Role of the solvent-surfactant duality of ionic liquids in directing two-dimensional particle assembly

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Figure S1. (A) Time series of TEM images showing the self-assembly process of gold NPs in a 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution. The electron dose rate was $10 \text{ e/Å}^2\text{s}$. (B) Statistical analysis of frequency versus interparticle separation (edge-to-edge) at 165 s is also depicted.



Figure S2. (A) Time series of TEM images showing the self-assembly process of gold NPs in a 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution. The electron dose rate was 5 e/Å²s.



Figure S3. Simulated interactions between gold NPs in 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution and structure of the interfacial layer. (A) Calculated disjoining pressure between two gold particles and (B) the zoom-in of the long-range region. (C) Mid-plane relative concentrations of [C₂OHmim]⁺ cations and AuCl₄⁻ anions in the gap between NPs. ρ is the mid-plane concentration of the ions and ρ_0 is their corresponding bulk value. (D) H-bonded configuration of two [C₂OHmim]⁺ cations decorating Au (111) surfaces with their aromatic rings vertical to the surfaces.



Figure S4. Variation in the size of gold NPs (NP0, NP4 and NP9) shown in the Figure 1 as a function of time.



Figure S5. (A) UV-Vis spectra showing variations in the surface plasmon absorption peak as a function of $[C_2OHmim][Cl]$ concentration. (B) Zeta-potential data showing the surface charge of as-synthesized gold NPs as a function of $[C_2OHmim][Cl]$ concentration.

To a certain extent, aggregation and self-assembly of gold NPs are a consequence of decreasing of colloidal stability, a property we evaluated by UV-vis absorption spectroscopy and zeta potential measurements. The absorption peak of the surface plasmon at ~517 redshifted, broadened, and a secondary peak appeared at higher wavelengths with increasing [C₂OHmim][Cl] concentrations relative to HAuCl₄. Such behavior is indicative of a transition from monodispersed to aggregated

gold NPs at higher ionic liquid concentrations. Zeta potential measurements showed the surface charge of the as-synthesized gold NPs increased with increasing $[C_2OHmim][Cl]$ concentrations. Collectively, these results imply that gold NPs tend to assemble or aggregate in the presence of $[C_2OHmim][Cl]$. It's worth mention, however, that the UV-vis absorption spectroscopy and zeta potential measurements were conducted on NPs synthesized ex situ with a chemical reducing agent, rather than by the electron-beam in the LC-TEM, and thus, comparisons are limited.

Movie S1. In situ liquid cell TEM video showing the self-assembly process of gold NPs in a 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution. The electron dose rate was 10 e/Å²s.

Movie S2. In situ liquid cell TEM video showing the self-assembly process of gold NPs in a 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution. The electron dose rate was10 e/Å²s.

Movie S3. In situ liquid cell TEM video showing the self-assembly process of gold NPs in a 5 mM HAuCl₄ and 500 mM [C₂OHmim][Cl] solution The electron dose rate was 5 e/Å²s.