Self-Organization into 2D and 3D Superlattices of Nanosized Particles Differing by Their Size

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Self-assembly of silver sulfide, Ag_2S , nanoparticles is reported for different particles sizes. Monolayers of particles organized in a hexagonal network are formed over very large domains. Small or large aggregates can also be produced. The observations indicate that the formation of self-assemblies of nanoparticles strongly depends on the preparation conditions of the samples. It is also shown that in the aggregates the particles are highly organized and form pseudocrystals with a face-centered cubic structure for various particles sizes.

I. Introduction

The fabrication of assemblies of perfect nanometer-scale crystallites (quantum crystal) identically replicated in unlimited quantities in such a state that they can be manipulated and understood as pure macromolecular substances is an ultimate challenge of modern materials research with outstanding fundamental and potential technological consequences. These potentialities are mainly due to the unusual dependence of the electronic properties with the size of the particles, either for metal^{1–3} or semiconductor^{1,4–6} particles, in the range 1–10 nm.

The preparation and characterization of these colloids have thus motivated a vast amount of work.⁷ Various colloidal methods are used to control the size and/or the polydispersity of the particles, using reverse¹ and normal⁸ micelles, Langmuir— Blodgett films,⁹ zeolites,¹⁰ two-phase liquid—liquid systems,¹¹ or organometallic techniques.¹² The achievements of an accurate control of the particles size, their stability, and a precisely controllable reactivity of the small particles are required in order to allow attachment of the particles to the surface of a substrate or to other particles without leading to coalescence and hence losing their size-induced electronic properties. Difficulties emerge when manipulating nearly monodispersed nanometer size crystallites of arbitrary diameter.

Moreover, the ability to assemble particles into well-defined two- and three-dimensional spatial configurations should produce interesting properties such as new collective physical behavior,¹³ and the development of a general procedure for the fabrication of "quantum" crystals is a major challenge of future research. The fabrication of such crystals of particles would, for example, lead to the production of optical gratings,^{14,15} optical filters,¹⁶ antireflective surface coating,^{17,18} selective solar absorbers,¹⁹ and data storage and microelectronic devices.²⁰

Several approaches have been used in order to obtain 2D and 3D structures: Syntheses of inorganic—organic superlattices have been obtained by using a multilayer cast film.²¹ Asher et al.^{22–24} developed a method for creating new submicron periodic organic and inorganic materials. By combination of syntheses



Figure 1. TEM micrograph of a monolayer of $5.8 \text{ nm } \text{Ag}_2\text{S}$ particles obtained by (A) depositing a drop of the colloidal solution, then drying the solvent, and repeating the procedure and (B) depositing several drops and then removing the solvent.

in reverse micelles with the precipitation of other materials, nanocomposites highly ordered are formed.²⁵ Another approach to obtain 2D and 3D structures is to assemble nanoparticles themselves in an ordered array. This requires only a hard sphere repulsion, a controlled size distribution, and the inherent van

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Figure 2. TEM micrograph at low magnification of monolayers ribbons (A–C) and at high magnification (D–F) for various particle sizes: 3 (A, D), 4 (B, E), and 5.8 nm (C, F).

der Waals attraction between particles and dispersion forces. The polydispersity in particle size prevents fabrication of such well-defined two- or three-dimensional structures. Hence, external forces are used to induce formation of monolayers made of particles. For example, electrodeposition²⁶ and Langmuir–Blodgett⁹ techniques favor the formation of submonolayer.

Recently, in our laboratory, we have demonstrated that reverse micelles have been used to produce silver sulfide particles differing by their sizes from 2 to 10 nm.²⁷ By dodecanethiol addition, the particles are coated and extracted from reverse micelles. The coated particles are dispersed in heptane, and an optically clear solution is obtained. The addition of a drop of this solution on a carbon grid induces the formation of monolayers of particles. This has been obtained for various

particle sizes. It is worth pointing out that the monolayers are formed without any external force. In these monolayers, the particles are organized in a hexagonal network. A 3D aggregate²⁸ has been observed with an area equal to 0.18 μ m².

Very recently, colloidal self-organization of nanocrystallites has been observed in the case of both metallic and semiconductor particles. In all cases, surface passivation with a coordinating ligand such as alkanethiol,^{28,29} alkyl phosphine³⁰ or dithiols³¹ has been used.

In this paper, we show the formation of very large monolayers and of very large aggregates of nanoparticles. In this last case, the particles are organized in a face-centered cubic structure. Both monolayers and crystals can be made for different silver sulfide particle sizes.



Figure 3. Monolayer on a large range made of 5.8 nm Ag_2S nanocrystallites: (A) TEM micrograph; (B) TM AFM image. *z* range: 50 nm from black to white. Insert: cross section of the monolayer corresponding to the straight line of AFM image.

II. Experimental Section

1. Products. Sodium bis(2-ethylhexyl) sulfosuccinate, usually called Na(AOT), was obtained from Sigma, isooctane from Fluka, and sodium sulfide (Na₂S) from Janssen. Silver bis(2-ethylhexyl) sulfosuccinate, Ag(AOT), has been prepared as described previously.³²

2. Apparatus. *2.1. Transmission Electron Microscopy (TEM).* Most of the TEM micrographs were obtained from a JEOL 100CX operating at 100 kV. Some samples were examined in a JEOL 200CX operating at 200 kV. A double-tilt holder has been used to image the samples in different orientations and thus to help in determining the stacking sequence of the particles.

The size distribution is deduced from histograms. They are obtained by measuring the diameter D_i of all the particles from different parts of the grid. About 500 particles are taken into account to establish the histogram. The standard deviation, σ , of the size distribution is calculated from the following equation:

$$\sigma = \{\sum [n_i(D_i - D)^2] / [N - 1]\}^{1/2}$$

where D and N are the average diameter and the number of particles, respectively.

2.2. Atomic Force Microscopy. The experiments were performed in tapping mode (TM AFM), using a silicon tip under air and at room temperature by using a Nanoscope III (Digital Instrument).

3. Synthesis of Ag₂S Nanocrystallites. Sodium bis(2ethylhexyl) sulfosuccinate, usually called Na(AOT), is known to form water-in-oil droplets called reverse micelles.³³ The diameter of the droplet is controlled by the water content, w =[H₂O]/[AOT].³⁴ Syntheses of Ag₂S nanocrystallites are performed by mixing two 0.1 M Na(AOT) micellar solutions having the same water content: One contains 8×10^{-4} M of sodium sulfide, Na₂S, and the second one contains 8×10^{-4} M Ag(AOT). Due to Brownian motion, some collisions between droplets are efficient, and the exchange process between water pools occurs. This favors the coprecipitation reaction between Ag⁺ and S²⁻ ions. A few minutes after mixing the micellar solutions, silver sulfide, Ag₂S, nanosized particles are formed. The size of the Ag₂S particles increases linearly with the water content (see Figure 2 in ref 27) with a size distribution closed to 30%.

Pure dodecanethiol (1 μ L/mL) is added to reverse micellar solution containing Ag₂S nanocrystallites. After evaporation at 60 °C, the precipitate is washed with ethanol and filtrated. The nanocrystallites coated by dodecanethiol are dispersed in heptane, forming an optically clear solution. This procedure does not permit to extract the largest particles (10 nm) from reverse micelles. Hence, the average size of coated particles increases from 3 to 5.8 nm (see Figure 4 in ref 28). The extraction induces a size selection with a strong decrease in the size distribution. It drops down from 30 to 14%.

4. Sample Preparations. Several techniques and supports are used to study these samples. The TEM experiments are performed using a carbon film supported by a copper grid. The TM AFM experiments are performed on cleaved graphite, but similar data are obtained by using mica instead of graphite.

The observations obtained by TEM and TM AFM strongly differ from the way the sample is prepared. Various procedures have been used to deposit particles on the support: (i) One drop of the colloidal solution is deposited on the support, and the solvent is evaporated. The procedure is repeated several times. (ii) Several drops are deposited on the support and solvent is



Figure 4. Islands on a large range made of 5.8 nm Ag_2S nanocrystallites: (A) TEM experiment; (B) TM AFM experiment. Surface plot (*z* range: 150 nm full scale). Insert: top view (*z* range: 200 nm full scale).

evaporated. (iii) The support is left inside a concentrated solution of colloidal particles.

III. Results and Discussion

1. Monolayer Made of Particles Differing by Their Size. By using a dilute solution of Ag₂S nanocrystallites (particle volume fraction, ϕ , equal to 0.01%), monolayers of particles are formed. The particles are organized in a hexagonal network. However, the area covered by the monolayer of Ag₂S nanocrystallites strongly differs with the preparation.

When particles are deposited on the support, drop after drop waiting for solvent evaporation before adding another droplet, monolayers are formed on a very small area. The particles are arranged in a hexagonal network with an average interparticle distance equal to 2 nm. However, the micrographs are not totally covered by particles, and large domains on the TEM grid are particles free (Figure 1A).

Instead of adding drop after drop of the solution, several drops are added immediately, and then the solvent is evaporated. Large domains of monolayer are obtained (Figure 1B). The surface of the TEM grid, which is not covered by particles, strongly decreases. The monolayer domain is very large, and it forms long monolayer ribbons.

As it is described above, by modifying the synthesis details, it is possible to vary the size of the particles. Figure 2 shows monolayer ribbons made of particles with different sizes. The length and width of the ribbons depend on the particle size, but whatever this size, the ribbons are always very long. Direct observations on the TEM allowed to estimate the length of the ribbons to be about 100 μ m, but this feature cannot be reproduced on a micrograph since the size of the particles is too small compared with the length of the ribbons. On the other



Figure 5. (A) Aggregate made of 5.8 nm Ag_2S nanocrystallites. (B) Same aggregate after 2 weeks.

hand, the width of monolayer ribbons varies from 0.3 to 1 μ m when the particle size increases from 3 to 5.8 nm. In some



Figure 6. (A) Enlarged view of one part of the aggregate shown in Figure 5A (black arrow). The white arrow shows a defect in the crystallinity. (B) High magnification of the aggregate shown in (A).

regions of the micrographs (Figure 2), differences in electronic contrast are observed. This shows a starting point of the particle arrangement in a three-dimensional structure.

2. Two- and Three-Dimensional Superlattices Made of Particles Having 5.8 nm as an Average Diameter. By using the second procedure described above, particles having an average size of 5.8 nm are deposited on TEM and TM AFM supports. Very large domains of monolayer (Figure 3A) as well as a small amount of aggregates of particles (Figure 4A) are observed by TEM on the same grid. Due to technical problems, it is not possible to explore simultaneously the monolayers and the aggregates by TM AFM. Thus, the atomic force microscopy experiments are performed separately.

Figure 3B shows the monolayer observed by TM AFM. This image shows formation of monolayer in a very large domain, with holes regularly distributed on the surface. A cross section of the monolayer is obtained (insert, Figure 3B). The average depth of the holes is found equal to 6 nm. This corresponds to the average diameter of the particles used to make the monolayer. The average distance of the holes in the monolayer is found equal to 40 nm. The cross sections of the monolayer confirm the formation of a rather compact arrangement of nanoparticles.

The region containing aggregates is explored by TM AFM. Figure 4B shows the presence of aggregates varying by their sizes. From a cross section of these islands, the largest aggregate is found to be 114 nm high and 1.8 μ m large. This corresponds to 15 layers of particles. The smallest aggregate corresponds to four layers.

When the support is left a few minutes in a concentrated solution of Ag₂S particles ($\phi = 0.1\%$), very large aggregates are formed. Figure 5A shows an aggregate having a very large area, equal to 3.2 μ m². It is surrounded by smaller aggregates.



Figure 7. Tilt experiment realized on one part of the aggregate shown in Figure 5B (black arrow). The white arrow shows a defect in the crystallinity. (A) TEM micrograph at zero angle; (B) TEM micrograph after tilting of 20°.



Figure 8. Tilt experiment realized on an other aggregate: (A) TEM micrograph at zero angle, (B) TEM micrograph after tilting of 45°.

In the middle of the large aggregate, a change is observed in the electronic contrast, indicating that the electron beam is less



Figure 9. Effect of time of immersion of the support in colloidal solution. Support immersed for 1 day: (A) TEM micrograph at low magnification and (C) magnification of (A). Support immersed for 3 days: (B) TEM micrograph at low magnification and (D) magnification of (B).

absorbed than in the other parts of the aggregate. This shows that the thickness of the aggregate is not constant. Tilted TEM experiments have been performed on the 2 week old sample. Figure 5B shows the new micrograph of the aggregate. Large dots are observed all over the aggregate. These dots are attributed to pollution of the carbon grid (see below) and not to coalescence of particles. The fact that this aggregate is not constituted by only one monolayer has later been confirmed with stereomicroscopy by taking pictures tilted by 20° and looking at them with a stereoscopic binocular. Furthermore, it is clearly observed that the large dots are on the surface of the aggregate.

Magnification of one part of the aggregate (indicated by a black arrow in Figure 5A) shows that it is made of nanosized particles (Figure 6A) which appear not to be placed at random but to be collectively organized (Figure 6B).

Figures 6A and 7A compare the same part of the aggregate before and after getting the dots, i.e., immediately after the preparation of the sample and 2 weeks later. Similar electronic contrast is obtained on the two micrographs, and the defect (white arrows in Figures 6A and 7) is still observed in the second case. This confirms that the structure is conserved and stable in time. (Similar behavior can also be observed after a few months.) The dots observed in Figure 7A do not correspond to a part of the aggregate containing a large amount of particles. Hence, the formation of these dots cannot be attributed to the coalescence of the particles but is rather due to a pollution of the TEM grid. This often takes place on TEM experiments, and it is usually attributed to hydrocarbon cracking.

It is clear from the TEM observations that Ag₂S layers are usually overlapping. This indicates a three-dimensional structure. By tilting of the sample it has been repeatedly demonstrated that it is always possible to find an orientation for which the stacking of monolayers appears to be periodic. This is illustrated in Figure 7, which clearly shows that the stacking of particles is not at random, but rather that it is periodic.

Monolayers of Ag₂S particles are composed by close-packed particles mimicking the stacking of atoms in a {111} plane of

a close-packed structure. It is thus believed that, when overlapping, the layers conserve this close-packed arrangement and that the particles adopt a three-dimensional close-packed structure, face-centered cubic (fcc) or hexagonal close-packed (hcp). In order to discriminate between the compact fcc and hcp stackings, tilt experiments have been performed using a TEM double-tilt holder: Figure 8 is an example of such an experiment. This aggregate has been chosen because it has an easily recognizable shape with a large contamination dot on its border. In Figure 8A, the projected positions of Ag₂S particles show a pseudohexagonal structure. The "hexagons" are in fact elongated along the vertical direction (insert, Figure 8A), but the ratio of the distances between particles positions in the horizontal and vertical directions is close to $\sqrt{2/2}$. This may correspond to the stacking of a {110} plane of the fcc structure, and there is no direction in a perfect hcp structure for which the projected positions of the particles would take this configuration. Tilting of the sample by 45° while keeping the horizontal direction of Figure 8A constant leads to the observation of Figure 8B, which shows a 4-fold symmetry. This symmetry is again characteristic of the stacking of {001} planes of the cubic structure (insert, Figure 8B) but cannot be found in the hexagonal structure. From these observations, we can undoubtedly conclude that multilayers of Ag₂S particles are composed by stacking of monolayers in a face-centered cubic arrangement.

Measurements of the distance between projected positions of particles as well as angles between directions joining particles positions are consistent with this conclusion. The distance between two particles core to core in the [010] direction of the superlattice of particles is about 11 nm, which corresponds to the cell parameter (a_0) of the pseudo-fcc crystal formed by Ag₂S particles. The average particle diameter is about 5.8 nm, while the shortest distance between particles is $a_0\sqrt{2/2} = 7.8$ nm, which gives a calculated spacing between two particles of 2 nm. This is in good agreement with the average distance between particles (2 nm) obtained from the observations of monolayers (see section III.1).



Figure 10. TEM of an island of Ag_2S in an {001} plane of a closepacked structure made of nanoparticles having an average size equal to 3 (A,B), 4 (C,D), and 5.8 nm (E,F).

In Figure 5 close to the large aggregate, several other crystals differing by their shape and size are observed. In all these cases, the particles are arranged in a face-centered cubic structure. Hence, on the same TEM micrograph large aggregates (Figure 5) coexist with smaller ones. This indicates that the control of the size and the shape of 3D superlattices are not yet reached.

Instead of leaving the support few minutes in a concentrated solution, it is left either 1 or 3 days. By increasing the time of immersion of the support, Figure 9 shows an increase in the surface area covered by the particles (Figure 9A,B). Figure 9C,D shows that the crystalline structure remains the same. However, the number of defects increases also. Other parameters would have to be studied to control the size and the shape of 3D superlattices.

3. Variation of the Particle Sizes in a 3D Superlattice. As shown in Figure 2, it is possible to make particles of differing sizes. Using the same procedure as described above, we have produced 3D superlattices for particles with an average size of 3 nm (Figure 10A) and 4 nm (Figure 10C). These aggregates are very similar to the ones formed with particles with an average size of 5.8 nm (Figure 10E). Higher resolution of these aggregates (Figure 10B,D,F) shows a 4-fold symmetry typical

of the fcc stacking. Furthermore, Figure 10E shows a stacking defect in the structure as in a crystal.

IV. Conclusion

In this paper, it has been shown that it is possible to form self-assemblies of silver sulfide nanoparticles for different particles sizes. Monolayers of particles can be formed over very large domains. Small or large aggregates can also be produced. In the aggregates, the particles are highly organized and form pseudocrystals with a face-centered cubic structure. The formation of these self-assemblies of nanoparticles strongly depends on the conditions of preparation of the samples. The next step is thus to control the size and shape of the crystals. This could be achieved by using a slightly different preparation procedure, as well as improving the quality of the support used.

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