



Highly aligned carbon nanotube/polymer composites with much improved electrical conductivities

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ABSTRACT

Carbon nanotube (CNT)/polymer composites are generally synthesized by coating CNT/polymer mixture solutions into films or powders. A main challenge is that CNTs are randomly dispersed in derived composites, which results in extremely low electrical conductivities. Here we report the synthesis of highly aligned CNT/polymer composites with much improved conductivities by incorporating polymers into aligned CNT arrays. The key point in this work is to grow dense and robust CNT arrays through a chemical vapor deposition process.

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1. Introduction

Carbon nanotube (CNT)/polymer composites have been extensively investigated due to their superior combined properties from both CNTs and polymers [1–3]. For example, CNTs impart good mechanical, electrical, and chemical performance into the composites, while polymers make the composite low-cost and easy to fabricate: a combined set of desired properties can not be found in the individual constituents, thus making these composite materials very useful in many applications [4]. Currently, CNT/polymer composites are mainly used as electrostatic-discharge components, in which multiple-walled CNTs slightly enhance the electrical conductivity of plastics [5]. CNT/polymer composites are generally synthesized by a solution process where three key steps are involved: dispersing CNTs in solvents, mixing CNTs with polymers, and casting mixtures into films or powders [6–8]. One of the main challenges using such an approach is that CNTs are randomly dispersed in resulted composite materials [5,9,10]. This leads to much reduced electrical conductivities of composites, e.g. $\sim 10^{-6}$ S/cm for CNT/poly(methyl methacrylate) composites at room temperature [11–13]. A possible solution is to directly use CNT arrays in which CNTs are highly aligned. Based on this concept, aligned CNT/polymer composites have been synthesized by infiltrating monomers into the arrays followed by in situ polymerization [11–13] or directly incorporating polymers into the arrays [14,15]. However, the conductivities of reported composite materials are very low, such as less than 1.31 S/cm at room temperature even for a CNT/conducting polymer composite [13]. This limitation has greatly deteriorated their wider applications. Here we synthesize highly

aligned CNT/polymer composites with much improved conductivities by synthesizing high-quality CNT arrays.

2. Experimental

Commercial polystyrene ($M_n = 1.4 \times 10^5$ g/mol, $M_w = 2.3 \times 10^5$ g/mol, M_n and M_w are number-average molecular weight and weight-average molecular weight, respectively) and poly(methyl methacrylate) ($M_w = 1.5 \times 10^4$ g/mol and 1.2×10^5 g/mol, respectively) from Aldrich were used in this work. Polystyrene and poly(methyl methacrylate) were dissolved in tetrahydrofuran with a concentration of 133 mg/mL. Poly(3,4-ethylenedioxythiophene) ($M_n = \sim 6000$ g/mol) end-capped with tetramethacrylate in nitromethane solution from Aldrich was used as received. Sulfonated poly(ether ether ketones) was synthesized via the nucleophilic aromatic substitution reactions of sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) and 3,3',5,5'-tetramethyl-4,4'-biphenol. The synthetic details are described elsewhere [2]. The sample with a M_n of 4922 g/mol was used in this work. Sulfonated poly(ether ether ketones) can be easily dissolved in water or dimethylformamide. CNT/polymer composites were then produced by dropcasting polymer solutions onto CNT arrays, followed by evaporation of solvents.

3. Results and discussion

The key point for this approach is to grow dense and robust CNT arrays. Most arrays will not maintain the initial alignment on the substrate when coated with solutions [16]. We have grown required CNT arrays with thickness up to 4 mm by a chemical vapor deposition process [17]. Fig. 1a shows a typical scanning electron microscopy (SEM) image of a CNT array with a thickness of ~ 1.1 mm. Fig. 1b shows a representative Raman spectrum of the

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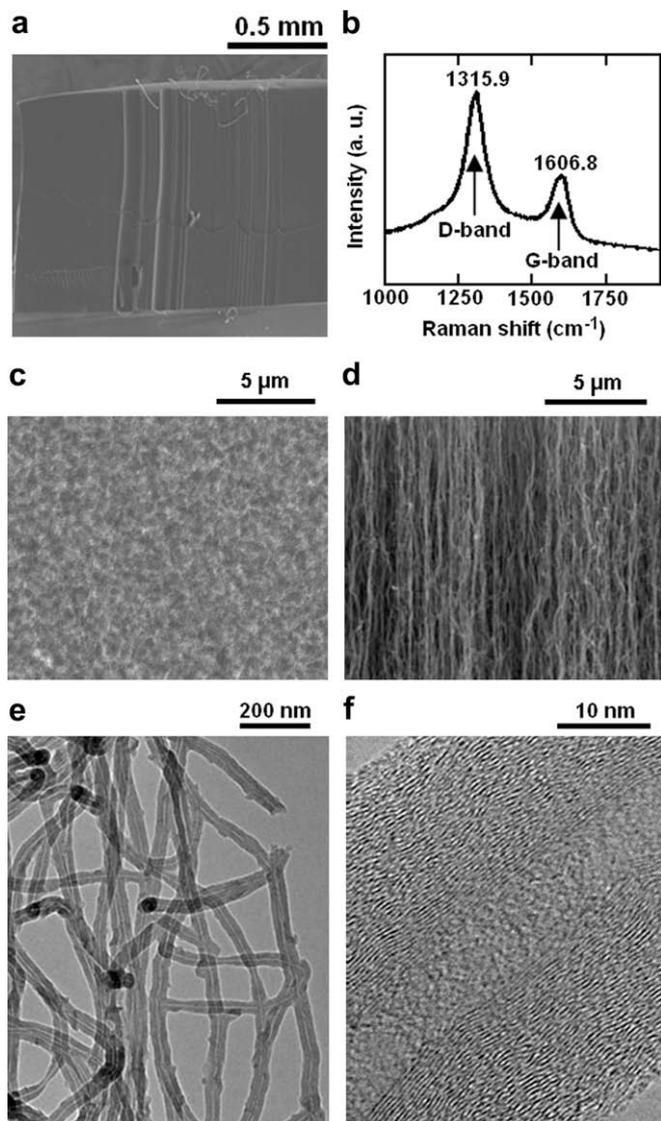


Fig. 1. A CNT array. (a) Scanning electron microscopy (SEM) image at low magnification. (b) Raman spectrum. (c) Top view of the array by SEM at high magnification. (d) Side view of the array by SEM at high magnification. (e) Transmission electron microscopy (TEM) image of CNTs. (f) High resolution TEM image of a CNT.

CNT array with D-band and G-band located at 1315.9 cm^{-1} and 1606.8 cm^{-1} , respectively, which agrees with other reported spectra of CNTs [18]. Fig. 1c shows the top view of the array. The top surface is flat, i.e., the CNTs at different locations are grown at almost the same rate. In addition, the surface of the array is very clean and no obvious dirty or undesirable particles are observed. Fig. 1d provides the side view of the array. The CNTs are highly aligned and vertical to the substrate. The density of CNTs in the array is 10^9 cm^{-2} . Fig. 1e and f shows the transmission electron microscopy (TEM) and high resolution TEM images of synthesized CNTs, respectively. They are multi-walled with diameter of $\sim 36\text{ nm}$.

Polystyrene and poly(methyl methacrylate) are among the most used polymers for composite materials. Here we synthesize CNT/polymer composites using these two polymers. CNT/polymer composites are prepared by directly dropcasting polystyrene or poly(methyl methacrylate) solutions into as-synthesized CNT arrays. Fig. 2 shows SEM images of aligned CNT/polystyrene and CNT/poly(methyl methacrylate) composites. The top views in Fig. 2a

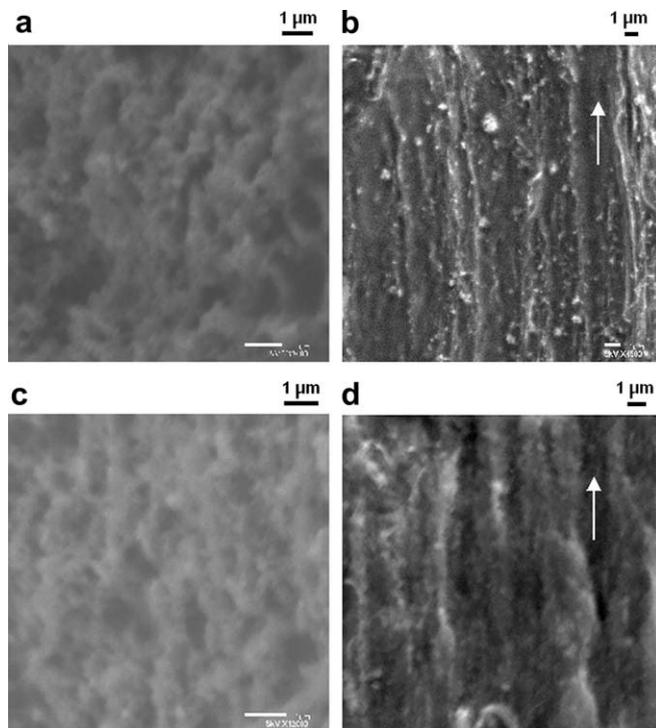


Fig. 2. SEM images of highly aligned CNT/polymer composites. (a) Top view of the CNT/polystyrene composite. (b) Side view of the CNT/polystyrene composite. (c) Top view of the CNT/poly(methyl methacrylate) ($M_w = 1.5 \times 10^4\text{ g/mol}$) composite. (d) Side view of the CNT/poly(methyl methacrylate) ($M_w = 1.5 \times 10^4\text{ g/mol}$) composite. The white arrows show the aligned directions of CNTs.

and c indicates that the surfaces of CNT/polymer composites remain even and flat. This property is important for their applications as electrodes which require even surfaces at contacting faces to show good electrical contacts [19]. The side views of the above two composites in Fig. 2b and d further confirm that the arrays maintain the original morphologies with highly aligned CNTs.

One main advantage of this synthesis over other approaches is the highly aligned CNTs, which enable the composite materials with much improved electrical conductivities. Here we measure the conductivities of these composites by a two-probe method, and the experimental setup is schematically shown in Fig. 3a. Two ends of a composite were first coated with thin layers of Ag, followed by the connections to copper wires. The small contact resistances between the composite and copper wires were neglected during the calculation of conductivities. The conductivities of CNT/poly(methyl methacrylate) composites with weight-average molecular weights of $1.5 \times 10^4\text{ g/mol}$ and $1.2 \times 10^5\text{ g/mol}$ were measured as 12.5 S/cm and 10.0 S/cm at room temperature, respectively. The CNT/polystyrene composite shows a conductivity of 13.3 S/cm at room temperature. For the above plastic polymers of poly(methyl methacrylate) and polystyrene with close molecular weights, the resulting composites do not show an obvious difference of conductivities. Nevertheless, the conductivities of these composites can be improved by using semiconducting polymers. For example, the conductivity of a CNT/poly(3,4-ethylenedioxythiophene) composite was measured as 25.0 S/cm at room temperature. Unexpectedly, compared to poly(3,4-ethylenedioxythiophene), the CNT composite derived from sulfonated poly(ether ether ketones) showed even a higher conductivity of 66.7 S/cm at room temperature, possibly due to a better solubility to form more uniform structures during the preparation. It should be also noted that this CNT/sulfonated poly(ether ether ketones) bulk material exhibited a higher conductivity than the reported CNT/sulfonated

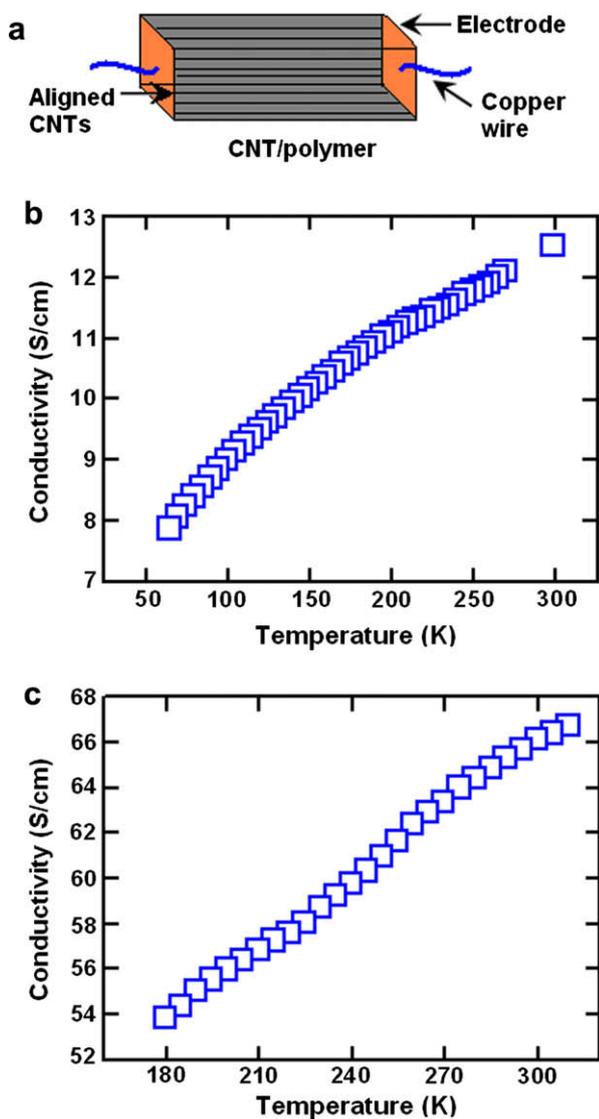


Fig. 3. Electrical properties of CNT/poly(methyl methacrylate) ($M_w = 1.5 \times 10^4$ g/mol) and CNT/sulfonated poly(ether ether ketones) composites. (a) Schematic illustration of the measurement of the conductivity by a two-probe method. (b) The temperature dependence of the conductivity for the CNT/poly(methyl methacrylate) composite. (c) The temperature dependence of the conductivity for the CNT/sulfonated poly(ether ether ketones) composite.

poly(ether ether ketones) film (~ 22 S/cm at room temperature) [2]. A main reason is that the used CNT arrays for the composite film are shorter than those at current system. Longer CNTs had

been demonstrated to improve the conductivities of aligned CNTs by minimizing their contact resistances [20]. Fig. 3b and c further shows the temperature dependence of the conductivity for the CNT/poly(methyl methacrylate) ($M_w = 1.5 \times 10^4$ g/mol) and CNT/sulfonated poly(ether ether ketones) composites, respectively. The conductivities for both of them increase with temperature, suggesting a semiconducting behavior for the above composite materials [21,22].

4. Conclusion

In summary, this work reports the synthesis of highly aligned CNT/polymer composites by directly casting polymer solutions onto dense and robust CNT arrays, followed by evaporation of solvents. Compared with other CNT/polymer composites, these composite materials exhibit much improved electrical conductivities and show potential applications as electrodes or in optoelectronic devices.

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