

# Fabrication of naked silver nanoparticles in functionalized ionic liquids

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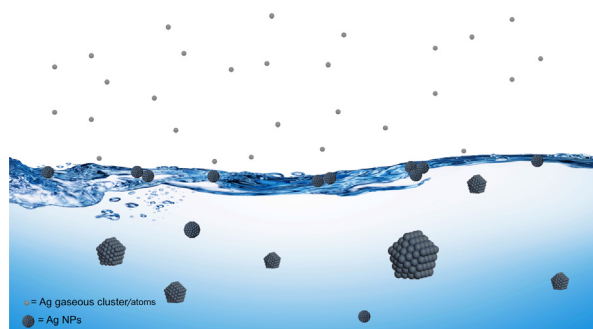
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## HIGHLIGHTS

- Ag nano particles (NPs) in functionalized ionic liquids (ILs) are prepared.
- The Ag NPs formation mechanism relies on stabilization provided by the substituted imidazolium cation.
- The smaller Ag NPs are located closer to the fluid surface while surrounded by a single monolayer of the IL.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Surface clean silver nanoparticles of 5–8 nm in size were prepared in functionalized imidazolium-based ionic liquids containing methoxy, cyano, and thio groups by magnetron sputtering deposition. The surface composition/organization of the ILs controls the size and location of NPs in these fluids. The simple model of metal–ligand interaction of surface-functionalized ILs can be used to explain and predict the structural organization of the sputtered NPs in these fluids. The sputtered NPs tend to penetrate deeper into the regions of the ILs containing lower coordinating groups (OMe), whereas those associated with strong sigma donating groups (CN and SH) tend to place the small nanoparticles close to the liquid surface. We estimate a single monolayer of IL surrounding the smaller Ag NPs located closer to the surface as determined by High-Sensitivity Low-Energy Ion Scattering (HS-LEIS).

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## 1. Introduction

The fabrication of well-defined (size, size distribution, and shape) surface-clean (naked) metal nanoparticles in liquids still remains a challenge [1]. Magnetron sputtering deposition promises a simple and easy approach to fabricate such nano devices, which

may display quite unique properties for several applications in fields such as electronics, sensors, biomedical and catalysis [2]. Indeed, this method allows the preparation of naked NPs in a single step, generating highly pure supported metal NPs in both solids and liquids supports, as opposed to classical chemical and electrochemical methods that usually require further purifications steps [3–7]. Indeed, since the pioneering reports by Kuwabata and Torimoto [8] that ionic liquids can be decorated by Au and Ag nanoparticles in ionic liquids [9,10], the field has flourished. In particular, the fabrication of metal nanoparticles in ionic liquids or hybrid IL materials [11–14] is a simple and controllable process for

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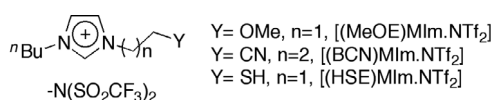


Fig. 1. Structure of the functionalized ILs employed in this study.

several applications, with huge advantages when compared to the classical wet methods. This method can nowadays be regarded as the method of choice for many applications [15]. However, little is known about the structural and electronic nature of the sputtered nanoparticles confined in functionalized ILs as compared to those in classical imidazolium, pyrrolidinium and phosphonium based ILs [16–19]. It is clear that more in-depth knowledge on the nature and structural organization of sputtered metal NPs in functionalized ionic liquids may open the way to design and predict the structure and electronic properties of naked NPs in ILs. For this purpose, we have employed imidazolium based ionic liquids containing methoxide [(MeOE)MIm.NTf<sub>2</sub>], cyanide [(BCN)MIm.NTf<sub>2</sub>], and thiol [(HSE)MIm.NTf<sub>2</sub>] groups at the alkyl side chain of imidazolium cation (Fig. 1) to investigate the structural organization of sputtered Ag nanoparticles in these liquids by High sensitivity low energy ion scattering spectrometry (HS-LEIS) analysis. Indeed, HS-LEIS is well known ultra-high surface sensitive technique that can provide the information of the top atomic layer of IL containing Ag NPs. This static depth profiling analysis provides information down to a depth of 10 nm. This mode also allows a quantitative measurement of the thickness of organic over-layers such as Langmuir–Blodgett films or self-assembled monolayers [20–22].

We compare our findings with those containing Au NPs obtained under similar conditions. The results clearly indicate that classical coordination chemistry (ligand–metal, the functionalized IL behave as a ligand-like and the surface as a metal centre) can be used to predict the size and location of sputtered Ag NPs in functionalized ionic liquids.

## 2. Experimental section

### 2.1. General

Ionic liquids 1-butyronitril-methylimidazolium bis(trifluoromethanesulfonyl)imide [(BCN)MIm.NTf<sub>2</sub>], 1-methoxyethyl-methylimidazolium bis(trifluoromethane sulfonyl)imide [(MeOE)MIm.NTf<sub>2</sub>], 1-thioethyl-methylimidazolium bis (trifluoromethanesulfonyl)imide [(HSE)MIm.NTf<sub>2</sub>] were synthesized by well known methods [23,24]. The IL was placed under vacuum, degassed for 3 h at room temperature and degassed with argon prior to its introduction into the sputter chamber as a liquid substrate for the sputter deposition of silver. MED model equipment 020 (Bal-Tech) was used for sputter deposition. TEM analysis was performed using a JEOL JEM1200 transmission electron microscope operating at 80 keV. For LEIS, the samples have been analysed with the Qtac 100 (ION-TOF). Its double toroidal analyzer allows for accurate measurements using HS-LEIS. The 3 keV <sup>4</sup>He<sup>+</sup> ion fluence for a complete spectrum was 1.4 × 10<sup>14</sup> ions/cm<sup>2</sup>. Assuming a sputter yield of 0.1 atoms/He ion, the sputter damage was 1–2% of a monolayer. A clean Ag surface was used for the reference spectrum. The change in the surface composition and thickness of the layer covering the Ag NPs is thus negligible (“static” analysis).

### 2.2. Ag NPs sputtering deposition in ILs

After drying the IL under reduced pressure, IL (3 g) was poured into a petri dish of 1 cm with a circular base of 3 cm in diameter, which was set horizontally into the sputter coater. The distance

between the liquid surface and the silver target (99.9% purity) was 50 mm. Deposition was performed with discharge voltages of 335 V (40 mA) under an argon pressure of 2 Pa at room temperature for 150 s. The black colloidal solution of IL and Ag NPs was stored under argon prior to the different analyses performed.

## 3. Results and discussion

Imidazolium-based ILs containing nitrile (-CN), thiol (-SH), and ether (-OMe) functionalized groups with the hydrophobic anion (NTf<sub>2</sub><sup>-</sup>) (Fig. 1) were selected in view of the presence of different coordinating groups that may act as ligand-like species towards the metal surface [25]. Moreover, they may act as both template and stabilizing media [26] to deposit the gaseous atomic Ag nanospecies prepared by magnetic sputtering (Scheme 1). This method is very simple and allows the generation of surface “clean” MNPs, since there are no other chemicals employed in the process [15]. The sputter deposition was conducted using 40 mA of discharge current for 150 s to obtain the MNPs, similar to conditions already employed for Au NPs [27].

TEM (Fig. 2) clearly indicates the presence of the NPs in ILs as well as their size distribution (Table 1). It was observed that monodispersed NPs with sizes of 5–14 nm were obtained in [(BCN)MIm.NTf<sub>2</sub>] IL, whereas the NPs obtained in [(HSE)MIm.NTf<sub>2</sub>] and [(MeOE)MIm.NTf<sub>2</sub>] ILs were 8.7–12 nm and 8.2–15.5 nm in size, respectively. As the NPs nucleate and grow on the ILs surface, the chemical configuration of the ILs surface plays an important role in controlling the size of the NPs. The small size of Ag NPs in [(BCN)MIm.NTf<sub>2</sub>] IL may be correlated with the presence of a nitrile functionalized moiety that presents two possible effects; (i) the dipole moment of the nitrile group causes the butyl nitrile side chain to fold into the ionic region of the surface to form H-bonds and/or dipole–dipole interactions and/or (ii) the orientation of the nitrile functionalized side chain towards the vacuum/IL interface [26]. In the latter case, it is very probable that in [(BCN)MIm.NTf<sub>2</sub>] the surface is enriched with the cyano group (pointed towards the vacuum/IL interface) that drives the anisotropic nucleation and growth of the NPs [26], as opposed to the less anisotropic [(MeOE)MIm.NTf<sub>2</sub>] fluid in which the functional group is located preferentially away from the liquid surface. Similarly, Ag NPs prepared in IL containing F-rich and low-coordinating anions [BMIm.PF<sub>6</sub>] under similar sputtering conditions display relatively large sizes (around 11 nm) [28], indicating that the NPs probably grow in the deeper regions of the less anisotropic fluid [17]. Moreover, the presence of these functionalized groups may affect the shape of NPs, relatively spherical shaped and well dispersed NPs were obtained in highly coordinated [(BCN)MIm.NTf<sub>2</sub>] and [(HSE)MIm.NTf<sub>2</sub>] ILs as compare to lower coordinated [(MeOE)MIm.NTf<sub>2</sub>] IL. In fact, the size and shape of Ag NPs in [(MeOE)MIm.NTf<sub>2</sub>] are similar to those prepared in non-functionalized ILs (4–15 nm) [28]. Hence, it appears that the size and shape of NPs prepared by magnetron sputtering in ILs are also related to the bulk organization (anisotropy) of these fluids akin to the observed using classical chemical methods. Indeed, [(MeOE)MIm.NTf<sub>2</sub>] is less anisotropic as compared to the other two functionalized ILs [17]. It is also worth noting that the same trend, i.e. larger Au NPs are formed by sputtering deposition in [(HSE)MIm.NTf<sub>2</sub>] than in the other two fluids, has been observed under identical experimental conditions [29]. In this case, the NPs growth probably occurs preferentially at the IL surface due to enhanced coordination properties of the SH group (sigma donor) towards Ag and Au. Therefore, the IL surface composition plays a central role in both nucleation and NP growth steps. Note that Ag NPs prepared by chemical, electro- and photo-chemical methods (reduction of Ag salts in ILs) can lead to a broad range of sizes and shapes [30–39] that may be reasonably correlated with the anion

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