

## First Correlation of Nanoparticle Size-Dependent Formation with the Ionic Liquid Anion Molecular Volume

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Stable silver nanoparticles are obtained reproducibly by hydrogen reduction of different inorganic precursors from Ag<sup>+</sup>X<sup>-</sup> salts (X = BF<sub>4</sub>, PF<sub>6</sub>, OTf) dissolved in the ionic liquids BMim<sup>+</sup>BF<sub>4</sub><sup>-</sup>, BMim<sup>+</sup>PF<sub>6</sub><sup>-</sup>, BMim<sup>+</sup>OTf<sup>-</sup>, or BtMA<sup>+</sup>NTf<sub>2</sub><sup>-</sup> [BMim<sup>+</sup> = *n*-butylmethylimidazolium, BtMA<sup>+</sup> = *n*-butyltrimethylammonium, NTf<sub>2</sub><sup>-</sup> = N(O<sub>2</sub>SCF<sub>3</sub>)<sub>2</sub>, and OTf<sup>-</sup> = O<sub>3</sub>SCF<sub>3</sub>] in the presence of *n*-butylimidazole (Bim) as the scavenger for the HX acid byproduct and with a narrow size distribution in the diameter range of 2.8–26.1 nm, which increases linearly with the molecular volume of the ionic liquid anion (transmission electron microscopy characterization).

Transition-metal nanoparticles are of great interest in several areas of science, including catalysis<sup>1</sup> and chemical sensors.<sup>2</sup> Silver nanoparticles (AgNPs) supported on Al<sub>2</sub>O<sub>3</sub><sup>3</sup> or titanium silicate zeolite<sup>4</sup> are of industrial importance for the gas-phase oxidation of olefins with molecular oxygen from air to their epoxides. The controlled and reproducible synthesis of defined and stable metal nanoparticles (MNPs) is of crucial importance.<sup>5</sup>

Ionic liquids (ILs) seem to be ideal for the stabilization of MNPs. The intrinsic ionic charge, high polarity, high dielectric constant, and supramolecular network<sup>6</sup> of ILs provide an electrostatic protection according to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory<sup>7</sup> in the form of a “protective shell” for MNPs, so that no extra

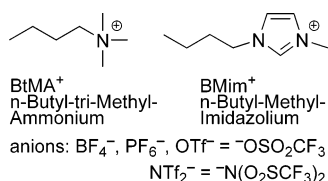
stabilizing molecules are needed.<sup>8</sup> The reduction of metal salts by hydrogen gas,<sup>9</sup> photochemical reduction, or electroreduction<sup>10</sup> can be used for MNP synthesis. Iridium nanoparticles were obtained via rapid reduction of [IrCl(cod)]<sub>2</sub> (cod = 1,5-cyclooctadiene) in BMim<sup>+</sup>PF<sub>6</sub><sup>-</sup> with hydrogen at 75 °C. A similar procedure has also been applied to prepare rhodium,<sup>6</sup> ruthenium,<sup>11,12</sup> and nickel<sup>13</sup> nanoparticles.

An intrinsic problem of MNP synthesis from MX<sub>n</sub> salts with hydrogen is the formation of strongly acidic HX (X = Cl, NO<sub>3</sub>, BF<sub>4</sub>, PF<sub>6</sub>, O<sub>3</sub>SCF<sub>3</sub>). An acidic reaction medium destabilizes MNPs and leads to their clustering.<sup>14</sup> N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-Tetramethylnaphthalene-1,8-diamine was present as a proton

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**Scheme 1** ILs Used

sponge in the preparation of iridium nanoparticles via reduction of [Ir(cod)(CH<sub>3</sub>CN)<sub>2</sub>][BF<sub>4</sub>] under hydrogen.<sup>15</sup>

Here we report the preparation of AgNPs through the reduction of silver salts, AgX, by hydrogen in monophasic ILs and the immediate neutralization of the HX formed through the presence of an imidazole scavenger. The imidazole and anion X is chosen, so as to lead to the formation of an IL preferably identical with the one already employed as the reaction medium. Even if the IL formed is only similar, it will be miscible with the main IL. In BASF's BASIL process (Biphasic Acid Scavenging utilizing Ionic Liquids), 1-alkylimidazoles are used to scavenge acid byproducts from organic chemical processes in order to prevent decomposition of the primary reaction product or to prevent unwanted side reactions.<sup>16</sup> Furthermore, we show that the average silver MNP particle size depends on and increases with the molar volume of the IL anion.

The silver precursor AgBF<sub>4</sub>, AgPF<sub>6</sub>, or AgOTf was dissolved, and Ag<sub>2</sub>O was suspended under argon in dried and deoxygenated ILs (Scheme 1) and reacted with hydrogen (4 atm, 85 °C). The reduction was carried out in the absence and presence of an *n*-butylimidazole scavenger (Bim) in a stainless steel reactor (Scheme 2).<sup>17,18</sup>

In the absence of the Bim scavenger, the AgNP particle size distribution is very broad, with a range of several tens or even hundreds of nanometers (Table 1 and Figure 1). This can be reasoned by proton (H<sup>+</sup>/H<sub>3</sub>O<sup>+</sup>) incorporation in the IL dynamic matrix (see below).<sup>6,19</sup> Also, the AgNP dispersion prepared without a scavenger is unstable as evidenced by

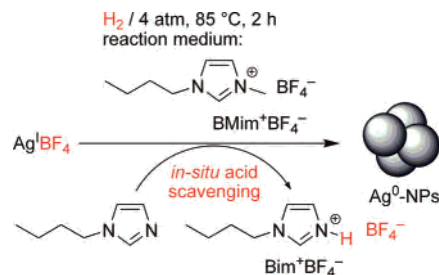
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(17) Materials and Instrumentation: Ag<sup>i</sup>X salts (X = BF<sub>4</sub>, PF<sub>6</sub>, OTf) were obtained from Aldrich and Merck, ILs and Bim from IoLiTec (H<sub>2</sub>O content < 100 ppm; Cl<sup>-</sup> content < 50 ppm). All manipulations were done using Schlenk techniques under argon because the AgX salts are very hygroscopic. The ILs were dried at high vacuum (10<sup>-3</sup> mbar) for 1–2 days. Transmission electron microscopy (TEM) photographs were taken at room temperature from a carbon-coated copper grid on a LEO 912 transmission electron microscope operating at an accelerating voltage of 120 kV.

(18) The hydrogen reductions were carried out in a stainless steel reactor connected to a hydrogen gas cylinder. In a typical experiment, the Ag<sup>i</sup> salt (0.0142–0.0426 g) and Bim (0.02–0.05 g) were dissolved and dispersed (~15 min) under argon at room temperature in 2–3 g of the IL (0.3–1 wt % Ag). Then, the reactor was evacuated and placed in an oil bath at 85 °C under stirring. The reaction was started by pressurizing with hydrogen to 4 atm. After 2 h, the reactor was evacuated for 1 h at 100 °C to remove excess hydrogen and Bim. After cooling to room temperature, an aliquot of the IL was collected under an argon atmosphere for in situ TEM characterization. The neutral pH of the reaction medium was ascertained by testing with pH paper.

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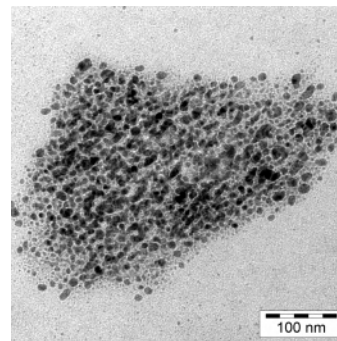
**Scheme 2** Formation and Stabilization of AgNPs by Hydrogen Reduction of AgBF<sub>4</sub> with the Imidazole Scavenging Process in BMimBF<sub>4</sub><sup>a</sup>

<sup>a</sup> The IL formed from the scavenging process should be similar to the main IL solvent.

**Table 1.** AgNP Size and Distribution from Different ILs and Silver Precursors Used and with or without a Scavenger

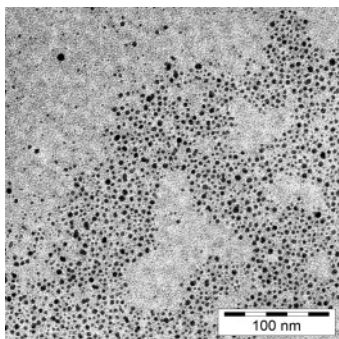
IL <sup>a</sup>	V <sub>IL anion</sub> /nm <sup>3 22</sup>	silver precursor	AgNP median (min–max diameter/nm), standard deviation σ <sup>b</sup>
Without a Scavenger; Soluble Silver Salts			
1 BMim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0.073 ± 0.009	AgBF <sub>4</sub>	66 (0.9–267) <sup>c</sup>
2 BMim <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	0.109 ± 0.008	AgPF <sub>6</sub>	9 (0.8–215) <sup>c</sup>
3 BMim <sup>+</sup> OTf <sup>-</sup>	0.131 ± 0.015	AgOTf	7.7 (0.6–27) <sup>c</sup>
Without a Scavenger; Insoluble Silver Precursor			
4 BMim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0.073 ± 0.009	Ag <sub>2</sub> O	5.7 (1.6–42) <sup>c</sup>
5 BtMA <sup>+</sup> Tf <sub>2</sub> N <sup>-</sup>	0.232 ± 0.015	Ag <sub>2</sub> O	8.6 (0.8–41) <sup>c</sup>
With Bim as the Scavenger; Soluble Silver Salts			
6 BMim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0.073 ± 0.009	AgBF <sub>4</sub>	2.8 (1.2–4.7), σ = 0.8
7 BMim <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	0.109 ± 0.008	AgPF <sub>6</sub>	4.4 (2.0–9.8), σ = 1.3
8 BMim <sup>+</sup> OTf <sup>-</sup>	0.131 ± 0.015	AgOTf	8.7 (3.5–18.4), σ = 3.4
9 BtMA <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>	0.232 ± 0.015	AgOTf <sup>l</sup>	26.1 (12.0–40.6), σ = 6.4
With Bim as the Scavenger; Insoluble Silver Precursor			
10 BMim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0.073 ± 0.009	Ag <sub>2</sub> O	6.5 (1.6–37) <sup>c</sup>

<sup>a</sup> BMim<sup>+</sup> = *n*-butylmethylimidazolium, BtMA<sup>+</sup> = *n*-butyltrimethylammonium, Bim = *n*-butylimidazole. <sup>b</sup> From TEM measurements, a statistical evaluation of the total sample pictures. <sup>c</sup> Very broad distribution curve, slowly tailing off to large particles; thus, no standard deviation is given. <sup>d</sup> Scavenging with 1-methylimidazole.

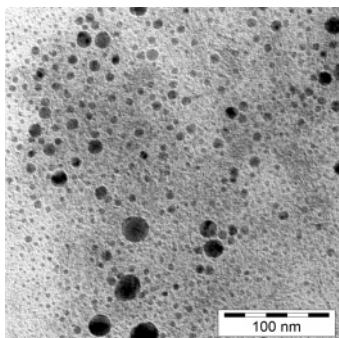
**Figure 1.** AgNPs from AgOTf in BMimOTf produced without a scavenger (entry 3 in Table 1; TEM photograph).

clearly visible metal particle precipitation within 1–2 h after reduction. In the presence of the Bim scavenger and soluble silver salts, the distribution of the AgNPs lies largely within 10 nm (Table 1 and Figure 2) and the dispersion is stable up to 3 days under argon. Under the reaction conditions, the median AgNP size ranges from 3 to 26 nm with uniform size distribution.

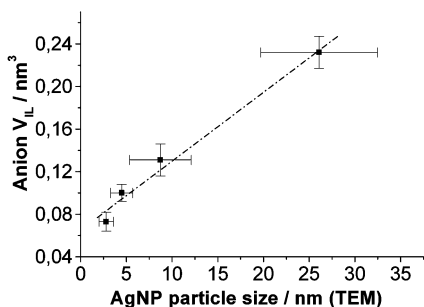
The scavenging process is crucial for the formation of well-defined, stable, and finely dispersed AgNPs in the IL



**Figure 2.** AgNPs from AgBF<sub>4</sub> in BMimBF<sub>4</sub> produced with Bim as the scavenger (entry 6 in Table 1; TEM photograph).



**Figure 3.** AgNPs from Ag<sub>2</sub>O in BMimBF<sub>4</sub> produced without a scavenger (entry 4 in Table 1; TEM photograph).



**Figure 4.** Correlation between the observed AgNP size (from TEM) and the molecular volume IL anion ( $V_{\text{IL, anion}}$ ).

matrix. The starting material silver(I) oxide, Ag<sub>2</sub>O, is insoluble in ILs and upon reduction gives AgNPs with a broad size distribution (Table 1 and Figure 3). Hence, dissolution of the metal containing starting material in ILs is important for the synthesis of AgNPs with narrow size distribution in ILs.

The AgNP size obtained with the Bim scavenger depends on the IL and increases roughly linearly with the molecular volume of the IL anion (Table 1 and Figure 4). MNPs (*core*) are considered stabilized in the ILs by the formation of “protective” anionic and cationic layers (shells) around them in a “core–shell system”.<sup>8,20</sup> We suggest that the thickness of the stabilizing shells around an AgNP depends on the IL

molecular ion volumes. According to the DLVO theory,<sup>7</sup> the first inner shell must be anionic, and then the IL anion will have the highest influence on the size and electrostatic stabilization of the AgNP. The anion molecular volume determines the region of the nanoparticle size. Other physical IL parameters like density, viscosity, or conductivity also correlate especially with the volume of the anion in the IL,<sup>21,22</sup> although the supramolecular imidazolium–anion clusters of the IL cation should be taken into account. The IL can be used as a fine-tuning tool in nanosynthesis.<sup>13</sup> “Pure” imidazolium-based ILs should be considered as three-dimensional networks of anions and cations, linked by weak interactions (such as hydrogen bonds and van der Waals and Coulomb forces). ILs should be regarded as supramolecular polymeric structures with a high degree of self-organization and weak interactions. When mixed with other molecules or MNPs, ILs should be described as nanostructured materials with polar and nonpolar regions.<sup>6,19,23,24</sup> AgNPs prepared with a scavenger in this medium are finely dispersed in the IL matrix (Figure 2). Protons from the reduction process without a scavenger will be incorporated in the cationic shells around the MNPs.<sup>25</sup> This proton incorporation weakens the cationic shells so that surface-energy-minimizing agglomeration can proceed to give larger particles and size distribution (Table 1 and Figure 1).

In summary, we describe here a simple and reproducible method for the tailored preparation of AgNPs with median diameters between 2.8 and 26.1 nm and narrow size distribution in ILs. The silver particle size depends upon and increases with the molecular volume of the anion in the IL (Figure 4). This should be useful for a tailoring of MNP sizes through an ab initio IL matrix selection.

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