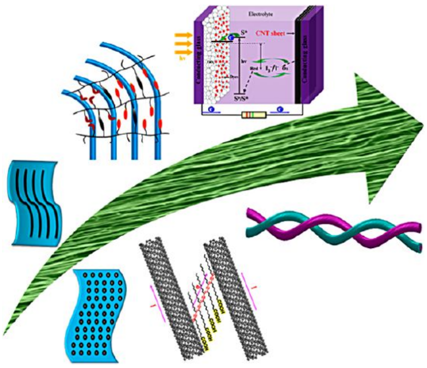
ACCOUNTS
of chemical research

The Alignment of Carbon Nanotubes: An Effective Route To Extend Their Excellent Properties to Macroscopic Scale

XUEMEI SUN, TAO CHEN, ZHIBIN YANG, AND HUISHENG PENG*
State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, Shanghai 200438, China

RECEIVED ON JULY 27, 2012

CONSPECTUS



To improve the practical application of carbon nanotubes, it is critically important to extend their physical properties from the nanoscale to the macroscopic scale. Recently, chemists aligned continuous multiwalled carbon nanotube (MWCNT) sheets and fibers to produce materials with high mechanical strength and electrical conductivity. This provided an important clue to the use of MWCNTs at macroscopic scale. Researchers have made multiple efforts to optimize this aligned structure and improve the properties of MWCNT sheets and fibers. In this Account, we briefly highlight the new synthetic methods and promising applications of aligned MWCNTs for organic optoelectronic materials and devices.

We describe several general methods to prepare both horizontally and perpendicularly aligned MWCNT/polymer composite films, through an easy solution or melting process. The composite films exhibit the combined properties of being flexible, transparent, and electrically conductive. These advances may pave the way to new flexible substrates for organic solar cells, sensing devices, and other related applications. Similarly, we discuss the synthesis of aligned MWCNT/polymer composite fibers with interesting mechanical and electrical properties. Through these methods, we can incorporate a wide variety of soluble or fusible polymers for such composite films and fibers.

In addition, we can later introduce functional polymers with conjugated backbones or side chains to improve the properties of these composite materials. In particular, cooperative interactions between aligned MWCNTs and polymers can produce novel properties that do not occur individually. Common examples of this are two types of responsive polymers, photodeformable azobenzene-containing liquid crystalline polymer and chromatic polydiacetylene. Aligning the structure of MWCNTs induces the orientation of azobenzene-containing mesogens, and produces photodeformable polymer elastomers. This strategy also solves the long-standing problems from the traditional mechanical rubbing method, which include production of broken debris and structure damage during fabrication and building up electrostatic charge during use. Aligning MWCNTs induces a conformational change in polydiacetylene, which causes the composite fibers to be electrochromatic, a previously unknown reaction in chromatic polymers.

Due to their large surface area, flexibility, electrical conductivity, and remarkable electrocatalytic activity, aligned MWCNT films can be used as counter electrodes to produce highly efficient dye-sensitized solar cells. In addition, chemists have developed new electrodes from the aligned MWCNT fibers to make a family of high-performing, wire-shaped dye-sensitized solar cells.

1. Introduction

Due to the unique structure and excellent mechanical, electrical, and thermal properties, carbon nanotubes (CNTs) have been widely studied for over 2 decades.[1−4] However, it remains difficult to make them for nanoscale devices at large scale as widely proposed.[1] To further improve their practical applications, more and more interest is attracted to exploring them for bulk materials.[2−6] To this end, it is critically important to extend the unique structure and excellent properties of CNTs from nanoscale to macroscopic scale. Recently, CNTs have been assembled into continuous sheets and fibers in which CNTs are highly

10.1021/ar300221r

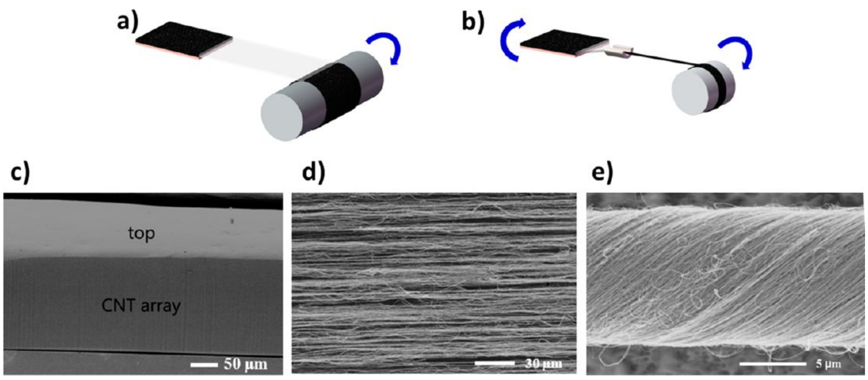


FIGURE 1. Preparation of MWCNT sheets and fibers from spinnable arrays. (a, b) Schematic illustrations of the sheet and fiber, respectively. (c, d, e) SEM images of array, sheet, and fiber, respectively. Adapted from ref 6.

aligned to enable mechanical strengths up to 6.7 GPa and electrical conductivities of 10^3 S cm^{-1}.[2,3] This strategy provides an efficient paradigm to the development of CNTs to maintain their remarkable properties at macroscopic scale, and much effort has been made to prepare aligned CNT materials.[4]

In this Account, we briefly review the recent efforts on the synthesis and application of aligned CNTs for organic optoelectronic materials and devices. First, several general methods are described to prepare highly aligned multiwalled carbon nanotube (MWCNT)/polymer composite films and fibers. Then, functional polymers with conjugated side chains and backbones are introduced to produce novel responsive properties due to the synergetic interactions between aligned MWCNTs and polymers. Finally, aligned MWCNT materials are shown for both planar and wire-shaped dye-sensitized solar cells with high performances.

2. New Synthetic Approaches to Highly Aligned MWCNT/Polymer Materials

CNTs have been widely incorporated into polymers to produce composite materials in which CNTs may provide excellent mechanical, electrical, and thermal properties, while polymers enable high flexibility, low cost, and easy fabrication.[5,6] Three typical methods, solution blending, melt blending, and in situ polymerization, are generally investigated. However, there remain common and critical challenges in the above methods, that is, random dispersion and low content of CNTs in polymer matrices. Therefore, the composites could not fully take advantage of the excellent properties of individual CNTs; for example, strength and conductivity are typically lower than 0.12 GPa and at 10^{-6} S cm^{-1}, respectively.[5] A general and effective solution has been recently recognized and explored: alignment of CNTs for better properties. The alignment could be realized before or after incorporation of polymers. For the former case, aligned CNTs are first synthesized prior to addition of polymers. For the latter case, external forces such as electric field, magnetic field, flowing, and stretching are used to induce alignment of CNTs in their mixtures with polymers;[7−9] for example, Poulin and co-workers found that CNTs could be aligned in their polymer composite fibers.[7,8] Besides the alignment of CNTs, a high content of CNTs had been also achieved in these two cases.

Here several new methods are described to prepare highly aligned MWCNT/polymer composites from aligned MWCNT arrays, sheets, and fibers, and a broad spectrum of soluble or fusible polymers are applicable. MWCNT arrays were first synthesized by chemical vapor deposition,[10−14] and both ultratall and spinnable MWCNT arrays could be prepared.

2.1. Preparation of Horizontally Aligned MWCNT/Polymer Composite Films. Free-standing MWCNT sheets were first pulled out of spinnable arrays by a dry spinning process (Figure 1a). The height of spinnable array was generally ranged from 100 to 300 μm, and Figure 1c shows a typical scanning electron microscopy (SEM) image. MWCNTs were highly aligned along the drawing direction (Figure 1d).[15] The areal density of sheets was 1.4 μg cm^{-2} and can be further improved by liquid densification, and they showed high conductivities up to 10^3 S cm^{-1} along the drawing direction.[16]

The MWCNT sheets could be stabilized on various substrates such as glass. Polymers were then directly incorporated to produce composite films through a solution or melting process. Of course, monomers could also be introduced first, followed by *in situ* polymerizations. The thicknesses of composite films were controlled by varying the layer number of MWCNT sheets. A wide variety of polymers such as polystyrene, poly(methyl methacrylate), poly(3-hexylthiophene-2,5-diyl), and sulfonated poly(ether ether

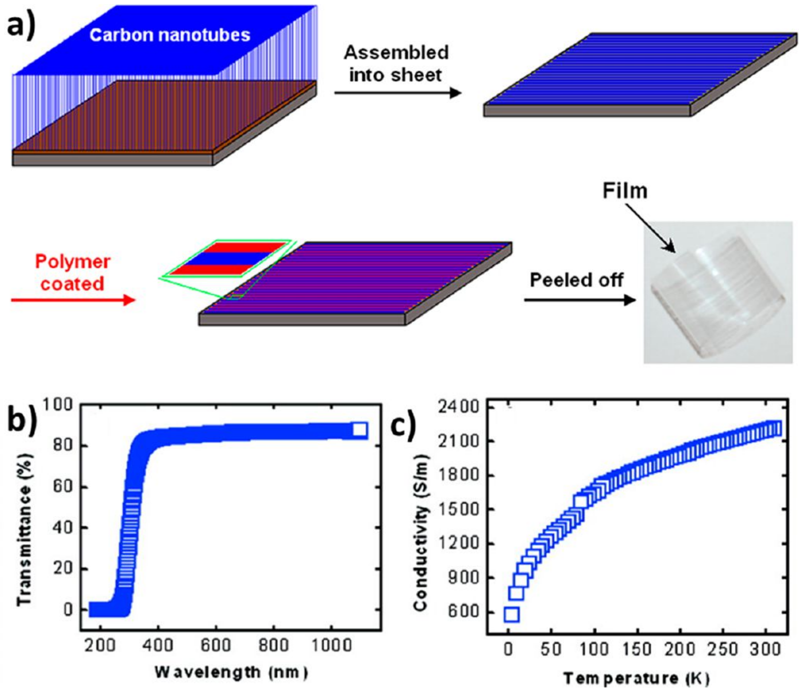


FIGURE 2. Horizontally aligned MWCNT/polymer films. (a) Schematic illustration of the preparation. (b) Optical transmittances measured by UV−vis spectrometer (5 μm in thickness). (c) Temperature dependence of the electrical conductivity. Adapted from ref 17.

ketones) have been studied for composite films in which MWCNTs remained highly aligned (Figure 2a).[17] The composite films were transparent based on the choice of specific polymers, for example, the use of sulfonated poly(ether ether ketones) produced a transmittance of ~86% for a film thickness of 5 μm (Figure 2b). The conductivity achieved 200 S cm^{-1} along the MWCNT-aligned direction and increased with increasing temperature, suggesting a semiconducting behavior for the composite film (Figure 2c). In addition, the composite films were flexible and strong.

On the other hand, the spinnable arrays were relatively short, though ultratall arrays with heights of millimeters had been easily synthesized. The mechanical and electrical properties of composite films were closely related to the length of MWCNTs, that is, longer MWCNTs had greatly increased both strength and conductivity.[18] To this end, horizontally aligned MWCNT/polymer films had been recently realized by the direct use of ultratall MWCNT arrays. Polymers or monomers were first coated onto ultratall MWCNT arrays, followed by slicing the composite array along the MWCNT length.[5,19] The composite films were also transparent (e.g., transmittance of higher than 90% at thickness of 125 nm) and flexible with a higher conductivity of 10^3 S cm^{-1}.

2.2. Preparation of Perpendicularly Aligned MWCNT/Polymer Films. Although the conductivity along the MWCNT length in horizontally aligned MWCNT/polymer films showed a high value, it was relatively low in the perpendicular direction due to high contact resistances among parallel MWCNTs, for example, 10^1 S cm^{-1}. However, a high perpendicular conductivity was critical to composite films for optoelectronic applications such as electrodes. An effective solution had been proposed to align MWCNTs in the perpendicular direction in composite films. The perpendicularly aligned MWCNTs may also provide composite films with other promising applications, for example, an ideal candidate for filtering membranes.[20]

Perpendicularly aligned MWCNT/polymer films could be directly prepared by coating polymers onto MWCNT arrays, and the film thicknesses were determined by heights of bare arrays. However, it was difficult to synthesize short arrays with thicknesses of several micrometers or lower due to rapid growth rates, for example, 60 μm/min. Even if short arrays had been synthesized, the coating of polymer solutions often destroyed the aligned structure of MWCNTs.[21] Therefore, no perpendicularly aligned MWCNT composite films could be obtained from short arrays. On the other hand, thin or even ultrathin films are highly required for optoelectronic applications.

Recently, a slicing method was introduced to prepare perpendicularly aligned MWCNT/polymer thin films from ultratall arrays. In a typical synthesis, the desired polymers were incorporated into bare MWCNT arrays, followed by cutting along the direction perpendicular to the MWCNT

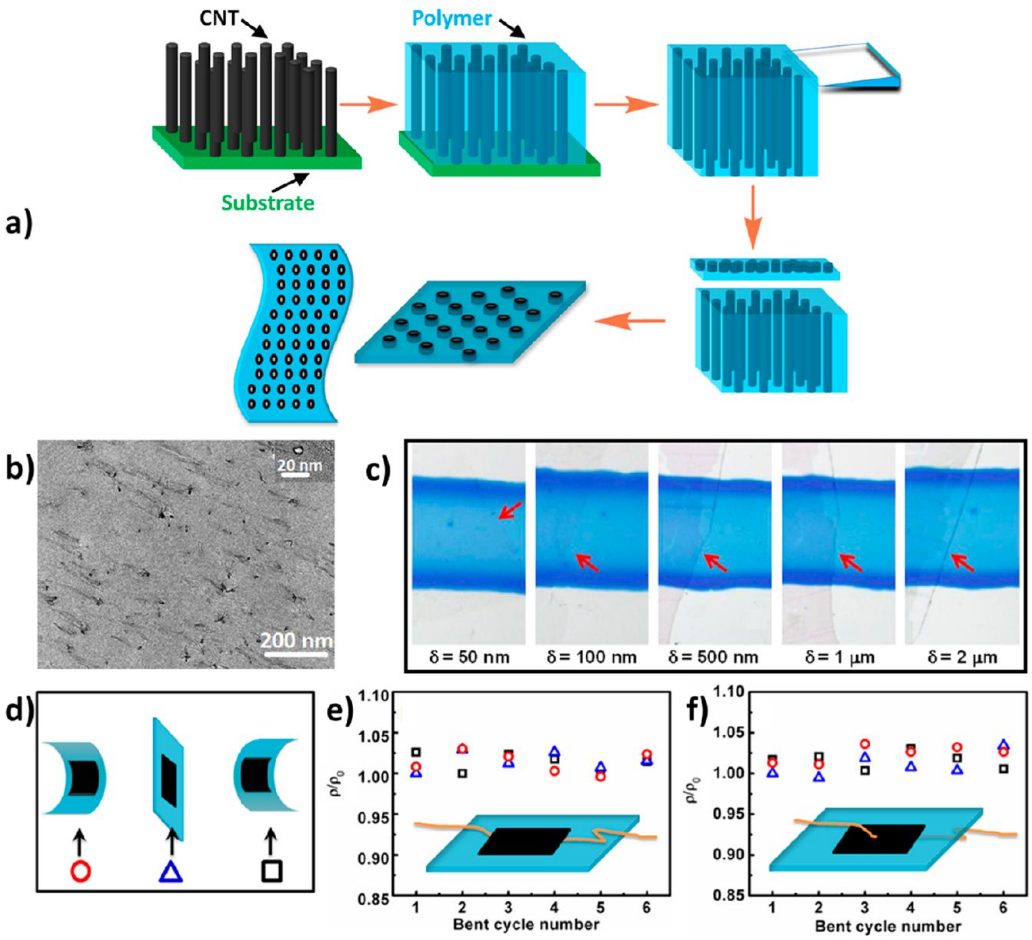


FIGURE 3. Perpendicularly aligned MWCNT/polymer films. (a) Schematic illustration to the preparation. (b) TEM image from a top view (inset, an open end of MWCNT). (c) A series of composite films on a blue ribbon-marked paper with thicknesses from 50 nm to 2 μm. (d) Schematic illustration of a repeating change of film morphologies. (e) In-plane and (f) perpendicular resistivities of a composite film under bending according to panel d; ρ_0 and ρ correspond to electrical resistivities before and after bending. Adapted from ref 23.

length (Figure 3a).[22,23] The film thicknesses were controlled from tens of nanometers to micrometers, while the number densities of MWCNTs were tuned from 10^{10} to 10^{12} cm^{-2}. MWCNTs penetrated through the composite film with open ends on both faces (Figure 3b). By appropriate choice of polymers such as epoxy resin, the composite films were transparent at thicknesses of less than 5 μm (Figure 3c). The composite films were stable in both structure and property. For instance, their electrical resistances remained almost unchanged after bending for many cycles (Figures 3d–f).

The MWCNT number density played a critical role in the preparation of such composite films, and the optimal density was $10^{10}-10^{12}$ cm^{-2}. At lower densities, the MWCNT array shrank during the coating process destroying the aligned structure, while organic molecules could not effectively infiltrate into the array at higher densities. In addition, polymers with comparable stiffness and toughness to MWCNTs should be used, so MWCNTs would not be pulled out during the slicing process. Some modifications such as the use of liquid nitrogen and electric current during the cutting process also helped to produce uniform films. Currently, thin composite films (thicknesses of hundreds of nanometers or lower) are typically prepared at sizes of millimeters, while thicker composite films can be made at centimeters or larger. The composite film can be continuously produced when the slicing process is designed automatically.

2.3. Preparation of Aligned MWCNT/Polymer Fibers. Similar to MWCNT sheets, MWCNT fibers were first spun from spinnable arrays (Figure 1b), which can be easily scaled up to produce long MWCNT fibers of hundreds of meters. The fiber diameters were varied between 2 and 40 μm by tuning the widths of initial ribbons, and MWCNTs were highly aligned (Figure 1e). MWCNT fibers showed a density of ~0.54 g cm^{-3} with strengths up to 3.3 GPa and conductivities of 10^3 S cm^{-1}. Similar to MWCNT sheets, the conductivity also increased with the increasing temperature,

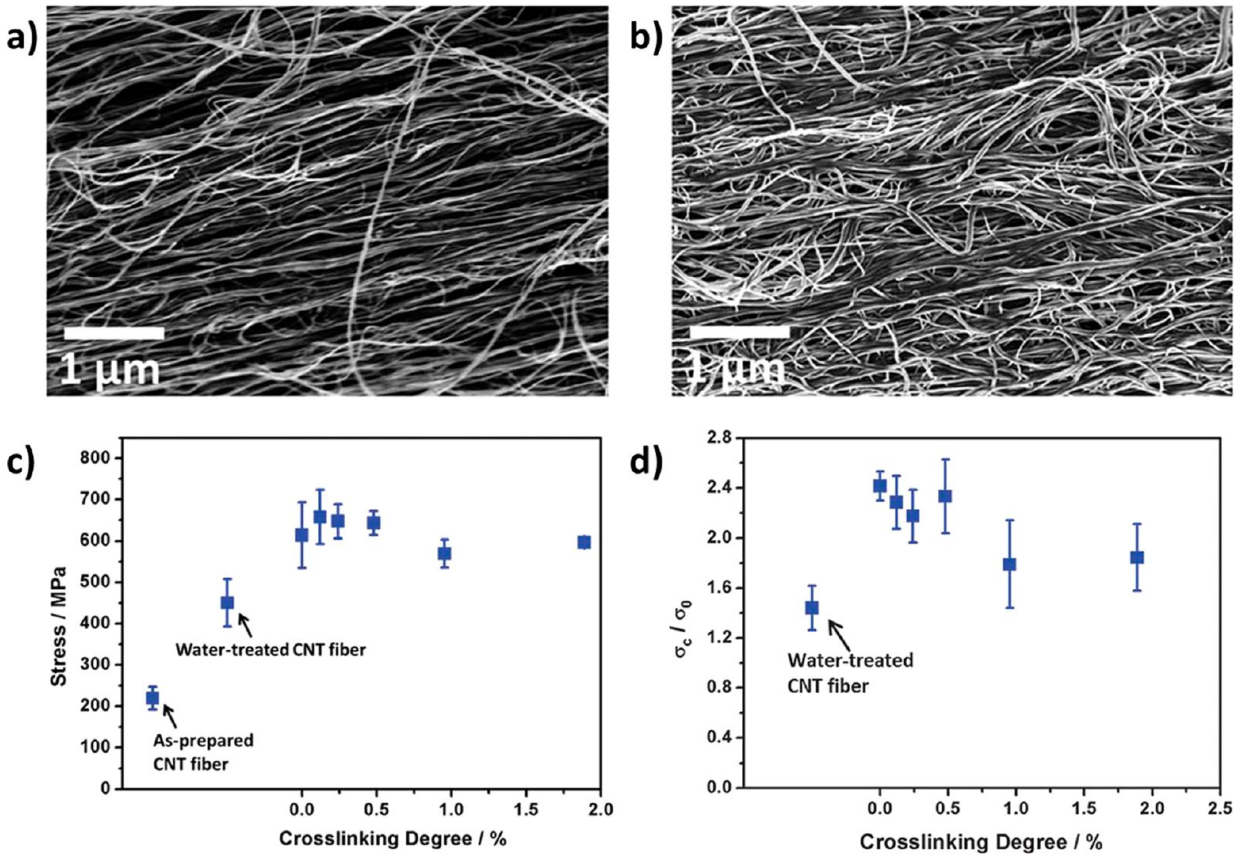


FIGURE 4. Aligned MWCNT/poly(acrylic acid) composite fibers. (a, b) SEM images before and after introduction of poly(acrylic acid). (c, d) Dependence of tensile strength and conductivity ratio on cross-linking degree of polymer. σ_0 and σ_c correspond to electrical conductivities of bare and composite fibers, respectively. Adapted from ref 27.

which indicated a semiconductive behavior of MWCNTs fibers. Both strength and conductivity could be further increased by optimizing the structure of individual MWCNTs and post-fabrication treatments.[24−26]

Polymers were then physically attached onto or chemically connected to MWCNTs in the fibers to produce aligned MWCNT/polymer composite fibers. However, because sizes of voids among MWCNTs typically ranged from 10 to 30 nm, polymer molecules with relatively large sizes could not effectively infiltrate into them, and it was difficult to obtain uniform composite fibers. To this end, monomers with much smaller sizes were often first incorporated into MWCNT fibers followed by *in situ* polymerization.[27] Figure 4 showed an aligned MWCNT/poly(acrylic acid) fiber by introduction of acrylic acid, followed by a radical polymerization. A uniform layer of poly(acrylic acid) was coated on MWCNTs, which maintained the highly aligned structure. The composite fibers exhibited much improved strength and conductivity compared with the direct use of polymers. Unexpectedly, both strength and conductivity were also higher than bare MWCNT fibers (Figure 4c,d), possibly because polymer chains interconnected neighboring MWCNTs to stabilize them and bundled MWCNTs more closely to decrease their contact resistances, respectively.

In summary, aligned MWCNT/polymer composite materials have been prepared from MWCNT arrays, sheets, and fibers. Compared with the conventional approaches, highly aligned MWCNT/polymer materials could be easily obtained, the number density of MWCNTs could be tuned in a wide range, and much longer MWCNTs were applicable. The performance of MWCNT/polymer composites strongly depend on the alignment, number density, and length of MWCNTs. For instance, tensile strengths had been increased from 320 to 850 MPa with the increasing length from 300 to 650 μm. Similar to the conventional approaches, it is also available to produce composite materials at a large scale because the array, sheet, and fiber could be continuously synthesized.

3. Novel Responsive Polymer Composites Induced by Aligned MWCNTs

Based on the alignment of MWCNTs, functional polymers could be further introduced to produce high-performance

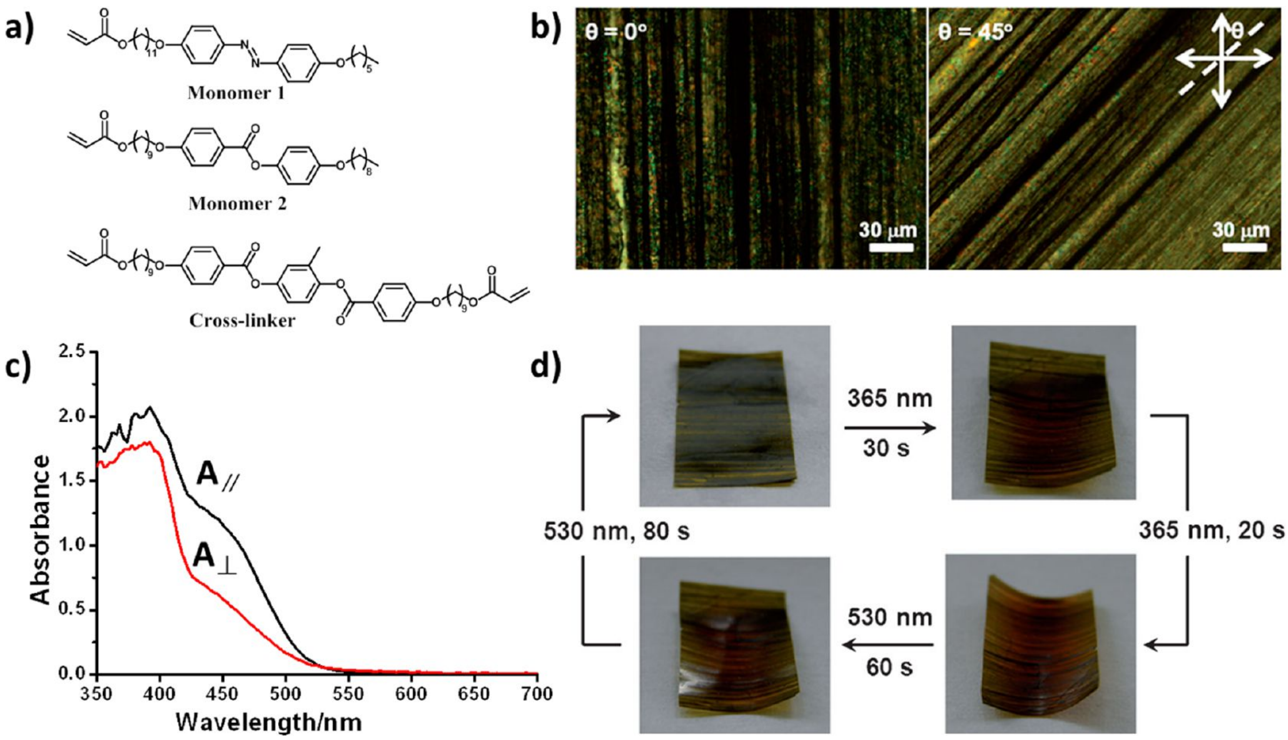


FIGURE 5. Aligned MWCNT/ALCP composite films. (a) Structures of two monomers and cross-linker. (b) Polarized optical micrographs. The white arrows and dashed white line indicate the directions of optical axes of the two polarizers and the alignment of MWCNTs, respectively. (c) Polarized absorption spectra. $A_{\parallel}$ and $A_{\perp}$ are the absorbance measured with the light being polarized to be parallel and perpendicular to the MWCNT-aligned direction, respectively. (d) Photographs of a composite film during one bending and unbending cycle after alternate irradiation by UV and visible lights at room temperature. Adapted from ref 31.

composite films and fibers. For instance, the synergetic interactions between aligned MWCNTs and polymers with conjugated side chains or backbones have been found to create some new properties that were unavailable to any individual component. Here two families of responsive polymers, photodeformable azobenzene-containing liquid crystalline polymer (ALCP) with conjugated side chain and chromatic polydiacetylene (PDA) with conjugated backbone, are studied as a demonstration.

3.1. Photodeformable MWCNT/ALCP Composite Film. Photodeformable ALCPs have been widely explored for various applications such as light-driven soft actuators due to a bending deformation derived from the reversible *trans*–*cis* photoisomerization of azobenzene.[28] To achieve high sensitivity and high stability, it is important to efficiently orient liquid-crystalline (LC) mesogens. Parallel micrometer-sized grooves on polyimide by mechanical rubbing are used to orient LC mesogens. However, there remain obvious challenges in this method, for example, production of broken debris and structural damage during the fabrication and accumulation of electrostatic charge during use. In addition, it is difficult to effectively control the orientation direction of mesogens, which determines the bending direction of the resulting ALCPs.

Aligned CNTs with parallel nanometer-sized grooves may represent a new and effective template to orient LC mesogens.[29] Aligned MWCNT sheets were shown as an effective substrate to orient small LC molecules with uniform structures.[30] Herein, the MWCNT sheets are further shown to effectively orient photodeformable ALCPs. MWCNT/ALCP composite film was synthesized by injecting the mixture of monomers and cross-linker (Figure 5a), which reacted to produce ALCPs into MWCNT sheets through a melting process.[31] The ALCP mesogens were effectively oriented along the MWCNT length without using any other aligning layer (Figure 5b,c). The resulting composite film underwent reversible bending and unbending toward the light under alternate irradiations of UV and visible lights (Figure 5d). In addition, the reversible deformation could be stably repeated for more than 100 cycles without obvious fatigue.

On the other hand, the orientation direction of mesogens could be further tuned by the fabrication process. The mesogens would be oriented in the direction perpendicular to the MWCNT length if the precursors were introduced by a solution process.[32] Therefore, the resulting MWCNT/ALCP films bent away from the UV light. Although these results could be effectively repeated and the interactions between

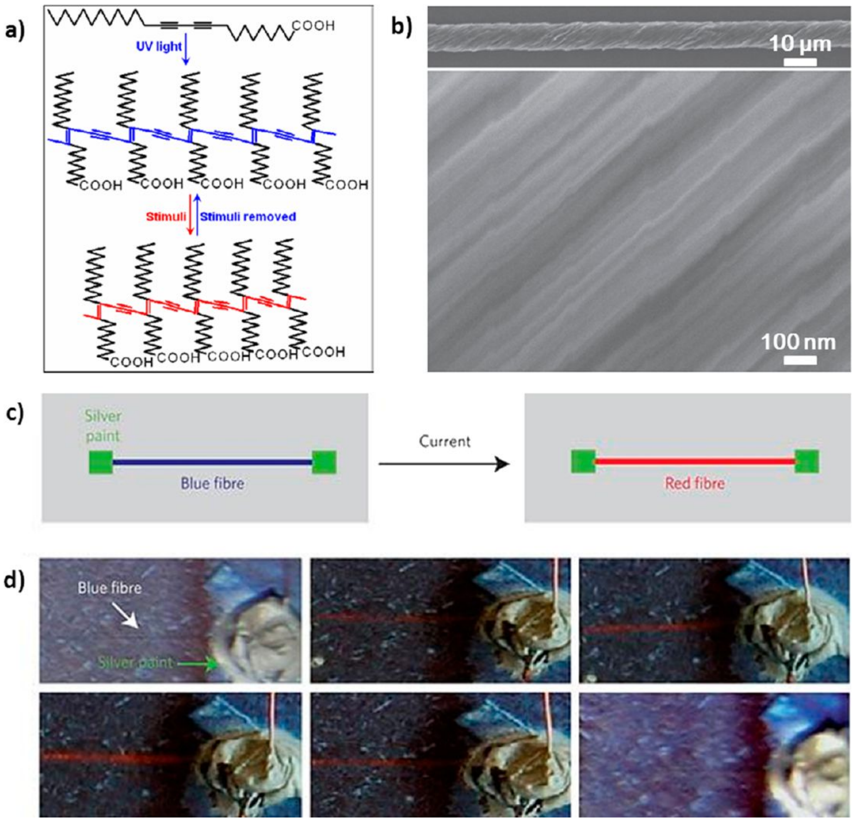


FIGURE 6. Aligned MWCNT/PDA composite fibers. (a) Polymerization of a diacetylenic monomer and reversible chromatism of the resulting PDA under stimulation derived from a reversible change of effective conjugation lengths. (b) SEM images of a composite fiber with different magnifications. (c) Schematic illustration to the color change of composite fiber from blue to red when a direct current is passed through it. (d) Electrochromatism of a composite fiber under a 10 mA direct current with on and off interval of 2 s. Adapted from ref 24.

MWCNT and ALCP were found to play a critical role on the different orientation, more effort is still required to clearly understand the mechanism and orientation process.

The introduction of aligned MWCNTs also provided the ALCP composites with excellent properties such as high strength up to ~1 GPa and conductivity of 10^2-10^3 S/cm. These properties had greatly improved the performance of ALCP materials, for example, prevention of charge accumulation, and enabled some unique applications, for example, a new actuation material for deformable optoelectronic devices such as electric switches.

3.2. Electrochromatic MWCNT/PDA Composite Fiber. PDA changes color under various external stimuli such as heating, pH, and mechanical rubbing and has been widely explored as a material for chromatic sensors. This color change, typically from blue to red, is caused by the conformation change of PDA backbone under external stimuli (Figure 6a). However, the practical applications have been largely hindered by their reversible chromatic transitions under limited stimuli. As a result, significant effort has been made to improve the reversibility and increase the scope of stimuli.[33−36] However, it remains difficult to realize electrochromatism due to a very low conductivity in PDA. MWCNT fibers showed excellent electrical properties such as high conductivities and may be incorporated with PDA to realize the desired electrochromatism.

MWCNT/PDA composite fibers were prepared by dipping bare MWCNT fibers into the solution of diacetylenic monomers followed by topochemical polymerization under UV light.[24] Figure 6b showed SEM images of a MWCNT/PDA fiber in which MWCNTs remained highly aligned and PDA was uniformly distributed. As a result, the composite fiber achieved a strength of 1.1 GPa and conductivity of 350 S cm^{-1}. Interestingly, the composite fiber showed a color change typically from blue to red upon pass of a direct current (10−30 mA) and returned to blue after removal of the current, and the chromatic transition could be rapidly completed in a second (Figures 6c,d). The electrochromatic mechanism had been elucidated on the basis of aligned MWCNTs. To summarize, when an electric current was passed through the composite fiber, the polar end groups of the side chain in PDA would be induced to reorganize

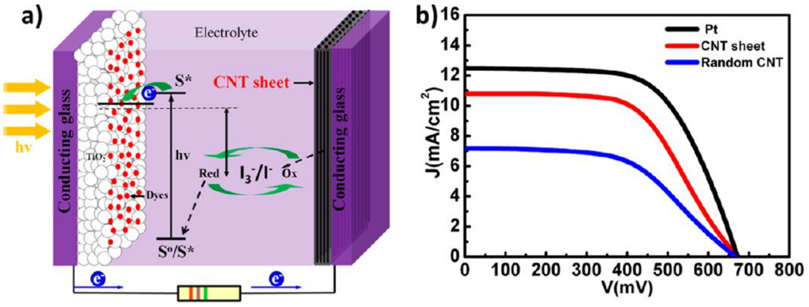


FIGURE 7. MWCNT sheets as counter electrodes in planar DSSCs. (a) Schematic illustration of a DSSC. (b) Current−voltage characteristics of DSSCs by using the randomly dispersed MWCNT film (blue line), aligned MWCNT sheet (red line), and Pt (black line) as counter electrodes under AM 1.5G illumination. Adapted from ref 16.

under the resulting electric fields among aligned MWCNTs, which further induced the conformation change of PDA backbones with a chromatic transition. Considering that the composite fiber was flexible, strong, and conductive, this electrochromatism could be particularly useful for nondestructive evaluation and structure monitoring in a broad spectrum of fields from aircraft to small electronic facilities.

4. Dye-Sensitized Solar Cells Based on Aligned MWCNTs

The dye-sensitized solar cell (DSSC) has been widely studied as an efficient photovoltaic device. It is typically composed of a working electrode (e.g., TiO_2 attached to dye), counter electrode (e.g., Pt), and electrolyte (e.g., I^-/I_3^-), and the working mechanism is summarized as follows: Photoelectrons are generated once the dye absorbs incident light and are injected into TiO_2 and transported to the counter electrode through an external circuit. The dye cations are reduced to the ground state by I^- ions with production of I_3^- ions, which reverted I^- by accepting electrons from the counter electrode. Although DSSCs have been demonstrated to be very useful, there remain several challenges to be overcome prior to practical applications. For instance, Pt as the conventional counter electrode is limited in source and produced under harsh conditions and becomes unstable during use. In addition, it is rigid, while flexible electrodes are required in many fields. Therefore, new electrode materials with easy fabrication, high flexibility, and high stability are urgently needed. MWCNTs have been widely investigated to replace Pt as counter electrodes to catalyze the reduction of triiodide.[37−39] However, the degree of improvement is far from expected due to the random dispersion of MWCNTs with many boundaries, which greatly decreases the charge separation and transport. To this end, the use of aligned MWCNT sheets or fibers provides an effective solution, and both planar and wire-shaped DSSCs had been developed with high performance.

4.1. Planar Devices Prepared from Aligned MWCNT Sheets. MWCNT sheets without and with polymers had been shown to be transparent, flexible, strong, and conductive, so they could be efficiently used as new counter electrodes on both rigid and flexible substrates. The cell structure based on an MWCNT sheet as the counter electrode is schematically shown in Figure 7a. The resulting DSSC typically exhibited an open-circuit photovoltage (V_{OC}) of 0.67 V, short-circuit photocurrent density (J_{SC}) of 10.80 mA cm^{-2}, and fill factor (FF) of 0.57 (Figure 7b). The energy conversion efficiency (η) is then calculated to be 4.18%. As a comparison, the cell derived from the randomly dispersed MWCNT film typically showed a V_{OC} of 0.67 V, J_{SC} of 8.11 mA cm^{-2}, and FF of 0.59 with η of 3.24%. Obviously, the η has been greatly increased by the alignment of MWCNTs. Compared with the Pt, the cell derived from the MWCNT sheet showed the same V_{OC} but decreased J_{SC} and FF.[16]

To further increase the performance of DSSCs, MWCNT sheets with longer MWCNTs had been prepared by peeling off rows of MWCNTs from ultratall arrays.[40] For the resulting MWCNT sheet with thickness of 4 μm from an array with height of 1.5 mm, the resulting cell typically showed V_{OC} of 0.74 V, J_{SC} of 18.02 mA cm^{-2}, and FF of 0.67, which produced an η of 9.00%. The cells showed better performances than those derived from Pt and MWCNT sheet as counter electrodes under the same condition. This phenomenon was mainly explained by the fact that MWCNTs in the ultratall array were more uniformly distributed with a higher degree of alignment. Similar, both horizontally and perpendicularly aligned MWCNT/polymer composite films could be also used as counter electrodes for DSSCs, particularly, flexible devices.[16] Compared with a rigid DSSC, the flexible cell showed a lower η of 2.77%, and more effort is required to further increase the cell efficiency. To this end, the optimization of electrode structures and fabrication parameters had been previously shown to be effective.

4.2. Wire-Shaped Devices Prepared from Aligned MWCNT Fibers. Compared with the conventional planar structure, wire-shaped solar cells have recently attracted increasing attentions due to the unique property of being wearable, which is required for various applications such as electronic textiles.[41] Generally, metal wires (e.g., Cu, Pt, and steel) and polymer fibers coated with a conductive layer (e.g., indium tin oxide) were used as electrodes in the wire-shaped cell. However, metal wires are easily corrupted by solvents, while the conductive layer on polymer fibers breaks during use. In addition, both of them are relatively less flexible and cannot be closely twined during the fabrication, so it remains difficult to further increase the cell efficiency. To this end, the aligned MWCNT fibers may represent an ideal candidate because they are flexible, strong, and conductive with high electrocatalytic activity.[42]

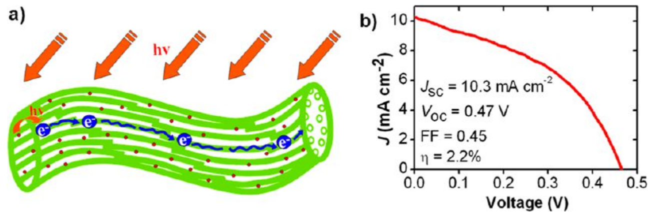


FIGURE 8. MWCNT fibers as working electrodes in DSSCs. (a) Schematic illustration to transportation of photoelectrons in an MWCNT/N719 fiber. The lime tube, red dot, and blue sphere correspond to MWCNT, dye N719, and photoelectron, respectively. (b) *J*−*V* curve of a cell under simulated 100 mW cm^{-2} illumination. Adapted from ref 43.

MWCNT fibers had been first proven effective as working electrodes in DSSCs,[43] and *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (generally called N719) was used as the dye. Due to the three-dimensional hopping conduction, the produced photoelectrons could be rapidly and efficiently transported through the MWCNT/N719 composite fiber (Figure 8a). The resulting DSSC showed V_{OC}, J_{SC}, and FF of 0.47 V, 10.3 mA cm^{-2}, and 0.45, respectively (Figure 8b), which produced η of 2.2%. However, the cell was not really wire-shaped with Pt film as the counter electrode. A free-standing and wire-shaped DSSC was recently realized by twining two MWCNT fibers with one coated with TiO_2 nanoparticles as working electrode and the other as counter electrode (Figure 9a,b).[44] The η achieved 2.94%. Due to the unique wire structure, all photovoltaic parameters were stable under different incident light angles and with increasing cell lengths (Figure 9c,d). In addition, the output voltage and current can be conveniently tuned by connection in series or in parallel.

Because TiO_2 nanoparticles with many boundaries had decreased electron mobility, aligned TiO_2 nanotubes had

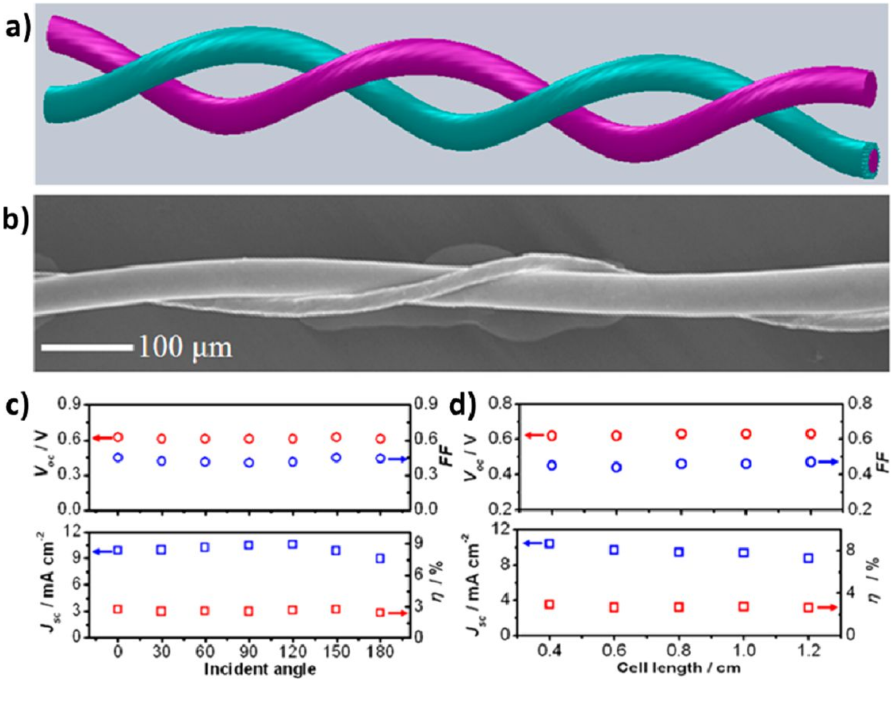


FIGURE 9. Wire-shaped DSSCs fabricated by twining two MWCNT fibers. (a) Schematic illustration. (b) SEM image for the middle part of a cell. (c, d) Dependence of V_{OC}, J_{SC}, FF, and η on the incident light angle and cell length. Adapted from ref 44.

been proposed and studied to enhance light harvesting, electron collection, and ion diffusion at the TiO_2−electrolyte interface for a higher efficiency.[45] Similarly, one Ti wire with perpendicularly aligned TiO_2 nanotubes grown on the outer surface had been used as the working electrode, while a bare MWCNT fiber was used as the counter electrode.[46] The two electrodes were twined to produce wire-shaped DSSCs with a higher η of ~4.6%.

Recently, all MWCNT fiber electrode-based wire-shaped DSSCs had been also fabricated without the use of TiO_2. One MWCNT fiber coated with a thin layer of poly(vinylidene fluoride) on the outer surface functioned as the counter electrode, while another MWCNT fiber absorbed with N719 was used as the working electrode.[47] The cell typically showed V_{OC}, J_{SC}, and FF of 0.08 V, 3.4 mA cm^{-2}, and 0.23, respectively, and the efficiency was lower than 0.1%. Therefore, the use of TiO_2 seemed critically important for wire-shaped DSSCs based on MWCNT fibers.

5. Conclusions and Perspectives

The alignment of MWCNTs has been proven effective to extend their remarkable properties from nanoscale to macroscopic scale, and the use of aligned MWCNT/polymer composites for optoelectronic materials and devices have been explored as a demonstration. Although much attention has been paid to the aligned MWCNT materials, it remains difficult or even impossible to compare the available studies because they were generally not performed quantitatively. For instance, the degree of alignment had not been measured although some characterization methods such as Raman and X-ray diffraction were shown to be effective to calculate the degree of alignment. Therefore, more efforts should be made to quantitatively study the dependence of material properties (e.g., electrical, mechanical, and optical properties) on the alignment degree of MWCNTs and number density of MWCNT in the future. Generally, a higher alignment of MWCNTs favors the improvement of properties, but there exist optimal number densities of MWCNTs for optoelectronic applications. A high number density increased the conductivity and strength, while it decreases the load of active materials such as dyes, which may decrease the efficiency of dye-sensitized solar cells. The optimal density depends on the size of dye molecules. According to previous studies, a number density of $10^{10}-10^{11}$ cm^{-2} in a MWCNT fiber was effective for the conventional dye of N719 (conductivity of 10^2 S/cm for the MWCNT fiber). In the case of aligned MWCNT/polymer composites, polymers are typically physically attached onto MWCNTs. More attention should be also paid to chemically connecting polymers, particularly, functional polymers and copolymers, to MWCNTs to further improve the structure uniformity and properties.

The wire-shaped photovoltaic device appears as a promising direction for the application of aligned MWCNT fibers. In this case, the MWCNT fiber must be flexible with conductivities higher than 10^2 S/cm and strengths higher than 10^2 MPa. The higher the conductivity and strength are, the higher efficiency the resulting photovoltaic wire shows. The MWCNT fibers should be also smooth on the outer surface if they are used in polymer solar cells. Otherwise, a short circuit will occur in them. Besides the organic optoelectronic materials and devices discussed in this Account, a wide variety of other applications such as high-performance structure materials and energy storage devices can be explored from aligned MWCNTs. It was found that perpendicularly aligned MWCNT/polymer composite films provided an unusual high capacity for lithium ion batteries when they were used as anodes.[23]

This work was supported by NSFC (Grants 20904006, 91027025, and 21225417), MOST (Grants 2011CB932503 and 2011DFA51330), STCSM (Grants 11520701400 and 12nm0503200), Fok Ying Tong Education Foundation, and The Program for Professor of Special Appointment at Shanghai Institutions of Higher Learning.

BIOGRAPHICAL INFORMATION

Xuemei Sun received her B.E. in Polymer Materials and Engineering from East China University of Science and Technology in 2008 and is currently pursuing her Ph.D. degree at Fudan University.

Tao Chen received his B.S. and M.S. in Polymer Materials both from Zhengzhou University in 2006 and 2009, respectively, and Ph.D. in Macromolecular Chemistry and Physics at Fudan University in 2012.

Zhibin Yang received his B.E. in Applied Physics from East China University of Science and Technology in 2009 and is currently pursuing his Ph.D. degree at Fudan University.

Huisheng Peng is currently a professor at Department of Macromolecular Science at Fudan University. His research centers on aligned MWCNT/polymer composite materials.

FOOTNOTES

*Corresponding author. E-mail address: penghs@fudan.edu.cn.
The authors declare no competing financial interest.

REFERENCES

1 Van Noorden, R. The Trials of New Carbon. *Nature* **2011**, *469*, 14–16.

2 Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cunniff, P.; Sennett, M.; Windle, A. High-Performance Carbon Nanotube Fiber. *Science* **2007**, *318*, 1892–1895.

3 Li, Q.; Li, Y.; Zhang, X.; Chikkannanavar, S. B.; Zhao, Y.; Dangelewicz, A. M.; Zheng, L.; Doorn, S. K.; Jia, Q.; Peterson, D. E.; Arendt, P. N.; Zhu, Y. Structure-Dependent Electrical Properties of Carbon Nanotube Fibers. *Adv. Mater.* **2007**, *19*, 3358–3363.

4 Jiang, K.; Wang, J.; Li, Q.; Liu, L.; Liu, C.; Fan, S. Superaligned Carbon Nanotube Arrays, Films, and Yarns: A Road to Applications. *Adv. Mater.* **2011**, *23*, 1154–1161.

5 Peng, H.; Sun, X. Highly Aligned Carbon Nanotube/Polymer Composites with Much Improved Electrical Conductivities. *Chem. Phys. Lett.* **2009**, *471*, 103–105.

6 Qiu, L.; Sun, X.; Yang, Z.; Guo, W.; Peng, H. Preparation and Application of Aligned Carbon Nanotube/Polymer Composite Material. *Acta Chim. Sin.* **2012**, *70*, 1523–1532.

7 Badaire, S.; Pichot, V.; Zakri, C.; Poulin, P.; Launois, P.; Vavro, J.; Guthy, C.; Chen, M.; Fischer, J. E. Correlation of Properties with Preferred Orientation in Coagulated and Stretch-Aligned Single-Wall Carbon Nanotubes. *J. Appl. Phys.* **2004**, *96*, 7509–7513.

8 Viry, L.; Mercader, C.; Miaudet, P.; Zakri, C.; Derre, A.; Kuhn, A.; Maugey, M.; Paulin, P. Nanotube Fibers for Electromechanical and Shape Memory Actuators. *J. Mater. Chem.* **2010**, *20*, 3487–3495.

9 Moniruzzaman, M.; Winey, K. I. Polymer Nanocomposites Containing Carbon Nanotubes. *Macromolecules* **2006**, *39*, 5194–5205.

10 Peng, H.; Jain, M.; Li, Q.; Peterson, D. E.; Zhu, Y.; Jia, Q. Vertically Aligned Pearl-like Carbon Nanotube Arrays for Fiber Spinning. *J. Am. Chem. Soc.* **2008**, *130*, 1130–1131.

11 Zhang, M.; Atkinson, K. R.; Baughman, R. H. Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology. *Science* **2004**, *306*, 1358–1361.

12 Peng, H.; Sun, X. Macroporous Carbon Nanotube Arrays with Tunable Pore Sizes and Their Template Applications. *Chem. Commun.* **2009**, 1058–1060.

13 Jiang, K.; Li, Q.; Fan, S. Spinning Continuous Carbon Nanotube Yarns. *Nature* **2002**, *419*, 801–801.

14 Li, L.; Zhang, L.; Ren, J.; Zhang, H.; Sun, X.; Li, H.; Chen, T.; Peng, H. Intriguing Hybrid Nanotubes with Tunable Structures. *Chem. Phys. Lett.* **2011**, *516*, 204–207.

15 Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. Strong, Transparent, Multifunctional, Carbon Nanotube Sheets. *Science* **2005**, *309*, 1215–1219.

16 Yang, Z.; Chen, T.; He, R.; Guan, G.; Li, H.; Qiu, L.; Peng, H. Aligned Carbon Nanotube Sheets for the Electrodes of Organic Solar Cells. *Adv. Mater.* **2011**, *23*, 5436–5439.

17 Peng, H. Aligned Carbon Nanotube/Polymer Composite Films with Robust Flexibility, High Transparency, and Excellent Conductivity. *J. Am. Chem. Soc.* **2008**, *130*, 42–43.

18 Zhang, X.; Li, Q.; Tu, Y.; Li, Y.; Coulter, J. Y.; Zheng, L.; Zhao, Y.; Jia, Q.; Peterson, D. E.; Zhu, Y. Strong Carbon-Nanotube Fibers Spun from Long Carbon Nanotube Arrays. *Small* **2007**, *3*, 244–248.

19 Huang, S.; Li, L.; Yang, Z.; Zhang, L.; Saiyin, H.; Chen, T.; Peng, H. A New and General Fabrication of an Aligned Carbon Nanotube/Polymer Film for Electrode Applications. *Adv. Mater.* **2011**, *23*, 4707–4710.

20 Majumder, M.; Chopra, N.; Hinds, B. J. Effect of Tip Functionalization on Transport through Vertically Oriented Carbon Nanotube Membranes. *J. Am. Chem. Soc.* **2005**, *127*, 9062–9070.

21 Li, Q.; DePaula, R.; Zhang, X.; Zheng, L.; Arendt, P. N.; Mueller, F. M.; Zhu, Y.; Tu, Y. Drying Induced Upright Sliding and Reorganization of Carbon Nanotube Arrays. *Nanotechnology* **2006**, *17*, No. 4533.

22 Huang, S.; Lin, H.; Qiu, L.; Zhang, L.; Cai, Z.; Chen, T.; Yang, Z.; Yang, S.; Peng, H. Perpendicularly Aligned Carbon Nanotube/Olefin Composite Films for the Preparation of Graphene Nanomaterials. *J. Mater. Chem.* **2012**, *22*, 16209–16213.

23 Li, L.; Yang, Z.; Gao, H.; Zhang, H.; Ren, J.; Sun, X.; Chen, T.; Kia, H.; Peng, H. Vertically Aligned and Penetrated Carbon Nanotube/Polymer Composite Film and Promising Electronic Applications. *Adv. Mater.* **2011**, *23*, 3730–3735.

24 Peng, H.; Sun, X.; Cai, F.; Chen, X.; Zhu, Y.; Liao, G.; Chen, D.; Li, Q.; Lu, Y.; Zhu, Y.; Jia, Q. Electrochromatic Carbon Nanotube/Polydiacetylene Nanocomposite Fibres. *Nat. Nanotechnol.* **2009**, *4*, 738–741.

25 Peng, H.; Jain, M.; Peterson, D. E.; Zhu, Y.; Jia, Q. Composite Carbon Nanotube/Silica Fibers with Improved Mechanical Strengths and Electrical Conductivities. *Small* **2008**, *4*, 1964–1967.

26 Yang, Z.; Sun, X.; Chen, X.; Yong, Z.; Xu, G.; He, R.; An, Z.; Li, Q.; Peng, H. Dependence of Structures and Properties of Carbon Nanotube Fibers on Heating Treatment. *J. Mater. Chem.* **2011**, *21*, 13772–13775.

27 Guo, W.; Liu, C.; Sun, X.; Yang, Z.; Kia, H.; Peng, H. Aligned Carbon Nanotube/Polymer Composite Fibers with Improved Mechanical Strength and Electrical Conductivity. *J. Mater. Chem.* **2012**, *22*, 903–908.

28 Yu, Y.; Nakano, M.; Ikeda, T. Directed Bending of a Polymer Film by Light. *Nature* **2003**, *425*, 145–145.

29 Russell, J. M.; Oh, S. J.; LaRue, I.; Zhou, O.; Samulski, E. T. Alignment of Nematic Liquid Crystals Using Carbon Nanotube Films. *Thin Solid Films* **2006**, *509*, 53–57.

30 Fu, W.; Liu, L.; Jiang, K.; Li, Q.; Fan, S. Super-Aligned Carbon Nanotube Films as Aligning Layers and Transparent Electrodes for Liquid Crystal Displays. *Carbon* **2010**, *48*, 1876–1879.

31 Wang, W.; Sun, X.; Wu, W.; Peng, H.; Yu, Y. Photoinduced Deformation of Crosslinked Liquid-Crystalline Polymer Film Oriented by a Highly Aligned Carbon Nanotube Sheet. *Angew. Chem., Int. Ed.* **2012**, *51*, 4644–4647.

32 Sun, X.; Wang, W.; Qiu, L.; Guo, W.; Yu, Y.; Peng, H. Unusual Reversible Photomechanical Actuation in Polymer/Nanotube Composites. *Angew. Chem., Int. Ed.* **2012**, *51*, 8520–8524.

33 Sun, X.; Chen, T.; Huang, S.; Li, L.; Peng, H. Chromatic Polydiacetylene with Novel Sensitivity. *Chem. Soc. Rev.* **2010**, *39*, 4244–4257.

34 Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. Polydiacetylene/Silica Nanocomposites with Tunable Mesostructure and Thermochromatism from Diacetylenic Assembling Molecules. *J. Am. Chem. Soc.* **2005**, *127*, 12782–12783.

35 Chen, X.; Li, L.; Sun, X.; Liu, Y.; Luo, B.; Wang, C.; Bao, Y.; Xu, H.; Peng, H. Magnetochromatic Polydiacetylene by Incorporation of Fe_3O_4 Nanoparticles. *Angew. Chem., Int. Ed.* **2011**, *50*, 5486–5489.

36 Sun, X.; Chen, T.; Huang, S.; Cai, F.; Chen, X.; Yang, Z.; Li, L.; Cao, H.; Lu, Y.; Peng, H. UV-Induced Chromatism of Polydiacetylenic Assemblies. *J. Phy. Chem. B* **2010**, *114*, 2379–2382.

37 Trancik, J. E.; Barton, S. C.; Hone, J. Transparent and Catalytic Carbon Nanotube Films. *Nano Lett.* **2008**, *8*, 982–987.

38 Zhu, H.; Zeng, H.; Subramanian, V.; Masarapu, C.; Hung, K. H.; Wei, B. Anthocyanin-Sensitized Solar Cells Using Carbon Nanotube Films as Counter Electrodes. *Nanotechnology* **2008**, *19*, No. 465204.

39 Lee, W. J.; Ramasamy, E.; Lee, D. Y.; Song, J. S. Efficient Dye-Sensitized Cells with Catalytic Multiwall Carbon Nanotube Counter Electrodes. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1145–1149.

40 Huang, S.; Yang, Z.; Zhang, L.; He, R.; Chen, T.; Cai, Z.; Luo, Y.; Lin, H.; Cao, H.; Zhu, X.; Peng, H. A Novel Fabrication of Well Distributed and Aligned Carbon Nanotube Film Electrode for Dye-Sensitized Solar Cell. *J. Mater. Chem.* **2012**, *22*, 16833–16838.

41 Zou, D.; Wang, D.; Chu, Z.; Lv, Z.; Fan, X. Fiber-Shaped Flexible Solar Cells. *Coord. Chem. Rev.* **2010**, *254*, 1169–1178.

42 Chen, T.; Cai, Z.; Yang, Z.; Li, L.; Sun, X.; Huang, T.; Yu, A.; Kia, H.; Peng, H. Nitrogen-Doped Carbon Nanotube Composite Fiber with a Core-Sheath Structure for Novel Electrodes. *Adv. Mater.* **2011**, *23*, 4620–4625.

43 Chen, T.; Wang, S.; Yang, Z.; Feng, Q.; Sun, X.; Li, L.; Wang, Z.; Peng, H. Flexible, Light-Weight, Ultrastrong, and Semiconductive Carbon Nanotube Fibers for a Highly Efficient Solar Cell. *Angew. Chem., Int. Ed.* **2011**, *50*, 1815–1819.

44 Chen, T.; Qiu, L.; Cai, Z.; Gong, F.; Yang, Z.; Wang, Z.; Peng, H. Intertwined Aligned Carbon Nanotube Fiber Based Dye-Sensitized Solar Cells. *Nano Lett.* **2012**, *12*, 2568–2572.

45 Zhu, K.; Neale, N. R.; Miedaner, A.; Frank, A. J. Enhanced Charge-Collection Efficiencies and Light Scattering in Dye-Sensitized Solar Cells Using Oriented TiO_2 Nanotubes Arrays. *Nano Lett.* **2007**, *7*, 69–74.

46 Chen, T.; Qiu, L.; Kia, H.; Yang, Z.; Peng, H. Designing Aligned Inorganic Nanotubes at the Electrode Interface: Towards Highly Efficient Photovoltaic Wires. *Adv. Mater.* **2012**, *24*, 4623–4628.

47 Cai, F.; Chen, T.; Peng, H. All Carbon Nanotube Fiber Electrode-Based Dye-Sensitized Photovoltaic Wire. *J. Mater. Chem.* **2012**, *22*, 14856–14860.