Single-Walled Carbon Nanotube-Based Coaxial Nanowires: Synthesis, Characterization, and Electrical Properties

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We report herein the template-directed synthesis, characterization, and electric properties of single-walled carbon nanotube- (SWNT-) based coaxial nanowires, that is, core (SWNT)—shell (conducting polypyrrole and polyaniline) nanowires. The SWNTs were first dispersed in aqueous solutions containing cationic surfactant cetyltrimethylammonium bromide (CTAB) or nonionic surfactant poly(ethylene glycol) mono-p-nonyl phenyl ether (O\(\sigma\)-10). Each individual nanotube (or small bundle) was then encased in its own micelle-like envelope with hydrophobic surfactant groups orientated toward the nanotube and hydrophilic groups orientated toward the solution. And thus a hydrophobic region within the micelle/SWNT (called a micelle/SWNT hybrid template) was formed. Insertion and growth of pyrrole or aniline monomers in this hybrid template, upon removal of the surfactant, produce coaxial structures with a SWNT center and conducting polypyrrole or polyaniline coating. Raman and Fourier transform infrared (FTIR) spectroscopy and scanning (SEM) and transmission (TEM) electron microscopy were used to characterize the composition and the structures of these coaxial nanowires. The results revealed that the micellar molecules used could affect the surface morphologies of the resulting coaxial nanowires but not the molecular structures of the corresponding conducting polymers. Electric properties testing indicated that the SWNTs played the key roles in the conducting polymer/SWNT composites during electron transfer in the temperature range 77 K to room temperature. Compared with the SWNT network embedded in the conducting polymers, the composites within which SWNTs were coated perfectly by the identical conducting polymers exhibited higher barrier heights during electron transfer.

Introduction

The past decade has witnessed significant progress in both the production and application of carbon nanotubes (CNTs) since their discovery in 1991.1–2 Following the first report of the preparation of a CNT/polymer composite by Ajayan et al.,3 many efforts have been made to combine CNTs 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-phenylenevinylene-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% multiwalled carbon nanotubes (MWNTs) to polystyrene results in a significant increase in the mechanical properties of the polymer because the external load can be effectively transferred to the nanotubes10 and the introduction of MWNTs to polyaniline composites enhances the electrical properties by facilitating charge-transfer processes between the two components.11 However, among these reports, carbon nanotube/polymer 1D composite nanostructures are seldom mentioned.

A most effective means of producing 1D nanostructures is by "template-directed synthesis" in which reactant materials are located within or in the immediate vicinity of the template.12 Many suitable nanoscale templates have been reported, including channels in porous materials (hard templates),13–14 mesoscale structures self-assembled from organic surfactants or block copolymers (soft templates),15–16 existing nanostructures including step edges on solid surfaces,17–19 biological DNA molecules and rod-shaped viruses,20–22 and other existing nanowires.23–24 More recently, carbon CNTs have begun to be used as hard templates to generate 1D nanomaterials with nanotubelike morphologies.25–27

In previous studies,28–31 we have described a rational approach to the synthesis of polyaniline/MWNT or polypyrrole/MWNT nanocables. Surfactant was applied to overcome the difficulty of CNT dispersing into insoluble and infusible polymer matrix, and aniline or pyrrole was polymerized in situ at the surface of the MWNT (core layer), ultimately forming the outer shell of the nanocables. These nanocables showed enhanced electrical properties due to the cablelike structure favoring charge transfer between polyaniline or polypyrrole and MWNTs.

Compared with MWNTs coated by conducting polymer, these would really show important quantum effects if the conducting polymer were well attached to the SWNT surface. In addition, it may be that the technique is more sensitive to either semiconducting or metallic nanotubes. So it would be more interesting to coat SWNTs with conducting polymers. However, to our knowledge, there are seldom reports on such coaxial nanowires. In the present study, we have attempted the synthesis of conducting polyaniline/SWNT (PAni/SWNT) and polypyrrole/SWNT (PPy/SWNT) coaxial nanowires. The SWNTs were first dispersed in aqueous solutions containing cationic surfactant cetyltrimethylammonium bromide (CTAB) or nonionic surfac-
The high-resolution TEM image (inset in Figure 1) clearly showed single walls and hollow cores of nanotubes.

PAni/SWNT coaxial nanowires were synthesized as follows: 0.124 g of cationic surfactant cetyltrimethylammonium bromide (CTAB) or 1.5 g of nonionic surfactant poly(ethylene glycol) mono-\(p\)-nonyl phenyl ether (O\(\alpha\)-10) were added into 35 mL of 1.0 M HCl solution containing 6.5 mg of SWNTs and sonicated for 4 h to obtain well-dispersed suspensions, then the suspension was cooled down to 0°–5 °C. Precooled solutions of 0.06 mL of aniline monomer and 6.25 mL of 1.0 M HCl containing 0.147 g of APS were added sequentially to the above suspensions. The reaction mixture was sonicated for 2 min and then left standing at 0°–5 °C for 24 h. After that, the resulting black precipitate was filtered and rinsed with distilled water and methanol several times. The remaining filter cake was then dried under a vacuum at room temperature for 24 h.

PPy/SWNT coaxial nanowires were synthesized as follows: 0.124 g of cationic surfactant CTAB or 1.5 g of O\(\alpha\)-10 were added into 35 mL of deionized water containing 6.5 mg SWNTs and sonicated for 4 h to obtain well-dispersed suspensions, and then the suspension was cooled down to 0°–5 °C. Precooled solutions of 0.06 mL of pyrrole monomer and 6.25 mL of deionized water containing 0.204 g of APS were added sequentially to the above suspensions. The reaction mixture was sonicated for 2 min and then left standing at 0°–5 °C for 24 h. After that, the resulting black precipitate was filtered and rinsed with distilled water and methanol several times. The remaining filter cake was then dried under a vacuum at room temperature for 24 h.

Raman spectra were recorded on a Renishaw system 1000 with 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. Infrared spectra were recorded on a Magna-IR 750 system by use of powder samples. SEM was conducted at 10 kV on a XL30S–FEG field-emission instrument and TEM was performed on JEM200CX at 200 kV. High-resolution transmission electron microscopic (HRTEM) images were recorded on Tecnai F30 at 300 kV. Samples for SEM and TEM were prepared by placing a drop of as-made nanowire aqueous dispersion onto a silicon wafer and carbon-coated copper grid, respectively. Electrical conductivity was measured by use of a Keithley 220-programmable current source and 181-nanovoltmeter, which was autocontrolled by a computer. Samples used in dc electrical-conductivity measurements were in the form of pressed pellets (12 mm in diameter and about 0.1 mm in thickness) obtained by applying a hydraulic pressure about 10 MPa.

Results and Discussion

Morphology. Figure 2 shows the SEM images of PAni/SWNT and PPy/SWNT composites, which were prepared by directed synthesis with different surfactants. For PAni/SWNT composites, when cationic surfactant CTAB was used for the micellar molecules, it was hard to find the wirelike structures (Figure 2a), but when nonionic surfactant O\(\alpha\)-10 was used, it was very easy to find the wirelike structures (Figure 2b). However, for PPy/SWNT composites, whichever surfactant was used for the micellar molecules, the as-prepared composites showed wirelike structures (Figure 2c,d). Both wirelike PAni/SWNT and PPy/SWNT were of uniform shape with diameters in the range of several tens of nanometers and lengths up to several micrometers. The surface morphologies of as-made wirelike composites were very different. For PAni/SWNT
wirelike nanostructures, there was much burr at the surfaces (Figure 2b). However, for PPy/SWNT, when cationic surfactant CTAB was used for the micellar molecules, their surfaces were relatively smooth (Figure 2c), but when nonionic surfactant O₅₋₁₀ was used, there were many spherical particles appearing at the surfaces (Figure 2d). These indicate that different types of surfactants have greatly affected the surface morphologies of as-made conducting polymer/SWNT composites.

Apparently these diverse surface morphologies came from the conducting polymers, so where were the SWNTs? Did these conducting polymers coat them? To answer these questions, special experiments were done. Take PPy/SWNT for example. Compared with the formula described in the Experimental Section, we halved the concentration of SWNTs, decreased the concentration of monomer to one-third, and used cationic surfactant CTAB as micellar molecules. The purpose of halving the SWNT concentration was to get better dispersion of SWNTs in the aqueous solutions, and the purpose of decreasing the monomer concentration was to get the thinner coating layers if it was true that the SWNTs were coated by the conducting polymers. Figure 3 shows the SEM and high-resolution TEM images of as-made products obtained by such a special formula. There were many wirelike PPy/SWNT composites still present; however, some nanostructures as thin as SWNT bundles appeared (arrows in Figure 3a). High-resolution TEM investigations indicated that these thin nanostructures were really small bundles of SWNTs and individual SWNTs coated with the thin conducting polymer layers. Figure 3b showed a bundle formed by two individual SWNTs. The diameter of one individual SWNT was 1.3 nm, and that of the other is 0.9 nm. Along the length direction, parts of the bundle being coated by amorphous conducting PPy were clearly seen, and other parts of the bundle were still naked. The reason for naked surfaces of the SWNT bundles is apparently ascribed to the absence of monomers in such a local region. In addition, in these naked parts of the SWNT bundles, their hollow cores were clearly seen, which demonstrated that monomers were only polymerized at the surfaces of the bundles, rather than in their hollow cores. Taken together, these investigations indicated that as-made conducting polymer/SWNT composites were coaxial structures: the outer layers were composed of the conducting polymers and the inner layers were composed of either the individual SWNTs or their small bundles. Compared with the fact that individual MWNTs

Figure 2. Conducting polymer/single-wall CNT composites directed by different micelle/CNT templates: (a) PANi/SWNT composites without coaxial nanostructures by using CTAB for micellar molecules; (b) PANi/SWNT composites with coaxial nanostructures by using O₅₋₁₀ for micellar molecules; (c) PPy/SWNT composites with coaxial nanostructures by using CTAB for micellar molecules; and (d) PPy/SWNT composites with coaxial nanostructures by using O₅₋₁₀ for micellar molecules.

Figure 3. (a) SEM and (b) TEM images of the nanostructures as thin as single-wall CNT bundles appeared within the PPy/SWNT composites by applying the micelle/CNT hybrid template-directed synthesis.
have served as the core layers of as-made nanocables, the reason for some small bundles of single-wall CNT as the core layers of as-made coaxial nanowires was ascribed to the difficulty of dispersing single-wall CNTs into aqueous solutions completely as the individual tubes by use of the surfactants. Previous work by other scientists showed that, in the presence of various surfactants, only parts of original single-wall CNT bundles were disintegrated into individual tubes, and the rest of them were just disintegrated into small bundles.

Along with our previous works, we put forward here a general mechanism, a micelle/CNT hybrid template-directed synthesis strategy, to explain the formation of the conducting polymer/SWNT coaxial nanowires. The strategy we have developed for template formation and template-directed synthesis of CNT-based coaxial nanowires is shown in Scheme 1. The CNTs were first dispersed in aqueous solutions containing anionic, cationic, or nonionic surfactants and block copolymers similar to the procedure reported by Islam et al. Each nanotube is thusencased in its own micellike envelope with hydrophobic surfactant groups orientated toward the nanotube and hydrophilic groups orientated toward the solution. Such micelle/CNT hybrid structures can be clearly seen by TEM. There is thus a hydrophobic region within the micelle/CNT hybrid structure. Insertion and growth of hydrophobic reactant materials in this region, upon removal of the surfactant, produces coaxial structures with a CNT center and grown material outer coatings. In the present study, we only investigate the role of both cationic and nonionic surfactant as micellar molecules. We have confirmed in our previous studies that anionic surfactant cannot be used for the micellar molecule when micelle/CNT hybrid template is used to direct the synthesis of conducting polymer/MWNT coaxial nanowires.

It was very interesting that when the micelle/CNT hybrid templates were used to direct the synthesis, for PPy/SWNT coaxial nanowires, both cationic and nonionic surfactant could be used for the micellar molecules, however for PANi/SWNT coaxial nanowires, only nonionic surfactant could be used as the micellar molecules. The reason for cationic surfactant not being usable for the micellar molecules when the micelle/SWNT hybrid template was used to direct the synthesis of PANi/SWNT coaxial nanowires was ascribed to the definite hydrophilicity of aniline monomers in 1 M HCl solutions and to the interactions between the surfactant CTAB and the oxidizing agent APS. In a previous study, we have demonstrated that the lamellar mesostructures can be formed between the cations of surfactant CTAB and anions of oxidizing agent APS. And we also have demonstrated that such mesostructures formed during the synthesis of the coaxial nanowires cannot affect the micelle/CNT hybrid template strategy. However, compared with MWNTs, the individual SWNTs or their small bundles were very thin; even their diameters were comparable to the layer spaces of lamellar mesostructures. In such a circumstance, when APS was added, the individual single-wall CNTs or their small bundles were located within the interlayers of lamellar. Furthermore, due to the definite hydrophilicity of aniline monomers in 1 M HCl solutions, the monomer could not wedge into the vicinities of hydrophobic CNTs completely to swell the layer spaces enough. So ribbonlike networks of PANi/SWNT composites were formed after reaction (Figure 2a). Some nanostructures as thin as single-wall CNT bundles (arrows in Figure 2a) have confirmed that single-wall CNT were embedded within the ribbonlike networks. By the way, the reason that the different surfactants result in different surface morphologies of as-made coaxial nanowires probably can be ascribed to the extraneous chemical process between cationic surfactant cations and oxidizing anions of APS but not between nonionic surfactant O10- and APS.

It seems from Figure 2 that the quality and uniformity of the wires is much better in the case of PPy than PANi. According to the micelle/CNT hybrid template-directed synthesis strategy we have proposed in this paper, one of the key steps is whether the monomer can enter hydrophobic regions within the micelle/CNT hybrid structures. By comparing aniline in 1 M HCl solution with pyrrole in neutral aqueous solution, it is obvious that pyrrole can more easily enter the hydrophobic regions within the micelle/CNT hybrid structures while it is difficult for aniline to enter, which is probably the reason that the quality and uniformity of the wires seem to be much better in the case of PPy than PANi.

Structural Characterization. Raman and IR spectra were used to characterize the molecular structure of the resulting conducting polymer/SWNT composites obtained by the above micelle/CNT hybrid template-directed strategy. Figure 4 shows the Raman and IR spectra of the resulting PANi/SWNT composites. It was found that, for PANi/SWNT composites, whichever surfactant was used as micellar molecules, both Raman and IR spectrum were similar. This indicates that micellar molecules cannot affect the molecular structure of the resulting PANi/SWNT composites during the synthesis. Although SWNTs were not perfectly coated by conducting PANi when CTAB was used as surfactant, the interaction between nanotubes and PANI did not exist, as similarly SWNT were perfectly coated by conducting PANI when O10- was used as surfactant. So the Raman and IR spectra of PANI (Figure 4) show no change in the molecular structure of PANI independent of the surfactant used. For the IR spectrum, the peaks at 1580 and 1494 cm-1 can be assigned to the C=C stretching vibration of quinoid and benzenoid rings, respectively, and the bands at 1300 and 1142 cm-1 correspond to C=N and C=N stretching vibration, respectively. These characteristic peaks are identical to those found in the emeraldine salt of polyaniline. The two very weak peaks around 2924 and 2854 cm-1, attributable to stretching modes of methylene groups, indicate that the surfactants were almost completely eliminated from the resulting composites (If the surfactants used had been retained in the composites, these IR peaks would be strong.) For the Raman spectrum, C-H bending of the quinoid/benzenoid ring at 1160 cm-1, weak C=N*+ stretching at 1328 cm-1, and C=C stretching of the benzenoid ring at 1586 cm-1 were observed, indicating the presence of slightly doped polyamine structures, and C=N stretching of the quinoid ring shifts to 1477 cm-1 (originally located at 1466 cm-1 for bulk PANI), 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. Figure 5 shows the Raman and IR spectra of the resulting PPy/SWNT composites. It was also found that, for PPy/SWNT composites, whichever surfactant was used for micellar molecules, the Raman and IR spectra were similar. This indicates that micellar molecules cannot affect the molecular structure of the resulting PPy/SWNT composites during the synthesis. For the IR spectrum, the peaks at 1565 and 1479 cm$^{-1}$ were due to the antisymmetric and symmetric ring-stretching modes of the PPy, respectively. Strong peaks near 1205 and 920 cm$^{-1}$ indicated the doping state of polypyrrole, and a broad band at 3000–3500 cm$^{-1}$ was attributed to N–H and C–H stretching vibrations. The peaks at 1045 and 1315 cm$^{-1}$ were attributed to C–H deformation vibrations and C–N stretching vibrations of the PPy, respectively. The two very weak peaks around 2924 and 2854 cm$^{-1}$ were attributed to the stretching vibration mode of methylene, indicating that surfactants had been almost completely eliminated from the final PPy/SWNT composites (If the surfactants used had been retained in the composites, these IR peaks would be strong.)

For the Raman spectrum, the strong peak at 1600 cm$^{-1}$ represents the backbone stretching mode of C=C bonds, and the weak peaks at ca. 1380 and 1075 cm$^{-1}$ belong to the ring stretching and the N=H in-plane deformation of the oxidized (doped) species of the PPy, respectively. The corresponding band of neutral species at 1045 cm$^{-1}$ is relatively strong. These indicated the doping level of the PPy was relatively low.

It was very interesting that, for various conducting polymer/single-wall CNT composite nanostructures, the vibration spectra almost showed the characteristic features of corresponding polymer, and the characteristic peaks of CNT were hardly seen. The present and previous works both have confirmed it. The reason should be ascribed to one or both of the following two points: (1) compared with the intensities of the vibration spectra of the conducting polymers, those of the CNTs are much lower at the same observing conditions, and (2) due to CNT being coated or embedded within the matrix of conducting polymers, the intensity of the transmission light to the CNTs was very low, and the corresponding reflective or scattering light has to transfer the matrix layers of the conducting polymers. However, the matrix layers of the conducting polymers have absorbed most of them.

Another interesting thing is that the vibration spectra (Raman and IR) of the conducting polymers coating in these coaxial nanowires differ from those of bulk conducting polymers. Take Raman spectra of PANi/SWNT coaxial nanowires for example. In comparing the spectra derived from PANi (not shown; see ref 29) with that of PANi/SWNT coaxial nanowires, 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. The similar interaction between other conjugated polymers and SWNTs was observed by other scientists.

**Electrical Conductivity.** Conducting polymer/SWNT composites directed by different micelle/CNT templates manifested typical nonmetallic behaviors as shown in Figure 6. The room-temperature conductivities, the values of $\sigma(300 \text{ K})$, of both PANi/
SWNT and PPy/SWNT were of the order of magnitude \(-2\), whichever surfactant was used for micellar molecules. The low room-temperature conductivities of those composites were ascribed to the fact that the corresponding conducting polymers were at a very low doping level, which is confirmed by the previous spectral analysis, and probably that most of the single-wall CNTs used here were semiconducting.

To further explore how the CNTs affect the conductivities of the composites, we measured the temperature dependence of the conductivity of the resulting conducting polymer/single-wall CNT composites as shown in Figure 6. Whichever surfactant was used for micellar molecules, the temperature dependence of the conductivity of both PANi/SWNT and PPy/SWNT showed \(\ln \sigma(T) \propto T^{-1/2}\) behavior, which could be interpreted in terms of a charge-energy-limited tunneling (CELT) model that described the charge transport in a system of metallic particles embedded in a dielectric matrix:46

\[
\sigma(T) = \sigma_0 \exp\left[-(D/T)^{1/2}\right]
\]

where \(D\) is a constant and depends on the barrier height and the charging energy. The values of \(D\) for the resulting conducting polymer/single-wall CNT samples were calculated from the slope of the \(\ln \sigma(T)\) vs \(T^{-1/2}\) plot and are shown in Figure 6. For PPy/SWNT composites, whichever surfactant was used for micellar molecules, the \(D\) values were of the order of magnitude 4. However, for PANi/SWNT composites, when nonionic surfactant O\(\sigma\)-10 was used for the micellar molecules, the \(D\) value was still of the order of magnitude 4, but when cationic surfactant CTAB was used for the micellar molecules, the \(D\) value was of the order of magnitude 3. The lower \(D\) value indicated the lower barrier height for electron transfer. Combining the morphologies of the resulting conducting polymer/single-wall CNT composites, we found that the resulting composites with coaxial nanostructure had higher \(D\) values and the ribbonlike network had lower \(D\) values. This indicated that when CNTs were coated perfectly by conducting polymers, their pressed pellet exhibited a higher barrier height during electron transfer, and when CNTs were coated imperfectly, such as in the ribbonlike network within which CNTs were embedded (actually CNT network was embedded), their pressed pellet exhibited a lower barrier height during electron transfer, which is to say, when an electron transfers from one CNT to another (namely, a CNT network) without conducting polymer barriers, it shows lower resistance. This tells us that the CNTs play the key roles in the conducting polymer/single-wall CNT composites during electron transfer in the tested temperature range, as is similar to the results on other conjugated polymer/CNT composites according to the classical percolation theory.31,47 It also tells us that, to get higher CNT-based composites, we should attempts to make a CNT network into the matrix directly.

**Conclusion**

We have attempted the synthesis of conducting polyaniline/SWNT (PANi/SWNT) and polypyrrole/SWNT (PPy/SWNT) coaxial nanowires. The SWNTs were first dispersed in aqueous solutions containing cationic surfactant cetyltrimethylammonium bromide (CTAB) or nonionic surfactant poly(ethylene glycol) mono-p-nonyl phenyl ether (O\(\sigma\)-10). Each individual nanotube (or small bundle) was then enced in its own micellelike envelope with hydrophobic surfactant groups orientated toward the nanotube and hydrophilic groups orientated toward the solution. Thus a hydrophobic region within the micelle/SWNT hybrid template was formed. Insertion and growth of pyrrole or aniline monomers in this hybrid template, upon removal of the surfactant, produces coaxial structures with a SWNT center and conducting polypyrrole or polyaniline coating. The micellar molecules used could affect the surface morphologies of the

![Figure 6](image_url)
resulting coaxial nanowires but not the molecular structures of the corresponding conducting polymers. The CNTs played the key roles in the conducting polymer/single-walled CNT composites during electron transfer in the temperature range 77 K to room temperature. Compared with the CNT network embedded in the conducting polymers, the composites within which CNTs were coated perfectly by the identical conducting polymers exhibited higher barrier heights during electron transfer. We believe that such a micelle/CNT hybrid template-directed synthesis strategy would have great potential applications in other CNT-based composite materials with coaxial nanostructures.

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References and Notes

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