We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Polymer Composites with Carbon Nanotubes in Alignment

Huisheng Peng, Xuemei Sun and Tao Chen
Key Laboratory of Molecular Engineering of Polymers of Ministry of Education,
Department of Macromolecular Science, and Laboratory of Advanced Materials,
Fudan University,
China

1. Introduction

Carbon nanotubes are typically considered as molecular-scale tubes of graphitic carbon. Depending on numbers of carbon layers, they are categorized as single-walled and multi-walled nanotubes (Zhao & Stoddart, 2009). The unique structure provides nanotubes with extraordinary mechanical and electrical properties, e.g., tensile strength up to 63 Gpa (Harris, 2004) and theoretically carrying electrical current density of 1,000 times higher than copper (Hong & Myung, 2007). Nanotubes have been extensively investigated with publication over 50,000 (searched from Web of Science) in recent ten years, and have been proposed for various applications in the fields of chemistry, physics, and engineering (Feldman et al., 2008; Guldi et al., 2005; Liu et al., 2009; Peng et al., 2008a; Shi, 2009).

Although nanotubes are very promising in a wide variety of fields, the large-scale applications of individual nanotubes remain challenging due to the difficulty in structure control, existence of impurities, and poor processability (Karousis et al., 2010). In order to improve their practical applications, bulk nanotube materials have recently attracted increasing attentions, particularly, by formation of composites with polymers (Moniruzzaman & Winey, 2006; Peng, 2008b). Here nanotubes may provide good mechanical, electrical, and thermal properties, while polymers enable them with high flexibility, low cost, and easy fabrication. Three typical methods, i.e., solution blending, melt blending, and in situ polymerization, have been widely explored (Moniruzzaman & Winey, 2006). Unfortunately, a common and critical challenge is yet to be solved, i.e., randomly dispersed nanotubes in polymer matrices (see Figure 1) (Peng, 2008b). As a result, the prepared composites could not fully take advantage of the exceptional properties of individual nanotubes. For instance, we found that a nanotube/poly(methyl methacrylate) composite showed low tensile strength and electrical conductivity of 10–100 MPa and 10^{-6}–10^{-1} S/cm, respectively.

Several groups have done extensive research in trying to solve the above challenge (Feldman et al., 2008; Guldi et al., 2005; Karousis et al., 2010; Liu et al., 2009; Moniruzzaman & Winey, 2006; Peng, 2008b). Various approaches such as the use of external field (Kimura et al., 2002), mechanical stretching (Jin et al., 1998), spin-casting (Safadi et al., 2002), melt fiber spinning (Haggenmueller et al., 2003), and electrospinning (Ge et al., 2004), have been
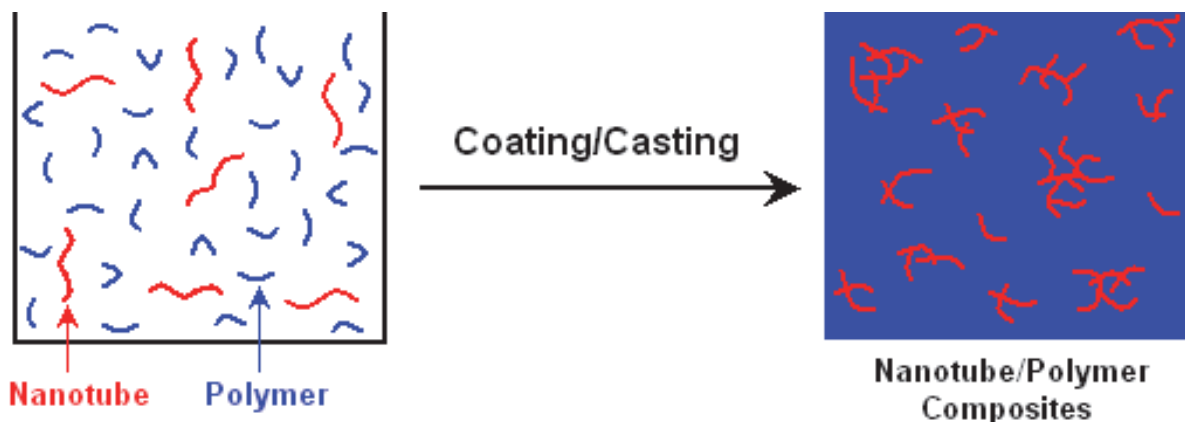
Fig. 1. Schematic illustration for the random aggregation of nanotubes in nanotube/polymer composites synthesized by traditional approaches. Reproduced with permission from Reference (Peng, 2008b). Copyright 2008, American Chemical Society.

investigated. However, alignment of nanotubes still needs to be improved, and properties of composites are not as good as expected. Recently, an effective approach has been developed by the use of nanotube arrays, sheets, and fibers with highly aligned nanotubes as building blocks to synthesize composite materials. Successful systems have been extensively reported by us and other groups. This chapter describes recent progress in aligned nanotube/polymer materials with excellent mechanical, electrical, and sensing properties.

For the convenience of readers, the basic synthesis and characterization of nanotube arrays, sheets, and fibers which are crucial to fabricate high-quality composites are first discussed in this chapter. Then the main efforts are paid to the preparation of aligned nanotube/polymer arrays, films, and fibers with emphasis on the improved mechanical, electrical, and sensing properties.

2. Aligned carbon nanotubes in forms of arrays, sheets, and fibers

2.1 Carbon nanotube arrays

Nanotube arrays are typically synthesized through a chemical vapor deposition process in which the catalytic metal (e.g., Fe, Co, or Ni) film on SiO_2/Si wafer form nanoparticles at high temperature to assist nanotube growth. High-efficiency catalysts are critical to grow high-quality aligned nanotube arrays. Iron possibly represents the most studied catalyst system (Fan et al., 1999). For the traditional direct coating of iron film on SiO_2/Si wafer, the iron layer generally becomes inactive within several minutes of nanotube growth due to its inter-diffusion with the substrate and accumulation of amorphous carbon. In order to grow longer nanotube arrays, catalyst precursors were continuously added to the system to nucleate new catalyst nanoparticles during the growth, however, the arrays were often composed of several stacked layers of nanotubes. In addition, the nanotubes grown in this way were often accompanied by excessive catalyst particles and amorphous carbon.

Recently, a new approach was reported, in which a thin Al_2O_3 layer was introduced between the catalyst and substrate to efficiently improve the growth of nanotubes (Li et al., 2006). The dense buffer layer enhances the Fe wettability during the preparation of catalyst. In addition, the Al_2O_3 layer functions as a buffer to prevent the inter-diffusion between Fe and substrate, and further improves the formation of stable catalyst nanoparticles during the nanotube growth.

For the Fe/Al_2O_3 catalyst system, the thickness uniformity of the Fe film is critical to grow good nanotube arrays. As compared in Figure 2, for the catalyst of Fe (thickness of 1 nm)/Al_2O_3 (thickness of 10 nm) under the same experimental conditions, the non-uniform Fe film melted to form polydisperse nanoparticles from which no nanotube array was grown (Figure 2a), while the uniform Fe film produced monodisperse nanoparticles which assisted the growth of long nanotube array (Figure 2b). The sizes of nanoparticles may be qualitatively controlled by the thickness of Fe film, which typically ranges from 0.2 to 1 nm. The resulting nanotubes are mainly multi-walled with diameters from 7 to 50 nm.
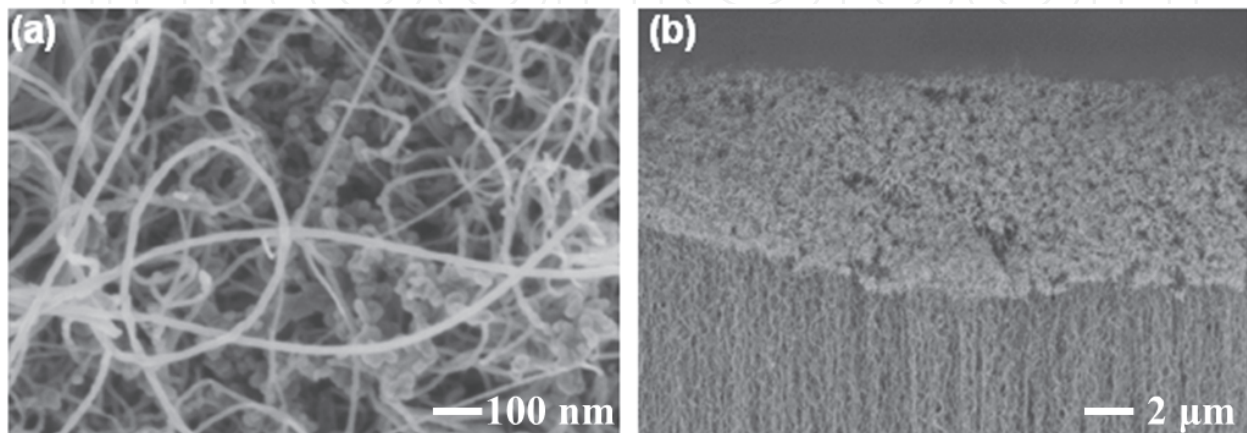

Fig. 2. The influence of the uniformity of Fe film on growth of aligned nanotube arrays. (a) Scanning electron microscopy (SEM) image of grown nanotubes by the use of non-uniform Fe film. (b) SEM image of grown nanotubes by the use of uniform Fe film. The thickness of the used Fe film was the same of 1 nm.

In a typical synthesis, the growth is fast (e.g., ~ 60 μm/min) in the first 20 min; afterwards, the growth gradually slows down and was normally terminated at 90 min. The growing rate also depends on the synthetic temperature. Zhu et al. had investigated a temperature range of 730–780 ºC, and found that the growing rates increased with increasing temperatures, e.g., 46 μm/min at 730 ºC, 64 μm/min at 750 ºC, and 74 μm/min at 780 ºC (Li, Q. et al., 2006). Water vapor, a weak oxidant, also greatly affected the growth of nanotubes in a more complex behavior. Introduction of water vapor did not obviously promote the growth of nanotubes at a lower temperature range of 730 to 750 ºC. In contrast, it significantly increased the growing rates of nanotubes at a higher temperature range from 750 to 780 ºC. In addition, water vapor had been found to prolong the growth time from 90 to 120 min, which produced longer nanotubes.

In order to further improve the production of nanotube arrays, an approach based on continuously moving substrates has been developed during chemical vapor deposition processes. As shown in Figure 3, the Fe/Al_2O_3 catalyst on Si substrate was fed continuously into the growth zone of the furnace through a moving stage driven by external motor, and nanotube arrays were then realized to be produced at large scale (de Villoria et al. 2009). Currently, the nanotube arrays could be grown at moving speeds of substrates up to 2.4 mm/s. No obvious differences had been observed for the resulting nanotube arrays between static and moving growth models.
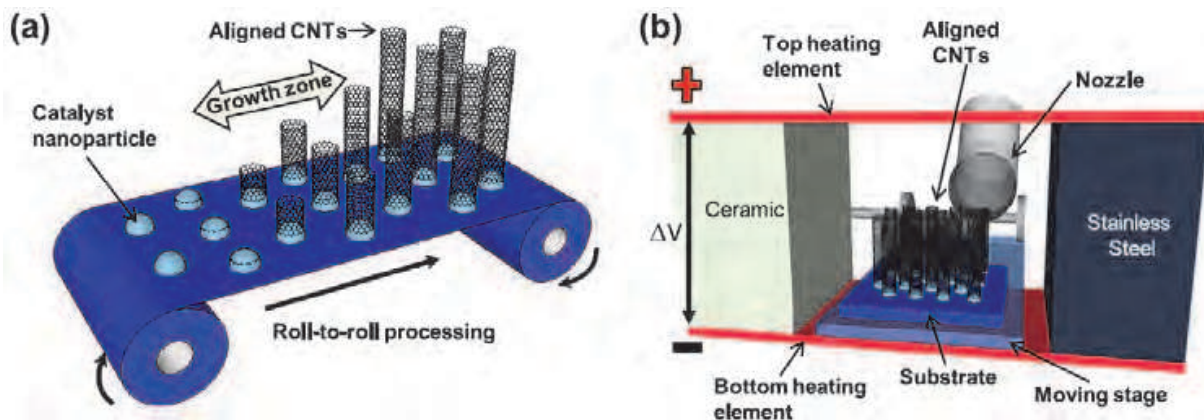
Fig. 3. (a) Schematic illustration of the continuous feeding of the catalyst. (b) Schematic construction of the synthetic system. Reproduced with permission from Reference (de Villoria et al., 2009). Copyright 2009, IOP Publishing.

2.2 Carbon nanotube sheets

A general and efficient route of preparing aligned nanotube sheets is to directly spin them out of the above array. Figure 4a schematically shows the formation of nanotube sheet spun from an array. Figure 4b and 4c further show scanning electron microscopy images of nanotube sheets in which nanotubes are highly aligned along the spinning direction as required. The measured areal sheet density was 2.7 $\mu g/cm^2$ and the volumetric density was 1.5 $\mu g/cm^3$. The density of nanotube sheet can be further improved, e.g., 0.5 g/cm^3, simply by immersing them into a liquid along the nanotube-aligned direction and then taking them out (Zhang, M. et al., 2005).

It should be noted that most nanotube arrays are not spinnable. In order to investigate their spinnability, nanotube arrays grown with increasing growth times from 10 to 180 min were first compared as model materials (Huynh & Hawkins, 2010; Sun & Peng, unpublished results). It was found that the prolonged growth time dramatically decreased the spinnability of the arrays, and the arrays grown longer than 30 min did not show good spinnability. For instance, long sheets up to meters were spun from the arrays grown in 15 min; sheets with length of centimeters were spun from the arrays grown in 40 min as the sheets easily broke during the spinning process; even worse, only short clumps were pulled out of the arrays grown in 180 min. The morphologies of the arrays were studied by scanning electron microscopy (Sun & Peng, unpublished results). The nanotube array shows very clean surfaces at growth times below 30 min. With the increase of growth time, a disordered layer was observed at the top of the arrays. The thickness of this layer increased with increasing growth time. Figure 5 compares the top and side views of arrays synthesized with different growth times of 15 and 90 min. The array grown in 15 min is clean without aggregates, while a lot of flake-like carbon aggregates are found at the top of the nanotube array grown in 90 min. These flakes are randomly piled, and their sizes decrease with increasing growth times. The flakes severely hinder the spinnability of synthesized arrays.

Besides growth time, the other experimental conditions including substrate, temperature, gas flow rate, and catalyst as well as its pre-treatment are also critical for synthesis of spinnable nanotubes. Huynh et al. and Zhang et al. had systematically investigated the effects of above variables that influence the spinnability of nanotubes, respectively (Huynh,
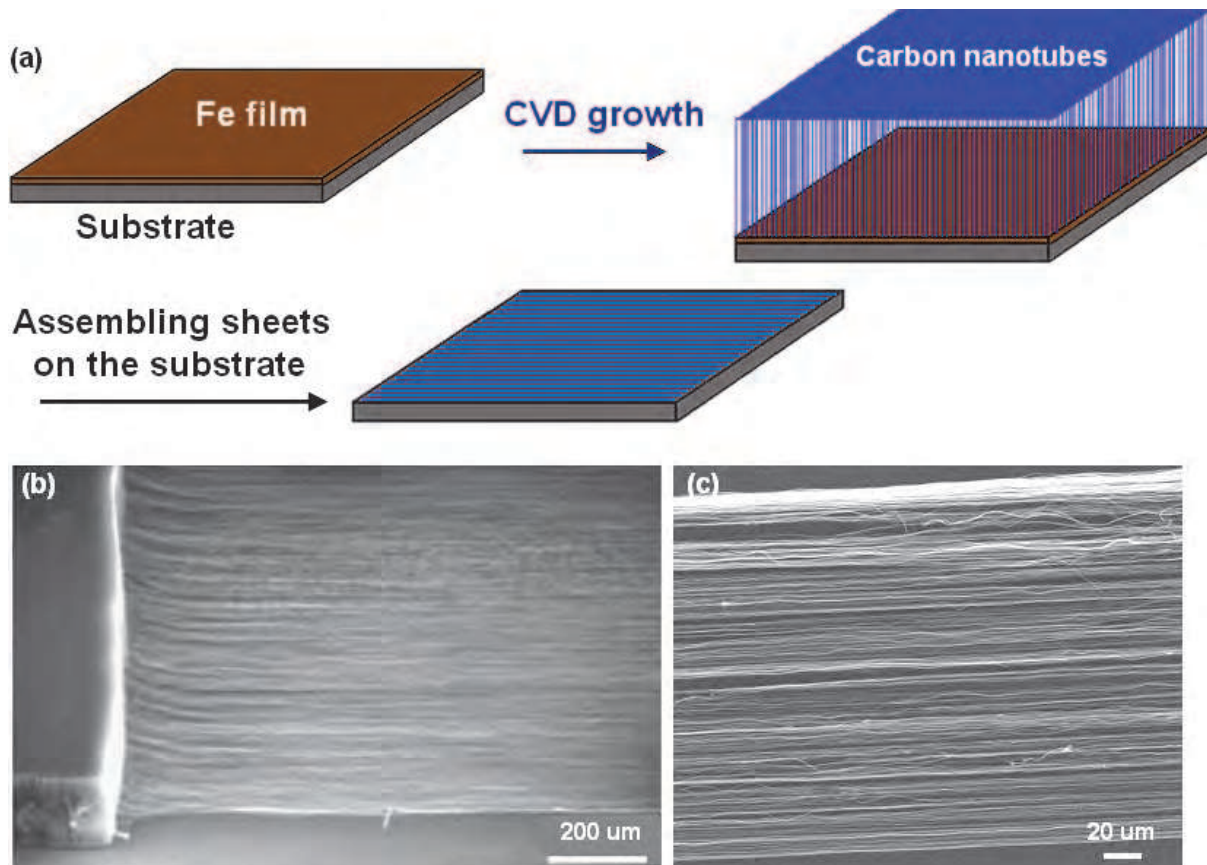
Fig. 4. Fabrication of nanotube sheets by a direct spinning method. (a) A schematic illustration. (b) SEM image for the formation of nanotube sheet from an array. Reproduced with permission from Reference 21. Copyright 2005, American Association for the Advancement of Science. (c) SEM image of a nanotube sheet. Reproduced with permission from Reference (Peng, 2008b). Copyright 2008, American Chemical Society.

2010; Zhang, Y. et al.; 2010). However, there is no simple reason or key factor for nanotube spinnability. In addition, although the surface morphology and alignment of nanotube arrays had been demonstrated to be very important for their spinnability, no unique characteristic is found to obviously distinguish a spinnable from a non-spinnable array. It was shown that nanotube arrays could be spinnable or not for a wide variety of height (80-900 μm) with nanotube diameters ranging from 7 to 11 nm and areal densities across an order of magnitude. Although it is difficult to fully understand the mechanism of nanotube spinnability currently, two possible models had been suggested by Fan et al. and Baughman et al., respectively (Zhang, M. et al., 2004; Zhang, X. et al., 2006). Fan and co-workers proposed that the unique features of spinnable nanotube arrays lied in that the nanotubes had very clean surfaces, and consequently there were strong van der Waals interactions among them (Zhang, X. et al., 2006). When nanotubes were pulled out of the arrays, it was the van der Waals force that made the nanotubes to join end to end to form a continuous sheet. Baughman and co-workers claimed that the spinnability was due to the disordered region at the top and bottom of the nanotube array, which entangled together forming a loop (Zhang, M. et al., 2004, 2005). The above mechanisms had been demonstrated to work for specific arrays. However, as spinnable nanotube arrays greatly vary for different systems or even for the same systems, it remains challenging to draw general conclusions.
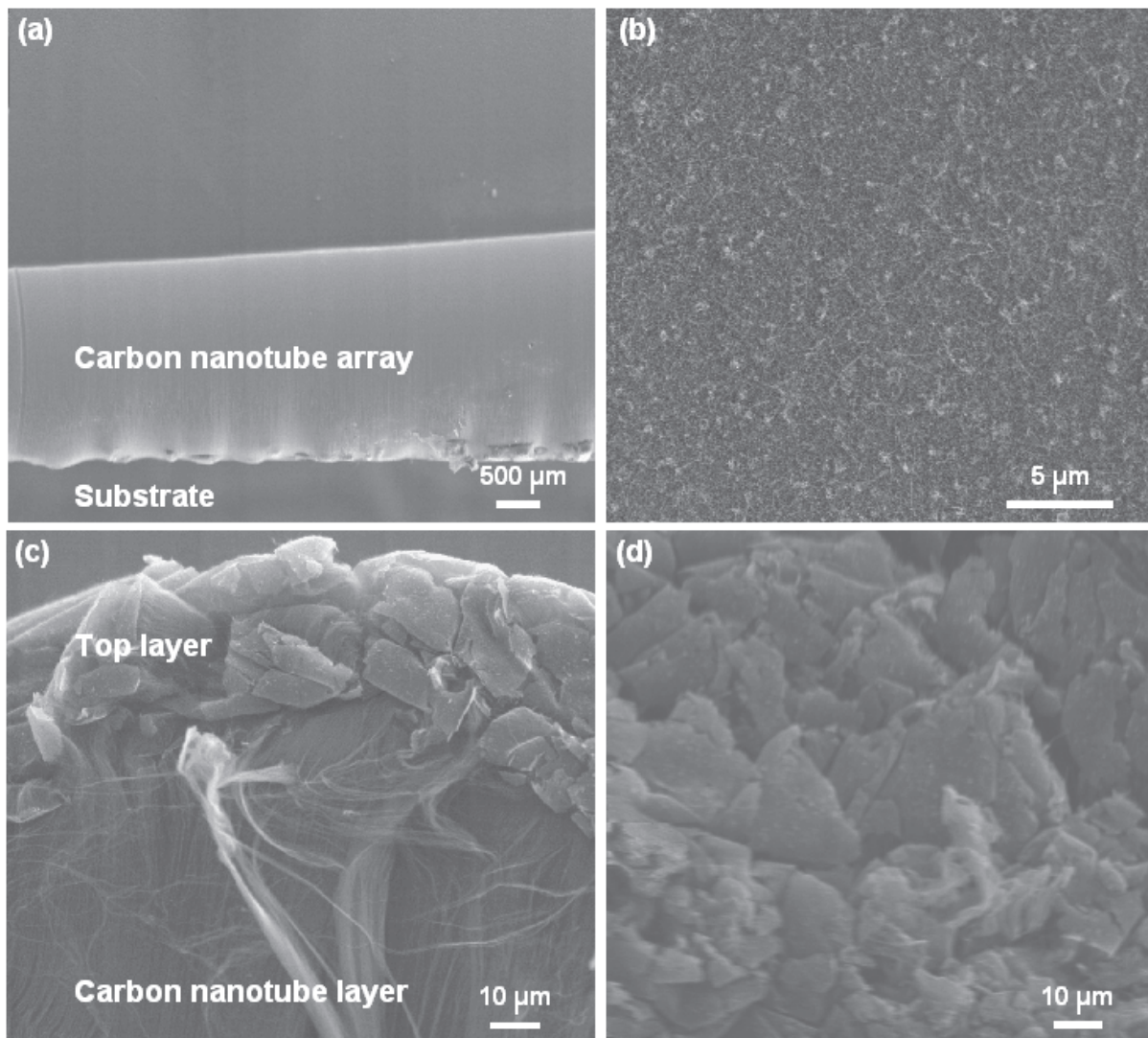
Fig. 5. Typical SEM images of (a) the spinnable nanotube array by side view, (b) the spinnable nanotube array by top view, (c) the non-spinnable nanotube array by side view, and (d) the non-spinnable nanotube array by top view.

2.3 Carbon nanotube fibers

Similar to nanotube sheets, nanotube fibers are mainly spun from nanotube arrays (Zhang, M. et al., 2004). Figures 6a and 6b show the formation of a fiber by twisting the nanotube sheet pulled out of an array. This spinning process can be easily scaled up to produce long nanotube fibers. The diameters of nanotube fibers can be controlled from 2 to 30 μm by tuning the initial ribbon width which is defined as a bunch of nanotubes pulled out of an array at the beginning of the spinning.

Although nanotube fibers are generally spun from aligned nanotube arrays, they had been also fabricated from nanotube cottons in which nanotubes were randomly arranged on substrates (Zheng et al., 2007). The cotton was composed of low-density nanotubes with length of centimeters and diameter of 100-380 nm, and these ultra-long nanotubes were entangled to form continuous fibers. The other methods, e.g., wet spinning of nanotube dispersions (Zhang, M. et al., 2004) and direct spinning from chemical vapor deposition reactions(Ericson et al.; 2004), had been also developed to fabricate nanotube fibers. Figure 6c shows a spool of 30-m
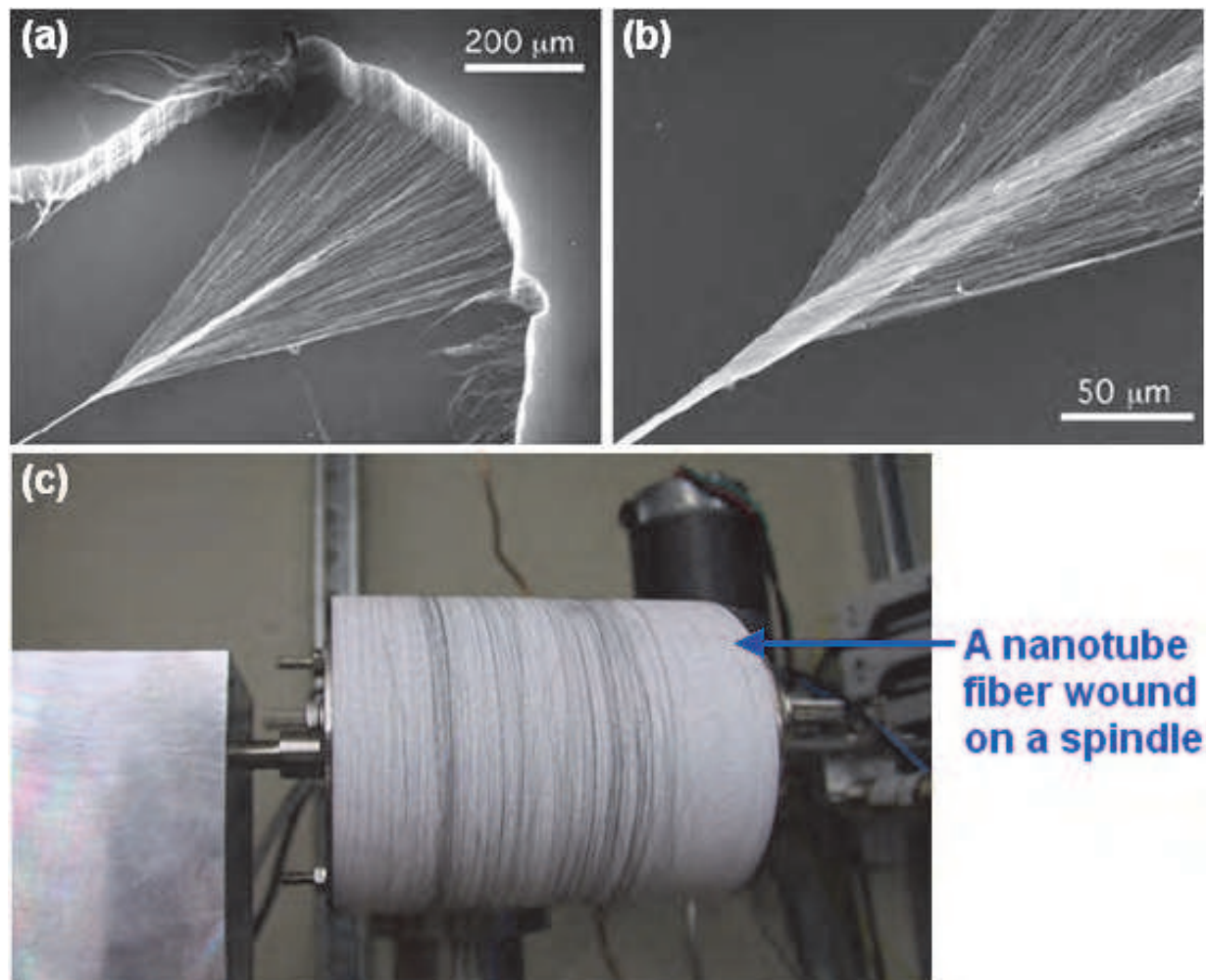
Fig. 6. (a) and (b) SEM images of a nanotube fiber spun out of an array. Reproduced with permission from Reference (Zhang, M. et al., 2004). Copyright 2004, American Association for the Advancement of Science. (c) A 30-m spool of nanotube fiber fabricated by a solution spinning process. Reproduced with permission from Reference (Ericson et al., 2004). Copyright 2004, American Association for the Advancement of Science.

nanotube fiber wound on a spindle via a solution spinning process (Ericson et al.; 2004). Nanotube fibers showed much higher density of ~ 0.8 g/cm^3 compared with nanotube sheets (Zhang, M. et al., 2004). The linear density is typically 10 μg/m compared with 10 mg/m and 20-100 mg/m for cotton and wool yarns, respectively. That is, about a million of nanotubes pass through the cross section of a fiber with diameter of 5 μm. As nanotubes are tightly bundled together inside, nanotube fibers had shown excellent mechanical and electrical properties, e.g., high tensile strengths and electrical conductivities.

In general, the tensile strength of a twisted fiber can be described by the equation of $\delta_f/\delta_{nanotube} \approx \cos\alpha[1 - (k\csc\alpha)]$, where δ_f and $\delta_{nanotube}$ are the tensile strengths of the fiber and the nanotube, respectively; α is the twist angle; and $k = (dQ/\mu)^{1/2}/3L$ with d of the nanotube diameter, L of the nanotube length, μ of the friction coefficient among nanotubes, and Q of the nanotube migration length (Li, Y. L. et al., 2004). Therefore, the fiber strength increases with increasing nanotube length and decreasing nanotube diameter. For instance, the nanotube fibers spun from arrays of 300, 500, and 650 μm in thickness showed tensile

strengths of 0.32, 0.56, and 0.85 GPa, respectively (Li, Y. L. et al., 2004); the diameter of spinnable nanotubes typically ranges from 7 to 11 nm. Post-spin twisting can also improve their tensile strengths with larger twist angle and higher density of building nanotubes. For instance, the twist angle of outer nanotubes increased from 10º to 21º; the density of nanotubes increased two times with decreasing fiber diameter from 10 to 7 μm, and the closer contact among nanotubes enhanced their van der Waals forces and frictions with better load transfers. Similarly, a solution treatment can also increase the fiber densities with improved tensile strengths. Zhu and co-workers reported that the specific strength of nanotube fiber could be 5.3 times the specific strength of the strongest commercial carbon fiber (T1000), and the specific stiffness of nanotube fiber could be 4.3 times the specific stiffness of the stiffest commercial carbon fiber (M70J) (Zhang, X. et al., 2007). Windle and co-workers further increased the tensile strength of nanotube fiber to ~9.6 GPa (Koziol et al., 2007). Figure 7 compares the specific strength and specific stiffness of the above nanotube fibers (the elliptical area at the top left corner of the graph) with other high-performance engineering fibers.
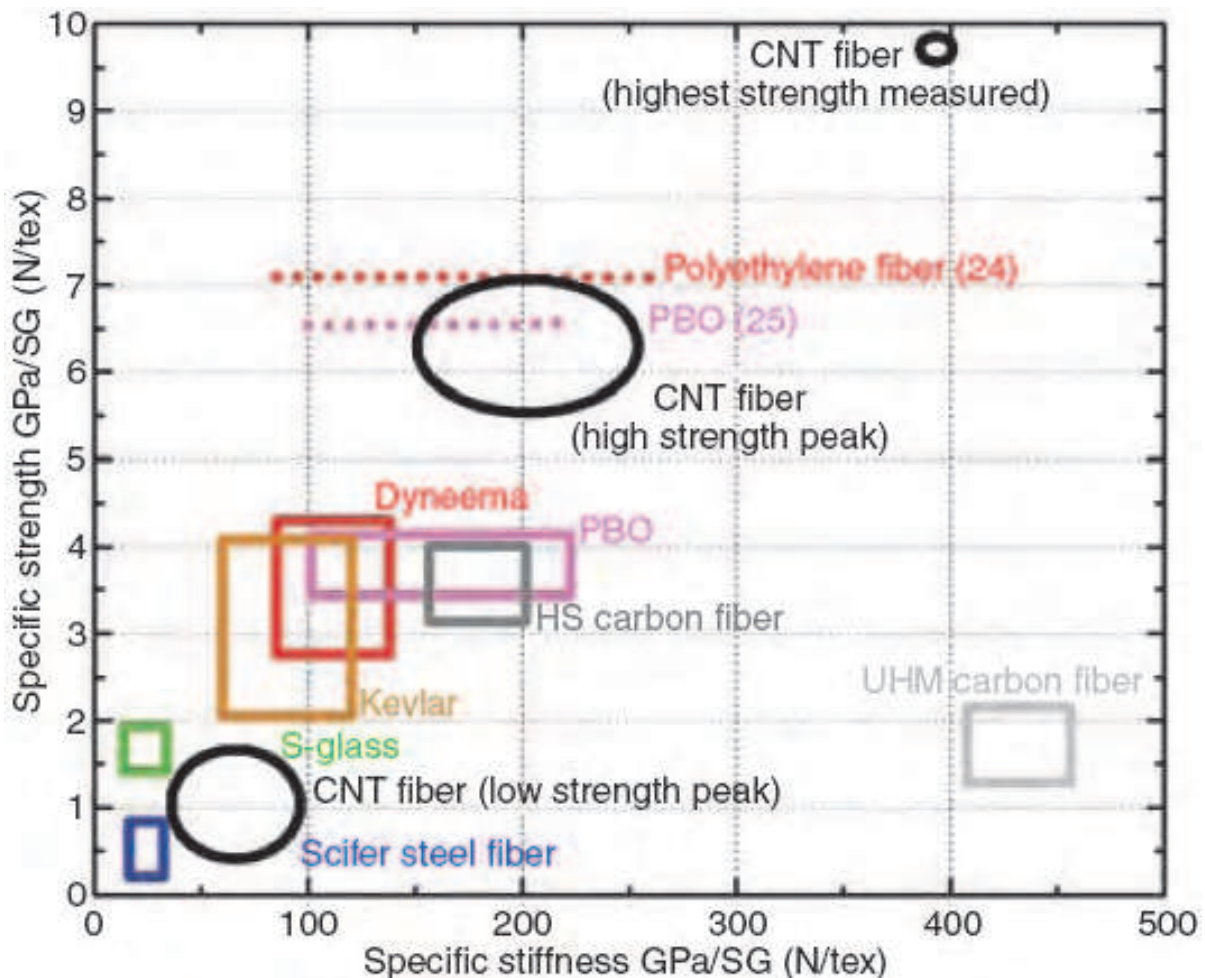

Fig. 7. Comparison of the specific strength and specific stiffness of nanotube fibers versus the properties of other commercially available high-performance fibers. Reproduced with permission from Reference (Koziol et al., 2007). Copyright 2007, American Association for the Advancement of Science.

Nanotube fibers showed excellent electrical conductivities up to 10^3 S/cm at room temperature. Figure 8a further indicates the temperature dependence of a nanotube fiber's conductivities measured by a four-probe method. The conductivity increases with the increase of the temperature, suggesting a semiconducting behavior. For the temperature dependence of conductivity, two main mechanisms had been suggested, i.e. variable range hopping mechanism and tunneling conduction mechanism (Li, Q. et al., 2007; Peng et al., 2008c). A systematic comparing study showed that the conduction in nanotube fibers was mainly controlled by the hopping mechanism. In more detail, the relationship between conductivity and temperature in hopping model can be also expressed as $\sigma \propto \exp(-A/T^{[1/(d+1)]})$, where A is a constant and d is the dimensionality. The plots of $\ln\sigma$ *vs.* $T^{-1/4}$ (for d=3), $T^{-1/3}$ (for d=2) and $T^{-1/2}$ (for d=1) show decreasing linear fitting coefficients (Figures 8b, 8c, and 8d), which suggests that the electron transport is more consistent with a three-dimensional hopping mechanism. This behavior is most likely due to the defect structures of nanotubes and a lot of contacting points among neighboring short nanotubes in fibers. Therefore, electrons cannot be confined in the one-dimensional channel along the nanotube-aligned direction. Instead, electrons hop from one localized site to another, or possibly from a nanotube to another.
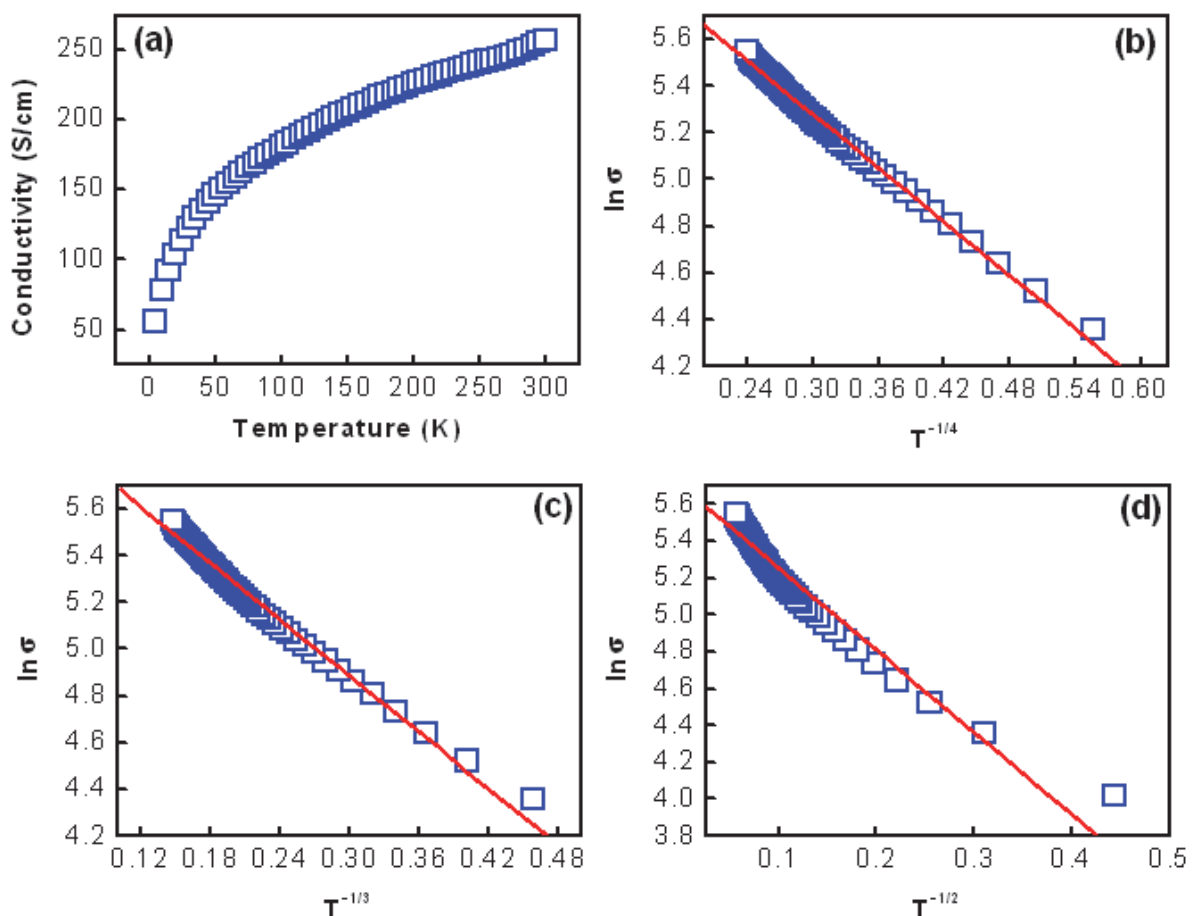

Fig. 8. Electrical properties of a nanotube fiber. (a) Temperature dependence of the conductivity measured by a four-probe method. (b) Three-dimensional hopping conduction model by plot of $\ln\sigma$ vs. $T^{-1/4}$. (c) Two-dimensional hopping conduction model by plot of $\ln\sigma$ vs. $T^{-1/3}$. (d) One-dimensional hopping conduction model by plot of $\ln\sigma$ vs. $T^{-1/2}$.

The electrical properties of nanotube fibers largely depend on structural changes of nanotubes. Therefore, their conductivities can be tuned by different chemical treatments. Oxidization on their surfaces increased the fiber's conductivities by introduction of acceptor dopant groups. The covalent link of metal nanoparticles onto nanotubes also enhanced the fiber's conductivities through an increase of carrier density. However, annealing of nanotube fiber in forming gas (94% Ar and 6% H_2) significantly lowered their conductivity due to the formation of sp^3 carbon bonds (Li, Q. et al., 2007).

3. Aligned carbon nanotube/polymer composites

3.1 Preparation of aligned carbon nanotube/polymer composites

The structures of aligned nanotube/polymer composites in the forms of arrays, films, and fibers have been schematically shown in Figure 9. Polymers are incorporated into nanotubes which maintain the high alignments. These composites are mainly synthesized through the use of above pure nanotube arrays, sheets, and fibers, and the other fabrication methods will be also compared later.

Aligned nanotube/polymer arrays are typically prepared by immersing a pure nanotube array into polymer solution, followed by evaporation of solvent (Peng & Sun, 2009). For this approach, a wide variety of polymers (either plastic or conjugated polymers) may be used to fabricate composite arrays. Figure 10 compares a nanotube array before and after incorporation with polystyrene. Obviously, nanotubes maintained the high alignment in polymer matrix. Similarly, aligned nanotube/polymer composites could be also synthesized by first immersing pure nanotube arrays into monomers, followed by polymerization of monomers (Feng et al., 2003; Raravikar et al., 2005; Yang et al., 2008). Recently, porous nanotube arrays were fabricated after heating treatment of as-synthesized dense nanotube arrays or through the use of polystyrene beads (Das et al., 2009; Dionigi et al., 2007), and polymers could be incorporated into the pores to form aligned nanotube composites.

The aligned nanotube/polymer films are produced by spin-coating or casting polymer solutions onto nanotube sheets, followed by evaporation of solvents. Film thickness may be controlled by varying concentrations of polymer solutions and coating times. After incorporation of designed polymers such as polystyrene, poly(methyl methacrylate), or sulfonated poly(ether ether ketones), the derived composite films were transparent and showed optical transparencies of higher than 80% (thickness of ~5 μm) (Peng, 2008b).

Alignment of nanotubes in both composite arrays and films had been also realized through the use of external stimuli such as mechanical force, magnetic field, and electrical field (Ahir et al., 2006; Ajayan et al., 1994; Jin et al., 1998; Kimura et al., 2002; Zhu et al., 2009). As to
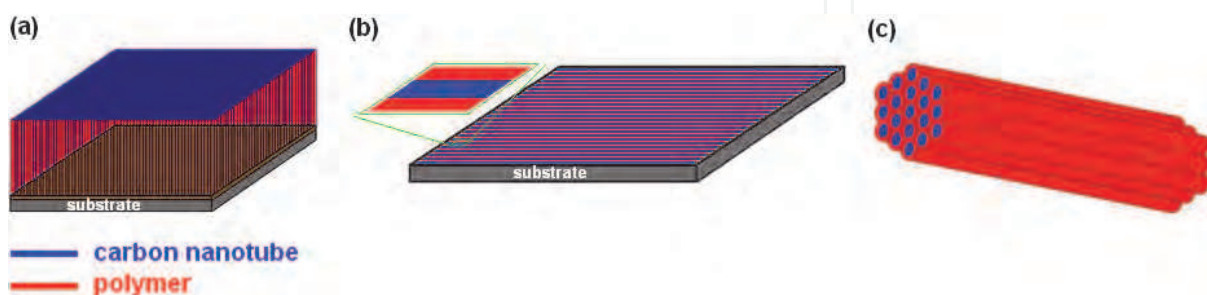

Fig. 9. Schematic illustration of the aligned nanotube/polymer composites in the forms of (a) array, (b) film, and (c) fiber.
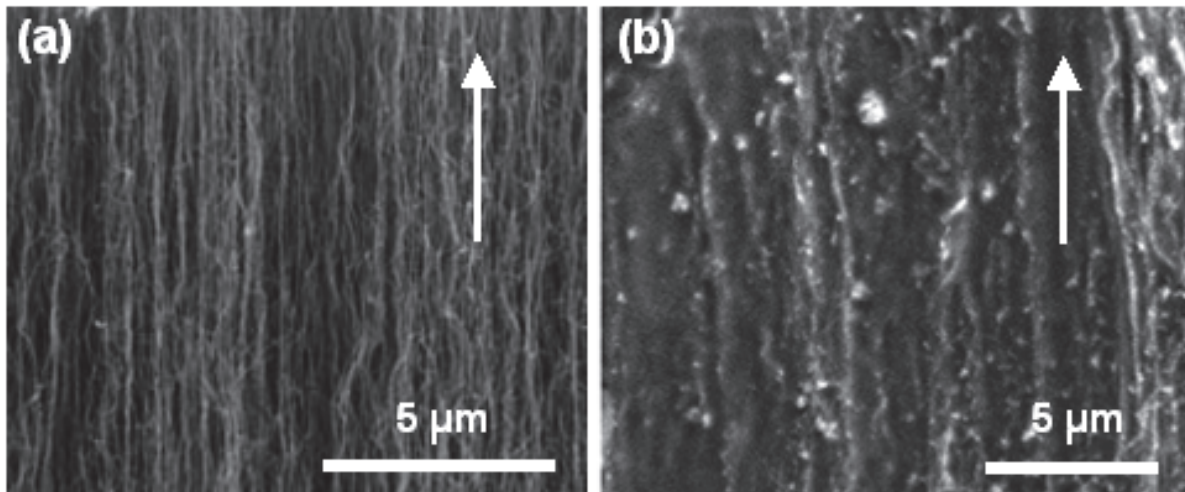
Fig. 10. SEM images of the aligned nanotubes (a) before and (b) after formation of composite with polystyrene. The white arrows show the aligned directions of nanotubes. Reproduced with permission from Reference (Peng & Sun, 2009). Copyright 2009, Elsevier.

mechanical force, cutting nanotube/resin composites induced nanotubes on the surface to align along the cutting direction (Kimura et al., 2002), or mechanical stretching of nanotube/polyhydroxyaminoether composites at high temperature aligned nanotubes in polymer matrix (Kimura et al., 2002). For the synthesis of aligned nanotube/polymer composites by magnetic field, monomers in nanotube solutions were polymerized in a mold under magnetic field (Kimura et al., 2002). Alignment of nanotubes was based on their anisotropic nature. Alignment of nanotubes in bulk epoxy matrix was available by application of electrical field, where nanotube/epoxy composites were prepared by a layer-by-layer method (Zhu et al., 2009). Alignment of nanotubes was due to polarization of their high aspect ratios under electrical field. However, composites by these methods show relatively low alignments of nanotubes compared to the use of nanotube arrays or sheets. The alignment of nanotubes may be assessed by microscopy technology, X-ray diffraction, and polarized Raman spectroscopy.

Aligned nanotube/polymer fibers can be directly prepared by physical attachment or chemical reaction of polymers onto nanotubes in pure nanotube fibers. To improve the uniformity of polymers, monomers may be first incorporated into nanotube fibers followed by polymerization as monomers can penetrate into much smaller voids in nanotube fibers and form more uniform composites through solution processes. For instance, high-quality nanotube/polydiacetylene composite fibers were produced by the physical attachment of diacetylenic monomers followed by topochemical polymerization of diacetylenic moieties under UV light (Peng et al., 2009).

Another widely explored method to aligned nanotube/polymer fibers is electrospinning, an electrostatically induced self-assembly process where nanoscale fibers were typically produced (Baji et al., 2010; Ge et al., 2004; Go et al., 2004; Kang et al., 2009). The surface tension, jet elongation, and slow relaxation of nanotubes contribute to orientation of nanotubes. Some other approaches including coagulation-based spinning (Razal et al., 2007; Vigolo et al., 2000 & 2002), melting spinning (Haggenmueller et al., 2003), dip coating method through microfluidic phenomena (Jang et al., 2009), and orientation by external stimuli such as mechanical interaction (Ji et al., 2009) had been also developed to synthesize

aligned nanotube/polymer fibers. However, similar to the composite arrays and films, the nanotube alignments in the resulting composite fibers are much lower compared to the direct use of pure nanotube fibers.

3.2 Improved mechanical, electrical, and sensing properties of aligned carbon nanotube/polymer composites

The alignment of nanotubes has greatly improved the mechanical properties of their polymer composites. Figure 11 compares the tensile strengths of less aligned nanotube/polymer fibers and aligned nanotube/polymer fibers. The nanotube/polymer fibers at Figure 11a were fabricated through a melting spinning process, i.e., the melting nanotube/nylon 6 mixtures were pressurized through a spinneret to form composite fibers (Gao et al., 2005). The nanotube/nylon 6 fibers showed relatively low strengths of less than 100 MPa. In contrast, the aligned nanotube/polymer fibers exhibited the strength of higher than 1000 MPa (Figure 11b).
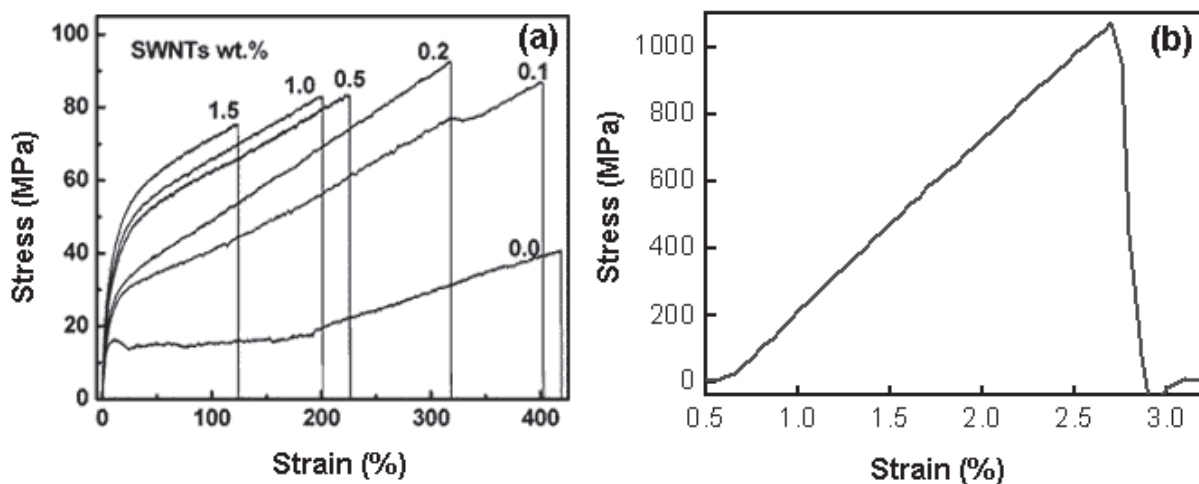

Fig. 11. Comparison of the mechanical strengths for (a) non-aligned nanotube/polymer fibers and (b) aligned nanotube/polymer fibers. Reproduced with permission from Reference (Gao et al., 2005). Copyright 2005, American Chemical Society.

The alignment of nanotubes has also greatly improved the electrical properties of their polymer composites. Figure 12 summarizes and compares the conductivities of randomly dispersed nanotube/polymer composites and aligned nanotube/polymer composites in forms of arrays, films, and fibers (Peng et al., 2008a, 2008b, 2008c; Peng & Sun, 2009). The non-aligned nanotube/polymer composites (including arrays, films, and fibers) fabricated through traditional solution blending or melt blending generally show conductivities lower than 10^{-1} S/cm at room temperature. As a comparison, the aligned nanotube/polymer arrays, films, and fibers show conductivities of 1-100 S/cm, 10-200 S/cm, and 10^2-10^3 S/cm at room temperature, respectively. The aligned nanotube/polymer composites followed a three-dimensional hopping conduction mechanism, which can be important for some optoelectronic applications (Peng et al., 2009).

The improved mechanical and electrical properties of above aligned nanotube/polymer composite have been realized through the direct use of nanotube arrays, sheets, and fibers. In the case of other approaches to align nanotubes (Baji et al., 2010; Ge et al., 2004; Go et al.,

2004; Haggenmueller et al., 2003; Jang et al., 2009; Ji et al., 2009; Kang et al., 2009; Razal et al., 2007; Vigolo et al., 2000, 2002), similar improvements were also observed. For instance, aligned nanotube/polyacrylonitrile fibers after hot-stretching treatment showed a significant enhancement of tensile strength by 320.7% (Ji et al., 2009), while aligned nanotube/epoxy arrays induced by electric field could improve electrical conductivities by four orders of magnitude in the direction of alignment (Zhu, Y. et al., 2009). However, possibly due to the relatively low degree of alignment, both strengths and conductivities were much lower compared with the direct use of aligned nanotube materials, e.g., strength below 325 MPa and conductivity of 10^{-10}–10^{-8} S/cm at room temperature for the discussed nanotube/polyacrylonitrile fibers and nanotube/epoxy arrays, respectively.

Orientation factor had been already used to quantitatively characterize the alignment degree of nanotubes through Herman's equation of $f = (3 <\cos^2\theta> - 1)/2$, where θ is the average angle between the nanotube and the aligned direction determined by Raman spectroscopy (Ge et al., 2004). However, the orientation factors were only available in very limited studies. Therefore, it remains difficult to quantitatively compare the experimental results (e.g., strengths and conductivities) of nanotube/polymer composites among different methods or different lab.
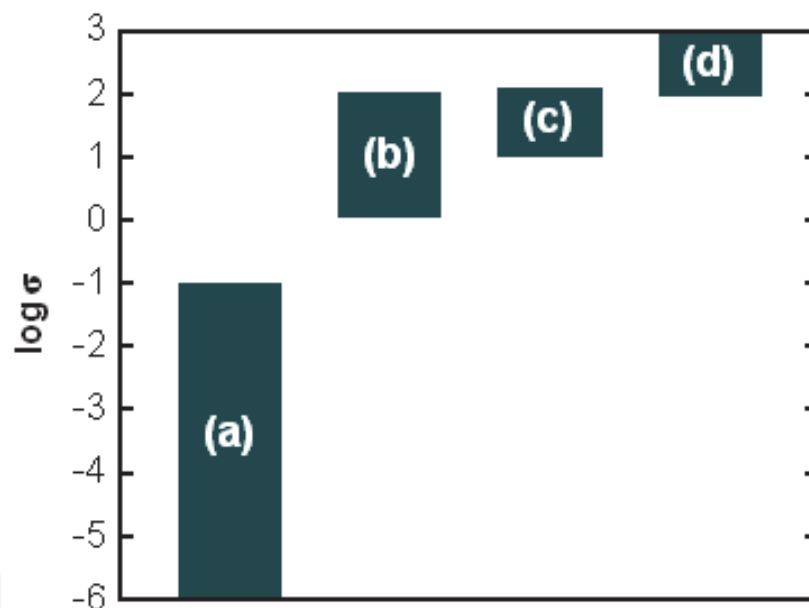

Fig. 12. Comparison of the electrical conductivities for (a) non-aligned nanotube/polymer composites, (b) aligned nanotube/polymer arrays, (c) aligned nanotube/polymer films, and (d) aligned nanotube/polymer fibers.

Nanotubes show the gas sensing capabilities through the changes of resistances after gas sorption. However, the use of non-aligned nanotubes for the sensing detection often needs tedious fabrication processes to integrate single nanotubes into sensors, and the number of analytes is also largely limited. In contrast, aligned nanotubes do not need direct manipulation of individual nanotubes. Particularly, the resistance changes of individual nanotubes could be greatly amplified as millions of nanotubes were collectively addressed through a common electrode (Lin et al., 2003; Wei et al., 2006; Zhu, Z. et al., 2010). For instance, Wei et al. reported that aligned nanotube/poly(vinyl acetate)

arrays showed high sensitivity and good selectivity to a wide variety of chemical vapors such as tetrahydrofuran, ethanol, and cyclohexane (Wei et al., 2006). The similar improvements at sensing capabilities after the nanotube alignment had been also observed for detections of the glucose and other biosensing applications (Lin et al., 2003; Zhu, Z. et al., 2010).

As previously discussed, the aligned nanotube/polymer composites show a semiconducting behavior with three-dimensional hopping conduction mechanism. This electrical property provides composites with other unexpected sensing properties. For instance, polydiacetylene is well known to change colors under external stimuli such as temperature, pH, solvent, and mechanical stress, mainly due to the conformation change of the conjugated backbone (Peng et al., 2007; Sun et al., 2010a, 2010b). By incorporation of polydiacetylene into aligned nanotube fibers, polydiacetylene was first realized to rapidly and reversibly change colors under electrical current, typically from blue to red (Figure 13) (Peng et al., 2009). The capability of forming strong electrical fields among aligned nanotubes was believed to induce the conformation change of incorporated polydiacetylene with the chromatic transition.
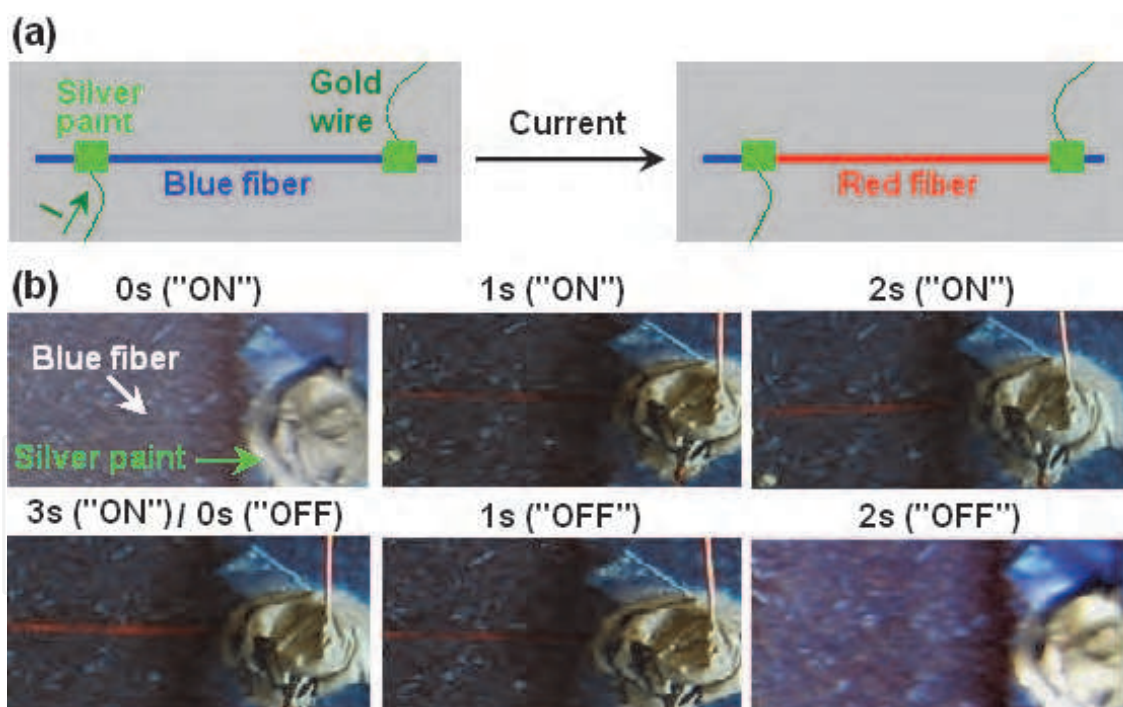

Fig. 13. Chromatic transitions of nanotube/polydiacetylene fibers in response to electric current. (a) Schematic illustration of experimental setups for current-induced chromatism. (b) Rapid and reversible electrochromatism. Reproduced with permission from Reference (Peng et al., 2009). Copyright 2009, Nature Publishing Group.

4. Conclusion

This chapter has mainly described the realization and importance of alignment of nanotubes in their polymer composites. Three typical forms of composites including arrays, films, and fibers are fabricated through the use of nanotube arrays, sheets, and fibers, respectively. The aligned nanotube composites have exhibited much improved mechanical, electrical, and sensing properties compared with those without alignment of nanotubes. The aligned nanotube/polymer composites may show promising applications in a wide variety of fields, particularly as high-end components for aerospace, energy, and other structural and optoelectronic materials.

Despite the great progresses having been made on fabrications, characterizations, and properties of aligned nanotube/polymer composites, here we also hope to call attention to a few key unmet challenges on further developing this new family of functional materials in the future.

Firstly, increasing attentions should be paid to establishing quantitative relationships between the alignment degrees of nanotubes and the properties (e.g., strengths and conductivities) of the composites. Therefore, it becomes available to accurately compare different fabrication approaches and different composite systems, which may provide important and general clues to improve the composite properties.

Secondly, most nanotube arrays are not spinnable, and more efforts are required to understand and control the spinnability of nanotube arrays to fabricate high-performance composite films and fibers. For instance, the mechanical and electrical properties of aligned nanotube/polymer composites strongly depend on the length of nanotubes. The longer the nanotubes, the better are the properties of composites. However, spinnable nanotube arrays range from 80 to 900 μm in height, and higher arrays are typically not spinnable. For the spinnability of nanotube arrays, another crucial issue is related to the nanotube alignment. It had been qualitatively shown that a high alignment of nanotubes was required for their spinnability (Sun & Peng, Unpublished results; Zhang, M. et al., 2005). However, as no quantitative characterizations have been made for the alignment degrees of nanotubes in arrays, it remains unclear for an accurate relationship between the alignment and spinnability of nanotube arrays.

Thirdly, polymers are mainly incorporated into aligned nanotubes through non-covalent interactions, and very few studies can be found to connect polymers and nanotubes by chemical bonds. Nevertheless, compared to physical attachment, polymers can be more uniformly incorporated into nanotubes by chemical modifications, and the resulting composites show more excellent properties, e.g., improved mechanical strengths as polymers cross-link neighboring nanotubes. Of course, some other issues such as uniformity in the composite and repeatability of the fabrication are also important for the development of aligned nanotube/polymer composites, particularly for their practical applications.

5. Acknowledgement

6. References

Ahir, S. V.; Squires, A. M.; Tajbakhsh, A. R. & Terentjev, E. M. (2006). Infrared actuation in aligned polymer-nanotube composites. Phys. Rev. B, Vol. 73, No. 8, (February 2006), pp. 085420(12).

Ajayan, P. M. & Tour, J. M. (2007). Nanotube composites. Nature, Vol. 447, (June 2007), pp. 1066-1068.

Ajayan, P. M.; Stephan, O.; Colliex, C. & Trauth, D. (1994). Aligned Carbon Nanotubes Arrays Formed by Cutting a Polymer Resin-Nanotube Composite. Science, Vol. 265, No. 5176, (August 1994), pp. 1212-1214.

Baji, A.; Mai, Y.; Wong, S.; Abtahi, M. & Du, X. (2010). Mechanical Behavior of Self-Assembled Carbon Nanotube Reinforced Nylon 6,6 Fibers. Compos. Sci. Technol., Vol. 70, No. 9, (September 2010), pp. 1401-1409.

Das, R. K.; Liu, B.; Reynolds, J. R. & Rinzler, A. G. (2009). Engineered Macroporosity in Single-Wall Carbon Nanotube Films. Nano Lett., Vol. 9, No. 2, (February 2009), pp. 677-683.

de Villoria, R. G.; Figueredo, S. L.; Hart, A. J.; Steiner III, S. A.; Slocum, A. H. & Wardle, B. L. (2009). High-yield growth of vertically aligned carbon nanotubes on a continuously moving substrate. Nanotechnology, Vol. 20, No. 40, (October 2009), pp. 405611(8).

Dionigi, C.; Stoliar, P.; Ruani, G.; Quiroga, S. D.; Facchini, M. & Biscarini, F. (2007). Carbon nanotube networks patterned from aqueous solutions of latex bead carriers. J. Mater. Chem., Vol. 17, No. 35, (September 2007), pp. 3681-3686.

Ericson, L. M. et al. (2004). Macroscopic, Neat, Single-Walled Carbon Nanotube Fibers. Science, Vol. 305, No. 5689, (September 2004), pp. 1447-1450.

Fan, S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M. & Dai, H. (1999). Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. Science, Vol. 283, No. 5401, (January 1999), pp. 512-514.

Feldman, A. K.; Steigerwald, M. L.; Guo, X. F. & Nuckolls, C. (2008). Molecular Electronic Devices Based on Single-Walled Carbon Nanotube Electrodes. Acc. Chem. Res., Vol. 41, No. 12, (August 2008), pp. 1731-1741.

Feng, W.; Bai, X. D.; Lian, Y. Q.; Liang, J.; Wang, X. G. & Yoshino, K. (2003). Well-aligned polyaniline /carbon-nanotube composite films grown by in-situ aniline polymerization. Carbon, Vol. 41, No. 8, (2003), pp. 1551-1557.

Gao, J.; Itkis, M. E.; Yu, A.; Bekyarova, E.; Zhao, B. & Haddon, R. C. (2005). Continuous Spinning of a Single-Walled Carbon Nanotube−Nylon Composite Fiber. J. Am. Chem. Soc., Vol. 127, No. 11, (March 2005), pp. 3847-3854.

Ge, J. J.; Hou, H. Q.; Li, Q.; Graham, M. J.; Greiner, A.; Reneker, D. H.; Harris, F. W. & Cheng, S. Z. D. (2004). Assembly of Well-Aligned Multiwalled Carbon Nanotubes in Confined Polyacrylonitrile Environments: Electrospun Composite Nanofiber Sheets. J. Am. Chem. Soc., Vol. 126, No. 48, (November 2004), pp. 15754-15761.

Go, J. B.; Yu, A. P.; Itkis, M. E.; Bekyarova, E.; Zhou, B.; Niyogi, S. & Haddon, R. C. (2004). Large-Scale Fabrication of Aligned Single-Walled Carbon Nanotube Array and Hierarchical Single-Walled Carbon Nanotube Assembly. J. Am. Chem. Soc., Vol. 126, No. 51 (December 2004), pp. 16698-16699.

Guldi, D. M.; Rahman, G. M. A.; Zerbetto, F. & Prato, M. (2005). Carbon Nanotubes in Electron Donor-Acceptor Nanocomposites. Acc. Chem. Res., Vol. 38, No. 11, (September 2005), pp. 871-878.

Haggenmueller, R.; Zhou, W.; Fischer, J. E. & Winey, K. I. (2003). Production and Characterization of Polymer Nanocomposites with Highly Aligned Single-Walled Carbon Nanotubes. J. Nanosci. Nanotech., Vol. 3, No. 1-2, (February 2003), pp. 105-110.

Harris, P. J. F. (2004). Carbon nanotube composites. International Materials Reviews, Vol. 49, No. 1, (February 2004), pp. 31-43.

Hong, S. & Myung, S. (2007). Nanotube Electronics: A flexible approach to mobility. Nature Nanotechnology, Vol. 2, (April 2007), pp. 207–208.

Huynh, C. P. & Hawkins, S. C. (2010). Understanding the synthesis of directly spinnable carbon nanotube forests. Carbon, Vol. 48, No.4, (April 2010), pp. 1105-1115.

Jang, E. Y.; Kang, T. J.; Im, H.; Baek, S. J.; Kim, S.; Jeong, D. H.; Park, Y. W. & Kim, Y. H. (2009). Macroscopic Single-Walled-Carbon-Nanotube Fiber Self-Assembled by Dip-Coating Method. Adv. Mater., Vol. 21, No. 43, (November 2009), pp. 4357-4361.

Ji, J.; Sui, G.; Yu, Y.; Liu, Y.; Lin, Y.; Du, Z.; Ryu, S. & Yang, X. (2009). Significant Improvement of Mechanical Properties Observed in Highly Aligned Carbon-Nanotube-Reinforced Nanofibers. J. Phys. Chem. C, Vol. 113, No. 12, (March 2009), pp. 4779-4785.

Jin, L.; Bower, C. & Zhou, O. (1998). Alignment of carbon nanotubes in a polymer matrix by mechanical stretching. Appl. Phys. Lett., Vol. 73, No. 9, (August 1998), pp. 1197-1199.

Kang, M. S.; Shin, M. K.; Ismail, Y. A.; Shin, S. R.; Kim, S. I.; Kim, H.; Lee, H. & Kim, S. J. (2009). The fabrication of polyaniline/singlewalled carbon nanotube fibers containing a highly-oriented filler. Nanotechnology, Vol. 20, No.8, (February 2009), pp. 085701(5).

Karousis, N.; Tagmatarchris, N. & Tasis, D. (2010). Current Progress on the Chemical Modification of Carbon Nanotubes. Chem. Rev., Vol. 110, No. 9, (June 2010), pp. 5366–5397.

Kimura, T.; Ago, H.; Tobita, M.; Ohshima, S.; Kyotani, M. & Yumura, M. (2002). Polymer Composites of Carbon Nanotubes aligned by a Magnetic Field. Adv. Mater., Vol. 14, No. 19, (October 2002), pp. 1380-1383.

Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cunniff, P.; Sennett, M. & Windle, A. (2007). High-Performance Carbon Nanotube Fiber. Science, Vol. 318, No. 5858, (December 2007), pp. 1892-1895.

Li, Q.; Li, Y.; Zhang, X.; Zheng, L.; Doorn, S. K.; Zhao, Y.; Dangelewicz, A. M.; Zheng, L.; Doorn, S. K.; Jia, Q.; Peterson, D. E. ; Arendt, P. N. & Zhu, Y. T. (2007). Structure-Dependent Electrical Properties of Carbon Nanotube Fibers. Adv. Mater., Vol. 19, No. 20, (October 2007), pp. 3358-3363.

Li, Q.; Zhang, X.; DePaula, R. F.; Zheng, L.; Zhao, Y.; Stan, L.; Holesinger, T. G.; Arendt, P. N.; Peterson, D. E. & Zhu, Y. T. (2006). Sustained Growth of Ultralong Carbon Nanotube Arrays for Fiber Spinning. Adv. Mater., Vol. 18, No. 23, (December 2006), pp. 3160-3163.

Li, Y. L.; Kinloch, I. A. & Windle, A. H. (2004). Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. Science, Vol. 304, No. 5668, (April 2004), pp. 276-278.

Lin, Y.; Lu, F.; Tu, Y. & Ren, Z. (2003). Glucose Biosensors Based on Carbon Nanotube Nanoelectrode Ensembles. Nano. Lett., Vol. 4, No. 2, (February 2004), pp. 191-195.

Liu, Z.; Tabakman, S. M.; Chen, Z. & Dai, H. J. (2009). Preparation of carbon nanotube bioconjugates for biomedical applications. Nature Protocols, Vol.4, No.9, (September 2009), pp. 1372-1382.

Moniruzzaman, M. & Winey, K. I. (2006). Polymer Nanocomposites Containing Carbon Nanotubes. Macromolecules, Vol. 39, No. 16, (July 2006), pp. 5194-5205.

Peng, H. & Sun, X. (2009). Macroporous carbon nanotube arrays with tunable pore sizes and their template applications. Chem. Commun., No. 9, pp. 1058-1060.

Peng, H. & Sun, X. (2009). Highly aligned carbon nanotube/polymer composites with much improved electrical conductivities. Chem. Phys. Lett., Vol. 471, No. 1-3, (March 2009), pp. 103-105.

Peng, H. (2007). Unusual Assembly of Small Organic Building Molecules in Common Solvent. J. Phys. Chem. B, Vol. 111, No. 30, (August 2007), pp. 8885-8890.

Peng, H. (2008). Aligned Carbon Nanotube/Polymer Composite Films with Robust Flexibility, High Transparency, and Excellent Conductivity. J. Am. Chem. Soc., Vol. 130, No. 1, (January 2008), pp. 42-43.

Peng, H.; Chen, D.; Huang, J.; Chikkannanavar, S. B.; Hanisch, J.; Peterson, D. E.; Doorn, S. K.; Lu, Y.; Zhu, Y. & Jia, Q. (2008). Strong and Ductile Colossal Carbon Tubes with Walls of Rectangular Macropores. Phys. Rev. Lett., Vol. 101, No. 14, (October 2008), pp. 145501(4).

Peng, H.; Jain, M.; Li, Q.; Peterson, D. E.; Zhu, Y. & Jia, Q. (2008). Vertically Aligned Pearl-like Carbon Nanotube Arrays for Fiber Spinning. J. Am. Chem. Soc., Vol. 130, No. 4, (January 2008), pp. 1130-1131.

Peng, H.; Sun, X.; Cai, F.; Chen, X.; Zhu, Y.; Liao, G.; Chen, D.; Li, Q.; Lu, Y.; Zhu, Y. & Jia, Q. (2009). Electrochromatic carbon nanotube/polydiacetylene nanocomposite fibres. Nat. Nanotechnol., Vol. 4, No. 11, (November 2009), pp. 738-741.

Raravikar, N. R.; Schadler, L. S.; Vijayaraghavan, A.; Zhao, Y. P.; Wei, B. Q. & Ajayan, P. M. (2005). Synthesis and Characterization of Thickness-Aligned Carbon Nanotube-Polymer Composite Films. Chem. Mater., Vol. 17, No. 5, (March 2005), pp. 974-983.

Razal, J. M.; Coleman, J. N.; Munoz, E.; Lund, B.; Gogotsi, Y.; Ye, H. H.; Collins, S.; Dalton, A. B.; Baughman, R. H. (2007). Arbitrarily Shaped Fiber Assemblies from Spun Carbon Nanotube Gel Fibers. Adv. Funct. Mater., Vol. 17, No. 15, (October 2007), pp. 2918-2924.

Safadi, B.; Andres, R. & Grulke, E. A. (2002). Multiwalled Carbon Nanotube Polymer Composites: Synthesis and Characterization of Thin Films. J. Appl. Polym. Sci., Vol. 84, No. 14, (June 2002), pp. 2660-2669.

Shi, D. (2009). Integrated Multifunctional Nanosystems for Medical Diagnosis and Treatment. Adv. Funct. Mater., Vol. 19, No. 23, (December 2009), pp. 3356-3373.

Sun, X. ; Peng, H. Unpublished results.

Sun, X.; Chen, T.; Huang, S.; Cai, F.; Chen, X.; Yang, Z.; Li, L.; Lu, Y. & Peng, H. (2010). UV-Induced Chromatism of Polydiacetylenic Assemblies. J. Phys. Chem. B, Vol. 114, No. 7, (February 2010), pp. 2379-2382.

Sun, X.; Chen, T.; Huang, S.; Li, L. & Peng, H. (2010). Chromatic polydiacetylene with novel sensitivity. Chem. Soc. Rev., Vol. 39, No. 11, (April 2010), pp. 4244-4257.

Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P. & Poulin, P. (2000). Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes. Science, Vol. 290, No. 5945, (November 2000), pp. 1331-1334.

Vigolo, B.; Poulin, P.; Lucas, M.; Launois, P. & Bernier, P. (2002). Improved structure and properties of single-wall carbon nanotube spun fibers. Appl. Phys. Lett., Vol. 81, No. 7, (August 2002), pp. 1210-1212.

Wei, C.; Dai, L.; Roy, A. & Tolle, T. B. (2006). Multifunctional Chemical Vapor Sensors of Aligned Carbon Nanotube and Polymer Composites. J. Am. Chem. Soc., Vol. 128, No. 5, (February 2006), pp. 1412-1413.

Yang, Z. H.; Gao, Z.; Sun, H. & Li, Y. (2008). Composite Films Based on Aligned Carbon Nanotube Arrays and a Poly(N-Isopropyl Acrylamide) Hydrogel. Adv. Mater., Vol. 20, No. 11, (June 2008), pp. 2201-2205.

Zhang, M.; Atkinson, K. R. & Baughman, R. H. (2004). Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology. Science, Vol. 306, No. 5700, (November 2004), pp. 1358-1361.

Zhang, M.; Fang, S. L.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R. & Baughman, R. H. (2005). Strong, Transparent, Multifunctional, Carbon Nanotube Sheets. Science, Vol. 309, No. 5738, (August 2005), pp. 1215-1219.

Zhang, X. B.; Jiang, K. L.; Feng, C.; Liu, P.; Zhang, L. N.; Kong, J.; Zhang, T. H.; Li, Q. Q. & Fan, S. S. (2006). Spinning and Processing Continuous Yarns from 4-Inch Wafer Scale Super-Aligned Carbon Nanotube Arrays. Adv. Mater., Vol. 18, No. 12, (June 2006), pp. 1505-1510.

Zhang, X.; Li, Q.; Tu, Y.; Li, Y.; Coulter, J. Y.; Zheng, L.; Zhao, Y.; Jia, Q. Peterson, D. E. & Zhu, Y. (2007). Strong Carbon-Nanotube Fibers Spun from Long Carbon-Nanotube Arrays. Small, Vol. 3, No. 2, (February 2007), pp. 244-248.

Zhang, Y.; Zou, G.; Doorn, S. K.; Htoon, H.; Stan, L.; Hawley, M. E.; Sheehan, C. J.; Zhu, Y. & Jia, Q. (2009). Tailoring the Morphology of Carbon Nanotube Arrays: From Spinnable Forests to Undulating Foams. ACS Nano, Vol. 3, No. 8, (July 2009), pp. 2157-2162.

Zhao, Y. L. & Stoddart, J. F. (2009). Noncovalent Functionalization of Single-Walled Carbon Nanotubes. Acc. Chem. Res., Vol. 42, No. 8, (August 2009), pp. 1161-1171.

Zheng, L.; Zhang, X.; Li, Q.; Chikkannanavar, S. B.; Li, Y.; Zhao, Y.; Liao, X.; Jia, Q.; Doorn, S. K.; Peterson, D. E. & Zhu, Y. (2007). Carbon-Nanotube Cotton for Large-Scale Fibers. Adv. Mater., Vol. 19, No. 18, (September 2007), pp. 2567-2570.

Zhu, Y. F.; Ma, C.; Zhang, W.; Zhang, R. P. & Koratkar, N.; Liang, J. (2009). Alignment of multiwalled carbon nanotubes in bulk epoxy composites via electric field. J. Appl. Phys., Vol. 105, No. 5, (March 2009), pp. 054319(6).

Zhu, Z.; Song, W.; Burugapalli, K.; Moussy, F.; Li, Y. & Zhong, X. (2010). Nano-yarn carbon nanotube fiber based enzymatic glucose biosensor. Nanotechnology, Vol. 21, No. 16, (April 2010), pp. 165501.
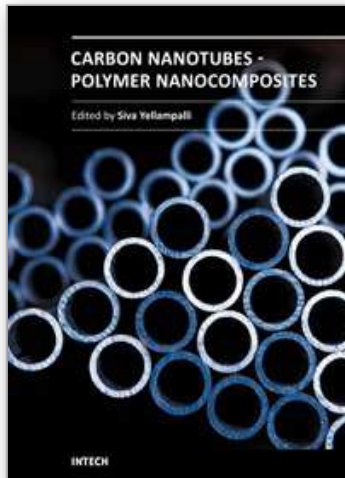
Carbon Nanotubes - Polymer Nanocomposites

Edited by Dr. Siva Yellampalli

Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This books focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

INTECH
open science | open minds