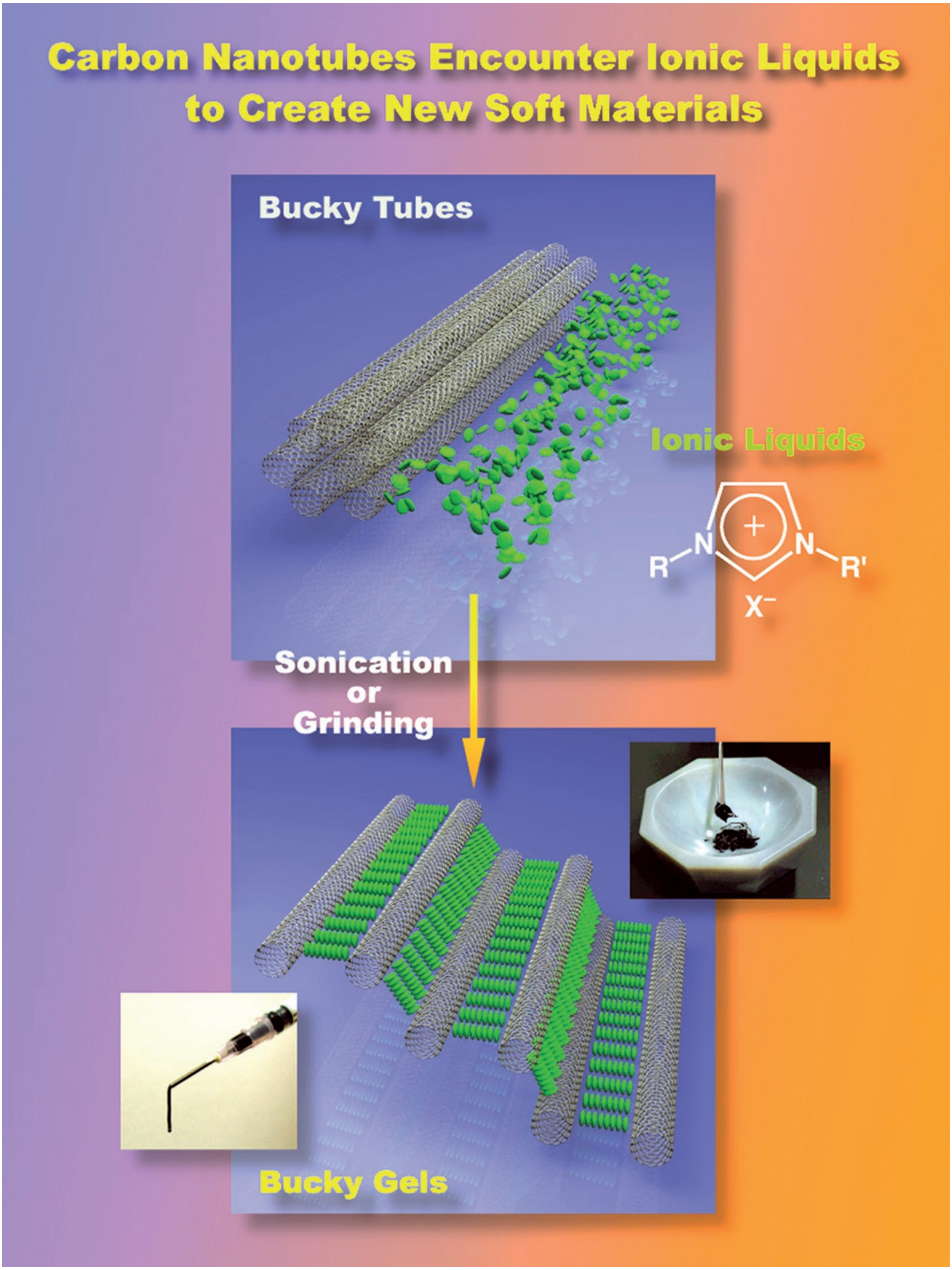
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700554



Ionic Liquids for Soft Functional Materials with Carbon Nanotubes

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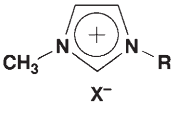
Abstract: A serendipitous finding that ionic liquids gel with carbon nanotubes has opened a new possibility of ionic liquids as modifiers for carbon nanotubes. Upon being ground into ionic liquids, carbon nanotube bundles are untangled, and the resultant fine bundles form a network structure. This is due to the possible specific interaction between the imidazolium ion component and the π-electronic nanotube surface. The resultant gelatinous materials, consisting of highly electroconductive nanowires and fluid electrolytes, can be utilized for a wide variety of electrochemical applications, such as sensors, capacitors, and actuators. Ionic liquids allow for noncovalent and covalent modifications of carbon nanotubes and fabrication of polymer composites with enhanced physical properties. The processing of carbon nanotubes with ionic liquids is not accompanied by the disruption of the π-conjugated nanotube structure and does not require solvents; therefore it can readily be scaled up. This article focuses on new aspects of ionic liquids for designer soft materials based on carbon nanotubes.

Keywords: conducting materials • gels • ionic liquids • materials science • nanotubes • soft materials

Introduction

The discovery of carbon nanotubes (CNTs)[1,2] has stimulated intense research activities, leading to remarkable scientific and technological advances in the development of nanostructured materials. This state-of-the-art carbon form consists of a rolled-up graphene sheet with hexagonally arranged sp^2-hybridized carbon atoms,[3,4] and can be regarded as an ultimate π-electronic architecture. Since CNTs provide extraordinary mechanical, electrical, and thermal properties, numerous potential applications are expected.[5] However, one major drawback is that CNTs are hard to process due to their poor dispersibility. In particular, single-walled CNTs (SWNTs) exist as ropes and bundles,[6] which are heavily entangled with each other to form agglomerates. For a better processability of CNTs, many chemical and physical approaches to the modification of the CNT surface have so far been attempted.[7,8] For example, adsorption of organic molecules onto the nanotube surface by means of van der Waals forces and/or π-stacking interactions has been shown to be promising for dispersing CNTs in fluid media, occasionally affording individual nanotubes. Compared with chemical approaches through covalent functionalization, such noncovalent approaches are easy to perform and have an additional advantage in that they can avoid disruption of the π-electronic conjugation of the CNTs.

Recently, we found imidazolium-ion-based ionic liquids (Figure 1) as a new class of dispersants for CNTs.[9] Previously reported dispersants include solid substances that are usable only by the combination with appropriate solvents. In contrast, ionic liquids are fluid at room temperature and



[emim][BF4] : $R = C_2H_5$, $X = BF_4$
[emim][Tf2N]: $R = C_2H_5$, $X = (CF_3SO_2)_2N$
[bmim][BF4] : $R = C_4H_9$, $X = BF_4$
[bmim][PF6] : $R = C_4H_9$, $X = PF_6$
[bmim][Tf2N]: $R = C_4H_9$, $X = (CF_3SO_2)_2N$
[omim][PF6] : $R = C_8H_{17}$, $X = PF_6$

Figure 1. Molecular formulas and schematic structures of typical imidazolium-ion-based ionic liquids.

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able to disperse CNTs by themselves, affording readily processible gelatinous substances. This feature gives a great advantage over the known examples, since one can "design" soft composite materials directly from the resulting gels, readily modify their physical properties, incorporate certain functionalities, and even transfer them into other fluid media or solid matrices. This method allows for large-scale processing of CNTs. Furthermore, ion-conductive properties of the media can be used for electrochemical applications. We and other groups have noticed several unique aspects of the physical gels from ionic liquids and CNTs, referred to as "bucky gels". This Concept article mostly describes the formation and fundamental properties of these gelatinous, soft composite materials and also highlights their applications to nanoscale materials sciences.

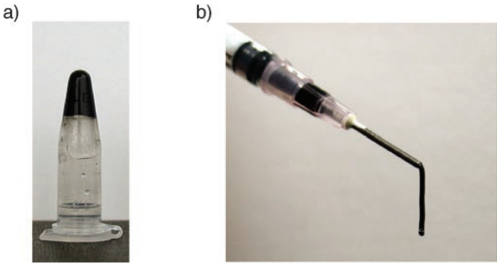


Figure 2. Photographs of a bucky gel formed from HiPco SWNTs and [bmim][BF$_4$]. a) Phase-separation behavior of the gel (upper phase) and excess [bmim][BF$_4$] (lower phase), observed after centrifugation of a ground mixture of SWNTs (2 mg) and the ionic liquid (0.6 mL). When the amount of [bmim][BF$_4$] in the starting mixture is lower than 0.2 mL, no ionic liquid phase is separated even upon prolonged centrifugation. b) Extrusion of the gel from a needle.

Formation and Properties of Bucky Gels

Ionic liquids are characterized by negligible vapor pressure, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical potential window.[10–13] Due to such unique properties coupled with an ability to dissolve a wide range of organic and inorganic substances, they have drawn increasing attention not only as a new class of electrolytes, but also for recyclable alternatives to conventional organic solvents for wet processes, including chemical syntheses, catalyses, liquid/liquid extractions, and so forth.[14–18]

Provided that CNTs are electroconductive and ionic liquids are ion conductive, we were motivated to explore if their composites might display any synergistic properties. When HiPco SWNTs were mixed with an ionic liquid such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-[BF$_4$], Figure 1), a suspension formed, which was then sonicated for 1 h in an ultrasound bath. During this time the suspension turned viscous, affording a gel. This observation implied that the ionic liquid may interact with the π-electronic surface of the SWNTs by means of cation–π and/or π–π interactions. However, unexpectedly, the gelation was not reproducible. After many trials, we eventually succeeded in reproducing the gelation by using a higher powered ultrasound generator or grinding this suspension in an agate mortar with a pestle.[9] The gelation occurs in a variety of imidazolium-ion-based ionic liquids (Figure 1) upon grinding with 0.5–1 wt% (critical gel concentration) of SWNTs. When SWNTs are ground into ionic liquid in excess with respect to the critical gel concentration, the gel and ionic liquid phases are clearly separated from each other by centrifugation (Figure 2a), indicating that the gel can trap a limited amount of the ionic liquid. Bucky gels thus obtained are easy to process into any shape. For example, through extrusion from a needle, one can fabricate a cable-like material that is not easily torn apart even when suspended (Figure 2b). Due to the negligible volatility of ionic liquids, bucky gels, in sharp contrast with ordinary organogels and hydrogels, are highly stable and can retain their physical properties even under a reduced pressure.

By means of transmission electron microscopy (TEM), we found that bucky gels contain highly exfoliated SWNT bundles (Figure 3). As observed by electronic absorption and Raman spectroscopy, SWNTs are not chemically disrupted, indicating that the gelation is induced only physically. Meanwhile, the rheological properties of the bucky gels suggested that the gel involves an elastic network. In oscillatory shear mode tests of a bucky gel of [bmim][BF$_4$] (Figure 4), the dynamic storage modulus (G') curve shows a plateau region at a low applied strain (γ), for example, $\gamma = 0.1$. On the other hand, over a wide range of the angular frequency (ω) from 100 to 0.04 rad s^{-1}, the loss modulus (G'') curve does not show any sign of relaxation, indicating that the system possesses permanent networks and therefore behaves as a gel. Another important observation is the large dependence of G' on γ at a low strain amplitude ($\gamma < 1.0$). When γ is increased to 1.0, the system starts to behave like a critical gel, for which the G' and G'' values both drop to a low modulus level and change with ω in a power law manner without any plateau. These rheological features suggest that an entanglement of SWNT bundles does not principally govern the elastic properties. Presumably, the system is ruled by a great number of weak physical cross-links among the SWNT bun-

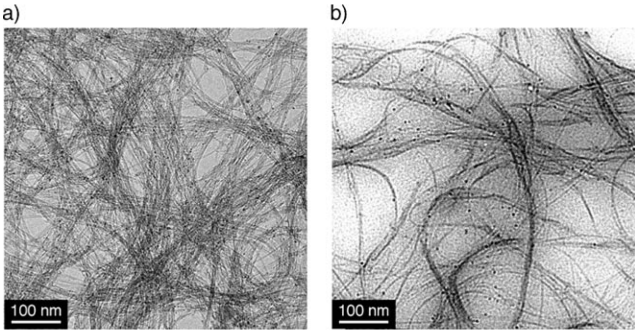


Figure 3. TEM micrographs of HiPco SWNTs a) received from a commercial source and b) obtained by dropping a bucky gel of [bmim][BF$_4$] into deionized water.

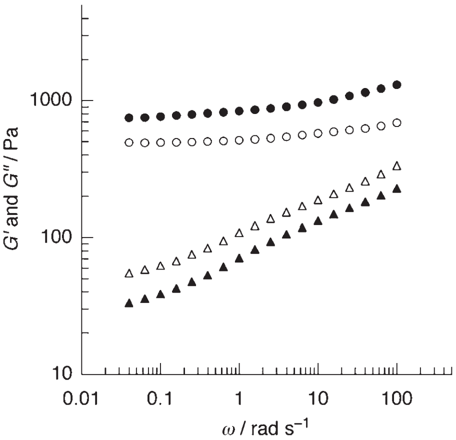


Figure 4. Angular frequency (ω) dependencies of dynamic storage (G', filled symbols) and loss moduli (G'', open symbols) of a bucky gel of [bmim][BF_4] at 25 °C at applied strain amplitudes (γ) of 0.1 (circles) and 1.0 (triangles). The sample was prepared by grinding 15 mg of SWNTs in [bmim][BF_4] (2 mL) for 1 h, followed by centrifugation of the resulting black paste at 9100*g* for 1 h to remove excess [bmim][BF_4].

dles, for which a long-range ordering of ionic liquid molecules, as suggested by X-ray diffraction and differential scanning calorimetry, is considered responsible. The imidazolium ions could be adsorbed through possible cation–π and/or π–π interactions onto the π-electronic surface of the nanotubes. As a seed crystal promotes crystallization, the adsorbed ionic liquid molecules probably trigger the clustering of the surrounding imidazolium ions in the bulk phase and interconnect neighboring SWNT bundles to form numerous physical cross-links. The exfoliated, fine nanotube bundles are weakly interlocked with one another by such a secondary ordering of the ionic liquid molecules, and the system therefore behaves as a gel. Since fullerenes and charcoal hardly gel ionic liquids upon grinding, the one-dimensional architecture of SWNTs with a large aspect ratio plays a role in the gelation.

Kim and co-workers investigated in detail the rheological properties of a [bmim][BF_4] gel with SWNTs, produced by an arc-discharged process.[19] Consistent with our observation, in oscillatory shear mode tests, the dynamic storage modulus of the bucky gel, even at a low concentration of SWNTs (1 wt %), is independent on the applied frequency, typical of network structures in a gel or rubber. Interestingly, the modulus of a gel prepared with purified SWNTs is one order of magnitude larger than that with raw SWNTs. Furthermore, in steady shear experiments, the gel with purified SWNTs behaves more like solid than that with raw SWNTs, and is considered to involve a larger number of cross-linking points and denser physical networks, thereby enduring a higher stress. All the rheological properties, in particular, high shear thinning, dynamic yield stress, and frequency-independent dynamic behavior, support the presence of a network structure in bucky gels.

Filtration of dispersed SWNTs is known to give a paper-like material called bucky paper,[20] which is rather strong but flexible, and usable for electrodes. Wallace and co-workers examined a change in mechanical properties of a bucky paper upon immersion in an ionic liquid such as [bmim][BF_4].[21] Interestingly, when immersed for only 30 s, the bucky paper significantly lost its breaking stress and elastic modulus. Such a quick and large deterioration in mechanical properties is hardly observed for a bucky paper after immersion, for example, in water. In creep tests, the bucky paper, after treated with [bmim][BF_4], showed a greater number of creeps than that untreated. It is likely that SWNTs absorb a large amount of ionic liquids by specific interaction, resulting in a big change in surface properties of SWNTs and their intertube interactions. Thus, the immersed sample eventually behaves like a viscous liquid.

Applications to Electrochemistry

Modified electrodes with bucky gels: CNTs are highly conducting and characterized by a large surface area and excellent chemical and physical stabilities. These properties are promising for electrode modifiers that are required to mediate electron-transfer reactions between electrodes and redox active species.[22–24] The use of bucky gels is beneficial for the fabrication of CNT-modified electrodes, since the large specific surface area of the highly dispersed CNTs can facilitate electron transfers more efficiently. Another advantage is a broader window of ionic liquids in applicable electrochemical potential than those of traditional electrolyte solutions, which enables electrochemical doping of carbon nanotubes.[25] Bucky-gel-modified electrodes can readily be fabricated from a variety of CNTs and ionic liquids.[26–33] For example, Dong and co-workers fabricated either gold or glassy carbon electrodes coated with a bucky gel prepared from multi-walled carbon nanotubes (MWNTs) and [bmim][PF_6].[26] Importantly, the redox potentials of $K_3Fe(CN)_6$, as evaluated by the modified and unmodified glassy carbon electrodes, are comparable to one another, indicating that the interfacial potential, possibly arising from the modification, is negligibly small. As supported by ac impedance and cyclic voltammogram measurements, electrical conduction governs the conductive properties of the bucky-gel layer deposited on the electrodes. Analogous to bucky gels with SWNTs, those with MWNTs most likely contain a well-developed nanotube network, which possibly serves as a conduction pathway from the electrodes. Very recently, Maleki and co-workers reported that graphite powder, when ground in an ionic liquid of *n*-octylpyridinium hexafluorophosphate, forms a paste-like soft composite material similar to bucky gels.[34] This black paste is useful for the modification of electrodes.

Bucky-gel-modified electrodes are used as electrochemical sensors, which can display a better performance than unmodified and even CNT-modified electrodes without ionic liquids. Zhuang, Zhu, and co-workers reported that a glassy carbon electrode modified with a MWNTs/[omim][PF_6] gel is capable of selectively detecting dopamine even in the presence of competing substrates such as ascorbic acid.[28] These substrates are hardly discriminated electrochemically by using the unmodified electrode. However, when the gel-modified electrode is used, a significant negative shift occurs preferentially for the anodic peak potential of ascorbic acid, so that the amount of dopamine can be quantified. Although a negative shift also takes place when using an electrode directly coated with MWNTs, the extent of the negative peak shift is more pronounced with the gel-modified electrode. Therefore, the gel layer provides the electrode with a higher electrocatalytic activity for the oxidation of substrates. The detection limit of this technique is 1.0×10^{-7} M, which is sufficient for the quantification of dopamine in a human blood serum, even in the presence of interfering substances such as uric acid. Similarly, a carbon fiber microelectrode, modified with a MWNTs/[bmim][PF_6] gel, exhibits a high electrocatalytic activity for the oxidation of NADH as well as dopamine and ascorbic acid.[29] This modified microelectrode also greatly promotes a direct electron transfer of glucose oxidase. As a more recent example, an electrode modified with a gel containing ferrocene-filled SWNTs (ferrocene peapods) has been reported, which efficiently catalyzes oxidation of H_2O_2 to O_2 and reduction to H_2O.[30]

Some ionic liquids are tolerated by biomolecules and hardly denature proteins, even promoting their refolding.[35] Furthermore, certain enzymes have been reported to exhibit enhanced biocatalytic activity and selectivity in ionic liquids.[36] Thus, when electrodes are modified with bucky gels containing catalytically active proteins, one may realize a substrate selectivity. Examples of such proteins include hemoglobin, microperoxidase, and horseradish peroxidase, which respond electrochemically on bucky-gel-modified glassy carbon or gold electrodes.[26,27,31]

Components for electrochemical devices: Inorganic and organic salts solubilized in organic solvents are important components for various electrochemical devices. However, since such organic electrolytes are flammable and volatile, a rigorous hermetic sealing is required for their use in practical applications. In this context, ionic liquids that are hardly flammable and volatile are advantageous and may be used as potential alternatives to organic electrolytes. For fabricating quasi-solid electrolytes useful for a long-time operation, a combination of ionic liquids with polymers,[37] nanoparticles,[38] and low-molecular-weight gelators[39] has been investigated. Bucky gels may serve as a unique class of quasi-solid electrolytes containing nanoscale electrodes, that is, carbon nanotubes. Watanabe et al., in collaboration with us, showed that bucky gels can be used as a component for electric double-layer capacitors (EDLCs).[40] EDLCs are energy storage devices, that accumulate electric charges at the interface between a polarizable electrode and an electrolyte. In a constant current mode, an [emim][Tf_2N]/SWNTs gel, sandwiched by metal electrodes with a separator, showed charging and discharging properties in response to an applied voltage. The capacitance (C_a) of the bucky-gel-based EDLC (7 $\mu F\,cm^{-1}$), normalized by its BET surface area, is greater than that fabricated with activated carbon and the same ionic liquid (5.5 $\mu F\,cm^{-1}$). On the other hand, the gravimetric capacitance (C_w) of the former is lower than that of the latter. Importantly, the dispersity of SWNTs affects the capacitance. When an unground mixture of SWNTs and [emim][Tf_2N] is used, the capacitance of the resultant EDLC is lower by approximately 30% than that with the corresponding bucky gel containing highly dispersed SWNTs. The bucky-gel-based EDLC also displays a smaller internal electrode resistance. In a preliminary report, fabrication of dye-sensitized solar cells was attempted by using [emim][Tf_2N] gels as electrolytes containing MWNTs and SWNTs. They show higher energy conversion efficiencies than that prepared with the ionic liquid alone.[41]

Plastic actuators based on bucky gels: By taking advantage of the capacitive properties of bucky gels, we developed a new class of electrochemical actuators,[42] which operate by the conversion of electrical energy into mechanical energy. Baughman and co-workers have reported the first carbon-nanotube-based actuators, in which two SWNT sheets (bucky paper), attached together with a double-sided Scotch tape, show a bending motion in aqueous electrolytes.[43] In sharp contrast, a bucky-gel-based actuator works in air without any support of external electrolytes. Furthermore, unlike conventional polymer actuators,[44] this actuator operates without deposition of a metallic electrode layer.

The bucky-gel-actuator adopts a simple bimorph configuration with a polymer-supported internal ionic liquid electrolyte layer,[37] which is sandwiched by bucky-gel electrode layers (Figure 5). The actuator film can readily be fabricated through layer-by-layer casting of electrode and electrolyte components in a gelatinous 4-methyl-2-pentanone solution of a vinylidene difluoride-hexafluoropropylene copolymer (PVdF(HFP)). Typically, the electrode layers are composed of SWNTs (13 wt%), [bmim][BF_4] (54 wt%), and PVdF(HFP) (33 wt%), while the electrolyte layer includes [bmim][BF_4] (67 wt%) and PVdF(HFP) (33 wt%). When an electric potential of ±3.5 V is applied with a frequency of 0.01 Hz, the actuator strip undergoes a bending motion

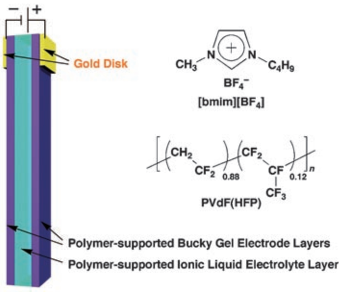


Figure 5. Schematic configuration of a PVdF(HFP)-supported actuator strip composed of a [bmim][BF_4] electrolyte layer sandwiched by SWNT/[bmim][BF_4]-gel electrode layers.

toward the anode side with a maximum displacement of 5 mm (Figure 6). The strain and stress, generated in the bucky-gel electrode layer, are 0.9 % and 0.1 MPa, respectively. The actuation takes place quickly in response to an applied alternating voltage of ±3.0 V even at a frequency of 30 Hz. Moreover, the bending motion (±2.0 V, 0.1 Hz) can be repeated for at least 8000 cycles in air without a notable decay (20 %).

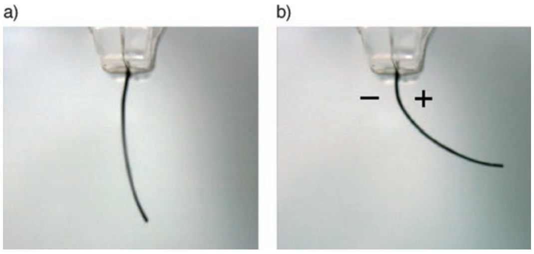
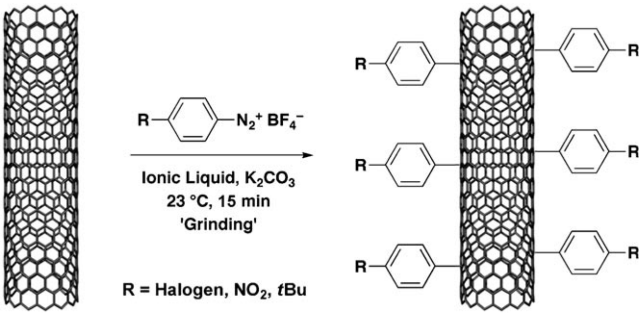


Figure 6. Bending motion (3.5 V, 0.01 Hz) of a PVdF(HFP)-supported actuator strip (15 mm in length, 1 mm in width, 0.28 mm in thickness) composed of a [bmim][BF$_4$] electrolyte layer sandwiched by SWNT/[bmim]-[BF$_4$]-gel electrode layers.

According to Baughman et al., the bucky-paper-based actuator operates by a dimensional change of SWNTs in the covalently bonded directions, due to quantum chemical and double-layer electrostatic effects caused by a charge injection into SWNTs.[43] However, for the bucky-gel actuators, this mechanism seems unlikely, considering the low loading level of SWNTs (13 wt %). We rather assume that a volume change of the electrode layers, arising from an interlayer ion transport, possibly contributes to the bending motion. Such an interlayer ion transport could be facilitated by the seamless connection of the electrode and electrolyte layers in the actuator. The soft-matter-based fabrication provides a large design flexibility of plastic actuators and may be combined with printing technologies for patterning.

Functionalization of Single-Walled Carbon Nanotubes from Bucky Gels

To provide CNTs with a high dispersibility and new functions, a number of protocols have been proposed for their covalent modification.[7] Recently, bucky gels have been utilized for chemical functionalization of CNTs. Aryl radicals, generated from, for example, aryl diazonium ions, are known to react to the sidewall of SWNTs. Tour and coworkers found that application of this reaction to a bucky gel results in smooth and uniform functionalization of SWNTs (Scheme 1).[45] For example, upon grinding 4-chlorobenzenediazonium tetrafluoroborate into a bucky gel of [bmim][PF$_6$] and SWNTs at room temperature for 15 min in the presence of K_2CO_3, the reaction takes place smoothly to give arylated nanotubes. This method is extremely simple and versatile, compared with other examples of SWNT-functionalizations that usually occur under harsh acidic or basic conditions and require enormous quantities of organic solvents. In the Raman spectra of the arylated SWNTs, the relative intensity of the diamondoid (1290 cm^{-1}) to graphitic bands (1590 cm^{-1}) is 0.51, which is as high as those reported previously with other methods. As observed by atomic force microscopy (AFM), the functionalized SWNTs exist predominantly as individuals. A wide variety of imidazolium and pyridinium salts with BF_4^- or PF_6^- can be used for this chemical transformation. As we have reported, SWNT bundles, upon being ground in ionic liquids, are exfoliated to give much finer bundles,[9] which likely contribute to the facile arylation on the SWNT surface. The chemical functionalization of SWNTs from bucky gels seems quite universal, unless the functionalization processes involve elementary steps that are hampered by ionic species.



Scheme 1. Covalent functionalization of dispersed SWNTs in bucky gels with aryldiazonium salts. The arylation of the sidewall of SWNTs occurs smoothly and homogeneously.

Electrochemical functionalization of CNTs[46] is important, but rarely proceeds homogeneously for large quantities of CNTs, since the reaction occurs locally on a limited surface of bundled SWNTs deposited on metal electrodes (Figure 7). An advantage of bucky gels of ionic liquids for

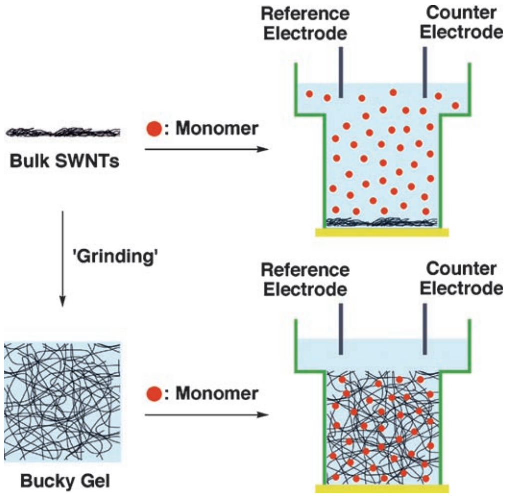
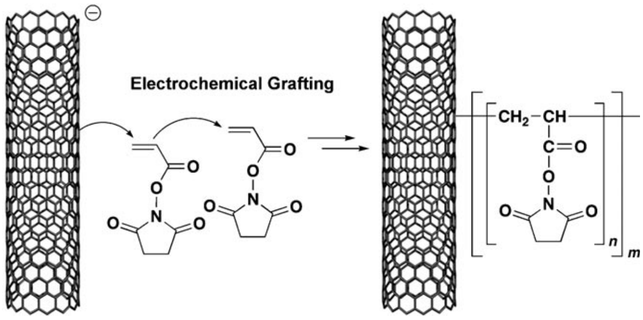


Figure 7. Schematic illustration of electrochemical polymer grafting of SWNTs on a metal working electrode (yellow). The new method through a bucky gel (lower) allows homogeneous grafting in comparison with a conventional approach using bulk SWNTs in a supporting electrolyte solution (upper).

the electrochemical functionalization of SWNTs is that the ionic liquid acts both as a dispersant of SWNTs and a supporting electrolyte. Examples include electrochemical grafting of an acrylate polymer from SWNTs (Scheme 2),[47] in which *N*-succinimidyl acrylate (NSA), chosen as the monomer, accepts one electron from electrochemically reduced SWNTs and reacts with the sidewall of the tube. Then, free-radical polymerization of NSA follows from the anchoring NSA to give a grafted polymer chain. In a typical experiment, NSA was ground into a gel of [bmim][PF_6] and SWNTs, and the resulting paste-like mixture was placed onto a gold electrode. When a reduction potential was applied to the electrode, the grafting reaction took place to form modified SWNTs, as confirmed by Raman and X-ray photoelectron spectroscopy. The resulting nanotubes are highly soluble in DMF. The active ester groups in the grafted poly-NSA can be utilized for further functionalization. For example, by the reaction with glucose oxidase, modified SWNTs with an electrocatalytic activity toward glucose can be fabricated.



Scheme 2. Schematic illustration of grafting of poly(*N*-succinimidyl acrylate) on SWNTs by electrochemical initiation. Symbols "*m*" and "*n*" represent the numbers of grafted polymer chains on a single SWNT and the repeating monomer units in the polymer chain, respectively.

Polymer Composites Derived from Carbon Nanotubes and Ionic Liquids

Carbon nanotubes have the potential to fabricate mechanically reinforced, electroconductive plastics.[7d,48] In particular, SWNTs are expected to behave as better dopants than MWNTs, because of their greater aspect ratio and mechanical modulus. Individual SWNTs possess a Young's modulus of ≈1 TPa,[49] which is comparable to that of graphite in-plane. On the other hand, bulk SWNTs show a high electrical conductivity in an order of 10^2–10^3 $S\,cm^{-1}$.[50] Despite these promising features, successful examples of such SWNT-based soft materials are limited, mainly due to an extremely poor dispersibility of bundled SWNTs in polymer matrices. Although covalently functionalized SWNTs are more easily dispersed,[7] some of the important properties of SWNTs arising from their extended π-conjugation are lost by chemical modifications. On the other hand, noncovalent wrapping of SWNTs with appropriate organic modifiers can avoid such an essential problem of π-electronic deterioration.[51] However, polymer composites of wrapped SWNTs, so far reported, rarely possess highly enhanced physical properties, most likely due to a poor compatibility of the surface modifiers with polymer matrices. If polymerizable modifiers for SWNTs are available, the resulting polymer composites could show enhanced physical properties.

We found that bucky gels formed from polymerizable ionic liquids and SWNTs, upon in-site free-radical polymerization, give rise to highly reinforced, electroconductive polymer composites of SWNTs.[9,52] Examples of polymerizable ionic liquids include acrylate, methacrylate (Figure 8), and vinyl groups appended with imidazolium ion functionalities. Similar to ordinary imidazolium-ion-based ionic liquids, the polymerizable ionic liquids gel with SWNTs. Upon heating in the presence of radical initiators such as azobisisobutyronitrile, the gels are transformed into black, homogeneous polymer materials (bucky plastics). A bucky-plastic film (Figure 9a), prepared from the methacrylate-appended ionic liquid monomer at a 7 wt% content of SWNTs, displays an electrical conductivity as large as 1 $S\,cm^{-1}$ and a 120-fold enhancement of the Young's modulus.[52] Such a large enhancement of the tensile modulus by SWNTs has rarely been re-

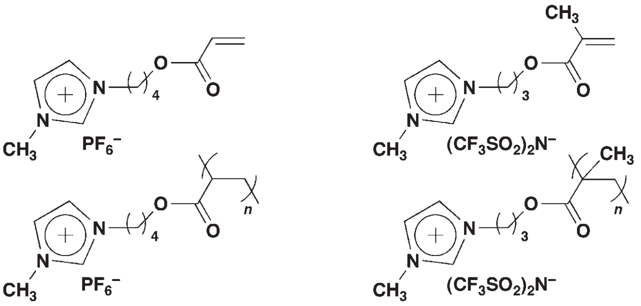


Figure 8. Schematic structures of imidazolium-ion-based polymerizable ionic liquids and their corresponding polymers.

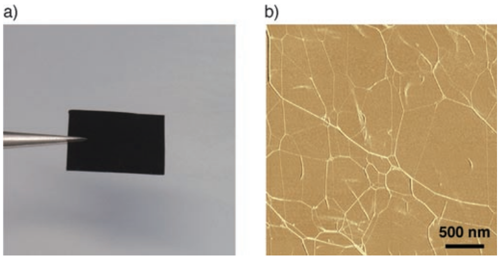


Figure 9. a) Photograph of a bucky plastic film containing 8 wt% of SWNTs and b) AFM phase image of its surface, prepared by free-radical polymerization of a methacrylate derivative of an imidazolium-ion-based ionic liquid gelled with SWNTs.

ported. Furthermore, the observed conductivity is one of the highest values so far reported for SWNT-doped polymers ($\sigma < 10^{-2}\,\mathrm{S\,cm^{-1}}$) at comparable loading levels of SWNTs.[51d,53] As confirmed by SEM and AFM (Figure 9b) microscopy, the bucky-plastic film possesses a well-developed cross-linked network consisting of finely dispersed SWNTs. This nanotube network may hamper slipping of entrapped polymer molecules through the strong interfacial interaction, and could also facilitate the intertubular charge carrier transport.

Mecerreyes and co-workers reported that polymeric ionic liquids (PILs), derived from 1-vinyl-3-ethylimidazolium salts with hydrophilic Br^- and hydrophobic Tf_2N^- ions, form stable dispersions of SWNTs in water and acetone, respectively.[54] The strong interaction between PILs and SWNTs here can be accounted for a multivalent interaction of a large number of the polymeric imidazolium ion moieties with the π-electronic surface of the nanotubes (Scheme 3). Interestingly, water and organic dispersions of SWNTs can be reversibly switched by simply exchanging in situ the counter anion of the attached PIL (Figure 10). When $LiTf_2N$ is added to an aqueous dispersion of SWNTs supported by PIL-Br, a precipitate forms, which in turn is dispersible in acetone. Tetrabutylammonium bromide is then added to this dispersion, whereupon a precipitate forms that is dispersible in water. The successful round trip of SWNTs by using a PIL vehicle is very simple and versatile, and may be useful for further processing of SWNTs.

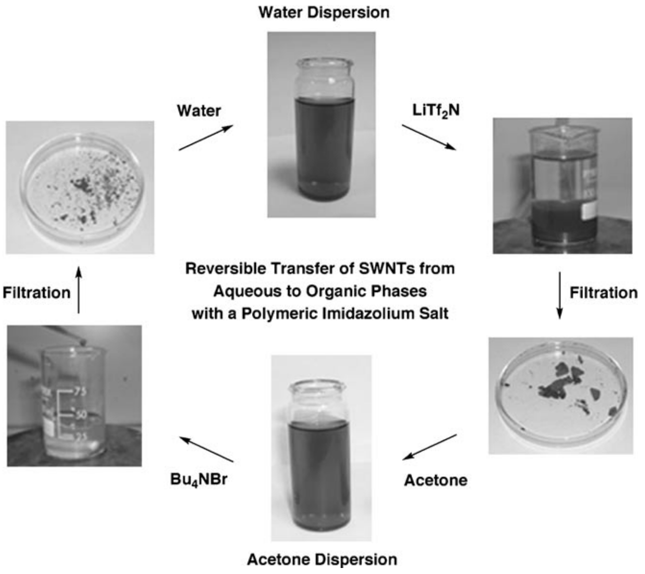


Figure 10. Reversible transfer of SWNTs between aqueous and organic media by counter anion exchange of the attached PIL. (Reproduced with permission from reference [54]. Copyright 2006 Wiley-VCH.)

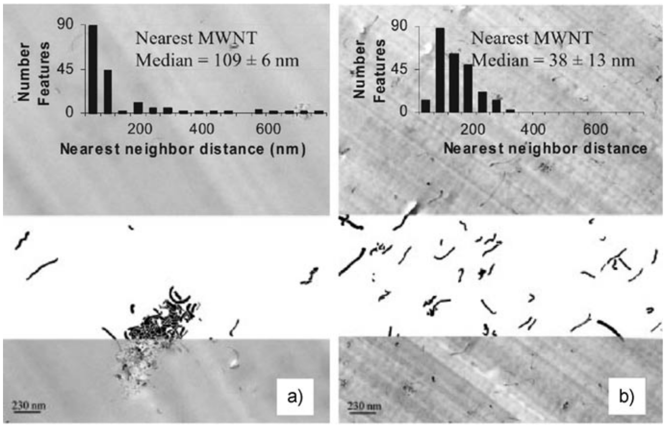
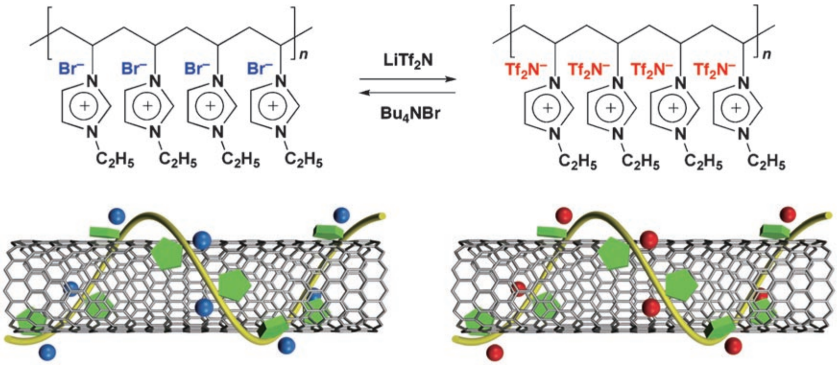


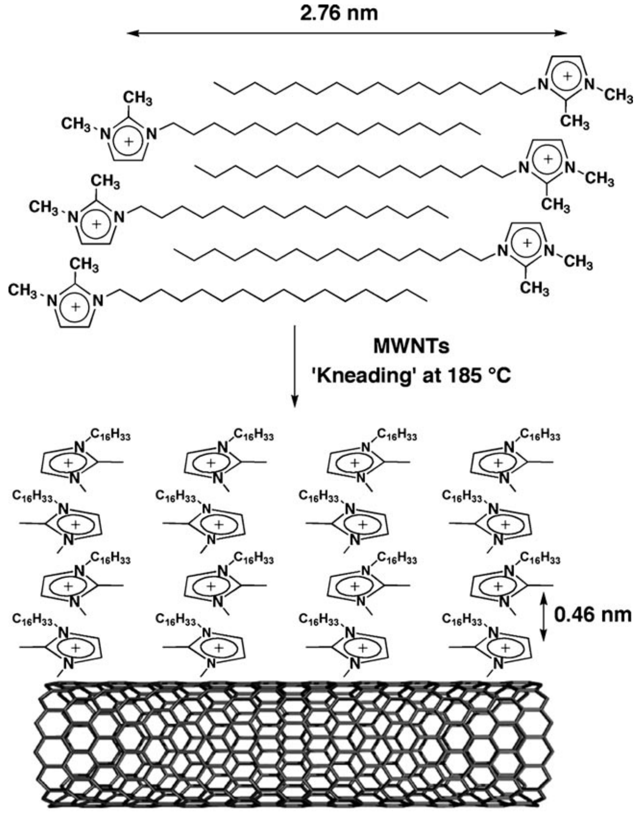
Figure 11. TEM micrographs and image analysis data of PS/MWNT composites fabricated by kneading at 185 °C a) without and b) with $[C_{16}dmim][BF_4]$. (Reproduced with permission from reference [55]. Copyright 2005 Wiley-VCH.)

The use of imidazolium ions paves a new way to the development of CNT composites with commodity polymers. Gilman and co-workers reported that 1-cetyl-2,3-dimethylimidazolium tetrafluoroborate ($[C_{16}dmim][BF_4]$) acts as an excellent compatibilizer for MWNTs toward polystyrene (PS).[55] $[C_{16}dmim][BF_4]$ is solid at room temperature and exhibits a liquid-crystal clearing point at 175 °C. By kneading with $[C_{16}dmim][BF_4]$, MWNTs are dispersed homogeneously in PS. Typically, a mixture of MWNTs and $[C_{16}dmim][BF_4]$ at a 1:1 weight ratio was kneaded at 185 °C, and the resulting mixture was further kneaded at 195 °C with a large amount of PS. As shown in Figure 11b, the PS composite (MWNT content; 0.5 wt %) contains highly dispersed, individual nanotubes. In contrast, MWNTs that are not pretreated with $[C_{16}dmim][BF_4]$ are hardly dispersed in PS, but form large agglomerates (Figure 11a). The imidazolium salt is not phase-separated in the composite, as supported by the absence of any apparent melting peaks of $[C_{16}dmim][BF_4]$ in the DSC profile. $[C_{16}dmim][BF_4]$ alone is known to exhibit XRD peaks assignable to an interdigitated-bilayer structure with a *d*-spac-



Scheme 3. Schematic structures of SWNTs noncovalently wrapped by an imidazolium ion polymer (PIL). Exchange of the counter anion of the attached PIL allows changing of the dispersibility of the composite.

ing of 2.76 nm. However, in place of this characteristic diffraction, the kneaded mixture of [C_{16}dmim][BF_4] and MWNTs displays a new peak with a *d*-spacing of 0.46 nm (Scheme 4). Of interest, this value is identical to that reported for a bucky gel prepared from a [bmim] salt and SWNTs.[9] Furthermore, as observed by infrared spectroscopy, the $C_{16}dmim^+$ and BF_4^- moieties in the kneaded mixture no longer form a hydrogen-bonded pair, suggesting that the $C_{16}dmim^+$ moiety leaves BF_4^- and sticks to the nanotube surface. Despite the low content of MWNTs (0.5 wt %) in PS, the onset and maximum degradation temperatures are higher by approximately 20 °C than intact PS. This may be of value to note, since blending with [C_{16}dmim][BF_4] or MWNTs alone does not improve the thermal properties of PS.



Scheme 4. Schematic illustrations of proposed assembled structures of [C_{16}dmim][BF_4] in the absence and presence of MWNTs. A columnar arrangement of the imidazolium ion is triggered by the interaction with MWNTs.

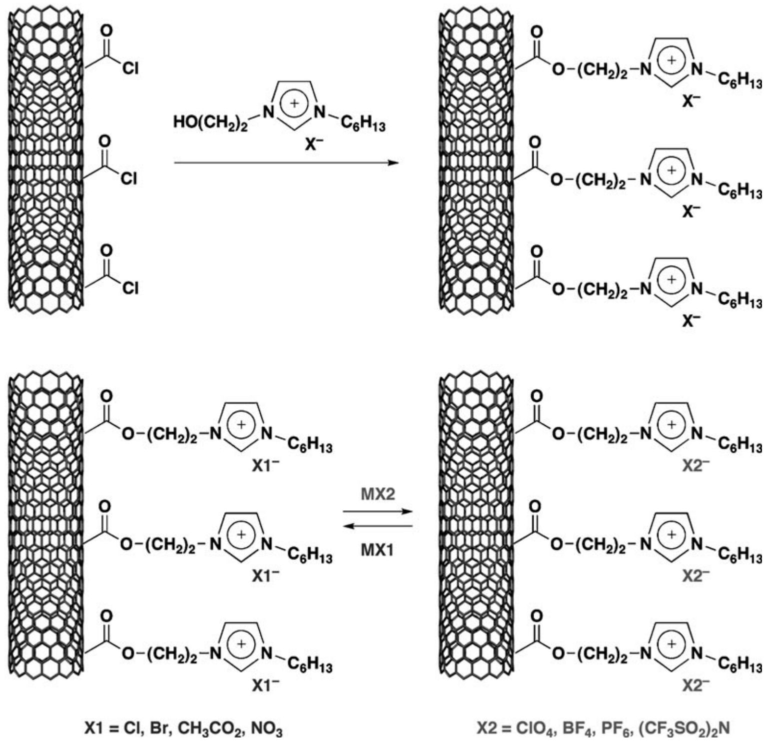
Carbon Nanotubes Covalently Modified with Imidazolium Ions

Several attractive features of noncovalently modified CNTs with ionic liquids have raised an interest in covalently modified CNTs.[56–58] A readily changeable hydrophilic/lipophilic balance of appended ionic liquid moieties by counter anion exchange may allow fine tuning of the dispersibility and compatibility of CNTs (Scheme 5).[56] For example, CNTs covalently modified with imidazolium ions are dispersible only in water when they bear Cl^- or Br^- as the counterion. In contrast, fluorine-containing anions such as BF_4^-, PF_6^-, and Tf_2N^- allow dispersion of the imidazolium-appended CNTs in organic solvents such as $CHCl_3$, affording black homogeneous solutions. In some cases, the modified CNTs are transferred reversibly between aqueous and organic phases by sequential addition of appropriate salts.[56,57] As expected, imidazolium-ion-functionalized CNTs are highly dispersible in ionic liquids of analogous chemical structures.

Imidazolium ion functionalities, covalently attached to the nanotube surface, may also allow incorporation of other functional groups. Phosphotungstic acid ($H_3[PW_{12}O_{40}]$) is a representative redox-active polyoxometalate (POM). Niu and co-workers incorporated the anionic form of this POM as the counter anion of an imidazolium ion-appended SWNTs and observed a charge transfer between the POM and SWNTs.[58] Typically, when an aqueous solution of the modified SWNTs with Br^- was stirred overnight in the presence of excess H_3POM, a precipitate formed, which was collected by centrifugation and thoroughly washed with water. As observed by infrared spectroscopy, the isolated product contains the POM. In cyclic voltammetry, the resulting material exhibits well-defined reversible redox waves due to the immobilized POM cluster. In contrast, without imidazolium ion functionalities on SWNTs, a product by an attempted composition with the POM shows a charging current of SWNTs predominantly.

Conclusions and Outlook

The specific interactions between CNTs and imidazolium ions, discovered from a serendipitous finding that ionic liquids gel with CNTs upon sonication, are opening a variety of new possibilities of soft composite materials of CNTs. In contrast, with known solid dispersants such as surfactants and π-conjugated substances, ionic liquids do not require solvents for dispersion of CNTs and allow large-scale processing of CNTs. Since ionic liquids are nonvolatile and nonflammable, the processing may be environmentally friendly. The processing is not accompanied by structural disruption of CNTs, as ionic liquids behave like a lubricant.[59] These features are advantageous over solid dispersants. In bucky gels, the exfoliated nanotubes are not free from one another, but are glued together by a great number of weak physical cross-links, for which secondary ordering of ionic liquids by means of interionic interactions may be responsible. This CNT network is preserved even after ionic liquid components are polymerized, so that the resulting polymer composites (bucky plastics) are mechanically reinforced and show an excellent electrical conductivity. While many trials for blending CNTs with polymers have been depressing, this achievement is outstanding and might encourage the related communities. Given that bucky gels are flexible, accommo-



Scheme 5. Schematic illustrations of MWNTs covalently functionalized with an imidazolium salt. Exchange of the counter anion of the attached imidazolium ion allows changing of the dispersibility of the nanotubes.

date a rather large amount of CNTs, and can also be transferred to commodity polymers, conductive soft materials with desired shapes such as cables and thin films can be fabricated. An enhanced surface area of CNTs, given by the high dispersion with ionic liquids, is not only beneficial for electrochemical applications, such as sensors, capacitors, and actuators, but also allows for the efficient covalent modifications of CNTs. Because ionic liquids are ion conductive, their composites with electroconductive CNTs are expected to be promising components for electrochemical devices, including solar cells. Bucky gels may further enhance the potentials of CNTs, considering that they can solubilize a variety of synthetic and natural substances including redox-active proteins.

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