

Morphosynthesis of gold nanorods using polyethyleneimine-capped seeds in ionic liquid

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1. Experimental

Materials

The ionic liquid 1-ethyl-3-methylimidazolium n-hexylsulfate (emimHexSO₄) (99%) was purchased from Merck. HAuCl₄ Ascorbic acid and sodium citrate were obtained from Sigma-Aldrich. Branched poly(ethyleneimine) with molar masses of 5000 g/mol and 1300g/mol were obtained from BASF and Sigma-Aldrich respectively. Cetyltrimethylammonium bromide (CTAB) surfactant was used as received from Fluka Analytical. Water used was deionized 18.2MΩ

Synthesis of Au nanoparticles seeds

Poly(ethyleneimine) (BASF Lupasol G100; Mw 5 000 g mol⁻¹) was neutralized and dried prior to use for several days at 50°C under high vacuum. For preparing a 0.5 wt. % PEI solution in the ionic liquid adequate amounts of the polymer were incorporated into emimHexSO₄ by applying ultrasound and heating up to 50 °C for 1 h. An alternative procedure to dissolve the polymer in ionic liquids is to use methanol as co-solvent which can be subsequently evaporated after incorporating the polymer. The precursor tetrachloroaurate (2 mM) solution in emimHexSO₄ was prepared at room temperature.¹ emimHexSO₄The obtained solutions were mixed in a 1:1 ratio (wt/wt) at room temperature and heated to 100 °C for 20 min. The change in color from yellow to dark red indicated the formation of gold nanoparticles. This was used as the stock solution.

The ionic liquid containing the nanoparticles was dissolved in a 1:10 volume ratio in chloroform and dropped on a copper grid, dried and examined in a transmission electron microscope (EM 902, Zeiss) at an acceleration voltage of 80 kV.

Synthesis of Au NRs (General procedure)

At the volume ratio of the seed solution to the 0.1M CTAB solution in the first step of the conventional three step seeding protocol reported by Murphy *et al.*², it was observed that the whole solution turned turbid white after which the precipitate settled down. As a result only a single step seed addition to the growth solution (GS) was carried out. The procedure adopted was as follows:

In 20 ml volume glass stopper bottle, 5 ml of GS was prepared by mixing 0.3 mM of HAuCl₄, 0.2 mM ascorbic acid and 0.1 M CTAB. 6 μL of concentrated HNO₃ was added to this GS and stirred well to ensure the HNO₃ was completely dissolved. Different growth conditions (discussed in Figure 2 of the manuscript) were formed by adding different additives to aforementioned 5 ml GS as follows.

Condition (A) GS + 8 μL of 50 wt% PEI in water

Condition (B) GS + 8 μL of 50 wt% PEI in water + 10 μL pure emimHexSO₄ IL

Condition (C) No extra additives to GS (reference growth condition)

Condition (D) GS + 10 μL pure emimHexSO₄ IL

5 μL of 20 % v/v IL Au nanoparticle seeds of stock solution were added to this GS and again stirred well and then put undisturbed in a water bath at 26 °C overnight.

2. UV-visible absorbance

Absorbance of freshly prepared and stored PEI-capped Au seeds in IL

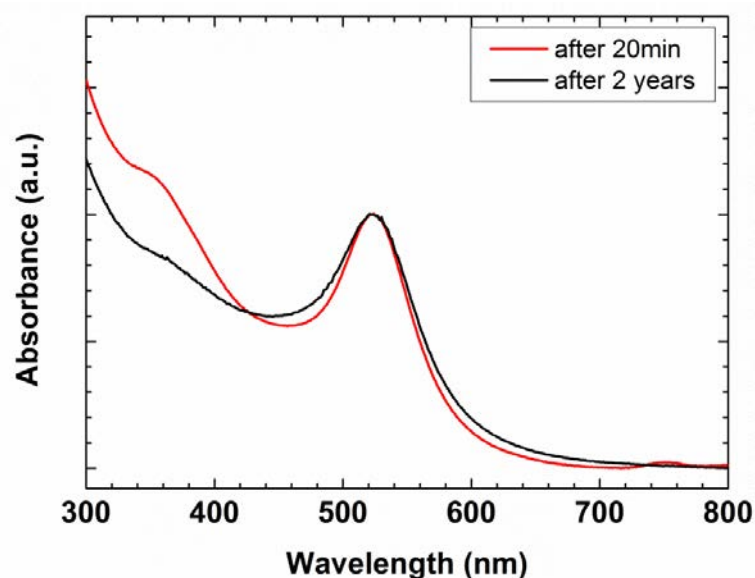


Figure S1: Absorption spectra of freshly prepared PEI-capped Au seeds in emimHexSO₄ ionic liquid (red) and of the same solution after 2 years of storage in ambient conditions (black)

Simulated spectra of 50x250 nm and 30x1000 nm Au nanorods in water

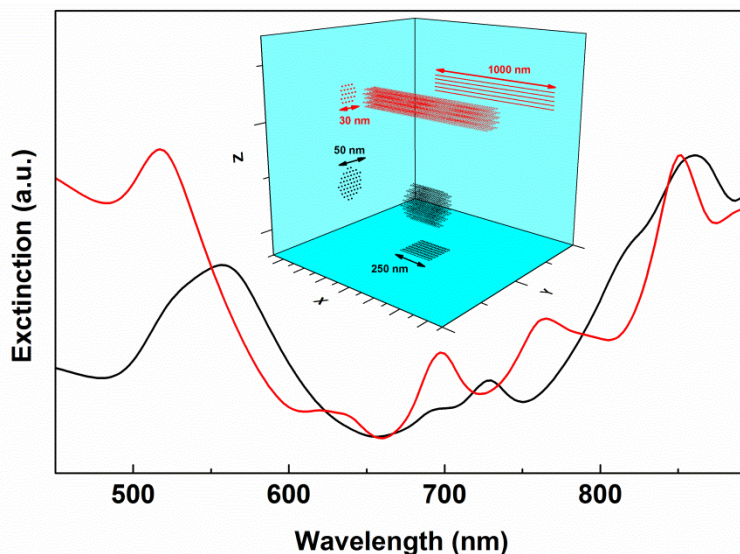


Figure S2: Calculated extinction spectra of short (250x50 nm) and long (1000x30 nm) Au nanorods in water ($n = 1.33$) representative of condition A (added PEI) and D (added IL) respectively. The dipolar models of nanorods used in the Green Dyadic Method simulation tool are shown in the 3D inset.³

The extinction spectra of Au nanorods were calculated by the established Green Dyadic Method³ in order to illustrate the influence of the aspect ratio on the spectral feature in the 500-800 nm window. Two spectra of extreme synthetic conditions A and D studied in this work and assimilated to their average size (250 x 50 nm and

1000 x 30 nm respectively) are represented in Figure S2. Several peaks are observed which are ascribed to dipolar and higher order Fabry-Perot modes as illustrated in numerous studies on near-field and far-field optical properties of Au and Ag nanorods.⁴

The spectrum of the shortest rods (250 x 50 nm) is dominated by a transverse and a longitudinal (dipolar) modes centered on 550 nm and 900-950 nm respectively. However, as the aspect ratio of the rod increases the dipolar mode shift into the infra-red region but higher order modes emerge in the 600-900 nm wavelength range. The energy of these modes are highly sensitive to the aspect ratio of the nanorods. Therefore, even in the case of nanorods having homogeneous diameter, accounting here for the 520-550 nm transverse plasmon mode, any polydispersity in their length translates into the superposition of peaks in the 550-900 nm energy range giving rise to the observed broad band the envelope of which varies with the average aspect ratio.

3. Morphological characterization of the Au NR

Au NR sample preparation for electron microscopy analysis

After the completion of growth, the particles settled down, forming a brownish gray film at the bottom of the bottles. The supernatant clear solution was discarded and the settled film was dispersed by addition of 2 ml of 10% (v/v) ethanolic water solution and centrifuged to 3000 rpm for 10 min and this process was repeated twice. The settled particles were then finally dispersed in a 10% (v/v) ethanol water solution and drop casted on a silicon substrate for scanning electron microscopy (SEM) analysis. SEM was performed on a ZEISS 1540XB Crossbeam with a Gemini SEM at 20kV voltage. Due to a remnant PEI/IL/CTAB layer on the particles, they tend to stick to each other forming agglomerates.

The crystallinity of the synthesized nanorods observed in Figure S1 is identical to the ones reported by Murphy *et al.* in the ‘zipping’ mechanism.⁵ All the numbered faces are indicated in the adjoining cartoons to the corresponding SEM images. This clearly indicates that the nanorod growth proceeds from the penta-twinning of the seeds.

With 0.8 mM PEI added to the GS, no nanorods were formed. Instead all the particles were irregularly spherical (Figure S2).

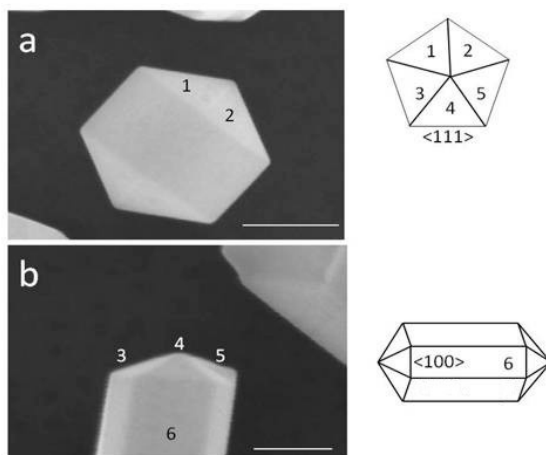


Figure S3: SEM micrograph showing the crystallinity of the AuNR synthesized from the Au seeds prepared in the ionic liquid medium with PEI as capping agent (scale bar 50 nm).

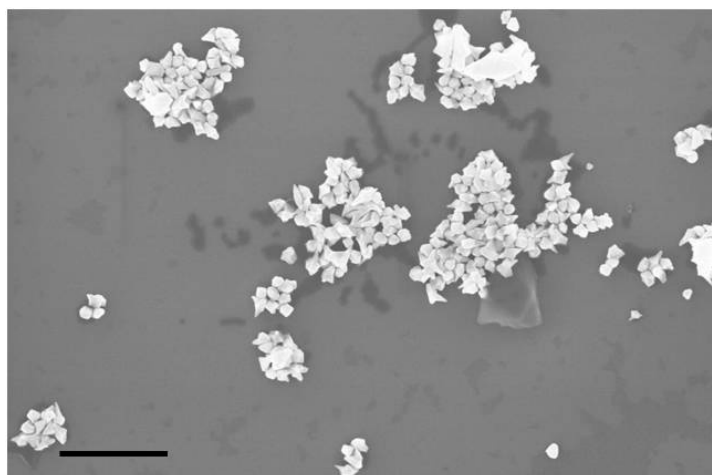


Figure S4: SEM micro graph of the sample with an excessive amount of PEI (0.8 mM) which led to complete inhibition of AuNR growth (scale bar 1 μ m).

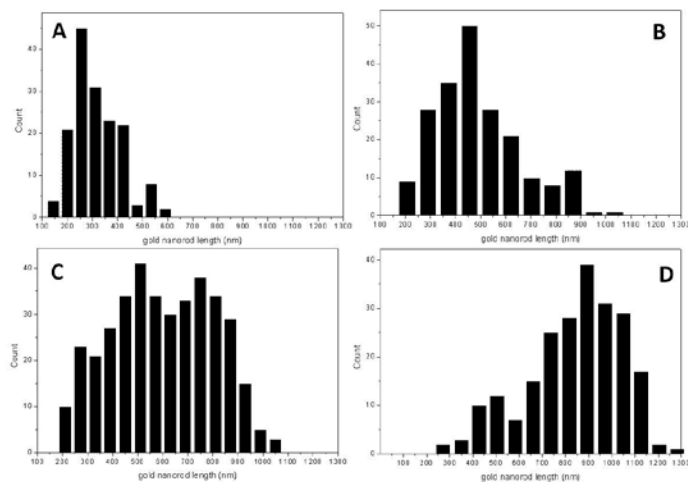


Figure S5: Histogram representation of the AuNR length shown in Figure 2.

4. Dynamic light scattering (DLS) experiments

DLS spectra were recorded using Zetasizer, Nano-ZS, Malvern Instruments.

Representative growth medium (RGS)

The growth medium was modified to suit DLS measurements. The concentration of the CTAB solution was reduced to 10 mM in order to avoid recrystallization and precipitation after IL addition. The PEI concentration was increased to enhance PEI capping over the Au seeds and to study the effect of added IL on its hydrodynamic diameter.

The final DLS sample of RGS was as follows:

2 mL of 10 mM CTAB, 4.1 mM emimHexSO₄, 0.38 mM of PEI solution in water.

Table S6: Samples used in the DLS measurements prepared from the aforementioned RGS with variation of IL content so as to investigate the CTAB-IL interaction with and without the presence of PEI coated seeds

Legend for data shown in Figure 4	DLS samples Figure S5, Figure S6	Sample medium	IL conc.	PEI from RGS	PEI coming with seeds	Au seed conc. % v/v
A	S5A	RGS (reference)	4.1 mM	0.38 mM	-	-
B	S5B	RGS	6.1 mM	0.38 mM	-	-
C	S5C	RGS	6.1 mM	0.38 mM	3 nM	1% (from stock)
D	-	RGS	8.2 mM	0.38 mM	3 nM	1% (from stock)
E	S6A	RGS	6.1 mM	0.38 mM	60 nM	20% (from stock)
F	S6B	RGS	8.2 mM	0.38 mM	60 nM	20% (from stock)

The DLS spectral peak spread (SPS) in A (Figure S5) is quite large. The signal comes from the inhomogeneous and unstable micelles formed by CTAB. As soon as extra IL was added to this medium, the SPS became quite narrow indicating that the medium was then organized due to added IL. Addition IL to AuNPs has a similar effect except with a slight increase in the apparent diameter. This may be due to the encapsulation of the AuNPs by the homogeneous pre-organized CTAB/IL micelles.

Figure S6A shows similar condition to S5C but with a 20 times higher AuNP concentration in the added IL. This makes the medium slightly unstable as indicated by the SPS broadening. However it narrowed down to a well-

organized state as soon extra IL was added to the medium. The extra IL made the IL concentration sufficient to regain condition C (Figure S5). But this came with an increased order in the medium which is indicated by the increase in apparent diameter by about 3 nm than in condition S6A.

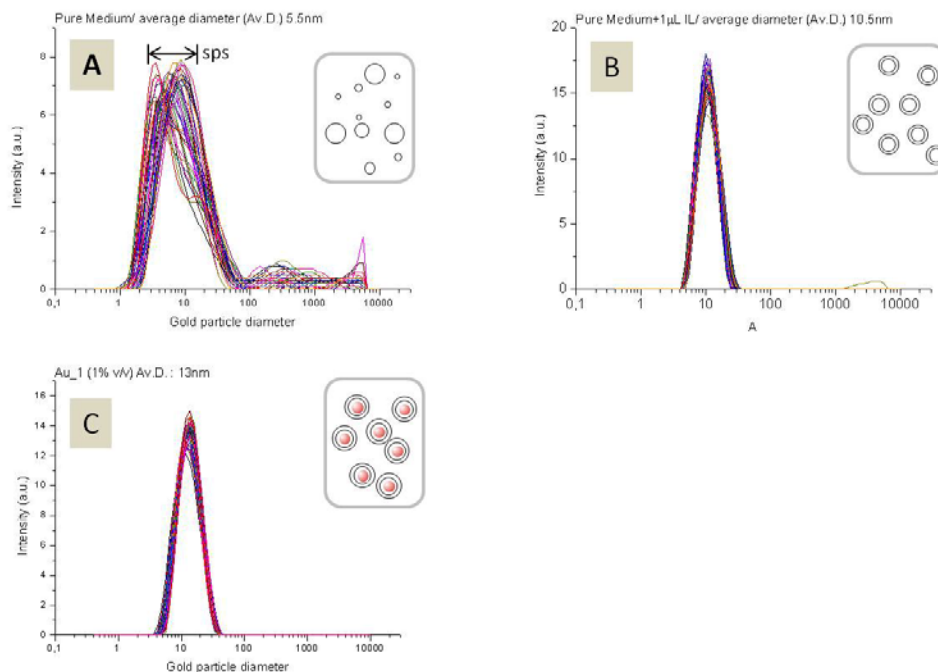


Figure S7: DLS spectra of the representative growth medium of different growth conditions reported in the manuscript. (A) Reference growth medium. (B) The addition of pure IL in medium (A) generates very homogeneous micelles (C) The addition of IL with Au seeds.

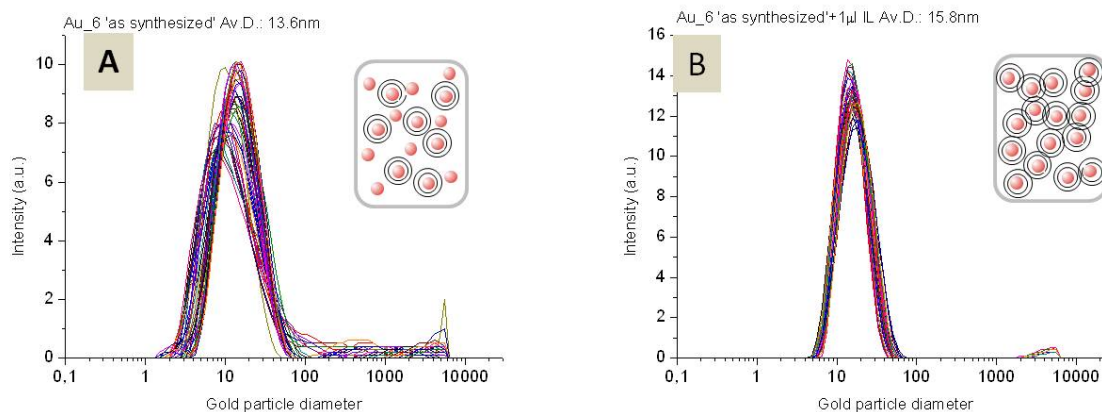


Figure S8: (A) Addition of IL with 20 times higher concentration of Au seeds, without extra IL addition. (B) Addition of extra IL in growth solution in condition (A) with the same seed concentration.

5. Atomic force microscopy (AFM) experiments

AFM studies were carried out using Veeco D300 for ambient atmosphere imaging. A Bruker bioscope catalyst AFM was used for liquid imaging.

NPs were immobilized on the Si/SiO₂ surface and wetted with the IL by drop casting. After some time the IL layer de-wetted the surface exposing the AuNPs again. This is shown in the AFM phase image in Figure S7A. The particles remain surrounded by the IL as seen as the dark corona around the particles. Figure S7B shows the height comparison between the dry particles and particles after de-wetting. It shows that the IL not only wets the PEI capped AuNP (after de-wetting from the rest of the surface) but also get absorbed in it to some extent. This can be seen by the slight increase in the height distribution of the particles. The change in the particle height under IL condition was about 3 nm, which is about 3 times more than in the case of IL de-wetting (Figure S8). This shows that the PEI layer is elastic and allows significant swelling under liquid.

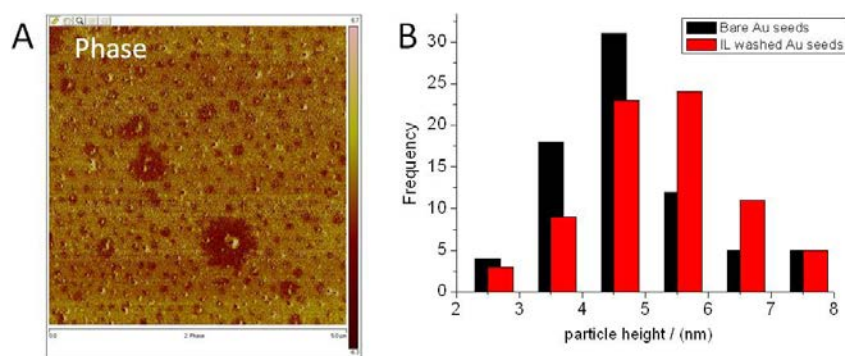


Figure S9: (A) The phase diagram shows the IL affinity towards the AuNPs. (B) Comparison of the AuNPs immobilized on a Si surface before (dry) and after wash with IL using AFM height signal.

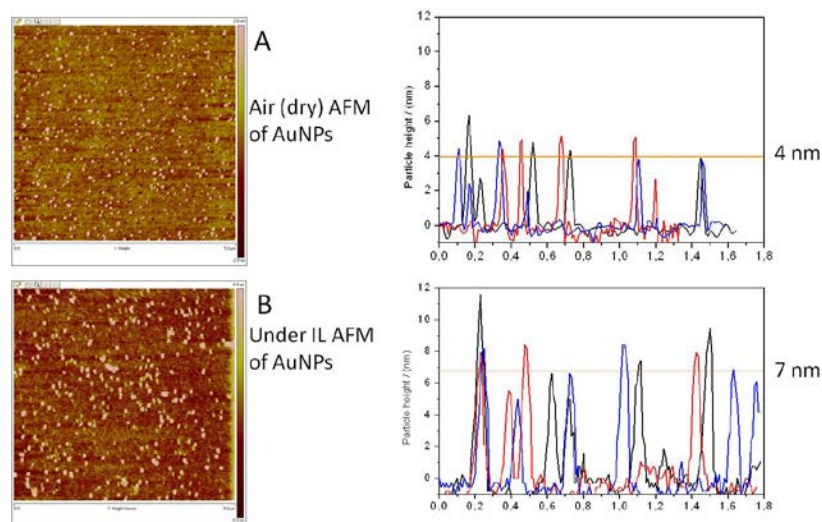


Figure S10: Change in AFM height signal of the dry and under liquid (IL) Au seeds. Height images of the (A) dry Au seeds (B) Au NPs under IL.

6. References

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