The electrolyte switchable solubility of multi-walled carbon nanotube/ ionic liquid (MWCNT/IL) hybrids†

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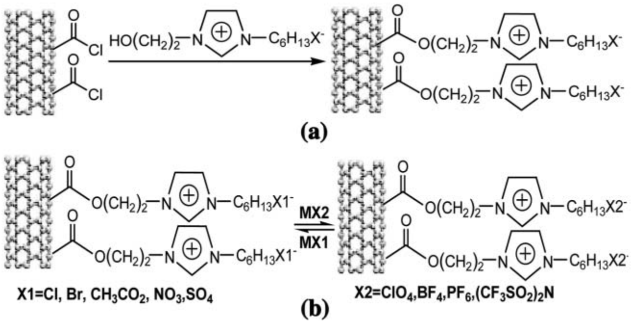
In this communication we report the first preparation of ionic liquid-modified carbon nanotubes with reversibly switchable solubility between aqueous and organic solvents, induced by anion exchange.

Since their discovery, carbon nanotubes (CNTs) have attracted tremendous research interest due to their potential applications in nanotechnology and materials science.[1] Chemical modification can not only add new functionality to CNTs, but also change their solubility,[2] of crucial importance in terms of purification and processibility.[3] Modifiers reported include small molecules,[2] biomolecules,[4] and polymer brushes.[5] CNTs can be made to be hydrophobic (organic-soluble) or water-soluble by specific modifications using respective types of molecules. Reversible solubility is especially intriguing, and can be realized by modification with responsive molecules that experience reversible soluble/insoluble transitions in response to environmental triggers.[4a] Room temperature ionic liquids (ILs) have controlled miscibility with other chemicals and are widely used as excellent green reaction media.[6] Modification of CNTs with ILs is expected to improve their compatibility and stability, creating more opportunity for applications of CNTs in sensors and actuators by improving the electrical contact with bulky media.[7] More interestingly, CNTs modified with ILs can be made reversibly water-soluble or non-water-soluble by switching electrolyte solutions. To our knowledge, this is the first report on the electrolyte-switchable solubility of modified CNTs.



Scheme 1 (a) Schematic depiction of the modification of MWCNTs with hydroxyl-functionalized ionic liquids. X = Cl, Br, NO_3, SO_4, CH_3CO_2, BF_4, PF_6, ClO_4 and $(CF_3SO_2)_2N$. (b) Anionic exchange that induces reversible solubility in aqueous and organic solvents.

The modification of multi-walled carbon nanotubes (MWCNTs) followed a standard method (Scheme 1).[2] Briefly, MWCNTs were activated in a nitric acid solution to give carboxyl group-functionalized MWCNTs (MWCNT-COOH), followed by reaction with thionyl chloride and 1-hydroxyethyl-3-hexyl imidazolium chloride (HEHImCl) in dry THF, resulting in IL-functionalized MWCNTs in their ammonium form (MWCNT-ImCl). Transformation to other IL forms was realized *via* anion exchange of the Cl^- counter-anions with an excess of other target anions such as Br^-, $CH_3CO_2^-$, NO_3^-, SO_4^{2-}, BF_4^-, PF_6^-, ClO_4^- and $(CF_3SO_2)_2N^-$ (Tf_2N). Experimental details are given in the supporting information.† To confirm the successful covalent attachment of IL molecules onto the MWCNTs, X-ray photoelectron spectroscopy (XPS) (Fig. 1) was used to analyze the presence of anions associated with the imidazole ring for the functionalized samples. In all spectra, the N-signal, centered around 402 eV, reveals the successful covalent attachment of ILs onto the MWCNTs. F1s at 685.2 eV and 687.1 eV, and 132.2 eV and 198.9 eV, corresponding to P2p and B1s for MWCNT-ImPF_6 and MWCNT-ImBF_4, respectively, and 198.7 eV and 207.3 eV for Cl2p in MWCNT-ImCl and MWCNT-ImClO_4, respectively, further verify the loading of other anions through corresponding anionic exchanges. FTIR was also used to follow reaction procedures. Figure S1 (ESI†) shows several samples modified with different ILs, coupled with different anions. The absorption band at 1708 cm^{-1}, attributed to the C=O stretching vibration in MWCNT-COOH, shifted to about 1725 cm^{-1} after esterification with HEHImCl. After anion exchange, absorbance peaks corresponding to the respective anions were observed. For example, the characteristic band at 840 cm^{-1} is assigned to the P–F stretching vibration in the sample MWCNT-ImPF_6, verifying the successful exchange of the desired anions. A TEM image of MWCNT-ImPF_6 is shown in Fig. 2, illustrating the integrity of the CNTs after chemical modification.

The ILs attached to CNTs were further evaluated by TGA. Figure S2 (ESI†) shows the TGA traces of MWCNT-COOH, MWCNT-ImCl, MWCNT-ImPF_6 and HEImPF_6. MWCNT-COOH decomposed at around 600 °C in air. After modification with ImCl, a first weight loss step at 210 °C was observed, intermediate between those of the neat ILs and the activated MWCNT sample, followed by a second step associated with the

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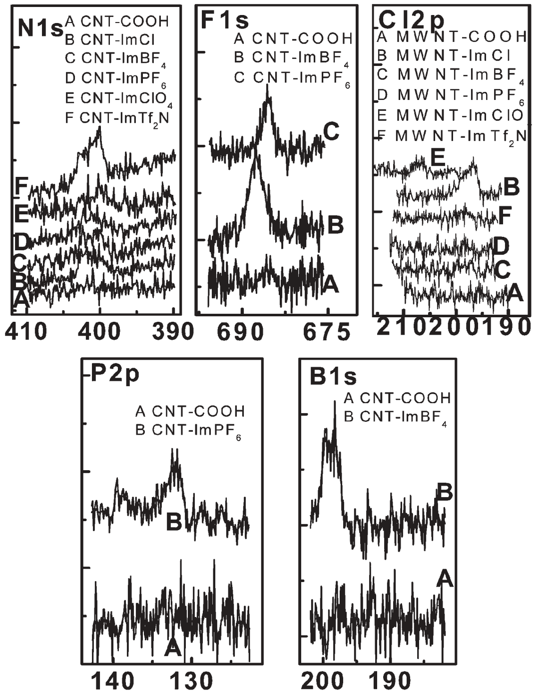

Fig. 1 XPS spectra of (a) N1s, (b) F1s, (c) Cl2p, (d) P2p and (e) B1s of MWCNTs modified with ILs in different forms.

decomposition of the CNTs. The weight loss of MWCNT-ImPF$_6$ is slight bigger than that of MWCNT-ImCl.

Modification by ILs greatly changes the solubility of the MWCNTs in different solvents. Fig. 3 shows photographs of (a) MWCNT-COOH, (b) MWCNT-ImCl, (d) MWCNT-ImBF$_4$, (e) MWCNT-ImPF$_6$, (f) MWCNT-ImClO$_4$ and (g) MWCNT-ImTf$_2$N dispersed in (c) a two-phase mixture of H_2O and CH_2Cl_2. MWCNT-COOH is water-soluble, although the MWCNT-COOH/water dispersion is quite unstable. Modification by ILs in their ammonium form (MWCNTs-ImCl) retains its water solubility. The same situation was found for MWCNT-ImAc, MWCNT-ImNO$_3$ and MWCNT-Im(SO$_4$)$_x$ (x = ½), which also exhibit good solubility in aqueous solution (data not shown). In contrast, MWCNTs substituted with other lipophilic anions

Fig. 2 TEM of MWCNT-ImPF$_6$.

BF_4^-, PF_6^-, ClO_4^- and $(CF_3SO_2)_2N^-$ are non-water-soluble but dissolve in CH_2Cl_2 easily. This indicates that the solubility of modified CNTs can be altered by anion exchange with the relatively hydrophobic anions BF_4^-, PF_6^-, ClO_4^- and $(CF_3SO_2)_2N^-$. These results corroborate earlier experiments on anion exchange with ionic liquid-terminated self-assembled monolayers.[8] We should point out that solubility will also relate to the length of alkyl chains in the ILs, but since they are present in every case (C2 and C6 for 1- and 3-N positions, respectively), we attribute the solubility in organic solvents primarily to the counter-anions.

Of great interest is the reversibly-altered solubility from organic-soluble back to water-soluble, when hydrophobic anion-coupled CNTs were treated again with concentrated hydrophilic anion solutions. From Fig. 3h–k it can be seen that the MWCNT-ImPF$_6$ switched from being hydrophobic to being hydrophilic after a stable dispersion of MWCNT-ImPF$_6$ in CH_2Cl_2 was mixed with an aqueous solution of NaCl, NaNO$_3$, NaAc or Na_2SO_4 (1.0 M). We did not check the threshold concentration needed for anionic exchange. Generally, for the hydrophilic to hydrophobic transition, a low salt concentration (1 mM) was sufficient, while the switch from hydrophobic to hydrophilic required a high salt concentration. This is apparently due to the different association

Fig. 3 Photographs of a series of MWCNT samples dispersed in H_2O (upper phase) and CH_2Cl_2 (lower phase) (0.2 mg mL^{-1}; note: this is not the saturated concentration) (a) MWCNT-COOH, (b) MWCNT-ImCl, (c) blank water/CH_2Cl_2, (d) MWCNT-ImBF$_4$, (e) MWCNT-ImPF$_6$, (f) MWCNT-ImClO$_4$, (g) MWCNT-ImTf$_2$N. MWCNT-ImPF$_6$ after anionic exchange with (h) NaCl, (i) NaNO$_3$, (j) NaAc and (k) Na_2SO_4 becomes hydrophilic and soluble in aqueous solution.

constants between the anions and imidazole cations in the ILs. The association constants and hydrophobicities of BF_4^-, ClO_4^-, PF_6^- and Tf_2N^- are generally larger than hydrophilic Cl^-, NO_3^-, Ac^- and SO_4^{2-}. Modification of MWCNTs by ILs can also improve the solubility of MWCNTs in ILs, especially in structurally similar ILs. Stable dispersions were obtained by adding IL-functionalized CNTs into the ILs (Figure S3, ESI†).

The anions in MWCNT-ImCl (MWCNT-ImBr, MWCNT-$ImNO_3$, MWCNT-$ImSO_4$, MWCNT-ImAc, *etc.*) are fully dissociated in water because of their hydration. Stable dispersions in water come from charge repulsion of the cationic imidazole rings that counterbalances the van der Waals interactions between CNTs.[9] In contrast, the dissociation of hydrophobic anions (BF_4^-, ClO_4^-, PF_6^- and Tf_2N^-) from imidazole rings is unfavorable because of poor solvation of the anions in water.[10]

In conclusion, we have demonstrated that IL-decorated CNTs exhibit a solubility dependence on the anions coupled with cationic imidazole rings. This represents a simple and convenient way to alter the solubility of CNTs by simply switching salt solutions under neutral conditions, which may prove useful in MWCNT purification and processibility. Due to the diverse structures and flexibility in molecular design of ILs, modification by ILs presents a promising way to functionalize CNTs. Moreover, positively-charged CNTs are particularly important in biological and biomedical science applications because of their potentially strong interactions with negatively-charged cell membranes.[9]

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