

Cationic surfactant directed polyaniline/CNT nanocables: synthesis, characterization, and enhanced electrical properties

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Abstract

We described here a new approach to the synthesis of size-controllable polyaniline/carbon nanotube (CNT) nanocables by in situ chemical oxidative polymerization directed by the cationic surfactant cetyltrimethylammonium bromide (CTAB). Carbon nanotubes were first dispersed in a high concentration (12-fold critical micelle concentration) CTAB solution, and thus the CTAB is adsorbed and arranged regularly at the CNT surfaces. Upon addition of the aniline monomer, some of the aniline hydrochloride is adsorbed at the surface of CNTs and wedged into the arranged CTAB molecules. When ammonium persulfate (APS) was added, aniline was polymerized in situ at the surfaces of the CNTs (core layer), ultimately forming the outer shell of the nanocables. Such polyaniline/CNT nanocables show enhanced electrical properties.

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1. Introduction

Rapid advances in the bulk synthesis of carbon nanotubes (CNTs), coupled with their remarkable mechanical and novel electrical properties offer the possibility of numerous novel applications via the generation of a host of CNT-based composite materials [1,2]. Following the first report of the preparation of a CNT/polymer composite by Ajayan et al. [3], many efforts have been directed towards combining CNT and polymers in order to produce functional composite materials with superior properties [4–7]. For example, epoxy resin loaded with 1% single-walled carbon nanotubes (SWNTs) showed a 70% increase in thermal conductivity at 40 K, increasing to 125% at room temperature [8]. The presence of SWNTs in poly(*m*-phenylene vinylene-*co*-2,5-dioctoxy-*p*-phenylene) (PmPV) composites shifts the radiative recombination region in

double-emitting organic light-emitting diodes (DE-OLEDs) without changing the PmPV emission energy [9]. Addition of only 1% multi-walled carbon nanotubes (MWNTs) to polystyrene results in 36–42% and 25% increases in elastic modulus and break stress respectively of the polymer because the external load can be effectively transferred to the nanotubes [10] and the introduction of MWNTs to polyaniline composites enhances the electrical properties (the room temperature resistivity is decreased by one order of magnitude as compared to polyaniline) by facilitating charge-transfer processes between the two components [11]. Several methods have been developed to prepare these polymer/nanotube composites efficiently. These include dissolving polymer into the MWNT suspension of organic solvents [12], melt mixing [13], in situ polymerization [14], grafting macromolecules to the CNT [15] and electrochemistry [16]. However, the systematic production of CNT-based structural composite materials, especially composite nanotubes or nanowires, remains a technological challenge. Applications for such technology would include polyaniline nanotubes doped with sulfonated CNTs made via a self-assembly process [17] and aligned

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coaxial nanowires of CNTs sheathed with conducting polyaniline or polypyrrole [18].

In the present study, we describe a new approach to the synthesis of size-controllable polyaniline/CNT nanocables by in situ chemical oxidative polymerization directed with the cationic surfactant cetyltrimethylammonium bromide (CTAB). Carbon nanotubes were first dispersed uniformly in the surfactant solution and then aniline was polymerized in situ at the surfaces of the CNTs (core layer), ultimately forming the outer shell of the nanocables. Such polyaniline/CNT nanocables show enhanced electrical properties due to their cable-like structure.

2. Experimental

Aniline monomer was distilled under reduced pressure. Multi-walled carbon nanotubes used in this work were synthesized by ethylene CVD using Al_2O_3 supported Fe catalysts as described in a previous study [19]. Other reagents were used without further purification.

Polyaniline/CNT nanocables were synthesized by in situ chemical oxidative polymerization directed with cationic surfactant cetyltrimethylammonium bromide (CTAB). In a typical nanocable synthesis experiment, 0.124 g CTAB and 6.6 mg CNT were added into 31 ml 1.0 M HCl solutions and sonicated for over 2 h to obtain well-dispersed suspensions, then cooled down to 0–5 °C. A pre-cooled solution of 0.06 ml aniline monomer and 6.25 ml 1.0 M HCl containing 0.147 g APS were added sequentially to the above suspensions. The reaction mixture was sonicated for 2 min, then left standing in the refrigerator at 0–5 °C for 24 h. After that, the resulting black precipitate was filtered and rinsed with distilled water and methanol for several times. The remaining filter cake was then dried under a vacuum at room temperature for 24 h.

Raman spectra were recorded with a Renishaw system 1000 using a 50 mW He–Ne laser operating at 632.8 nm with a CCD detector. The final spectrum presented is an average of 10 spectra recorded at different regions over the entire range of the sample. SEM was conducted at 25 kV and TEM at 200 kV and at 300 kV for the high resolution studies. Samples used in dc electrical-conductivity and magnetoresistance measurements were in the form of pressed pellets, 12 mm in diameter and about 0.1 mm in thickness. The standard Van Der Pauw DC four-probe method [20] was used to measure the electron transport behavior of polyaniline and nanocables. Electrical conductivity was measured using Keithley 220-programmable current source and 181-nanovoltmeter, which was auto-controlled by a computer. Magnetoresistance was measured using PPMS (Physical Properties Measurement System from Quantum Design, USA).

3. Results and discussion

The morphology of the resulting nanostructures was characterized by SEM and TEM (Fig. 1). SEM images clearly show that the nanostructures were of uniform shape with diameters in the range of several tens of nanometers and lengths up to several micrometers (Fig. 1a). Some irregularities, appearing as “dents” or surface depressions were observed at their edges (Fig. 1b). TEM images (insets in Fig. 1a and b, respectively) revealed the

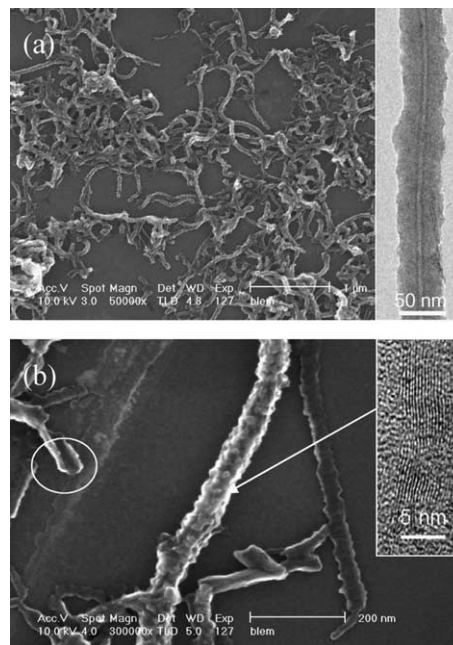


Fig. 1. SEM images of polyaniline/CNT nanocables with a (a) large scale (inset: TEM image of single nanocable) and (b) small scale (inset: HRTEM image with clear crystalline phase of inner layer of single nanocable).

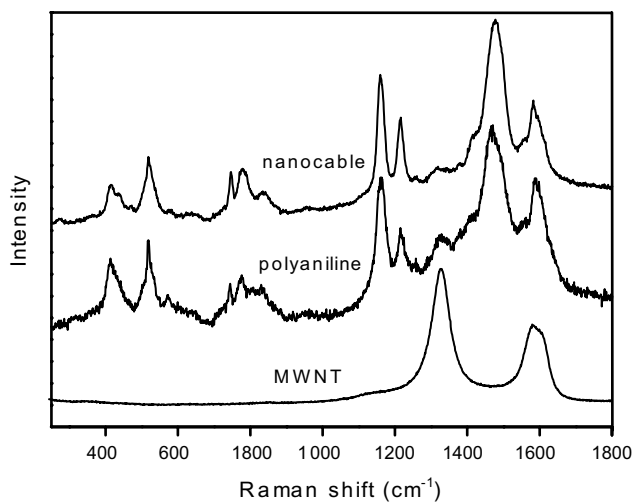


Fig. 2. Raman spectra for polyaniline, MWNT and polyaniline/CNT nanocable.

cable-like morphology of the nanostructures in which the outer layer was apparently amorphous and the inner layer crystalline. A lattice spacing of about 0.34 nm along the nanocable can be readily resolved, indicating that the inner layer was comprised of multi-walled CNTs [21]. Taken together, these data suggest that the aniline monomers polymerized not in the hollow core but at the surface of the MWNTs. The rough outer amorphous polyaniline layer had an average thickness of about several tens of nanometers (Fig. 1).

Raman spectroscopy was used to characterize the chemical composition of the polyaniline/CNT nanostructures (“nanocables”). Fig. 2 shows the Raman spectra of MWNT, polyaniline and polyaniline/CNT

nanocables. For the pure carbon nanotubes, two strong peaks were observed around 1580 and 1326 cm^{-1} , which can be assigned to the D and G modes of CNTs respectively [22]. The Raman spectrum for polyaniline was essentially similar to that reported previously [23]. C–H bending of the quinoid/benzenoid ring at 1160 cm^{-1} , C–N⁺ stretching at 1328 cm^{-1} , C=N stretching of the quinoid ring at 1466 cm^{-1} , and C–C stretching of the benzenoid ring at 1586 cm^{-1} were observed, indicating the presence of doped polyaniline structures [17]. In the case of the polyaniline/CNT nanocables, Raman typical characteristics of polyaniline were apparent, suggesting that the CNTs were entirely encapsulated by polymer. In comparing the spectra derived from polyaniline with

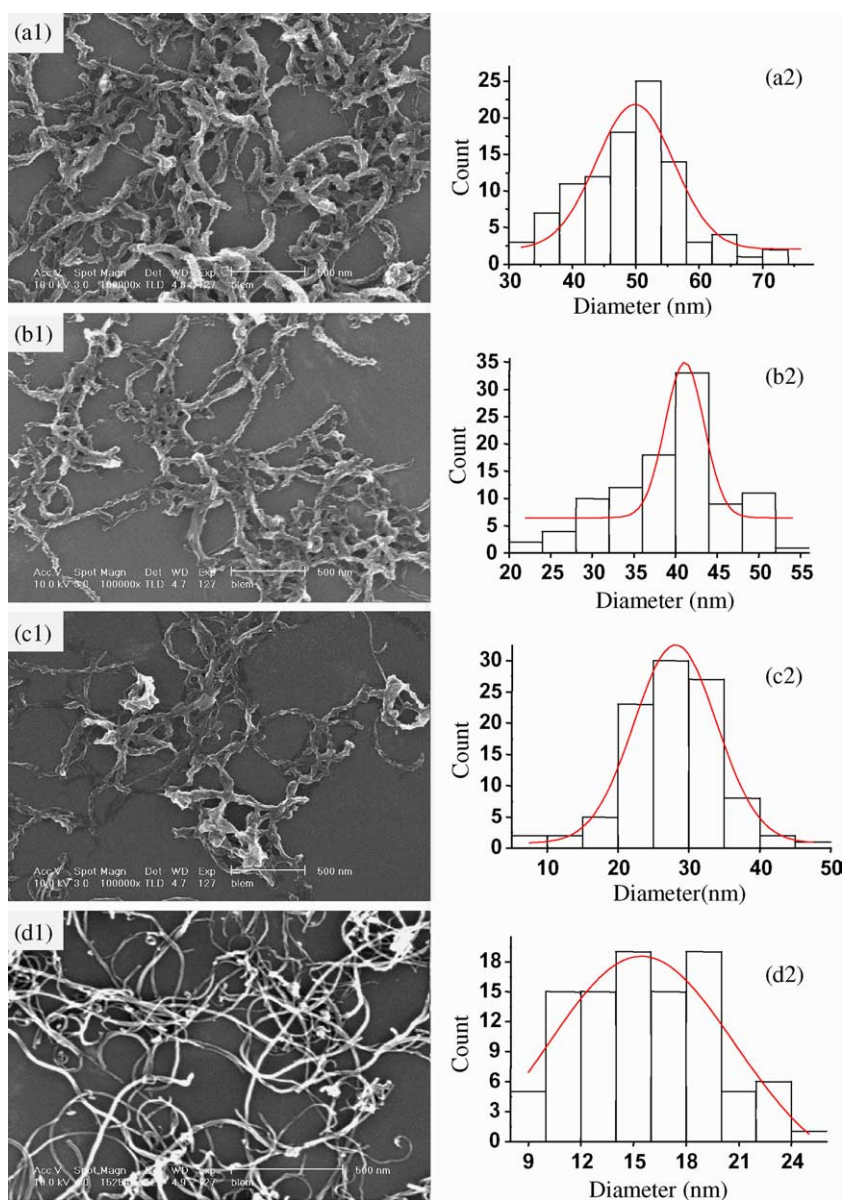


Fig. 3. SEM images and diameter distributions of polyaniline/CNT nanocables with different aniline/CNT mass ratios: (a) 300:33; (b) 200:33; (c) 100:33 and (d) 0:33.

that of polyaniline/CNT nanocables, two points should be noted: (1) the remarkable decrease in relative intensity of C–N⁺ stretching at 1328 cm⁻¹ with respect to that of C–H bending at 1160 cm⁻¹, indicating that the degree of protonic acid doping decreases in the presence of CNTs and (2) the C=N stretching of the quinoid ring shifts from 1466 to 1477 cm⁻¹, suggesting that a site-selective interaction between the quinoid ring of the doped polymer and the CNTs had occurred as a consequence of the in situ polymerization. This interaction probably facilitates charge-transfer processes between the polymer and CNTs [11].

The average diameter of the nanocable can be controlled by changing the aniline/CNT mass ratio. Typical MWNTs without polyaniline coatings are uniform with diameters in the range of 8–25 nm and length up to several hundreds of nanometers (Fig. 3d), the distribution of diameter sizes (obtained from measurements of hundreds of SEM images) at different sample locations showed a peak centered at 16 nm. In addition, nanocables with different aniline/CNT mass ratios are apparently different from CNTs in both morphology and size (Fig. 3a–c). For any given aniline/CNT mass ratio, the nanocables were all relatively uniform but the average diameter of nanocables with different aniline/CNT mass ratios were different. The smaller the aniline/CNT mass ratio, the smaller the average diameter. This trend can be clearly seen from the histograms of the diameter size distributions. A new peak value, at 27 nm, emerged in the nanocable diameter distribution plot corresponding

to a 100:33 aniline/CNT mass ratio (though diameters as small as pure CNTs were also still present). Increasing the aniline/CNT ratios to 200:33 and 300:33 resulted in mean diameter sizes of 41 and 50 nm respectively. Thus it can be seen that nanocable diameter is apparently proportional to the aniline/CNT mass ratio. However, further increasing the aniline/CNT ratio to greater than 300:33 resulted in the presence of a number of “nanogrooves” (groove-like structures indicated by the circle in Fig. 1b) and decreasing the aniline/CNT ratio to less than 100:33, indicated the presence of many nanostructures with diameter corresponding to that of CNTs. These data indicate that the optimum aniline/CNT mass ratio range lies between 100:33 to 300:33 and we can control the average diameter by simply changing the ratio in this range.

A model describing the mechanism of polyaniline/CNT nanocable formation by in situ chemical oxidative synthesis directed with cationic surfactant CTAB is as follows. The surfactant CTAB appears to play an important role in the synthetic pathway (shown in Fig. 4). CTAB initially breaks the CNT bundles into individual tubes during sonication in 1.0 M HCl solutions. Secondly, the surfactant is adsorbed and arranged regularly at the CNTs surfaces due to the relatively high concentration (12-fold critical micelle concentration). Upon addition of the aniline monomer, aniline immediately reacts with HCl to form aniline hydrochloride. Some of the aniline hydrochloride is adsorbed at the surface of CNTs and wedged into the arranged CTAB

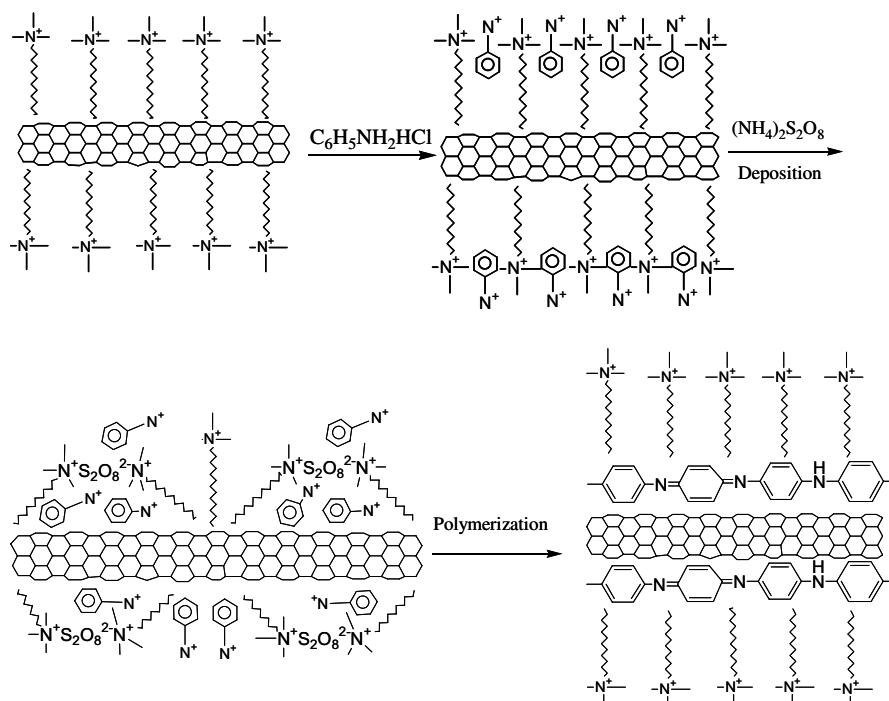


Fig. 4. Schematic diagram of the formation mechanism of a polyaniline/CNT nanocable.

molecules. The remaining aniline hydrochloride is in solution and a dynamic equilibrium is set up between the two. When APS was added, a heavy floccular precipitate instantly appeared, presumably due to electrical neutralization between the quaternary ammonium cation of the CTAB and $S_2O_8^{2-}$ of APS ($((CTA)_2S_2O_8$ is insoluble in water or in 1.0 M HCl). The surfactant CTAB is therefore deactivated and some of aniline hydrochloride and individual CNTs become encapsulated during precipitation. Aniline hydrochloride and $S_2O_8^{2-}$ will collide due to Brownian motion and electron exchange will occur, resulting in a redox reaction. Aniline hydrochloride is oxidized to produce the oligomer and $S_2O_8^{2-}$ is reduced to SO_4^{2-} . Once $S_2O_8^{2-}$ is reduced to SO_4^{2-} , surfactant CTAB is then regenerated ($((CTA)_2SO_4$ is soluble in water or in 1.0 M HCl), and the floccular precipitate can be seen to gradually disappear. When aniline hydrochloride encapsulated during precipitation is oxidized, the aniline hydrochloride remaining in solution would be expected to diffuse towards the unreduced floccular precipitate $(CTA)_2S_2O_8$ and be further oxidized. Polyaniline oligomers and polymers are insoluble and this, together with the site-selective interaction between the quinoid ring of the doped polymer and the CNTs, would result in the deposition of polyaniline at the surface of the CNTs. The resulting polyaniline/CNT nanocables are then stabilized by regeneration of the surfactant CTAB.

No polyaniline/CNT nanocables were obtained when cationic surfactant CTAB was replaced by anionic surfactant sodium dodecyl sulfate (SDS). A number of different organic sulfonic acids, including camphorsulfonic acid [24] and dodecyl benzene sulfonic acid [25] have been used as dopants to modify the solubility of doped polyaniline. SDS in 1.0 M HCl solutions probably plays the same role as organic sulfonic acid in that dodecyl sulfate acted as the counter-ion in doping the polyaniline. So SDS and other anionic surfactants could not serve as surfactant in in situ chemical oxidative synthesis of polyaniline/CNT nanocables.

Polyaniline synthesized in the presence of CTAB shows a typical non-metallic behavior [26] with a room temperature conductivity of 7.77×10^{-3} S/cm (Fig. 5). (The room temperature conductivity of MWNT is 0.23 S/cm [27].) The low room temperature conductivity of polyaniline probably has something to do with its low protonic acid doping degree and amorphous morphology. The overall pattern of conductivity temperature dependence of polyaniline is well expressed in the form $\sigma \sim \exp[-(T_0/T)^{0.5}]$ [28,29]. In contrast, the electron transport properties of polyaniline/CNT nanocables exhibit the following remarkable characteristics: (1) the low and room temperature conductivity are both increased as the fraction of CNT increases; (2) the maximum room temperature conductivity of 1.35 S/cm is two orders of magnitude higher than that of polyaniline;

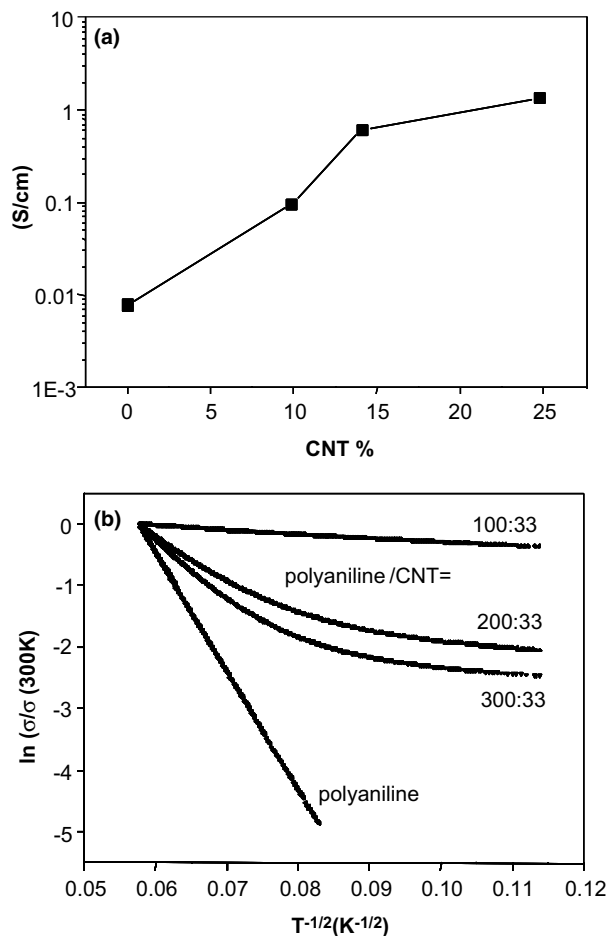


Fig. 5. (a) Room temperature conductivities of nanocables with the fraction of CNT varying from 0 to 25%; and (b) normalized conductivity temperature dependence for nanocables with different polyaniline/CNT mass ratios.

(3) the low temperature conductivity is much higher than that of polyaniline; (4) the temperature dependence of the conductivity is much weaker than that of polyaniline, probably due to the fact that the conductivities at different temperatures are dominated by different components [11]; (5) the conductivity is not well expressed in the form $\sigma \sim \exp[-(T_0/T)^{0.5}]$. Taken together, these facts indicate that electrical contacts between the polyaniline and CNT have been improved and that the cable-like structure favors the charge transfer between polyaniline and CNT.

Magnetoresistance (MR) is sensitive to the extent of structural disorder and therefore serves as an especially useful probe for identifying microscopic transport mechanisms and scattering processes [30]. As shown in Fig. 6a, polyaniline synthesized in the presence of CTAB shows negative MR at 200 K, which is in agreement with earlier results [31] (polyaniline shows positive MR at very low temperature). Nanocables with different polyaniline/CNT ratios show negative MR at 200 K (Fig. 6a)

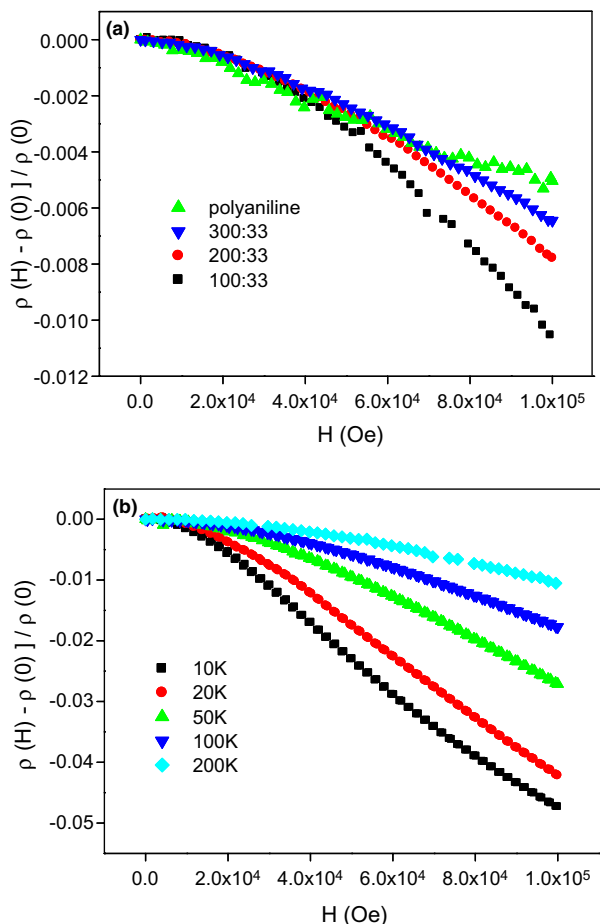


Fig. 6. (a) Magnetoresistance of nanocables with different polyaniline/CNT mass ratio as a function of the magnetic field at 200 K; and (b) magnetoresistance of nanocables (polyaniline/CNT mass ratio 100:33) as a function of the magnetic field at different temperatures.

while 100:33 ratio polyaniline/CNT nanocables show negative MR at 10–200 K (Fig. 6b). The data indicate that electrons transferred within the nanocable form a conventional diffusive system, describable within the framework of weak-localization theory, wherein the effect of e - e interaction can be treated as a perturbation [32] (MWNT synthesized by CVD also show negative MR at low temperature).

4. Conclusion

We have described a new approach to the synthesis of size-controllable polyaniline/CNT nanocables. Surfactant was applied to overcome the difficulty of CNT dispersing into insoluble and infusible polymer matrix, and aniline was polymerized in situ at the surface of the CNT (core layer), ultimately forming the outer shell of the nanocables. By changing the aniline/CNT ratio, we can easily control the sizes of as-prepared nanocables. Polyaniline/CNT nanocables produced in this way show

enhanced electrical properties (the conductivity of nanocables is two and one orders of magnitude higher than polyaniline and CNT, respectively) due to the cable-like structure favoring the charge transfer between polyaniline and CNT. Negative temperature coefficient of resistance at 77–300 K and negative magnetoresistance at 10–200 K were also observed. These characteristics of size-controllability and enhanced electrical properties provide new potential for applications for nanocables across a number of scientific and technological fields.

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