

Supporting Information

On the formation of anisotropic gold nanoparticles by sputtering onto a nitrile functionalized ionic liquid

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1. Experimental Details

TEM and HRTEM sample preparation. The samples for TEM and HRTEM were prepared by dispersion of the gold nanoparticles (AuNPs) deposited on ILs in isopropanol at room temperature and then collected on a carbon-coated copper grid. The histograms of the AuNPs were obtained from the measurement of more than 1000 particles and were reproduced in different regions of the Cu grid, found in arbitrarily chosen areas of enlarged micrographs.

SFM sample preparation and measurements. AuNPs colloids were dissolved in acetone and then centrifuged. The precipitate was dissolved again in acetone and the centrifugation process was repeated. Finally, the precipitate was dissolved in acetone and dropped onto Si foil. After evaporation of the solvent the topography of the samples was characterized *ex situ* in a Nanoscope IIIa (Digital Instruments) scanning force microscope (SFM)

in the Tapping ModeTM, with NanosensorsTM CNT-NHC SFM tips (with nominal carbon nanotube radius <2.1nm and length <750nm). SFM was carried out in the samples to characterize the height and shape of the tiny particles in order to define the real morphology of the disk-shaped AuNPs. Typical drive amplitudes were set to give a detector signal around 3V. In order to minimize tip–surface interactions when scanning a sample surface, the damping of the free oscillation of the cantilever was kept to the minimum value compatible with stable imaging of the sample probed. The scanning frequency was always 1 or 2 Hz and quantitative analysis of the SFM data was performed on images captured with high-quality tips in order to minimize systematic errors due to the tip shape common in SFM.

UV-Vis spectroscopy. The experiments were conducted in a Varian Cary 100 spectrophotometer in the pure AuNPs-ILs colloidal samples using 1 mm quartz cuvettes in order to investigate the formation of AuNPs. Figure S1 shows the absorption spectra of the colloidal samples after sputtering deposition of Au onto (BCN)MI.N(Tf)₂ for 150 s at different discharge voltages.

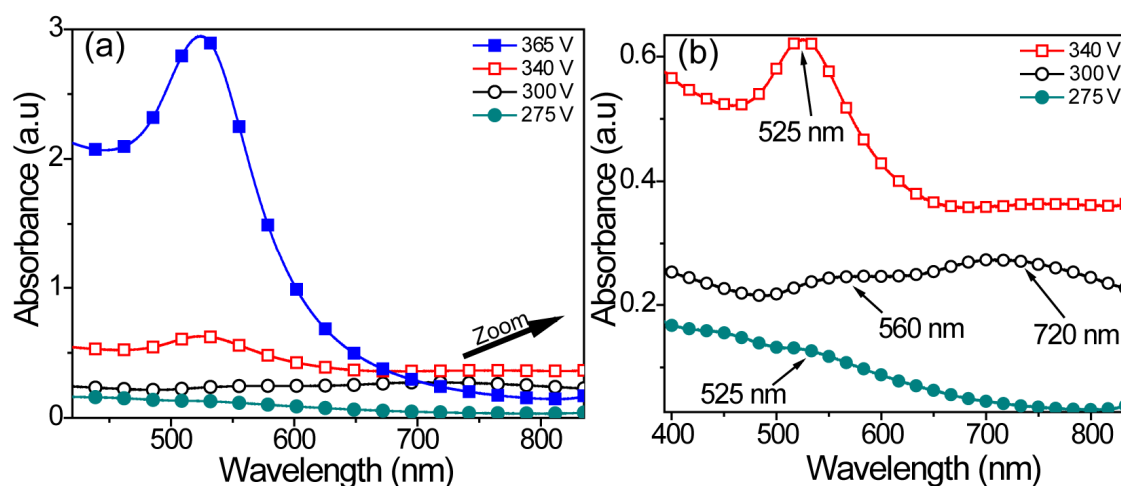


Fig.S1 UV-Vis absorption spectra of (BCN)MI.N(Tf)₂ after sputtering of an Au target for 150 s with discharge voltages of 275, 300, 340, and 365 V (a). Scale enlarged absorption spectra of the first three curves (b), where it can be seen that a second absorption band at 720 nm is present only for the sample sputter deposited at 300 V.

2. SAXS Experiments and Analysis

Small angle X-ray scattering (SAXS) experiments were performed in NPs solutions at the SAXS1 beamline of Brazilian Synchrotron Light Laboratory (LNLS), with $\lambda = 1.488$ Å and $0.05 < q < 3.33$ nm⁻¹, where $q = 4\pi \cdot \sin(2\theta) / \lambda$; q is the scattering vector, θ is the scattering angle, and λ is the X-ray wavelength. The colloidal solutions were injected by a syringe into a cell with mica windows specially designed for liquids.¹ The fitting procedures of the experimental SAXS data have been made using the SASfit program which uses the least-squares fitting approach, consisting in minimizing the squared chi (χ^2). The SASfit software package was developed by J. Kohlbrecher and is available free of charge at <http://kur.web.psi.ch/sans1/SANSSoft/sasfit.html>.

As shown in Figure 4 of the main text, the experimental SAXS curves clearly presents a strong structure factor, which is highest for the sample sputtered at 300 V and decreases with discharge voltage increases. In the hard sphere model for the structure factor, two parameters were taken into account during the fit: the hard sphere repulsion radius (RHS), which is linked with the structure correlation of the particles, and the volume fraction (f_p). The strong correlation between NPs in the sample sputtered at 300 V ($RHS = 4.3$ and $f_p = 0.5$) indicates that the NPs are assembled as superlattices in the ILs solutions, which corroborates that the second resonance band at 720 nm observed in the UV-Vis, Figure S1(b), might be due to the very small distance between the NPs.

Figure S2 shows the size distribution of the colloidal AuNPs obtained by sputtering at 340 V onto the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMI.N(Tf)₂] IL. Only the formation of spherical AuNPs with mean diameter of 5.2 ($\sigma = 1.0$) nm could be observed, without any traces of anisotropic NPs, in agreement with previous reports.^{2, 3} This result is indicating that the surface composition of the (BCN)MI.N(Tf)₂ differs from the short alkyl chains bases ILs, as the EMI.

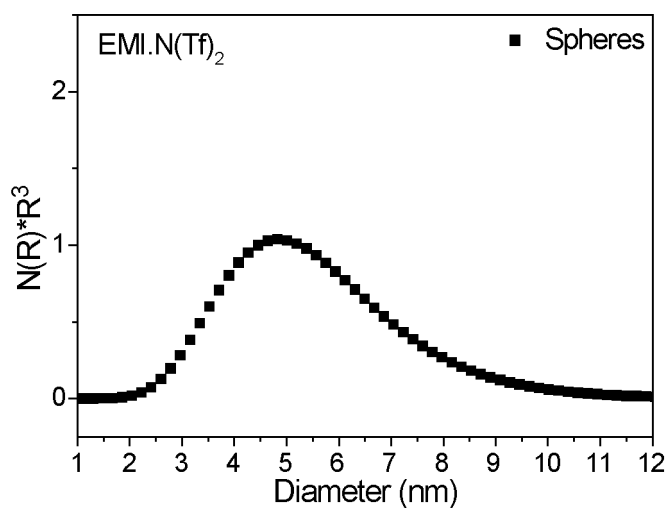


Fig.S2 Size distribution of the AuNPs obtained by sputtering at 340 V for 150 s onto the EMI.N(Tf)₂ IL.

References

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