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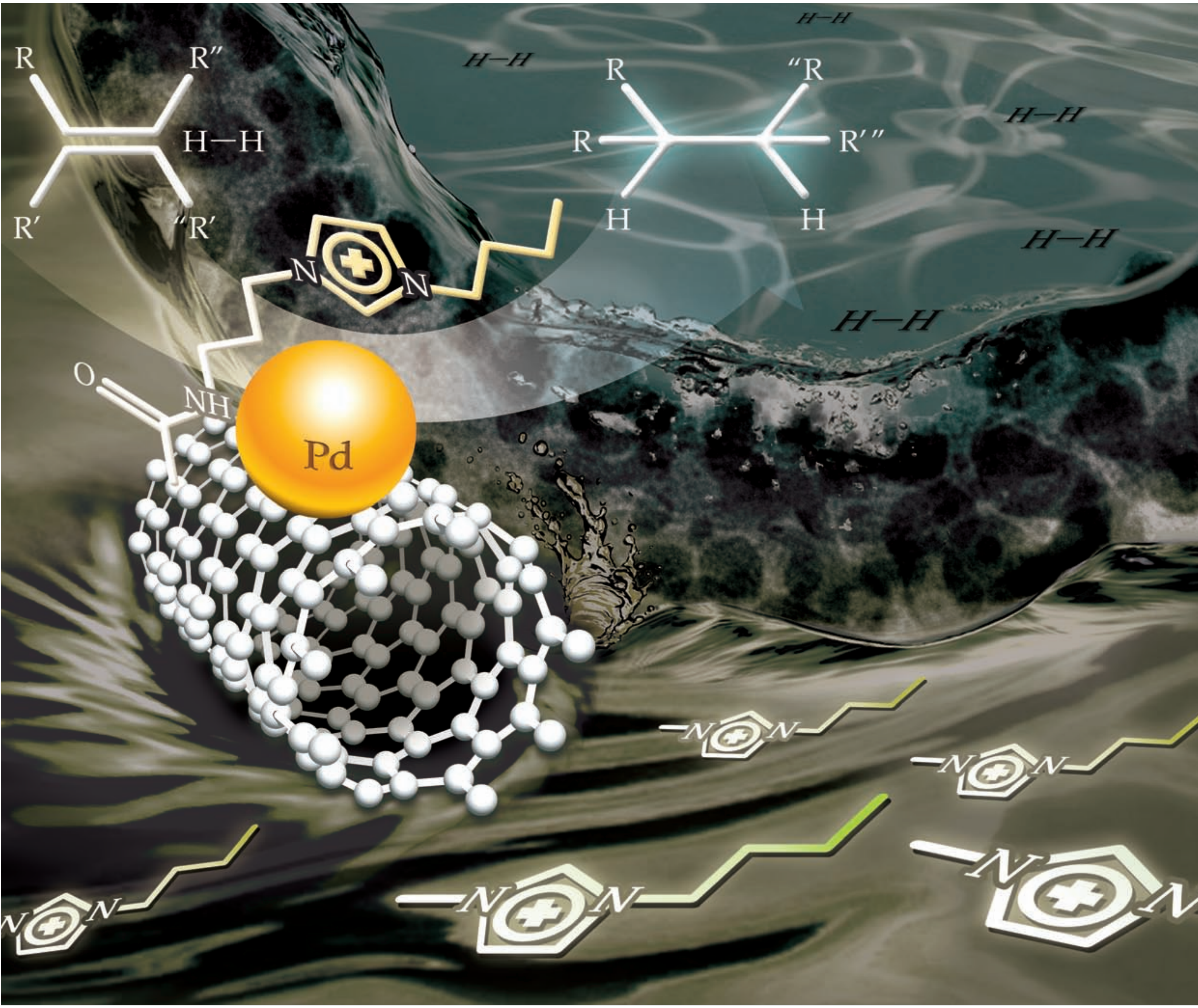

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Palladium nanoparticles supported onto ionic carbon nanotubes as robust recyclable catalysts in an ionic liquid†

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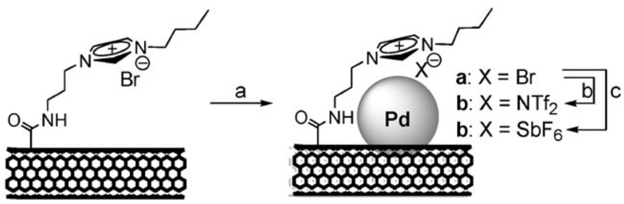
Palladium nanoparticles have been deposited onto imidazolium bromide-functionalized ionic MWCNTs through hydrogen reduction of Na_2PdCl_4 in water without aid of surfactants under extremely mild conditions, and combined with an ionic liquid to create a new recyclable ionic liquid-based catalytic system allowing up to 50 times recycling.

Metallic nanoparticles are known to present a very high catalytic activity because of their size effects.[1] However, having very active surface atoms could often lead to kinetic liability with respect to aggregation to the bulk metal and decreases in catalytic activity. Methods currently employed to solve the problem are stabilization of nanoparticles by addition of an additive stabilizers or supporting the nanoparticles onto a solid material.[2] Although, as homogeneous catalysts, the additive-stabilized nanoparticles show high catalytic activity, difficulties in separation and reuse limit their practical applications. In contrast, the solid-supported nanoparticles allow recycling as they work heterogeneously, but often result in significant loss of catalytic activities. Therefore, development of new catalytic systems composed of nanoparticles that are not only stable and active, but also easy to separate and reuse are highly desirable to facilitate actual practical applications.

Ionic liquids (ILs) are attracting considerable attention as an alternative reaction medium for homogeneous and heterogeneous catalysis as well as for the formation of nanomaterials.[3] Dupont *et al.* reported for the first time that catalytic nanoparticles can be stabilized by imidazolium ILs and utilized in catalytic hydrogenations in ILs.[4] Much of the recent studies suggested imidazolium ILs stabilize nanoparticles electrostatically and by coordination involving the imidazolium cations.[5] Although imidazolium ILs are believed to be effective stabilizers for nanoparticles, aggregation was determined in some cases to result in loss of activity. Different thiol,[6] nitrile[7] functionalized or polymeric[8] imidazolium ILs have also been used to stabilize metal nanoparticles. Our new approach, described in this communication, is a combination of imidazolium-functionalized ionic multi-walled CNT (IL-*f*-MWCNT)-supported nanoparticles with an ionic liquid. Due to the unique properties of CNTs such as mechanical strength, chemical stability, and a large surface area-to-volume ratio, they have potential as a new support material for catalytically active nanoparticles. Known methods for depositing catalytically active nanoparticles onto CNTs, including reduction of metallic precursors in supercritical CO_2, water or in the solid state, usually require harsh conditions, *i.e.*, high temperatures and high hydrogen pressures or large amount of surfactants.[9] Moreover, it is also important to note that the CNTs have extremely low solubility in ionic liquids as exemplified by the formation of gels with CNTs.[10] We have recently found that covalently functionalized MWCNTs with imidazolium salts (IL-*f*-MWCNTs) exhibited preferential solubility in ionic liquids as compared to water and/or organic solvents.[11] Moreover, the IL-*f*-MWCNTs **1** bearing a hydrophilic bromide anion showed high solubility in water. Based on these observations, we reasoned that the water-soluble hydrophilic IL-*f*-MWCNTs **1** might potentially be capable of acting not only as surfactants during deposition of nanoparticles by hydrogen reduction in water, but also as stabilizers when dissolved in ILs.

An aqueous solution of IL-*f*-MWCNTs **1** and Na_2PdCl_4 in H_2O was hydrogenated under 1 atm of H_2 pressure for 30 min at room temperature, and the resulting black Pd nanoparticles deposited on the IL-*f*-MWCNTs **1** were filtered by using a 0.2-μm Millipore® polycarbonate membrane, and washed successively with deionized water and methanol several times, and dried under vacuum for 24 h at room temperature to provide Pd/IL-*f*-MWCNTs **2a** (Scheme 1).

Transmission electron microscope (TEM) images of the Pd/IL-*f*-MWCNT **2a** (Fig. 1(a)) clearly showed that the Pd nanoparticles are well deposited on IL-*f*-MWCNTs surfaces with an average size distribution of 10 ± 0.5 nm.[12] Inductively coupled plasma atomic adsorption emission (ICP-AES) analyses indicated 55.3 wt% of palladium was deposited onto Pd/IL-*f*-MWCNT **2a** corresponding to 87.8% of the Pd



IL-*f*-MWCNT **1**   Pd/IL-*f*-MWCNT **2**

[a]H_2 (1 atm), Na_2PdCl_4, H_2O, RT, 30 min. [b]$LiNTf_2$, H_2O, RT, 12 h. [c]$NaSbF_6$, H_2O, RT, 12 h.

Scheme 1 Synthesis of palladium nanoparticles supported on imidazolium-functionalized multi-walled carbon nanotubes in water.‡

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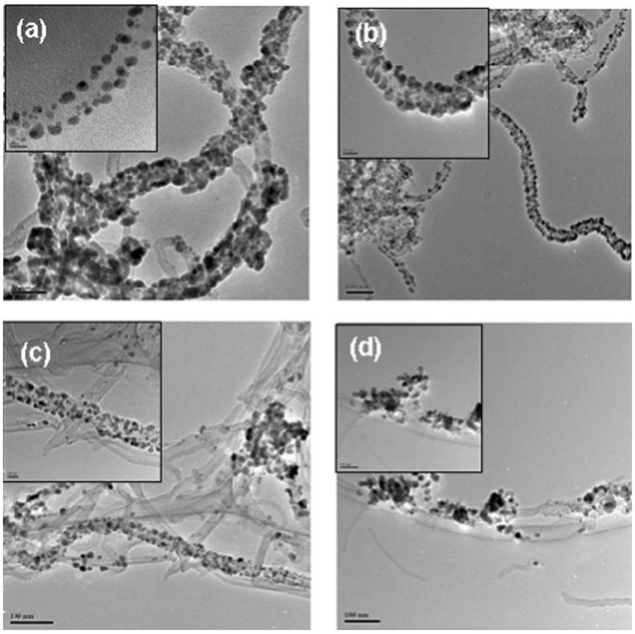


Fig. 1 TEM images of (a) Pd/IL-*f*-MWCNT **2a** (scale bar: 50 nm, 10 nm for inset); (b) Pd/IL-*f*-MWCNT **2c** prepared by anion exchange of **2a** with $NaSbF_6$ (scale bar: 100 nm, 20 nm for inset); (c) Pd/IL-*f*-MWCNT **2c** after 50 runs (scale bar: 100 nm, 20 nm for inset); (d) Pd/IL-*f*-MWCNT **2c** after the 51st run (scale bar: 100 nm, 50 nm for inset).

used. X-Ray photoelectron spectroscopy (XPS) of Pd/IL-*f*-MWCNT **2a** showed typical Pd(0) binding energies at 334.9 ± 0.5 eV for Pd($3d_{5/2}$) and 340.0 ± 0.5 eV for Pd($3d_{3/2}$), with asymmetric line shape. X-Ray diffraction (XRD) measurements of Pd/IL-*f*-MWCNTs **2a** also showed sharp peaks at $2\theta = 40.2°$ {111}, 46.6° {200}, 68.2° {220} and 86.8° {311} demonstrating the crystallized structure of these Pd nanoparticles (see XPS and XRD spectra of Pd/IL-*f*-MWCNT **2a**–**2c** in ESI†).

It is well known that the availability of potentially hydrophobic and hydrophilic ILs attests to the ease in the manipulation of their physical properties.[13] Especially, the choice of anions yields the greatest effect on hydrophilicity/phobicity. Recently we have demonstrated that surface properties of self-assembled monolayers (SAMs) presenting imidazolium salts can be tuned by anion exchange.[14] Taking advantage of the anion-directed tunable property of imidazolium ILs, we expected that dispersion of the Pd/IL-*f*- MWCNTs **2** in solvents could also be varied by changing the counter anion.

Thus, direct anion exchange of the Br in Pd/IL-*f*-MWCNTs **2a** to hydrophobic NTf_2 and SbF_6 anions in water could be possible without changing the size and distribution of the Pd nanoparticles, and provided the hydrophobic Pd/IL-*f*-MWCNTs **2b** (X = NTf_2) and **2c** (X = SbF_6, Fig. 1(b)).[15] XPS analysis clearly indicated the Br anion was completely exchanged with NTf_2 and SbF_6 anion (see ESI†). As shown in Fig. 2, the Pd/IL-*f*-MWCNTs **2a** bearing the hydrophilic Br anion is well-dispersed in water (Fig. 2(A)), whereas Pd/IL-*f*-MWCNTs **2b** and Pd/IL-*f*-MWCNTs **2c** having hydrophobic NTf_2 and SbF_6 (Fig. 2(B)) anions, respectively, are precipitated. Although all of the Pd/IL-*f*-MWCNTs **2a**, **2b** and **2c** are dispersed in alcohols such MeOH (Fig. 2(C) and (D)) and ^{i}PrOH (Fig. 2(E)), they are preferentially dispersed in an imidazolium IL (Fig. 2(F)).

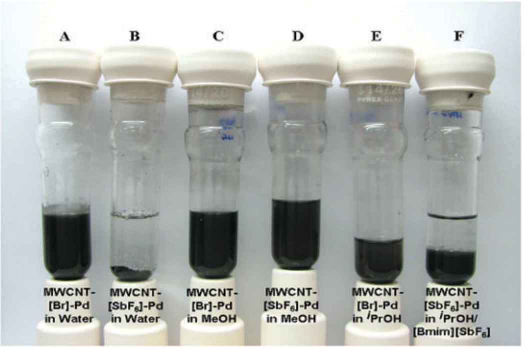


Fig. 2 Photo of Pd/IL-*f*-MWCNTs: (A) **2a** in H_2O, (B) **2c** in H_2O, (C) **2a** in MeOH, (D) **2c** in MeOH, (E) **2c** in ^{i}PrOH, (F) **2c** in ^{i}PrOH–[bmim][SbF_6] (1 : 1 v/v).

The catalytic activities of Pd/IL-*f*-MWCNTs **2a–2c** were tested first for the hydrogenation of *trans*-stilbene in MeOH solvent (entries 1–7 in Table 1). To our delight, the Pd/IL-*f*-MWCNTs **2** exhibited high catalytic activities with up to 2820 mol h^{-1} turnover frequency (entry 6 in Table 1). Interestingly, it has been found that the catalytic activity of the palladium nanoparticles were affected by the anion of imidazolium salt. The Pd/IL-*f*-MWCNT **2c** having SbF_6 anion showed superior catalytic activity compared to **2a** having Br and **2b** bearing NTf_2 anions (compare entries 2, 5 and 7 in Table 1). The catalytic activity of Pd/IL-*f*-MWCNT **2c** was retained in ^{i}PrOH (entry 8 in Table 1), or in a both of the mono- (entries 10) and biphasic alcohol–ionic liquid (entry 11) co-solvent systems. In the case of Pd/IL-*f*-MWCNT **2b** having NTf_2 anion, the catalyst activity was increased when the catalysis was conducted in a mixture of MeOH–[bmim][NTf_2] solvent (compare entries 3 and 9 in Table 1) suggesting a positive effect of ionic liquid on catalytic activity.

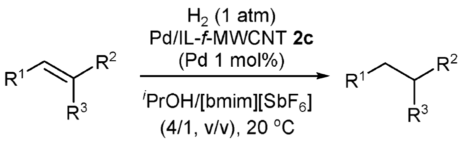
Noteworthy is that as we expected, the Pd/IL-*f*-MWCNT **2c** was effectively immobilized in an ionic liquid, [bmim][SbF_6], with extraordinary stability. Thus, the Pd/IL-*f*-MWCNT **2c**/[bmim][SbF_6] can be recovered by simple phase separation, and reused 10 times without any loss of catalytic activity (entries 1 and 7–10 in Table 2).‡

Table 1 Hydrogenation of *trans*-stilbene using Pd/IL-*f*-MWCNTs **2a–2c**[a]

Entry	**2** (Pd mol%)	*t*/min	Conv.[b] (%)	TOF/mol h^{-1}
1	**2a** (1.0)	10	100	600
2	**2a** (0.1)	20	22	660
3	**2b** (1.0)	10	65	390
4	**2b** (1.0)	20	100	300
5	**2b** (0.1)	20	9	270
6	**2c** (1.0)	10	100	600
7	**2c** (0.1)	10	47	2820
8[c]	**2c** (1.0)	10	100	600
9[d]	**2b** (1.0)	10	100	600
10[d]	**2c** (1.0)	10	100	600
11[d]	**2c** (1.0)	10	100	600

[a] Stilbene (1.0 mmol) in MeOH (10 mL) was hydrogenated under 1 atm of H_2 pressure at 20 °C in the presence of Pd/IL-*f*-MWCNT **2**. [b] Determined by GC. [c] Reactions in ^{i}PrOH (10 mL). [d] Reactions in MeOH–[bmim][NTf_2] (8 mL–2 mL). [e] Reactions in MeOH–[bmim][SbF_6] (8 mL–2 mL). [f] Reactions in ^{i}PrOH–[bmim][SbF_6] (8 mL–2 mL).

Table 2 Hydrogenation of olefins using Pd/IL-*f*-MWCNTs **2c** in [bmim][SbF_6] and recycling of **2c**/[bmim][SbF_6][a]



Entry	R^1	R^2	R^3	*t*/min	Runs[b]	Conv.[c] (%)
1	Ph	Ph	H	10	1–10	100
2[d]	Ph	H	H	5	11–20	100
3[d]	Ph	Me	H	10	21–30	100
4[d]	Ph	Me	Me	10	31–40	100
5[d]	4-$MeOC_6H_4$	H	H	10	41–50	100
6[d]	$MeOC_6H_4$	H	H	10	51	65
7	4-$CF_3C_6H_4$	H	H	5	1–10	100
8	4-ClC_6H_4	H	H	10	1–10	100
9	Ph	CO_2Me	H	15	1–10	100
10	4-Pyridyl	H	H	10	1–10	100

[a] Substrate (1.0 mmol) in ^{i}PrOH–[bmim][SbF_6] (8 mL–2 mL) was hydrogenated under 1 atm of H_2 pressure at 20 °C in the presence of **2c** (1 mol% of Pd). [b] The **2c**/[bmim][SbF_6] recovered from previous run was used. [c] Determined by GC. [d] **2c**/[bmim][SbF_6] recovered from previous entry was used, and 0.3 mL of [bmim][SbF_6] was additionally added every 20 times reusing.

ICP-MS analysis of the ^{i}PrOH layer separated from each run indicated no detectable Pd was leached out. Moreover, after 10 times of reuse, the Pd/IL-*f*-MWCNT **2c**/[bmim][SbF_6] recovered was still active, and therefore was subsequently reused for the hydrogenations of four additional substrates (entries 2–5 in Table 2) with total turnover number of 5000. During phase separation, it has been observed that a tiny amount of [bmim][SbF_6] was leached out into ^{i}PrOH layer, and thus, 0.3 mL of [bmim][SbF_6] was additionally added after every 20 times recycling. As shown in Fig. 1(c), although aggregations of Pd particles are observed, much of the Pd nanoparticles still remained on the CNT surfaces after 50 times recycling. However, the catalytic activity was decreased after 50 runs, and the conversion in the 51st run decreased to 65% (entry 6 in Table 2). The TEM image in Fig. 1(d) suggested that the decreased catalytic activity may largely be due to the aggregation of the palladium nanoparticles. Nevertheless it should be noted that, to the best of our knowledge, this is the first demonstration of the combination of Pd nanoparticles supported onto ionic CNTs with ionic liquids to generate a robust recyclable ionic liquid-based catalytic system.

In summary, Pd nanoparticles have been deposited on imidazolium bromide-functionalized ionic MWCNTs through hydrogen reduction of Na_2PdCl_4 in water without the aid of surfactants under extremely mild conditions (1 atm H_2 at 25 °C). Direct anion-exchange of the hydrophilic Br anion with NTf_2 and SbF_6 afforded the hydrophobic Pd/IL-*f*-MWCNTs **2b** and **2c**, respectively, which preferentially dispersed in ionic liquids over water and ^{i}PrOH. A combination of the Pd/IL-*f*-MWCNTs **2c** having SbF_6 anion with an ionic liquid created a new robust recyclable ionic liquid-based catalytic system. This concept will be extrapolated to catalysis in ionic liquids with other ionic CNT-supported nanocatalysts, and investigations along this line are underway.

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‡ For experimental details: see ESI.†

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15 We also attempted to deposit Pd nanoparticles using IL-*f*-MWCNTs having hydrophobic NTf_2 anion. However, as shown in Fig. S1 (ESI†), the palladium nanoparticles are deposited onto the only limited CNTs, which may largely due to the insolubility of the hydrophobic IL-*f*-MWCNTs having NTf_2 anion. However, the size distributions are similar with that of the Pd/IL-*f*-MWCNTs **2a** having hydrophilic Br anion.