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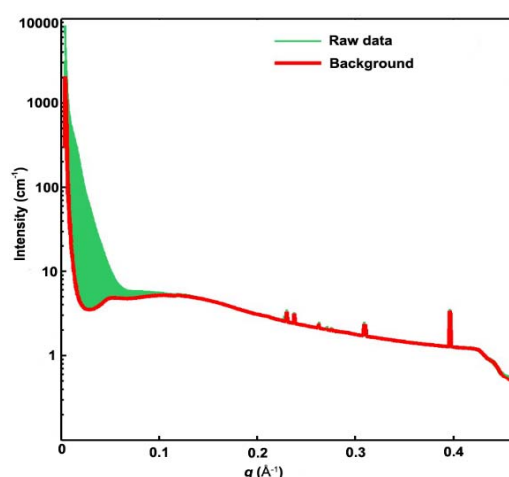
**Volume 54 (2021)**

**Supporting information for article:**

***In situ* small-angle X-ray scattering investigation of X-ray-induced gold nanoparticle synthesis without stabilizer**

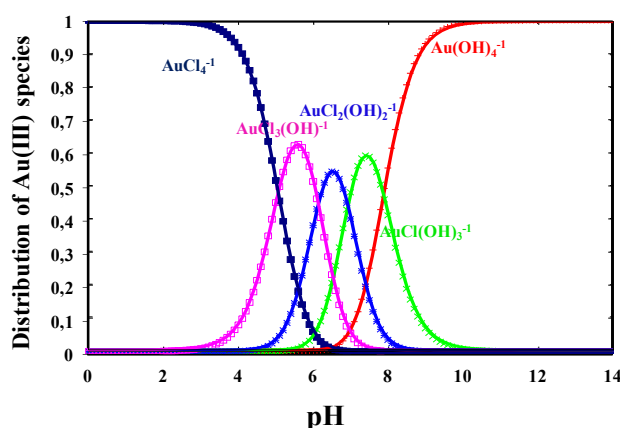
**Fangzuo Li, Qianqian Xu, Wenjing Xia, Xiang Zhang, Weidong Zhao, Lili Zhou, Haijian Zhong, Weijie Peng, Zhiguo Liu and Tianxi Sun**

**SAXS subtraction procedure.** As the experiment is designed to follow the early nucleation and further growth of nuclei and particle coalescence of AuNPs, a special attention was devoted to the correction of the background. Indeed, there are significantly two main physical backgrounds contribute to a scattering pattern. First, the walls of the capillary containing the solution are contributing at low  $q$ . At large  $q$ , just after the mixing of the  $[\text{HAuCl}_4]_{\text{aq}}$  and  $[\text{NaOH}]_{\text{aq}}$ , there is an addition of the contribution from the solvent (a flat contribution in the  $q$ -range used) and from the different solute still unreacted. As a matter of fact, the two separated solutions present a very weak (but measurable) structuration containing very small objects (less than 1nm). Accordingly, a capillary filled with solvent is not the correct background to subtract when one wants to observe the scattering by the gold nuclei alone. Fortunately, the first scattering diagram is obtained after only 100ms shows that the gold reduction is still in course. Moreover this scattered intensity is very weak at every  $q$  (as compared to what it becomes later) and contains all the contributions we are looking for. Therefore, the first diagram was considered as the background of all the subsequent diagrams in the sequence and was then directly subtracted to them since nor the thickness of the sample nor the transmission evolve with time, as shown in Fig. S1. It is nevertheless an approximation, since the solute concentration evolves with time due to the formation of the particles. However, the evolution of the background with time could not be measured independently and the present approximation was effective not only at short time where the background contribution was indeed comparable to the signal but also at longer time since the background effect was far less than the signal of the particles at large  $q$ .



**Figure S1** Background correction: the first frame (red line) is subtracted from all subsequent data (green).

**The speciation of Au(III) chloride complexes at different pH.** From the difference of UV-spectra of the hydrolysis species, the speciation diagram gold(III)  $\text{AuCl}_{(4-n)}\text{OH}_n$  versus pH can be obtained as shown by Mironov et al., (Mironov, et al., 2009), and reproduced it here on Fig. S2.

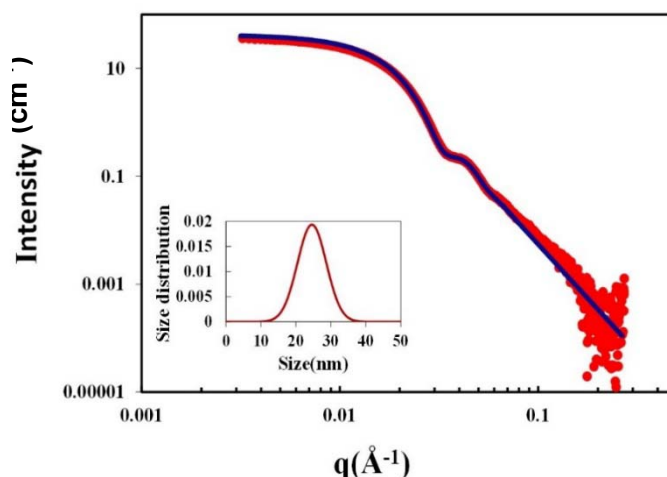


**Figure S2** molar fraction (d) of Au(III) chloride complexes as a function of pH ( the dissociation constants for stepwise hydrolysis of Au(III) complexes were obtained from the Auk overall equilibrium constants are:  $\log_{10}\beta_{10} = 7.87$ ,  $\log_{10}\beta_{20} = 14.79$ ,  $\log_{10}\beta_{30} = 20.92$  and  $\log_{10}\beta_{40} = 25.98$  at the ionic strength  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$  and  $t = 25^\circ\text{C}$  ). Data are taken from the literature (Mironov, *et al.*, 2009).

**SAXS fitting procedure.** In order to extract the number density  $n$ , the radius  $r_0$  and the polydispersity  $\sigma$  of the nuclei and growing nanoparticles, the scattering from a population of objects is calculated and compared to the SAXS data. The size distribution and number of particles are adjusted to give the best fit using a Levenberg-Marquardt algorithm. In the case of a diluted assembly of spherical particles, the scattered intensity is given by:

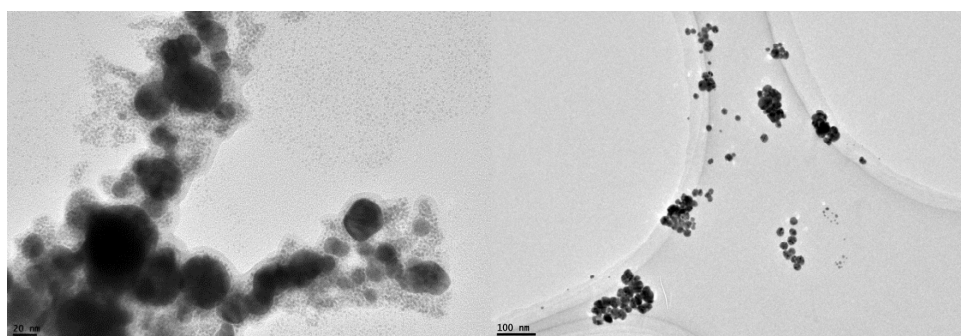
$$I(q) = \Delta\rho^2(n \int f(r)V(r)^2P(q,r)dr) \quad (2)$$

Where  $V(r)$  and  $P(q,r)$  are the volume and the form factor of a sphere of radius  $r$ .  $f(r)$  is the size distribution function of the particles. The best results were obtained for a population  $f(r)$  of spheres with a gaussian size distribution. A representative scattering curve recorded at 17s and the corresponding fitting curve and size distribution was shown in Fig. S2.



**Figure S3** SAXS data: a representative scattering curve recorded at 17s and the corresponding fitting curve for measurement in the AuNPs synthesis experiment with the chemical condition:  $[\text{Au(III)}]=2\text{ mM}$  without NaOH, the fixed pH= 2.3. Inset: The size distribution correspond to the fitting.

**TEM images for the final collected AuNPs.** The produced AuNPs have been collected and the final states have been characterized by TEM (see Fig. S3). The bare particles are not stable with time. The TEM shows the AuNPs aggregate in some area and big particles in well-defined shapes and sizes are obtained.



**Figure S4** Left: The TEM images of final states of produced AuNPs. Right: sharp shape of AuNPs.

## References

1. Mironov, I. V. & Makotchenko, E. V. (2009). *J. Solution Chem.* **38**, 725.