

# Oleic acid as the capping agent in the synthesis of noble metal nanoparticles in imidazolium-based ionic liquids†

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This paper reports the synthesis and automatic separation of solvent dispersible silver and platinum nanoparticles in 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ([BMIM][Tf<sub>2</sub>N]) ionic liquid (IL) using oleic acid as the major capping agent.

Recent results suggest that ILs can be the preferable solvents in the synthesis and modification of nanostructured materials because of their unique properties, such as extended hydrogen bonding.<sup>1</sup> They have been used in making mesoporous metal oxides, polyaniline nanoparticles, morphologically interesting nanoflakes and nanosheets, and in controlling the composition of PtCo alloys.<sup>2–8</sup> Imidazolium-based ionic liquids have also been used in the surface modification of carbon nanotubes.<sup>9</sup> While ionic liquids have been used in the synthesis of nanostructured materials, identification of appropriate surface capping agents in these new solvents remains an important issue. Several currently used capping agents tend to cause irreversible aggregation of nanoparticles.<sup>8,10</sup> This phenomenon has been successfully applied in making mesoporous titania.<sup>2</sup> Amphiphilic molecules have been used for the synthesis of uniform nanoparticles in non-hydrolytic systems, as they not only govern the size and shape but also the stability of resulting particles. Long alkane chain carboxylic acids and amines have been proven very effective for synthesis conducted in various conventional non-hydrolytic solvents.<sup>11,12</sup> This work shows some unique aspects of using oleic acid as capping agent when [BMIM][Tf<sub>2</sub>N] IL is used as solvent. It can not only stabilize the metal nanoparticles formed but also lead to a settling process which the resultant nanoparticles automatically separate out from the IL reaction mixtures. Unlike most of the previously reported colloidal nanostructures made in ILs, these metal nanoparticles can be readily dispersed in conventional organic solvents and the synthetic approach can potentially facilitate the development of continuous production of high quality nanoparticles.

Silver is chosen in part because of its size-dependent surface plasmon and other unique properties, which have found increasingly broad applications.<sup>13–15</sup> Oleic acid-capped Ag nanoparticles also possess an interesting surface mediated phase transfer property.<sup>16</sup> Most recently, oleic acid-capped Ag nanoparticles have been found to be an excellent candidate as ink for printable Ohmic contacts for high-mobility organic thin-film transistors

(TFT).<sup>17</sup> In this paper, we used silver trifluoroacetate as precursor which can be readily reduced to form Ag nanoparticles.<sup>17–20</sup> Although this precursor had a low solubility in [BMIM][Tf<sub>2</sub>N] at room temperature, the mixture of silver trifluoroacetate, oleic acid, and [BMIM][Tf<sub>2</sub>N] formed a homogenous and light yellowish solution at ~150 °C.

The reaction was conducted at either 160 or 200 °C. Under these conditions, the product could settle out from [BMIM][Tf<sub>2</sub>N] ILs after about 20 min. Upon the completion of the reaction, the color of the mixture turned into transparent yellow. The ionic liquid could be easily removed from the reaction vessel directly by a pipette, leaving behind the black solid stuck to the wall of the flask. This product could then be dispersed readily in hexane.† Fig. 1 shows a photograph of two vials that contained the [BMIM][Tf<sub>2</sub>N] IL mixture after the reaction and the hexane suspension of nanoparticles. The suspension contained highly concentrated nanoparticles, which could be further cleaned and separated using ethanol as anti-solvent.

Fig. 2 shows a TEM image of the nanoparticles made at silver trifluoroacetate/oleic acid molar ratio of 1 : 6. These particles had an average diameter of  $4.5 \pm 0.4$  nm. Unlike the nanoparticles made in ILs previously reported, an extended ordered hexagonal arrangement was observed, suggesting monodispersity in size and excellent solvent dispersibility of these nanoparticles. The average size of the nanoparticles increased to  $5.1 \pm 0.7$  nm if the precursor concentration was double while all other conditions were kept the same. The resultant particles however had a standard deviation of about 14% in size, which was broader than that for 4.5 nm particles, Fig. S1.† The silver trifluoroacetate/oleic acid molar ratio played an important role in determining the particle size and size distribution. The yield of silver nanoparticles was also affected by

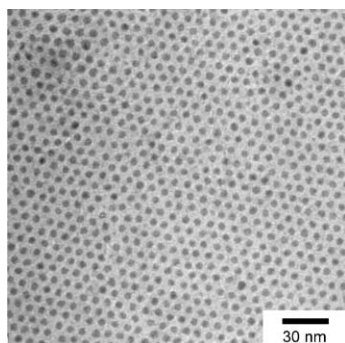


**Fig. 1** Photograph of the [BMIM][Tf<sub>2</sub>N] IL mixture after the reaction (left vial) and the dispersion of nanoparticles in hexane (right vial). The reaction was conducted using silver trifluoroacetate and oleic acid at 200 °C. The reaction time was 40 min.

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**Fig. 2** TEM images of silver nanoparticles made at silver trifluoroacetate/oleic acid molar ratio of 1 : 6.

this molar ratio. This value increased from about 54% to 70%, when the precursor/surfactant ratio changed from 1 : 3 to 1 : 6, Table 1. We noted that some insoluble yellowish solid could be found at the bottom of the hexane suspension. TEM and powder X-ray diffraction (PXRD) analyses indicated that this solid could be the products of the intermediates formed from oleic acid and the silver precursor. It appears that oleic acid was essential in this reaction. It not only stabilized the resulting metal nanoparticles, but also facilitated the settling of nanoparticles from the IL reaction mixture and ensured an excellent dispersity of nanoparticles in conventional organic solvents, such as hexane. This auto-separation phenomenon was most likely due to the changing interactions between ionic liquid and capped nanoparticles.

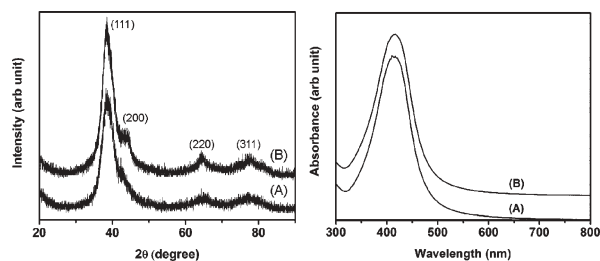
Fig. 3 shows the PXRD patterns and UV-vis absorption spectra of 4.5 and 5.1 nm particles obtained at 200 °C. These two samples had the similar X-ray diffraction patterns, which could be assigned to metal silver in *Fm3m* space group, [ICDD PDF: 04-0783]. They had the maximum absorbance centered at ~416 nm, which could be attributed to the surface plasmon resonance of the silver nanoparticles. Their full width at half maximum (FWHM) was ~84 nm. The UV-vis absorption appeared to be not sensitive enough to detect the difference in size and size distribution between these two types of samples.

The particles formed at 160 °C became less uniform in size in comparison with those formed at 200 °C, Fig. S2.† The average diameters were  $4.1 \pm 0.5$  nm for particles made at the precursor/surfactant molar ratio of 1 : 6, and  $6.1 \pm 0.8$  nm for those with this ratio of 1 : 3. These values represented a standard deviation of

**Table 1** Comparison of average diameter and yield of the silver nanoparticles made at different temperatures and precursor/surfactant molar ratios.

	T/°C	Molar ratio	Average diameter/nm	Yield <sup>a</sup> (%)
1	200	1 : 6	$4.5 \pm 0.4$	69.9
2	200	1 : 3	$5.1 \pm 0.7$	53.9
3	160	1 : 6	$4.1 \pm 0.5$	21.2
4	160	1 : 3	$6.1 \pm 0.8$	17.7

<sup>a</sup> The yield was estimated based on silver. After the reaction, the particles were extracted using a designed amount of hexane. About 100  $\mu$ L of the extracted product was transferred into an alumina pan in a thermogravimetric analyzer (TGA). The stable value at ambient room temperature was the weight of particles with surfactants. The residue weight obtained after heating the specimen to 800 °C under N<sub>2</sub> flow was used to calculate the amount of silver nanoparticles in the sample, and subsequently the yield of silver nanoparticles.



**Fig. 3** PXRD patterns (left panel) and UV-vis spectra (right panel) of (A) 5.1 and (B) 4.5 nm silver nanoparticles, respectively.

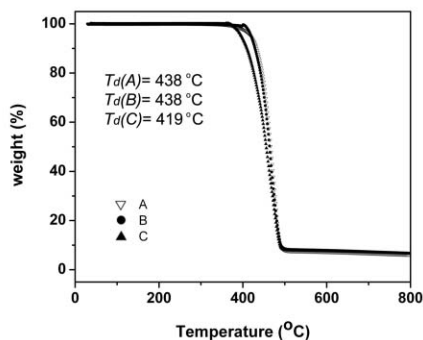
12–13%. The overall yields of the nanoparticles were substantially lower for those reactions conducted at 160 °C. Slow nucleation rate and the inefficiency in size focusing of nanoparticles at the relatively low temperature could be the main reasons.<sup>11</sup> Table 1 summarizes the size and yield of the nanoparticles obtained under the above conditions. The temperature threshold for the formation of relatively uniform Ag nanoparticles in [BMIM][Tf<sub>2</sub>N] was around 160 °C, while the acceptable surfactant/precursor molar ratio was around three or above.

The size and size distribution of silver particle formed in the [BMIM][Tf<sub>2</sub>N] reaction mixtures were also affected by the reaction time. The diameters of the Ag particles formed were  $4.8 \pm 1.1$  nm for reaction time of 2 h at 160 °C, Fig. S3.† This value decreased slightly to  $4.4 \pm 1.0$  nm at 200 °C. The long reaction time resulted in the broadening of particle size distribution.

The IL mixtures after reaction were studied using both UV-vis spectrometer and TGA based on the 5.1 nm silver nanoparticles at 200 °C. No absorption peak was observed between 400 and 800 nm for the mixture after the synthesis. This observation indicated that the Ag nanoparticles settled out completely from the IL mixtures. The change in the interaction between this ionic liquid and the nanoparticles during the growth could be important for the settling process.<sup>16</sup> The silver precursors could form complexes with oleic acid through the carboxyl acid groups and gradually grew into clusters.<sup>20</sup> As these clusters were covered by the alkyl chains pointing toward surrounding IL environment, they exhibited a dramatically different solubility (or dispersity) from the molecular precursors and were eventually driven out from the ionic liquid upon reaching the critical sizes. Based on the TGA data, the onset temperature of the decomposition of this IL mixture was 438 °C, Fig. 4, which was the same as that for pure [BMIM][Tf<sub>2</sub>N]. This result suggests that the IL kept its thermal stability after the reaction.

A control experiment with no addition of oleic acid was conducted at 200 °C and a concentration of silver precursor of 0.06 M. In this case, the settling of particles did not occur. The silver species remained in the IL reaction mixtures and could not be extracted out from the mixture of [BMIM][Tf<sub>2</sub>N] IL using hexane. This control study further indicated the dual functions of oleic acid.

Besides the single-molecule precursor approach, the reduction of a metal salt by a reducing agent was also examined. The latter route can have broad ramifications because of the easy access to various metal salts. Platinum was chosen for this demonstration, in part because of its excellent catalytic property in the hydrogenation and other reactions.<sup>21</sup>

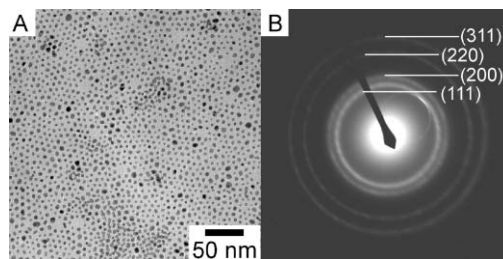


**Fig. 4** TGA traces of (A) pure [BMIM][Tf<sub>2</sub>N], the [BMIM][Tf<sub>2</sub>N] IL mixture after the syntheses (B) with and (C) without the presence of oleic acid.  $T_d$ : temperature onset for the thermal decomposition of various IL mixtures.

Platinum acetylacetonate (Pt(acac)<sub>2</sub>) was used as the Pt precursor and 1,2-hexandecandiol was the reduction agent. Besides oleic acid, oleylamine was used as the coordinate capping agent, as it has been shown in previous studies that long chain amine can help to stabilize Pt colloidal nanoparticles.<sup>12</sup> The reaction was conducted in [BMIM][Tf<sub>2</sub>N] IL at 230 °C following a similar procedure. The color of the reaction mixture turned bright yellow after Pt(acac)<sub>2</sub> and 1,2-hexandecandiol dissolved at about 75 °C. The color of this mixture subsequently turned brown at about 200 °C and became black when the reaction temperature reached 230 °C.

Fig. 5A shows a representative TEM image of the Pt nanoparticles obtained. The nanoparticles could also settle out from the IL during the reaction. The particles were found having an average diameter of  $4.5 \pm 0.8$  nm with a standard size deviation of less than 20%. The selected area electron diffraction (SAED) pattern indicated these particles were face centered cubic Pt metal (*Fm3m*), Fig. 5B. The combination of oleic acid and oleylamine was necessary in this synthesis. The reaction without oleic acid resulted in large faceted and irregularly shaped crystals. When only oleic acid was used, aggregates consisting of small particles with diameter of  $\sim 5$  nm were obtained. These aggregates could not be dispersed readily as individual nanoparticles using hexane or other common solvents.

In short, noble metal nanoparticles with relatively narrow size distributions can be obtained using an imidazolium-based ionic liquid as solvent. The combination of oleic acid with [BMIM][Tf<sub>2</sub>N] ionic liquid leads to an automatic separation of colloidal metal nanoparticles from the IL mixtures through a settling process. No obvious degradation in IL has been observed based on the onset of the decomposition temperature. Our results



**Fig. 5** (A) TEM image and (B) SAED of platinum nanoparticles.

show the potentials of using ionic liquids in the development of a recyclable method for making metal nanoparticles.

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## Notes and references

- (a) M. Antonietti, D. B. Kuang, B. Smarsly and Z. Yong, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988; (b) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156; (c) G. A. Baker, S. N. Baker, S. Pandey and F. V. Bright, *Analyst*, 2005, **130**, 800.
- Y. Zhou and M. Antonietti, *J. Am. Chem. Soc.*, 2003, **125**, 14960.
- H. X. Gao, T. Jiang, B. X. Han, Y. Wang, J. M. Du, Z. M. Liu and J. L. Zhang, *Polymer*, 2004, **45**, 3017.
- H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, **126**, 3026.
- A. Taubert, *Angew. Chem., Int. Ed.*, 2004, **43**, 5380.
- Y. J. Zhu, W. W. Wang, R. J. Qi and X. L. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 1410.
- Z. H. Li, Z. M. Liu, J. L. Zhang, B. X. Han, J. M. Du, Y. N. Gao and T. Jiang, *J. Phys. Chem. B*, 2005, **109**, 14445.
- Y. Wang and H. Yang, *J. Am. Chem. Soc.*, 2005, **127**, 5316.
- M. J. Park, J. K. Lee, B. S. Lee, Y.-W. Lee, I. S. Choi and S.-g. Lee, *Chem. Mater.*, 2006, **18**, 1546.
- C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke and J. Dupont, *J. Am. Chem. Soc.*, 2005, **127**, 3298.
- Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664.
- S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- Y. G. Sun, B. Mayers, T. Herricks and Y. N. Xia, *Nano Lett.*, 2003, **3**, 955.
- Y. N. Xia and N. J. Halas, *MRS Bull.*, 2005, **30**, 338.
- P. Raveendran, J. Fu and S. L. Wallen, *Green Chem.*, 2006, **8**, 34.
- T. Bala, A. Swami, B. L. V. Prasad and M. Sastry, *J. Colloid Interface Sci.*, 2005, **283**, 422.
- Y. Wu, Y. Li and B. S. Ong, *J. Am. Chem. Soc.*, 2006, **128**, 4202.
- X. Z. Lin, X. W. Teng and H. Yang, *Langmuir*, 2003, **19**, 10081.
- X. Z. Lin, A. D. Terepka and H. Yang, *Nano Lett.*, 2004, **4**, 2227.
- P. J. Cowdery-Corvan and D. R. Whitcomb, in *Handbook of Imaging Materials*, ed. A. S. Diamond and D. S. Weiss, Dekker Inc., New York, 2002.
- A. Wieckowski, E. R. Savinova and C. G. Vayenas, *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Marcel Dekker, Inc., New York, 2003.