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Micelle-Encapsulated Carbon Nanotubes: A Route to Nanotube Composites

Youngjong Kang and T. Andrew Taton*

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

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The unique properties of single-walled carbon nanotubes (SWNTs) have led researchers to investigate their use in composite materials for a variety of applications, including electrostatic discharge,[1] structural reinforcement,[2] and thermal dissipation.[3] Despite this potential, the study of SWNT composite materials has been hindered by the poor solubility and processibility of SWNTs. Researchers have addressed these problems by high-energy sonication or processing techniques,[4] by wrapping nanotubes with polymer chains,[5] and by modifying the surfaces of nanotubes both covalently[6] and noncovalently.[7] Herein, we report an alternative, noncovalent method of modifying SWNTs by encasing the nanotubes within cross-linked, amphiphilic copolymer micelles. This encapsulation significantly enhances the dispersion of SWNTs in a wide variety of polar and nonpolar solvents and polymer matrices. In addition, because the copolymer shell is permanently fixed, the encapsulated SWNTs are stabilized with respect to typical polymer processing and recovery from the polymer matrix.

The general strategy for encapsulating SWNTs within amphiphilic block copolymer shells (Scheme 1) is similar to that

Scheme 1
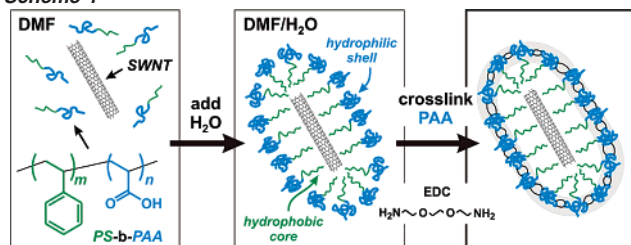
demonstrated by Wooley et al. for forming empty cross-linked polymer micelles.[8] Amphiphilic poly(styrene)-*block*-poly(acrylic acid) copolymer (PS_{49}-*b*-PAA_{54}, PS_{159}-*b*-PAA_{58}, or PS_{106}-*b*-PAA_{16}, Polymer Source Inc., Dorval, Canada) was first dissolved in dimethylformamide, a solvent in which both blocks are well solvated and micelles do not form. SWNTs (Carbon Nanotechnologies, Houston, TX) were then suspended in this solution by ultrasonication. Micellization of the amphiphile was induced by gradually adding H_2O to the nanotube suspension.[8-10] As has been observed for other neutral surfactants such as Triton-X 100,[11] PS-*b*-PAA copolymers were effective at stabilizing SWNT dispersions in aqueous solution and water mixtures. However, nanotubes that were simply codispersed with PS-*b*-PAA could not be isolated and resuspended in other media.

The PAA blocks of the micellar shells were permanently cross-linked by addition of a water-soluble diamine linker and a carbodiimide activator.[10] The SWNTs remained solubilized throughout the cross-linking process for polymer concentrations between 10^{-3} and 10^{-7} g/mL. After the cross-linking, excess reagents were removed by dialysis of the suspension against deionized water. Micelle-encapsulated SWNTs (e-SWNTs) were purified from empty micelles by three or more consecutive cycles of centrifuging the
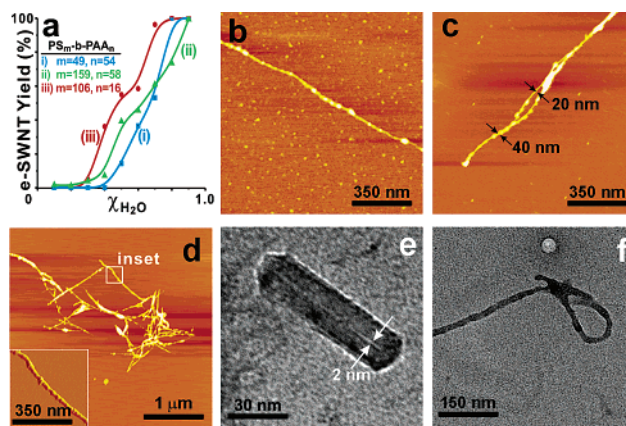
Figure 1. (a) Fraction of initial SWNT material recovered as copolymer-encapsulated e-SWNTs, for copolymer cross-linking performed at different H_2O:DMF ratios. [PS-*b*-PAA] = 10^{-3} g/mL. e-SWNT yield was determined by comparing the extinction of SWNT and e-SWNT dispersions at 500 nm. The line is provided as a guide to the eye only. (b–d) Height-mode AFM images of e-SWNT samples, deposited as droplets of suspension onto freshly cleaved mica and dried in air. (b) Unpurified e-SWNT material. Both an e-SWNT and empty polymer micelles are visible. (c) A bundled pair of e-SWNTs from unpurified material. It is not clear from the image whether the two SWNTs are encapsulated together or separately. (d) Purified e-SWNTs. (e,f) TEM images of purified e-SWNTs, prepared by depositing droplets of suspension onto Formvar/graphite-coated copper grids, allowing the grids to dry, and then staining the material with ~1 μL 2% methylamine vanadate.

dispersion and discarding the supernatant. Purified e-SWNTs could be redispersed in pure water at a concentration of over 0.5 g nanotubes/L with minimum sonication (less than 10 s), as determined by measuring the optical extinction of the solution at 500 nm and by using a reported specific extinction coefficient for SWNTs of $\epsilon_{500} = 2.86 \times 10^{-14}$ g/cm².[12]

The extent of shell cross-linking could be varied by adjusting the amount of diamine linker added and monitored by IR spectroscopy.[10] Complete cross-linking of the PAA blocks was not necessary to stabilize e-SWNTs; cross-linked product could be successfully isolated as long as at least 25% of the acid groups were converted to amides. The total yield of isolated e-SWNT product, measured as a fraction of the SWNT material suspended before cross-linking, was greatest when the cross-linking was performed at a high H_2O:DMF ratio (Figure 1a). This is presumably due to kinetic stabilization of the insoluble, glassy polystyrene core at high water content,[9] which traps the micelle around the nanotube as the PAA block is being cross-linked. Consistent with this hypothesis, cross-linking at low H_2O:DMF ratio produced insoluble flocs of polymer and SWNT material. Also, SWNTs could not be stabilized by simply mixing empty, preformed or precross-linked PS-*b*-PAA micelles with nanotube dispersions; micelles had to be assembled in the presence of SWNTs for e-SWNT material to be successfully isolated.
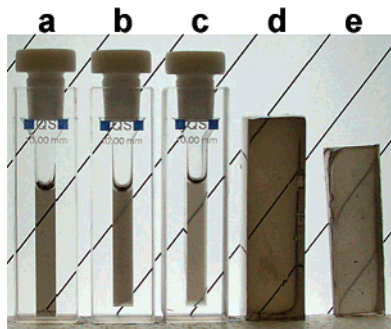
Figure 2. Purified e-SWNTs redispersed in: (a) H_2O, (b) THF, (c) CH_2Cl_2, (d) 1% agarose gel (0.01 wt % SWNT), (e) SBS elastomer (0.03 wt % SWNT).

Both the nanostructure of SWNTs encapsulated within PS_{159}-*b*-PAA_{58} micelles and their separation from empty micelles was characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Tapping mode AFM images of unpurified e-SWNT material revealed a mixture of spherical, empty micelles and straight, cylindrical e-SWNTs (Figure 1b,c). The cylindrical objects were much straighter than is typical for empty, "wormlike" micelles,[13] indicating that straight SWNTs were captured inside. AFM images after repeated centrifugation and redispersion (Figure 1d) showed that empty micelles had been successfully removed from the composite material to yield pure e-SWNTs. TEM demonstrated that the micelles contained individual SWNTs rather than SWNT bundles (Figure 1e), and that the toroidal and lariat shapes that are commonly observed for SWNTs[14] are also found in e-SWNTs (Figure 1f). The diameter of the polymer shell varied slightly ($d \approx 25$ nm by TEM), but correlates roughly with the diameter of empty cross-linked micelles (30 nm by AFM; 20 nm by static light scattering). In general, the cross-linked shells appear more irregular by AFM than by TEM, and occasionally look more like a periodic array of spheres than a continuous cylinder. This observation is not due to spherical micelles bound to the outer surface of carbon nanotubes; AFM images taken from mixtures of SWNTs and either cross-linked or uncross-linked PS_{159}-*b*-PAA_{58} micelles showed no accumulation of the micelles at SWNT surfaces. The difference between the observed AFM and TEM morphologies may be due to the fact that the outer, hydrogel block of e-SWNTs is swollen with water under the ambient conditions of AFM imaging and free of water in the high vacuum of the TEM instrument.

The e-SWNT material could be lyophilized to dryness and easily redispersed in both hydrophobic and hydrophilic solvents and polymer solutions with brief sonication (Figure 2a–c). Neither the visible absorbance nor the scattered light intensity of these fluid suspensions changed over the course of weeks, indicating that the suspended material did not flocculate with time. We attribute the high solubility of e-SWNTs to the fact that at least one of the polymer blocks, and sometimes both blocks, are well solvated in all solvents tested (including H_2O, THF, $CHCl_3$, and DMF) except saturated hydrocarbons, which fail to give stable e-SWNT dispersions. ^1H NMR spectroscopy of the e-SWNT material in $CDCl_3$ showed identifiable signals for the PS block, and in D_2O showed signals for the PAA block.[10] This behavior can be attributed to effective solvation of the polymer blocks in each of these solvents.[15] In all cases, solvent could be removed in vacuo to regenerate solid e-SWNT material without desorption of the cross-linked polymer, as confirmed by AFM re-imaging.

Casting combined solutions of e-SWNTs and polymers yielded bulk e-SWNT composite gels, rubbers, and solids in which the SWNTs were well dispersed in the solid state (Figure 2d,e). For example, e-SWNTs could be suspended in a hot, aqueous solution of agarose polysaccharide (1% w/v) and then stably cooled to form a nanotube−hydrogel composite (Figure 2d). The same e-SWNTs can also be dispersed in concentrated $CHCl_3$ solutions of polystyrene-*block*-polybutadiene-*block*-polystyrene thermoplastic elastomer (SBS D-1102K, Kraton, Houston, TX). This solution can either be directly cast to form nanotube composite films (Figure 2e), or the solvent can be removed in vacuo to form bulk composite plastic that can be molded. We are currently investigating the physical properties of these materials, which may be significantly different from those of past SWNT composites due to improved dispersion of the nanotubes.

In conclusion, we have demonstrated a topological, noncovalent solution to improving the dispersion of SWNTs by encasing them in cross-linkable surfactant micelles. Because micelle-encapsulated SWNTs are compatible with a wide variety of solvent and polymer matrices, e-SWNTs could be used as an alternative starting material to pure SWNTs for the production and investigation of nanotube composite materials.

Supporting Information Available: Experimental details for nanotube encapsulation, imaging, IR and ^1H NMR spectra of cross-linked materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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