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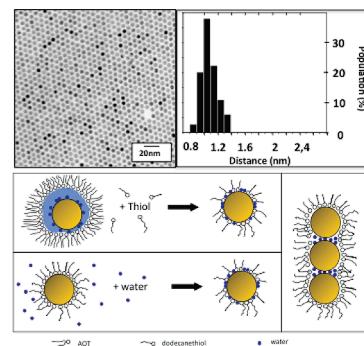
How to Tune the Au Internanocrystal Distance in Two-Dimensional Self-Ordered Superlattices

Caroline Salzemann, Wei Zhai, Nicolas Goubet, and Marie-Paule Pilani*

UPMC Université Paris 06, UMR 7070, Laboratoire LM2N, F-75005 Paris, France

ABSTRACT Hydrated and anhydrous Au nanocrystals with the same size dispersion and coating agent are synthesized from two procedures. Intriguing, the interparticle distance in two-dimensional (2D) self-ordered Au nanocrystals can be tuned by the amount of water molecules added to anhydrous Au nanocrystal solution. This behavior could be attributed to adsorption of water molecules either to the Au nanocrystal surface or on the dodecanethiol alkyl chains inducing their shrinkage. Taking into account various syntheses performed in hydrated media and the influence of water molecules on the appearance of attractive interactions between nanocrystals (measured by others), we claim that the presence of water molecules induces a competition between their adsorption at the metallic hydrophilic surface of Au nanocrystals and the chemisorption of the dodecanethiol. These adsorbed water molecules lead to additional attractive adhesion forces, which decrease the internanocrystal distance, whereas the strong thiol–Au bonding maintains the 2D long-range ordering of the nanocrystals.

SECTION Nanoparticles and Nanostructures



Au nanocrystals are extensively studied because of their outstanding potentialities in catalytic, electrical, optical, and biomedical applications.^{1–3} In particular, a very large number of groups have produced Au nanocrystals self-ordered in compact hexagonal networks.^{4–8}

Indeed, self-organizations of nanocrystals represent a new generation of materials having specific properties compared with those of the isolated nanocrystals and the bulk material. It has been shown that two-dimensional (2D) self-ordered silver and cobalt nanocrystals exhibit collective optical and magnetic properties due to dipolar interactions.⁹ Recently, it has been shown that the collective optical properties due to the self-ordering of silver nanocrystals markedly depend on the average internanocrystal distance.¹⁰ Until now, the interparticle distance is mostly controlled by the dispersion solvent and the alkyl chain length of the coating molecules stabilizing the particles.^{11,12} The microscopic mechanism for self-organization of ligand-stabilized nanocrystals is well established as a competition between the interparticle van der Waals interaction, which provides attractive forces inducing the self-assembly of the nanocrystals, and the steric repulsion due to the ligand molecules providing stable structures.^{9,13–16}

Here we show that the internanocrystal distances in 2D self-ordered Au nanocrystals can be tuned, keeping the same size and coating agent. We show that the presence of water molecules in colloidal solution of Au nanocrystals induces a competition between their adsorption at the metallic hydrophilic surface of Au nanocrystals and the chemisorption of the dodecanethiol. These adsorbed water molecules lead to additional attractive adhesion forces,

which decreases the internanocrystal distance whereas the strong thiol–Au bonding maintain the 2D long-range ordering of the nanocrystals.

Au nanocrystals have been synthesized by using two different methods. The syntheses have been repeated several times, and all the data described below are highly reproducible. The first procedure (I) is based on a chemical reduction by hydrazine of an aqueous solution of HAuCl₄ solubilized in Na(AOT) reverse micelles.^{15,17,18} The second procedure (II) is based on the chemical reduction of chlorotriphenylphosphine Au dissolved in toluene by a *tert*-butylamine borane complex. At the end of the syntheses, Au nanocrystals are washed by ethanol to remove the residual surfactants and dispersed in toluene. A drop of a solution containing the nanocrystals is deposited on a transmission electron microscopy¹⁹ (TEM) grid covered with highly oriented pyrolytic graphite (HOPG). A sheet of filter paper placed underneath the grid absorbs the solvent inducing a flux of the colloidal solution on the substrate. For either procedure (I or II) a long-range assembly of Au nanocrystals ordered in a compact hexagonal network is observed (Figure 1A,C, respectively). The average diameters²⁰ and size dispersions²¹ of Au nanocrystals deduced from the TEM image, corresponding to a large covering of the substrate, are 5.5 ± 0.4 nm and 5.3 ± 0.3 nm. In fact, here we produce, by two different procedures, Au nanocrystals having similar diameters, size dispersions, and coating agents. By

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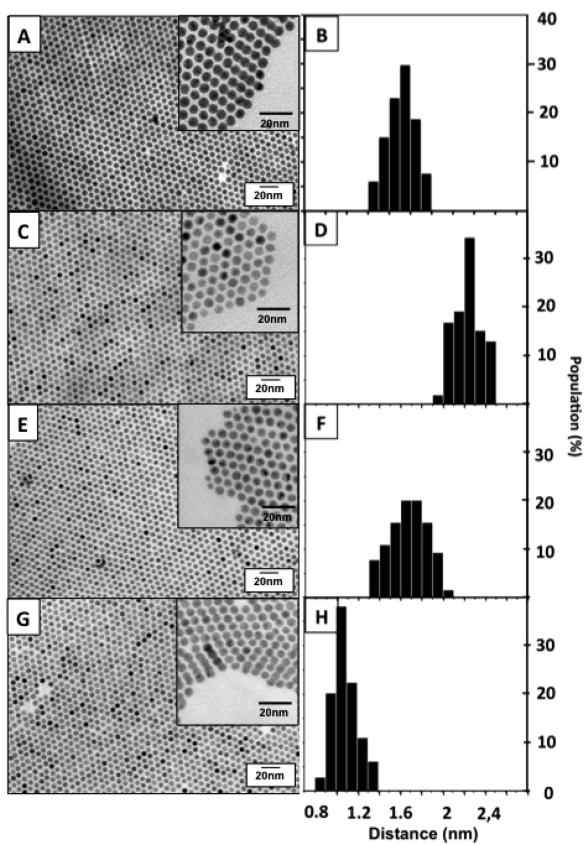


Figure 1. 2D self-ordered Au nanocrystals on HOPG. Long-range self-assembly of Au nanocrystals obtained from procedure I (A), from procedure II without water (C), with 4 % water (E), and with 20 % water (G). Insets: the corresponding monolayer edges. (B,D,F,H) Corresponding interparticle distances.

procedure I, the average distance between Au nanocrystals (border-to-border), measured on the long-range area of the nanocrystals ordering (Figure 1A) is 1.6 ± 0.2 nm (Figure 1B). At the edge of the nanocrystal monolayer, coalescence is observed in the direction of the hexagonal network where the internanocrystal distance is the smallest (Figure 1A inset). For nanocrystals produced via procedure II (Figure 1C) the interparticle distance is 2.2 ± 0.2 nm (Figure 1D), and, conversely to procedure I, no coalescence is observed at the monolayer edges (Figure 1C inset). This change in the average internanocrystal distance is related to the procedure used to obtain the nanocrystals and cannot be attributed either to the nanocrystal size, the solvent, or the deposition process. A careful comparison of the synthesis modes (see below) shows that the significant difference between the two procedures (I and II) could be due to residual water molecules when nanocrystals are produced from reverse micelles (water-in-oil droplets), whereas no aqueous solution is involved in procedure II. To support such claim, let us consider the addition of water from $20 \mu\text{L}$ (4 %) to $100 \mu\text{L}$ (20 %), or none, to a 0.5 mL colloidal 5.3-nm Au nanocrystal solution obtained by procedure II. Note that the colloidal solution remains optically clear after water addition. In the absence of any water molecules, we observe large monolayer domains (Figure 1C) without

coalescence at their edges (inset). For any amount of added water molecule, a large compact monolayer of Au nanocrystals is observed (Figure 1E,G). However, the internanocrystal distance progressively decreases, with increasing the amount of water in the initial colloidal solution, from 2.2 ± 0.2 nm in the absence of water (Figure 1D) to 1.7 ± 0.2 nm (Figure 1F) and 1.1 ± 0.2 nm (Figure 1H) by addition of 4 % and 20 % aqueous solution, respectively. At the monolayer edges, the internanocrystal distance remains the same over all the monolayer when 4 % of water is added (inset Figure 1E), whereas for 20 % there is a marked decrease in the internanocrystal distance, and coalescence between nanocrystals occurs (Figure 1G inset). Hence, the decrease in the internanocrystal distance with appearance of coalescence of nanocrystals at the monolayer edges is the same for Au nanocrystals produced either in reverse micelles (Figure 1A) or by procedure II in the presence of 20 % water solution. From these results, it is clear that the changes in the internanocrystal distance of long-range ordered nanocrystals are related to the presence of water in the colloidal solution. A question arises: What is the influence of water on the interparticle distance control when Au nanocrystals are deposited on a substrate? To answer this question, the best would be to detect the water molecules either freely trapped in alkyl-chains or adsorbed at the Au nanocrystal interface and/or on the alkyl-chains. Different methods such as NMR, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIRS) cannot be used because of the too low amount of valuable matter and also the presence of signals due to other compounds such as alkyl-chains, residual chemicals, and/or solvent. A colloidal solution of Au nanocrystals is optically clear. We know that UV-visible technique is very sensitive, and a well-defined Plasmon-resonance peak, which is highly sensitive to the environment, characterizes the absorption of Au nanocrystal colloidal solution. A slight change in the maximum of the Plasmon resonance peak has been observed, indicating a slight change in the surrounding Au surface. However, this can be due either to adsorption of water molecules at the Au nanocrystal interface or to water molecules solubilized in toluene, which could change the dielectric constant of the surrounding media. Hence, this technique cannot distinguish between both behaviors, which could explain such short interparticle distance. Indeed, a rather large amount of water molecules solubilized in toluene could change the interactions between nanocrystals in the hydrated toluene solution ²² and the hydrophobic alkyl-chains should begin to constrict, forming bundles containing trapped free water molecules and consequently inducing a decrease of the interparticle distance. This cannot be retained for the following reasons: (i) from procedure I, Au nanocrystals are extracted from the micellar solution and redispersed in anhydrous toluene before being deposited, and (ii) by annealing the Au nanocrystal 2D superlattices at 150°C , no change in the interparticle distance is observed, indicating no free water molecules are trapped to the bundles. However, the presence of bound water molecules on the dodecanealkyl chains used to coat the Au nanocrystals cannot be excluded. At this point we conclude that

it will not be possible to give direct proof if the control of the interparticle distance is due to the water molecules bonded either on the alkyl chain or at the Au surface. To differentiate between these two processes, we have to take into account results obtained by others^{4,5,14} and from our own group¹⁸ to propose a mechanism consistent with the data obtained:

- (i) *Water molecules penetrate at the Au surface.* This has been well demonstrated by Israelashvili et al.¹⁴ The addition of traces of water induces the aggregation of ZnS nanoparticles, coated either with hexadecyl or octadecylamine, into semirigid flocs. Because the coating agent is not strongly bound to the ZnS nanoparticles (physisorbed), the water molecules penetrate between the head-polar group of the coating agent and the ZnS–nanocrystal interface, which involves a drastic increase in the interparticle adhesion forces inducing aggregation.¹⁴
- (ii) *Strength of attachement of coating agent at the Au surface.* Dodecanethiol is attached to the Au nanocrystal interface by a quasi-covalent bond,²³ which favors the nanocrystal self-assembly over a very long-range. Indeed, the strength of the bonding between the coating agent and the nanocrystal surface prevents (or not) the aggregation between particles. This is supported by previous data obtained in our group with Pd nanocrystals produced in the presence of water molecules in which, by using dodecylamine as coating agent, spherical particles aggregate forming worm-like particles, whereas, with dodecanethiol, only spheres are formed (see ref 24, Figures 1 and 5). This is due to a stronger bonding of the Pd surface with alkylthiol than with alkylamine. This clearly shows that the strength of the binding of coating agent at the nanocrystal interface is a key parameter to retain the nanocrystal shape and prevent against coalescence. When a rather large amount of water molecules (50 % in volume) is present during the synthesis of Co nanocrystals coated by covalent bonding,²⁵ very large

domains (several micrometers) in compact hexagonal networks are observed.

Hence, taking these results into account, it is reasonable to say that there is a strong competition between the forces involved in water molecules penetrating between the surfactant head-polar group and the Au surface and the quasi-covalent bonding between the Au surface and the thio-derivative. The presence of both surfactant and water molecules makes it possible to produce a self-ordered monolayer over a long range and an increase in the interparticle adhesion forces,¹⁴ inducing a decrease in the interparticle distance. Hence adsorption of water molecules at the Au nanocrystal interface is the key parameter in the interparticle distance tuning. The mechanisms in reaching equilibrium differ between the two procedures. In reverse micelles (I) at the end of the synthesis, water molecules surround the Au nanocrystals. By dodecanethiol addition to the micellar solution, some of the water molecules are removed from the Au nanocrystal interface and are replaced by dodecanethiol molecules. After extraction from the micellar solution, the nanocrystals retain surfactant and water molecules at the interface (Figure 2A). For nanocrystals produced via procedure II, some dodecanethiol molecules bound to the Au nanocrystal interface, before water addition, are removed and replaced by water molecules at the Au nanocrystal interface to finally reach the same partition between water molecules and dodecanethiol on the Au nanocrystal interface as with procedure I (Figure 2B). At the edge of the monolayer, when the amount of water molecules adsorbed at the Au nanocrystal interface is large enough, the capillary forces induced by the solvent flux are added to the competitive forces between water and thiol adsorption on the Au nanocrystal interface.²⁶ This induces an additional attractive force favoring particle–particle interactions, and, consequently, Au nanocrystals coalesce along the flux direction (Figure 2C). We have to note that the interdigitation between alkyl chains is not possible because the interparticle distance is smaller than one zigzag chain length. This shows that the attractive interactions between Au nanocrystals are large enough to constrict the alkyl chains.

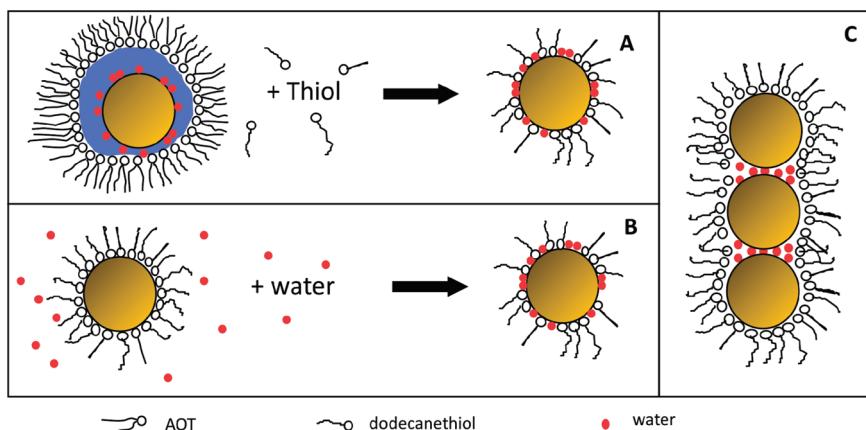


Figure 2. Schematic representation of the water/thiol adsorption at the metallic surface: (A) nanocrystals produced in reverse micelles (procedure I); (B) nanocrystals produced from the Brust method (procedure II); (C) the influence of adsorbed water on the interparticle distance.

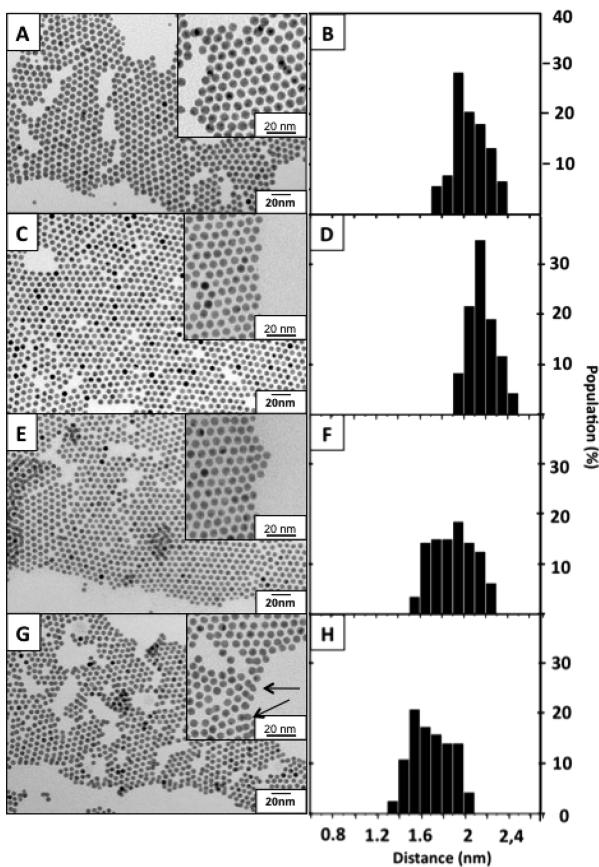


Figure 3. 2D self-ordered Au nanocrystals on AC. Long-range self-assembly of Au nanocrystals obtained from procedure I (A), from procedure II without water (C), with 4% water (E), and with 20% water (G). Insets: the corresponding monolayer edges. (B,D,F,H) Corresponding interparticle distances.

One of the key questions concerns the influence of the surface diffusion of nanocrystals on their ordering. To answer this question, the HOPG substrate is replaced by amorphous carbon (AC). We know that HOPG is characterized by a very smooth surface parallel to basal planes, in which carbon atoms are ordered hexagonally, whereas AC has a rough surface with carbon atoms randomly arranged on the film with many mosaic blocks. Hence, conversely to HOPG, the nanocrystals as well as the solvent are partially trapped by AC, which changes their diffusion rates.²⁷ Similar behavior was observed with silver nanocrystals deposited on HOPG and AC substrates.²⁸ Thus, by replacing HOPG substrate by AC for either procedure (I and/or II), local 2D self-assembled nanocrystals are observed (Figure 3A,C). Conversely to what is observed above on HOPG, the internanocrystal distances, obtained by procedures I and II, are similar with values of 2.1 ± 0.2 nm and 2.2 ± 0.2 nm, respectively (Figure 3B,D). In addition, for both procedures, no coalescence is observed either in the monolayer or at their edges (Figure 3A,C insets). Hence the internanocrystal distance, produced by procedure I, markedly differs upon replacing HOPG by AC (from 1.6 to 2.1 nm), whereas with nanocrystals produced from II, in the absence of water molecules, no change is observed

(2.2 nm). These results suggest that the AC roughness induces a decrease of both the diffusion rate of nanocrystals and solvent on the substrate. This allows the alkyl chains to freely diffuse and the capillary forces that are not strong enough to favor coalescence.

However, the dodecanethiol molecules remain partially attached to the Au nanocrystal interface, and their amount is sufficient to prevent any coalescence. The water molecules are still adsorbed on the Au surface when the particles are produced via procedure I, but the above observations suggest that their influence is reduced. This is confirmed by the fact that the average distance between nanocrystals, produced via procedure II, decreases from 2.2 ± 0.2 nm (Figure 3D) to 2.0 ± 0.3 nm (Figure 3F) and 1.8 ± 0.2 nm (Figure 3H) by increasing the water molecule percentage from 0% to 4% and 20%, respectively. Thus on AC, the average distance decreases with increasing the amount of water added to the colloidal solution. However, this is much less than that observed by deposition of the nanocrystals on HOPG. If we consider the edge of the monolayer, no coalescence is observed for either substrate (HOPG, AC), either with no water (Figure 3C inset) or with 4% water (Figure 3E inset). For 20% water addition, some coalescence of few nanocrystals is observed at the edges (inset of Figure 3G). This confirms our claim that water molecule addition in colloidal solution increases the forces involved between nanocrystals. However, because the bonding of dodecanethiol to the Au nanocrystal interface is very strong, no aggregation of nanocrystals takes place in the monolayer domains (except at the edges for a large amount of water and a very smooth surface). These two processes control the attractive interaction between nanocrystals and, consequently, the internanocrystal distance in long-range nanocrystal self-assemblies.

In conclusion, the internanocrystal distance can be tuned by addition of aqueous solution to the inorganic colloidal solution. The presence of water molecules induces a strong attraction between the water and Au surface. Because of the rather strong interaction between the dodecanethiol and the Au nanocrystal interface, a competition between these two processes takes place. The dodecanethiol bonding to the Au nanocrystal interface is strong enough to prevent nanocrystals from aggregation and keeps, when the substrate is smooth enough, the nanocrystals ability to order over a long-range. The presence of residual water at the Au surface favors the attractive nanocrystal–nanocrystal interactions and consequently decreases the interparticle distance. This process is mainly controlled by the nanocrystals and solvent mobility on the surface. At the edges, because of the force induced by the flux during the deposition process, the interparticle interactions increase, favoring directional ordering of nanocrystals characterized by a very short interparticle distance and consequently coalescence at the monolayer edges. This result opens a new research area related to the compactness of the monolayer. We could expect to observe change in the absorption spectra of the planar arrays differing by their interparticle distance with a progressive appearance of a splitting of the surface plasmon resonance (SPR) bands as predicted by DDA simulation.¹⁰

Experimental Methods

Procedure I. Au nanocrystals in reverse micelles^{15,17,18} are prepared by mixing three solutions (together). First, an aqueous solution of HAuCl₄ is added to an isoctane solution of AOT (0.2 M). Hydrazine, the reducing agent, is then added to the reverse micelles. There is a large excess of the former with the stoichiometric ratio of $R = [\text{N}_2\text{H}_4]/[\text{AuCl}^{4-}] = 3$. The water-to-surfactant molar ratio, $w = [\text{H}_2\text{O}]/[\text{AOT}]$, is kept at 5, corresponding to a droplet diameter of 15 nm. Immediately after adding the reducing agent, the mixed solution color turns from yellow to dark red, indicating formation of Au nanocrystals. After a 15-min reaction waiting time, 20 μL of dodecanethiol (C₁₂H₂₆S) is added to the reaction mixture. After 2 h, ethanol is added to the solution followed by centrifugation at 4500 rpm for 5 min to remove the AOT surfactant. This washing step is repeated twice, and then the black precipitate is redispersed in toluene.

Procedure II. Au nanocrystals are synthesized by using a modified Stucky's protocol.²⁹ Briefly, 0.25 mM chlorotriphenylphosphine gold(I) is dissolved in toluene, and then 500 μL of dodecanethiol is added to the solution. The metal precursor is reduced using a solution of *tert*-butylamine borane complex at 2.5 M in toluene. After the addition, the mixture turns slowly from colorless to dark red. During the synthesis, the temperature is fixed at 373 K, and after 5 min the reaction is stopped. A part of the solution is dried, and ethanol is added to the solid product followed by centrifugation at 2000 rpm for 2 min. After washing, the black precipitate is dispersed in toluene.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed.

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- (20) The average size is determined by counting almost 500 nanocrystal diameters.
- (21) To determine the mean nanoparticle size, D , and the corresponding size distribution, s , around 500 nanoparticles are measured for each sample and presented in a histogram. The standard deviation, σ , is calculated according to $\sigma = \{\sum(D_i - D)^2\}/[n - 1]^{1/2}$. The corresponding size distribution, s , is defined as the ratio s/D .
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