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Temperature and pH-Responsive Single-Walled Carbon Nanotube Dispersions

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ABSTRACT

Solubilization of single-walled carbon nanotubes (SWNTs) using noncovalently interacting polymer surfactants in aqueous media has opened up a new vista of SWNTs in biology and medicine. In many potential applications, it is desirable to control the dispersion or aggregation of SWNTs in solvents with external stimuli. Here we report two "smart" SWNT dispersions that respond to temperature and pH changes in poly(*N*-isopropylacrylamide) and poly-L-lysine solutions.

Single-walled carbon nanotubes (SWNTs) are a unique family of all-carbon one-dimensional nanomaterials that offer extraordinary mechanical, electrical, and thermal properties leading to great promises in applications ranging from composite materials and field emission displays to nanoelectronics.[1,2] Recent breakthroughs that as-produced bundles of SWNTs can be disrupted into individual nanotubes in aqueous media via covalent or noncovalent modifications[3−5] have enabled investigations of previously inaccessible properties such as ensemble optical electronic spectroscopy in solution.[6,7] More importantly, introducing individually dispersed SWNTs to biologically compatible media has opened up a new vista in biology and nanomedicine.[8−10] New concepts such as using an SWNT as optical sensor, drug and gene transporter, gene expression regulator, cancer therapy agent, and neuron stimulating electrode are being intensively explored.[11−17]

Among various functionalization schemes, noncovalent methods using polymer surfactants are particularly interesting because SWNTs are shown to be dispersed with high efficiency and stability while their intrinsic structure and properties are preserved. Since noncovalent interactions with SWNT sidewalls ($\pi-\pi$ stacking, van der Waals interaction, and hydrophobic interactions) do not require specificity and directionality, a surprisingly large variety of water-soluble polymers containing nanotube-interacting structural moieties are suitable for this purpose.[3,18−24] The synthetic control of polymer structure also allows multi-functional polymer surfactants to be engineered for the separation,[22,24−26] alignment,[27,28] and hierarchical assembly of SWNTs,[29] as well as the tagging of fluorescent chromophore and biologically active cargos to SWNTs.[14,30] In many potential applications such as SWNT-based switching devices, sensors, drug and gene delivery systems, it is desirable to control the dispersion or aggregation of SWNTs in solvents with external stimuli.[31] Poly(acrylic acid)- and lysozyme-dispersed SWNTs are shown to respond to pH value changes of the environment.[32,33] Here we report two "smart" SWNT dispersions that respond to temperature and pH changes in poly(*N*-isopropylacrylamide) (PNIPAAm) and poly-L-lysine (PLL) solutions.

SWNT Dispersion in PNIPAAm. About 1 mg of purified HiPCO SWNT powders (lot number P0276, Carbon Nanotechnologies, Inc., Houston, TX) was added to 3 mL of a solution of 10 mg/mL PNIPAAm ($M_n = 20\,000-25\,000$, Aldrich) and 0.02 M NaOH. The mixture was sonicated for 90 min in an ice−water bath at 5 W power, followed by centrifugation for 5 min at 800g and 3 min at 2300g to yield PNIPAAm−SWNT complexes in the supernatant. The resulting dispersion is stable at room temperature for weeks with little or no precipitation, but it cannot withstand high-speed centrifugation. Dialysis removal of free unbound PNIPAAm molecules in solution causes significant flocculation. Further experiments also reveal that SWNTs cannot be stably dispersed if PNIPAAm concentration is lower than 5 mg/mL.

Optical spectra demonstrate the dispersion of SWNTs in PNIPAAm solution. The absorption peaks of SWNTs (Figure 1A) appear broader than the reported van Hove transitions of well-dispersed HiPCO SWNTs in solution, but the peak positions are in good agreement.[3] The Raman spectrum in Figure 1B shows the radial breathing mode, the disorder-induced D-band, and the tangential G-band of SWNTs.[34] Covalent functionalizations, which convert sp^2 carbon atoms to sp^3 hybridization and disrupt the extended π-conjugation systems, lead to the loss of structures in absorption spectra

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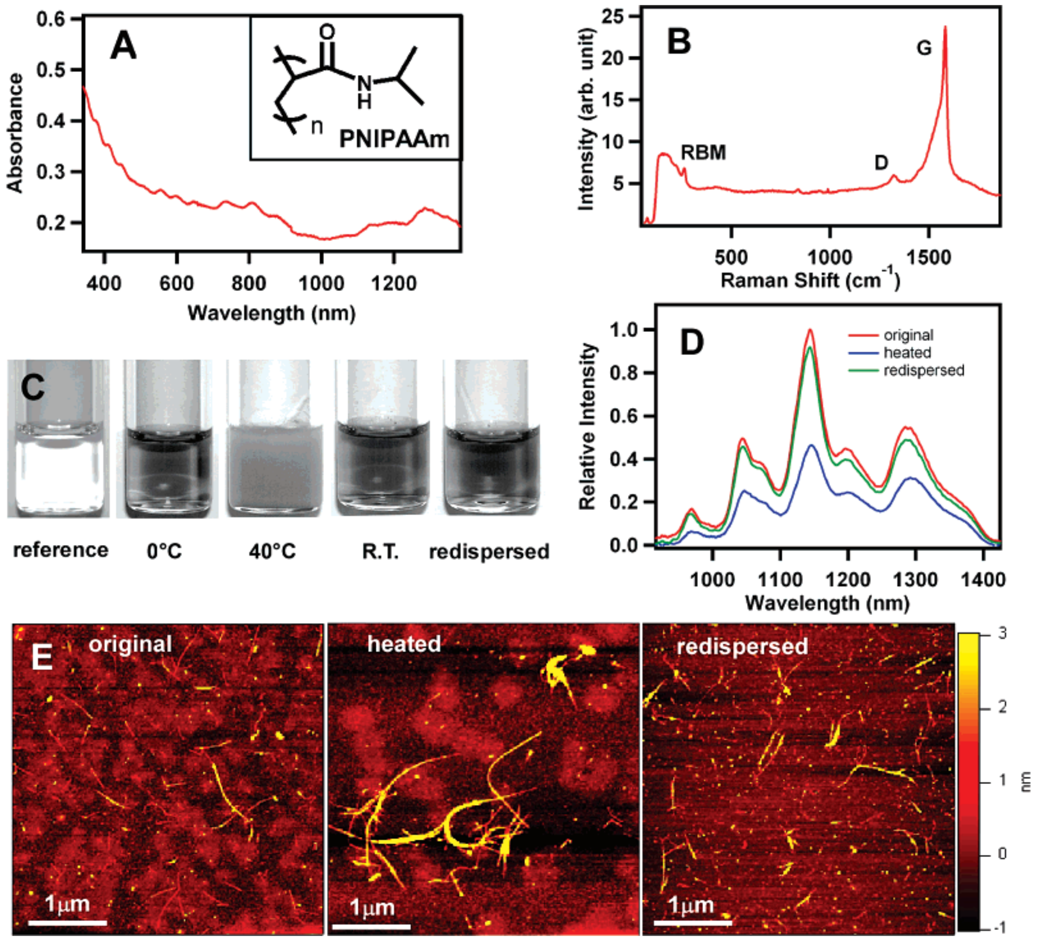

Figure 1. (A) Absorption spectrum and (B) Raman spectrum of a PNIPAAm−SWNT dispersion; inset in A is the structure of PNIPAAm. (C) From left to right: photographs of a pure PNIPAAm solution at room temperature as a reference, PNIPAAm−SWNT dispersions at 0 °C, 40 °C, cooled to room temperature, and redispersed by a 2 min sonication at 0 °C. (D) Fluorescence spectra of PNIPAAm−SWNT dispersions before (red line) and after (blue line) heating in 40 °C, and after redispersion via 2 min of sonication at 0 °C (green line). Spectra were all taken at room temperature and excited at 658 nm using an NS1 NanoSpectralyzer (Applied NanoFluorescence, LLC, Houston, TX). No fluorescent light could be detected at 40 °C due to strong scattering by aggregated free PNIPAAm at this temperature. (E) AFM images of PNIPAAm−SWNT complexes; from left to right: original dispersion, dispersion heated at 40 °C for 2 min, dispersion redispersed by sonicating at 0 °C for 2 min. AFM samples were prepared by spin coating fleshly cleaved mica with 10 μL of 0.1% w/v polylysine solution and then 10 μL of the PNIPAAm−SWNT dispersion. The samples were then rinsed with deionized water and dried with argon gas. Images were taken at room temperature and ambient conditions using an MFP3D microscope (Asylum Research, Santa Barbara, CA) in AC mode. Probes with resonance frequency around 325 kHz (NSC15/AlBS, MikroMasch USA, Wilsonville, OR) were used in imaging. The typical free amplitude and set point were 35 and 20 nm, respectively.

and cause a significant increase in the disorder-induced D-band intensity in Raman spectra.[35−39] Thus, the van Hove peaks in the absorption spectrum and the low intensity of the D-band in the Raman spectrum indicate that PNIPAAm molecules are noncovalently physisorbed on the sidewall of SWNTs. Consistent with spectroscopic observations, atomic force microscopy (AFM) images of PNIPAAm−SWNT complexes deposited on mica surfaces show both individually dispersed SWNTs and small bundles with diameters less than 5 nm (Figure 1E). The presence of small bundles explains the broadening of absorption peaks.

We reason that the hydrocarbon main chain and the isopropyl side chains of PNIPAAm could interact with SWNT sidewalls through nonspecific van der Waals and hydrophobic interactions, while the hydrophilic amide bonds maintain the water solubility of PNIPAAm−SWNT complexes. The instability of the dispersion under high-speed centrifugation and the requirement of free unbound PNIPAAm molecules in solution indicate that the affinity of PNIPAAm to SWNT sidewalls is modest, and there is a dynamic equilibrium between free unbound PNIPAAm in solution and PNIPAAm molecules physisorbed on SWNT surfaces.

Temperature Response of PNIPAAm−SWNT Complexes. PNIPAAm has been extensively studied as a temperature-responsive polymer.[40] The C═O and N−H bonds in PNIPAAm can form intermolecular hydrogen bonds with surrounding water, which gains in enthalpy but pays an entropic price for limiting the motion of bound water molecules; alternatively, the C═O and N−H bonds can also form intramolecular hydrogen bonds, which is less exothermic than the intermolecular H-bonding conformation but is entropically favored for releasing water.[41] The structure of PNIPAAm is subtly balanced such that, at temperatures below the lower critical solution temperature (LCST, ~33 °C for PNIPAAm), the equilibrium shifts toward the enthalpically favored intermolecular H-bonding conformation, but moves toward the entropically favored intramolecular H-bonding conformation at temperatures above the LCST. This structural transition leads to insoluble aggregates above the LCST in linear PNIPAAm, a volume-shrinking phase transition of cross-linked PNIPAAm hydrogels,[42] and the switching of water wettability for PNIPAAm-coated surfaces.[43]

To test the temperature response of the SWNT dispersion in PNIPAAm, the PNIPAAm−SWNT dispersion was heated in a 40 °C water bath for 2 min. The solution quickly become turbid, mostly due to the aggregation of free PNIPAAm. When the solution was cooled to room temperature, it became clear again (Figure 1C). However, AFM images of PNIPAAm−SWNT complexes cooled back to room temperature (Figure 1E) show that SWNTs aggregate into larger bundles (4−20 nm diameter) than before the heat/cool cycle. Partial quenching of nanotube fluorescence, regardless of tube diameter (i.e., fluorescence wavelength), also suggests roughly uniform bundling of all size SWNTs in the dispersion (Figure 1D).[44] Sonicating the dispersion at ∼5 W power while it is heated at 40 °C yields the same response and AFM characterization and thus does not prevent the complexes from aggregating. The retention of increased bundle size at room temperature in spite of the redissolution of free PNIPAAm reflects the kinetic stability of the temperature-induced switching of aggregation states. Indeed, the redispersion barrier can be circumvented by a short period of sonication. After 2 min of sonication in a 0 °C ice−water bath, the solution stays clear, and AFM images show that the SWNTs are redispersed individually or in small bundles similar to those from the original dispersion (<5 nm) (Figure 1E). The fluorescence intensity also recovers to the level of the original dispersion, irrespective of nanotube size after redispersion (Figure 1D), which indicates that the temperature-stimulated switching is reversible.

The reversible switch of PNIPAAm−SWNT dispersion/aggregation states controlled by temperature could be understood based on the thermal switching behavior of PNIPAAm chain conformation. At temperatures lower than the LCST, the hydrocarbon backbone of a PNIPAAm molecule interacts with the SWNT sidewalls, and the hydrophilic amide motifs solvate the complexes in water. When the temperature is raised above the LCST, the amide bonds form intramolecular H-bonds, which results in a compact chain conformation with a hydrophobic surface.[41,43] The compact conformation of PNIPAAm chains at high temperatures may result in a reduced coverage on the SWNT sidewalls and cause the fusion of multiple PNIPAAm−SWNT complexes in order to cover the nanotube surface and minimize the SWNT−water interfacial energy. This observation also indirectly implies that PNIPAAm chains are unlikely to wrap around SWNTs, as proposed for single-stranded DNA,[22,26] but instead are more likely to form “a loose and swollen cylinder” around SWNTs, as described for poly(styrene-*co*-maleic acid) and gum Arabic.[45]

SWNT Dispersion in PLL. PLL is a naturally occurring polyelectrolyte that contains a high density of partially protonated primary amine groups. Due to its high density of positive charges, PLL has been widely used in modifying the electric potential of surfaces, in the layer-by-layer assembly of polyelectrolytes, and in drug and gene delivery systems.[46−48] Since it has been reported that amine groups can strongly physichemisorb on the sidewalls of SWNTs,[49−51] we explore whether the high density of amine groups on PLL could result in the dispersion of SWNTs in an aqueous environment.

Figure 2C shows a photograph of SWNT dispersion in a PLL solution obtained by sonicating 1 mg of purified HiPCO SWNT powders (lot number P0276, Carbon Nanotechnologies, Inc., Houston, TX) in 2 mL of 0.1% w/v PLL solution (Sigma-Aldrich) for an hour in an ice−water bath followed by centrifugation for 10 min at 9300g. The pH of the as-prepared PLL−SWNT complex solution is about 7.0. The absorption spectrum of SWNTs dispersed in PLL solution show sharp peaks due to van Hove transitions (Figure 2A), which, in addition to low Raman D-band intensity (Figure 2B), indicates that SWNTs are well-dispersed via noncovalent interactions. An AFM micrograph (Figure 2D) of PLL−SWNT complexes deposited on freshly cleaved mica shows that most SWNTs are individually dispersed.

pH Response of PLL−SWNT Complexes. We serendipitously discovered that SWNTs could not be dispersed in PLL solution in strong basic environments. This led us to investigate the pH response of PLL−SWNT complexes. We first adjusted the pH of the PLL−SWNT solution to 4.1, then increased it to 9.7, decreased it back to 8.3, and finally decreased it to 5.1 by adding 1.5 M HCl or NaOH solutions. Each change in pH was followed by 10 min of sonication in an ice−water bath. The photographs in Figure 2C show homogeneous solutions with dark color at all other pH values except for 9.7, at which the solution becomes cloudy. Additional experiments reveal that sonicating SWNTs in PLL solutions with pH values greater than 9 does not lead to stable dispersions. AFM images show that SWNTs are individually dispersed or in small bundles (<5 nm) in acidic and neutral environments but aggregate into large bundles at pH 8.3 (Figure 2D). At pH 9.7, the SWNTs precipitated out of the solution and could not be imaged with AFM. The redispersion of precipitated SWNTs after adjusting the solution back to acidic pH excludes the possibility that precipitation at high pH is caused by the irreversible hydrolysis of peptide bonds in the PLL chain. The dispersion or aggregation states of PLL−SWNT complexes are further verified by nanotube fluorescence spectra. Figure 2E shows that SWNT emission is partially quenched due to aggregation at pH 9.7, but remains largely unchanged at other pH conditions.

The fact that PLL could not solubilize SWNTs at high pH reflects that the interaction between PLL and SWNTs in acidic and neutral pH aqueous environments is fundamentally different from that observed between organic amines and SWNTs in organic solvents. It has been reported that nitrogen atoms in organic amines partially donate electron density to SWNTs in organic solvents, which results in the physichemisorption of amine on SWNTs and the solubilization of SWNTs.[49−51] In aqueous environments, however, the amine groups in PLL are protonated under acidic or neutral pH and cannot interact with SWNTs via the electron-donating

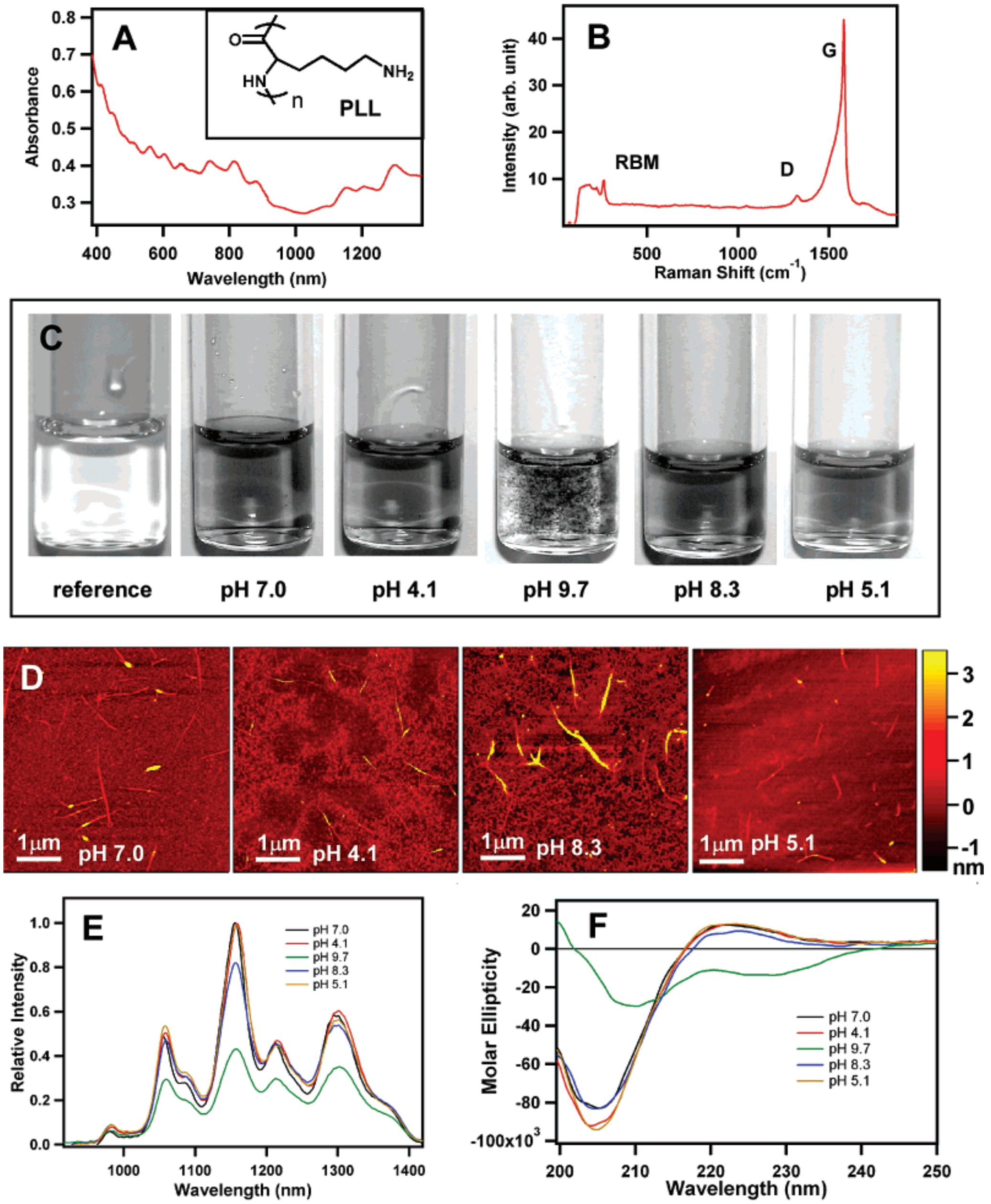

Figure 2. (A) Absorption spectrum and (B) Raman spectrum of PLL−SWNT dispersion; inset in A is the structure of PLL. (C) Photographs of a pure PLL solution as a reference and PLL−SWNT dispersions at different pH values. (D) AFM images of PLL−SWNT complexes. AFM samples were prepared by spin coating 10 μL of the PLL−SWNT dispersion onto a fleshly cleaved mica substrate followed by rinsing with deionized water and drying with argon gas. Imaging conditions were the same as those described in Figure 1E. (E) Fluorescence spectra of PLL−SWNT dispersions at different pH values excited at 658 nm. (F) CD spectra of PLL−SWNT complexes at different pH values. The spectra were recorded on a Jasco-715 spectropolarimeter (Jasco, Inc., Easton, MD).

mechanism. At alkaline pH, uncharged amine groups instead prefer to donate electrons to dissolved oxygen, a much better oxidizing agent than SWNTs. Therefore, the mechanism through which SWNTs interact with PLL in an aqueous environment could only be (1) hydrophobic interactions between the PLL hydrocarbon linker moieties ($-C_4H_8-$) and the SWNT sidewalls and/or (2) cation-π interaction[52,53] between protonated amine groups and the π-electron system of the SWNTs. Both mechanisms would respond to the pH change of the solution.

The cation-π interaction is completely turned off at pH > 9.7, the isoelectric point of lysine, due to the deprotonation of $-NH_3^+$ groups. The hydrophobic interaction between the $-C_4H_8-$ linker and the SWNT is not directly altered by the acid−base titration of the amine groups, but it could be indirectly affected through changes in the secondary structure of PLL. It is well characterized that uncharged PLL assumes an α-helix conformation at high pH, but adopts an uncoiled conformation in acidic or neutral pH due to the electrostatic repulsion among side-chain cations.[54,55] Due to the electrostatic repulsion, the uncoiled structure is more extended than the α-helix, and thus the hydrocarbon linker moieties are more accessible to SWNTs. We verify that the pH response of the PLL secondary structure is not strongly affected by the presence of SWNTs in PLL−SWNT complexes. Circular dichroism (CD) spectra (Figure 2F) of PLL−SWNT complexes in an acidic or neutral pH show a single negative peak around 200 nm, which is characteristic of an uncoiled conformation. At pH 9.7, the spectrum displays two negative bands in the 200–230 nm range, characteristic of the α-helix conformation.[55,56]

In summary, we report the dispersion of SWNTs in PNIPAAm and PLL solutions and their responses to external stimuli. The suspended SWNTs in PNIPAAm and PLL solutions can be reversibly switched between dispersed and aggregated states by changing temperature or pH. The environment-responsive polymer–SWNT complexes may have potential applications in nanoelectronics, sensing, and drug and gene delivery systems.

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