Covalent Cross-Linked Polymer/Single-Wall Carbon Nanotube Multilayer Films

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Layer-by-layer films have been constructed from a cationic diazo resin and poly(sodium 4-styrenesulfonate)-functionalized single-wall carbon nanotubes (SWNT). Raman and near-IR absorption spectra indicate that some diazonium ions reacted with SWNT during film construction. The ionic bonds in the film between diazonium ions and sulfonate ions converted to covalent bonds upon UV irradiation as shown by the disappearance of diazonium ion peaks in the UV and IR spectra and appearance of an arenesulfonate peak in the IR spectra. The resistance of the film toward etching by polar solvents increased significantly after irradiation.

Introduction

Incorporation of single-walled carbon nanotubes (SWNT) into materials is of great interest because of their unique electronic, mechanical, optical, and thermal conductivity properties. Because of their low density and high surface area, SWNT reinforcement of polymer composites should enable the formation of ultra-lightweight, high-strength materials. However, the formation of SWNT composite materials has been hampered by the poor solubility of pristine SWNT in most solvents and polymers. Bundles of SWNT are difficult to break up into individual tubes, which would be the most effective reinforcing material. The functionalization of SWNT confers solubility and can be realized by either noncovalent or covalent approaches. Functionaization should be an effective route to homogeneous dispersions of carbon nanotubes in polymer matrixes.

Layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes is a simple and powerful method for the construction of composites that are self-assembled on a nanometer scale. Many different types of nanoparticles, including SWNT, can be incorporated into LBL films. LBL assembly allows excellent control of thickness and composition and diminished phase segregation compared with other methods of construction of SWNT composites.

In addition to electrostatic interactions, LBL composite materials have been constructed based on hydrogen bonding, charge-transfer interactions, and coordination bonding. So far, all LBL composites containing SWNT have been constructed via electrostatic interactions or hydrogen bonding. However, both the electrostatic and the hydrogen bonding attractions may be insufficient to stabilize the composites in some cases, such as against etching by polar solvents. The strength of SWNT composites depends on strong adhesion between the SWNT and the polymer. SWNT/polymer LBL composites have been strengthened by covalent cross linking. The tensile strength of the cross-linked composites was several times higher than that of a similar SWNT composite made by mixing.

Here we report the cross linking of multilayer LBL films of SWNT-poly(sodium 4-styrenesulfonate) (PSS) and a diphenylamine-4-diazoresin. The SWNT–PSS was 55 wt % SWNT. Covalent linkage of the PSS ensures adhesion...
of the SWNT to the polymer matrix. Diazoresins (DRs), polycondensation products of a diarylamine-4-diazonium salt, and its derivatives with formaldehyde are important photosensitive materials for the manufacture of negative presensitized plates for lithographic printing. Multilayer films of DR and anionic polyelectrolytes are very stable toward polar solvents after UV irradiation because the ionic bonds between layers convert to covalent bonds. Diazonium groups also react with SWNT thermally at room temperature in aqueous solution to form chemically functionalized SWNT. Therefore, LBL films from anionic polyelectrolyte-functionalized SWNT and DR, having chemical crosslinking both between SWNT and DR and between polyelectrolytes, and DR should have excellent stability and strength.

Experimental Section

Materials. DR was synthesized as reported and stored at −5 °C in the dark. SWNT−PSS (55/45 in weight ratio) was synthesized by in situ free radical polymerization of sodium 4-styrenesulfonate (NaSS) in the presence of pristine HiPco SWNT. PSS was the unattached polymer produced during the SWNT functionalization, which was separated from SWNT−PSS by ultrafiltration through a 0.2-μm PTFE membrane and precipitated into acetone. Water was triply deionized with a Barnstead E-pure system to conductivity less than 1 × 10⁻⁶ Ω⁻¹ cm⁻¹. All other reagents and solvents were used as received from Aldrich or Acros Chemicals.

Instruments and Measurements. All spectra were obtained from dry polymer films using a Perkin-Elmer 2000 FTIR instrument, a Hewlett-Packard 8453A diode array UV−vis spectrophotometer, a Jovin Yvon-Horiba Lab Raman spectrometer equipped with a charge-coupled device detector and 633-nm laser excitation, and a Cary5/Cary500 UV−vis−NIR spectrophotometer. Atomic force micrographs (AFM) were obtained using a Multimode Nanoscope IIIa SPM (Digital Instruments, St. Barbara, CA) operating in the tapping mode under ambient conditions. The Si cantilevers had a spring constant of about 20 N/m and a resonance frequency of about 265 kHz. The set-point amplitude ratio was maintained at 0.9 to minimize sample deformation by the tip.

Film Preparation. The LBL film was constructed on a quartz slide for UV−vis, NIR, Raman, and AFM measurements or on a calcium fluoride (CaF₂) plate for Fourier-transform (FT)IR spectroscopy. Before LBL construction, the quartz wafer was cleaned with 30% H₂O₂ and concentrated sulfuric acid (3:7 by volume) at 100 °C for 30 min and rinsed 10 times with water, and the CaF₂ wafer was cleaned by washing 10 times with water. The concentrations of DR, PSS, and SWNT−PSS in water for dip coating were 1.0, 1.0, and 0.5 mg/mL, respectively. In all cases, DR was the first layer. For (DR/PSS), multilayer films, the deposition time for each layer was 20 min, followed by washing three times for 1 min with water. For the (DR/SWNT−PSS)ₙ multilayer film, the deposition time for SWNT−PSS layers was 40 min; otherwise the procedure was the same as for (DR/PSS)ₙ films. All fabrications were performed in the dark, and DR solutions and films were kept in the dark until the intended irradiation. The irradiation of the DR/SWNT−PSS and DR/PSS films employed a 75-W “black” incandescent lamp filtered to transmit mainly UV light at a 20-cm distance from the film.

Results and Discussion

LBL films of DR and PSS have been fabricated before based on electrostatic interaction between cationic polyelectrolyte DR and anionic polyelectrolyte PSS. The ionic bonds between these two components converted to covalent bonds during UV irradiation. To be compared, multilayer films of both DR/SWNT−PSS and DR/PSS were constructed using aqueous solutions for LBL deposition. Figures 1 and 2 show the UV−vis absorption spectra of the DR/SWNT−PSS and DR/PSS multilayer films. The absorbance of the film at 380 nm, which is due mainly to the diphenylamine-4-diazonium group, increases linearly with the increasing number of bilayers in both cases as shown in insets of Figures 1 and 2, indicating deposition of the same amount of DR in each bilayer. However, the absorbance at 380 nm increases about 0.017 per bilayer for DR/SWNT−PSS and 0.028 per
bilayer for DR/PSS, although the concentration and deposition time is the same for DR in both films. One reason for this difference is the concentration of PSS used during deposition: 0.5 mg/mL for SWNT-PSS, which corresponds to 0.25 mg/mL PSS, and 1.0 mg/mL for PSS. The SWNT themselves also may affect deposition behavior. Still another reason for the difference is that some diazonium groups were consumed by chemical reaction with SWNT. (See the discussion of Raman spectra.) A constant amount of SWNT-PSS per bilayer was deposited, as shown in the inset of Figure 1, where the absorbance of SWNT at 700 nm increases linearly with the number of bilayers.

The diazonium groups decompose easily by mainly a cationic mechanism under UV irradiation and a radical mechanism under heating.26 Figure 3 shows the changes in UV-vis spectra of the films after irradiation. The absorbance at 380 nm of both the DR/SWNT-PSS film and the DR/PSS film decreases dramatically due to the decomposition of the diazonium group.23 At the same time, the absorbance of SWNT at >480 nm did not change during the process. Previously the irradiation of DR/PSS films was said to cross link the DR to PSS via conversion of the diazonium ions to phenyl cations and then combination of sulfonate anions from PSS with the cations to form aryl 4-styrenesulfonate groups.27 Thus the ionic bond between diazonium and sulfonate group converts to a covalent bond by photoreaction. To confirm this reaction, films of 10 bilayers of DR/SWNT-PSS and DR/PSS were constructed on CaF₂ plates, and their FTIR spectra were recorded before and after irradiation as shown in Figure 4. The spectra of DR/SWNT-PSS and DR/PSS are basically the same (parts A-a and B-a of Figure 4), due to strong absorption of DR at 2168 and 1580 cm⁻¹. The ~2–4-cm⁻¹ shift of the characteristic absorption peaks in DR/SWNT-PSS film compared with those in DR/PSS film was found in three different samples. The shifts may be due to interactions between SWNT and DR. As seen in Figure 4A, the asymmetric stretching vibration of the −N₂⁺ at 2168 cm⁻¹ in DR/SWNT-PSS film decreased completely after UV irradiation, indicating the decomposition of the diazonium group.23 At the same time, the symmetric stretching of SO₃⁻ in the DR/SWNT-PSS film at 1182 cm⁻¹ shifted to 1172 cm⁻¹, which corresponds to the symmetric stretching of an anenesulfonate group.23 Furthermore, the absorption at 1580 cm⁻¹ corresponding to the vibration of the arene ring conjugated with an unsaturated group in DR/SWNT-PSS film shifted to 1599 cm⁻¹, the normal absorption of an arene.28 All of this evidence shows that the ionic bonds in the DR/SWNT-PSS multilayer film were converted to covalent bonds by photoreaction, the same as in the DR/PSS multilayer film shown in Figure 4B.

Besides the photoreaction between DR and PSS, chemical reaction of diazonium groups with SWNT during the film construction and irradiation is also possible. Dyke and Tour reported that aryldiazonium tetrafluoroborate salts can react thermally at 23 °C with individual SWNT in an aqueous SDS (sodium dodecyl sulfate) dispersion.25 They proposed

a radical mechanism for the thermal reaction. In our preparation, the SWNTs were dispersed well in water in the form of individual tubes or small bundles by covalent functionalization with PSS. Because the degree of functionalization of the SWNT is very low, the electronic structure of SWNT is still intact in the SWNT-PSS. After LBL construction with DR, the diazonium groups in the film are close to the SWNT surface as counterions of the PSS, which is similar to the diazonium ions and adsorbed SDS on the SWNT surfaces reported by Dyke and Tour. To confirm this, Raman spectra of DR/SWNT-PSS multilayer films were recorded before and after UV irradiation. Compared with the spectrum of SWNT-PSS, which shows a small disorder mode (D-band) at 1315 cm\(^{-1}\) (Figure 5A-a), and the spectrum of (DR/PSS)\(_{12}\) (Figure 5A-b), the spectrum of (DR/SWNT-PSS)\(_{14}\) before irradiation (Figure 5A-c) contains all of the signals from both SWNT and DR/PSS. However, Figure 5A-c shows a significant decrease in the large tangential mode (G-band) relative to the D-band, indicating an increase in the degree of the functionalization of SWNT. This demonstrates that the SWNTs were already functionalized during the film construction, which we attribute to reaction between the diazonium groups and the SWNT. Covalent bonds to the side walls of SWNT increase the intensity of the D-band relative to the G-band. Because only a fraction of the diazonium groups in the (DR/SWNT-PSS)\(_{14}\) film were consumed, the film still absorbs at 380 nm as shown in UV-vis spectra in Figure 3A. The UV irradiation had no further effect on the Raman spectra of the SWNT in either the SWNT-PSS film or the DR/SWNT-PSS film as shown in spectra a and c of parts A and B of Figure 5; the D-band and G-band ratios in the spectra of SWNT-PSS and/ or DR/SWNT-PSS films are almost unchanged, indicating no further reaction between SWNT and diazonium groups.

Another change in the Raman spectrum of (DR/SWNT-PSS)\(_{14}\) upon irradiation is the intensity of the 1589-cm\(^{-1}\) G-band of SWNT relative to the intensities of the DR peaks at 1659, 1701, and 1763 cm\(^{-1}\) as shown in parts A-c and B-c of Figure 5. A possible cause is a change of the film surface morphology upon UV irradiation. Before irradiation, the force for film formation is electrostatic attraction between diazonium and sulfonate groups. During irradiation, N\(_2\) was released, the ionic bonds in the film converted to covalent bonds, the bilayers contracted, and more SWNTs were exposed to the film surface, which accounts for stronger signals in Raman spectra. This is supported by AFM images. Before irradiation, only several big SWNT bundles can be observed clearly on the rough (DR/SWNT-PSS)\(_{14}\) film surface, as seen in Figure 6A. After irradiation, besides several big bundles, numerous individual or small bundles of SWNTs several hundred nanometers to several micrometers in length appear clearly in Figure 6B.

The reaction between diazonium groups and SWNT during the film construction was also confirmed by near-IR absorption spectra. The cast SWNT-PSS film shows the characteristic van Hove singularities at 500–1700 nm both before and after irradiation (parts A-a and B-a of Figure 7). These
peaks became very weak after construction of the DR/SWNT−PSS film (Figure 7A-b), indicating the covalent functionalization of the sidewall of SWNT even before irradiation. The weak transitions in the NIR after self-assembly also account for the weak absorbance of SWNT in the UV−vis spectra in Figures 1 and 3A. In our previous work on self-assembly of multilayer films of SWNT−poly-(4-vinylpyridine) and −poly(acrylic acid), the absorbance of SWNTs in UV−vis spectra was stronger than here.14 After irradiation, the spectrum of the DR/SWNT−PSS film (Figure 7B-b) did not change. Thus, the overall chemical reactions during the film construction and further irradiation are as illustrated in Scheme 1. During construction, some of the diazonium groups in the film reacted thermally with SWNT,25 and the rest of them bonded ionically to sulfonate groups. These ionic bonds converted to covalent bonds via a cationic mechanism after release of N2 by UV irradiation.23

The stability of the film toward etching by polar solvents increases greatly after irradiation. When the unirradiated DR/SWNT−PSS film was immersed in a ternary mixture of H2O−DMF−ZnCl₂ (3:5:2 by weight), nearly 50% of the film was dissolved after 10 min according to the decrease of the absorbance at 250 and 380 nm. This ternary system was chosen because of the high solubility of the polyelectrolyte complex of DR/PSS in this solvent.23 For an irradiated DR/SWNT−PSS film, no detectable change of the absorbance at 250 nm was observed after immersion in the same ternary solvent for 30 min even with sonication. Chemical cross linking between SWNT/DR and DR/PSS made the multilayer film more robust.

In conclusion, alternating layers of cationic DR and anionic SWNT−PSS films have been constructed using the LBL technique. Some of the diazonium groups reacted to form covalent bonds to SWNT during film formation. Ionic bonds between the diazonium ions and the sulfonate ions converted to covalent bonds upon UV irradiation, which improved greatly the stability of the film toward etching by polar solvent.

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