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Carbon nanotube/poly(2,4-hexadiyne-1,6-diol) nanocomposites prepared with the aid of supercritical CO_2

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Poly(2,4-hexadiyne-1,6-diol) (poly(HDiD)) was coated on the outer walls of carbon nanotubes (CNTs) with the aid of supercritical CO_2, resulting in poly(HDiD)/CNT nanocomposites, which possess optical properties originated from poly(HDiD).

Since their discovery, carbon nanotubes (CNTs) have attracted more and more interest due to their outstanding structural, mechanical, and electrical properties.[1–5] CNTs are becoming increasingly available, and considerable attention from both academia and industry is focused on the applications of CNTs in bulk quantities, including use as a conductive filler in insulating polymer matrices,[6] and as reinforcement in structural materials.[7] Other potential applications use CNTs as a template to grow nanosized, and hence ultra-high surface-to-volume ratio catalyst, or aim to combine CNTs to form nanoelectronic elements. Strategies for functionalizing CNTs are crucial for the pursuit of these applications. The developed approaches for functionalizing CNTs involve the introduction of functional groups onto the CNTs surfaces covalently. For example, functionalized CNTs with carboxylic acid have been used to covalently attach proteins,[8] oligonucleotides,[9] polymers,[10] and nanocrystals[11] to CNTs. However, it also desirable to develop methods for functionalizing CNTs noncovalently to retain their attractive electronic and mechanical properties. Some functional molecules, such as 1-pyrenebutanoic acid and succinimidyl ester,[12] pyrene-like initiator,[13] surfactants and polymer layers,[14] SiO_2 thin film,[15] and gold nanoparticles,[14f] have been attached onto the surfaces of CNTs through noncovalent bonds. The functionalization of CNTs makes them possess some new properties, probably resulting in new materials.

Diacetylenes (DAs) $R_1–C{\equiv}C–C{\equiv}C–R_2$ are unusual in that they can be converted into macroscopic polymer single crystals *via* solid state polymerization by heat, pressure, and UV or γ–ray irradiation.[16] The resultant polymers give rise to some novel properties such as electrical transport, nonlinear optical and thermochromic properties. Based on the structures of DAs and CNTs, it is possible for DAs to be adsorbed on the surfaces of CNTs through π–π interaction between DAs and CNTs, and CNTs/DAs composites can be prepared. The composites may possess both optical properties from DAs and good mechanical properties from CNTs.

As is well known, supercritical fluids (SCFs), due to their special properties such as low viscosity, high diffusivity, near zero surface tension, and strong solvent power for some small organic compounds, have been widely used in the field of material science.[17] Among SCFs, supercritical (SC) CO_2 is the most popular because it is non-flammable, non-toxic, cheap, and easy to obtain. SC CO_2 can dissolve many organic compounds, and carry them into micropores.[18] On the other hand, the solubility of SC CO_2 or compressed CO_2 in many organic solvents is very high, leading to a reduction in the solvent strength of the organic solvents, *i.e.*, CO_2 acts as an antisolvent because the solvent power of CO_2 is much weaker than that of organic solvents for many solutes. The special properties of SC CO_2 have been used to fabricate nanomaterials which are difficult to prepare by traditional techniques. For example, Pt nanoparticles have been deposited into mesoporous alumina templates through the H_2 reduction of metal precursors in SC CO_2,[19] and metal nanowires were filled into multiwalled CNTs using SC CO_2 as the reaction medium.[20] In this communication, 2,4-hexadiyne-1,6-diol (HDiD), which is a fluorescent organic compound and can form a polymer with optical properties at temperatures higher than 180 °C, was selected as a model molecule to synthesize the DAs/CNT composites. We developed a facile route to synthesize the CNT/poly(HDiD) composites with the aid of SC CO_2.†

The micro-FTIR spectra of virgin CNTs and the composites are shown in Fig. 1.‡ The composites possess hydroxyl groups (3424 cm^{-1}) and CH_2 groups (2930 cm^{-1}), which confirm that poly(HDiD) is present in the composites.

XPS analysis‡ of the as-prepared composites shows a predominant presence of carbon (88.2%) and oxygen (11.8%), while the amounts of carbon and oxygen in the virgin CNTs are 96.5% and 3.5%, respectively. The increase in oxygen amount is an indication of the loading of poly(HDiD) onto the CNTs substrate.

The C 1s spectrum of the composites is displayed in Fig. 2. It can be deconvolved into three peaks, which are shown at the bottom of Fig. 2(a). The main peak at 284.6 eV is assigned to the C 1s binding energy for the CNTs, representing the elemental sp^2 and sp^3 carbon atom. The peak at 286.6 eV is due to the carbon atom bound to one oxygen atom, *i.e.*, to the carbon atoms bound to hydroxyl groups from the poly(HDiD). The peak at 289.8 eV is due to the π–π* conjugation of CNTs walls. The O 1s core level of the composite, shown in Fig. 2, is located at 533.1 eV. This binding energy is consistent with that of O 1s in hydroxyl group. Therefore, both C 1s and O 1s spectra confirm the presence of hydroxyl groups in the composites, implying poly(HDiD) is present in the as-prepared composites.

The TEM images of the composites are shown in Fig. 3. It can be clearly observed that the CNT is coated with a polymer layer. From the detailed inspection of high resolution TEM image (Fig. 3(b)), it seems that the interior cavity of CNT was also filled with poly(HDiD). The TEM results illustrate that poly(HDiD) exists in the composites in two ways: coating on the outer surfaces and impregnating in the inner caves of the CNTs. This can be explained by the following.

In this work, CO_2 was used to adjust the solvent power of ethanol for dissolving HDiD. For comparison, we performed the experiment for depositing HDiD on CNTs in ethanol solution.

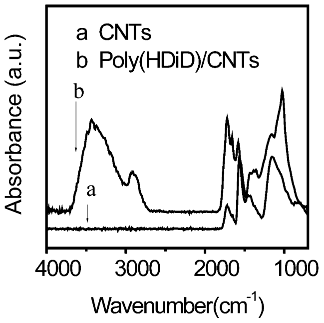

Fig. 1 The micro-FTIR spectra of pristine CNTs and the composites.

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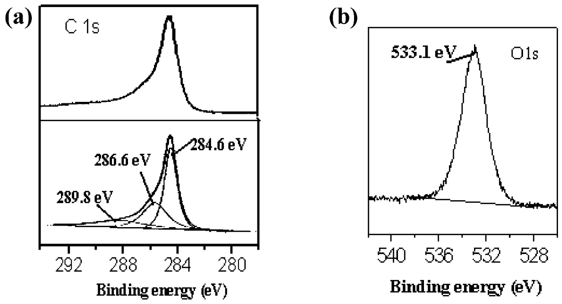

Fig. 2 The XPS C 1s (a) and O 1s (b) spectra of the composites.

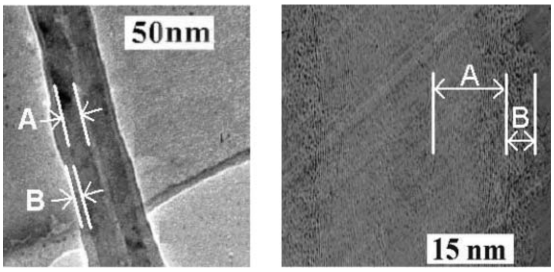

Fig. 3 TEM images of the composites (a) low magnification, (b) high magnification. A: CNT walls, B: poly(HDiD) layer.

However, there was little HDiD adsorbed on the surface of CNTs because the strong solvent power of ethanol for HDiD made most of the HDiD dissolve, thus no CNTs coated with poly(HDiD) were obtained. Under our experimental conditions, an experiment using an optical cell showed that the fluid was in the one phase region during the soaking process, and the solvent contained about 86 wt% CO_2. The solvent power of ethanol for dissolving HDiD was reduced due to the antisolvent effect of CO_2, which was favorable for the adsorption of HDiD on the outer surfaces of CNTs. At the same time, the CO_2–ethanol mixture under the experimental conditions had near zero surface tension and larger diffusivity, which could help the HDiD molecules diffuse into the interior cavities of CNTs easily. Thus, in this study, SC CO_2 might have two functions. Firstly, it worked as an antisolvent to enhance the adsorption of HDiD molecules on the surfaces of the CNTs. Secondly, it reduced the viscosity and surface tension of the solvent, which enhanced the diffusion of HDiD molecules into CNTs. The special properties of SC CO_2 led to the characteristic morphology of the as-prepared CNT/poly(HDiD) composites.

The optical properties of the as-prepared composites were investigated by UV/Vis spectroscopy and fluorescence (FL) spectroscopy‡. The UV and FL spectra of the composites are illustrated in Figs. 4(a) and (b), respectively. It can be seen that the UV and FL spectra of the composites are similar to the corresponding spectrum of poly(HDiD). This implies that the as-prepared composites possess the optical properties of poly(HDiD), which can make the CNT/poly(HDiD) composites work as optical materials. Meanwhile the mechanical strength of poly(HDiD) is also improved through incorporation of CNTs.

In summary, CNT/poly(HDiD) composites with poly(HDiD) coated on the surfaces of the CNTs have been synthesized successfully with the aid of SC CO_2. The resultant composites have the potential to be used as optical materials. The method may be expanded to the fabrication of some other CNT/poly(DAs) composites with useful optical properties.

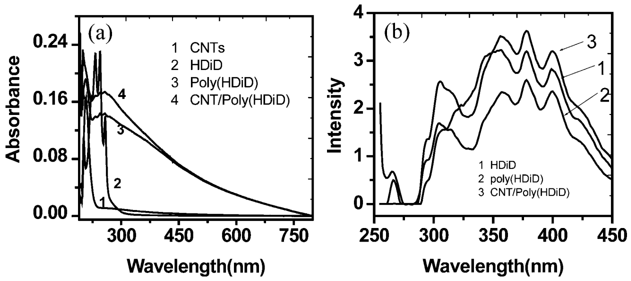

Fig. 4 The UV (a) and FL (b) spectra of samples.

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Notes and references

† *Synthesis of carbon nanotubelpoly(HDiD) nanocomposites*. The multi-walled CNTs were supplied by Shenzhen Nanotech Port Corporation (China) with a purity of >95%, and their outer diameter was in the range from 30 to 40 nm, and inner diameter was in the range from 5 to 10 nm. HDiD was purchased from Aldrich. In an experiment, 10 mg of CNTs were dispersed in 3 mL of HDiD–ethanol solution with a HDiD concentration of 1 mg mL^{-1}. The solution was ultrasonically vibrated for 10 min so that the CNTs were homogeneously dispersed in the solution, and the dispersion was then transferred into a 22 mL high-pressure vessel. The vessel was put into a water bath at 35 °C, and CO_2 was then charged into the vessel up to 12.0 MPa. The CO_2 and ethanol mixture was released from the vessel after an equilibration time of about 10 h, and CO_2 was charged into the vessel to dry the sample. Then the obtained sample was heated to 200 °C for 4 h for the polymerization of HDiD.

‡ *Characterization*. The micro-FTIR spectra were recorded with a Nicolet Magna IR-750 spectrometer using BaF_2 windows. UV spectra were obtained on a UV-Visible spectrophotometer (UV-1601 PC, Shimadzu). Fluorescence (FL) spectra were collected at the excited wavelength of 245 nm under continuous Xe lamp excitation with a spectrofluorometer (Hitachi F-4500) at room temperature. X-Ray photoelectron spectra (XPS) were collected on an ESCALab220i-XL spectrometer at a pressure of about 3×10^{-9} mbar using Al Kα as the exciting source ($h\nu = 1486.6$ eV) and operating at 15 kV and 20 mA. TEM images were taken using a Hitachi 200 under a charge voltage of 300 kV.

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