

## References

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## Fabrication and characterization of well-dispersed single-walled carbon nanotube/polyaniline composites

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Since the discovery of carbon nanotubes (CNTs), extensive research in the fields of applied physics, chemistry and materials science and engineering has rapidly emerged [1–3]. The potential applications of nanotubes are many, and include nanoelectronic devices [4,5], field emitters [6], probe tips for scanning probe microscopy [7], etc. As theoretically anticipated, the tensile modulus and strength of the nanotubes are about 1 TPa and 200 MPa, respectively [8,9]. These nano-structural elements could also be used as nano-fillers and nano-reinforcements for improving the mechanical, thermal and impact resistance properties of advanced composite materials. It has been shown experimentally that the introduction of CNTs into a polymer matrix improves the electrical conductivity as well as the mechanical properties of the original polymer matrix [10–12]. As a result, CNT-based nanostructures and functional materials have become popular subjects of study. Many efforts have focused on the design and preparation of nanotubes-polymer composites and a large number of composites based on CNTs have been prepared. For instance, CNTs can be used as a conductive filler for CNTs/poly(3-octylthiophene) composites [13], and some other composites have also been reported, such as CNT/

poly(phenylenevinylene) (PPV) [14], CNT/polypyrrole [15], and CNT/PMMA [16]. Moreover, carbon nanotubes have been suggested to increase the efficiency of polymer-based light-emitting diodes [17].

Among various conducting polymers, polyaniline (PANI) is a unique and promising candidate for practical applications due to its good processability, environmental stability, and reversible control of electrical properties by both charge-transfer doping and protonation [18,19]. To date, several studies concerning CNT/PANI composites have been reported [20–22]. However, realization of the expected enhancement in properties has not been demonstrated. This is in part because of the difficulties in material processing arising from insolubility of the pristine CNTs in most solvents. In addition, CNTs and polymer chains interact only weakly through van der Waals bonds. There is therefore interest in increasing the strength of the bonding between the nanotubes and the polymer matrix so that the overall strength and toughness of the composite materials can be increased.

Recent studies have shown that CNTs can be dissolved in aniline via formation of donor-acceptor complex [23]. The solubility of single-walled carbon nanotubes (SWNTs) in aniline is up to 8 mg/ml. To our knowledge, this presents the first observation of significant dissolution of pristine CNTs in standard organic solvents. This aniline-nanotube solution can be readily diluted with other organic

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solvents such as acetone, THF, and DMF [23]. Here, we report the fabrication and characterization of SWNT/PANI composites by in situ polymerization of an aniline solution containing different SWNT contents. Electron microscopy and conductive analysis showed that they have good uniformity, nanotube dispersion, and electric conductivity.

SWNTs were produced by a chemical vapor deposition method. The process of preparation and purification were described in detail elsewhere [24,25]. In this work, SWNTs were synthesized by using methane as carbon reactant and MgO-supported Fe nanoparticles as catalyst, and the reaction was carried out at 850 °C under Ar atmosphere for 30 min. The obtained SWNTs were then added to 5 ml of aniline with different contents of 1, 2, 4, 8 wt.% (weight percent with respect to aniline monomer). The mixture was heated at reflux for 3 h in the dark. After reflux for a short time, the original colorless aniline solution first became brownish and then turned dark red, indicating that SWNTs have been dissolved into aniline. After being cooled to room temperature, a SWNT solution was obtained by filtration through a  $\varnothing 0.1 \mu\text{m}$  Supor Membrane Disc Filters (Gelman).

Polymerization was carried out as follows: a solution of 1 M HCl containing 0.325 M aniline dissolved SWNTs in various mixture ratios was stirred at 0–5 °C and then an equal volume of precooled (5 °C) oxidant solution containing 0.125 M ammonium persulfate in 1 M HCl was slowly added dropwise to the well-stirred solution. The mixture was left for polymerization for 2 h at 0–5 °C under constant stirring. The polymerization of aniline-dissolved SWNTs can be observed by the color change of the solution. After a few minutes, the solution became green. The SWNT/PANI composites were obtained by filtering and rinsing the reaction mixtures with deionised water followed by drying under vacuum at 80 °C for 24 h.

Fig. 1 shows the typical SEM image of the purified SWNTs. It can be seen that the SWNTs are very long and

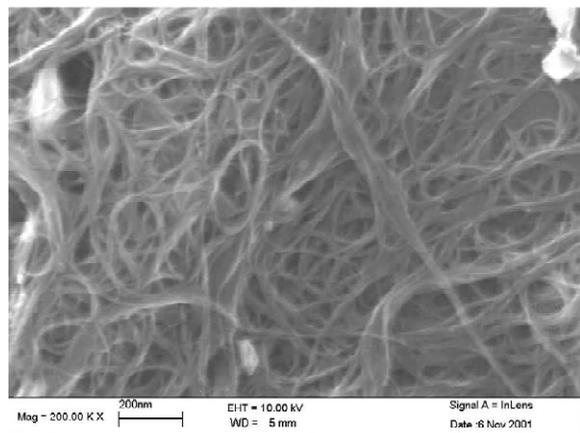


Fig. 1. Typical SEM image of the purified SWNTs.

highly entangled in the solid state to form a dense, robust, network structure. It is very difficult for the SWNTs to be well dispersed in polymer matrix because of their tendency to agglomerate into thick ropes or bundles, and their inherent insolubility in most solvents [26]. Interestingly, experiment indicates that SWNTs can be well dispersed in most solvents such as acetone, THF, DMF, etc., after refluxing in aniline, which is consistent with the result reported by Sun et al. [23]. Fig. 2a shows the typical tapping mode AFM image of SWNT-aniline solution diluted with acetone after evaporation on a Si wafer. It was obvious that the SWNTs have been completely peeled off and were present as individual tubes or thin bundles. From the AFM section profile measurement, the SWNTs are 0.8–2 nm in height with a well-defined dispersion. To assess quantitatively the diameters of the nanotubes, we have systematically analyzed a large number of AFM images. As shown in Fig. 2b, quantitative analysis demonstrates relatively narrow distributions with average diameter of  $1.83 \pm 0.02 \text{ nm}$ .

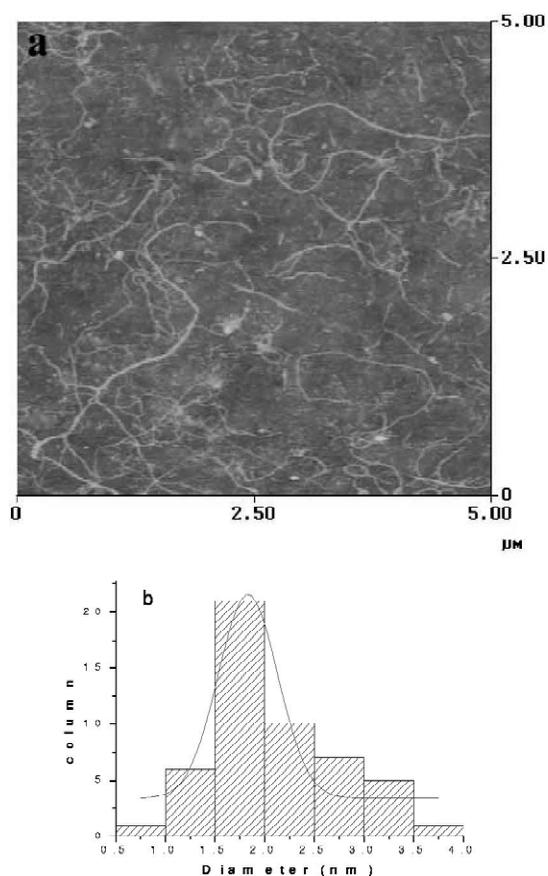


Fig. 2. The typical tapping mode AFM image of SWNT-aniline solution diluted with acetone after evaporated on Si wafer (a) and histogram of the diameter of the dissolved SWNTs (b). The solid line in (b) corresponds to Gaussian fits.

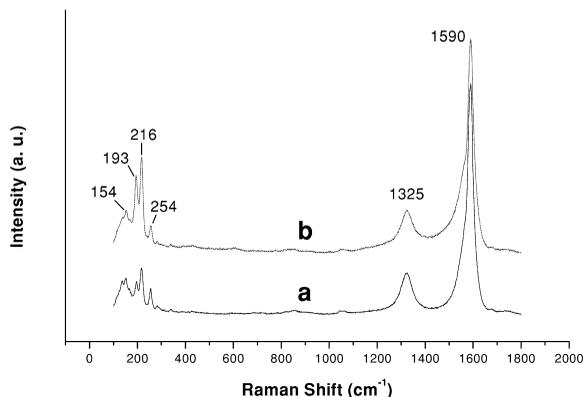


Fig. 3. Raman spectra of SWNT samples before (a) and after refluxing in aniline (b).

In order to make sure that no damage had occurred to the SWNTs, Raman spectroscopy was used to investigate their microstructure. Fig. 3 shows Raman spectra of SWNT samples (a) before and (b) after refluxing in aniline. Both spectra show typical SWNT features for the tangential and radial breathing modes near 1600 and 200  $\text{cm}^{-1}$ , respectively [27]. It can be seen that there is also a small band located around 1350  $\text{cm}^{-1}$  in both spectra. The band in this region is usually assigned to the amorphous carbon residuals. Compared with the Raman spectrum of the original SWNTs, a stronger and sharper peak of RBM in the spectrum of the SWNTs refluxed in aniline was observed, suggesting that the obtained SWNTs are well dispersed into individual and thin bundles. The radial breathing mode present near 200  $\text{cm}^{-1}$  is directly related to the diameter of the SWNTs and the relationship between them can be estimated from the formula  $\omega = 223.75/d$ , where  $d$  is the tube diameter in nanotubes and  $\omega$  is the frequency of the radial breathing mode in wavenumbers [28]. According to this formula, the peaks present correspond to SWNTs with diameters of 1.45, 1.16, 1.04, and 0.88 nm, respectively. The result indicates that no damage occurred to the SWNTs after refluxing in aniline and the resulting SWNTs are of good quality.

Fig. 4 shows UV-visible adsorption spectra of (a) the original SWNTs, (b) aniline, and (c) the SWNT-aniline solution diluted with acetone. No adsorption peak was observed in the spectrum of the original SWNTs (Fig. 4a). A single peak appeared around 320 nm in the spectrum of aniline (Fig. 4b), which is originated from the  $\pi$ - $\pi^*$  transition of the benzene rings and the excitation of the quinoid rings. In the spectrum of the SWNT-aniline solution (Fig. 4c), new peaks appear around 362, 455, 510, and 550 nm, respectively, which suggested the formation of an aniline-SWNT charge-transfer complex. It is reported that carbon nanotubes should be a good electron acceptor, while aniline is a fairly good electron donor. At elevated

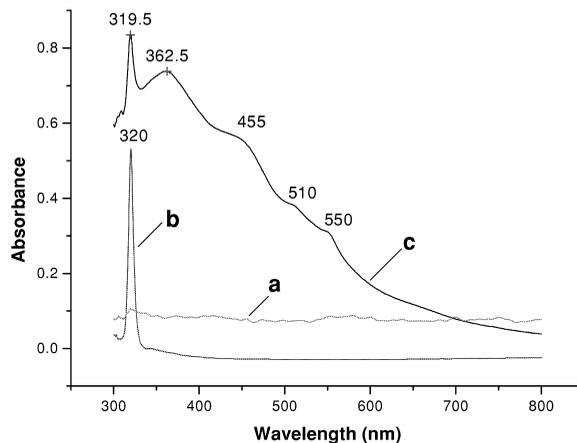


Fig. 4. UV-visible adsorption spectra of the SWNTs (a), aniline (b), and the SWNT-aniline solution (c) diluted with acetone.

temperatures, nanotubes and aniline may form a charge-transfer complex in their ground state [23].

The SWNT/PANI composites were obtained by polymerization of aniline dissolved SWNTs with different concentrations. Fig. 5 shows the TEM image of the composites obtained by polymerization of aniline dissolved SWNTs with a concentration of 8 wt.%. As shown in Fig. 5, a single SWNT was visible with the hollow core at the center of the composites. It can be seen that the diameter of the SWNT is 1–2 nm and the PANI coating is approximately 10 nm thick. This is indicative of good interaction between nanotubes and aniline, as each SWNT supports a quite considerable mass of PANI. This conclu-

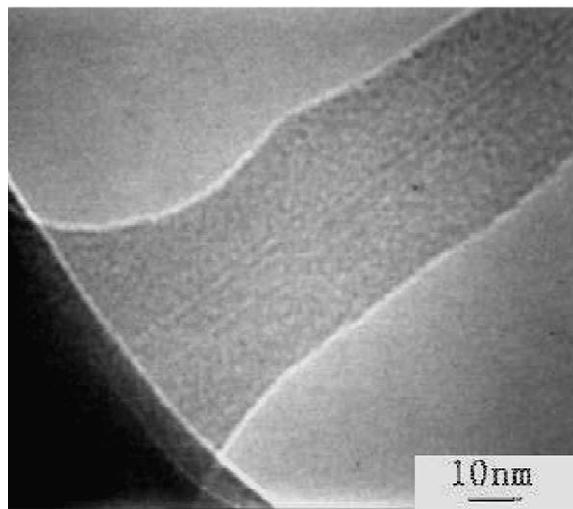


Fig. 5. Typical TEM image of the SWNT/PANI composites obtained by polymerization of aniline dissolved SWNTs with concentration of 8 wt.%.

sion was also proved by UV–vis spectra. The nanotubes stick strongly to the PANI matrix by the formation of charge-transfer complex rather than the weak van der Waals interactions between the nanotubes and polymer chains [29].

To further confirm the validity of the TEM image, we measured the electrical conductivity of the composites at room temperature. When the SWNTs content is increased to 8%, the conductivity of the composite is  $1.26 \times 10^{-2} \text{ S m}^{-1}$ , which is 14 times higher than that of the pure PANI measured under similar conditions. Even 1% of SWNTs can improve the conductivity of the composite to more than twice than that of the PANI. This enhancement of conductivity may be due to the dopant effect or charge-transfer from the PANI to carbon nanotubes. In addition, due to the large aspect ratio and surface area of SWNTs, they may serve as conductive bridges connecting PANI conducting domains and increasing the electrical conductivities of the composites.

In summary, SWNT/PANI composites with good uniformity and dispersion have been formed by the polymerization of aniline containing well-dissolved SWNTs. Raman spectroscopy indicated that no damage had occurred to the SWNTs after refluxing in aniline and the resulting SWNTs were of good quality. UV–vis adsorption spectroscopy and TEM studies show that the nanotubes adhere strongly to the PANI matrix by the formation of a charge-transfer complex rather than the weak van der Waals interactions between them. This facilitates improved dispersion of SWNTs into the PANI matrix, and results in enhanced electric conductivity.

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