DOI: 10.1002/cplu.201200108

Application of a Versatile Nanoparticle Stabilizer in Phase Transfer and Catalysis

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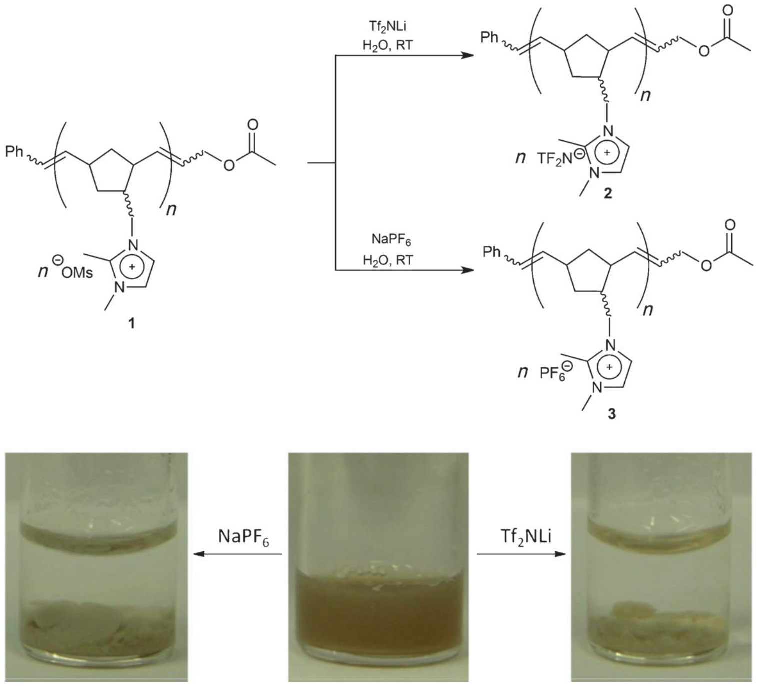
Gold and rhodium nanoparticles stabilized by a cationic polymer can be readily modified by anion exchange to afford nanoparticles that may be dispersed in a wide range of organic solvents and ionic liquids. The catalytic activity of the Rh nanoparticle dispersions have been evaluated in the selective hydrogenation of limonene and the nature of the solvent has been shown to play a critical role.

Introduction

Metallic nanoparticles, NPs, have applications in catalysis, medicine[1,2] and in optical devices.[3] Although mostly used in the solid state, NP dispersions are important in certain applications, and the ability to transfer NPs into different physicochemical environments is consequently a fundamental issue of considerable importance. The most common strategy used to transfer NPs prepared in an aqueous to an organic phase involves coating the NPs with ligands that directly coordinate to the metal surface.[4] However, the strong covalent interaction between the ligands and the NP surface decreases the number of available surface atoms for catalysis and consequently these types of stabilizers are not very suitable for catalytic applications.[5] It would therefore be preferable to find an alternative method to transfer NPs from water to other solvents using a noncovalent NP stabilizer. Polymer stabilizers such as poly(vinyl pyrrolidone), PVP, or poly(vinyl alcohol), PVA, exhibit poor solubility in most organic solvents and ionic liquids (ILs).[6] Recently, it has been shown that NPs coated with a polymer-ionic liquid, P-IL, may be transferred from aqueous solution into ILs.[7] It has also been shown that NPs stabilized by PVP can be prepared in functionalized ILs, but this procedure is limited to very hydrophilic ILs.[8]



Scheme 1. P-IL **1** and the synthesis of **2** and **3** by anion exchange.

Herein, we describe the preparation and characterization of NPs decorated with a P-IL that may be readily switched into a wide range of different solvents. The catalytic properties of some of the resulting NPs were also evaluated and show that the P-IL does not impair the catalytic activity of the NPs.

Results and Discussion

The water-soluble P-IL, poly-(3-((2,4-divinylcyclopentyl)methyl)-1,2-dimethyl-1H-imidazolium methanesulfonate) **1**, was synthesized in high yield from 3-(bicycle[2.2.1]hept-5-en-2-ylmethyl)-1,2-dimethyl-1*H*-imidazolium methanesulfonate through ring-opening metathesis polymerization, ROMP, using commercially available second-generation Grubbs catalyst as described previously (Scheme 1).[9] The solubility properties of **1** are readily modulated by anion exchange, for example exchange of the methanesulfonate anion, MsO$^-$, by bis(trifluoromethylsulfonyl)imide or hexafluorophosphate anions by reaction with an excess amount of LiTf$_2$N or NaPF$_6$ affords the hydrophobic P-ILs **2** and **3**, respectively, that precipitate from aqueous solution. The reactions are fast and quantitative with the immedi-

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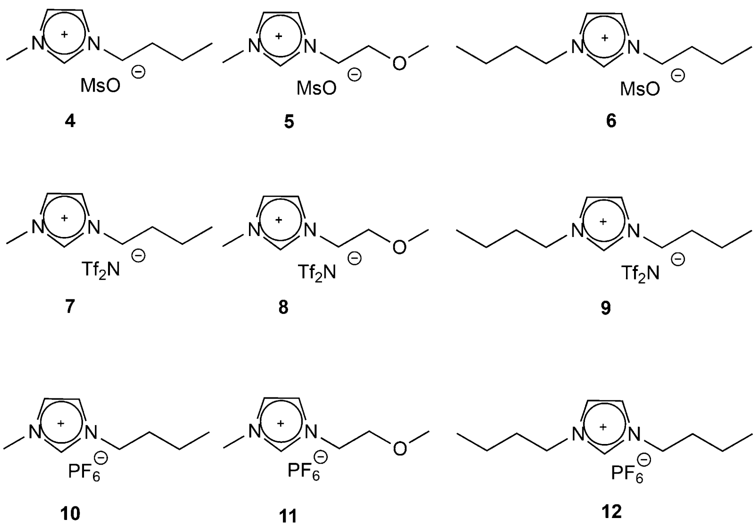
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201200108.

ate precipitation of **2** and **3** from the aqueous solution observed. These precipitates can be subsequently separated, washed, and dried to afford white solids.

The solubility of **1–3** was studied in nine imidazolium-based ILs **4–12** (Scheme 2); **1** is soluble in the hydrophilic ILs **4–6** whereas **2** and **3** are soluble in the hydrophobic ILs **7–9** and **10–12**, respectively. P-IL **1** was used in the synthesis of gold NPs, **NP-1**, using $HAuCl_4$ as a precursor (Au/polymer 1:1) and $NaBH_4$ as the reducing agent (Au/$NaBH_4$ 1:2 w/w). On addition of the $NaBH_4$ to the $HAuCl_4$ solution the color of the solution changes from pale yellow to red indicative of the formation of NPs. Successful NP synthesis was also confirmed by an intense absorption peak at 517 nm in the UV/VIS spectrum corresponding to the gold surface plasmon band[10] and TEM analysis revealed the particle size of the NPs is in the range 3–10 nm (see Figure 1 and the Supporting Information).



Scheme 2. ILs used in solubility studies of **1**–**3**.

Two different approaches were explored to transfer **NP-1** into the hydrophobic ILs **7**–**12**. In one approach the aqueous **NP-1** solution and the appropriate IL are vigorously mixed in the presence of a saturated aqueous solution of $LiTf_2N$ or $NaPF_6$ (see the Supporting Information). Once the methanesulfonate counter anion of the P-IL in **NP-1** is switched to Tf_2N^- in **NP-2**, or PF_6^- in **NP-3**, the NPs rapidly transfer into ILs **8**–**13**. Alternatively, **NP-1** is directly precipitated from the aqueous solution through anion exchange with $LiTf_2N$ or $NaPF_6$ to afford **NP-2** and **NP-3** as solids, respectively. **NP-2** and **NP-3** may be separated by filtration and after drying **NP-2** may be dispersed in ILs **7–9** and **NP-3** in ILs **10–12**. Characterization of the transferred NPs by TEM reveals that the size of the transferred NPs is essentially unchanged (see the Supporting Information).

In aqueous NP solutions stabilized by surfactants such as tetradecyltrimethylammonium bromide, TTAB, the transfer of the NPs into ILs is related to the charge stabilization of surface-adsorbed anions.[5,11] For example, gold and silver NPs stabilized by TTAB can be transferred from water to CH_2Cl_2 containing a small amount of [bmim][PF_6].[12] The [TTA]$^+$ cations on the particle surface interact with the PF_6^- anion of the IL leading to the formation of a hydrophobic ion pair, which changes the surface properties of the NPs and allows their transfer into CH_2Cl_2.

A similar mechanism can be invoked for the transfer of the NPs described here and to confirm whether the exchange reaction is complete X-ray photoelectron spectroscopy (XPS) was used to analyze the NP surfaces. XPS analysis has been successfully employed to analyze the near-surface electronic structure of several ILs, leading to a better understanding of the specific interactions occurring between the cation and anion in imidazolium-based ILs and hence to their physical properties.[13–18] Furthermore, this technique had been widely used to investigate transition-metal NPs in ILs providing deeper insights in the stabilization mode.[19–24]

As expected, the high resolution survey spectra obtained on **NP-2** and **NP-3** contain the characteristic Au 4f doublet (Figure 2). Notably, the spectra also confirm that the anion-exchange process is effectively quantitative, as shown by the appearance of an F 1s peak, an additional N 1s peak for **NP-2**, and additional P 2s and P 2p peaks for **NP-3**. Moreover, no S signal is observed in the **NP-3** sample. Comparisons with literature data confirm the presence of the Tf_2N^-

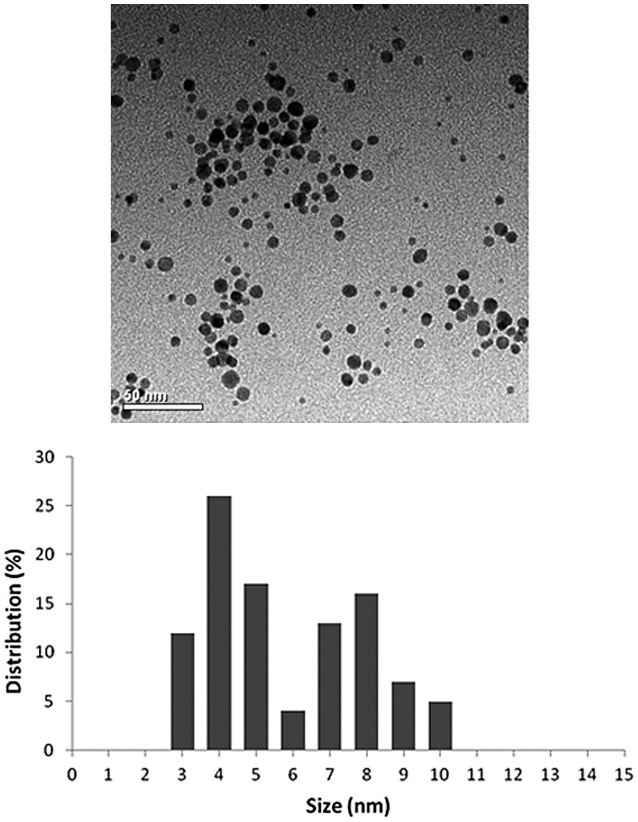


Figure 1. TEM image and size distribution histogram for **NP-1** (scale bar: 50 nm).

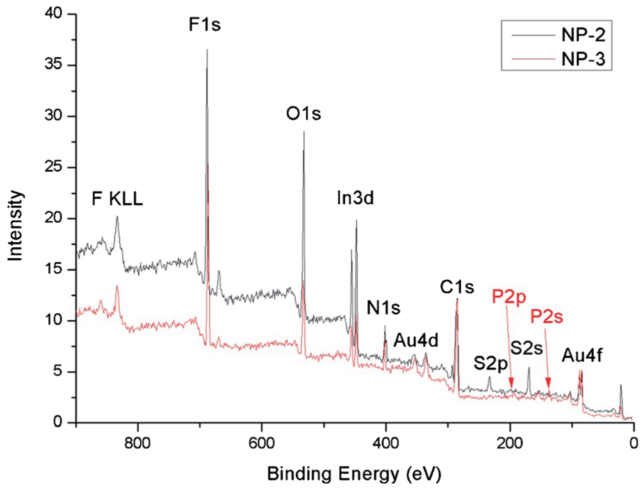


Figure 2. XPS survey spectra for **NP-2** and **NP-3** (the indium 3d doublet originates from the indium foil used to support the samples).

anion in **NP-2**[18] and the PF_6^- anion in **NP-3**.[17,20] The atomic ratio calculated from the high-resolution spectra is very close to the expected stoichiometric atomic ratio (see the Supporting Information).

The stabilization of NPs by **1** is presumably due to a combination of steric and electrostatic effects. Because of the incomplete coordination of the surface atoms and the electrophilic character of the NP surface, the MsO^- anions presumably form a layer immediately adjacent to the NP surface, thus providing electrostatic stabilization.[5] Replacement of **1** with the corresponding monomer in the preparation of NPs resulted in the immediate precipitation of the NPs from the aqueous solution, strongly suggesting that a steric effect is also involved in the stabilization process. After addition of $LiTf_2N$ or $NaPF_6$ to **NP-1**, the cationic chain moieties of **1** rapidly interact with the Tf_2N^- or PF_6^- anions forming the corresponding hydrophobic polymers **2** and **3** and consequently modifying the surface properties of the NPs such that they become hydrophobic. The hydrophilic polymer **1** is not only soluble in water, but it is also soluble in methanol and ethanol, and the hydrophobic polymers **2** and **3** are soluble in acetone, acetonitrile, dimethyl sulfoxide (DMSO), and *N*,*N*-dimethylformamide (DMF). Consequently, **NP-2** and **NP-3** were also redispersed in acetone, acetonitrile, DMF, and DMSO. Analysis by UV/VIS spectroscopy shows an absorption peak at 517 nm for all the samples, indicating the NPs are essentially unchanged and verified by TEM images (see the Supporting Information).

Rhodium NPs stabilized by **1** were synthesized from the reduction of $RhCl_3$ with $NaBH_4$ (Rh/polymer 1:1). On addition of the reducing agent the solution immediately turned from orange to black, indicative of NP formation, **NP-4**. TEM analysis of **NP-4** confirmed the presence of rhodium NPs with a diameter <3 nm (Figure 3).

Transfer of the aqueous **NP-4** solution into ILs **7** and **10** (to afford **NP-5** and **NP-6**) was achieved using the same anion-exchange reaction applied to the gold NPs (see above and the Supporting Information for characterization). XPS analysis confirmed that the anion-exchange reaction went to completion (see the Supporting Information).[17,18,20]

The NPs were evaluated in the hydrogenation of limonene, a cyclic terpene occurring in many essential oils,[25] and a renewable material obtained in large quantities as a by-product in orange juice manufacture. Limonene contains a terminal and an internal C=C bond, and partial hydrogenation (of the terminal C=C bond) provides carvomenthene, which can be converted into *para*-menthane after hydrogenation of the internal C=C bond (Scheme 3). The hydrogenation of related substrates by ruthenium and platinum NPs has been reported previously,[26,27] and reviews describing the application of rhodium NPs in catalysis have been published.[28,29]

The catalytic reactions were performed using a catalyst/substrate ratio of 1:2000 at 80 °C under 40 bar of hydrogen. After 30 minutes with the **NP-4** solution carvomenthene is selectively obtained in 35 %. A longer reaction time increased the conversion to 74 %, and provided carvomenthene in 71 % (Table 1, entries 1 and 2). The selective hydrogenation of limonene with rhodium complexes in aqueous solution has been reported before,[30] but this appears the first report of aqueous rhodium

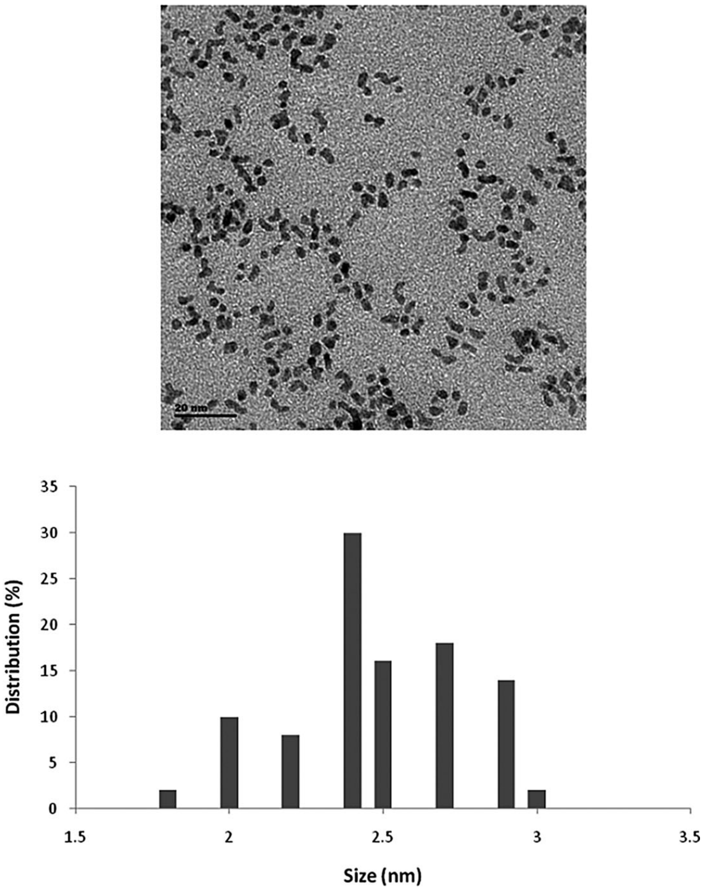
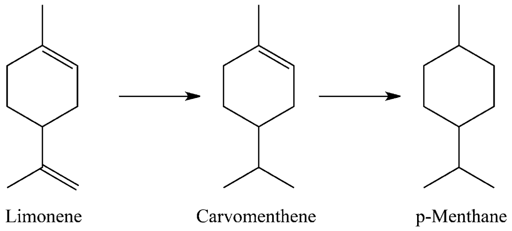


Figure 3. TEM image and size distribution histogram for **NP-4** (scale bar: 20 nm).



Scheme 3. Hydrogenation of limonene.

Table 1. Hydrogenation reactions using **NP-4–NP-6.**[a]

Entry	Catalyst	Solvent	Substr.	Conv. [%][b]	Product	Selec. [%]	Yield [%][c]
1	NP-4	water		35		100	35
2[d]	NP-4	water		74		96	71
						4	3
3	NP-5	IL 7		76		100	76
4	NP-6	IL 10		>99		75	74
						25	25

[a] Hydrogenation reactions performed at 40 bar of hydrogen, 80 °C for 30 min. [b] Determined by NMR spectroscopy. [c] Yield of isolated product.[d] 60 min reaction time.

NPs catalyzing this reaction. In ILs the rate of reaction and the selectivity both increase—**NP-5** and **NP-6** are extremely active and the selectivity toward the partially reduced product is very high (Table 1, entries 3 and 4).

Indeed, in recent years ionic liquids (ILs) have received increasing attention as reaction media because of their favorable properties such as high polarity, negligible vapor pressure, high ionic conductivity, high thermal stability, and low interfacial surface tension.[31–38] The latter feature makes ILs good media for NP synthesis because a low interfacial surface tension results in high nucleation rates, allowing the formation of very small particles which undergo weak Ostwald ripening.[19,39–42] Moreover, ILs have also been shown to influence the selectivity of numerous reactions.[43,44]

Conclusion

The solubility properties of the hydrophilic ionic polymer **1** described here are readily modulated by exchanging the counter ion allowing NPs to be dispersed in a wide range of solvents. XPS analysis demonstrates that efficient and quantitative anion exchange takes place. Because the polymer stabilizer interacts with the NP surface mostly through noncovalent interactions (note that the oxygen atoms can potentially coordinate) the catalytic activity of the NPs is not suppressed and excellent activities can be obtained. Moreover, when dispersed in ILs the selectivity of catalytic reactions can be modified, and thus, the appropriate combination of NP stabilizer and dispersion solvent is vital to afford nanocatalysts with optimum properties.

Experimental Section

Reagents were purchased from Aldrich or Acros and used as received. Water was double distilled using a Water purification Milli-Q Gradient, Elix 3 with 30 L reservoir. Membrane dialysis tubes (MWCO 1000 and 2000) were purchased from Spectrum Laboratories. P-IL **1**[9] and ILs **4–6**,[45,46] **7–9**[47–49], and **10–12**[48,50,51] were synthesized according to literature procedures. The UV/VIS spectra were recorded on a Jasco V-550 spectrometer. The NMR spectra were measured on a Bruker DMX 400 using $SiMe_4$ as an external standard at 20 °C. The TEM images were obtained on a PHILIPS/FEI CM20 transmission electron microscope (200 KeV) using Quantifoil Carbon film Cu grids on 200 mesh as specimen supports. The size distribution was estimated from 200 particles. The XPS data were obtained on an Axis Ultra instrument (Kratos Analytical) under ultra-high vacuum ($<10^{-8}$ Torr), using a monochromatic $Al_{K\alpha}$ X-ray source (1486.6 eV). The source power was maintained at 150 W and the emitted photoelectrons were sampled from a 700×350 μm^2 area with a 90° photoelectron take-off angle. The analyzer pass energy was 80 eV for survey spectra and 40 eV for high-resolution spectra. The adventitious carbon 1s peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. Both curve fitting of the spectra and quantification were performed with the CasaXPS software, using relative sensitivity factors given by Kratos.

General procedure for the synthesis of 2 and 3

To **1** (10 mg, 0.033 mmol of monomer units) dissolved in double-distilled water (0.5 mL), $LiTf_2N$ (29 mg, 0.1 mmol) or $NaPF_6$ (17 mg, 0.1 mmol) was added with the immediate precipitation of an off-white solid observed. The solution was stirred at RT for 1 min, centrifuged (30 s, 16000 rpm), and the supernatant water removed. Double-distilled water (1 mL) was added, the solution stirred at RT for 1 min, centrifuged (30 s, 16000 rpm), and the water removed. This procedure was repeated four times and poly-(3-((2,4-divinylcyclopentyl)methyl)-1,2-dimethyl-1H-imidazolium bis-(trifluoromethylsulfonyl)-imide) **2** or poly-(3-((2,4-divinylcyclopentyl)methyl)-1,2-dimethyl-1H-imidazolium hexafluorophosphate **3** were dried under vacuum for 12 h. ^1H NMR (25 °C, 400.1 MHz, [D_6]acetone) for **2**: $\delta=$ 7.56, 5.64, 5.52, 5.43, 5.25, 4.31, 4.22, 4.08, 3.91, 3.43, 3.24, 2.96, 2.86, 2.72, 1.85, 1.75, 1.30 ppm; for **3**: $\delta=$7.46, 5.61, 5.50, 5.42, 5.24, 4.22, 4.16, 4.02, 3.84, 3.35, 3.20, 3.06, 2.83, 2.67, 2.29, 1.79, 1.53, 1.28 ppm.

Synthesis of NP-1

An aqueous solution of $HAuCl_4$ (1 mL, 1 mg mL^{-1}, 2.5 μmol of Au), an aqueous solution of **1** (13 μL, 0.1905 M, 2.5 μmol), and water (3 mL) were added together and stirred for 2 min at RT. After this time an aqueous solution of $NaBH_4$ (1 mL, 0.5 mg mL^{-1}, 12.5 μmol) was rapidly added and the color of the reaction mixture immediately turned from pale yellow to red. The solution was stirred for additional 30 min at RT and then dialyzed for 24 h (MWCO: 1000). The solution was stored at 4 °C.

General procedure for the transfer of NP-1 from aqueous solution to ILs 7–12

Method 1: The hydrophobic IL **7**–**12** (1 mL), **NP-1** solution (0.5 μmol of Au, 2.6 μL of **1**, 1 mL) and an aqueous solution of $LiTf_2N$ (0.1 mmol, 287 mg, 1 mL) or $NaPF_6$ (1 mmol, 168 mg, 1 mL) were stirred for 1 min. The NPs immediately transferred from the aqueous phase to the IL phase. The solution was stirred for additional 5 min, then the aqueous layer was removed, and the IL layer was washed with water (5×2 mL) and dried under vacuum at 80 °C for 10 h.

Method 2: The **NP-1** solution (0.5 μmol of Au, 2.6 μL of **1**, 1 mL) and an aqueous solution of $LiTf_2N$ (30 μmol, 9 mg, 0.1 mL) or $NaPF_6$ (30 μmol, 5 mg, 0.1 mL) were stirred for 1 min; the immediate precipitation of the NPs was observed, affording **NP-2** and **NP-3**, respectively. The solution was filtered and the precipitate was washed with water (5 mL). The NPs were dried under vacuum for 24 h and then re-dispersed in the appropriate IL, **7–9** for **NP-2** and **10**–**12** for **NP-3**.

Synthesis of NP-4–NP-6

An aqueous solution of $RhCl_3$ (1 mL, 1 mg mL^{-1}, 5.06 μmol of Rh), an aqueous solution of **1** (27 μL, 0.1905 M, 5.0 μmol of monomeric unit), and water (4.0 mL) were stirred together for 2 min at RT. After this time $NaBH_4$ (2.0 mg, 54 μmol) was rapidly added to the solution and the color immediately changed from orange to black. The solution was stirred for 2 h at RT and then dialyzed for 24 h (MWCO: 1000). The black solution was stored at 4 °C. The NPs were transferred into the ILs in the same way as that described above for the gold NPs.

General procedure for the preparation of TEM samples

The NP solutions (0.1 mL) were diluted in water or acetone (0.5 mL) and ultrasonicated at 20 °C for 5 min. One drop of the solution was deposited on a carbon film copper grid (200 mesh) and dried under vacuum for 24 h prior to analysis (2 h for **NP-1**).

Catalytic studies

Catalytic experiments were performed using a home-built multicell autoclave containing an internal temperature probe. Each glass reaction vessel was loaded with the NP solution (1 mL) and the substrate (1 mmol, 10 mmol, or 81 mmol) and then placed inside the autoclave and sealed. After flushing with H_2 (5×10 bar), the autoclave was heated to 80 °C under H_2 (10 bar) and maintained at 40 bar for the appropriate time (see Table S2). The autoclave was then cooled to RT using an external water-cooling jacket and the pressure released. Conversions were determined by ^1H NMR spectroscopy and GC-MS analysis.

Acknowledgements

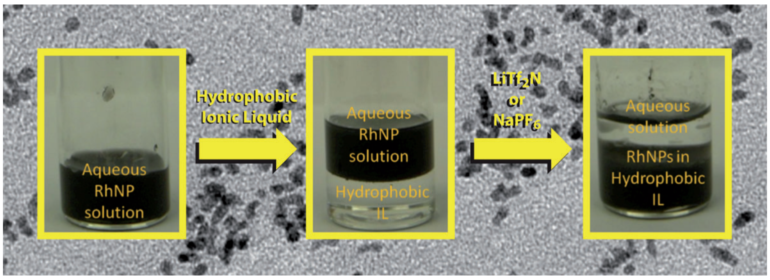
We thank the EPFL and Swiss National Science Foundation for financial support. We also thank Prof. Philippe André Buffat, Dr. Marco Cantoni and the staff at the Interdisciplinary Centre for Electron Microscopy (CIME) at the EPFL for assistance and useful discussions regarding TEM analysis.

Keywords: heterogeneous catalysis · hydrogenation · ionic liquids · gold · nanoparticles · rhodium

[1] *Microspheres, Microcapsules and Liposomes: Smart Nanoparticles in Nanomedicine, Vol. 8* (Eds.: R. Arshady, K. Kono), Kentus Books, London, **2006**.
[2] *Cancer Nanotechnology: Methods And Protocols in Methods in Molecular Biology, Vol. 624* (Eds.: S. R. Grobmyer, B. M. Moudgil), Springer, Berlin, **2010**.
[3] *Colloidal Gold: Principles, Methods, and Applications, Vol. 1* (Ed.: M. A. Hayat), Academic Press, San Diego, **1989**.
[4] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* **1994**, 801.
[5] L. S. Ott, R. G. Finke, *Coord. Chem. Rev.* **2007**, *251*, 1075.
[6] N. Yan, J.-G. Zhang, Y. Tong, S. Yao, C. Xiao, Z. Li, Y. Kou, *Chem. Commun.* **2009**, 4423.
[7] D. B. Zhao, Z. F. Fei, W. H. Ang, P. J. Dyson, *Small* **2006**, *2*, 879.
[8] X. Yang, N. Yan, Z. F. Fei, R. M. Crespo-Quesada, G. Laurenczy, L. Kiwi-Minsker, Y. Kou, Y. D. Li, P. J. Dyson, *Inorg. Chem.* **2008**, *47*, 7444.
[9] I. Biondi, G. Laurenczy, P. J. Dyson, *Inorg. Chem.* **2011**, *50*, 8038.
[10] M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
[11] S. Özkar, R. G. Finke, *J. Am. Chem. Soc.* **2002**, *124*, 5796.
[12] C. Y. Lee, C. H. Huang, G. T. Wei, *Colloids Surf. A* **2010**, *367*, 24.
[13] T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, R. Wolfel, P. S. Schulz, P. Wasserscheid, H. Weber, J. Thar, B. Kirchner, F. Maier, H. P. Steinruck, *Chem. Eur. J.* **2010**, *16*, 9018.
[14] O. Höfft, S. Bahr, M. Himmerlich, S. Krischok, J. A. Schaefer, V. Kempter, *Langmuir* **2006**, *22*, 7120.
[15] T. Ikari, A. Keppler, M. Reinmoeller, W. J. D. Beenken, S. Krischok, M. Marschewski, W. Maus-Friedrichs, O. Hofft, F. Endres, *e-J. Surf. Sci. Nanotechnol.* **2010**, *8*, 241.
[16] A. Keppler, M. Himmerlich, T. Ikari, M. Marschewski, E. Pachomow, O. Hoefft, W. Maus-Friedrichs, F. Endres, S. Krischok, *Phys. Chem. Chem. Phys.* **2011**, *13*, 1174.
[17] C. Kolbeck, T. Cremer, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid, F. Maier, H. P. Steinruck, *J. Phys. Chem. B* **2009**, *113*, 8682.
[18] C. Kolbeck, M. Killian, F. Maier, N. Paape, P. Wasserscheid, H. P. Steinruck, *Langmuir* **2008**, *24*, 9500.
[19] G. S. Fonseca, G. Machado, S. R. Teixeira, G. H. Fecher, J. Morais, M. C. M. Alves, J. Dupont, *J. Colloid Interface Sci.* **2006**, *301*, 193.
[20] C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos, J. Dupont, *J. Phys. Chem. B* **2006**, *110*, 13011.
[21] F. Bernardi, J. D. Scholten, G. H. Fecher, J. Dupont, J. Morais, *Chem. Phys. Lett.* **2009**, *479*, 113.
[22] M. Shigeyasu, H. Murayama, H. Tanaka, *Chem. Phys. Lett.* **2008**, *463*, 373.
[23] H. Zhang, H. Cui, *Langmuir* **2009**, *25*, 2604.
[24] Z. Yinghuai, E. Widjaja, S. L. P. Sia, W. Zhan, K. Carpenter, J. A. Maguire, N. S. Hosmane, M. F. Hawthorne, *J. Am. Chem. Soc.* **2007**, *129*, 6507.
[25] K. Bauer, D. Garbe, H. Surburg, *Common Fragrance and Flavor Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, **2006**, pp. 1–5.
[26] W. Yu, M. Liu, H. Liu, X. An, Z. Liu, X. Ma, *J. Mol. Catal. A* **1999**, *142*, 201.
[27] W. Yu, M. Liu, H. Liu, X. Ma, Z. Liu, *J. Colloid Interface Sci.* **1998**, *208*, 439.
[28] A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757.
[29] Y. Yuan, N. Yan, P. J. Dyson, *Catal.* **2012**, *2*, 1057.
[30] R. Grzybek, *React. Kinet. Catal. Lett.* **1996**, *58*, 315.
[31] P. Dash, N. A. Dehm, R. W. J. Scott, *J. Mol. Catal. A* **2008**, *286*, 114.
[32] T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459.
[33] C. Daguenet, P. J. Dyson, *Organometallics* **2004**, *23*, 6080.
[34] P. J. Dyson, *Chimia* **2005**, *59*, 66.

[35] P. J. Dyson, T. J. Geldbach, *Electrochem. Soc. Interface* **2007**, *16*, 50.
[36] Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122.
[37] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876.
[38] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, G. Laurenczy, P. J. Dyson, *Helv. Chim. Acta* **2005**, *88*, 665.
[39] M. Antonietti, D. B. Kuang, B. Smarsly, Z. Yong, *Angew. Chem.* **2004**, *116*, 5096; *Angew. Chem. Int. Ed.* **2004**, *43*, 4988.
[40] G. Machado, J. D. Scholten, T. da Vargas, S. R. Teixeira, L. H. Ronchi, J. Dupont, *Int. J. Nanotechnol.* **2007**, *4*, 541.
[41] J. Dupont, D. d O. Silva, *Nanopart. Catal.* **2008**, 195.
[42] P. Migowski, J. Dupont, *Chem. Eur. J.* **2006**, *13*, 32.
[43] Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem.* **1995**, *107*, 2941; *Angew. Chem. Int. Ed. Engl.* **1996**, *34*, 2698.
[44] E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. J. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner, J. Dupont, *Chem. Eur. J.* **2004**, *10*, 3734.
[45] C. C. Cassol, G. Ebeling, B. Ferrera, J. Dupont, *Adv. Synth. Catal.* **2006**, *348*, 243.
[46] M. C. Uzagare, Y. S. Sanghvi, M. M. Salunkhe, *Green Chem.* **2003**, *5*, 370.
[47] P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.
[48] Q. B. Liu, M. H. A. Janssen, F. van Rantwijk, R. A. Sheldon, *Green Chem.* **2005**, *7*, 39.
[49] D. S. Newman, D. Y. Chen, X. Zeng, R. X. Ren, *Proc. Electrochem. Soc.* **2006**, *2004–24*, 426.
[50] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.
[51] S. S. Palimkar, S. A. Siddiqui, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *J. Org. Chem.* **2003**, *68*, 9371.

Received: May 7, 2012



Polymer coated: Metal nanoparticles coated with an ionic polymer may be readily dispersed in a wide range of solvents including ionic liquids (see figure). In catalysis the nature of the solvent strongly influences the outcome of the reaction and consequently the solvent can be used to fine-tune the surface features of the nanoparticles and their corresponding catalytic properties.

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Application of a Versatile Nanoparticle Stabilizer in Phase Transfer and Catalysis