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Solubilization and Purification of Single-Wall Carbon Nanotubes in Water by in Situ Radical Polymerization of Sodium 4-Styrenesulfonate

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Because of outstanding electrical conductivity, thermal conductivity, and mechanical strength, single-wall carbon nanotubes (SWNT) have enormous potential in field emission displays, supercapacitors, molecular computers, and ultrahigh-strength materials.[1,2] For optimal performance in most applications, the SWNT should be separated into individual tubes or bundles of only a few tubes. However, the as-prepared SWNT contain impurities of metal catalyst particles and amorphous carbon, and because of strong van der Waals attraction, the SWNT pack into bundles that aggregate into tangled networks. Dissolution of SWNT in water, which is important because of potential biomedical applications and biophysical processing schemes, has been facilitated by surfactants and polymers and by chemical modification.[3−11] Here we report a method by which pristine SWNT are solubilized, separated from catalyst particles, and separated from excess dispersant to produce SWNT with grafted poly(sodium 4-styrenesulfonate) (PSS) as an aqueous solution that is stable indefinitely. The method is illustrated in Scheme 1.

As in some other functionalizations of SWNT,[12−14] the process requires no pretreatment. Debundling and functionalization of SWNT are achieved in one step with no high shear mixing or heavy sonication, which break down SWNT to shorter lengths.[5,15] A mixture of 40 mg of pristine HiPco SWNT, 4.0 g of sodium 4-styrenesulfonate (NaSS), and 40 mg of potassium persulfate as a free radical initiator was stirred at 65 °C for 48 h. Catalyst residues and amorphous carbon were removed by gentle centrifugation, and excess unbound PSS was removed by ultrafiltration and ultracentrifugation. The final solution contained 68 mg of SWNT−PSS in 100 mL of water. A detailed procedure is in the Supporting Information. Elemental analysis (CHS) corresponded to 45 wt % of PSS in the SWNT/PSS composite. The ^{1}H NMR spectra of the PSS in the ultrafiltrate and the SWNT−PSS were the same, which suggests that the molecular weight of the attached PSS is high. In control experiments, stirring pristine SWNT with preprepared PSS or with potassium persulfate and sodium *p*-toluenesulfonate but no monomer by the method used during the polymerization or sonicating in a cleaning bath failed to disperse the SWNT. SWNT also can be dispersed into water by surfactants and by high shear mixing or sonication with PSS, but large excesses of the surfactants or PSS are required.[5,15]

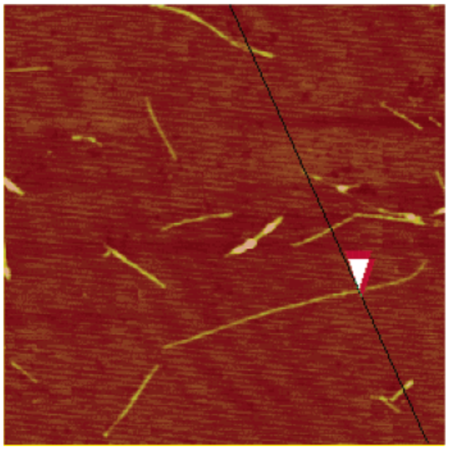
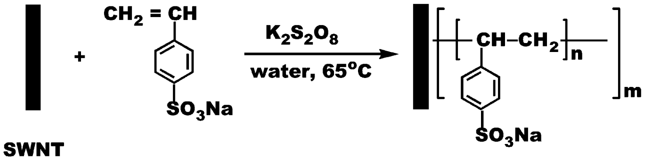


Figure 1. AFM height image of SWNT−PSS (3 μm × 3 μm). The arrows point to a 1.2 nm height difference.

Scheme 1



We attribute the stability of the SWNT with such a small amount of PSS to covalent bonding of the polymer to the SWNT. One attached polymer coil protects a large area of the SWNT surface from van der Waals attraction to other SWNT. By analogy to the addition of polystyryl radicals at diffusion-controlled rates to aggregates of [60]fullerene in solution,[16] bundles of SWNT should also react with polymer radicals, although at lesser rate constants because of the lesser strain of the sidewalls of SWNT than of [60]fullerene. Additions of nonpolymeric radicals to SWNT are well-known.[17]

The distributions of diameters and lengths of the functionalized SWNT were analyzed by tapping mode atomic force microscopy (AFM). Figure 1 shows contour lengths from several hundred nanometers to several micrometers and a representative diameter of 1.2 nm. The range of diameters of pristine HiPco SWNT is 0.6−1.3 nm.[18] Larger area AFM images and transmission electron microscopy (TEM) images at resolution too low to detect individual tubes show bundles of the SWNT−PSS that are much smaller than the bundles of the pristine SWNT (Figures S1 and S2). TEM shows none of the catalyst particles that were abundant in the pristine SWNT (Figures S2a and 2b).

The Raman spectrum of the functionalized SWNT in Figure 2a shows a disorder (D) band at 1315 cm^{-1} in addition to the radial breathing band (180−260 cm^{-1}) and tangential (G) band at 1590 cm^{-1}. The intensity of the D band is indicative of the degree of covalent functionalization of the nanotube framework. The radial breathing bands are shifted an average of 5 cm^{-1} to higher frequency by functionalization with the PSS, which indicates debundling during the polymerization.

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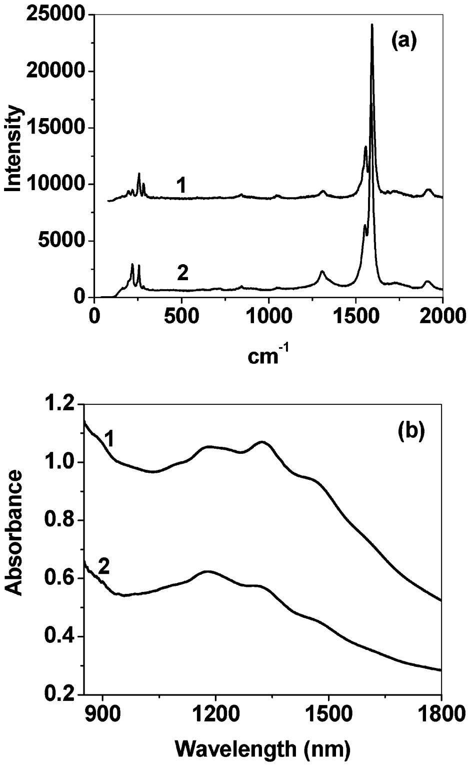


Figure 2. (a) Raman spectra of pristine HiPco SWNT (1) and SWNT−PSS (2) from 633 nm excitation. (b) Near-IR spectra of pristine HiPco SWNT (1) and SWNT−PSS (2).

The near-IR absorption spectrum of the functionalized SWNT displays less sharp features compared to the spectrum of pristine SWNT (Figure 2b), indicating some alteration of the van Hove transitions of semiconducting SWNT. Both the near-IR spectrum and the Raman spectrum indicate that PSS is covalently attached to the sidewalls of SWNT, not simply wrapped around the SWNT.[5] On the other hand, the remaining near-IR peaks indicate that the nanotube is not functionalized heavily.[19] Thus, the electronic conductivity of the SWNT−PSS should be largely retained.[20]

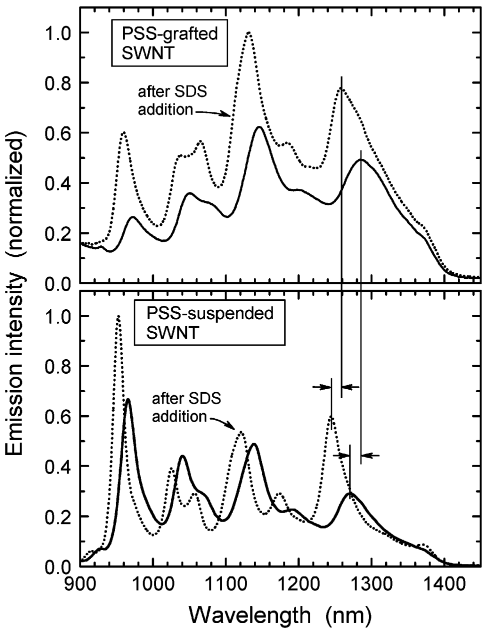
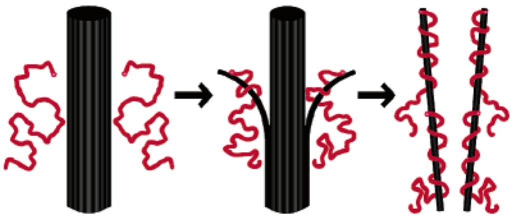


Figure 3. Fluorescence emission spectra of SWNT samples in water measured using 670 nm excitation. Top frame: SWNT grafted with PSS, before (solid curve) and after (dotted curve) the addition of SDS surfactant. Bottom frame: chemically unmodified SWNT suspended in 0.1% PSS solution, before (solid curve) and after (dotted curve) the addition of SDS surfactant. Vertical lines illustrate the substantial spectral red shift of the PSS-grafted sample compared to the PSS-suspended sample.

Scheme 2



Fluorescence spectra of the grafted SWNT−PSS in water (Figure 3) show a series of van Hove transitions that indicate presence of individual semiconducting SWNT. However, the peaks are shifted to longer wavelengths and broadened compared to spectra of pristine SWNT dispersed with sodium dodecyl sulfate (SDS). The emission is much weaker and broader than that of intact SDS- or PSS-wrapped SWNT due to covalent modification of the SWNT. As with pristine SWNT, the intensity of the photoluminescence from SWNT−PSS is reduced in acidic solution. Figure 3 shows that the van Hove transitions of the SWNT suspended with PSS, using PSS from the filtrate of the grafted SWNT−PSS, are all at shorter wavelength than the transitions of grafted SWNT−PSS. Addition of SDS to the SWNT suspended with PSS shifts the transitions to shorter wavelength to give a spectrum the same as that of SWNT suspended directly with SDS. Addition of SDS to the grafted SWNT−PSS also shifts the transitions to shorter wavelength, but the spectrum differs significantly from all other spectra obtained by suspending HiPco SWNT in SDS solution. The spectra are consistent with partial SDS adsorption to the surface of the grafted SWNT−PSS without displacing the PSS. On the other hand, SDS completely displaces the PSS from the solution of SWNT suspended by PSS. Thus, the fluorescence results indicate that the SWNT and PSS are linked chemically. At the same time, the existence of fluorescence demonstrates that the number of chemical bonds to the side walls per unit of the SWNT length is small.[21] The SWNT structure is altered, but not completely modified, as often happens with many methods of chemical treatment and purification applied to SWNT material.[17,22,23]

The mechanism in Scheme 2 proposes that propagating PSS macroradicals are capped by SWNT bundles. The attached water-soluble PSS chains and stirring help the outermost SWNT separate from the bundles and dissolve in water. Continued attachment of PSS breaks down the large bundles to single tubes and smaller bundles to give a solution in which 55/45 (by weight) SWNT/PSS are stable indefinitely (12 months at the date of submission of this paper). Without grafted PSS the pristine SWNT precipitate in 5 min. No other method of which we are aware stabilizes SWNT in water with so little polymer or surfactant. The stability of the SWNT with less PSS than SWNT by weight also supports the conclusion that the PSS from in situ polymerization is bound covalently rather than adsorbed to the SWNT. Grafting of polystyrene to multiwall carbon nanotubes in water/styrene mixtures by radical addition to produce MWNT−polystyrene that is soluble in organic solvents also is known.[24]

In conclusion, in situ polymerization of sodium 4-styrenesulfonate is a facile method for functionalization, solubilization, and purification of HiPco SWNT. This method should be applicable to at least gram-scale purification of SWNT and may be applicable to a wide range of water-soluble and organic-soluble polymers. Preparation of polyelectrolyte thin films containing the SWNT−PSS using layer-by-layer deposition is in progress with the aim of improving both the electrical conductivity and the mechanical strength of the films.

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Supporting Information Available: Experimental section and AFM and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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