

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

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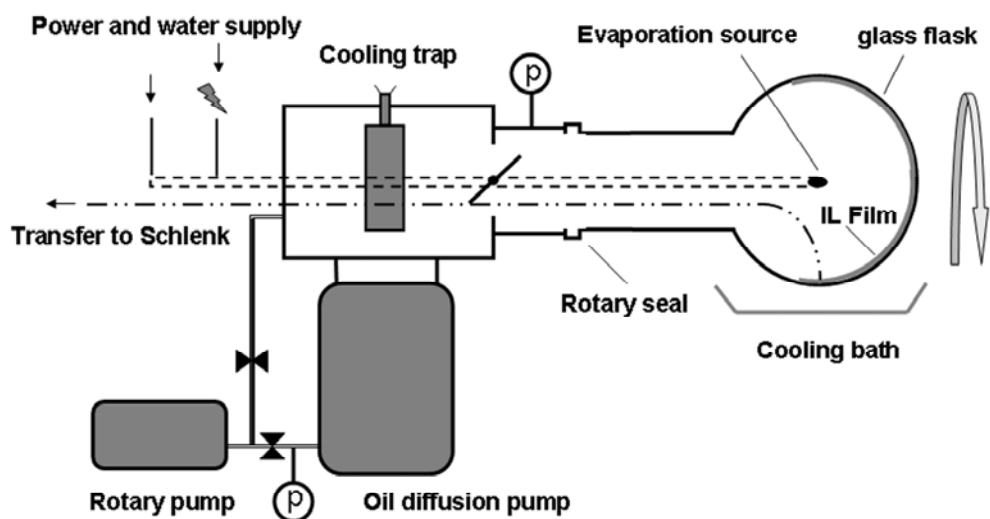
Supporting Information

1. Synthesis of the ILs

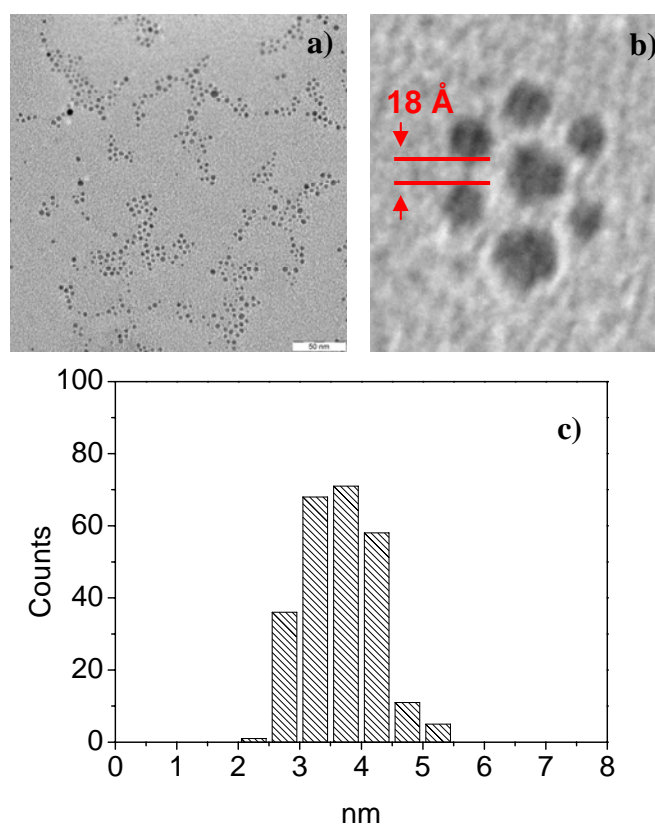
[P66614][DCA]: Trihexyl(tetradecyl)phosphonium chloride (50 g, 0.0963 mol) and sodium dicyanamide (10.3 g, 0.116 mol) were added to a mixture of 150 ml acetone and 150 ml water. The mixture was stirred over night at room temperature. After removal of acetone under vacuum the residue was extracted with dichloromethane (4 x 50 ml). The combined organic layers were washed intensively with deionised water (10 x 15 ml) to remove any excess of dicyanamide. The solvent was evaporated to give a colourless low viscous liquid. Yield: 95.2%, 50.41 g. ^1H NMR (250MHz, δ /ppm; CDCl_3): 0.89 (m, 12 H), 1.25 (m, 32 H), 1.47 (m, 16 H), 2.10 (m, 8 H).

[C₄mim][DCA]: 1-Butyl-3-methyl-imidazolium chloride (50 g, 0.286 mol) was molten at 80 °C in an argon flushed three neck flask. Sodium dicyanamide (28.00 g, 0.315 mol) was added into the melt. The mixture was then stirred at 80°C under argon over night. After cooling the solid which formed was dissolved with 100 ml dichlormethane and the organic layer was extracted with a small amount of deionised water. The solvent was evaporated to give a low viscous, colourless liquid. Yield: 92.8%, 54.48 g. ^1H NMR (250MHz, δ /ppm; CDCl_3): 0.88 (t, 3 H), 1.32 (m, 2 H), 1.84 (m, 2 H), 4.02 (s, 3 H), 4.24 (t, 2 H), 7.46 (s, 1 H), 7.51 (s, 1 H), 9.36 (s, 1 H).

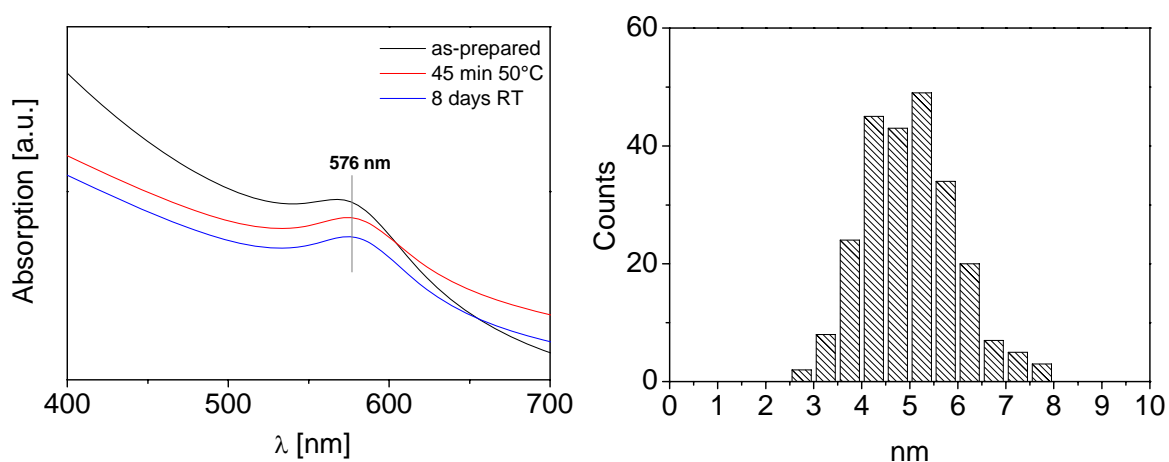
2. Plan of the used SMAD equipment:



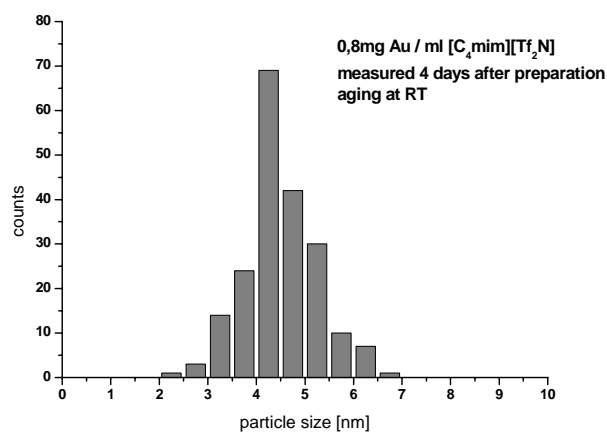
3. Analytics



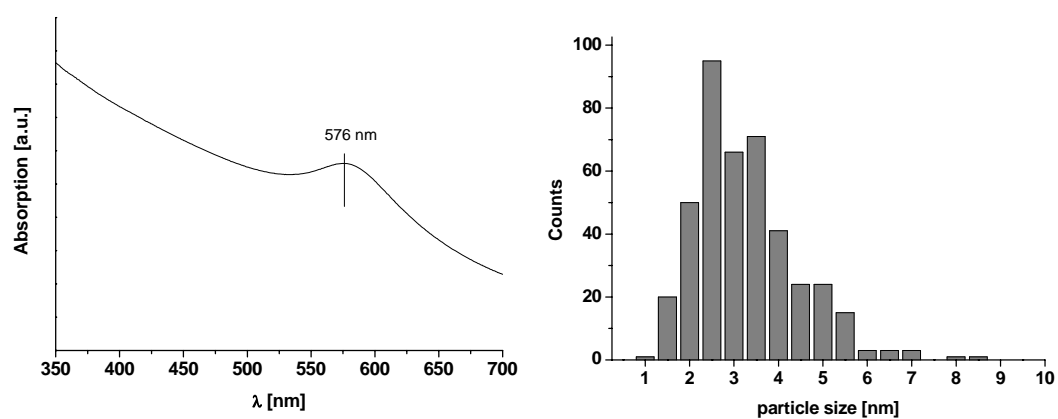
SI-Figure 1. TEM image of copper nanoparticles in the ionic liquid $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ (a,b). Scale bar: 50 nm. Particle size distribution of the as-prepared copper particles (c).



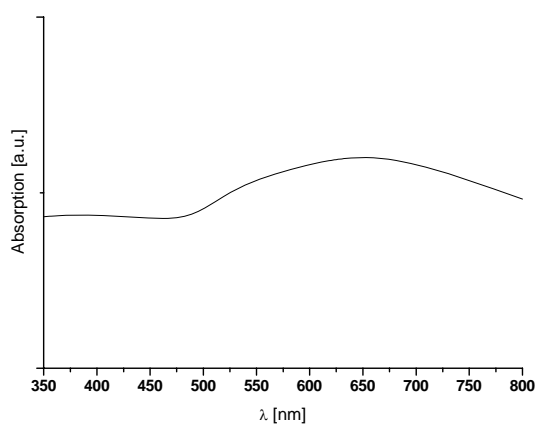
SI-Figure 2. UV/vis-spectrum of copper particles ($c=0.2$ mg/ml) in the ionic liquid $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ (left). Size distribution after heating for 45 min at 50 °C (right).



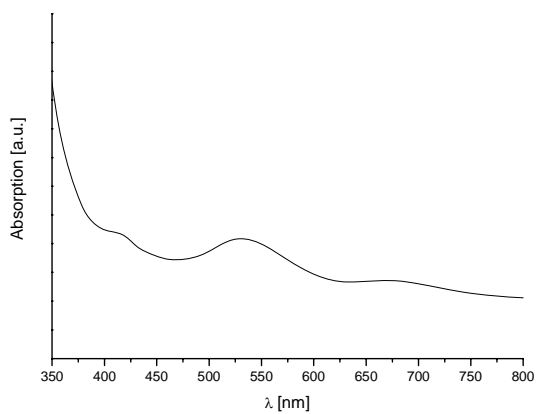
SI-Figure 3. Size distribution of Au NPs in [C₄mim][Tf₂N] after 4 days.



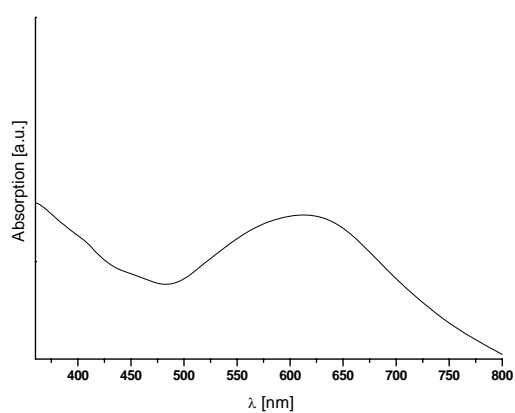
SI-Figure 4. UV/vis spectrum of Cu NPs (c=4 mg/ml) in [C₄mim][Tf₂N] after 14 days (left) and size distribution (right)



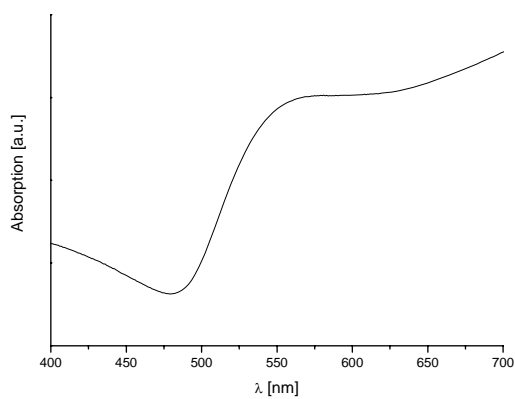
SI-Figure 5. UV/vis spectrum of Au NPs in [C₄mpyr][Tf₂N] after evaporation.



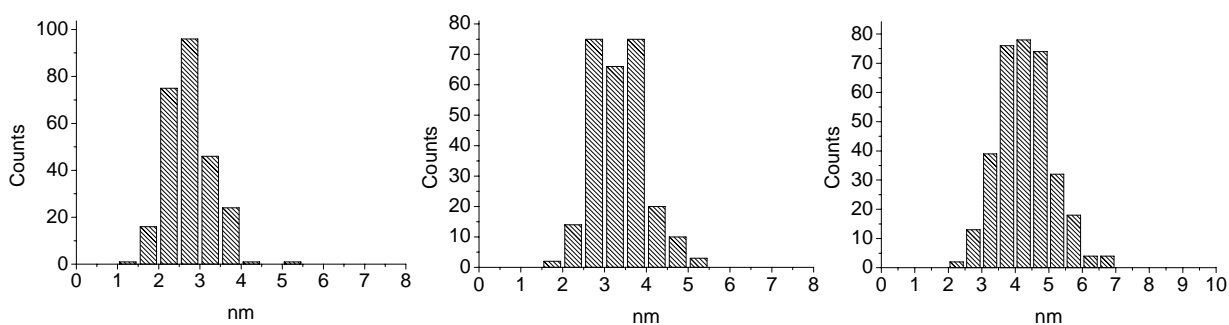
SI-Figure 6. UV/vis spectrum of Au NPs in [C₄mim][DCA] after evaporation.



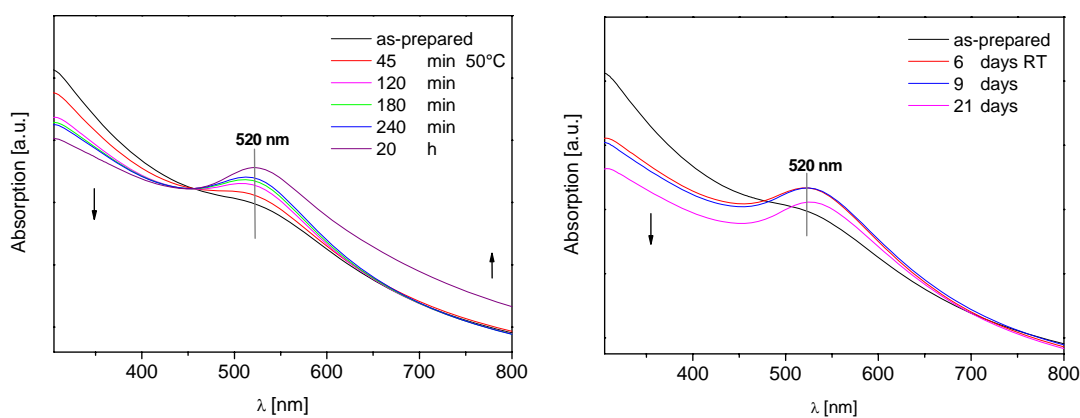
SI-Figure 7. UV/vis spectrum of Au NPs in [P66614][DCA] after evaporation.



SI-Figure 8. UV/vis spectrum of Au NPs in [C₈mim][PF₆] after evaporation.



SI-Figure 9. Particle size distribution of Au NPs in $[C_4mim][PF_6]$, as-prepared (left), after 120 min at 50°C (middle) and after 20 h at 50°C (right).



SI-Figure 8. UV/vis spectra of Au NPs ($c=0.2\text{mg/ml}$) in $[C_4mim][PF_6]$, during heat treatment (left), upon aging at room temperature (right).