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A Biomimetic "Polysoap" for Single-Walled Carbon Nanotube Dispersion

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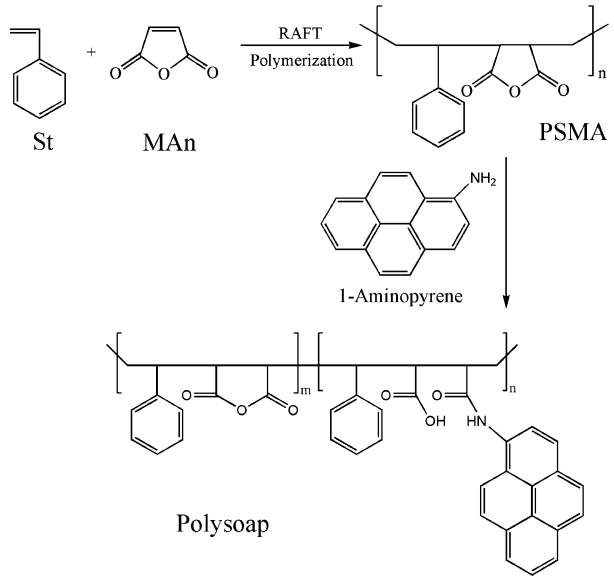
Single-walled carbon nanotubes (SWNTs) exhibit extraordinary mechanical, thermal, and electrical properties due to their unique one-dimensional all-carbon structure.[1] They have demonstrated great potential in applications ranging from composite materials and molecular electronics to sensors and electrochemical electrodes.[2] As-produced carbon nanotubes are typically bundled mixtures of various species due to strong inter-tube van der Waals interactions and hydrophobic interactions in aqueous environments. Thus, SWNTs have to be first dispersed in organic or aqueous solvents before solution-phase processing, separation, and assembly can become successful.

Individually dispersed SWNTs can be obtained by covalently functionalizing the end or the sidewall of nanotubes, but the electronic structure of the SWNT is arguably altered in this way.[3] Recent developments show that SWNTs can be incorporated into micelles formed by various surfactants in aqueous solutions, such as lipids,[4,5] sugars,[6] proteins,[7] DNA,[8,9] and commodity polymers.[10] The detection of band-gap fluorescence of SWNT-containing complexes in the near-infrared region indicates that the electronic structure of nanotubes is preserved in the local environment of surfactant micelles.[4,11] Among these surfactants, single-stranded DNA (ssDNA), used by Zheng et al., is particularly intriguing because the resulting SWNT−DNA complexes can be separated, using ion-exchange HPLC, into fractions that are rich in metallic or semiconducting SWNTs.[8,9] It is proposed that the DNA molecules wrap around SWNTs with the aromatic base interacting with the SWNT wall and the charged backbone staying at the exterior of the micelles. This work constitutes an important step toward (*n*,*m*) specific production of SWNTs; however, DNA is not readily available in large quantities like surfactants. In addition, the structure of DNA lacks flexibility for further improvement of the SWNT dispersion property, except that the base sequence can be varied.[9]

We design a "polysoap" surfactant (Scheme 1) that mimics the structure of DNA to disperse SWNTs in aqueous solution. The backbone of the polysoap consists of alternating styrene (St) and maleic acid (Ma) units, and the maleic acid groups are functionalized with aminopyrene. The pyrene moiety has a strong tendency to adsorb on SWNTs, but the charged backbone tends to dissolve in water.[12] The designed "polysoap" thus mimics ssDNA in SWNT wrapping functions.

As shown in Scheme 1, the polysoap is synthesized in two steps. First, 2.08 g (0.02 mol) of styrene and 1.96 g (0.02 mol) maleic anhydride (both from Beijing Chemical Reagent Co., China) monomers are polymerized using radical reversible addition−fragmentation chain transfer (RAFT) polymerization, resulting in poly(St-*alt*-Ma) (PSMA) with 80% yield.[13] The molecular weight of the PSMA is measured by GPC to be 8400, and the molecular weight distribution ($M_w/M_n \approx 1.34$) is much narrower than for

Scheme 1



ordinary radical copolymerization products (see Supporting Information). Second, 1 g of the PSMA is allowed to react with 20 or 50 mg of 1-aminopyrene (Sigma-Aldrich) in 1,4-dioxane. The reaction leads to polysoaps with pyrene side chain content of 1.15 and 2.30%, with yields of 95 and 94%, respectively. To disperse SWNT, 1 mg of the polysoap is dissolved in 1 mL of 0.1 M NaOH solution in a test tube, and ∼2 mg of purified HiPCO SWNT powder (Carbon Nanotechnology Inc.) is added. The solution is then sonicated for 1 h at ∼5 W power. The resulting suspension is centrifuged for 1 h at 14000 rpm to give the solution of SWNT−polysoap complexes in the supernatant.

The absorption and fluorescence spectra in Figure 1 indicate that the SWNTs are dispersed in the solution. The absorption peaks in the visible region agree well with reported spectra of SWNT mixtures.[8,9] The polysoap solution displays the characteristic fluorescence of pyrene in an aqueous environment, but the fluorescence is completely quenched when SWNTs are incorporated in the complexes. This verifies that the pyrene side chains directly interact with SWNTs in the complexes as designed.

We measure the solubility of SWNTs in polysoap solutions by adding THF to the SWNT−polysoap solution. The addition of THF results in the destabilization of the micelles and the precipitation of SWNTs. The pyrene fluorescence in the UV is no longer quenched after addition of THF. This indicates that the polysoap desorbs from SWNTs and remains in the solution. The sample is then centrifuged, and the precipitated SWNTs are dried and weighted. The solubility of SWNT, expressed as the mass ratio of SWNT over surfactant, is summarized in Table 1.

The control experiment using PSMA shows that hydrolyzed

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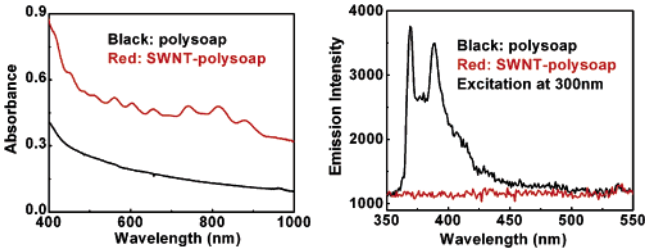

Figure 1. Absorption and fluorescence spectra of the polysoap and the SWNT−polysoap complexes.

Table 1. SWNT Dispersion Property of the Polysoaps

surfactant	pyrene content (molar %)	SWNT solubility (mass ratio SWNT:surfactant)
PSMA	0	0.7:1
polysoap 1	1.1	1.2:1
polysoap 2	2.3	1.3:1

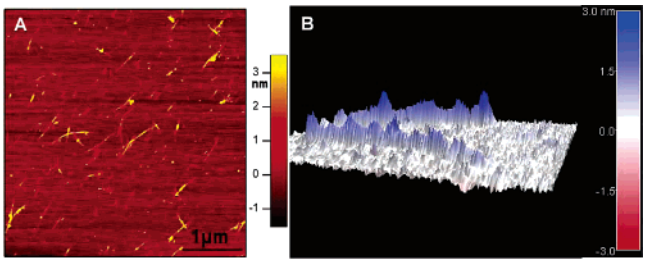

Figure 2. (A) AFM images of the SWNT−polysoap complexes. (B) 3D representation of complexes in 1 μm × 1 μm scale.

alternating copolymer of St and Ma without pyrene side chains is also effective in dispersing SWNTs. We reason that the dispersion property comes from the benzene ring in the styrene units, which may interact with SWNTs in a fashion similar to pyrene. The pyrene functionalization of side chains significantly increases the solubility of SWNTs to more than 1.2:1. The solubility of SWNTs is reported to be less than 0.4:1 in ssDNA,[8] and ∼25 mg/L in sodium dodecyl sulfate (SDS) solution.[4] Testing under the exact same conditions, we find the solubility of SWNTs in polysoap is about 1.3 times better than that in ssDNA and ∼5 times better than that in SDS (Supporting Information).

To study the structure of SWNT−polysoap complexes, we image the complexes with atomic force microscopy (AFM). A drop of the SWNT−polysoap solution was spin-coated onto a piece of freshly cleaved mica. The sample was imaged with an Asylum Research (Santa Barbara, CA) MFP3D atomic force microscope in ambient. Figure 2A shows that SWNTs are individually dispersed. A zoom-in 3D image in Figure 2B shows that the height profile along the axis of the complex has quasi-regular corrugation. The variation is much higher than the noise on the mica background and is not seen on bare SWNT samples (Supporting Information). Thus, the height corrugation must come from quasi-periodic wrapping of the polysoap around SWNTs.

We have reported DNA mimicking polysoap surfactants for dispersion of SWNTs in aqueous solutions. The polysoap surfactants prepared through pyrene functionalization of PSMA disperse SWNTs more effectively than ssDNA. Molecular engineering of the polysoap surfactants, including systematic tuning of structural parameters such as molecular weight, polymer backbone charge, side-chain structure, and the linker length between the backbone and the side chain, could further optimize the SWNT dispersion efficiency. The "living" nature of the RAFT polymerization used for PSMA synthesis allows block copolymerization of other monomers,[13] which may lead to direct coupling of the SWNT dispersing property with other functions, such as matrix adhesion for SWNT composite materials and biocompatibility or target specificity for SWNT-related biomedical engineering. The synthetic nature of the polymer surfactant also provides the possibility for large-scale and low-cost preparative production in the future. We thus believe this work opens a new vista in SWNT processing and application.

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Supporting Information Available: Characterization of PSMA, comparison of SWNT solubility in different surfactant solutions, and AFM images of bare SWNTs. This materials is available free of charge via the Internet at http://pubs.acs.org.

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