Transition of Ionic Liquid [bmim][PF_6] from Iiquid to High-Melting- Point Crystal When Confined in Multi-Walled Carbon Nanotubes

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Supporting Information

Experimental details

Commercially available MWNTs (purity >95%, length >5 μm, the average internal and external diameters are about 5-10 nm and 40-60 nm, respectively. CVD method, Shenzhen Nanotech Port Co., Ltd, China) were purified and opened via sonication in a mixture of concentrated sulfuric and nitric acids (3:1, 98% and 70%, respectively) at 50 °C.[1] The resultant solid was washed thoroughly with deionized water until the pH was 7.0, and tip opened short nanotubes in length between 400 to 600 nm were obtained. The [bmim][PF_6] was prepared by the method described previously.[2, 3] According to the methods reported by Sloan *et al*.[2, 3] for improving the filling yield of SWNTs incorporating species, herein, an optimum procedure including annealing opened carbon nanotubes and incubating at 90 °C under vacuum was employed. In a typical filling experiment, 186.5 mg opened MWNTs was put into a two necked flask (one of the necks was sealed by a rubber stopper and the other was

connected with a high-vacuum line). The flask was broiled by gas burner for 4 hrs under vacuum to draw out the gas inside MWNTs. Then 20 mL [bmim][PF_6] was transferred into the flask through a syringe and the mixture was ultrasonically vibrated for 3 hrs at 90 °C, to fill the opened MWNTs with the ionic liquid. The resultant mixture was cooled for 3 h to room temperature. The filled samples were separated from the mixture by centrifugation and purified by six cycles of washing with methanol and filtration to completely remove the absorbed [bmim][PF_6] from the nanotube surface.[4] The final product (named as IL@MWNTs for simplicity) was obtained by overnight drying under high vacuum. To further investigate the filling behavior of [Bmim][PF_6] in the interior channel of MWNTs, the mixed solution with methanol (v/v=1:1) was introduced into the cavities of MWNTs in a similar manner and the final product was named as IL/MeOH@MWNTs.

Characterizations

The X-ray diffraction (XRD) measurements were carried out on an X'Pert Pro diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. High resolution transmission electron microscopy (HRTEM) images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. The samples for TEM observation were prepared by dispersing the filled nanotubes in ethanol and drying a few drops on a carbon-coated copper grid, then allowing them to dry in a desiccator. Melting points of the encapsulated [bmim][PF_6] were determined by differential scanning calorimetry (DSC-822e, Mettler-Toledo Corp.). The sample was scanned from 223 K to 573 K at a programmed heating rate of 10 °C /min, using indium to calibrate the temperature and heat flow of the DSC device.

XRD Patterns

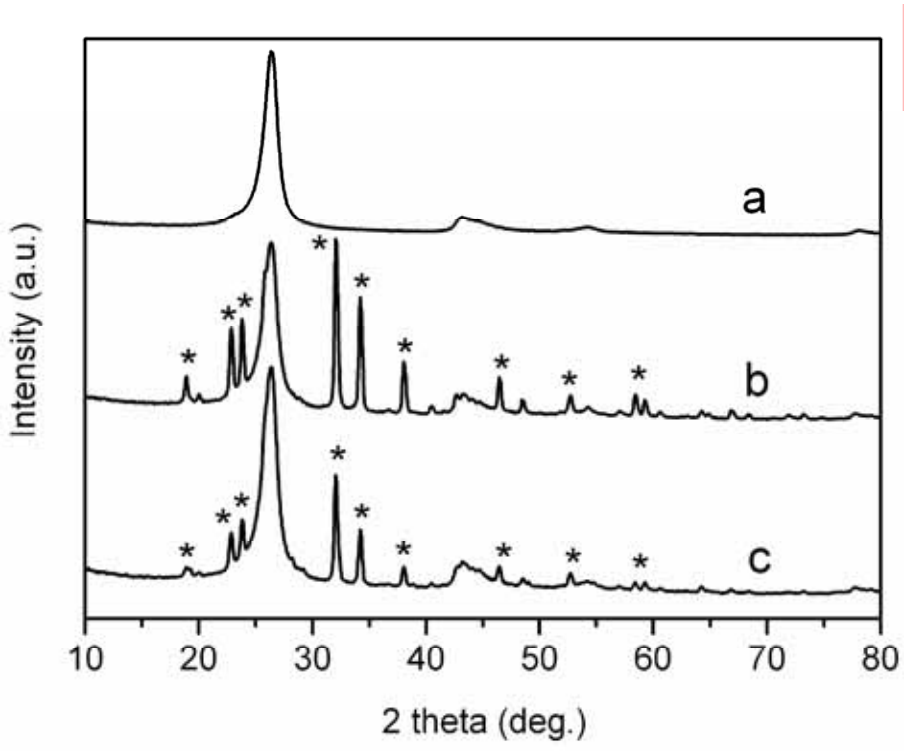

Figure S-1. X-ray diffraction patterns of opened MWNTs (a), IL@MWNTs (b), and IL/MeOH@MWNTs (c). (* indicates the peaks of [bmim][PF_6] crystals encapsulated in MWNTs)

Figure S-1 shows the XRD patterns of the opened MWNTs and the filling products. Compared with the opened MWNTs, many new peaks appear in the IL@MWNTs and IL/MeOH@MWNTs samples (marked by asterisk). The diffraction peaks appearing at 2θ=18.9°, 22.9°, 23.8°, 32.1°34.2°, 38.1°, 46.5°, 52.7°, and 58.4°should correspond to different crystal planes of [bmim][PF_6] inside MWNTs. However, the peaks calculated from the CIF file of the low-temperature crystal structure of [bmim][PF_6] reported by Choudhury, et al.[5] are at 2theta = 10.41, 11.08, 11.64, 11.82, 13.11, 15.11, 16.42, 16.85, 17.82, 19.05, 19.46, 19.80, 20.78, 20.91, 21.15, 21.69, 22.26, 22.6, 23.18, 23.4, 23.84, 24.94, 25.24, 25.86, 26.2, 30.92, 36.1. It is indicated that a different solid phase was formed inside MWNTs in this study.

References

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(4) To check the efficiency of this purification method, 102 mg pristine MWNTs (length >5 μm, the tips are closed) was mixed with 20 mL [bmim][PF_6], then MWNTs were separated from the mixture by centrifugation and purified by six cycles of washing with methanol. Thermal gravity analysis of the as-obtained MWNTs showed no weight loss (Perkin-Elmer Pyris-1 series thermal analysis system, under a flowing nitrogen atmosphere at a scan rate of 10 °C/min from 50 to 800 °C). FT-IR measurement (Nicolet Avater-360) showed no existence of [bmim][PF_6] in the purified sample, indicating the centrifugation method can remove the absorbed [bmim][PF_6] completely.

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