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Reversible Dispersion and Release of Carbon Nanotubes Using Foldable Oligomers

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Abstract: Foldamers are synthetic and designable oligomers that adopt a conformationally ordered state in selected solvents. We found that oligo(*m*-phenylene ethynylene)s, which are single-stranded foldamers, can be made to reversibly disperse and release single-walled carbon nanotubes (SWCNTs) simply by changing the solvent, consistent with a change from an unfolded state to a folded state. Using absorption spectroscopy, atomic force microscopy, Raman spectroscopy, and electrical measurements, we observed that the foldamer-dispersed SWCNTs are individually well-dispersed and have a strong interfacial interaction with the foldamers. In contrast, the released SWCNTs appeared to be free of foldamers. Under illumination, transistors based on the foldamer-dispersed SWCNTs demonstrated significant photoresponse, apparently due to photoinduced charge transfer between the foldamers and SWCNTs. The reported nanocomposites may open an alternative way of developing optoelectronic devices or sensors based on carbon nanotubes.

Introduction

Since their discovery,[1,2] single-walled carbon nanotubes (SWCNTs) have inspired intense studies because of their unique electrical, optical, and mechanical properties as well as various potential applications in electronics, optoelectronics, and composites.[3−12] Although a great deal of work with SWCNTs has been carried out, there are still many technical difficulties to overcome before these nanomaterials can actually be employed in practical applications. One such difficulty lies in the fact that the as-produced SWCNTs often aggregate as bundles and thus are very hard to disperse in solvents, imposing difficulties in their purification and incorporation into devices. Bundle aggregation also diminishes the unique properties intrinsic to the individual nanotubes and weakens their performance when employed in devices. Therefore, how to prepare stable, individually dispersed SWCNTs still remains an interesting research topic.

To date, several methods for the dispersion of SWCNTs have been developed, including covalent[13,14] and noncovalent[15−18] surface modification. Covalent methods involve permanent chemical reactions of the side walls of the SWCNTs with functionalizing groups, consequently causing undesirable disruption of the electronic and/or mechanical properties of the SWCNTs. In contrast, noncovalent approaches, which are typically realized through surface binding of surfactants[19] or

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Scheme 1. Solution Process for Dispersion and Release of SWCNTs by *m*PE-13mers
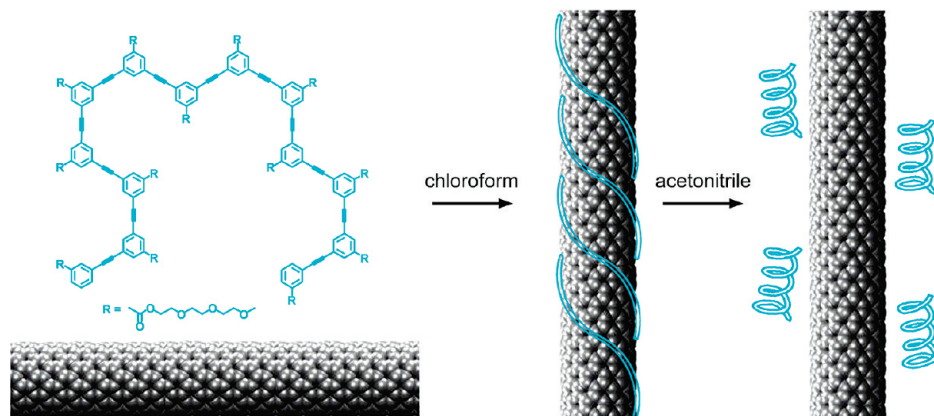
wrapping with polymers[15,20−23] or biomolecules,[24−26] present obvious advantages over covalent approached and have drawn increasing attention. Instead of dramatically changing the intrinsic properties of the SWCNTs, as often occurs when covalent methods are used, the noncovalent methods only slightly tune the properties of the SWCNTs.[27]

In this paper, we demonstrate a simple, reversible route for dispersion and release of SWCNTs involving the use of a particular kind of foldable oligomer (foldamer), oligo(*m*-phenylene ethynylene)s (named *m*PE-13mers), simply by controlling their conformational states in different solvents (Scheme 1). Reversible dispersion and release of SWCNTs through control of light,[28] temperature and pH,[29] or oxidation−reduction reactions of Cu^I/Cu^{II} [30] have been reported previously. However, the dispersion produced using these methods was either stable for only a week or involved only partial debundling, and the dispersion based on light irradiation was actually a one-way process, as the photoconversion from PEG-MG to PEG-MG+ is a permanent, irreversible reaction. *m*PE-13mers are single-stranded foldamers that adopt a helical conformation in solvents other than chlorinated hydrocarbons.[31] The folding is primarily controlled by the π−π interaction between nonadjacent monomer units in conjunction with the solvophobic interaction between the hydrophobic backbone of the oligomer and the polar solvent.[31−34] It has been found that *m*PE-13mers are effective in dispersing SWCNTs while in the unfolded state in chlorinated

hydrocarbon solvents. The dispersion presumably relies on the subtle balance of intramolecular π−π interactions versus intermolecular ones between oligomers and nanotubes. When the solvent is changed from chloroform to a polar solvent, the *m*PE-13mers become folded and are conformationally unsuitable for interfacial π−π interactions with the nanotubes. As a result, the bare nanotubes are released into the solvent, resulting in their precipitation. The dispersed SWCNTs have also been built into network field-effect transistors (FETs), for which interesting phototransistor behavior was observed, indicating photoinduced charge separation between the *m*PE-13mers and the SWCNTs.

Results and Discussion

It has previously been established that the conformational state of *m*PE-13mer foldamers in solution is controlled by changing the solvent. They are conformationally disordered when dissolved in chloroform or other chlorinated hydrocarbons but folded into a helical conformation when dissolved in polar solvents (e.g., acetonitrile). The driving force for the folding is mainly due to the solvophobic effect caused by the hydrophobic aromatic backbone of the oligomer, which thus achieves the maximum π−π interaction between the nonadjacent monomer units, leaving the hydrophilic side chains stretched out into the polar solvent. When the oligomers are dissolved in the unfolded state, their π faces are exposed and able to wrap or stack onto the surface of SWCNTs through intermolecular π−π interactions. The high conformational flexibility of *m*PE-13mers is conducive to surface attachment in a way that maximizes the intermolecular π−π contact, thus affording the maximal free-energy change. Strong interfacial π−π interactions have previously been noted for other aromatic molecules upon mixing with carbon nanotubes.[18,27,35−40] As indeed evidenced in this study, SWCNTs could be well-dispersed in a solution of *m*PE-13mers when chloroform was used as the solvent (Figure 1). The dispersion thus obtained was very stable, remaining clear for

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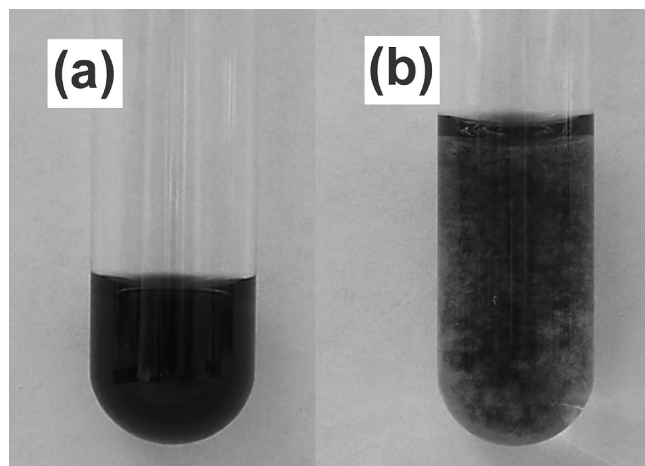(39) Sun, Y. P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002**, *35*, 1096–1104.

(a)   *(b)*

Figure 1. Photograph of (a) an SWCNTs/*m*PE-13mer dispersion in chloroform and (b) the same dispersion after addition of acetonitrile, showing the precipitated nanotubes.
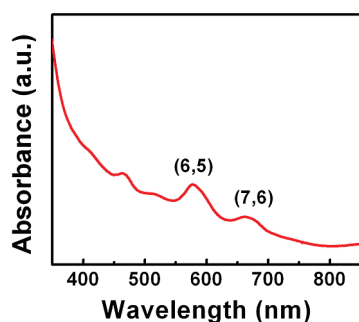

Figure 2. Absorption spectrum of an SWCNT/mPE-13mer dispersion in chloroform.

longer than 6 months of storage in a cabinet. Even upon high-speed centrifugation, only a very slight amount of residue was found at the bottom of the tube. The solubility of SWCNTs in chloroform was estimated to be ∼100 mg/L when the concentration of *m*PE-13mers was 700 mg/L.

It was interesting to see that the dispersed SWCNTs could be rapidly released from the postulated oligomer wrapping simply by addition of acetonitrile into the dispersion (Figure 1b), which results in a solvent composition where *m*PE-13mers
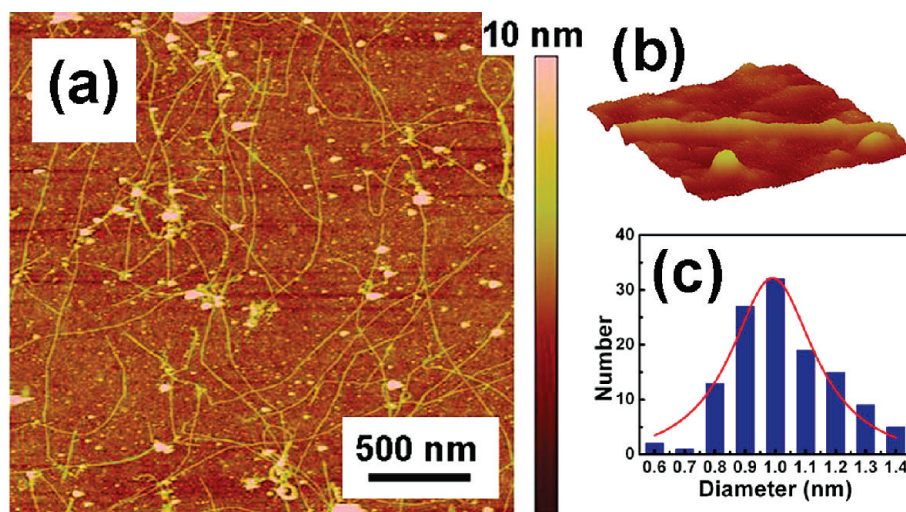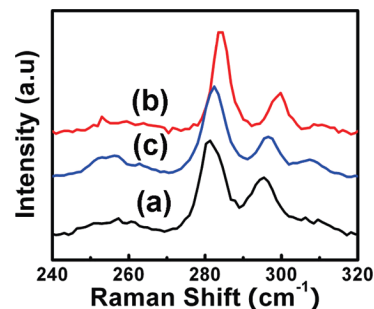

Figure 4. Raman spectra of (a) as-received SWCNTs, (b) *m*PE-13mer-wrapped SWCNTs, and (c) released SWCNTs.

switch their conformational structure from disordered to helical. The folded state is presumably unsuitable for stacking onto the surface of the nanotubes because of the compact conformation, in which most of the monomer π faces are no longer accessible to the nanotube's surface. The released nanotubes (initially floating in the solution) could easily be collected either by membrane filtration or centrifugation.

Absorption spectroscopy has widely been used for characterizing the dispersion of carbon nanotubes. Figure 2 shows an absorption spectrum of an SWCNT/mPE-13mer dispersion in chloroform. The spectrum displays two well-resolved absorption peaks around 576 and 663 nm, which are characteristic of (6,5) and (7,6) carbon nanotubes, respectively. The well-resolved spectral structure indicates that the SWCNTs are well-dispersed in chloroform upon wrapping with mPE-13mers, producing minimal scattering that may otherwise be caused by bundles.

Figure 3a shows a typical AFM image obtained from a spin-cast sample of a diluted SWCNTs/*m*PE-13mer solution, where well-dispersed, individual nanotubes can be observed. When we performed the same AFM scanning over many different areas, we found few nanotubes in bundles. Figure 3b shows a three-dimensional (3D) AFM image revealing a nonuniform height along the nanotube axis. We interpret these undulations as the surface wrapping with *m*PE-13mers. Such surface wrapping of oligomers was further examined by measuring the diameter of the dispersed SWCNTs and comparing it with that of the as-received nanotubes. Measurement of the diameter of the SWCNTs was based on the height profile obtained from AFM raster scanning. By analyzing the height profile of more

Figure 3. (a) AFM image of individually separated SWCNTs spin-cast onto a SiO₂ substrate from a diluted SWCNT/*m*PE-13mer solution. (b) Typical 3D AFM image obtained over a single SWCNT (image size 120 nm × 120 nm). (c) Diameter distribution of the oligomer-wrapped SWCNTs (blue) and the Lorentzian fit (red).
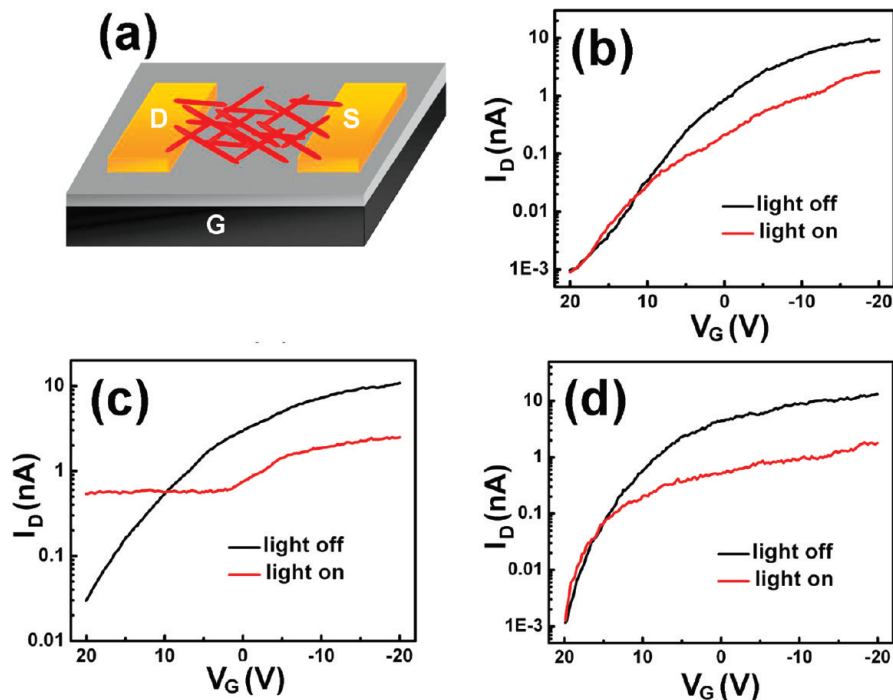
Figure 5. (a) Schematic illustration of the SWCNT network FET. (b−d) Transfer characteristics (I_D−V_G curves) of (b) the as-received SWCNTs, (c) *m*PE-13mer-wrapped SWCNTs, and (d) released SWCNTs. All of the measurements were performed at a bias voltage (V_{DS}) of 5 V. The light source was a 200 W mercury lamp.

than 100 SWCNTs, we found that the diameter ranged from 0.8 to 1.3 nm with an average of 1.0 nm (Figure 3c). For the as-received nanotubes (from the same batch of sample purchased, SWeNT SG 65), the diameter was ∼0.8 nm. The slight increase in diameter observed for the dispersed SWCNTs is apparently due to the wrapping with *m*PE-13mers.

Raman spectroscopy has proven to be an effective way to characterize the surface modification of carbon nanotubes. The low-wavenumber Raman radial breathing mode (RBM) of SWCNTs is strongly dependent on the diameter of the nanotube as well as the surface-absorbed chemical species.[41−45] The relationship between the RBM frequency (ω_{RBM}) and the nanotube diameter (d_t) can be expressed as in eq 1:[45]

$$\omega_{RBM} = \frac{C_1}{d_t} + C_2 \qquad (1)$$

where C_1 and C_2 are 223.5 nm cm^{-1} and 12.5 cm^{-1}, respectively. Previous studies have demonstrated that the absorption of DNAs on the SWCNTs induces an upshift in the RBM, and the upshift is relevant to the wrapping compactness, or the degree of

interaction between DNAs and the carbon nanotubes. Stronger interfacial interactions usually result in a larger upshift in the RBM.[44] Figure 3 shows Raman spectra recorded from the as-received SWCNTs, the SWCNT/*m*PE-13mer blend, and the released SWCNTs, for which the main RBMs are located around 281 and 295 cm^{-1} for the bare nanotubes. Using eq 1, we estimated the diameter of the SWCNTs to be ∼0.8 nm, which is consistent with the size obtained from the manufacturer. In comparison with the as-received nanotubes (Figure 4a), the oligomer-wrapped nanotubes (Figure 4b) exhibited a significant upshift of 3.5 cm^{-1} for the two RBM peaks, indicating the strong electronic (π−π) interaction between the adsorbed oligomers and nanotubes. On the other hand, the released SWCNTs (Figure 4c) demonstrated almost the same Raman spectrum as the as-received nanotubes, indicative of a surface free of oligomers.

The strong electronic interaction between carbon nanotubes and surface-absorbed or -bound molecules is often accompanied by charge transfer, which in turn affects the electrical properties of the nanotubes and can be used to develop chemical or biosensors,[46−49] or photoswitches.[50,51] In order to characterize the electrical properties of the dispersed and released SWCNTs, we spin-coated the nanotubes onto a photolithography-defined electrode pair with a channel length of 8 μm, forming a bottom-contact FET. Since the SWCNTs we used were ∼1 μm in length, they piled together to form fibril-like networks within the large gap of the electrode pair (Figure 5a). In view of the good conductivity intrinsic to nanotubes, no contact problem

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would be expected for the networks thus formed. For the as-received SWCNTs, typical p-type FET behavior was observed in measurements under ambient conditions (Figure 5b), where the surface-absorbed oxygen acts as an electron-withdrawing species, leading to the generation of holes as the charge carriers.[52] Upon illumination with white light from a 200 W mercury lamp, some of the surface oxygen was eliminated through so-called photodesorption, as previously observed by others,[52] thereby resulting in a decrease in the conductivity of the nanotubes (Figure 5b). For comparison, the same electrical and optical examinations were performed on the oligomer-wrapped nanotubes, as shown in Figure 5c. Although quite similar FET performance was observed in the dark, the oligomer-wrapped nanotubes exhibited dramatically different behavior under illumination, where a clear "off" state could be seen in the transfer curve and a threshold gate voltage that was negatively shifted relative to that observed for the as-received nanotubes was seen. Such a negative shift in the gate threshold voltage usually implies electron transfer from the adsorbed oligomers to the nanotubes, as previously observed for other molecules attached to SWCNTs.[51,53] In great contrast, the FET properties of the released SWCNTs (Figure 5d) remained the same as those of the as-received SWCNTs (Figure 5b) both in the dark and under white-light illumination. This, in combination with the Raman spectroscopy results (Figure 4), indicates that the surface of the released SWCNTs had become free of *m*PE-13mers.

Conclusion

In summary, we have demonstrated that *m*PE-13mers, which are single-stranded foldamers, can be made to reversibly disperse and release SWCNTs simply by controlling their conformational state through a change in solvent. When dispersed in a nonpolar solvent, the oligomers exist in a flexible unfolded conformation, causing association between the surface of the oligomers and the SWCNTs via intermolecular $\pi-\pi$ interactions, resulting in a stable dispersion of the nanotubes. Increasing the polarity of the solution by adding acetonitrile forces the oligomers to fold into the rigid helical structure, becoming unsuitable for the surface $\pi-\pi$ stacking with the SWCNTs. As a result, all of the oligomers dissociate from the surfaces of nanotubes and dissolve back into the solution, leaving the bare nanotubes to precipitate from the solution. Such dispersion and release were well-characterized by various experimental techniques, including absorption spectroscopy, atomic force microscopy, Raman spectroscopy, and electrical measurements. The oligomer-wrapped nanotubes demonstrated significant photoresponse for the FET behavior, implying potential applications of these nanocomposites in phototransistors, optical sensors, or photoswitches.

Supporting Information Available: Experimental details of synthesis and structural characterization of the foldamers; dispersion and AFM measurements on SWCNTs; Raman spectroscopy characterization of foldamer adsorption onto nanotubes; fabrication of FET devices with the foldamer-wrapped SWCNTs and measurements of the photoresponse; estimation of the number of foldamers wrapped per nanotube and the number of electrons transferred per foldamer; and complete ref 42. This material is available free of charge via the Internet at http://pubs.acs.org.

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