A New and General Fabrication of an Aligned Carbon Nanotube/Polymer Film for Electrode Applications

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For current optoelectronic and electronic devices, electrodes are mainly composed of platinum, indium tin oxide, or both.[1–6] High-temperature or vacuum processes are typically required to fabricate them, resulting in high costs. These electrode materials have been also shown to be unstable in many conditions, e.g., platinum may be dissolved in corrosive electrolytes and indium tin oxide is fragile and not resistant to acid.[4–6] In addition, there are limited sources for either platinum or indium. These disadvantages have largely hindered their practical applications in a wide variety of fields. Therefore, it is highly desired to develop new electrode materials with good stability, high efficiency, and low cost. Recently, increasing interest has been paid to carbon nanotube (CNT)/polymer composite films, which may represent a family of promising electrode materials to simultaneously solve the above challenges due to incorporated excellent properties from CNTs and polymers. CNTs exhibit high mechanical strength and electrical conductivity, while polymers provide good flexibility, high transparency, easy processing, and low cost.[7,8] CNT/polymer films have been typically fabricated by dispersing two moieties in solvent, followed by spin coating or other solution processes.[9] Although it is easy to operate with relatively high efficiency, random dispersion of CNTs in polymer matrices greatly decreases the physical properties of resulting composite films.[10] For instance, electrical conductivities of CNT/polymer films at room temperature are often less than 10^{-3} S cm^{-1}, which largely reduces their electrode applications. In order to improve their electrical conductivities, aligned CNT/polymer films by using CNT sheets as templates have been recently realized, and conductivities up to 10^{2} S cm^{-1} along the CNT-aligned direction were obtained.[11,12] However, the synthesis of spinnable CNT arrays, which are required to fabricate CNT sheets, remains challenging as most CNT arrays are non-spinnable.[13] In addition, spinnable CNT arrays are generally less than 1 mm in height, which limits the further improvement of conductivities in the resulting aligned CNT/polymer films.[14] Therefore, new and more general routes are urgently required to prepare aligned CNT/polymer films with longer CNTs, higher efficiencies, and lower costs.

Here, we report such a new and general approach to make aligned CNT/polymer composite films that are transparent, flexible, and highly conductive. CNT lengths may be increased to millimeters or even longer, depending on the heights of used CNT arrays, to provide much improved electrical conductivities in the resulting composite films. These novel composite films exhibit promising applications as a new family of electrodes. Herein, the use of aligned CNT/polymer films as counter electrodes as replacements for platinum in the fabrication of novel dye-sensitized solar cells are investigated as an application example.

Figure 1 schematically shows the preparation of aligned CNT/polymer composite films from CNT arrays. First, high-quality CNT arrays are easily grown by chemical vapor deposition with aluminum oxide or iron as the catalyst and ethylene as the carbon source. These CNT arrays typically show thicknesses of millimeters in most cases and may achieve a height of centimeters. CNT densities of as-synthesized arrays range from 10^{10} to 10^{11} cm^{-2}, and they can be further improved by pressing as-synthesized arrays from one or both sides. Polymers are then infiltrated into CNT arrays to prepare composite arrays through solution or melting processes. In fact, a wide variety of polymers have been incorporated to form vertically aligned CNT composite arrays with high quality.[15,16] These composite arrays exhibit much improved mechanical properties,[15] which are important for the next and critical slicing procedure. Finally, composite arrays are sliced by ultramicrotome or microtome along CNT-aligned direction. Epoxy has been chosen as a model in this work as it is a widely used general polymer.

Figure 2a,b show scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of aligned CNT/epoxy films fabricated from an as-synthesized CNT array. It can be found that CNTs are well dispersed and highly aligned with each other in the epoxy matrix. Figure 2c,d show SEM images of the aligned CNT/epoxy films fabricated from a pressed CNT array, which has a density four times that of the as-synthesized one. CNTs remain uniformly dispersed and highly aligned in the epoxy, and CNT densities are about three times higher than those derived from the as-synthesized array. In other words, CNT densities in these composite materials can be easily controlled through post-growth treatments of as-synthesized arrays. CNT densities may be also controlled by varying experimental parameters during growth, e.g., thickness of the catalytic iron film. The iron film breaks into nanoparticles, which induce growth of CNTs, so a thicker iron film generally produces more nanoparticles with a higher density of CNTs in

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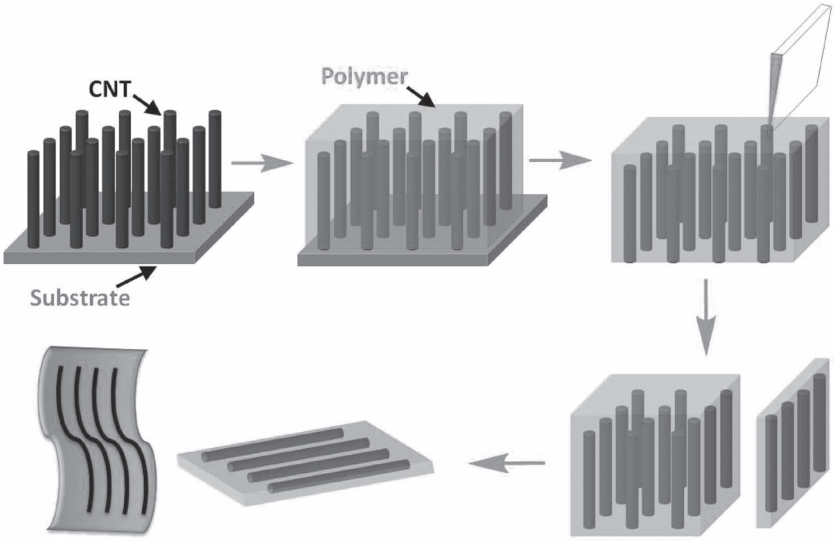

Figure 1. Schematic illustration to the fabrication of the aligned CNT/polymer composite film.

the array if the other experimental parameters are the same. In this work, iron films are increased from 0.25 to 1 nm in thickness, and CNT densities can be accordingly improved for about 2–5 times, depending on the growth conditions, which include temperature and the flow rate of gases.

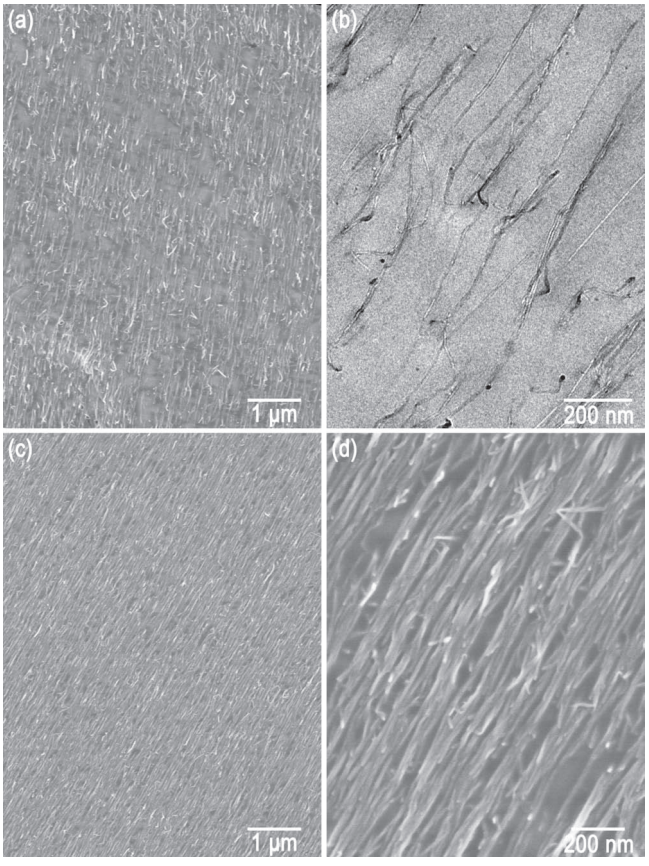

Figure 2. Structure characterizations of aligned CNT/epoxy films by SEM and TEM. a,b) SEM and TEM images, respectively, of the aligned CNT/epoxy film derived from an as-synthesized CNT array. c,d) SEM images of the aligned CNT/epoxy film derived from a pressed CNT array (improved three times in CNT density) at low and high magnification, respectively.

Aligned CNT/epoxy films can be accurately controlled from 50 nm to 50 μm in thickness and may be up to centimeters in width. These composite films exhibit excellent flexibility, and they can be deformed for many times without breaking. **Figure 3**a shows optical graphs of a composite film during a deformation. No breaking was observed by optical microscopy during the above process. In addition, SEM was used to monitor the structure integrity of this composite film at the nanoscale. Similarly, no obvious changes in structure were detected for such aligned CNT/epoxy films. For instance, no CNTs were found to be pulled out of composite films. Therefore, aligned CNT/epoxy films are also mechanically stable.

The aligned CNT/epoxy film in Figure 3a seems not to be transparent due to a high thickness of 20 μm. With the decrease in the thickness to less than 5 μm, which has been generally used in electrodes, these composite films become transparent. For instance, composite films with thicknesses from tens to hundreds of nanometers are required as working electrodes to replace indium tin oxide in various organic solar cells. Figure 3b compares a series of aligned CNT/epoxy films with thicknesses ranging from 75 to 250 nm. The red line under the composite films can be clearly observed. A UV-vis spectrometer was used to quantitatively measure the transmittances in a wavelength range from 300 to 800 nm. Figure S1 (Supporting Information) shows a typical graph of a composite film with a thickness of 125 nm and the transmittances is higher than 90%.

Electrical resistances of the composite film in two directions, i.e., along the CNT alignment in plane and normal to plane, were carefully measured using a typical two-probe method. For convenience of discussion, the directions are simplified as parallel and normal directions, respectively. The fabrication and characterization details can be found in the Experimental Section. For a composite film with a dimension of 3 mm × 2.5 mm × 0.01 mm derived from as-synthesized CNT array, it exhibited resistances of 2.8 Ω in the parallel direction and 2×10^{-4} Ω in the normal direction. For a composite film with the same dimension from a pressed CNT array (CNT density increased three times), the resistances decreased by 67% in the parallel direction and 49% in the normal direction.

In order to study potential applications as flexible electrodes, we measured the electrical resistances of composite films in the two directions during the deforming processes. **Figure 4**a compares the electrical resistances of a composite film in the parallel direction before and after being bent from 0° to 180°. The resistances are nearly unchanged during the bending process. In addition, the resistances were almost the same after being bent for 500 cycles (Figure 4b). Figure 4c compares the electrical resistances of the composite film in the normal direction during the same bending process. Similarly, no resistance changes were measured when the composite film was bent from 0° to 180°. Furthermore, the resistances in the normal direction were stable after being bent for 500 cycles (Figure 4d).

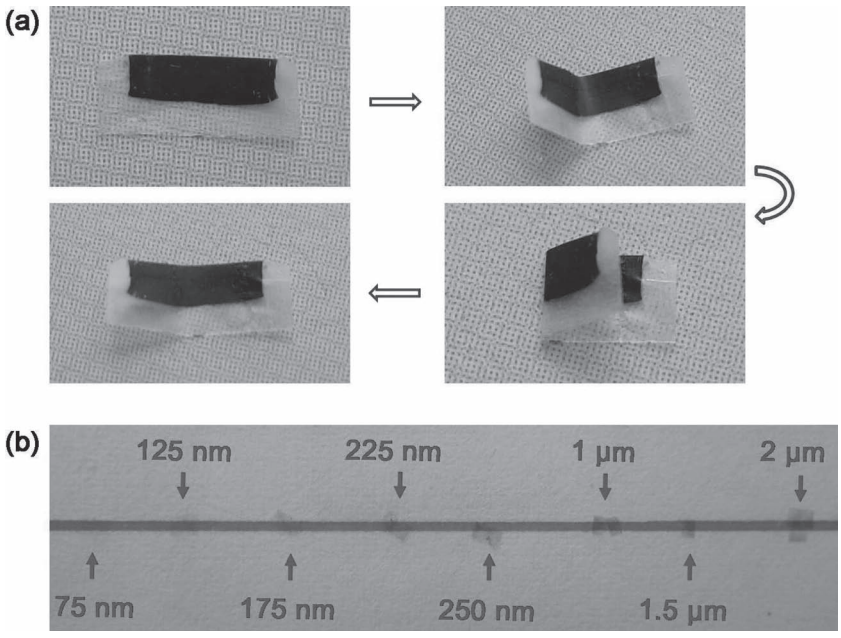

Figure 3. Photographs of aligned CNT/epoxy films. a) Good flexibility of a composite film, which is bent without breaking. b) High transmittances of composite films with different thicknesses.

These results also suggest that aligned CNT/epoxy composite films are mechanically stable, which agrees with previous SEM observations of their structure integrity during deformations. For comparison with the other CNT/polymer composite materials, electrical resistances were further transformed to electrical conductivities. Electrical conductivities of aligned CNT/epoxy films may achieve 10^2–10^3 S cm^{-1} in the parallel direction and 10^2 S cm^{-1} in the normal direction at room temperature, which are much higher than the other CNT/polymer composite films.[17] It should be also noted that the electrical conductivities of composite films with different thicknesses were almost the same because the CNTs were highly aligned with each other.

Due to the combined high conductivity, flexibility, stability, and transparency, these aligned CNT/epoxy films show great potential as electrode materials in a wide variety of fields. Here, we fabricated a series of dye-sensitized solar cells by using aligned CNT films in counter electrodes as replacements

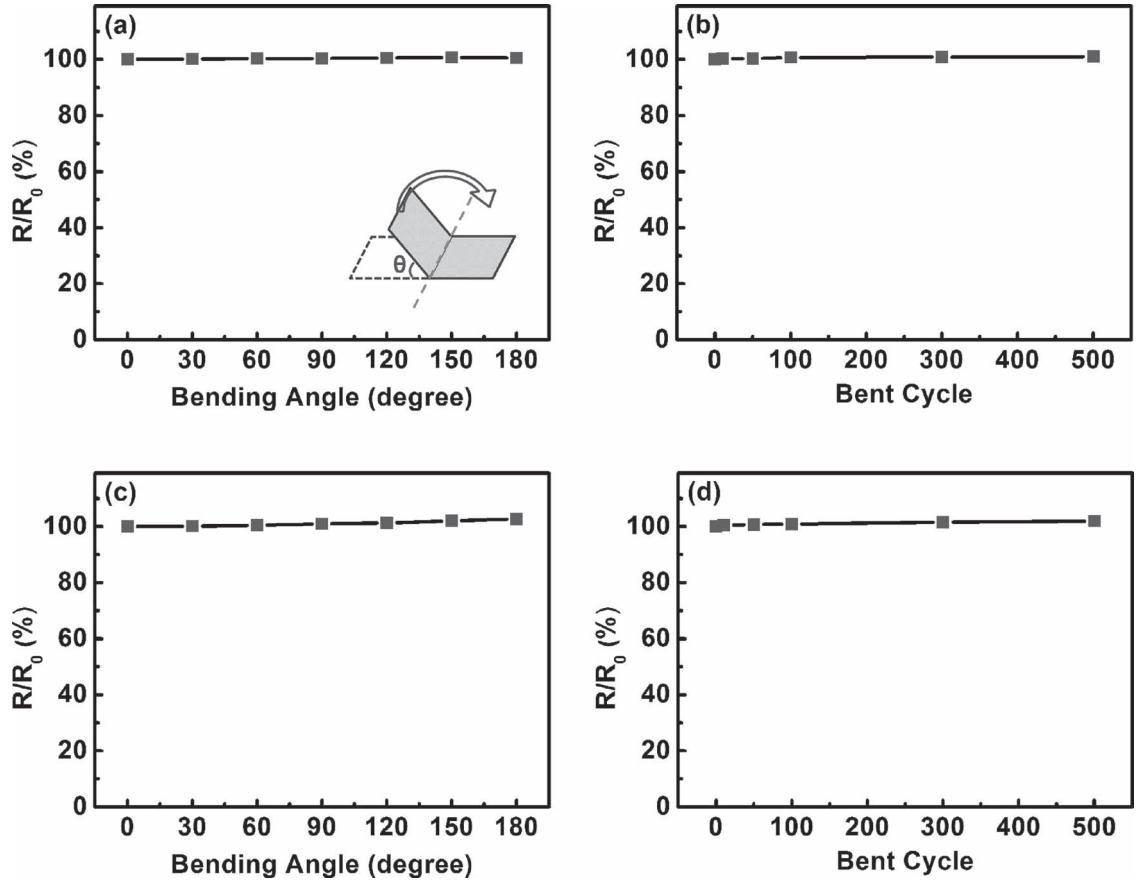

Figure 4. Electrical resistances of aligned CNT/epoxy films during the deforming process as a function of bending angle and bent cycle. a,b) Along the CNT-aligned direction in the film plane and c,d) in the normal direction to the film plane. R_0 and R correspond to electrical resistances of composite films before and after deformation. The inserted image in (a) schematically defines the bending angle and one bent cycle means the recovery of a composite film after the deforming process with bending angles from 0° to 180° in (a).

for platinum (Figure S2, Supporting Information). As previously discussed, platinum is expensive with limited sources and may be dissolved in corrosive electrolytes with limited stability.[4] These disadvantages have largely hindered the practical application of dye-sensitized solar cells. As a comparison, the CNT/polymer materials may efficiently solve the above problems because they are cost-effective and stable. The resulting cells typically showed an open-circuit voltage, short-circuit current density, and fill factor of 0.65 V, 1.30 mA cm^{-2}, and 0.16, respectively, under one sun illumination (100 mW cm^{-2}, AM 1.5G). The cell efficiencies may be further improved by the optimization of the fabrication, including the increase in CNTs on the surfaces of composite films and improvement of their contacts with substrates.

In summary, a general route to fabricate aligned CNT/polymer composite film with good flexibility and high transparency has been developed with high efficiency and low cost. This fabrication also show several other advantages compared to the reported approaches in the preparation of aligned CNT/polymer films: 1) it greatly improves the alignment of CNTs compared with the traditional solution or melting methods; 2) it greatly increases the fabrication efficiencies and overcomes the limitations of CNT lengths and structure uniformity in the CNT-sheet-based methods; 3) the thicknesses of composite films can be accurately tuned from the nanometer to micrometer scale; and 4) it produces composite films with excellent electrical conductivities. These composite films have exhibited promising applications as a family of new electrodes for the replacement of platinum or indium tin oxide in organic solar cells. Novel dye-sensitized solar cells using aligned CNT/polymer films as the counter electrodes have been investigated with great potential. These composite films may also show potential applications in many other fields including touch screens and gas sensors.

Experimental Section

CNT arrays were grown on a 1 × 1 cm^2 silicon substrate with Fe (1 nm)/Al_2O_3 (10 nm) deposited on top as the catalyst using a chemical vapor deposition process.[11,18–20] The growth was carried out at 750 °C with ethylene as the carbon source and a mixture of argon and hydrogen as the carrying gas. The flowing rates were 600, 40, and 120 standard cubic centimeters per minute for argon, hydrogen, and ethylene, respectively. Densification of the CNT arrays was realized by pressing their two sides and animprovement of three times in density for CNTs was mainly investigated in this work. CNT/polymer composite arrays were prepared by dipping as-synthesized or densified pure arrays into liquid epoxy, followed by curing treatment at 60 °C for 36 h.[19] The resulting composite arrays were sliced into thin films with thicknesses from nanometers to micrometers using ultramicrotome or thick films with thicknesses from micrometers to millimeters using microtome. The electrical resistances of the composite films along the CNT alignment were measured using a two-probe method, and two electrodes were connected to the same plane. Electrical resistances in a normal direction to composite film (between two planes) were measured by coating a thin layer of silver paint on each plane, followed by the connection of copper wires.

Aligned CNT/epoxy films (typical thickness of 5 μm) were further transferred onto FTO (fluorine-doped SnO_2, 15 ohm per square, transmittance 90%, Nippon Sheet Glass Co., Japan) to construct counter electrodes. The working electrode was prepared by printing a layer of TiO_2 onto indium tin oxide substrate, followed by immersion into a 0.5 mM solution of N719 dye in acetonitrile/tert-butanol (volume ratio of 1:1) for 16 h. After being rinsed with acetonitrile and dried, the dye-incorporated TiO_2 electrode was assembled with the counter electrode based on the composite films. An electrolyte was injected into the cell through a hole on the counter electrode. Finally, the hole was sealed with surlyn and a piece of glass.

The structures of aligned CNT/epoxy films were characterized SEM (Hitachi FE-SEM S-4800, operated at 1 kV) and TEM (JEOL JEM-2100F, operated at 200 kV). The electrical resistances of the composite films were traced by an Agilent 34401A digital multimeter. The dye-sensitized solar cells were measured by recording the current density–voltage (*J–V*) curves with a Keithley 2400 Source Meter under illumination (100 mW cm^{-2}) of simulated AM1.5G sun light from a solar simulator (Oriel-91193 equipped with a 1000 W Xe lamp and an AM1.5 filter). The stray light was shielded by a mask with an aperture that was slightly smaller than the working electrode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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