Stability and growth behavior of transition metal nanoparticles in ionic liquids prepared by thermal evaporation: how stable are they really?

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Stability and growth behavior of transition metal nanoparticles in ionic liquids prepared by thermal evaporation: how stable are they really?†

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Recently we developed an access to metal- and metal-oxide colloids based on thermal evaporation of metals into ionic liquids (ILs). Here we present systematic studies on the long-time stability of gold and copper nanoparticles (NPs) in different ILs. The influence of metal concentration and temperature on the ripening of the as-prepared gold NPs in different ILs was investigated by transmission electron microscopy (TEM) and UV-vis absorption measurements. Short alkyl chain-length-methyl-imidazolium salts with weakly coordinating perfluorinated counter anions (PF$_6^-$, BF$_4^-$ or Tf$_2$N, bis(trifluoromethanesulfonyl)amide) were found to be better stabilizers compared to ILs with cations bearing long alkyl chains (triethylytridecylphosphonium, 1-octyl-3-methylimidazolium) and anions of higher coordination strength (DCA, dicyanamide). In the latter ILs fast particle growth and agglomeration was observed. In the well-stabilizing ILs initially very small NPs form which undergo a similar ripening process at room temperature as at higher temperatures. The final particle size depends largely on the used IL and the metal and to a minor extent on the temperature. The metal concentration seems to be an unimportant factor.

1. Introduction

Ionic liquids (ILs), especially room temperature liquid ILs (RTILs), are recently receiving substantial attention in the field of synthesis of inorganic nanomaterials as they offer a unique combination of properties such as wide liquid range, good thermal stability, a large electrochemical window and considerable electric conductivities. Among these, the often negligible vapour pressure renders them attractive for vacuum applications. Furthermore, ILs are known not only to be advantageous for the synthesis of nanomaterials but often are also able to provide electrostatic and steric stabilization for nanoparticles (NPs). For example, in 1,3-dialkylimidazolium ILs a continuous three-dimensional hydrogen bond network between acidic protons of IL cations and the IL anions forms a matrix around transition metal nanoparticles which prevents particle coalescence and precipitation. One of the first reports of using ILs as both a stabilizer for a metal-NP catalyst and the reaction medium was a Heck reaction where palladium NPs were generated from the Pd(0) precursor under ultrasound irradiation. Later Dupont and co-workers developed chemical approaches to NP-IL colloids by thermal decomposition or reduction of low-valent metal-organic precursors with hydrogen in ILs. This route has been further explored and it has recently been shown that surface hydrogen plays a crucial role in the NP stabilization. Aside from using elemental hydrogen as a clean reducing agent task-specific ILs have been developed that can act as a solvent, stabilizer and reducing agent. Also a microwave assisted decomposition of metal-carbonyl complexes leads to long time stable NP-IL colloids.

It is well known that ligands, counter ions and side products may influence particle size and morphology as well as the stability of the colloids. Side products can influence or decrease the catalytic reaction or activity by poisoning the as-prepared catalyst or the IL can be damaged by harsh synthesis conditions. Physical methods that omit the use of additional chemicals thus should be advantageous in that context. It was shown that larger metal particles or aggregated could be converted to much smaller NPs with a narrow size distribution by laser ablation. Metal nanoparticles in ILs could also be obtained by electrolytic dissolution of a metal and subsequent plasma reduction. By sputter deposition of metals onto ionic liquids it was not only possible to yield metal NPs but also alloy NPs. For this versatile method the influence of the IL surface composition and sputter conditions on the NP size was recently investigated. However, the comparatively high kinetic energy of the particles and thus the impact when the metal fragments hit the IL surface may lead to IL decomposition. In addition, it is quite difficult to manufacture large quantities of metal NPs in a short time. Therefore even milder and more efficient methods are sought. In our previous
report we described the synthesis of copper, gold and metal-oxide nanoparticles by thermal evaporation of the metal onto an IL film under high vacuum conditions using weakly coordinating ILs.\textsuperscript{29} In contrast to the sputter deposition the gas phase of the evaporated metal consists of 99% atoms and the kinetic energy is substantially lower (0.1–0.25 eV).\textsuperscript{30} However, we realized a strong influence of the chemical nature of the IL on its ability to stabilize NPs. Also the final particle size was found to be dependent on the IL. To the best of our knowledge there is at this time no detailed investigation on the long-term stability and the ripening behavior of as-prepared transition metal particles in different ILs using this thermal evaporation technique. For our studies we chose the ILs \([\text{C}_4\text{mim}][\text{DCA}]\) (1-butyl-3-methylimidazolium-dicyanamide), \([\text{C}_4\text{mim}][\text{Tf}_2\text{N}]\) (1-butyl-3-methylimidazolium-bis(trifluorosulfonyl)amide), \([\text{C}_4\text{mim}][\text{BF}_4]\) (1-butyl-3-methylimidazolium tetrafluoroborate), \([\text{C}_4\text{mpyr}][\text{PF}_6]\) (1-butyl-3-methylimidazolium-hexafluorophosphate), \([\text{C}_8\text{mim}][\text{BF}_4]\) (1-oktyl-3-methylimidazolium-hexafluorophosphate), \([\text{C}_7\text{pyr}][\text{BF}_4]\) (N-butyl-pyridinium tetrafluoroborate), \([\text{C}_7\text{mpyr}][\text{Tf}_2\text{N}]\) (N-butyl-N-methyl-pyridinium-bis(trifluorosulfonylamide) and \([\text{P66614}][\text{DCA}]\) (trihexyltetradecylphosphonium-dicyanamide) to determine the influence of the different cation and anion combinations on the particle formation mechanism and the colloid stability. These ILs were chosen to allow for a comparison between the influence of the cation alkyl-side chain length, aromatic and aliphatic core, hydrogen bonding ability (e.g. the 2-H proton of the imidazolium cation is highly acidic whilst pyrrolidinium cations have no protons of appreciable acidity) and the anion donor strength (DCA as a strongly coordinating anion vs. tetrafluoroborate as a weakly coordinating anion).

2. Experimental

2.1 Materials

All ILs except \([\text{P66614}][\text{DCA}]\) and \([\text{Bnim}][\text{DCA}]\) were purchased from IoLiTec, Denzlingen, Germany. They were dried at 80 °C under vacuum for 2 days prior to use. For the preparation of \([\text{P66614}][\text{DCA}]\) and \([\text{Bnim}][\text{DCA}]\) see ESI. Copper (99.9995%) and gold (99.99%) were purchased from www.smart-elements.com, Wien, Austria.

2.2 Preparation of Cu/Gold nanoparticles

To prepare the copper colloids a SMAD setup (TVP 800, Torrovap, Canada, Fig. 1) based on initial developments by Timms, was used.\textsuperscript{31,32}

In a typical experiment 40 ml of the IL was placed in the glass bulb of the reactor and the desired metal was placed in a tungsten crucible for evaporation. The setup was pumped with an oil diffusion pump to 10\textsuperscript{-6} Torr; the ionic liquid was allowed to degas for 4 h. Then the glass bulb was started to rotate (5 rpm). When a homogeneous thick film of the IL had formed on the glass surface the metal started to evaporate under dynamic vacuum onto the continuously renewing IL film. After evaporation of the desired amount of metal (estimated by time and evaporation rate, the exact metal concentration in the IL was finally calculated from the weight loss of the evaporation source after the experiment) the as-prepared colloid was then siphoned into a Schlenk tube under argon and subjected to further analysis. The temperature of the IL during evaporation process was about 50 °C.

2.3 Growth study of the as-prepared colloid

For the growth study, the as-prepared colloidal solutions were stirred under argon at room (25 °C) and elevated temperatures (50 °C) in a Schlenk tube. After the desired time the colloid was transferred into a UV/vis cuvette (2 mm pathway, special optical glass, Helma, D) and the absorption spectra were recorded with a Varian Cary 5000 UV/vis spectrometer. Transmission electron microscopy (TEM) studies were carried out with a Hitachi H-8100 microscope equipped with an LaB\textsubscript{6} cathode, operated at an acceleration voltage of 200 kV. Samples were prepared by dropping a small amount of the NP–IL colloid on the grid. Excess liquid was wiped away with a tissue. The size distributions were experimentally derived by TEM analysis and the deviation is given as mean deviation \(\sigma_1\).

3. Results and discussion

3.1 Formation of NPs by thermal evaporation of metal particles onto ILs

The stability of the colloids was measured by UV/vis spectroscopy (Table 1). The time of stability is defined as the time without a significant decrease in absorption intensity.

As can be seen only in the case of the 1-butyl-3-methylimidazolium ILs a long-term stable colloid could be obtained. Closely after the start of the evaporation process onto the 1-butyl-3-methylimidazolium ILs the formation of yellow-brown streaks on surface IL was observed indicating the initial nucleation of the evaporated metal to small clusters or particles. However, soon a transparent colloidal solution is formed. In the case of the other ILs black streaks were observed following the formation of turbid dark-blue dispersions. For the IL with the extremely hydrophobic phosphonium cation and strongly coordinating anion, \([\text{P66614}][\text{DCA}]\), even the formation of a metallic layer on top of the IL surface was observed during the evaporation process. This observation is similar to the one observed for the evaporation of silver and chromium on the polar IL 1-ethyl-3-methyl-imidazolium-ethanesulfate leading to the formation of a metallic layer.\textsuperscript{33} It was observed that the growth of the chromium layer occurred much faster than that of the silver layer, which was attributed to different diffusion rates of the metal into the bulk IL.\textsuperscript{33} It is believed
that the strong interaction between the imidazolium cation and the strongly coordinating alkyl-sulfate anion creates an impermeable surface. Indeed, in the case of thermal evaporation of metals onto ILs the vacuum–IL surface interface seems to play an important role. Angle resolved X-ray photoelectron spectroscopy (ARXPS) paired with theoretical investigations has recently suggested that the apolar alkyl-chains of the IL cation assemble at the IL surface and point into the surrounding vacuum.4,34,35 Thus, it is likely that the long alkyl tails of the tris(hexyl)tridecylphosphonium form an apolar surface which prevents the condensed gold atoms from diffusing into the bulk IL, leading to the formation of a metallic layer on top of the IL surface. A similar observation was made in the case of [C8mim][PF6]. Here we observed only the formation of metal–NP dispersions. On the other hand, if the alkyl side chain of the imidazolium cation is shortened to 4 carbon atoms, as in the case of [C4mim][PF6] the evaporation leads to the formation of stable particles. Interestingly, in contrast to our findings, Hatakeyama and co-workers obtained small gold nanoparticles by sputtering gold onto [C4mim][BF428] which shows that sputtered particles with higher kinetic energy penetrate directly through the apolar surface. It might also be anticipated that a high surface tension could lead to the formation of metallic films or larger aggregates. Typically the surface tension of an IL decreases with increasing the alkyl chain length of the cation. The surface tension at RT of [C4mim][PF6] (36.2 mN m−1) is lower than that of [C8mim][PF6] (42.9 mN m−1). But for the IL with lower viscosity the formation of a film was found and not for the one with the higher surface tension. Thus high surface tension does not lead to the formation of a metal film on the IL surface and the diffusion of the metal particles through the surface is independent of the IL surface tension. It rather seems that for ILs with longer alkyl tails a hydrophobic, oil-like IL–vacuum interface is formed which prevents the metal from diffusing into the bulk and favours the formation of metal films. A factor important for mass transport within the IL is viscosity. One could anticipate that in the case of a lower viscosity higher mass transport rates in the IL would lead to metal particle collision and coalescence, finally leading to larger particle sizes or reduced colloid stability. Typically viscosity increases with longer alkyl chains on the IL cation, e.g. the viscosity of [C4mim][PF6] at RT is 247.1 mPa s and of [C8mim][PF6] is 690.6 mPa s.36 However, for [C4mim][PF6] with the lower viscosity the formation of small particles which are stable for weeks is observed whilst for [C8mim][PF6] fast metal precipitation occurs. Thus, mass transport related to IL viscosity does not play an important role in the formation of small particles and their stability.

It appears that diffusion into the bulk and formation of a colloid or the formation of a metallic film is only dependent on the chemical composition of the vacuum/IL interface and not on the IL surface tension or viscosity for our experimental conditions. For sputtering metals on IL conflicting literature reports exist—one claiming an influence of IL surface tension and viscosity28 and one neglecting it.26

### 3.2 Growth behavior of the as-prepared particles

The size distribution of particles prepared in [C4mim][TF2N] (concentration \(c = 0.2 \text{ mg Au ml}^{-1}\) IL) has a tailored shape which is typical for a random nucleation process.37

Particles with a diameter between 2 nm and 7 nm with a strong maximum around 3 nm were observed (Fig. 2a, e). After heating for 45 min at 50 °C a shift of the mean particle size to 5.5 nm occurs and the shape of the distribution is more Gaussian-like. Now we found particles between 3 and 9 nm (Fig. 2b, f).

The absorption at 510 nm is due to the surface plasmon resonance (SPR) of the Au NPs and the weak absorption at 650 nm could be attributed to the larger aggregates (Fig. 3).38

The ripening process of the gold NPs in [C4mim][PF6] is different. The particle size distribution of the as-prepared colloid (\(c = 0.2 \text{ mg ml}^{-1}\)) is Gaussian-shaped with a maximum at 2.7 nm (\(\sigma = 0.61 \text{ nm}\)) (Fig. 4a, c). After heating for 120 min at 50 °C a shift of the maximum to 3.3 nm accompanied by an increase of the mean deviation (\(\sigma = 0.68 \text{ nm}\)) is observed. After 20 h at 50 °C particles with a diameter of 4.3 nm (\(\sigma = 0.88 \text{ nm}\)) are observed (Fig. 4b, d). Similar to the particles in [C4mim][TF2N] after heat treatment a tendency to form aggregates is observed (Fig. 4b). Nearly the same particle size maximum (4.8 nm, \(\sigma = 0.88 \text{ nm}\)) was observed by Torimoto and co-workers after heating a gold [C4mim][PF6] colloid at 100 °C for 30 minutes.39

During heat treatment a shift of the SPR to higher wavelengths is observed (Fig. 5). After 240 min the maximum is at 515 nm and shifts after 20 h to 520 nm, accompanied

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### Table 1

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Metal</th>
<th>Absorption max/nm(^a)</th>
<th>System(^b)</th>
<th>Stability(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4mim][TF2N]</td>
<td>Au</td>
<td>510</td>
<td>Colloid</td>
<td>1 week</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>575</td>
<td>Colloid</td>
<td>1 week</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Cu</td>
<td>576</td>
<td>Colloid</td>
<td>Several weeks</td>
</tr>
<tr>
<td>[C4mim][BF4]</td>
<td>Au</td>
<td>520</td>
<td>Colloid</td>
<td>Several weeks</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Au</td>
<td>520</td>
<td>Colloid</td>
<td>1 week</td>
</tr>
<tr>
<td>[C4mim][DCA]</td>
<td>Au</td>
<td>531</td>
<td>Colloid</td>
<td>3 days</td>
</tr>
<tr>
<td>[P6614][DCA]</td>
<td>Au</td>
<td>(\sim 600)</td>
<td>Dispersion</td>
<td>1 day</td>
</tr>
<tr>
<td>[C4mpyr][TF2N]</td>
<td>Au</td>
<td>(\sim 650)</td>
<td>Dispersion</td>
<td>Fast precipitation</td>
</tr>
<tr>
<td>[C4mpyr][PF6]</td>
<td>Au</td>
<td>(\sim 570)</td>
<td>Dispersion</td>
<td>Fast precipitation</td>
</tr>
</tbody>
</table>

\(^a\) Measured after ripening (for complete spectra see ESI+). \(^b\) Dispersion means in this context a metal/IL mixture which shows typical light scattering by shining red laser-light through the sample. In contrast, a colloidal solution does not show this effect. \(^c\) Stability without significant decrease of absorption intensity at RT.
by an increase of the baseline. The increase of the baseline could also be attributed to the formation of aggregates. However, the total amount of gold is constant indicated by the isosbestic point. In the control sample after 9 days at RT (c). Light scattering of the sample after heat treatment (d). TEM image of gold NPs in [C₄mim][Tf₂N] with a concentration of 0.2 mg ml⁻¹ as-prepared and after heat-treatment at 50 °C for 45 min (e, f). Scale bar: 50 nm.

Fig. 3 UV/vis spectra of gold NPs in [C₄mim][Tf₂N] with a concentration of 0.2 mg ml⁻¹ as-prepared and after heat-treatment at 50 °C for 45 min. Inset: colour change of the sample.

In the case of gold in [C₄mim][DCA] a less stable colloid with an absorption maximum at 530 nm was obtained. The higher absorption wavelengths indicate larger particles and aggregates. The reason for the lower particle stability is not completely clear. We assume that the extremely low viscosity in contrast to [C₄mim][BF₄] and in consequence of the higher particle movement leads to the coalescence and fast precipitation.40

In order to compare the influence of the metal on the ripening process, the same experiment with copper NPs in [C₄mim][Tf₂N] was carried out. Fig. 6a shows the size distribution of the as-prepared copper colloid (c = 0.2 mg ml⁻¹). The particles are assembled in domains with the tendency to hexagonal arrangements on the TEM grid. After heating for 45 min at 50 °C (Fig. 6b–d) the mean particle size shifts to 5.0 nm (σ ± 2.1 nm). In contrast to the gold particles we found after heating no agglomerates on the TEM grid. The particles show the same arrangements in groups and all particles have the same distance between each other (18 Å). This indicates a stronger interaction between the IL and the copper particle surface during the ripening process. The obtained mean particle size after heating is nearly the same as in the case of gold. The absorption maximum shifts during heating to 575 nm. The absorption maximum of the
control sample at RT shows after 8 days the same value (see ESI†).

All together these results lead us to the assumption that the final particle size is independent of the aging conditions. However, the tendency to form aggregates depends on the metal and the IL.

The stability of the colloids increases with using weak coordinating and fluorinated anions. The most long-time stable colloid was obtained in the case of [C4mim][PF6]. All obtained particle sizes dependent on concentration and aging time are summarised in Table 2.

4. Conclusions

We found that only the imidazolium containing ILs in combination with weakly coordinating perfluorinated anions are suitable for the long term stabilization of transition NPs. The stability of the colloid increases in the rank of the anions [Tf2N] < [BF4] < [PF6] which is in agreement with the Lewis basicity of the IL anions. With highly coordinating anion like DCA no NP formation could be achieved. The IL cation also plays an important role. In the case of hydrophobic cations the formation of a metal film on the IL is found and no stable colloids could be observed. The use of the aromatic pyridinium cation where π-metal interactions could be discussed does not lead to the formation of long-time stable colloids. Also in the pyrrolidinium salts no stable colloids could be obtained. Apparently the acidic 2-H proton of the imidazolium cation plays an important role in the metal-NP-IL interaction that stabilizes the colloid. If a similar-sized cation without acidic protons like C4mpyr is used this kind of stabilization is absent and the colloid is less stable. It seems that these specific metal-IL interactions are rather important for the stability of the colloids, and also for the final particle size compared to bulk properties like surface tension and viscosity.

From our results the formation of the nanoparticles can be subdivided into different processes (Fig. 7): (i) the mass transport to the surface, (ii) the condensation and nucleation of metal atoms on the surface, (iii) the diffusion through the surface, and (iv) the further ripening process in the bulk IL. If the rate of the mass transport and the rate of nucleation is higher than the diffusion through the surface, metallic layers or larger aggregates which result from a breaking of the initial IL film and diffusion of the particles into the bulk IL are observed. The diffusion rate through the surface depends on the specific composition of used ILs. Imidazolium ILs with weak coordinating anions seem to be substantial.

After the initial NP formation in the IL, the as-prepared NPs undergo a ripening process by coalescing until their final energetically optimum size is reached. This final size seems to be independent of the concentration of metal and bulk properties of the IL and depends on the chemical identity of the respective IL matrix.

![Fig. 6](https://example.com/f6.png) TEM image of copper NPs in [C4mim][Tf2N] with a concentration of 0.2 mg ml\(^{-1}\) as-prepared (a) and after heat-treatment at 50 °C for 45 min (b). Size distribution before (c) and after (d) heat treatment.

![Fig. 7](https://example.com/f7.png) Postulated steps of the growth mechanism of nanoparticles by evaporation of transition metals onto an IL film: (i) mass transport to the surface, (ii) the condensation and nucleation of metal atoms on the surface, (iii) the diffusion through the surface, and (iv) the further ripening process in the bulk IL. In order to obtain small initial particles the diffusion rate \(k_3\) must be higher than the mass transport to the surface.

### Table 2  Size distribution of gold and copper colloids in different ILs

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Metal</th>
<th>Metal concentration/mg ml(^{-1})</th>
<th>Aging</th>
<th>Mean particle size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Au</td>
<td>0.2</td>
<td>As-prepared</td>
<td>2.7 (±1.4)</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Au</td>
<td>0.2</td>
<td>45 min, 50 °C</td>
<td>5.5 (±1.5)</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Au</td>
<td>0.8</td>
<td>4 days, RT</td>
<td>4.2 (±0.9)</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Au</td>
<td>4.8</td>
<td>11 days, RT</td>
<td>5.5 (±3.1)</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Au</td>
<td>0.2</td>
<td>As-prepared</td>
<td>2.7 (±0.61)</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Au</td>
<td>0.2</td>
<td>120 min, 50 °C</td>
<td>3.3 (±0.68)</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Au</td>
<td>0.2</td>
<td>20 h, 50 °C</td>
<td>4.3 (±0.88)</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Cu</td>
<td>0.2</td>
<td>As-prepared</td>
<td>3.7 (±1.2)</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>Cu</td>
<td>0.2</td>
<td>45 min, 50 °C</td>
<td>5.0 (±2.1)</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>Cu</td>
<td>4</td>
<td>14 days, RT</td>
<td>3.0 (±1.2)</td>
</tr>
</tbody>
</table>

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These results cast a new light on the stabilization and formation of transition metal NPs prepared by physical vapour deposition (PVD) processes.

Acknowledgements

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Notes and references