## Gold Nanoparticle Superlattice Crystallization Probed In Situ

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The nucleation and growth of three-dimensional superlattices of gold nanoparticles has been followed directly *in situ* by means of small angle x-ray scattering. These assemblies spontaneously form in a dilute solution providing the particles are large enough to generate a van der Waals driven attraction sufficient to counterbalance the thermal energy. The superlattices nucleate very soon after the birth of the individual particles and their growth kinetics is slower than predicted by a mechanism of simple diffusion of the nanoparticles towards the superlattices. The superlattices are first limited in size (170 nm in diameter) and have a globular shape with a low polydispersity. They present a fcc inner structure with nanoparticles being separated by a capping agent bilayer yielding a low gold internal volume fraction ( $\phi_{SL} = 0.33$ ). In a second stage, these superlattices coalesce with time.

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Self-assembly of particles into ordered structures is a matter of interest from both fundamental and applicative standpoints. Organization is triggered by short or long range interactions between the elementary building blocks and can lead to photonic crystals through crystallization of (sub)-micrometer particles (synthetic opals) [1] or nucleation of protein crystals which is a crucial step toward subsequent structure elucidation. Decreasing the size of the elementary units has opened new routes for future devices [2] based on nanoparticle (NP) superlattices (SL). SL can be obtained either in the form of extended 2D monolayers or 3D aggregates through the evaporation of a NP dispersion onto a substrate. In that case, they can eventually present a large structural diversity [3,4]. The role of hydrodynamic forces during drying might be of importance in the organization process, as recently shown in the case of CdS nanorods self-assembly [5]. Out of equilibrium configurations can prevail depending on the balance between interparticle forces (van der Waals, dipolar, steric forces) [6,7], substrate-particle interaction and flow induced in the evaporating droplet. As a matter of fact, recent in situ scattering experiments have shown that the kinetics of evaporation strongly influences the structure of nanocrystal superlattices [8,9]. A few publications [10–13] report on 3D arrays of NP spontaneously formed in solution, and they do not include time resolution or in situ structural characterization. Accordingly, until now, the spontaneous occurrence of 3D superlattice from dilute dispersions without the help of drying forces has not received a complete kinetical and structural description. Here, we use in situ time-resolved small angle x-ray scattering (SAXS) to follow *in solution* the rapid self-assembly of gold nanoparticles yielding face cubic centered 3D superlattices. This spontaneous process occurs in very dilute dispersion ( $\Phi_{\rm NP} = 2 \times 10^{-5}$ ) and only a few seconds after the initial formation of the nanoparticles. The gold NPs were synthesized by mixing two toluene solutions containing a cationic surfactant (DDAB) as described

by Jana and Peng [14]. In the first one a gold salt (AuCl<sub>3</sub>) was solubilized and in the second one an oil soluble borohydride reducing agent and decanoic acid were mixed. Gold concentration after mixing was  $[Au] = 3.5 \times 10^{-3} M$ and the other components concentrations obeyed the following ratios : [DDAB]/[Au] = 8; [borohydride]/[Au] =4;  $[C_{10}OOH]/[Au] = 28$ . In order to be studied by time resolved SAXS experiments [performed at the ID2 beam line at the European synchrotron radiation facility (ESRF)], the two solutions were mixed using a SFM-400 stopped flow apparatus [15–17] from Biologic. This system enables a fast and turbulent mixing in a micrometer size chamber followed by an injection (in a few ms) in a glass capillary where flow is further stopped by a pneumatic system enabling steadiness and sequential acquisitions of the SAXS diagrams. The sample detector distance was initially set at 1.5 m for an incident beam energy (11.5 keV) just below the L3-edge of gold. Figure 1 shows the scattering patterns of the solution after mixing as a function of time. Starting from an initially flat scattering pattern, characteristic of a salt solution, a rapid increase in intensity is observed until  $t_1 = 10$  s. No trace of inter-



FIG. 1. SAXS patterns as a function of time during the formation of the gold nanoparticles superlattice.

actions between the particles can be seen, in agreement with the very small volume fraction of total gold in the mixture. More precisely, the diagrams during this phase can be fitted to the intensity scattered by a (noninteracting) Gaussian distribution of spheres. The intensity scattered by an assembly of spheres of volume V in interaction is sensitive to their size through the form factor  $P(\vec{q})$  and their organization through the average structure factor  $S(\vec{q})$ :

$$I(\vec{q}) = \Phi V P(\vec{q}) S(\vec{q}), \tag{1}$$

where  $\Phi$  is the volume fraction of the particles and  $\vec{q}$  the scattering vector. This first phase reveals the particles' formation processes, which have been detailed in a previous paper [18] for other concentrations conditions. It was shown that when an alkylamine was used as the ligand (instead of the carboxylic acid), a single burst of nucleation yields small NPs (r = 1.5 nm in average) which do not further grow. When using carboxylic acid ligands (with a acid/gold concentrations ratio of 14), the nucleation stage is followed by a growth regime yielding larger particles (r = 3.7 nm). In both cases no further evolution of the patterns was observed during the experiment, which lasted no longer than a few minutes. In the present case, the concentration of carboxylic ligand has been doubled, inducing a decreasing power of the reducing agent [18], and hence a smaller nucleation rate and larger particles. However, invariant calculation time shows again that the particle growth is finished at  $t_1$ . At this time, the scattering pattern can be fitted with a Gaussian distribution centered at 5 nm with a standard deviation of 0.9 nm. Surprisingly and despite the very low volume fraction, strong correlation peaks appear after  $t_1$ , revealing an organization between nanoparticles. These peaks are increasing in intensity during a period of 40 s and finally remain steady until the end of our experiment. In order to extract an average structure factor S(q) using Eq. (1), the scattering patterns after  $t_1$  were divided by the experimental scattered intensity obtained just before the appearance of the peaks. This procedure yields S(q) as a function of time as shown in Fig. 2(a). The peaks can be readily indexed to Bragg positions of a face cubic centered (fcc) lattice with a lattice parameter  $(a_{SL})$  of 21.5 nm leading to 15.2 nm for the center to center distance between two closest neighbors. This value is in close agreement with the average radius of the stabilized gold nanoparticles. Indeed, the NPs are stabilized by a ligand monolayer whose thickness  $\delta$  can be estimated to 1.4 nm in the present case of  $C_{10}$  alkyl chain by using the Tanford formula [19]. Thus, due to polydispersity of the core, the observed center to center distance  $\bar{d}$  between two first neighbors in the crytals has to be averaged over the size distribution [f(r)] with the respective scattering power (proportional to  $r^6$ ) of each particle:



FIG. 2 (color online). (a) Apparent structure factors S(q) obtained by dividing the experimental pattern by the one obtained at  $t_1$ . (b) Theoretical S(q) for a fcc crystal of limited size (85 nm) obtained from Debye formula in equilibrium with a variable amount of free particles  $\alpha = 0.1, 0.35$ , and 0.9

$$\bar{d} = 2(\bar{r}+\delta) = 2\left(\frac{\int r^6 f(r)rdr}{\int r^6 f(r)dr} + \delta\right).$$
 (2)

The obtained values ( $\bar{d} = 14.5 \text{ nm}$ ,  $\bar{r} = 5.85 \text{ nm}$ ) mean that the particles covered by a layer of ligands are in close contact within the superlattices. Thus, the gold volume fraction  $\phi_{SL}$  inside the SL obtained from :  $\phi_{SL} = \frac{16\pi}{3}\bar{r}^3/a_{SL}^3$  is low and only equal to 0.33. The size of the superlattice particles can be obtained by using SAXS patterns acquired at a larger sample to detector distance (10 m). In the Porod plot shown in the inset in Fig. 3, oscillations are clearly seen at low q in the time regime where Bragg peaks are present and are the signature of the external envelope of the superlattice. Their presence is a proof of a globular shape with low polydispersity for the SLs. Assuming a spherical shape, the average size of the minimum of oscillation by  $q^*R_{SL} = 4.5$ . In addition, the



FIG. 3 (color online). (Top)  $N_{\rm SL} \approx I_{\rm min}^{\rm SL}/R_{\rm SL}^6$  versus time,  $I_{\rm min}$  is the intensity at the minimum of oscillation. Inset: Porod plot of the small angle intensity at different times. (Bottom) Radius  $R_{\rm SL}$  of the superlattice in formation versus time.

intensity  $I_{\min}^{SL}$  at  $q^*$  is proportional to the number  $N_{SL}$  of superlattices as stated by the classical relation:  $N_{\rm SL} \simeq \frac{I_{\rm SL}^{\rm SL}}{R_{\rm SL}^6}$ . Both  $R_{\rm SL}$  and  $\frac{I_{\rm SL}^{\rm SL}}{R_{\rm SL}^6}$  are reported in Fig. 3. Three different phases in time are observed. First, from 10 to 50 s the radius of the superlattices increases up to 85 nm, meanwhile their number is constant. The complete fitting of the oscillations leads to  $81 \pm 12$  nm, recovering the 85 nm determination by the minimum position. This is a pure growth regime meaning that the nucleation phase cannot be extracted from the data either because it is too rapid or the signal of the NPs themselves is masking it. Then, from 50 to 300 s the radius and number are strictly constant. Finally, beyond 300 s, the radius increases again and the number of superlattices is decreasing. The persistence of an oscillation in the Porod plot in this time phase means that a globular shape is preserved after the fusion and strongly supports a coalescence process between SL against an aggregation scenario. The low internal volume fraction of gold (0.33) in the SL can explain this possible rapid reorganization. The growth of the SL by coalescence is accompanied by their sedimentation as shown by the decrease of the SL volume fraction  $N_{\rm SL}R_{\rm SL}^3$ . In the stationary regime, the number of NP inside one superlattice grain is in average:  $N_P = \frac{16\pi}{3}R_{\rm SL}^3/a_{\rm SL}^3$  leading to around 1000 particles in each superlattice of 85 nm radius. As NPs are joining the SLs from the solution, at any time, the scattered intensity comes from a fraction  $\alpha(t)$  of free NPs and  $1 - \alpha(t)$  of NPs involved in SLs [20]. In that model the average structure factor *S* is a linear combination of the structure factor of the dilute suspension of free NPs ( $S_{\rm NP} = 1$ ) and of the SLs structure factor  $S_{\rm SL}$ :

$$S = \alpha(t) + [1 - \alpha(t)]S_{\rm SL}.$$
(3)

Equation (3) can be applied for the fully developped SLs [t = 59.7 s in Fig. 2(a)] using the Debye formula to calculate the structure factor  $S_{SL}$  of a fcc crystal of limited size. Theoretical structure factors are shown in Fig. 2(b) with different  $\alpha$  values keeping  $R_{\rm SL}$  equal to 85 nm as already obtained. At very low q the theoretical structure factor is dominated by the strong increase of  $S_{SL}$ . At larger q, on a small q range (0.02–0.03 nm<sup>-1</sup>), S is equal to  $\alpha$  due to the deep depression in  $S_{SL}$ . This allows to determine the final fraction of NPs in equilibrium with the SLs ( $\alpha^* =$ (0.35) with a good accuracy. In that case, the amplitude of the experimental first peak is slightly too high and the clear theoretical separation between 220 and 311 is not recovered experimentally. This can be explained by the lower resolution of the S(q) extraction in this q region due to the oscillation of the P(q) of the NP. The lower experimental Bragg peak amplitude may come either from the slight polydispersity of NPs or from the fact that the SL contains a few domains of smaller size. A last important point is the kinetics of apparition of these crystals. Their final total number is set by their internal average population (1000). The total number of gold nanoparticles per unit volume  $n_{\rm NP}$  at  $t_1$  was  $6.0 \times 10^{-8}$  mol/L as determined by the fitting of the scattering pattern at this time and thus the maximum total numbers of SLs per unit volume  $N_{SL}$ was accordingly  $3.9 \times 10^{-11}$  mol/L (taking  $\alpha^* = 0.35$ ). Assuming that they all nucleate on a very short time scale, a growth limited by diffusion of the nanoparticles towards the crystals would give the following time dependence of the radius  $R_{SL}$  of the superlattices [21]:

$$\frac{dR_{\rm SL}}{dt} = v_{\rm NP} \frac{D_{\rm NP}}{R_{\rm SL}} \left( n_{\rm NP} (1 - \alpha^*) - \frac{N_{\rm SL}}{v_{\rm NP}} \frac{4\pi}{3} R_{\rm SL}^3 \right), \quad (4)$$

where  $v_{\text{NP}}$  is the volume of one NP in the superlattice (not in solution) is 2500 nm<sup>3</sup> considering the fcc structure and the thickness of the organic layer,  $D_{\text{NP}}$  their diffusion coefficient in the organic solution. The solubility of the superlattice in nanoparticle is taken into account by  $\alpha^*$  in Eq. (4). Assuming that the nucleation started at  $t_1$  and is very rapid, we consider that  $t_1$  is the initial time for the growth in Eq. (4). The calculated radius is reported as a full line in Fig. 3. The experimental radius is increasing slightly



FIG. 4 (color online). van der Waals interaction between two gold particles in toluene versus their face to face separation.

less rapidly than predicted by a diffusion limited model, showing that a supplementary activation barrier has to be passed for a NP to join a SL or that the nucleation stage is not instantaneous and spans over a few seconds. The last point to be discussed is the origin of the driving force for this crystallization obtained in very diluted conditions in large contrast with the classical SL obtained by evaporation and concentration. In the present system, the chemical nature of the ligand and the gold to ligand quantity could be used to tune the final size of the particle [14, 18] and over the different experimental conditions tested these SLs happened to form when the final radius of the gold particles was over 4 nm. This shows that a force depending on the size of the particles is involved in the formation of the SLs. Accordingly, the van der Waals (vdw) attraction between particles is a good candidate since gold is one of the most polarisable material. Figure 4 reproduces the vdw potential for gold particles as a function of the distance between them for 3 different radiuses using an Hamaker constant of 1.9 eV [22]. At separation distances comparable to the one observed in the SL ( $\simeq 2.8$  nm), the amplitude of vdW potential is sufficient to counterbalance the thermal energy only when the gold particles are sufficiently large. If the particles are too small, thermal energy will disperse the particles and self-assembly will not be possible. On the other side, if the particles are too large, the attractive force are too strong for the clusters to organize into crystalline equilibrium structures. In this case, irreversible aggregation occurs and amorphous (fractal) precipitates are preferred. The size dependent adhesion energy also explains that the smaller particles in the distribution will have difficulties to find a correct stable position in the SL which supports the existence of a fraction of free NPs. In conclusion, our experiments show that nanoparticles selfassembly can occur in solution without any specific interaction between them and in the absence of any hydrodynamic interaction and substrate effect. The crystalline assemblies are of fcc nature with a low volume fraction. The methodology used here to follow the spontaneous crystallization of superlattice can be extended to many other systems and open new insights in the understanding of crystallization process by allowing comparison of measurable quantities with predictive model.

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