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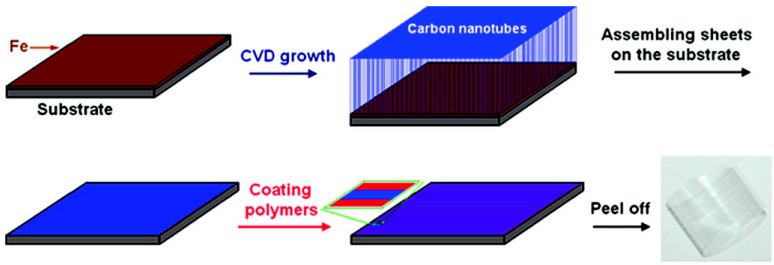

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Aligned Carbon Nanotube/Polymer Composite Films with Robust Flexibility, High Transparency, and Excellent Conductivity

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Transparent and flexible conductors are essential supporting materials for many device applications such as paper displays and plastic solar cells.[1] Traditionally, Sn-doped In_2O_3 (ITO) is deposited on flexible substrates to meet the demands. However, the performance of ITO is generally reduced compared to that on glass; for example, conductivities of ITO on polyethylene terephthalate are about 5 times lower than that on glass.[2] In addition, cracks appear after repeated bending or strain, and it is not resistant to acid.[2] Due to these technical problems, alternative materials have to be developed in the near future to meet wider applications.

Carbon nanotube (CNT)/polymer composites represent a new direction to these materials.[3] CNTs exhibit excellent mechanical and electrical properties, while polymers provide good flexibility, high transparency, easy processing, and low cost. Three main fabrication approaches (i.e., solution blending, melt blending, and in situ polymerization) have been extensively explored.[4] Unfortunately, advances in processing transparent CNT/polymer composites have been hindered by the aggregation and random dispersion of carbon nanotubes inside (Figures S1 and S2), which results in an extremely low electrical conductivity for composite materials. For example, the conductivity is less than 10^{-6} S/cm at room temperature for CNT/poly(methyl methacrylate) nanocomposites synthesized by a melt spinning process.[5] Here we report a novel and general synthesis of CNT/polymer composites with highly aligned nanotubes inside. The resulting composite films show high optical transparency, robust flexibility, and excellent conductivity.

Figure 1 schematically shows the synthesis of transparent and flexible CNT/polymer composite films. CNT arrays are first grown on silicon by a chemical vapor deposition (CVD) process. Uniform CNT sheets are then pulled out of the arrays and stabilized on glass. Composite films are finally produced by spin-coating or casting polymer solutions onto CNT sheets, followed by evaporation of solvents. Film thickness can be controlled by varying the concentration of polymer solutions and coating times. Transparent and flexible films can be readily peeled off the substrate. For this approach, the fabrication is simple and efficient, and a wide range of polymers and monomers may be used to synthesize functional composite materials.

A key point for this method is to grow long and spinnable CNT arrays which produce high-grade sheets. The catalytic iron film on the Al_2O_3 buffer layer has been proved to be active for several hours, which is critical for growing long CNT arrays.[6] We synthesized spinnable CNT arrays up to 4 mm using this catalyst system (Supporting Information). Figure 2a shows a typical scanning electron microscopy (SEM) image of a CNT array on silicon. Synthesized CNTs are highly aligned and vertical to the substrate. The surface of the array was very clean and smooth. No obvious dirty or undesirable particles were observed. Representative Raman spectrum (Figure S2a) shows a strong peak at 1308 cm^{-1} for D-band and a weak peak at 1598 cm^{-1} for G-band, similar to other spinnable CNT arrays.[6] Figure S3b shows the transmission

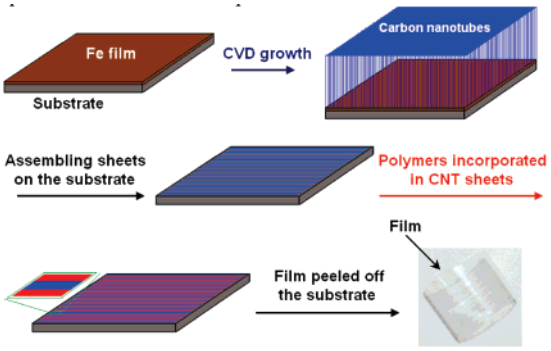


Figure 1. Synthesis of aligned carbon nanotube/polymer composite films.

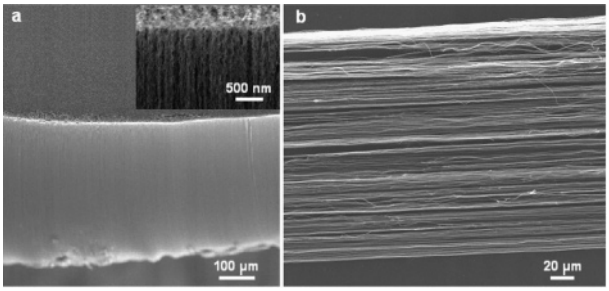
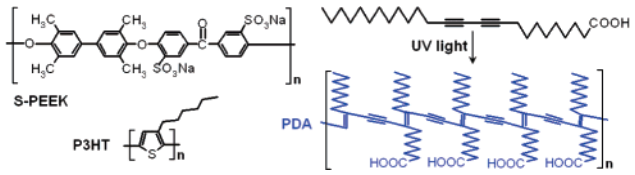


Figure 2. (a) SEM image of a CNT array (inset: high magnification). (b) SEM image of CNT sheets pulled out of the array.

Scheme 1. Chemical Structures of Three Building Polymers



electron microscopy (TEM) and high-resolution TEM images of synthesized CNTs. They are multiwalled with a diameter of ~10 μm. CNT sheets are readily assembled on glass from these high-quality CNT arrays (Figure 2b).

Both plastic and semiconducting polymers have been studied in this work. Polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(3-hexylthiophene-2,5-diyl) (P3HT) are purchased from Aldrich, synthesis of sulfonated poly(ether ether ketones) (S-PEEK) is detailed in the Supporting Information, and polydiacetylene (PDA) is synthesized by polymerizing 10,12-pentacosadiynoic acid under UV light (Scheme 1). For PS-, PMMA-, and S-PEEK-derived composite films, they are transparent and show an optical transparency higher than 80% with a thickness of ~5 μm. Figure 3a shows the S-PEEK-derived film (15 μm in thickness) on a labeled paper, and the symbol on the paper can be clearly observed. UV−vis spectroscopy further shows a transparency of ~86% at the wavelength of 400−1100 nm (Figure 3b) for a film of 5 μm in

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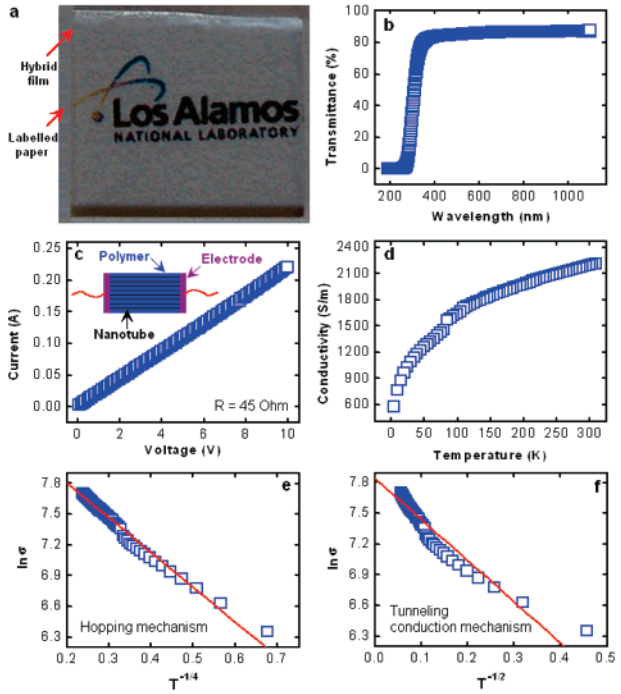

Figure 3. Optical and electrical properties of CNT/S-PEEK composite films. (a) Transparent film on a labeled paper. (b) Optical transmittance measurement. (c) Typical $I-V$ curve at room temperature. (d) Temperature dependence of the conductivity measured by a two-probe method. (e) Scaling of the conductivity with the variable range hopping mechanism on a plot of ln σ versus $T^{-1/4}$. (f) Scaling of the conductivity with the tunneling conduction mechanism on a plot of ln σ versus $T^{-1/2}$.

thickness. Before polymerization, CNT/10,12-pentacosadiynoic acid films are transparent; after polymerization, PDA exhibits a blue color and films are not transparent. P3HT shows a red color, and derived composite films are not transparent.

For all studied polymers, their composite films show high conductivities along the CNT-aligned direction. For example, conductivity of S-PEEK-derived films at room temperature is 22 S/cm, approximately the same order of magnitude as films of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic) acid.[7] Conductivity can be further increased to 200 S/cm by growing longer spinnable CNT arrays and engineering CNT sheets. Synthesized CNT/polymer films are very stable, and their conductivity keeps constant after being bent many times. Figure 3d further shows the temperature dependence of the conductivity of CNT/S-PEEK films. The conductivity increases with the increase of the temperature, suggesting a semiconducting behavior.[8a] The high conductivity provides these composites other interesting properties. For example, CNT/PDA composites quickly change their colors from blue to red under the stimulation of the current. More effort is underway.

For the temperature dependence of conductivity, two main mechanisms have been suggested, that is, a variable range hopping mechanism[8b] and a tunneling conduction mechanism.[8c] These two mechanisms are, respectively, described by the following two equations: $\sigma = \sigma_0 \exp(-A/T^{1/4})$ and $\sigma = \sigma_0 \exp(-B/T^{1/2})$, where σ is the conductivity, σ_0, A, and B are constants, and T is the temperature. As shown in Figure 3e,f, ln σ versus $T^{-1/4}$ based on the first equation shows a much higher degree of linearity than that of ln σ versus $T^{-1/2}$ based on the second equation. This indicates that the conduction in this system is mainly controlled by the hopping mechanism. In more detail, the relationship between conductivity and temperature in Mott's hopping model can also be expressed as $\sigma \propto \exp(-A/T^{[1/(d+1)]})$, where A is a constant and d is the dimensionality.[8a] The plots of ln σ versus $T^{-1/4}$ (for $d = 3$), $T^{-1/3}$ (for $d = 2$), and $T^{-1/2}$ (for $d = 1$) have linear fitting coefficients of 0.961, 0.946, and 0.915, respectively (Figure S5−S7). This result suggests that the electron transport is consistent with a three-dimensional hopping mechanism. This behavior is most likely due to the defect structures of CNT composites, in which electrons cannot be confined in the one-dimensional channel along the CNT-aligned direction. Instead, electrons hop from one localized site to another, or possibly from a CNT to another.

Note that aligned CNT/polymer films can also be prepared by inserting flexible and transparent poly(ethylene terephthalate) films into CNT solutions, followed by evaporation of solvents.[7] Although derived films show high transparency, the conductivity is low. CNTs pasted on the surface of films are also easy to be pulled out and are not stable. In addition, available polymers are largely limited. As a comparison, this novel approach overcomes the above problems and will be more promising in applications.

In summary, this work reports a novel and general synthesis of transparent and flexible CNT/polymer composite films with much improved conductivities compared to other approaches. These composite films show many potential applications such as flexible conductors for optoelectronic devices.

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Supporting Information Available: Synthesis and characterization of nanotube arrays and composite films, and complete refs 1b, 6, and 8a. This material is available free of charge via the Internet at http://pubs.acs.org.

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