then Lin et al. [23] reported the development of twisted, aligned multi-walled CNT/Si composite fiber anodes for flexible, fiber-shaped lithium ion batteries (Figure 13). A thin layer of silicon was coated on the outer surface of the aligned multiwalled CNTs to form a core-sheath structure that can effectively and simultaneously exploit the high specific capacity of the silicon and high electrical conductivity of the multiwalled CNTs, while the designed space with sizes of tens to hundreds of nanometers among the aligned composite nanotubes can effectively counterbalance the volume change of the silicon component. As a result, the aligned multiwalled CNTs/Si fiber electrode shows a combined high specific capacity and cyclic stability. And this fiber electrode offers unique advantages, such as being lightweight and weavable compared with the conventional planar structure. This core-sheath architecture and aligned structure of the multiwalled CNTs/Si composite nanotubes display a remarkable electrochemical performance, including high specific capacity and cyclic stability.
3.4. The Integrated Wire-Shaped Device Based on Carbon Nanotube Fibers. The solar energy is converted into electric energy which is transferred through external electric wires to electrochemical devices, such as lithium ion batteries and supercapacitors. To further improve the energy conversion and storage efficiency, it is important to simultaneously realize the two functions, photoelectric conversion (PC) and energy storage (ES), in one device. Recently, attempts have been made to directly stack a photovoltaic cell and a supercapacitor into one device which can absorb and store solar energy. Chen et al. [48] developed an integrated energy fiber to simultaneously realize PC and ES with high efficiency (see Figure 14). A titanium wire was modified in sections with aligned titania nanotubes on the surface. Active materials for PC and ES were then coated onto the modified parts within titania nanotubes. CNT fibers were twisted with the modified Ti wire to produce the desired device. The Ti wire and CNT fiber had been used as electrodes. Figure 14(a) schematically shows a wire in which one part is capable of PC and one part is capable of ES. This integrated fiber device exhibits an overall photoelectric conversion and storage efficiency of 1.5%. The fiber structure also enables unique and promising applications; for example, it is envisaged that it can be easily integrated into electronic textiles by a well-defined weaving technique and serve as a self-powering system for portable microelectronic devices and equipment.

Zhang et al. [33] have developed an all solid-state, coaxial, and self-powered “energy fiber” which simultaneously converts solar energy to electric energy and stores it (Figure 15). The design of a coaxial structure in the “energy fiber” enables promising advantages for both PC and ES. For the PC part, it is similar to the efficient planar polymer solar cell in the radial direction, so the generated charges can be rapidly separated and transported to produce high photocurrents. For the ES...
part, different from the explored twisted structure of two fiber electrodes with high electrical resistances, the coaxial structure with much higher effective contact area also favors a rapid charge transport. In addition, the use of flexible, transparent, strong, and conductive multiwalled CNT sheets can also greatly improve the photoelectric conversion and energy storage. The “energy fiber” is flexible and can be scaled up for the practical application by the well-developed textile technology and may open a new avenue to future photoelectronics and electronics.

And then Chen et al. [49] have developed an energy fiber which can simultaneously realize energy conversion and storage by integrating dye-sensitized solar cell and electrochemical capacitor (see Figure 16). A Ti wire substrate modified with perpendicularly aligned titania nanotubes on the surface and horizontally aligned CNT sheets serves as two electrodes in the integrated “energy fiber” device. The maximal photoelectric conversion efficiency achieved 2.73%, while the energy storage efficiency reached 75.7% with specific capacitances up to 0.156 mFcm$^{-1}$ or 3.32 mFcm$^{-2}$ and
power densities up to 0.013 mW cm\(^{-1}\) or 0.27 mW cm\(^{-2}\) at a current of 50 mA. The “energy fiber” is flexible and stable and shows promising applications for various portable electronic devices that require lightweight and weavable materials.

4. Conclusions

The recent studies of the CNT fibers for optoelectric conversion and energy storage are summarized. The CNT has been extensively applied to fiber-shaped dye-sensitized solar cell, lithium ion battery, supercapacitor, and their integrated device. These “energy fibers” are flexible, stable, and stretchable and show promising applications to be integrated into electronic textiles by a well-defined weaving technique and serve as a self-powering system for portable microelectronic devices and equipment.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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