

Dispersion of modified carbon nanotubes in 1-butyl-3-methyl imidazolium tetrafluoroborate

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Carbon nanotubes (CNTs) have been promising materials owing to their unique structures and properties since their discovery by Iijima in 1991 [1]. Various applications based on this novel material have been studied from both the fundamental and practical views [2, 3], such as fuel storage [4, 5], polymer reinforcement [6, 7], nanoelectronic devices [8, 9], and field electron emitters [10, 11]. However, carbon nanotubes tend to aggregate into packed ropes or entangled networks. Thus, the dispersion and dissolution of CNTs is recognized to be an important step in many of the applications that are contemplated for this unique material.

Basically, one strategy to improve the dispersion of CNTs in solvents is to use a surface-active reagent [12, 13]. This procedure is easy to be realized, however, the surface-active reagent is introduced to make the solution or dispersion difficult for further investigations and applications. The other is to modify CNTs chemically [14, 15], which bonds polymeric or long chain organic molecules on their surface. It is effective to get stable solution. Both of the above two approaches are well investigated to disperse CNTs in conventional organic solvents, such as ethanol, chloroform, tetrahydrofuran, which are usually volatile and harmful to the environment. In this paper,

we report an approach to disperse the CNTs in ionic liquids, (e.g. 1-butyl-3-methylimidazolium tetrafluoroborate), a novel class of green solvents [16]. It has been shown effective in obtaining dispersion. The new dispersion system has incredible significances in material, electrochemistry and so on [17–19].

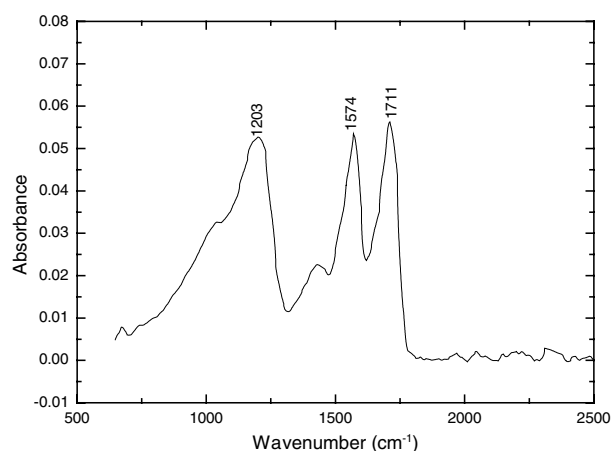


Figure 1 FTIR spectrum of modified MWNTs. The peak at 1711 cm^{-1} is the C=O stretch of the carboxylic groups ($-\text{COOH}$), and the peaks at 1574 and 1203 cm^{-1} are the C=C and the C–C stretch of the modified MWNTs.

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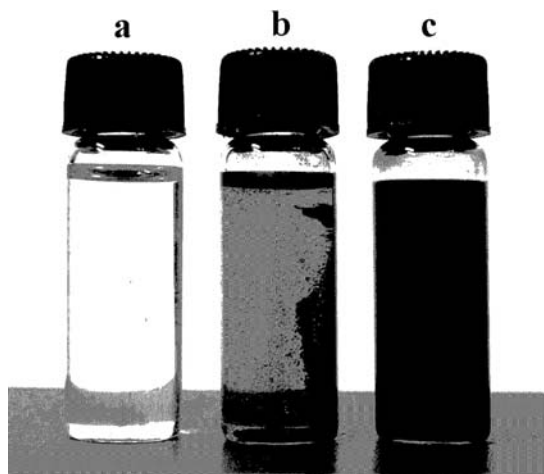


Figure 2 (a) The pure [bmim]BF₄. (b) The suspension of pristine MWNTs in [bmim]BF₄ after centrifuged at 2000 rpm for 30 min. (c) The suspension of modified MWNTs in [bmim]BF₄ after centrifuged at 2000 rpm for 30 min.

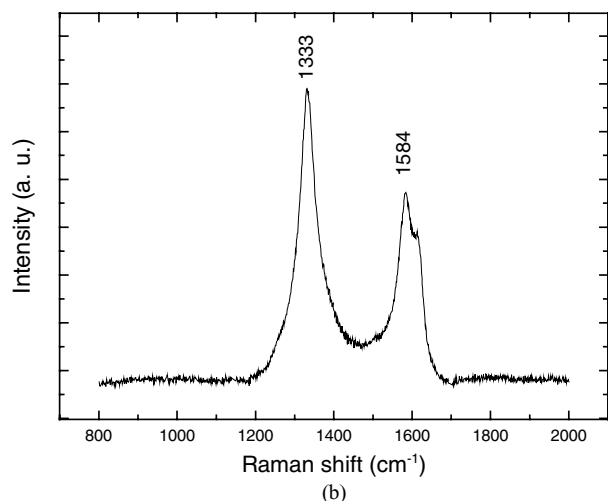
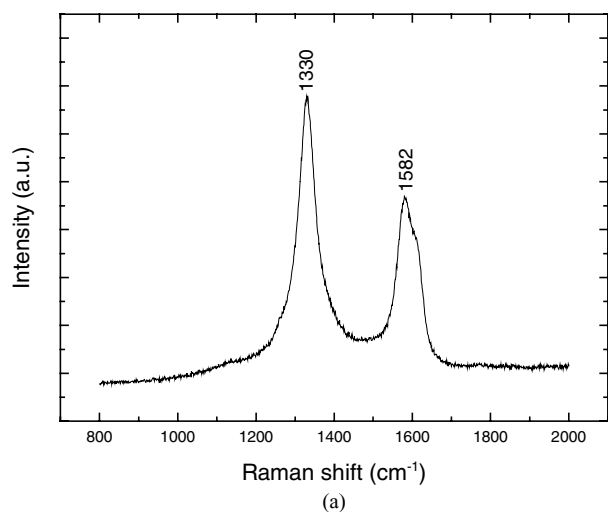


Figure 3 (a) Raman spectrum of the modified MWNTs upon excitation at 633 nm. (b) Raman spectrum of the modified MWNTs gel upon excitation at 633 nm.

Multi-walled carbon nanotubes (MWNTs) produced via the chemical vapor deposition method were bought from Sun Nanotech Co. Ltd. (Nanchang, China). The pristine MWNTs were purified and converted to acid-modified MWNTs via sonication in nitric-sulfuric acid (1/3, v/v) at ca. 50 °C according to Shi *et al.* [20]. The modified MWNTs were terminated with carboxylic groups (–COOH) on the surface, which can be identified clearly in FTIR (Fig. 1).

The modified MWNTs were added into 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) and the dispersion system of concentration (1 mg/g) was made. Black homogeneous ink-like suspension was formed after dispersing for half an hour in an ultrasonic bath. Then the ink-like sample centrifuged at 2000 rpm for 30 min, the suspension was found to be still ink-like and a small portion of precipitate to be centrifuged out. However the suspension of pristine MWNTs was separated clearly at the same conditions. Photographic images are shown in Fig. 2, it can be seen that the modified MWNTs are more stable in [bmim]BF₄.

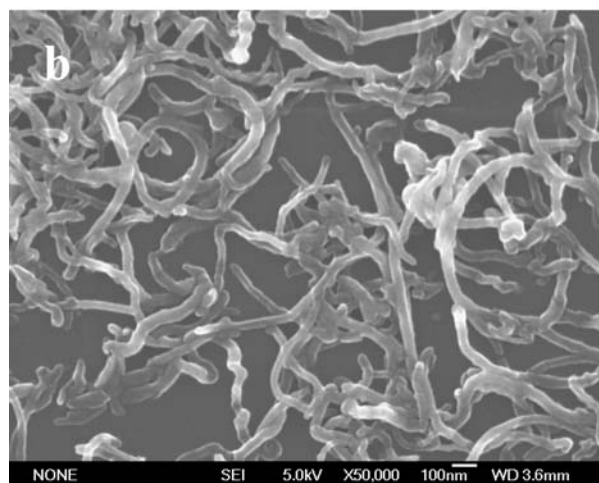
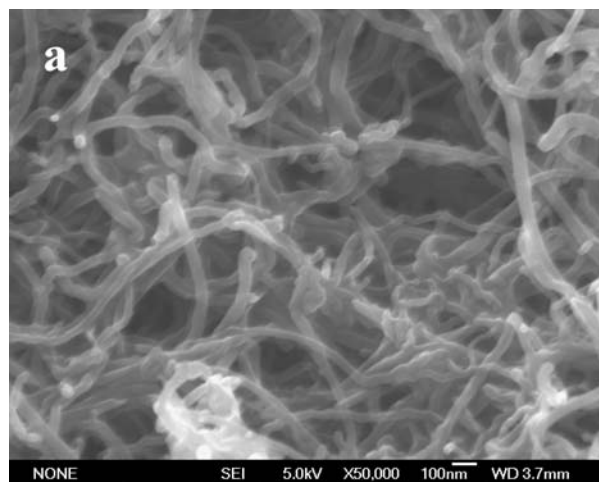


Figure 4 (a) SEM image obtained by dispersing the pristine MWNTs gel of [bmim]BF₄ in ethanol. (b) SEM image obtained by dispersing the modified MWNTs gel of [bmim]BF₄ in ethanol.

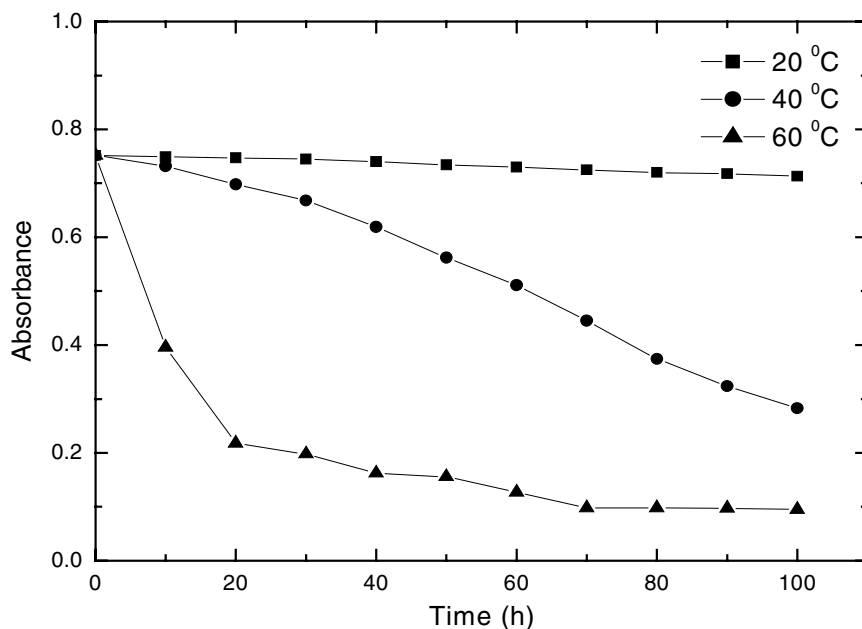


Figure 5 Absorbance of UV-vis changing with time.

For the centrifuged suspension, the featureless UV-vis absorption spectrum can be obtained. Absorbance of UV-vis increases with the concentration of modified MWNTs and the standard curve of absorbance-concentration at certain wavelength follows the Lambert-Beer's law well [15, 21]. For a thick suspension, it may be diluted to a proper concentration in which the absorbance at the wavelength can match the standard curve. So concentration of the modified MWNTs in [bmim]BF₄ is calculated. Because the dispersion system is not a real solution, there isn't a solubility for the modified MWNTs in [bmim]BF₄.

After the sample was further centrifuged at 4000 rpm for 2 h, the suspension of modified MWNTs was separated to produce two phases, colorless liquid phase and the modified MWNTs gel phase. The gel phase was estimated to entrap up to 0.843×10^{20} [bmim]BF₄ molecules per mg modified MWNTs [3.2 wt % (wt %)] [17]. By comparing Raman spectra of the modified MWNTs (Fig. 3a) with the modified MWNTs gel (Fig. 3b), it was found that the G lines and D lines [15], typical of MWNTs, shifted only 2 cm^{-1} , 3 cm^{-1} respectively, which indicates that the gelation doesn't denature the modified MWNTs chemically. At the same time, it was proved that the modified MWNTs (Fig. 4b) are dispersed better than the pristine MWNTs (Fig. 4a) by analyzing the MWNTs gels with Scanning Electron Microscopy (SEM) at the same conditions.

To analyze the thermal stability, a certain concentration of suspension of the modified MWNTs in [bmim]BF₄ was ultrasonicated for half an hour and divided into three quartz containers. The three quartz containers were placed at 20 °C, 40 °C and 60 °C respectively. The absorbance of UV-vis at the corresponding temperature without stirring during the period of testing is shown in Fig. 5. It can be found that the absorbance decreased sharply and

the suspension aggregated into big granules quickly at 60 °C; the absorbance decreased steadily and the suspension aggregated into small granules slowly at 40 °C; the absorbance kept almost constant and the suspension remained almost unchanged at 20 °C. Therefore, increasing temperature agitates the modified MWNTs and provides more chances for the modified MWNTs to collide with each other and aggregate from small to big granules, thus the stability of the dispersion system was destroyed.

In summary, it has been showed a good way to disperse MWNTs in the ionic liquid. In the dispersing process, the MWNTs are not denatured in chemistry, and the dispersion system is sensitive to temperature.

Acknowledgments

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