Electrolyte Switchable Solubility of Multi-Walled Carbon Nanotube/Ionic Liquid (MWCNT/IL) Hybrids

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Experimental Section Materials

MWCNTs prepared by the catalytic decomposition of CH_4 ^[1] were purchased from Shenzhen Nanoport Company, China. (CF₃SO₂)₂NLi was obtained from Aldrich and used as received.1-hydroxyethyl-3-hexyl imidazolium chloride (HEHImCl) was synthesized in our labratory^[2]. Other reagents were of analytical grades and used as received. All aqueous solutions were prepared with the deionized water with a Millipore-Q system (18.2 M Ω).

Instruments

The X-ray photoelectron spectroscopy (XPS) analysis was obtained on a PHI-5702 multifunctional XPS, using Al K α radiation as the exciting source. The binding energies of the target elements were determined at a pass energy of 29.35 eV, with a resolution of ± 0.3 eV, using the binding energy of the gold (Au4f: 84.0 eV) as the reference. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker IFS 66v/S FTIR spectrometer (4 cm⁻¹). Thermogravimetric analysis (TGA) was conducted out on a ZRY-2P TGA at a heating rate of 10 ° C min⁻¹ in flowing air. Transmission electron microscopy (TEM) was carried out on a JEOL model JEM-2010Ex/S electron microscope.

Preparation of MWCNT-ImCl and other MWCNT samples

A 100 mL flask charged with 2.0 g crude MWCNTs and 50 mL of 60% HNO3 aqueous solution was sonicated in a bath (40 KHz) for 30 min. The mixture was then stirred for 24h under reflux. After cooling to room temperature, it was diluted with 200 mL of deionized water and then centrifuged under 10000 rpm. The solid was washed with deionized water until the pH of the suspension reached 6. The solid was then dried under vacuum for 12 h at 60 °C to give 1.28 g of carboxylic acid-functionalized MWCNT (MWCNT-COOH).^[3] Dried MWCNT-COOH (1.1 g) was treated in an ultrosonator in dry THF for 2 h to give a homogeneous suspension, and refluxed in neat SOCl₂ at 65 °C for 24 h under N₂. The solid was then separated by centrifugation and washed with anhydrous THF. Subsequently, it was dried under vacuum at 40 °C to give 0.87 g carbonyl chloride group-functionalized MWCNT (MWCNT-COCI). Then, a small amount of MWCNT-COCl dispersed in dry THF was added to 1-hydroxyethyl-3-hexyl imidazolium chloride (HEHImCl), and stirred at room temperature for 2 h. The solid was washed with anhydrous THF, ethanol and deionized water and separated by centrifugation. The black solid was collected and dried under vacuum overnight. MWCNT-ImCl was dissolved in deionized water. The solutions of aqueous NaBF₄, NH₄PF₆, NaClO₄ and (CF₃SO₂)₂NLi were added drop-wise into the aqueous MWNT-ImCl under vigorous stirring for 12 h at room temperature. Then the product will be dissolved in CH₂Cl₂. After centrifugation and washing with THF, the precipitates were vacuum-dried overnight.



Fig S1 FTIR spectra of MWNTs and MWNTs modified with different ILs. MWNT-ImBF₄ exhibits a band at 1060 cm⁻¹ which attributed to B-F stretching vibration. The characteristic band at 840 cm⁻¹ was assigned to the P-F stretching vibration in the sample MWCNT-ImPF₆. The peak at about 1086 cm⁻¹ was assigned to the Cl-O stretching vibration in MWNT-ImClO₄.



Fig S2 TGA trace of the MWNT-COOH, MWNT-ImCl, MWNT-ImPF₆ and HEImPF₆ It is seen that the onset temperature with apparent weight loss occurs above 600 $^{\circ}$ C in the presence of air. The onset temperature is intermediate for ionic liquid modified MWCNT, lying between those of the neat ILs and the activated MWCNT sample.



Fig S3 MWCNT-COOH (left), and MWCNT-ImPF₆ (right) dissolved in IL of 1-methyl-3-hexylimidazolium hexafluorophosphate.

MWNT-COOH and MWNT-ImPF₆ dispersed in ionic liquid for 3 h with the assistance of ultrasonication. It is seen that MWNT-ImPF6 can form stable suspension in ionic liquid, whereas MWCNT-COOH precipitate after while.

References

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