Stop-and-go, stepwise and "ligand-free" nucleation, nanocrystal growth and formation of Au-NPs in ionic liquids (ILs)[†]

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Ionic liquids function as a nanosynthetic template for a "ligand-free" stepwise formation of gold nanoparticles (Au-NPs) which can be stopped and resumed at different color steps and Au-NP sizes (between 2.6 and 200 nm median diameter) and which can be reasoned by the DFT-calculation stabilization order: H_2O (no Au-NP stabilization) < IL anion, *e.g.* $BF_4^- \approx PH_3 < citrate < Cl^-$ (which inhibits Au-NP growth).

From the antique cranberry (gold ruby) glass to the Purple of Cassius and modern day catalysts,¹ sensors,² coatings³ and bio-medical applications,⁴ gold nanoparticles (Au-NPs) have a long-standing importance⁵ as colloidal metals in nanotechnology applications due to their size,⁶ shape,⁷ and nanoenvironment-dependent optical properties.⁸ Au-NPs are typically synthesized by the Turkevich HAuCl₄-citrate reduction route;9 recent work demonstrated that the size and shape of Au-NPs can be controlled by the type of reducing agent.¹⁰ However, the possibility of a "ligand-free" step-bystep (crystal) growth of Au-NPs, essential for an understanding of the mechanism of nucleation, crystallization and nanocrystal formation, is not known. Ionic liquids (ILs) can stabilize metal nanoparticles on the basis of their high ionic charge, high polarity, high dielectric constant and supramolecular network,^{11–13} so that no extra stabilizing molecules are needed.14 Thus, monitoring and control of the nanocrystal formation and growth could be performed by using ILs as a novel matrix for nucleation and nanocrystal growth studies. Recently, Au particle growth in organic solvents was monitored (but without control) by synchrotron small/wide angle X-ray spectroscopy¹⁵ and optical single particle spectroscopy.¹⁶ Yet, mostly, we do not understand the nucleation and growth processes of nanocrystals.17

Here we report the step-by-step, "ligand-free" nucleation and nanocrystal growth of Au-NPs by the reduction of KAuCl₄ with SnCl₂ in ILs. The growth process is steered through the controlled dropwise addition of a KAuCl₄ solution to a mixture of SnCl₂/IL (eqn (1)). During the



Fig. 1 Selected colors with given molar Au: Sn ratios during the step-by-step Au-NP growth process (see also Table 1 and Fig. 3). The color change represents the transition of Au-NPs from non-metallic (white/yellow) to metallic and crystalline (red and purple) particles.

addition of KAuCl₄/IL to excess SnCl₂/IL the color changes from light-yellow through yellow, yellow-orange, orange-red, red-purple (Fig. 1), purple-brown, to brown-black and finally black-blue. Au-NP nucleation and nanocrystal growth can be stopped and resumed reproducibly at different color steps, representing the corresponding Au particle sizes (Fig. 1 and Table 1), by discontinuing the controlled KAuCl₄ addition.

$$2\left[KAuCl_{4}\right] + 3 \underset{(excess)}{SnCl_{2}} \xrightarrow{ILs}_{RT} 2Au^{0}_{(Au-NP)} + 2 SnCl_{4} + K_{2}[SnCl_{6}] (1)$$

The characteristic Au surface plasmon resonance (SPR) band^{6,18,19} (~520 nm) evolves in the UV/VIS spectrum (Fig. 2) and increases in relative intensity during addition of KAuCl₄, which we ascribe to the formation of larger (>4 nm) metallic and simultaneously crystalline Au-NPs (see Table S1 in ESI†).²⁰ Still, the short wavelength maximum at 360–380 nm, assigned to 1–3 nm non-crystalline Au-NPs²⁰ is retained, so that UV/VIS does not only show the growth of larger particles, but also the formation of new small Au-NPs during the addition of KAuCl₄. HRTEM and TEM measurements (Table 1, Fig. 3) show a bimodal particle size distribution upon continuous KAuCl₄ addition when the median larger particle size surpasses ~5 nm.

From transmission electron diffraction (TED/SAED, ESI[†] Fig. S8 and Table S1) and UV/VIS studies (Fig. 2) we observed a critical transition point from 1–3 nm amorphous and non-metallic Au-NPs to crystalline and metallic Au-NPs (\sim 3–5 nm) at a molar Au:Sn ratio of about 1:10 (Fig. 3), indicated by an increase in the gold plasmon band at around 520 nm. The median metal nanoparticle size depends on the added Au content and ranges from \sim 1.7 to max. 200 nm. (Table 1). It is suggested that the *in situ* formed precritical clusters (1–3 nm) of low structural order will grow by colliding and coalescing to form crystalline Au-NPs.²¹ A bimodal particle size distribution was observed due to the presence of

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Table 1 Au-NP size and range analyzed by (HR)TEM during the stepwise growth^a

No.	V(KAuCl ₄ /IL)/ molar Au:Sn ratio	TEM/HRTEM median diameter/nm (standard deviation σ) ^{<i>b,c</i>}		TEM/HRTEM size range/nm	
1	0.15 ml/1:24	2.6 ± 0.6		1.7–4.0	
2	0.3 ml/1:12	4.1 ± 1.0		2.3-5.6	
3	0.6 ml/1:6	4.9 ± 1.4	1.9 ± 0.4	4.4-6.8	1.3-2.6
4	0.7 ml/1:5	6.5 ± 1.5	3.2 ± 0.6	4.4-11	2.1-4.9
5	0.8 ml/1:4.5	7.6 ± 2.3	3.6 ± 0.7	5.0-16	2.0-5.5
6	0.9 ml/1:4	22 ± 6	4.1 ± 0.4	6.9-32	2.0-8.5
7	1.2 ml/1: 3	36 ± 10	5.9 ± 1.3	20-60	2.7-9.3
8	1.5 ml/1:2	200 ± 76	n.p. ^d	75–440	n.p. ^d

^{*a*} Brief experimental conditions: 30.0 mg (0.08 mmol) KAuCl₄ in 3.0 g (2.5 ml) IL, $c(Au) = 0.03 \text{ mmol ml}^{-1}$ from which a specified amount was added to 20.0 mg (0.106 mmol) SnCl₂ in 2.0 g (1.7 ml) IL, BMIm⁺BF₄⁻⁻ IL density 1.208 g cm⁻³. ^{*b*} Statistical evaluation of the total sample pictures (see ESI Fig. S2–S8). (HR)TEM = (high resolution) transmission electron microscopy. ^{*c*} Bimodal particle distribution for No. 3–7. ^{*d*} No small particles present any more.



Fig. 2 UV/VIS spectra of Au-NPs from KAuCl₄/SnCl₂ in BMIm⁺BF₄⁻. The spectral changes with the appearance and increased intensity of the Au SPR band around 520 nm (green arrows) indicate the transition of Au-NPs from non-metallic to metallic particles with a critical transition point at an Au:Sn ratio of $\sim 1:10$.

small and large Au-NPs (Table 1) because new nucleation and continuous nanocrystal growth processes occur simultaneously during the stepwise addition of the Au precursor solution. No size focusing effect was found during the synthesis as is known for, *e.g.*, colloidal nanocrystals with steric protecting ligands.²² The growth rate of larger Au nanocrystals does not seem to slow down and in addition aggregation between existing particles (Au_n + Au_{n'} → Au_{n+n'}) seemed to occur from a certain particle size on, as suggested by the more than doubling of the particle size between entries 5 and 6 in Table 1 (see ESI[†], Fig. S6 and S7). Agglomeration to larger Au nanocrystals in ILs is not prevented because of the only weak interaction of the IL species with the Au-NPs and, thus, is driven by the known



Fig. 3 HRTEM and TEM pictures of Au-NPs from $KAuCl_4/SnCl_2$ in BMIm⁺BF₄⁻⁻ (see ESI[†] Fig. S2–4 for enlarged versions). Molar Au:Sn ratios: (a) 1:24; (b) 1:12; (c) 1:6; (d) 1:4.5 (No. 1, 2, 3, and 5, respectively, in Table 1). HRTEM pictures (a) and (b) show no crystallinity. Crystalline Au-NPs are only indicated in (c) by the presence of lattice layers (interplanar spacing 2.35 Å in the cubic Au phase), see TED/SAED in ESI[†] Fig. S8 and Table S1).

strong aurophilic Au–Au interaction (Au cohesive energy 3.8 eV, $\sim 88 \text{ kcal mol}^{-1}$).²³

We have compared here for the first time the binding of different substrates to the electrophilic Au_n cluster surface *via* density functional theory (DFT) calculations (see ESI†). We have modelled the Au_n -substrate contact *via* the interaction of single substrate molecules with gas phase gold clusters. The relative binding energies (BE) of different substrates to the gold clusters are taken here as measures of the relative strength of their interactions.

Fig. 4 shows Au_n -substrate binding configurations and the variation of the BE with cluster size *n*. The BE of BMIm⁺ is found to be very weak (see Tables S2 and S3 in ESI† for the explicit numbers, other substrates and variation of the functional used). All the substrates show a smooth dependence of the BE with cluster size with a maximum for Au_2 (n = 2).

The BE of the IL BF_4^- anion is weaker than the BE of the usual stabilizing ligands (like citrate or PH₃) and never exceeds the gold–gold interaction. This suggests that a dynamic Au nanocrystal growth mechanism is responsible for the formation and stabilization of Au-NPs in ILs. BE comparison with chloride, citrate, PH₃ and H₂O illustrates the critical influence of the ionic charge and electron delocalization from the ligand to Au_n (Fig. 4). The softer the anion or ligand, that is, the more charge transfer or electron delocalization (according to Pearson's hard–soft concept and the nephelauxetic series)²⁴ to Au_n is possible, the better the stabilizing effect. H₂O as a hard and neutral ligand offers the least stabilization, hence, reduction of gold salts by SnCl₂ in water led immediately to the red purple solution (known as the Purple of Cassius).



Fig. 4 (a) Binding energies (BE) and addition energies depending on the cluster size. (b–f) Relaxed configurations of Au_6 bound to (b) Cl⁻, (c) citrate⁻ (C₆H₇O₇⁻) (d) PH₃, (e) BF₄⁻ and (f) H₂O. (g) Relaxed configuration of Au_7 . The bond lengths are given in Å.

Remarkably, the relatively soft chloride anion shows the largest BE in agreement with the strong covalent binding of chloride ions to the Au(111) surface found in recent DFT simulations.²⁵ Furthermore, its BE exceeds the gold-gold interaction for small n. This theoretical result suggests that the chloride anion is able to stop the growth process of gold clusters completely. Indeed, experimentally, the presence of free Cl⁻ by using a mixture of BMIm⁺ BF_4^- and the analogous BMIm⁺ CI^- inhibits the Au-NP growth and results in an almost colorless solution (see ESI[†] Fig S9). We propose that the dissolved KAuCl₄ is first reduced by the SnCl₂ salt to give zero valent Au-metal atoms. These zero valent Au atoms collide in solution with other Au atoms or add to the surface of small clusters that have already formed (nucleation and surface growth). To initiate nucleation, the concentration of metal atoms in solution must be high enough to reach "supersaturation".²⁶ After reaching a critical Au_n concentration secondary growth can occur by bimolecular aggregation of Au_n particles (Au_n + Au_{n'} \rightarrow Au_{n+n'}).

If surface and secondary growth are of comparative rate a bimodal particle size distribution will be obtained (Table 1).²⁷ Normally the secondary growth process is faster than surface growth and is slowed down until it is finally stopped by the presence of a surface-capping ligand.²⁸ ILs are not acting as strong capping ligands (Fig. 4), but as a *kinetically* stabilizing, dynamic molecular network in which the reduced Au⁰ atoms and clusters can move by diffusion and cluster together. Thus, the Au nanocrystals can nucleate and grow in a step-by-step manner through the controlled addition of new gold precursor material in an efficient way. At the desired size the Au-NPs can be *thermodynamically* stabilized through the post-synthetic addition of a capping ligand, *e.g. n*-butylimidazole, see ESI[†].

In conclusion we describe here a simple and reproducible method for a "ligand-free", stop-and-go step-by-step nucleation and nanocrystal growth process of Au nanoparticles in ILs as a "novel nanosynthetic template" through the controlled addition of the reactants. A DFT-calculated weak binding energy (BE) of the IL BF_4^- anion to gold clusters never exceeds the gold–gold interaction and supports the model of a dynamic Au_n···IL stabilization, nucleation and nanocrystal growth process.

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