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Selective Band Structure Modulation of Single-Walled Carbon Nanotubes in Ionic Liquids

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Single-walled carbon nanotubes (SWCNTs) form a type of promising nanomaterial with extraordinary physical properties.[1] Unfortunately, SWCNTs are typically synthesized as a mixture of metallic and semiconducting tubes, which poses great obstacles to the application of SWCNTs, especially in high-performance devices. It is therefore of crucial importance to separate metallic and semiconducting SWCNTs. However, their similar properties make the separation a big challenge. Another critical issue for the application of SWCNTs is the selective and rational tuning and controlling of their electronic properties. Some chemical and physical approaches have been developed to meet these goals.[2] However, the disadvantages of causing damage to the SWCNTs, introducing too many components into the SWCNT dispersions, and making the procedures too complicated greatly restrict their applicability. Therefore, more effective and convenient nondestructive methods for the identification, separation, and modification of metallic and semiconducting SWCNTs are desired.

Imidazolium-based room-temperature ionic liquids were found to be excellent solvents for the dispersion of SWCNTs,[3] in which the SWCNTs can be well-dispersed and untangled into very fine bundles at contents as high as ∼1 wt %. Recently, we demonstrated that such solvents have the additional advantage of retaining the intrinsic structure and properties of the SWCNTs.[4] Because of these merits, imidazolium-based ionic liquids are ideal solvents for property studies and large-scale manipulation and application of SWCNTs. In addition, the unique physicochemical characteristics of ionic liquids may also introduce novel properties into this dispersion system.

Anionic surfactants have been widely used for the dispersion of SWCNTs in water.[5] Their tail parts adsorb on the nanotube walls through hydrophobic interactions without modifying the inherent properties of the SWCNTs.[5] However, it was found in the present work that anionic surfactants can selectively absorb on different SWCNTs and modify their band structures in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) ionic liquids. This method is very simple and effective, and the modification is reversible.

Figure 1a and Figure S2 in the Supporting Information (the latter including baseline correction) show the absorption spectra of SWCNTs suspended in [BMIM]PF_6 before and after the addition of various most commonly used anionic surfactants. It can be seen that some of them, including perfluorooctanoic acid (PFOA), sodium dodecyl sulfate (SDS), and lithium dodecyl sulfate (LDS), induced changes in the absorption bands of the SWCNTs, while for the other surfactants, such as potassium perfluorooctanesulfonate (PPFOS) and potassium dodecyl sulfate (PDS), the absorption bands remained unchanged even at a very high surfactant concentration. These facts imply that special interactions exist between SWCNTs and the cations of certain surfactants. This process is reversible. After removal of the surfactants, the absorption bands recovered.

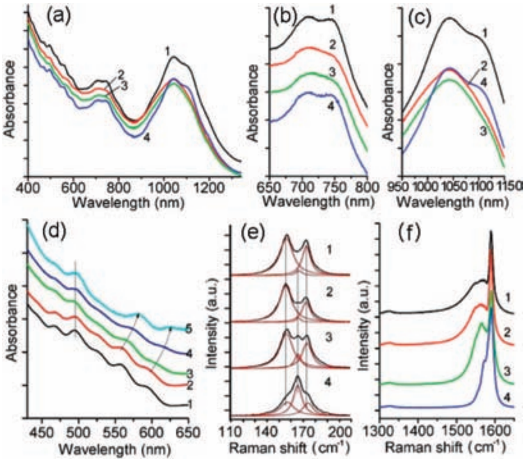

Figure 1. Spectra of SWCNTs suspended in [BMIM]PF_6 before and after addition of various surfactants. (a) Absorption spectra, from top to bottom, containing (1) no additive, (2) 3.3 mM PFOA, (3) 4.7 mM SDS, and (4) 5.0 mM PPFOS. (b, c) Magnifications of portions of (a). (d) Absorption spectra, from bottom to top, after addition of (1) 0.0, (2) 1.6, (3) 2.5, (4) 3.3, and (5) 6.6 mM PFOA. (e) RBM and (f) G bands of Raman spectra ($E_{\mathrm{laser}} = 1.96$ eV), from top to bottom, after addition of (1) 0.0, (2) 1.6, (3) 3.3, and (4) 6.6 mM PFOA. The RBM bands were fitted with Lorentzian profiles.

More interesting is the fact that the changes in the absorption spectra are absorption-band-selective, SWCNT-type- and diameter-selective, and dependent on the anionic surfactant concentration. The SWCNTs used had diameters of ∼1.2−1.7 nm. After the additions of PFOA, LDS, and SDS, different absorption features exhibited different behaviors (Figure 1a−d). Type-I absorption features, corresponding to E_{22} transitions (∼1100 nm) of the large-diameter (∼1.5−1.7 nm) semiconducting nanotubes[6] and E_{11} transitions (∼750 nm) of the metallic nanotubes with diameters of ∼1.5 nm, diminished in intensity, and type-II absorption bands (∼550−650 nm), arising from E_{33} transitions of the semiconducting nanotubes with diameters of ∼1.5−1.7 nm, were red-shifted to longer wavelengths with increasing surfactant concentration; in contrast, type-III absorption bands (∼400−500 nm), assigned to E_{33} electronic transitions of the small-diameter semiconducting nanotubes (∼1.2−1.4 nm), did not show any shift at the tested concentrations. These facts show that only metallic SWCNTs and large-diameter semiconducting SWCNTs interact with the surfactants and that their electronic band structures can be tuned over a range by changing the surfactant concentration. These facts also demonstrate that the high-energy electrons in the vicinity of the Fermi level are more easily affected than the lower-energy electrons.[7] This was further verified by first-principles calculations of the band structures and densities of states of positively charged

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SWCNTs (see Figure S8 in the Supporting Information). PFOA, LDS, and SDS show differing abilities to modulate the SWCNTs' transition energy. It can be seen from Figure S2 that LDS shifts the transition energy more than PFOA and SDS at the same molar concentration.

Figure 1e shows the radical breathing mode (RBM) in the resonance Raman spectra of SWCNTs at various PFOA concentrations ($E_{\mathrm{laser}} = 1.96$ eV). A more detailed discussion of the Raman spectra is available in the Supporting Information. As the PFOA concentration increased, the metallic and large-diameter semiconducting SWCNTs lost intensity in their RBM bands (at ~173 and ~156 cm^{-1}, respectively), while the small-diameter semiconducting SWCNTs maintained the intensity of their RBM band (at ~166 cm^{-1}). The results show further evidence that the surfactant molecules primarily interact with metallic and large-diameter semiconducting SWCNTs. Another obvious change in the Raman spectra was the diminishment of the Breit−Wigner−Fano (BWF) G band at high PFOA concentrations (Figure 1f), indicating a reduction of the density of states near the Fermi level for metallic SWCNTs. There was no increase in the disorder mode (~1325 cm^{-1}) after addition of PFOA. This result shows that no defects were introduced into the SWCNTs and no covalent bonds were formed between PFOA and the SWCNTs. Therefore the structure of the SWCNTs was well-retained after the addition of PFOA.

It has been stated above that only surfactants with small cations (H^+, Li^+, Na^+) can selectively modify SWCNTs. There are at least two additional pieces of evidence showing that cations play the key role in this process. First, the addition of crown ether to the system made the absorption spectra recover because the cations were coordinated by the crown ether (see Figure S7 in the Supporting Information). Second, the absorption spectra did not change when the positive charge density of the cation was reduced by the strong interaction between the anions and the cations when octanoic acid, dodecyl acid, or sodium stearate was used (see Figure S5 in the Supporting Information). Our further study revealed that the tails of the surfactant molecules play a supplementary role in the interaction between the cations and SWCNTs. When we replaced the surfactants with inorganic salts or organic salts with short alkyl chains, there was no change in the SWCNTs' transition band (see Figure S5). These facts indicate that the tail and head parts of the surfactant molecules acted integratively and that the surfactant molecules were undissociated for PFOA, SDS, and LDS in $[\mathrm{BMIM}]\mathrm{PF}_6$. Anionic surfactants are normally dissociated and form micelles in $[\mathrm{BMIM}]\mathrm{BF}_4$,[8] and therefore, anionic surfactants in $[\mathrm{BMIM}]\mathrm{BF}_4$ cannot change the band structure of SWCNTs because the dissociated cations cannot absorb on the SWCNT walls (see Figure S4 in Supporting Information).

On the basis of the above results, the possible interaction mechanism between SWCNTs and the surfactants (PFOA, SDS, and LDS) in $[\mathrm{BMIM}]\mathrm{PF}_6$ shown in Figure 2 is proposed. The undissociated surfactants are absorbed onto the SWCNT walls through solvatophobic interactions between the tails of the surfactants and the SWCNTs. Because of the large positive charge density of the cations, the high-energy electrons of the SWCNTs near the Fermi level transfer to the lowest unoccupied orbitals of the cations. A stable "cation−π" complex is formed at the nanotube surface. The metallic SWCNTs have finite a density of states near the Fermi level. The large-diameter semiconducting SWCNTs have a small gap near the Fermi level. For small-diameter semiconducting SWCNTs, a large gap exists. Thus, the energy of the highest occupied band in the three kinds of SWCNTs decreases correspondingly, as does the strength of the interaction between the SWCNTs and the cations of the surfactants. The positive charge density of the cations varies with their type and can be further altered by changing the anions. Therefore, the strength of the cation−SWCNT interaction can be tuned. Then the SWCNTs can be modified in a more controlled manner according to their electronic structures. This may also provide a potential approach for chirality-dependent separation of SWCNTs.

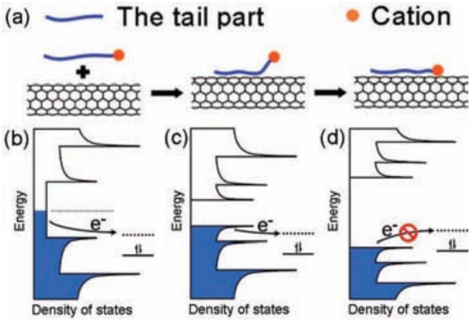

Figure 2. Scheme showing the selective modification mechanism. (a) Adsorption of anionic surfactants on SWCNTs. (b−d) Schematic representations showing electron transfer from (b) metallic, (c) large-diameter semiconducting, and (d) small-diameter semiconducting SWCNTs to the lowest unoccupied orbital of the cation.

In conclusion, we have demonstrated in this communication a simple method for the reversible and selective modification of metallic and large-diameter semiconducting SWCNTs in $[\mathrm{BMIM}]\mathrm{PF}_6$ ionic liquids by addition of certain anionic surfactants. Their electronic band structures can be controlled and tuned over a range by varying the surfactants used and their concentration. This method is mild and does not destroy the structure of the SWCNTs. A charge-transfer "cation−π" complex model is proposed as the mechanism.

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Supporting Information Available: Experimental procedures and additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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