Covalent Modification of Multiwalled Carbon Nanotubes with Imidazolium-Based Ionic Liquids: Effect of Anions on Solubility

Min Jeong Park,[†,‡] Jae Kyun Lee,[‡] Bang Sook Lee,[†,‡] Yong-Won Lee,[§]
Insung S. Choi,[*,§] and Sang-gi Lee[*,†]

Division of Nano Science, Ewha Womans University, 11-1 Daehyun-Dong, Seodaemun-Gu, Seoul, 120-750, Korea, Life Sciences Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea, and Department of Chemistry and School of Molecular Science (BK21), KAIST, Daejeon 305-701, Korea

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Multiwalled carbon nanotubes (MWCNTs) were covalently modified with imidazolium salt-based ionic liquids (ILs). Coupling of acid chloride-functionalized MWCNTs with commercially available (3-aminopropyl)imidazole, followed by the reaction with *n*-butyl bromide, afforded 1-butylimidazolium bromide salt-functionalized MWCNTs (***f*-3a**). The bromide anion of ***f*-3a** could be exchanged with BF_4^-, PF_6^-, and NTf_2^- (*N*,*N*-bis((trifluoromethyl)sulfonyl)amide) by metathesis and afforded functionalized MWCNTs, ***f*-3b** (BF_4^-), ***f*-3c** (PF_6^-), and ***f*-3d** (NTf_2^-), bearing different counteranions. Raman, IR, NMR, TGA, and XPS analyses clearly confirmed covalent functionalization and imidazolium salt formation as well as anion exchange of the IL-functionalized MWCNTs. UV−vis data imply that counteranions have an effect on the relative solubility of the IL-functionalized MWCNTs in water: the solubility of ***f*-3** in water is of the order ***f*-3a** (Br^-) > ***f*-3b** (BF_4^-) > ***f*-3c** (PF_6^-) > ***f*-3d** (NTf_2^-), and the water-soluble ***f*-3a** was phase-transferred from the aqueous phase to the chloroform phase via simple anion exchange with NTf_2^-. All of the IL-functionalized MWCNTs, including the water-soluble ***f*-3a**, exhibited a preferential solubility in an ionic liquid, [bmim][NTf_2].

Introduction

Ionic liquids (ILs), consisting of imidazolium cations and counteranions, have attracted increasing interest as an alternative to conventional organic solvents for a wide range of synthesis, catalysis, electrochemistry, and liquid−liquid extractions.[1−5] In addition, their use as a new material has recently expanded to the formation of nanometer-sized metal particles,[6,7] nanorods,[8] biomaterials,[9] CO_2 capture,[10] etc. The physicochemical properties, especially the hydrophilicity and hydrophobicity of the ILs, can easily be tuned by varying alkyl appendages of the imidazolium cation and/or counteranions, and consequently the miscibility of ILs with organic solvents and water can be varied.[11,12] Utilization of the tunable properties of the ILs in surface science or nanometer-sized materials could provide a new way to control properties of the surfaces and materials. Quite recently, Itoh et al. reported a phase-transfer of Au nanoparticles coated with thiol-functionalized ionic liquids from aqueous to organic phase through the anion exchange.[13] We also have recently demonstrated that the tunable property of the ILs could be transferred to the solid surfaces, leading to the control over the surface wettability of the gold[14,15] and Si/SiO_2 surfaces,[16] which were coated with imidazolium-terminated self-assembled monolayers.[17] On this line, we attempted a combination of the tunable ILs with carbon nanotubes (CNTs) to open a new way to the utilization of the ILs and CNTs. Herein we report covalent modification of multiwalled carbon nanotubes (MWCNTs) with imidazolium salt-based ionic liquids and the effect of anions on the solubility of the IL-functionalized MWCNTs.

During the past few years, CNTs have attracted much attention due to their unique electrical and mechanical

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[*] Corresponding authors. S.-g.L.: phone, (+82)-2-3277-4505; fax, (+82)-2-3277-3419; e-mail, sanggi@ewha.ac.kr. I.S.C.: phone, (+82)-42-869-2840; fax, (+82)-42-869-2810; e-mail, ischoi@kaist.ac.kr.
[†] Ewha Womans University.
[‡] Korea Institute of Science and Technology.
[§] KAIST.

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properties.[18,19] The chemical functionalization of CNTs is expected to play a vital role in tailoring the properties of these materials and engineering CNT-based devices. A number of research groups have focused on the chemical modification of CNTs through covalent or noncovalent functionalizations, and they have made great progress in this field.[20−25] Recently, Fukushima et al. reported that the imidazolium ion has a strong affinity toward the π-electronic surface of single-walled CNTs and mixing pristine single-walled CNTs with imidazolium cation-based ILs formed gels (Bucky Gel).[26,27] Herein we report our finding that the covalent modification of multiwalled carbon nanotubes (MWCNTs) with imidazolium salt-based ILs provided IL-soluble functionalized MWCNTs. Moreover, the solubility of the IL-functionalized CNTs in water and organic solvents could be varied by anion exchange.

Experimental Section

Materials. MWCNT (multiwalled carbon nanotubes) were provided by Iljin Nanotech Co., Ltd. (purity, >95%; length, 10−50 μm; diameter, 10−30 nm), and used without further purification. All reagents were used as received, and all solvents were distilled prior to use. Ionic liquids were prepared according to the reported procedures[28] and contained less than 10 ppm of chlorine in chlorine analysis at Analysis Center in Korea Institute of Science and Technology and less than 15 ppm of water in Karl Fischer analysis (Metrolm model 756KF coulometer).

Measurements. Fourier transform infrared (FT-IR) spectra were obtained with a Bruker Equinox 55 FT-IR spectrometer. The nuclear magnetic resonance (^{1}H NMR) measurements were carried out on a Brüker DPX-300 MHz spectrometer. Raman spectra were acquired using the samples in the solid state in the backscattering mode on the “microstage” of a Renishaw RM1000-Invia spectrometer. Spectra were recorded over the range of 1000−2000 cm^{-1} and an excitation wavelength of 642.8 nm (1.96 eV). The field emission-scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4200 field-emission microscope, and the samples were loaded on the glass surface previously sputter-coated with a homogeneous gold layer for charge dissipation the SEM imaging. Scanning transmission electron microscopy (TEM) analyses were conducted on a Philips CM 30 electron microscope at 200 kV, and the samples for TEM measurements were prepared by placing one drop of sample on copper grids coated with carbon. Thermogravimetric analyses (TGA) were carried out on a TGA 2050 thermogravimetric analyzer with a heating rate of 20 °C/min and air flow (20 mL/min). The X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5800 ESCA system using a monochromatized aluminum Kα anode (350 W, 25 mA). Ultraviolet−visible (UV−vis) spectra were measured on a Cary 1E UV−visible spectrophotometer. The photographs of the samples placed in solvent were taken with a digital camera (Canon, A80).

Preparation of Carboxylic Acid-Functionalized MWCNTs (*f*-1). The chemical oxidation of the pristine MWCNTs (1.0 g) was carried out by cutting them in 60% HNO_3 under the sonication (Bransonic, model 1510R-PTH, 42 kHz) for 1.5 h at 50 °C.[29,30] The black mixture was diluted with 2 L of water, centrifuged at 14 000 rpm for 1 h (Hanil Science, micro 17R+), and washed with distilled deionized water and acetone several times successively. The oxidized MWCNTs were washed with distilled water and vacuum-filtered through a 0.2-μm Millipore polycarbonate membrane until the pH of the filtrate was 7.0. The filtered solid was dried under vacuum for 24 h at 60 °C.

Preparation of 1-(3-Aminopropyl)imidazole-Functionalized MWCNTs (*f*-2). A suspension of ***f*-1** (100 mg) in $SOCl_2$ (30.0 mL) was stirred at reflux under nitrogen atmosphere for 24 h. The solid was separated by filtration, washed with anhydrous THF, and subsequently dried under vacuum at room temperature for 2 h to give the acid chloride-functionalized MWCNTs (MWCNT-COCl, 99 mg), which were used for the next reaction. A mixture of MWCNT-COCl (99 mg) and 1-(3-aminopropyl)imidazole (30.0 mL) was stirred at 120 °C for 24 h under nitrogen atmosphere. The solid was separated by filtration through a 0.2-μm poly(tetrafluoroethylene) (PTFE) membrane and washed successively with anhydrous THF followed by 1 N aqueous HCl solution, saturated $NaHCO_3$ solution, and water until the pH of the filtrate was 7.0. The resulting solid was finally washed with ethanol and dried overnight in a vacuum at 60 °C to give ***f*-2** (90 mg).

Preparation of 1-(3-Aminopropyl)imidazole Salt with Carboxylic Acid-Functionalized MWCNTs (*f*-2′). A mixture of ***f*-1** (CNT-COOH, 100 mg) and 1-(3-aminopropyl)imidazole (10.0 mL) was stirred at room temperature for 24 h. The solid was separated by filtration through PTFE membrane and thoroughly washed with anhydrous THF. The resulting solid was dried overnight in a vacuum at 60 °C to give ***f*-2′** (90 mg).

Control Experiments To Confirm Covalent Functionalization in *f*-2. Each solution of ***f*-2** (50 mg) and ***f*-2′**(50 mg) in 1 N aqueous HCl (10 mL) was stirred at room temperature for 2 h. The solid was separated by filtration and washed with saturated $NaHCO_3$ solution and water until the pH of the filtrate was 7.0. The resulting solid was dried overnight in a vacuum at 60 °C and subjected to XPS analysis.

Preparation of *n*-Butylimidazolium Bromide Salt-Functionalized MWCNTs (*f*-3a). A mixture of ***f*-2** (500 mg) and 1-bromobutane (20 mL) was stirred at 80 °C for 24 h under nitrogen atmosphere. The solid was separated by filtration through 0.2-μm PTFE membrane and thoroughly washed with anhydrous THF several times to remove the excess bromobutane. The resulting solid was dried under vacuum at room temperature for 24 h to give ***f*-3a** (490 mg).

Typical Procedure for Anion Exchange. To a solution of ***f*-3a** (100 mg) in water (4.0 mg) was added excess amount (200 mg) of solid $NaBF_4$ for ***f*-3b** ($NaPF_6$ for ***f*-3c**, $LiNTf_2$ for ***f*-3d**) all at once

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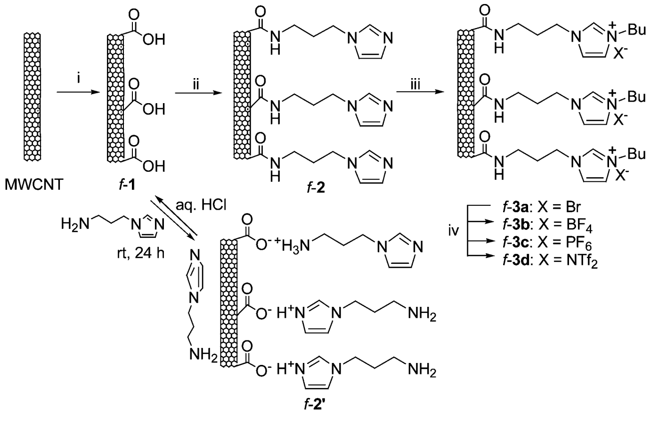
Scheme 1[a]



[a] Key: (i) 60% aqueous HNO_3, sonication for 1.5 h, 50 °C; (ii) (a) $SOCl_2$, reflux, 24 h, (b) (3-aminopropyl)imidazole, 120 °C, 24 h; (iii) **_f_-3a**, *n*-BuBr, 80 °C, 24 h; (iv) for **_f_-3b**, **_f_-3a** + $NaBF_4$ in H_2O, 24 h, for **_f_-3c**, **_f_-3a** + $NaPF_6$ in H_2O, 24 h, and, for **_f_-3d**, **_f_-3a** + $LiNTf_2$ in H_2O, 24 h.

at room temperature, and the mixture was stirred at room temperature for 24 h. The homogeneous black solution became colorless, and black solids were precipitated. The solid was separated by filtration and washed with water to remove the water-soluble species such as $NaBF_4$ residue and NaBr. After repeated washing with water, the resulting solid was dried overnight in a vacuum to give **_f_-3b** (90 mg).

Results and Discussion

Methods for the functionalization of MWCNTs with imidazoluim salts are depicted in Scheme 1. The chemical oxidation of MWCNTs were carried out in a 60% aqueous HNO_3 under sonication condition to yield carboxylic acid-functionalized MWCNTs, **_f_-1**.[29,30] In Raman spectra (Figure 1a), increased *R* value (area ratio of D_a/G_a) of **_f_-1** ($R = 1.4$) was observed compared with pristine MWCNTs ($R = 1.3$), suggesting that defects in MWCNTs were increased during functionalization. The presence of carboxylic acid groups was confirmed by IR analysis, in which the C=O bands appeared at 1718 and 1568 cm^{-1} with about 1:1 intensity (Figure 1b). The carboxylic acid group of **_f_-1** was converted to acid chloride, which was subsequently reacted with an excess amount of (3-aminopropyl)imidazole at 120 °C for 24 h under nitrogen atmosphere. The resulting MWCNTs were washed thoroughly successively with THF and 1 N aqueous HCl solution to remove the excess (3-aminopropyl)imidazole and any noncovalently adsorbed substances. Finally, the substrates were washed with deionized water and ethanol and dried to afford (3-aminopropyl)imidazole-functionalized MWCNTs (**_f_-2**). In the IR spectrum of **_f_-2**, the C=O band of the carboxylic acid group at 1718 cm^{-1} in **_f_-1** was shifted to 1646 cm^{-1}, indicating the formation of the amide bond (see Figure S1b in the Supporting Information). The qualitative X-ray photoelectron spectroscopy (XPS) analysis of **_f_-2** also showed the nitrogen atom (N 1s, 401 eV) (Figure 2a), suggesting the presence of imidazole moiety in **_f_-2**. To confirm the covalent bond formation in **_f_-2**, the control experiments were also carried out with the (aminopropyl)imidazole salt **_f_-2′**, which was prepared independently by mixing **_f_-1** and (3-aminopropyl)imidazole at room temperature for 24 h. Both the substrates, **_f_-2** and **_f_-2′**, were treated with 1 N aqueous HCl solution at room temperature, and the resulting substrates were subjected to the XPS analysis. As shown in Figure 2, the nitrogen peaks were retained from **_f_-2** (Figure 2a), whereas they disappeared from **_f_-2′** (Figure 2b), where **_f_-2′** was converted to the carboxylic acid-functionalized MWCNT, **_f_-1**. These results clearly indicate that the (aminopropyl)imidazole moiety in **_f_-2** was covalently bonded onto the surface of MWCNTs and the noncovalently adsorbed (3-aminopropyl)imidazole moieties onto the surface of MWCNTs could be removed by washing with aqueous HCl solution.

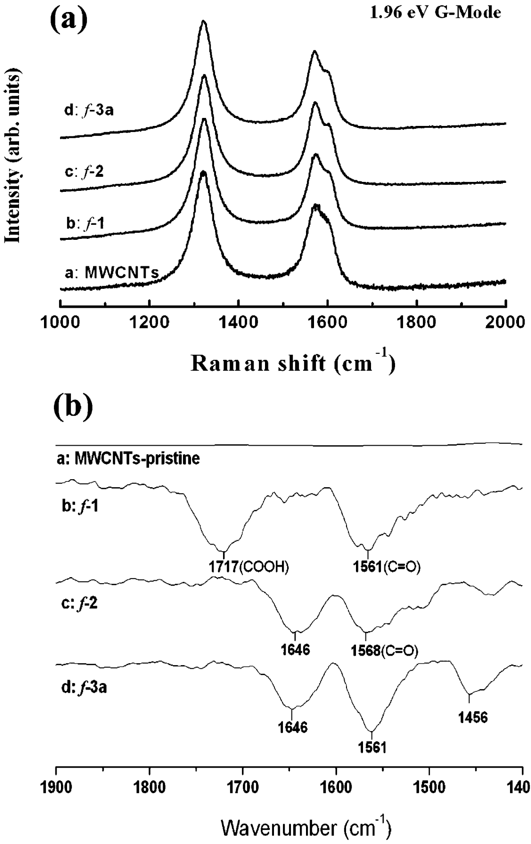


Figure 1. (a) D and G bands of Raman spectra for (a) pristine MWCNTs, (b) **_f_-1**, (c) **_f_-2**, and (d) **_f_-3a**. (b) C=O bands of FT-IR spectra of (a) pristine MWCNTs, (b) **_f_-1**, (c) **_f_-2**, and (d) **_f_-3a**.

The quantity of the (aminopropyl)imidazole in **_f_-2** was determined from the thermogravimetric analysis (TGA) of **_f_-2**, which showed a 11.7 wt % loss corresponding to the (aminopropyl)imidazole fragments, and from this value the mol % of the (aminopropyl)imidazole moiety on the surface of MWCNTs ($[AI]_{MWCNT} = 1.13$ mol % with respect to carbon) was calculated by using the weight percent and the molecular weight of the aminoimidazole fragment (124.16 g mol^{-1}) (see Figure S1 in the Supporting Information).[31] The *N*-butylimidazolium bromide-functionalized MWCNTs (**_f_-3a**) was prepared by the reaction of **_f_-2** with excess *n*-butyl bromide (Scheme 1). In the ^1H NMR spectrum of **_f_-3a**, the protons of the imidazolium ring resonated at δ 8.9 and 7.5 ppm, which clearly indicated the formation of imidazolium

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(31) Calculated according to the following equation: $[AI]_{MWNT} = [(\text{weight } \% \text{ of aminoimidazole from TGA/mol wt of aminoimidazole fragment})/(100/\text{mol wt of carbon})] \times 100$. Baskaran, D.; Mays, J. W.; Bratcher, M. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2138.

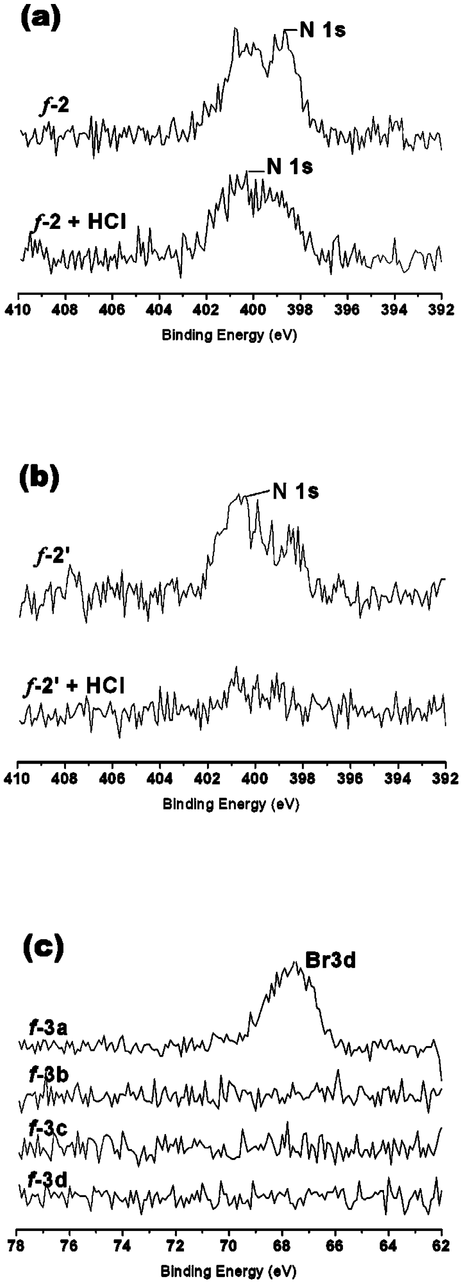

Figure 2. N(1s) region in XPS spectra of (a) ***f*-2** and (b) ***f*-2′** before (top spectrum) and after (bottom spectrum) treatment with aqueous HCl solution. (c) Br(3d) region in XPS spectra of ***f*-3a** and the anion-exchanged ***f*-3b**, ***f*-3c**, and ***f*-3d**.

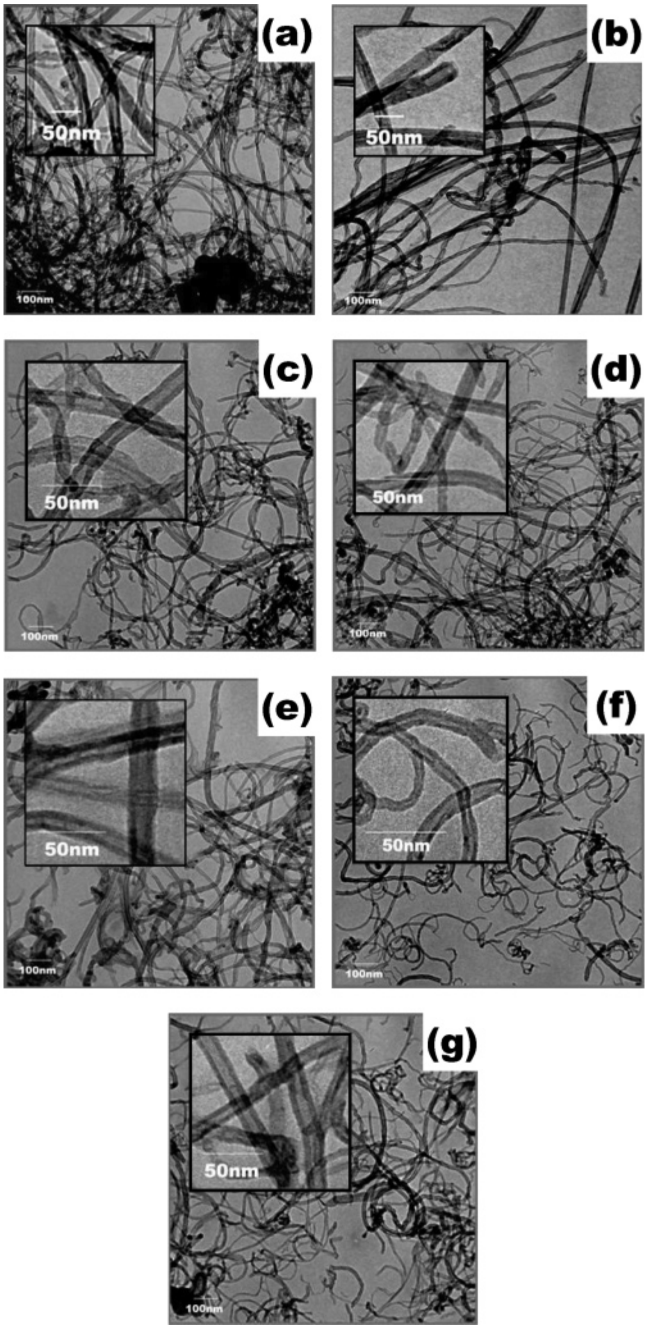

Figure 3. TEM images of the (a) pristine MWCNTs, (b) ***f*-1**, (c) ***f*-2**, (d) ***f*-3a**, (e) ***f*-3b**, (f) ***f*-3c**, and (g) ***f*-3d**.

bromide salts (see Figure S3 in the Supporting Information). The XPS analysis of ***f*-3a** further confirmed the formation of imidazolium bromide salt (Br: $3d_{3/2}$, 70 eV, and $3d_{5/2}$, 69 eV) (Figure 1c). The bromide anion of ***f*-3a** could be exchanged with other anions such as BF_4 (***f*-3b**), PF_6 (***f*-3c**), and NTf_2 (***f*-3d**) by treatment with $NaBF_4$, $NaPF_6$, and $LiNTf_2$, respectively, in deionized water at room temperature for 24 h. During the anion exchange, it was observed that the homogeneous black solution became colorless and the anion-exchanged MWCNTs were precipitated. The XPS analyses of ***f*-3b**, ***f*-3c**, and ***f*-3d** clearly indicated that the Br anion of ***f*-3a** was completely exchanged (Figure 2c) with BF_4^- (B 1s, 194 eV, and F 1s, 688 eV), PF_6^- (P $2p_{1/2}$, 137 eV, $2p_{3/2}$, 136 eV; F 1s, 687 eV), and NTf_2^- (N 1s, 401 eV, 399 eV; S 1s 168 eV; F 1s 688 eV) (see Figures S3-1−S3-5 in the Supporting Information). The morphology and tubular structure of the functionalized MWCNTs were observed in field-emission scanning electron microscopy (FE-SEM) (see Figure S4 in the Supporting Information) and transmission electron microscopy (TEM), suggesting that the functionalization and anion-exchange processes did not deteriorate the structural integrity of MWCNTs (Figure 3).

The thermostability of the functionalized CNTs was investigated by using TGA (heating rate, 20 °C/min; air flow, 20 mL/min). As shown in Figure 4, the crude MWCNTs (Figure 4a) and ***f*-1** (Figure 4b) were thermally stable below 600 °C. In contrast, the aminoimidazole-functionalized ***f*-2** (Figure 4c) and the imidazoluim salt-functionalized ***f*-3a-d** (Figures 4d−g) decomposed at much lower temperature with two main weight-loss regions. The first weight-loss region

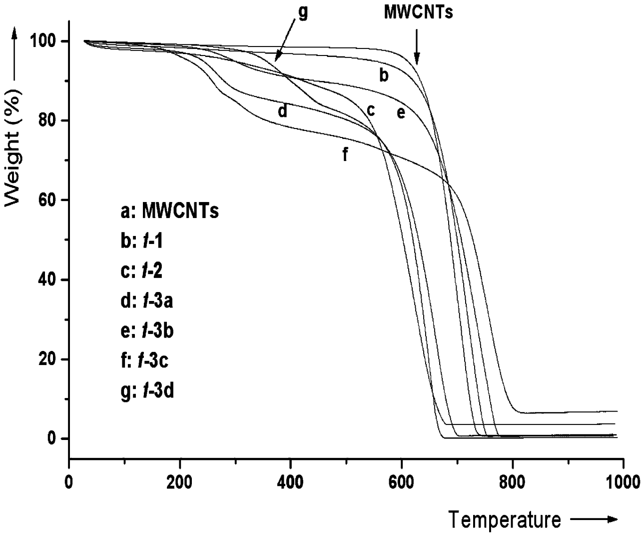

Figure 4. TGA curves (heating rate, 20 °C/min; air flow, 20 mL/min) of the pristine and the functionalized MWCNTs, **_f_-1**, **_f_-2**, and **_f_-3a−d**.

Table 1. Absorbance at 600 nm (A_{600}) of the Functionalized MWCNTs (*f*-1, *f*-2, *f*-3a−d) with a Content of 1 mg of Sample/10 mL of Water and Chloroform

		f-MWCNT					
solvent	param	*f*-1	*f*-2	*f*-3a	*f*-3b	*f*-3c	*f*-3d
H_2O	A_{600}	1.2317	1.2367	1.5784	0.3079	0.018	0.014
	R_{600}^{a}	1.000	1.004	1.281	0.250	0.015	0.011
$CHCl_3$	A_{600}	0.9375	0	1.4457	1. 2593	1. 0999	2.0419
	R_{600}^{a}	1.000	0	1.542	1.343	1.173	2.178

[a] *R* is the ratio of A_{600} of the sample to A_{600} of **_f_-1**.

below ~350 °C may be attributed to the decomposition of the surface-attached aminoimidazole and (aminopropyl)-imidazolium salt. The significant weight reduction in the second region (~580 °C) is likely due to the decomposition of MWCNTs. The comparison of the TGA curves of the imidazolium salt-functionalized MWCNTs (**_f_-3a−d**) suggests that the counteranion has influence on the thermostability of MWCNTs. However, the exact nature of the effect of anions on the thermal stability of MWCNTs is not yet clear and remains to be solved.

Table 2. Qualitative Solubility of the Functionalized MWCNTs in a Variety of Solvents[a]

	solvent						
f-MWCNT	H_2O	EtOH	EtOAc	$CHCl_3$	[bmim] $[BF_4]$	[bmim] $[PF_6]$	[bmim] $[NTf_2]$
f-1	0	−	−	0	−	−	−
f-2	−	−	−	0*	−	−	0*
f-3a	+	+	−	+	0	0	+
f-3b	−	+	0	−	+	0	+
f-3c	−	−	−	+	0	+	+
f-3d	−	+	−	+	+	+	+

[a] Solubilities: −, not soluble; 0, faintly colored solution; +, dark black solution; ∗, very faintly colored solution. The content of the sample is 1 mg/mL of solvent.

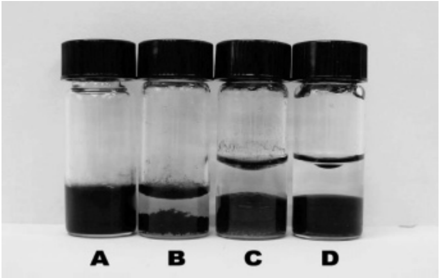

Figure 5. Photograph showing phase-transfer of the functionalized MWCNTs (1 mg/mL) via anion exchange (1 mg/mL): (A) **_f_-3a** in H_2O; (B) **_f_-3a** + $LiNTf_2$ in H_2O; (C) extraction of (B) (**_f_-3a** + $LiNTf_2$ in H_2O) with $CHCl_3$ (top layer is H_2O and bottom layer is $CHCl_3$, v/v = 1); (D) extraction of (A) (**_f_-3a** in H_2O) with [bmim]$[NTf_2]$ (v/v = 1) (the top layer is H_2O and the bottom layer is [bmim]$[NTf_2]$).

The solubility and the dispersibility of the functionalized MWCNTs, **_f_-1**, **_f_-2**, and **_f_-3a−d**, were semiquantitatively characterized with a UV−vis spectrophotometer at 600 nm in water and chloroform (Table 1 and Figure S5 in the Supporting Information). The relative absorbance of **_f_-3a−d** in water implies that the effect of counteranions on hydrophilicity/hydrophobicity of the IL-functionalized MWCNTs; i.e., solubility in water is the following order: **_f_-3a** (Br^-) > **_f_-3b** (BF_4^-) > **_f_-3c** (PF_6^-) > **_f_-3d** (NTf_2^-). The order is quite consistent with the results obtained previously from the water contact angle of the monolayered surfaces coated with the 1-methylimidazolium cation.[14] The **_f_-3d** bearing NTf_2 anion, which is known to be the most hydrophobic counteranion in 1-butyl-3-methylimidazolium cation-based ionic liquids, showed the lowest absorbance in water but the highest value in chloroform. Consistent with the UV−vis data, **_f_-3a**, which was functionalized with *n*-butylimidazolium bromide, was completely dissolved in water, leading to the formation of homogeneous black aqueous solution. The homogeneity of **_f_-3a** in water remained after several months, and no precipitation was observed. It was also found that the imidazolium salt-functionalized MWCNTs (**_f_-3a−d**) were quite soluble in a hydrophobic ionic liquid, [bmim]$[NTf_2]$ (bmim = 1-buthyl-3-methylimidazolium), whereas the carboxylic acid- (**_f_-1**) and (aminopropyl)imidazole-functionalized MWCNTs **_f_-2** were not soluble (see Figure S6c in the Supporting Information). Among the IL-functionalized MWCNTs, **_f_-3d** bearing the NTf_2 counteranion exhibited the highest solubility in all ionic liquids. However, the other IL-functionalized MWCNTs showed preferential solubility in the ionic liquid having the same counteranion. Therefore, although the possibility of the counteranion exchange between the IL-functionalized MWCNTs and ILs, when they have different counteranions, could not be excluded, **_f_-3b**,**c** showed preferential solubility in [bmim]$[BF_4]$ and [bmim]-$[PF_6]$, respectively. The qualitative solubility of the samples in ionic liquids was summarized in Table 2. The anion effects on the solubility of the imidazolium salt-functionalized MWCNTs allowed the phase-transition of the MWCNT via direct anion exchange. Figure 5 shows the optical micrograph of the phase-transition of the functionalized MWCNTs. Upon the addition of $LiNTf_2$ (3 mg), the homogeneous black aqueous solution (1.0 mg/mL) of **_f_-3a** (Figure 4a) became clear and precipitates were observed (Figure 4b), which could be extracted with $CHCl_3$ (Figure 4c). These results clearly indicate that the anion exchange of the Br^- with NTf_2^- changed the solvent preference of the imidazolium salt-functionalized MWCNTs between H_2O and $CHCl_3$. Moreover, the imidazolium salt-functionalized MWCNTs, even the water-soluble **_f_-3a**, exhibited a high preferential solubility in an ionic liquid, [bmim]$[NTf_2]$. The addition of 1 mL of [bmim]$[NTf_2]$ to the aqueous solution of **_f_-3a** followed by vigorous shaking resulted in the complete transfer from the aqueous layer to the IL layer (Figure 4d). The preferential solubility of the imidazolium salt-functionalized MWCNTs in [bmim][NTf_2] could be ascribed to strong ionic interactions between the imidazolium ions, which were covalently linked with the modified MWCNTs, and [bmim][NTf_2].

Conclusions

In conclusion, we have covalently functionalized the multiwalled carbon nanotubes (MWCNTs) with imidazolium cation-based ionic liquids and investigated the effect of counteranions on the solubility of the functionalized MWCNTs. The relative solubility of the functionalized MWCNTs in water and organic solvents could be varied by the anion exchange, and the phase-transfer of the functionalized MWCNTs from aqueous solution to $CHCl_3$ was also achieved. In addition, the imidazolium salt-functionalized MWCNTs showed a high preferential solubility in the ionic liquids, which may open up a new avenue for further investigations toward the modifications and applications of CNTs in ionic liquids.

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Supporting Information Available: TGA of ***f*-2**, an ^{1}H NMR spectrum of ***f*-3a** in D_2O, XPS spectra of ***f*-2** and ***f*-3a−d**, SEM images of MWCNTs, ***f*-1**, ***f*-2**, and ***f*-3a−d**, UV−vis spectra of the functionalized MWCNTs in water and chloroform, and photographs of the funtionalized MWCNTs in water, chloroform, and [bmim]-[NTf_2] (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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