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Debundling of Single Walled Carbon Nanotubes by HPC in 1-propanol and Water

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Abstract. A novel surfactant, hydroxypropyl cellulose (HPC), was firstly used to debundle Meijo single walled carbon nanotubes (SWNTs) in distilled water and 1-propanol. As comparison, common surfactants (SDBS and Triton) were used to disperse Meijo SWNTs in 1-propanol and distilled water. And the dispersibility of mixed surfactants, HPC/SDBS and HPC/Triton, were also tested. After short ultrasonication and centrifugation, stable supernatant of HPC-SWNTs has been obtained, and HPC show the best dispersibility to Meijo SWNTs. The HPC-SWNTs solution was used to prepare transparent conductive films on PET substrate by spray coating method. After being soaked in 1-propanol and HNO_3, the sheet resistance decreased from 8,440 Ω/ϒ to 4,175Ω/ϒ at 90% transmittance. TEM, UV-Vis-NIR spectra, and Raman spectra were performed to characterize the SWNT solutions and films.

Introduction

A great deal of attention has been attracted by single walled carbon nanotubes (SWNTs) since it was found in 1993, which have excellent properties and potential applications.[1-3] As we know, the amazing properties of SWNTs is original from its perfect 1D tube and C-C surface structure. However, the lack of solubility and the difficulty in manipulation of SWNTs in any solvents have also imposed great limitations to their application. To solve these issues, a variety of covalent and non-covalent functionalization methods have been developed to achieve effective debundling and dispersion, such as HNO_3 refluxing, strong power and long time ultrasonication, and using surfactants.[4,5] Although covalent methods can debundle SWNTs, they were found to destroy the surface structure and deteriorate the intrinsic properties of carbon nanotubes seriously. The more perfect structure SWNTs kept, and the better their properties are. So the choice of suitable surfactants and solvents is very important for debundling SWNTs to improve its application. HPC is a derivative of cellulose with both water solubility and organic solubility, which is used as a topical ophthalmic protectant and lubricant. For its formula structure and high molecular weight, it was used to disperse Meijo SWNTs as a novel surfactant.

Flexible highly-conducting electric devices, such as touch screens, solar cells and displays, have been increasingly developed. Carbon nanotube transparent conductive films have been broadly investigated as an alternative to commonly used conductive oxides, such as ITO.[6-8] Various methods, such as spraying coating vacuum filtration, bar coating, and spin coating have been reported to prepare transparent conductive SWNT films. In our work, HPC-SWNT solution was used to prepare transparent conductive films by spray coating and HNO_3 soaking had been applied to decompose the residual surfactants.

Materials and methods

The Meijo SWNTs used in this study were synthesized by FH-arc discharge method at Meijo University. According to the provider, the contents of carbon was about 90 wt%. All solvents were of reagent grade and were used without further purification. Hydroxypropyl cellulose (HPC), Sodium dodecyl benzene sulfonate (SDBS), and Triton X-100 surfactants were purchased from Sigma-Aldrich Corporation.

1 mg/mL HPC, SDBS, Triton X-100, SDBS/HPC, and Triton/HPC surfactants solutions were dissolved in 1-propanol. The molar ratios of the two surfactants in the mixed surfactant solutions were controlled at 1:1. 5 mg Meijo SWNTs were added into 50 mL surfactant solutions and ultrasonicated in a water bath for 2 h. Then the SWNT-solutions were centrifuged at 30,000 rpm for 15 min and the supernatants were carefully collected. Five SWNT-surfactant supernatant solution had been obtained. 3 mL supernatant solution was use to prepare films on PET substrate by spray coating. And then the films were soaked in HNO_3 solution to remove residual surfactant. Distilled water is used to replace 1-propanol to do the same procedure.
The UV-Vis–NIR absorption spectra of the SWNT dispersions were recorded on a Perkin Elmer spectrophotometer. Transmission electron microscope (TEM) was employed to study the dispersion of SWNTs on a JEM 2100F JEOL with an accelerating voltage of 200 kV. Raman spectra were obtained using a Renishaw MicroRaman with an excitation wavelength of 632.8 nm. Measurements of the sheet resistances were carried out with a four-point probe resistivity meter on a Loresta EP MCP-T360.

Results and Discussions

Fig. 1 shows the photographs of (a) SWNT-1-propanol suspensions and (b) SWNT-distilled water suspensions, after standing for two weeks. Comparing the two series of solutions, SWNT-1-propanol solutions are more stable than the SWNT-distilled water solutions. HPC can disperse Meijo SWNTs in both 1-propanol and water, however, Triton X-100 can not disperse Meijo SWNTs well in these two solvents. SDBS show better dispersibility in 1-propanol than in water. The mixed surfactant, SDBS/HPC and Triton X-100/HPC, also show the good dispersibility to Meijo SWNTs in 1-propanol.

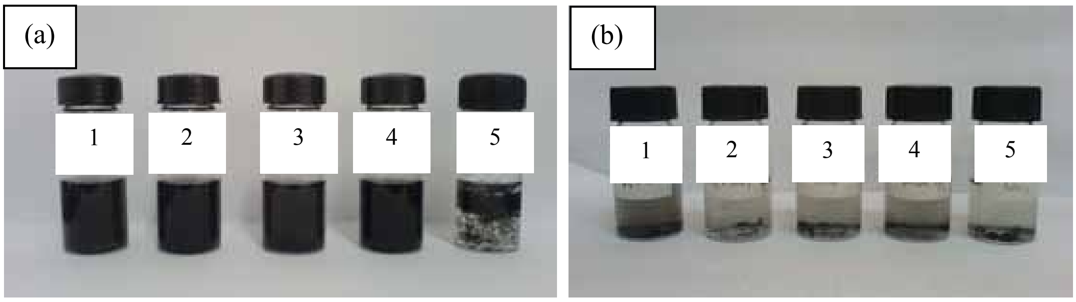

Fig. 1 Photographs of (a) SWNT-1-propanol suspensions; (b) SWNT-distilled water suspensions. The surfactants of Sample 1-5 are HPC, SDBS/HPC, SDBS, Triton/HPC, and Triton, respectively.

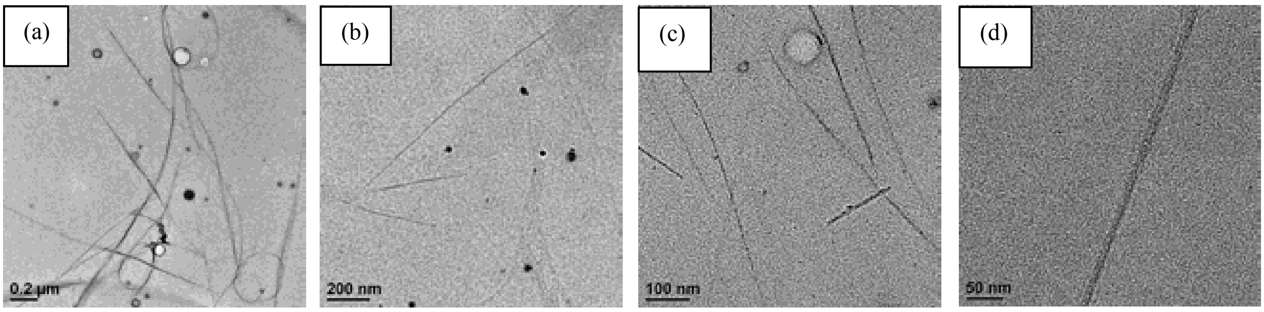

Fig. 2 TEM image (a) and (b) of SWNTs dispersed by SDBS/HPC and Triton/HPC in 1-propanol; (c) and HRTEM image (d) of SWNTs dispersed by HPC in 1-propanol.

To show the structures of SWNTs, TEM is applied here. The Meijo SWNTs were dispersed by SDBS/HPC and Triton/HPC in 1-propanol, whose bundle size was not uniform and ranged from 20 nm to 50 nm, as seen in Fig. 2 (a) and (b). And Fig. 2 (c) and (d) reveals the TEM and HRTEM images of HPC-SWNT solution. In contrast to the other two samples, HPC can disperse SWNTs uniformly and the bundle size was about 10 nm composed of eight SWNT ropes. The application of HPC surfactant can disperse Meijo SWNTs stably and uniformly. For all the samples, there are some shorter SWNT tubes in the TEM images, indicating that partly fragmentation of SWNTs might have occurred during the ultrasonication.

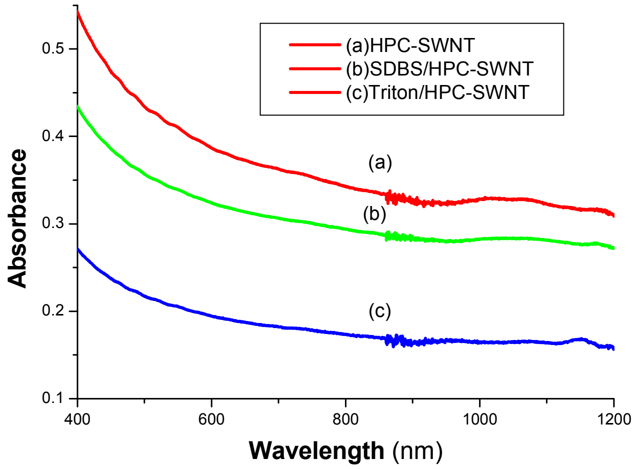

Fig 3. UV-Vis-NIR spectra of (a) HPC-SWNT, (b) SDBS/HPC-SWNT, and (c) Triton/HPC-SWNT.

Fig. 3 shows solution-phase UV-Vis-NIR spectra of HPC-SWNT, SDBS/HPC-SWNT, and Triton/HPC-SWNT after centrifugation, which were dispersed in 1-propanol. The absorbance of 550 nm is always used to calculate the relative concentration of SWNTs. As seen in Fig. 3, the curve (a) shows the concentration of HPC-SWNT, which is the highest in the three samples. This suggests Meijo SWNTs can not only be dispersed well by HPC, but also can obtain a higher concentration with comparison of the other two surfactants.

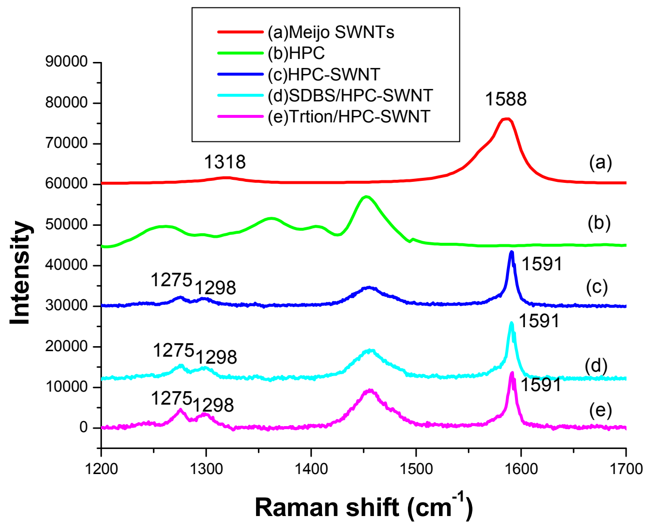

Fig 4. Raman spectra of (a) pristine Meijo SWNTs, (b) HPC, (c) HPC-SWNT, (d) SDBS/HPC-SWNT, and (e) Triton/HPC-SWNT.

To investigate the physical structure and the interaction between the SWNTs and the solubilizers, Raman spectroscopy is used to characterize the SWNTs. Fig. 4 shows Raman curves of Meijo SWNTs, HPC, HPC-SWNT, SDBS/HPC-SWNT, and Triton/HPC-SWNT. The D-band of 1318 cm^{-1} is always used to characterize the SWNT sidewall damage caused by functionalization. The D/G ratio of pristine Meijo SWNTs is about 0.1. After ultrasonication and centrifugation, the D-band of SWNT downshifts from 1318 cm^{-1} to 1298 cm^{-1}, which indicates that the HPC can functionalize on the surface of SWNTs. The D/G ratio of HPC-SWNT sample is lower than the other two samples, which suggests that the HPC caused the fewest damages the SWNTs under the same experimental condition.

The HPC-SWNT solution were used to prepare transparent conductive films on the flexible PET substrate. When the transmittance is about 90%, the sheet resistance is 8,440 Ω/ϒ. And then, after soaking in the 1-propanol and HNO_3, respectively, the sheet resistance decreased to 4,175 Ω/ϒ and the transmittance is almost no change. It indicates that soaking in the 1-propanol and HNO_3 can remove residual HPC successfully.

Summary

In summary, a novel dispersant of HPC is used to disperse the SWNTs in 1-propanol. Compared with TEM, UV-Vis-NIR spectra and Raman spectra, HPC exhibits better dispersibility than SDBS, Triton X-100 and mixed surfactants under this experimental condition. Meijo SWNTs can be dispersed uniformly by HPC in 1-propanol with the bundle size of 10 nm and the final supernatant solution of Meijo SWNTs can be stable for over three months. The HPC-SWNT supernatant solution is also used to prepare transparent conductive film by spray coating on flexible PET substrate. After post-treatment, the residual surfactant can be decomposed and the sheet resistance decreased from 8,440 Ω/ϒ to 4,175 Ω/ϒ when the transmittance is 90%.

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