Research Article

Utilizing Fullerenols as Surfactant for Carbon Nanotubes Dispersions Preparation

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Dispersionsofindividualcarbonnanotubes(CNTs)arecrucialfornanodevicesandpolymer/CNTsnanocomposites.Inthispaper,stableandhomogenousdispersionsofindividualmultiwalledcarbonnanotubes(MWCNTs)havebeensynthesized.Thefactorsinfluencingthedispersibilitymechanism,includingthesurfactantconcentrationandthePHvalue,havebeenvanished. SEM imagesdisplaytheimpuritiesstickingonMWCNTswhichhavemorebeenremoved.Theoxygentaininggroupsonthesurfaceof MWCNTssamplehavebeendetectedthroughFT-IRandRamanspectra.Allexperimentalresultsillustratethatusingfullerenols asurfactantcangreatlyimprovethedispersibilityofMWCNTs.Moreover,theprepareddispersionsexhibitgoodstabilitythatthesedimentpercentageoffullerenols-MWCNTsisonly5.2%after5days.

1. Introduction

Asanewtypeofone-dimensionalnanomaterials,CNTshaveattractedconsiderableattentionduetoitsnovelstructureand uniquephysicalandchemicalpropertiesinrecentyears[1–3].Themethodtoimprovethedispersibilityofindividual CNTs is urgently requested because of the demand for high performance devices, such as transistors, sensors, and oscillators [4–8].

Generally, CNTs can be synthesized by arc discharge, laser ablation, and chemical vapor deposition (CVD), which inevitably contained amorphous carbon, carbon nanoparticles (CNPs), and metal catalyst particles [1, 9–11]. To date, various methods to rarefy MWCNTs, including physical and chemical purification, have been explored. However, physical methods are always complicated and less effective, whereas the chemical methods usually destroy the MWCNTs’ structure, especially one-step liquid phase oxidation [12, 13]. Therefore, two-step liquid phase oxidation, which causes less damage to MWCNTs, has been exploited extensively over the recent years.

Inmostcommonsolvents, van der Waals’ force holds MWCNTs together and severely impedes its manipulation and application. To resolve this problem, various types of surfactants have been proposed to improve the dispersion properties, such as sodium dodecylbenzene sulfonate (NaD-DBs) whose dispersibility is limited and polyvinylpyrrolidone (PVP) which is hard to be removed [14, 15]. Besides, fullerenols exhibit unique structure where polar hydroxyl groups bond on the carbon cages and possess strong electronic adsorption capacity. This characteristic induces the physically adsorption of fullerenols onto the sidewall of MWCNTs by 𝜋-𝜋 interactions, which enhances the dispersions homogeneity and stability significantly [16].
In this work, MWCNTs were purified by two-step liquid phase oxidation with NaOH and a mixture of nitric and sulfuric acids (H$_2$SO$_4$/HNO$_3$, volume 1 : 3). Fullerolns serving as surfactants were used to disperse MWCNTs. The effects of fullerols concentration and solution pH on the dispersibility of MWCNTs were investigated, respectively. Based on the experimental results, a possible mechanism of improvement of dispersibility was proposed.

2. Materials and Methods

2.1. Materials. The N-doped MWCNTs produced by chemical vapor deposition (CVD) were supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. Fullerenes C$_{60}$ were purchased from Suzhou Dade Carbon Nano Science and Technology Co. Ltd. NaDDBs and PVP were bought from Aladdin Reagent. All other reagents were of analytical reagent (AR) pure grade and were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of MWCNTs Dispersions. To obtain the purified MWCNTs (P-MWCNTs), raw MWCNTs (R-MWCNTs) were refluxed in 2 mol/L NaOH for 12 h. Then, MWCNTs were sonicated (400 W, KQ-500DE) for 30 min in a mixture of nitric/sulfuric acids (volume 1 : 3) and washed with deionized water until the eluate reached neutral. Finally, P-MWCNTs were dried at 80°C under vacuum.

The fullerols were synthesized from powdered Fullerene C$_{60}$ by a novel method reported by Chiang et al. [17]. For preparing the MWCNTs dispersions, 25 mg P-MWCNTs and 5 mg surfactants (fullerols, NaDDBs, and PVP) were sonicated for 30 min in 10 ml methanol, respectively. Then, the stable dispersions were collected by centrifuging separation (3000 rpm, TG16-WS) to remove sediment and impurities underlying. Finally, dispersion 1, dispersion 2, and dispersion 3 of MWCNTs were obtained, respectively. Furthermore, the dispersion 1-1, dispersion 1-2, and dispersion 1-3 were prepared based on dispersion 1, in which the amount of fullerols was adjusted by 2.5 mg, 5 mg, and 10 mg, respectively.

2.3. Characterization. The morphologies and chemical compositions of the P-MWCNTs were characterized by scanning electron microscopy (SEM, JEOL JSM-7001F), atomic force microscope (AFM, Bruker Veeco Dimension-5), and Fourier transform infrared spectrometer (FT-IR, Bruker Tensor 27).

The optical absorbance of dispersions was measured by UV-Vis spectrum (METASH UV-8000A), and then the suspensions were collected, dried, and weighed to obtain the quality and concentration. Standard spectra of optical absorbance and the MWCNTs concentration can be obtained since the dispersion concentration is proportional to the dispersion absorbance.

3. Results and Discussion

3.1. Morphologies and Compositions Analysis. Figure 1 shows SEM images of R-MWCNTs and P-MWCNTs. R-MWCNTs with impurities, including amorphous carbon and metal particles, exist in large bundles (Figure 1(a)). P-MWCNTs contained fewer inclusions (Figure 1(b)) than R-MWCNTs since the metal particles can be dissolved by acid and amorphous carbon used to be oxidized under gentle conditions. The P-MWCNTs are prepared by sonication of R-MWCNTs in the binary mixture of H$_2$SO$_4$/HNO$_3$ acid. Therefore, P-MWCNTs possess more intrinsic properties considering that less damage has been brought to MWCNTs than refluxing in the mixed acid [18].

Figure 2 shows FT-IR spectra of R-MWCNTs and P-MWCNTs. For the FT-IR spectrum of R-MWCNTs in Figure 2(a), the weak peaks at 3752 cm$^{-1}$ and 690 cm$^{-1}$ are attributed to the stretching vibration mode and rocking
vibration mode of C-H, while the peaks which locate at 1500 cm$^{-1}$ and 2300 cm$^{-1}$ can be ascribed to the C-N rocking vibration and C≡N stretching vibration in N-doped R-MWCNTs, respectively. Compared with the R-MWCNTs, several different absorption peaks are appeared in the FT-IR spectrum of P-MWCNTs, as shown in Figure 2(b). Considering the influence of water has been already eliminated, the broad peak which appears at 3430 cm$^{-1}$ is ascribed to the O-H stretching vibration modes. The peak which appears at 1620 cm$^{-1}$ is related to C=O stretching in carboxyl groups, whereas the increased strength of the peak at 1250 cm$^{-1}$ may be associated with C-O stretching in phenols [19]. The FT-IR spectra indicate that a two-step purification using NaOH-mixed acid as a solvent is capable of enhancing MWCNTs’ chemical reaction activity, which is beneficial to functionalize hydroxyl and carboxyl groups and improve the performance of dispersions.

Differences of Raman spectra between R-MWCNTs and P-MWCNTs are illustrated in Figure 3. The G-band (1590 cm$^{-1}$) represents the in-plane bond-stretching motion of the pairs of C sp$^2$ atoms (E$_{2g}$ phonons), while the D-band (1350 cm$^{-1}$) corresponds to breathing modes of rings or K-point phonons of A$_{1g}$ symmetry [20]. The structural integrity of the MWCNTs is characterized by ratio of D-band and G-band intensities ($I_D/I_G$). The decrease of $I_D/I_G$ intensity ratio from 1.03 (R-MWCNTs) to 0.83 (P-MWCNTs) demonstrates that the purity of MWCNTs is improved obviously. Compared with R-MWCNTs, both the intensities of D-band and G-band of P-MWCNTs are reduced. The weakening of the D-band is due to the removal of carbonaceous impurities such as amorphous carbon and carbon nanoparticles [21]. The weakening of the G-band indicates that parts of defects are oxidized to hydrophilic groups such as hydroxyl and carboxyl [22], which are consistent with the results of FT-IR spectra.

3.2. Analysis of the Stability of Dispersions. Stability of the MWCNTs dispersion is of great importance in its applications. Dispersion 1 of P-MWCNTs was synthesized by using fullerenols as the surfactant. Figure 4 shows the UV-Vis absorbance spectra of the dispersion 1. Because of 1D van Hove singularities of individual CNTs [23], the characteristic bands of P-MWCNTs corresponding to an intense absorption peak at 260 nm can be clearly observed. Besides, the absorbance intensity is substantially linear in the concentration of dispersion 1 (the inset in Figure 4). The linear fashion indicates that a homogeneous suspension of fullerenols-MWCNTs is formed following the Beer–Lambert law.

The absorbance peak at 260 nm of all dispersions could characterize the concentration of MWCNTs seeing that the concentration of MWCNTs is proportional to the absorbance intensity of UV-Vis spectra. Generally, the sediment percentage used to characterize the suspension stability could be calculated by the following equation:

$$S = \frac{A_0 - A_1}{A_0},$$

where $A_0$ is the absorbance at 260 nm for the fresh dispersion, and $A_1$ is the absorbance at 260 nm for the dispersed suspension at a certain time.
where $A_0$ and $A_1$ are the absorbance intensity of the original solutions and the quiescent solutions. In our experiment, the sedimentation percentage was measured every 12 hours (Figure 5); the concentrations of surfactants including fullerenols, NaDDBs, and PVP were $500 \times 10^{-6}$ g/ml for dispersion 1, dispersion 2, and dispersion 3, whereas the concentrations of P-MWCNTs were about $1080 \times 10^{-6}$ g/ml, $720 \times 10^{-6}$ g/ml, and $530 \times 10^{-6}$ g/ml, respectively.

The results show that the sedimentation percentage of the dispersion 1 is the minimum, which is only 5.2% after 5 days standing. However, the sedimentation percentage of the dispersion 2 and dispersion 3 is 47.5% and 83.1%, almost 10 and 20 times as much as that of dispersion 1. In right inset, it is also clearly observed that NaDDBS-MWCNTs and PVP-MWCNTs dispersions contain coagulated bundles at the bottom while fullerenols-MWCNTs dispersions are homogeneous.

The authors declare that they have no competing interests.

Figure 5: Variation of sediment percentage of dispersion 1, dispersion 2, and dispersion 3. The inserts are the optical images of P-MWCNTs dispersions with fullerenols, NaDDBs, and PVP after 120 h standing (from left to right), respectively.

3.3. Dispersing Mechanism of P-MWCNTs with Fullerenols.

Fullerenols are soluble in polar solvents such as water and alcohol because of decorating of polar hydroxyl groups on the carbon cages. Further experimental results illustrated by SEM images in Figure 5 show that fullerenols can improve the dispersibility of P-MWCNTs significantly. Moreover, the cage structure of fullerenols would result in a strong capacity of electrons adsorption. Therefore, a physical adhesion between fullerenols and MWCNTs could be achieved by $\pi-\pi$ interaction, which can weaken the van der Waals force between MWCNTs and further improve the dispersibility and stability of MWCNTs [16].

In the experiment, the fullerenols concentrations in dispersion 1-1, dispersion 1-2, and dispersion 1-3 were 250 $\times 10^{-6}$ g/ml, 500 $\times 10^{-6}$ g/ml, and 1000 $\times 10^{-6}$ g/ml, respectively. Accordingly, the concentrations of P-MWCNTs in the above dispersions were about $420 \times 10^{-6}$ g/ml, $1080 \times 10^{-6}$ g/ml, and $1250 \times 10^{-6}$ g/ml. Figures 6(a)–6(c) show SEM images of dispersion 1-1, dispersion 1-2, and dispersion 1-3, respectively.

The quantity of P-MWCNTs which adheres to the substrate is proportional to the concentrations of fullerenols mentioned above. The phenomenon is consistent with the results of UV-Vis investigation. Figure 6(d) is the magnified SEM image of the area marked in Figure 6(b); it demonstrates that some individual P-MWCNTs have been taken from dispersion 1-2. More detailed information can be obtained from a quantitative AFM investigation (Figure 6(e)), which further shows the height profiles of an individual P-MWCNT. The diameter is about 26.8 nm as illustrated in Figure 6(f).

The dispersibility also could be tuned by solutions pH. In this work, the pH values of dispersion 1 have been adjusted by HNO$_3$ and NaOH. Figure 7 shows the SEM images of P-MWCNTs of dispersions under acidic (pH = 5) and alkaline (pH = 9) conditions. It can be clearly observed that the dispersibility of P-MWCNTs in alkaline solution is better than that of the acid solution. These can be ascribed to two presumable reasons. Firstly, the dissociation of the oxygen-containing groups could lead to a rise in the concentration of negative charges on the surface of P-MWCNTs. This enhances the electrostatic repulsion between adjacent P-MWCNTs and results in a great improvement of dispersibility. Inversely, the dissociation is usually suppressed in the acidic condition. Secondly, the oxidations of fullerenes can readily proceed under alkaline condition and contribute to the oxygen-containing groups in the functionalization reaction. Nevertheless, this process is difficult to occur under acidic and neutral conditions because of the high energy barriers [24].

4. Conclusions

P-MWCNTs have been produced using two-step liquid phase oxidation treatment with NaOH and a mixture of nitric and sulfuric acids (1:3 by volume). SEM images have shown that oxidative treatment could remove the impurities in MWCNTs. Moreover, hydroxyl groups and carboxyl groups have also been identified on the surface of MWCNTs applying FT-IR and Raman spectroscopy. The results indicated that an effective route has been developed to disperse P-MWCNTs in methanol using the fullerenols as a surfactant. The conspicuously enhanced homogeneity and stability of dispersions can be attributed to excellent electronic absorption ability and weak acid dissociation properties of fullerenols in the solution. This approach of preparing dispersions of MWCNTs is promising to be used in the area of nanodevices and polymer/CNTs nanocomposites fabrication.

Competing Interests

The authors declare that they have no competing interests.
Figure 6: (a) SEM image of dispersion 1-1; (b) FESEM image of dispersion 1-2; (c) FESEM image of dispersion 1-3; (d) a further magnified SEM image from the area marked in image (b); (e) AFM image of dispersion 1-2; (f) cross sections along the solid lines in the image (e).
Figure 7: SEM images of dispersion 1-2: (a) acidity (pH = 5); (b) alkalinity (pH = 9).

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