1 Self-Organization of Inorganic Nanocrystals

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1.1 Introduction

Self-organization of inorganic nanocrystals opens a new and challenging area in nanotechnology [1, 2]. We already know that nanomaterials are a new generation of advanced materials that are expected to exhibit unusual chemical and physical properties, different from those of either the bulk materials or isolated nanocrystals [3–5]. Engineering of nanophase materials and devices is of great interest in several domains such as electronics, semiconductors, optics, catalysis, and magnetism. During the past decade, nanocrystal research has been focused on two major properties of finite-size materials: quantum size effects and surface/interface effects [6, 7]. A new trend, however, has emerged in the past few years: the arrangement of the nanocrystals into two- and three-dimensional (2D and 3D) superlattices.

It was found that inorganic nanocrystals are able to self-assemble in compact hexagonal networks [8], rings [9, 10], lines [11, 12], stripes [13], tubes [14, 15], columns and labyrinths [16-18], and in large "supra" crystals characterized by a face centered cubic (fcc) structure [8, 19-23]. The physical properties of such mesoscopic assemblies differ from those of isolated nanocrystals and from the bulk phase [1, 2]. Furthermore, the mesoscopic structure itself is also a key parameter in the control of the physical properties [11, 15, 24-26]. In the last five years, collective magnetic, optical, and transport properties were demonstrated [1]. They are mainly due to dipole-dipole interactions. Intrinsic properties due to self-organization also open a new research area, which concerns the physical, chemical, and mechanical properties of these assemblies. Recently it has been demonstrated that vibrational coherences of nanocrystals occur when they are organized in fcc structures [27]. These coherences could explain the change in the transport properties observed previously with silver nanocrystal self-organizations [28]. Similarly, a gentle annealing process (below 50 °C) produces large monocrystals like those observed under ultravacuum by epitaxial growth [29]. This opens a new approach in the crystal growth mechanism. The nanocrystals can also be used as masks for

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nanolithography and their self-assemblies are then transferred onto a substrate, which is a completely new technique in this field [30, 31]. The nanocrystal stability in an annealing process is markedly improved by the self-organization [32]. All these new approaches make it possible to claim that self-organization of nanocrystals opens a large number of new research areas which involve many of the present research domains.

Several groups have obtained 2D and 3D superlattices of various nanomaterials such as semiconductors (Ag₂S, CdSe, PbSe) [8, 19, 33, 34], metals (Ag [20, 21, 27, 29, 35-46], Au [47-62], Pd and Pt [63, 64], Co [11, 13, 22, 23, 25, 26, 32, 65-70] etc.), and oxides (ferrites) [71, 72]. The most common crystalline structure of these organizations is hexagonal at 2D and fcc at 3D. The nanocrystal self-organization is induced by "internal" forces already present in the system. For nanometer-size particles, these forces are usually van der Waals interactions and capillarity forces. Furthermore, the 2D and 3D superlattices are most often obtained by evaporation of a size-selected nanocrystal solution on a substrate. Thus, the particle-particle and particle-substrate interactions have to be taken into account in their formation. Moreover, the solvent plays a role in the nanocrystal self-organization through wetting properties, and it interacts with the substrate and the nanocrystals via the capillarity forces. Other types of mesoscopic nanocrystal organizations such as rings [9, 10, 73, 74], chains and ribbons [11–15, 24–26, 75–82], columns and labyrinths [16–18] etc. are obtained by application of "external" forces (temperature gradient, magnetic field, pressure) during the solvent evaporation process.

This chapter is divided into four major parts. In the first two parts, the various forces involved in nanocrystal self-organizations are described. In the third and fourth parts, the formation of 2D and 3D assemblies in the absence or presence of external forces, and the parameters controlling the ordering and/or the meso-scopic shapes of the nanocrystal assemblies are discussed.

1.2

Surface Modification of Nanocrystals and Interparticle Forces in Solution

To produce well-defined 2D and 3D superlattices of nanocrystals, highly stable materials are needed. Furthermore various forces have to be taken into account. Let us first list the various parameters involved in the nanocrystal self-assemblies.

Due to van der Waals interactions, particles in the nanometer-size range have a strong tendency to agglomerate (Fig. 1.1). It is therefore important to develop synthetic methods by which the particles can be stabilized, i.e., where repulsive and attractive forces between particles balance each other. Mainly electrostatic and steric forces prevent agglomeration of nanoparticles. Electrostatic stabilization involves creation of an electrical double layer arising from ions adsorbed on the surface and associated counterions that surround the particle. Thus, if the electric potential associated with the double layer is sufficiently high, the Coulombic repulsions between the particles prevent their agglomeration (Fig. 1.2A). Steric stabili-



Fig. 1.1 Uncharged particles are free to collide and agglomerate.

zation is achieved by adsorption of organic molecules containing suitable functional groups, such as -SH, -COOH, and -NH₂, at the particle surface (Fig. 1.2 B). Indeed, the lengths of the alkyl chains are usually greater than the range over which the attraction forces between nanocrystals are active. In addition, dipolar magnetic interactions are to be taken into account for single-domain magnetic nanocrystals.

Hence the stability of a colloidal solution is governed by the total interparticle potential energy V_{total} , which can be expressed as:

$$U_{\text{total}} = U_{\text{vdW}} + U_{\text{dd}} + U_{\text{elec}} + U_{\text{steric}} \tag{1}$$

where U_{vdW} , U_{dd} , U_{elec} , and U_{steric} are the attractive potential energy due to longrange van der Waals interactions between particles, the attractive potential energy



Fig. 1.2 Schematic illustration of the interaction potential energy and relevant length scales for (A) electrostatic and (B) steric contributions, where κ^{-1} is the effective double-layer thickness and δ the adlayer thickness.

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due to long-range dipolar interactions between magnetic particles, the repulsive potential energy resulting from electrostatic interactions between like-charged particle surfaces, and the repulsive potential energy resulting from steric interactions between particle surfaces coated with adsorbed organic molecules, respectively.

1.2.1

Van der Waals Forces

 $U_{\rm vdW}$ exhibits a power-law distance dependence whose strength varies with the Hamaker constant and a geometrical factor [83, 84]. The Hamaker constant ($A_{\rm p-o-p}$) depends on the dielectric properties of the interacting colloidal particles (p) and intervening solvent (oil) and it is higher for metallic materials than for semiconductors. The geometrical factor depends on the particle size and the contact distance between nanocrystals. For spherical particles (*i*, *j*) of equal size, $U_{\rm vdW}$ is given by the Hamaker expression:

$$U_{\rm vdW} = -\frac{A_{\rm p-o-p}}{12} \left\{ \frac{d^2}{\left(r_{ij}^2 - d^2\right)} + \frac{d^2}{r_{ij}^2} + 2\ln\left(\frac{r_{ij}^2 - d^2}{r_{ij}^2}\right) \right\}$$
(2)

where A_{p-o-p} , d, and r_{ij} are the Hamaker constant, the particle diameter, and the distance between the particles (r = d + l with l the distance of separation), respectively. At the minimum separation distance, the l value is directly correlated to the surface coating agent and U_{vdw} scale as l^{-1} :

$$U_{\rm vdW} = -\frac{A_{\rm p-o-p}}{24} \left(\frac{d}{l}\right) \tag{3}$$

1.2.2 Magnetic Dipolar Forces

The magnetic dipolar energy between spherical nanocrystals of equal size and with the same magnetic properties is expressed as [85]:

$$U_{\rm dd} = \frac{1}{4\pi\mu_0} \left\{ \frac{\vec{m}_i \cdot \vec{m}_j}{r_{ij}^3} - \frac{3}{r_{ij}^5} \left(\vec{m}_i \cdot \vec{r}_{ij} \right) \left(\vec{m}_j \cdot \vec{r}_{ij} \right) \right\}$$
(4)

where *m* and μ_0 are the magnetic moment of the nanocrystals and the magnetic permeability, respectively.

At small interparticle separation distances, U_{dd} is:

$$U_{\rm dd} = \frac{m^2}{4\pi\mu_0 \left(d+l\right)^3}$$
(5)

When this dipolar energy is larger than 3kT, it is expected that there will be a spontaneous organization of the nanocrystals in linear chains [86].

1.2.3 Electrostatic Forces

The electrostatic potential energy between charged particles, U_{elec} , exhibits an exponential distance dependence whose strength varies with the surface potential induced on the interacting colloidal particles and with the dielectric properties of the intervening medium [87]. Exact analytical expressions for the electrostatic potential energy cannot be given. Therefore, analytical approximations or numerical solutions are used. For equal-size spherical particles that approach one another under constant potential conditions, U_{elec} is given by:

$$U_{\text{elec}} = \pi \varepsilon_{\text{r}} \varepsilon_0 \, d\Psi_0^2 \exp\left(-\kappa h\right) \tag{6}$$

where $\varepsilon_{\rm p} \varepsilon_0$, Ψ_0 , *h*, and $1/\kappa$ are the dielectric constant of the solvent, the permittivity of vacuum, the surface potential, the minimum separation distance between particles, and the Debye–Hückel screening length, respectively. κ is given by:

$$\kappa = \left(\frac{F^2 \sum_i N_i z_i^2}{\varepsilon_r \, \varepsilon_0 \, kT}\right)^{1/2} \tag{7}$$

where N_i and z_i are the number density and valence of the counterions of type *i*, respectively, and *F* is the Faraday constant [88].

1.2.4 Steric Forces

Steric stabilization provides an alternate route to controlling colloidal stability and is used in aqueous and nonaqueous solutions. In this approach, adsorbed organic molecules are utilized to induce steric repulsion. To be effective, the adsorbed layers must be of sufficient thickness and density to overcome the van der Waals attraction between particles and to prevent bridging flocculation. Such species should be strongly anchored to avoid desorption during particle collisions. Steric interactions occur when particles approach one another at a separation distance less than twice the adlayer thickness (δ). U_{steric} is given by [89]:

$$U_{\text{steric}} = \pi d^2 N k T \left\{ 1 - \frac{r_{ij} - d}{\delta} - \frac{r_{ij}}{\delta} \ln \left(\frac{d + \delta}{r_{ij}} \right) \right\}$$
(8)

1.2.5 Solvation Forces

The use of appropriate solvents is required for high particle stabilization. The stabilizing agent has to possess high affinity with the solvent in order to solvate the particles and form an extended layer for screening the attraction between particles [90].

1.3

What is Required to Provide Highly Ordered Self-Assemblies?

Usually, self-assemblies of nanocrystals are obtained by evaporation of the solution containing nanocrystals on a given substrate. Various parameters play a role in the nanocrystals' organization.

1.3.1 Nanocrystal Size Distribution Effect

The size distribution of nanocrystals is the key parameter to obtain ordered nanocrystal superlattices. This is well illustrated in Fig. 1.3, which shows TEM images of the various arrangements of cobalt nanocrystals characterized by various size distributions (σ). (All the depositions are made in the same way, i.e., by deposition of a colloidal solution on an amorphous carbon grid [67]). The nanocrystals self-assemble in a 2D hexagonal network when σ is equal to or lower than 13%. The Fourier transform (insert in Fig. 1.3 E) made on a 200 × 200-nm array displays three orders of reflections and thus confirms the long-range hexagonal network.

1.3.2

Substrate Effect

The long-range order of the organization depends on the particle–substrate interactions. Hence, compact monolayers are produced on a large scale by deposition of silver nanocrystals [91] on a highly oriented pyrolytic graphite (HOPG) substrate (Fig. 1.4 B). Conversely, with amorphous carbon as substrate, the order is local and the monolayer shows vacancies (Fig. 1.4 A).

The strength of the particle–substrate interaction depends on the Hamaker constant, A_{p-o-s} , which takes into account the nature of the nanocrystals, the solvent (oil), and the substrate (s). It is given by the expression [83, 84]:

$$U_{\rm vdW} = -\frac{A_{\rm p-o-s}}{6} \left\{ \frac{d}{(2r_{ij}-d)} + \frac{d}{(2r_{ij}+d)} + \ln\left(\frac{(2r_{ij}+d)}{(2r_{ij}+d)}\right) \right\}$$
(9)

where r_{ij} is the distance from the particle (*i*) center to the wall (*j*). At the minimum separation distance, $r_{ij} = d/2 + l$ and the interaction energy becomes:

$$U_{\rm vdW} = -\frac{A_{\rm p-o-s}}{12} \left(\frac{d}{l}\right) \tag{10}$$



Fig. 1.3 Transmission electron microscopy (TEM) images of 7.2-nm cobalt nanocrystals obtained at various size distributions (σ : (A) 30%, (B) 18%, (C) 13%, (D) 12%, (E) 12%, (F) 8%. Inset of (E): corresponding Fourier transform).

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Fig. 1.4 TEM images of 2D self-assemblies of silver nanocrystals (A) on amorphous carbon and (B) on HOPG substrates.

1.3.3 Capillary Forces

Capillary forces arise when, during the evaporation process, the thickness of the film reaches the particle diameter. They depend on the contact angle (ϕ) of the solvent meniscus (surface tension γ) between two neighboring particles of diameter *d* (Fig. 1.5).

The capillary force [92] is:

$$F = 2\pi d\gamma \cos\phi \tag{11}$$

When capillary forces act, their strengths are greater than those involving particle–particle and/or particle–substrate interactions. They induce the cohesion of the organization.



Fig. 1.5 Schematic illustration of capillary forces acting between nanocrystals.

1.3.3.1 Solvent Evaporation Process

Removal of the liquid vehicle during the evaporation process can induce nanocrystal aggregation and film cracking (see Chapter 13). This is illustrated in Fig. 1.6. By increasing the amount of cobalt nanocrystals deposited on a substrate, 3D assemblies are obtained. When the evaporation [13] takes place in air (fast evapora-



Fig. 1.6 Scanning electron microscopy (SEM) images of 3D assemblies of cobalt nanocrystals obtained by drying the colloidal solution in air (A) and in a quasi-"saturated" atmosphere of solvent (B).

tion process), nanocrystals tend to aggregate (Fig. 1.6 A, whereas on decreasing the evaporation rate a smooth film with cracks is observed (Fig. 1.6 B).

1.3.3.2 Application of a Magnetic or Electric Field During the Evaporation Process

The application of a field (magnetic or electric) during the evaporation process involves dipolar interactions between nanocrystals. Coupled to van der Waals interactions, they can have a considerable influence on the nanocrystal organization. Hence, the drying process is a critical step in the formation of self-assemblies. It is a multistage process that involves, as well as fluid flow, evaporation processes, nanocrystal diffusion, nanocrystal interactions, etc.

1.4 Self-Assemblies in the Absence of External Forces

In 1995, large-scale arrays of semiconductor nanocrystals were produced simultaneously by French and American groups [12, 13]. Later on, a large number of groups succeeded in forming 2D networks of various materials: metallic as silver, gold, or cobalt, and oxide as ferrite etc. [14–20, 41, 42]. The nanocrystals are characterized by a low size distribution. Furthermore, their surfaces are passivated (with either thiol, carboxylic acid or phosphine) in order to prevent their coalescence. Usually, the 2D organizations are obtained after evaporation of a drop deposition of a diluted nanocrystal solution on a TEM grid. A typical hexagonal 2D nanocrystal organization is shown in Fig. 1.7 [93]. For any amount of material deposited on the substrate, the nanocrystals are always organized in a hexagonal network. Note that the organization occurs on larger scale when the amount of nanomaterial deposited is rather large (compare Fig. 1.7 A and B). Moreover, due to **10** 1 Self-Organization of Inorganic Nanocrystals



Fig. 1.7 TEM images of a monolayer of 5.8-nm Ag₂S nanocrystals after evaporation of a colloidal solution containing (A) 3.6×10^{17} and (B) 6×10^{17} nano-crystals mL⁻¹.



Fig. 1.8 TEM images at low magnification of monolayers (A–C) and at high magnification (D–F) for various Ag_2S nanocrystals diameters: (A, D) 3 nm, (B, E) 4 nm and (C, F) 5.8 nm.

van der Waals forces [94], the long-range ordering increases with increasing nanocrystal size (Fig. 1.8).

By deposition of a concentrated solution, 3D superlattices are obtained in coexistence with monolayers (Fig. 1.9A). A typical TEM pattern of 3D superlattices is shown in Fig. 1.9 B. The high-magnification image of an aggregate shown in Fig. 1.9 B exhibits a large degree of ordering of nanocrystals in fourfold symmetry (Fig. 1.9 C). This can be attributed to the [001] plane of an fcc lattice [19, 94]. The large aggregate (1 µm wide and 116 nm high) corresponds to a stacking of 20 layers (Fig. 1.9D). The 3D arrays are very inhomogeneous in size and shape (Fig. 1.9 A). In order to obtain more regular 3D superlattices, also called "supra" crystals, control of the solvent evaporation rate is required. For this, the substrate is directly immersed in the colloidal solution and the solvent is allowed to evaporate. The evaporation rate is controlled by either the substrate temperature or the solvent saturation degree of the surrounding atmosphere. By using this deposition process, "supra" crystals made of silver [20, 21] (Fig. 1.10A) or cobalt [22] (Fig. 1.10 B) nanocrystals form. They look like paving stones characterized by welldefined shapes and rims. The "supra" crystal thickness is about 10 µm with silver nanocrystals. This corresponds to the regular stacking of around 1000 monolayers whereas for cobalt nanocrystals, the number of monolayers is smaller by almost a factor of 2. The optimal temperatures to reach the highest-ordered "supra" crystals



Fig. 1.9 TEM images of 3D aggregates in coexistence with monolayers of Ag_2S nanocrystals (A); high magnification of one aggregate (B, C); AFM image of one aggregate (D).



Fig. 1.10 SEM images of "supra" crystals of silver (A) and cobalt (B) nanocrystals obtained by deposition on HOPG substrate at 35 °C. Scanning electron microscopy images of 3D amorphous assemblies of silver (C) and cobalt (D) nanocrystals obtained by deposition on HOPG substrate at 10 °C.

are around 35 and 45 °C for silver and cobalt nanocrystals, respectively. The ordering decreases with decreasing the substrate temperature to reach, at 10 °C, amorphous aggregates, highly polydispersed in size and shape, and forming a nonhomogeneous film. This is observed for silver [21] (Fig. 1.11C) and cobalt [23] (Fig. 1.11D) nanocrystals. Small-angle X-ray diffraction (XRD) measurements in a grazing incidence show, for silver [20, 21, 27] and cobalt [22, 23] "supra" crystals, an fcc packing. For cobalt "supra" crystals, nine spots are recorded (Fig. 1.11). Their coordinates, which are reciprocal distances, are in good agreement on conversion into d-spacing, with the calculated coordinates of diffraction spots assuming an fcc structure (Table 1.1).

The XRD pattern of the amorphous aggregates described above shows a diffuse ring (insert Fig. 1.12 A). Hence the ordering of the "supra" crystals is tuned by controlling the substrate temperature. This is well demonstrated with cobalt nanocrystals where the Bragg reflections, typical of the (111) lying planes, become more and more intense whereas the diffuse ring intensity progressively decreases when the substrate temperature increases from 10 to 45 °C (Fig. 1.12 and Table 1.2). This behavior clearly indicates an increase in both size and out-of-plane ordering of the "supra" crystals. The center-to-center nanocrystal distance calcu-



Fig. 1.11 X-ray diffraction pattern obtained in a grazing incidence geometry of a "supra" crystal of Co nanocrystals. The intensity is reduced by a factor of 20 in the central inset.

Table 1.1 Comparison of experimental and calculated coordinatesof diffraction spots assuming an fcc structure; coordinates areexpressed in *d-spacings*.

Reflection label (see Fig. 1.11)	{h,k,l } indices	X (measured) [nm]	X (calculated) [nm]	Y (measured) [nm]	Y (calculated) [nm]	d _{hki} (measured) [nm]	d _{hki} (calculated) [nm]
1	1,1,-1	25.15	25.56	9.05	9.04	8.52	8.52
2	2,0,0	12.89	12.78	9.19	9.04	7.48	7.38
*	1,1,1	8.54	8.52	0	0	8.52	8.52
*	2,2,2	4.24	4.26	0	0	4.24	4.26
3	-1,3,1	8.53	8.52	5.24	5.22	4.46	4.45
4	1,1,3	5.12	5.11	9.51	9.04	4.51	4.45
5	2,2,-2	13.22	12.78	4.52	4.52	4.28	4.26
6	1,1,-3	26.09	25.56	4.47	4.52	4.41	4.45
7	4,0,0	6.38	6.39	4.55	4.52	3.70	3.69
8	3,3,1	3.67	3.65	10.10	9.04	3.45	3.39
9 +	4,2,0	4.31	4.26	5.44	5.22	3.38	3.30

lated from the stacking parameter is 10.75 nm, when the nanocrystals are ordered, against 11.75 nm for the disordered system. As expected, the packing of Co nanocrystals is less compact in the amorphous phase than in the "supra" crystal. Similar behavior with the substrate temperature was observed previously in the fabrication of "supra" crystals made of silver nanocrystals [21, 27]. The second-order Bragg reflection is observed from 22 °C and the interparticle distance is minimal at this temperature. At substrate temperatures above 22 °C, the "supra" crystal size increases [27]. The dependence of the structural organization upon the deposition temperature is mostly related to the nanocrystal diffusion on the substrate. At low temperature, this diffusion is limited; hence, nanocrystals rapidly



Fig. 1.12 Diffractograms of cobalt films obtained from HOPG substrate immersed in a highly concentrated cobalt colloidal solution. The different substrate temperatures (*T*) are: (A) 10 °C, (B) 25 °C, (C) 35 °C, (D) 45 °C. Insets: diffraction patterns.

Substrate temperature [°C]	12	25	35	45
Inner ring distance [nm]	9.60	8.80	8.80	8.70
$\delta q_{1/2} [nm^{-1}]$	0.19	0.050	0.035	0.034
$R_{\rm int}$: $I_{\rm ref}/I_{\rm halo}$	1.6	11	87	674
D _{center-center} [nm]	1.75	10.80	10.80	10.65
D _{interpart.} [nm]	4.55	3.60	3.60	3.45

Table 1.2 Various parameters extracted from the diffraction patterns and thecorresponding diffractograms in Fig. 1.12.

 $\delta q_{1/2}$: the half width at half maximum; R_{int} : the reflection intensity to the halo intensity ratio; $D_{center-center}$: center-to-center nanocrystal distance; $D_{interpart.}$: border-to-border nanocrystal distance.

stick on the substrate which hinders their compact organization. Moreover, it is also possible that the coating "fluidity" plays a role during the organization step. On increasing the partial vapor pressure of the solvent during the evaporation process to close to 100%, i.e., by slowing down the solvent evaporation rate, crackfree homogeneous cobalt nanocrystal "supra" crystals with terraces are obtained (Fig. 1.13). XRD measurements confirm that they are highly crystallized and have the same structural characteristics as the fcc "supra" crystals described above. The change in the "supra" crystal morphology is related to the variation of the surface



Fig. 1.13 SEM image of "supra" crystal of cobalt obtained from HOPG substrate immersed in a highly concentrated cobalt colloidal solution. The solvent evaporation rate is very low.

tension arising during solvent evaporation. Similar behavior was previously observed with silver nanocrystals with well-defined "supra" crystals in quasi-saturated vapor with a high degree of ordering (Fig. 1.10 A), whereas a low extent of ordering and defects are found when the evaporation takes place in air (Fig. 1.14 A and B).

Another growth technique to obtain 3D superlattices is based on slow diffusion of a nonsolvent in the bulk of a concentrated solution of nanocrystals in a solvent. By this method, 3D superlattices of CdSe [95] and Au [96] are obtained. The building blocks are also aligned in a regular fcc-like 3D superlattice. Recently, "supra" crystals made of mercaptosuccinic acid-coated Au nanocrystals have been obtained in aqueous solution. In this case, the crystalline structure corresponds to hexagonal close packing (hcp) [97].

The ability to make "supra" crystals provides a new horizon to study the physical (optical, magnetic, electron transport, etc.) collective properties due to the particle interactions [1]. Furthermore, for devices, it is important to obtain these different arrays on the required substrate. Therefore, it is crucial to control various parameters like the interparticle gap and particle crystallinity. Obviously, such mesostructures must be stable in time and must also be thermally stable, in the parti-



Fig. 1.14 SEM patterns at a 45° tilt and at different magnifications obtained by drying the silver colloidal solution on a hot substrate at 35 °C in air (A and B).

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cular case where a thermal treatment is necessary to improve the nanoparticle crystallinity. These various points are described below.

1.4.1

Control of the Interparticle Gap Via the Coating Agent

A large amount of data concern the 2D organization of nanocrystals surfacecoated with thiol molecules with different alkyl chain lengths. Self-organizations in 2D networks are produced with Ag_2S [93] as well as Ag nanocrystals [91], coated with thiols with different lengths, with the number of carbon atoms, *n*, going from 8 to 14. For gold and palladium nanocrystals, *n* is between 6 and 14 [62] and between 6 and 16 [63, 64], respectively. This is related to the coating process as well as to the difference in the material–thiol headgroup bonding strength. However, the minimum and the maximum chain lengths making it possible to obtain 2D nanocrystal organizations differ with the nature of the materials.

1.4.1.1 Silver Sulfide Nanocrystals

The TEM images of Ag₂S nanocrystals coated with various alkyl chain lengths show nanocrystal self-organization in compact hexagonal networks (Fig. 1.15). The interparticle spacings change with the alkanethiol chain length. However, the edge–edge separation distances (d_{pp}) do not correspond exactly to the distances one might expect from the alkyl chain lengths in trans zigzag conformation (d_{zigzag}) (Fig. 1.15). The experimental d_{pp} values are considerably shorter than twice the chain length. In the case of octanethiol and decanethiol, d_{pp} is longer than the expected length of one chain. For dodecanethiol-coated nanocrystals, d_{pp} is about equal to d_{zigzag} . For C₁₄-thiol-derivative particles, d_{pp} is actually shorter than d_{zigzag} . These trends are explained by the change in chain conformation and the various defects that depend on chain length [93]. Indeed, the number of gauche defects near the particle surface decreases as the alkyl chain length increases. However, the incidence of gauche defects near the terminal (methyl) end of the chain increases with chain length. Hence, the shortest chains (C_6) behave almost as free alkanes, and are thus not prone to 2D organization or interdigitation. As the chain length increases, interdigitation between alkyl chains on adjacent particles occurs, leading to a d_{pp} value that approaches the length of a single chain, d_{zigzag} (C₁₀- and C₁₂-thiol systems). In the case of C14-thiol surface groups, the increase in gauche defects near the chain terminal end allows pseudorotational motion of the chain about the R-S bond axis. This explains why the d_{pp} value is smaller than d_{zigzag} for the C₁₄-thiol system.

Hence, the interparticle spacing, d_{pp} , is dependent on chain length, and does not evolve linearly. However, very short-chain alkanethiol groups behave more as free alkanes and the 2D superlattices are not produced.



Fig. 1.15 TEM images of monolayers of 4-nm Ag₂S nanocrystals surfacecoated with (A) 1-octanethiol (C₈), (B) 1-decanethiol (C₁₀), (C) 1-dodecanethiol (C₁₂), and (D) 1-tetradecanethiol (C₁₄). (E) Experimental average interparticle gap (d_{pp}) to theoretical alkyl chain length in trans zigzag comformation (d_{zigzag}) ratio and evolution of the gauche defect with alkyl chain length for thiol molecules.

1.4.1.2 Silver Nanocrystals

The mean interparticle distance remains more or less the same (1.8 nm) for any thiol alkyl chain length between C_8 and C_{12} thiols [91], with an optimal interdigitation obtained with a C_{12} alkyl chain. Furthermore, the long-range order of the organization increases with the alkyl chain length (Fig. 1.16). Note that the interdigitation obtained for dodecanoic acid-coated cobalt nanocrystals [67] is not as pronounced (2.5 nm) as those obtained for Ag (1.8 nm) or Ag₂S (1.8 nm) nanocrystals coated by dodecanethiol.

Theoretically it has been found [60] that the ratio, r, of the capping ligand chain length, $\langle L \rangle$, to the metal core radius, R, controls the superlattice struc-

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ture: the packing in an fcc structure is favored for r < 0.69, whereas it evolved to a less compact structure like bcc for r > 0.69. Most of the coated nanocrystals used for fabricating 2D or 3D superlattices are in the scale range r < 0.69. As expected from these considerations, the crystalline structure of the 3D superlattices is usually fcc. This is illustrated with Ag₂S nanocrystals coated with thiols with different alkyl chain lengths (Fig. 1.17). The nanocrystals coated with C8 and C10 thiols, and with the same average size, form well-faceted aggregates with fourfold symmetry, as observed for the C12-thiol-coated nanocrystals (Fig. 1.17 A-C). Conversely, C14-thiol-coated nanocrystals do not form well-defined supracrystals (Fig. 1.17 D). The difference in self-assembly behavior when C_{14} alkanethiols are used is related to the d_{pp} edge-to-edge spacing parameter discussed earlier. For the alkyl chain lengths shorter than C_{14} , the d_{pp} value is either similar to (for example, n = 12) or slightly longer ($8 \le n \le 12$) than the calculated chain length assuming complete trans (zigzag) conformation. The interdigitation of alkyl chains in these systems leads to a dense packing of the nanocrystals, which in turn results in well-defined 3D lattices. In the case of the C_{14} alkyl chains, the small d_{pp} value implies strong interparticle van der Waals attraction [Eq. (9)], in addition to the presence of a large number of gauche defects and poor interdigitation.



Fig. 1.17 TEM images of 3D assemblies of Ag_2S nanocrystals surface-coated with (A) 1-octanethiol (C_8), (B) 1-decanethiol (C_{10}), (C) 1-dodecanethiol (C_{12}), (D) 1-tetradecanethiol (C_{14}).

Similar results are obtained with thin superlattices made of silver nanocrystals [29] with different thiol alkyl chain lengths (C_8 to C_{14}). The average center-to-center nanocrystal distance for "supra" crystals of silver as well as cobalt nanocrystals is determined from XRD measurements. It is found to be larger than that determined by TEM for the monolayers. Such a difference is attributed to the presence of defects inside the "supra" crystals (cf. Fig. 1.10), which are also taken into account by the XRD technique.

1.4.2 Influence of the Substrate

The nature of the substrate used in the deposition of the nanocrystals markedly changes the nanocrystal organization. This has been well demonstrated with silver sulfide nanocrystals [98]. On HOPG, Ag₂S nanocrystals self-organize in compact monolayers and form small microdomains over the entire surface (Fig. 1.18A). The gray region in Fig. 1.18A corresponds to Ag₂S nanocrystal monolayers and the darkest is due to the bare substrate (designated hole). The brightest regions correspond to 3D faceted aggregates characterized by a thickness less than 1 μ m and 4–8 μ m width (Fig. 1.18B). Holes are found within the large monolayer regions as observed with atomic force microscopy (AFM; Fig. 1.18C). The cross section (Fig. 1.18C insert) along the line shows that the depth of a hole is about 6 nm, cor-



Fig. 1.18 SEM (A, B) and AFM (C, D) images obtained by using HOPG as the substrate, showing 3D aggregates in coexistence with monolayers. Insert: cross section along the line.

responding to the average nanocrystal diameter and indicating a very dense monolayer, and the coated alkyl chain lines on the substrate surface. Figure 1.18 D shows, by high-resolution AFM, that Ag_2S nanoparticles are organized in hexagonal networks with the same interparticle gap as that observed with TEM.

By replacing HOPG with MoS_2 , the self-organization markedly differs with large interconnected domains of monolayers in coexistence with holes (Fig. 1.19 A). Furthermore, conversely to what is observed on HOPG substrate, aggregates build on the top of the monolayers (Fig. 1.19 B). They are small compared to those observed previously, around 2 μ m width and 150 nm height. The AFM pattern shown in Fig. 1.19 C at a large scale confirms the data observed with SEM (Fig. 1.19 B): rather large holes are trapped inside the monolayer (Fig. 1.19 C). The high-resolution AFM pattern (Fig. 1.19 D) confirms the formation of small islands made of particles arranged in a hexagonal network. Hence, conversely to HOPG substrate, the monolayers on MoS_2 are less dense and the aggregates grow on the top of the monolayers.

These changes were correlated to the interparticle effects [Eq. (1)], particle– substrate interactions [Eq. (9)], and to solvent–substrate interaction (wetting).



Fig. 1.19 SEM (A, B) and AFM (C, D) images obtained by using MoS_2 as the substrate, showing 3D aggregates in coexistence with monolayers. Insert: cross section along the line.

Calculations of the Hamaker constant A_{p-o-p} and A_{p-o-s} indicate that, with HOPG substrate, the interactions between the nanocrystals are dominant compared to particle-substrate interactions. Moreover, the heptane solvent on HOPG forms a nonzero contact angle $(5-10^\circ)$, which means that as evaporation occurs, the solvent film becomes unstable and droplets begin to form. The dynamics of these droplets play a key role in the evolution of the Ag2S nanocrystal assembly on HOPG (Fig. 1.20). Immediately after deposition of a drop of solution containing the nanocrystals, the solvent starts to evaporate (Fig. 1.20 A). The Ag₂S nanocrystals themselves are fully solvated by the heptane, thus preventing their assembly into dense structures. As the droplets grow and begin to merge, some of the Ag₂S nanocrystals (which are still mobile because of the thin solvent layer present on the HOPG surface) are expelled from the merge center (see arrows in Fig. 1.20 B). These coated nanocrystals form compact monolayer islands, whose density increases after all of the solvent evaporates and interdigitation of the alkyl chains on the Ag₂S nanocrystal occurs. Other particles are caught in the center of the droplet merge point. The pressure exerted on these nano-



Fig. 1.20 Sketch of formation of a monolayer and a multilayer on HOPG substrate.

crystals by the droplet menisci is large, and while a monolayer initially forms, continued droplet coalescence engenders the formation of a 3D structure (Fig. 1.20 C). This process may be viewed as analogous to the collapse of Langmuir films when the lateral pressure on the monolayer is too high. The sizes of the 3D aggregates of Ag_2S are similar, which implies that the merge regions between growing solvent droplets are also similar in size. A key point implied by the scheme in Fig. 1.20 B and D is that the formation of monolayers and 3D aggregates occurs essentially simultaneously.

With MoS_2 as substrate, the Hamaker constant indicates that the particle–substrate interactions are higher than those between particles. This favors the sticking of the nanoparticles on the substrate. At this point, this random process induces a



nonordered monolayer. However, because of the surface diffusion and attractive particle–particle interactions (van der Waals and capillary forces), small islands of ordered particles are formed. Once monolayers are formed, the particle–substrate interactions do not play any role in the aggregate growth. Because the nanocrystals interact they tend to form small aggregates. This suggests a layer-by-layer growth following the monolayer formation.

With silver nanocrystals, self-assemblies in a compact hexagonal network are obtained by using a rather large variety of substrates such as HOPG, gold, and silicon (Fig. 1.21) [36]. The vacancies observed in Fig. 1.21 C are probably due to the fact that not enough nanocrystals were deposited on the silicon. Similarly, "supra" crystals are produced with these substrates and also with Al_{0.7}Ga_{0.3}As (Fig. 1.22). X-ray diffraction measurements show reflectograms similar to those observed with HOPG (Fig. 1.11) and characteristic of fcc crystalline structures. All of these substrates are characterized by low-roughness surfaces that favor the particles' diffusion and their organization in 2D and thus in 3D structures.



Fig. 1.22 SEM images of "supra" crystals made of silver nanocrystals deposited on different substrates: (A) HOPG, (B) gold, (C) silicon, and (D) $Al_{0.7}Ga_{0.3}As$.

1.4.3

Thermal and Time Stabilities

To be used, superlattices have to be highly ordered, and thermally and time stable.

1.4.3.1 Crystallinity Improvement Related to the Atomic and Nanocrystal Ordering

The thermal stability of the arrays was specially studied in the case of cobalt particles coated either with dodecanoic acid [32, 68] or with oleic acid [69]. As expected, the annealing of cobalt nanocrystals improves their crystallinity. Native cobalt nanocrystals coated with dodecanoic acid, self-organized in 2D (Fig. 1.23 A) or in 3D (Fig. 1.23 D) superlattices, are made of poorly crystallized fcc particles (Fig. 1.23 B and C). The annealing of the monolayers at 300 °C (Fig. 1.23 E) does not change either the particle diameter (7.2 nm) or the average distance between their neighbors (3.55 nm). The 3D superlattices remain similarly ordered (Fig. 1.23 H). However, in both cases, the annealing process improves the crystallinity of the particles with formation of pure hcp nanocrystals



Fig. 1.23 TEM images of 7.2-nm cobalt nanocrystals coated with dodecanoic acid and ordered in a compact hexagonal network: not annealed (A) and annealed at 300 °C (E). The corresponding high-resolution images (B, F) and electron diffraction patterns (C, G). Multilayers of cobalt nanocrystals: not annealed (D) and annealed at 300 °C (H).

(Fig. 1.23 F and G). Furthermore, by annealing cobalt nanocrystals coated with dodecanoic acid in powder form at 275°C, it is possible to redisperse them in a non-polar solvent and to obtain the same organization as those formed before annealing. In addition, the crystallinity is improved with formation of pure hcp nanoparticles [68]. It must be noted that when the annealed monolayers [32] are left in air for a few weeks, nanocrystals can be superficially oxidized (Fig. 1.24 B), whereas their organization remains unchanged (Fig. 1.24 A). When these oxidized nanocrystals are not implied in the array, i.e., when they are isolated, coalescence takes place (Fig. 1.24 C). Thus, it is concluded that self-organization of nanocrystals prevents coalescence. This claim is confirmed in Fig. 1.24 D where obviously the nanocrystals in the superlattice are protected from coalescence. This is one of the first intrinsic properties of the self-organization process. This fact can be explained in terms of collective entropy gained by nanocrystal ordering, which contributes a substantial amount of stabilization energy to the superlattice.

Similarly, the annealing at 300 °C of monolayers of Co nanocrystals coated with oleic acid [69] does not alter the organization, but material oxidation is observed. With 3D superlattices, there is coalescence of the particles [69]. This is correlated to the removal of the oleic acid molecules during the annealing process. Note that the absence of coalescence in 2D organizations, expected after the coating agent removal, is explained by the absence of mobility of nanocrystals on the substrate, due to their interactions with the latter. In the same way, it has been reported that thin 3D superlattices of FePt [70] nanocrystals are stable up to 550 °C; above this temperature, the mixed coating made with oleic acid and oleyl amine evaporates, inducing again particle coalescence [70].

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Fig. 1.24 TEM images of 7.2-nm cobalt nanocrystals after annealing at 300 °C: ordered in a compact hexagonal network (A) and the corresponding electron diffraction pattern (B). The sample is examined a few weeks after its preparation. Individual dispersed cobalt nanocrystals (C) and the same sample having self-assembled and isolated nanoparticles (D).

As observed for 2D and thin 3D superlattices made of dodecanoic acid-coated cobalt nanocrystals, annealing at 300 °C of "supra" crystals does not change the ordering and keeps the fcc structure [32]. Furthermore, from the XRD patterns, the ordering of the "supra" crystals increases, with an increase in the Bragg peak of the (111) reflection to ring intensity ratio (insert Fig. 1.25 F) and a decrease in the Bragg peak width (Fig. 1.25 F) compared to that of the native sample (Fig. 1.25 C and insert). Note that the interparticle gap decreases from 0.90 nm with increasing the temperature from 25 to 300 °C. Furthermore, cracks appear (Fig. 1.25 D) favoring the decrease of the constraints existing in the native superlattice. The reduction of the interparticle gap is due to the coating agent compaction. From this, it is concluded that thermal treatment of "supra" crystals induces,



Fig. 1.25 SEM images of 7.2-nm cobalt nanocrystals ordered in "supra" crystals not annealed (A, B), annealed at 300 °C (D, E), and annealed at 350 °C (G, H). Corresponding diffractograms obtained by imaging plate scanning and corresponding to the X-ray diffraction patterns obtained in a grazing incidence geometry (insets C, F, I).

as in the bulk phase, an increase in the nanocrystal order. A further increase in the annealing temperature to 350 °C induces formation of small domains (Fig. 1.25 G) and breaks the "supra" crystal ordering with a shift of the Bragg peak towards a smaller angle in the XRD pattern (Fig. 1.25 I and insert). This indicates a dilatation of the (111) planes of about 0.8 nm compared to the "supra" crystal annealed at 300 °C.

1.4.3.2 A New Approach to Crystal Growth

Another annealing process that totally differs from that presented above can be used to form large, flat, silver single crystals with a triangular shape [29]. A colloidal solution of coated silver nanocrystals is evaporated and kept for several days at 50 °C. Immediately after solvent evaporation the nanocrystals are organized in fcc 3D superlattices (Fig. 1.26 A). With time, the nanocrystals coalesce to give rise to



Fig. 1.26 TEM and HRTEM images obtained by immersing HOPG substrate in a silver nanocrystal solution heated at 50 °C for 3 h (A) and for 6 days (B–D). (A) 3D fcc superlattices of silver nanocrystals; in insets, a higher resolution of part of the superlattices and the corresponding power spectrum. (B) Large triangular-shape silver single crystals. (C) HRTEM images of a single triangular particle and (D) the corresponding power spectrum.

large silver single crystals characterized by a regular triangular shape and an average size around 100 nm (Fig. 1.26B). HRTEM images and image processing by the square Fourier transform (power spectrum, PS; Fig. 1.26 C and D) show that these triangular particles are very well crystallized in an fcc structure and are very flat. The reflections observed in the PS correspond to 1/3 (422) reflections that are normally forbidden and indicate very thin particles, which has been confirmed by TEM weak field/dark field techniques.

The nature of the substrate plays an important role in the nanocrystal growth. By replacing HOPG with amorphous carbon, small silver polycrystals (average size around 15 nm) are produced (Fig. 1.27 B–D). As the silver nanocrystals are not initially as well organized on amorphous carbon as on HOPG, this shows the



Fig. 1.27 TEM observations of annealing-time effect on the crystal growth of silver nanocrystals deposited on a amorphous carbon grid: (A) after 3 h (in inset, the corresponding power spectrum); (B, C) after 6 days; (D) HRTEM images of Ag particles in (C).

key role of the nanocrystal organization in the crystal growth process. This feature gives rise to a new area of research in the crystal growth domain and shows a new intrinsic property of the self-organization of inorganic nanocrystals in a well-defined structure.

1.4.3.3 Stability with Time

The stability with time of "supra" crystals is also a real challenge. After a few weeks, the silver nanocrystal monolayers are damaged [20]. The nanocrystals start indeed to coalesce. This finding indicates a desorption of the coating agent with time and thus its weak bonding with silver nanocrystals, which has been observed for various coating agents. Nevertheless, this aging has not been observed in the



Fig. 1.28 SEM images obtained from HOPG substrate immersed in a highly concentrated colloidal silver solution (3×10^{-6} mol L⁻¹), dried 9 h at 35 °C in a hexane vapor atmosphere and then left in air at room temperature for one month (A, B) and five months (C, D). In (B) and (D) the sample is tilted by 45°.

case of monolayers made of cobalt nanocrystals coated by dodecanoic acid [22]. This is mainly due to the fact that the bonding of dodecanoic acid with cobalt atoms at the interface is covalent [99] whereas that of dodecanethiol with silver nanocrystals is weaker. After several months, the "supra" crystals of silver nanocrystals show cracks and holes on their surfaces (Fig. 1.28) and their edges are no longer well defined [20]. The roughness of the surface increases with aging (Fig. 1.28 B and D). From XRD patterns, the evaporation of the residual solvent with time reduces the mean distance between the nanocrystals with a less well-defined second-order peak as for the freshly prepared sample, indicating a decrease in the ordering inside the "supra" crystals. After five months' aging, the "supra" structure is totally destroyed. This is explained as follows: the evaporation of the residual solvent remaining inside the thick "supra" crystals induces the desorption of the alkyl chain used to coat the nanocrystals and thus their coalescence. This confirms the loss in the edge and very rough surfaces observed on the sample (Fig. 1.28 D). Conversely to cobalt nanocrystals, "supra" crystals remain stable in time [22].

1.5 Self-Assemblies in the Presence of External Forces and Constraints

2D hexagonal networks of nanocrystals and 3D fcc superlattices are the most commonly observed organizations with low-size-distribution nanocrystals. Furthermore, it was shown that the use of external force as in the Langmuir–Blodgett technique can improve the 2D hexagonal nanocrystal organization [100–103] and the monolayer is transferred on various substrates. Other external forces, such as convection modes in the liquid phase and application of a magnetic field, either parallel or perpendicular to the substrate during evaporation, induce the formation of new patterns.

1.5.1 Fluid Flow

The deposition method and the evaporation rate of the solvent used to disperse the nanocrystals are two parameters that can also strongly influence the 2D and 3D arrangements of the nanoparticles. Thus, when a droplet of diluted colloidal solution is deposited on a TEM grid maintained with an anticapillary tweezer, nanocrystal ring formations are observed (Fig. 1.29), depending on the solvent evaporation rate [9, 10]. In this deposition mode, the droplet remains on its support until the solvent is totally evaporated (solvent cannot escape from the grid). Ring formation has been observed with different nanomaterials like spherical silver (Fig. 1.29 A), silver sulfide (Fig. 1.29 B), cobalt (Fig. 1.29 C), maghemite (Fig. 1.29 D), nanocrystals and flat triangular CdS (Fig. 1.29 E), and cigar-shaped hematite (Fig. 1.29 F) nanoparticles. This organization is obtained by using a highly volatile solvent as hexane. Both parameters, deposition mode and the solvent evaporation rate, are correlated. A fast evaporation process induces a high gradient temperature between the interface and the substrate, which results in an increase of the surface tension perturbation and convective flow. After complete evaporation of the solvent, the nanocrystal organization is the replica of this flow. By decreasing the evaporation rate (use of a low-volatility solvent, such as decane), the system equilibrates faster than the heat loss by the evaporation process and instabilities disappear. With nanocrystals having a low size distribution, the nanocrystals organized in rings are self-organized in a hexagonal array (Fig. 1.7); otherwise, they are randomly dispersed on the substrate.

By increasing the particle concentration, more complex organizations [9, 10] such as honeycombs or chaotic structures are observed (Fig. 1.30A and B) after evaporation of the solvent. Again, this result is obtained whatever the nature of the nanocrystals. These patterns are similar in shape to those observed in Bénard's experiment with liquid films [104] and attributed to a Marangoni effect. In this case, the concentration gradient appearing during the evaporation favors a convective flux. The patterns observed after evaporation are a replica of the liquid flows and instabilities. This is confirmed by evaporation of a highly concentrated



Fig. 1.29 TEM images of ring organizations of spherical silver (A), silver sulfide (B), cobalt (C), maghemite (D), nanocrystals and flat triangular CdS (E), and cigar-shaped hematite (F) nanoparticles.

nanocrystal solution on a substrate (Fig. 1.31). At the wetting front, during the droplet spreading, fingering instability is observed. An increase in the fingering periodicity is observed from 120 to 200 μ m during the evaporation stage. When the solvent is totally evaporated, fingering patterns are still homogeneous in shape and periodicity (Fig. 1.31 C). Again, these instabilities reflect the migration of the solvent on a substrate and can be observed because it contains nanocrystals dispersed in the solution.



Fig. 1.30 Honeycombs (A) and chaotic structures (B) obtained after evaporation of a concentrated solution containing silver nanocrystals on a TEM grid.



Fig. 1.31 Fingering patterns obtained from a concentrated solution of silver nanocrystals dispersed in hexane. The images are obtained at different times during the spreading of the droplet (A, B) and after evaporation of the solvent (C).

1.5.2

Application of a Magnetic Field

1.5.2.1 Applied Field Parallel to the Substrate

Magnetic nanocrystals with dominant dipolar attractions tend to organize in chainlike structures. This was well demonstrated with iron [75] and magnetite [76] nanocrystals [Eq. (5)]. Similar organizations can be obtained with weakly dipolar nanocrystals by evaporation of the ferrofluid in a magnetic field applied parallel to the substrate. Such experiments were made with spherical cobalt ferrite [14], maghemite [12, 77, 78], and cobalt [13, 25] and with acicular nickel [79] and maghemite [80] nanocrystals. Two types of coating agent are used: an ionic agent like citrate ions, or alkyl chains like carboxylic acid. Then the stability of the ferrofluid is governed on the one hand by electrostatic interparticle repulsion (Fig. 1.2A) and on the other hand by steric repulsion (Fig. 1.2 B). A polar solvent such as water is used to stabilize nanocrystals coated with citrate ions or with short alkyl chain length. An apolar solvent like hexane or cyclohexane is used for long alkyl chain lengths. Depending on the solvent, the deposition modes differ: with polar solvents, a drop of ferrofluid is deposited on the substrate; with apolar solvents, the substrate is dipped into the solution. Evaporation takes place in the presence or absence of a magnetic field. Conversely to ring and honeycomb formation, the deposition mode and solvent used are not key parameters for obtaining chainlike organizations. Using spherical 10-nm γ -Fe₂O₃ nanocrystals [12, 77], surface-passivated with octanoic (C_8), decanoic (C_{10}), and dodecanoic (C_{12}) acids, the TEM patterns markedly differ (Fig. 1.32) Without a magnetic field applied during the evaporation process, large spherical aggregates are produced with C₈ nanocrystals (Fig. 1.32 A), whereas smaller ones are obtained with the C_{10} derivative (Fig. 1.32 B) and, finally, randomly dispersed nanocrystals with C12 (Fig. 1.32C). When nanocrystals are deposited in a 0.59-T magnetic field, an evolution of the organization from chains to a random dispersion is observed (Fig. 1.32 E-G). Such a change in nanocrystal organization is correlated to the total interparticle potential energy which can be expressed as $U_{\text{total}} = U_{\text{vdW}} + U_{\text{dd}} + U_{\text{steric}}$ (see Chapter 3). The interaction between particles increases when the interparticle distance decreases [Eq. (3)]. The length of the alkyl chain used as coating molecule modulates this distance. Large van der -Waals interactions (short interparticle distance) usually lead to spherical aggregations of particles. This is observed experimentally using C₈ nanocrystals in the absence of a magnetic field. In this case the steric repulsion is not sufficient to overcome the van der Waals and dipolar interactions between nanocrystals. The application of a magnetic field during evaporation induces a total magnetic dipole in each aggregate, which is much larger than that of a single nanoparticle. Therefore, the aggregates attract each other and form a chainlike structure. Conversely, by increasing the alkyl chain length of the coating agent (C₁₂ nanocrystals), the steric repulsion is active and particles are then randomly deposited due to a large size dispersion ($\sigma = 20\%$). With a magnetic field, dipolar interactions between nanocrystals are too weak to induce chain formation (see Chapter 3). An intermediate behavior is observed for nanocrystals coated with C10 chains. This explanation is sup-



Fig. 1.32 TEM images of spherical γ -Fe₂O₃ nanocrystals, deposited in the absence (A–D) and in the presence (E–H) of a magnetic field. Nanocrystals are surface-passivated with octanoic acid (A, E), decanoic (B, F), dodecanoic acid (C, G), and citrate ions (D, H).

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ported by Brownian dynamic simulations [12, 77]. Chainlike structures are also obtained with maghemite nanocrystals coated with citrate ions (Fig. 1.32 H). With no magnetic field, spherical aggregation is observed (Fig. 1.32 D).

The structures observed with or without a magnetic field can be explained with the same process described for C8 nanocrystals. Of course, with citrate-coated nanocrystals, electrostatic repulsion has to be taken into account ($U_{\text{total}} = U_{\text{vdW}}$ + $U_{\rm dd}$ + $U_{\rm elec}$). During evaporation, the overlap of the ionic double layer occurs and the Debye-Hückel screening length decreases. Large van der Waals interactions are expected, inducing aggregation in the absence of a magnetic field. Indeed, with a field, dipolar interactions between aggregates are sufficiently high to induce chainlike organizations. By increasing the amount of material deposited on the substrate, similar types of mesostructures are observed (Fig. 1.33). In this way, spherical maghemite nanocrystals [15, 77] coated with short chains (C₈ nanocrystals) or with citrate ions organize in spherical highly compact aggregates (Fig. 1.33 A and D) without an applied magnetic field, and form long cylinders with a very regular structure in its presence (Fig. 1.33 E and H). By tilting the sample, it is seen that the structure corresponds to superimposed cylinders. Conversely, when nanocrystals are coated with long alkyl chain length acids (C12 nanocrystals), without a field, a dense film with a flat surface is observed (Fig. 1.33C) and the application of a magnetic field induces only a slight undulation at the surface of the film (Fig. 1.33 E). An intermediate behavior is observed with C₁₀ nanocrystals (Fig. 1.33 B and F).

As in the case of diluted ferrofluids, such changes in the mesoscopic structure are correlated to interactions between nanocrystals (see Chapter 3) [12, 77]. Hence, the disappearance of structural organization for dodecanoic acid-coated nanocrystals is a result of the significant decrease in the interaction between nanocrystals due to the large interparticle distance. Cobalt nanocrystals coated with dodecanoic acid and deposited under an applied magnetic field show the formation of stripes (in concentrated systems) [13, 25]. This finding markedly differs from that observed with C12 maghemite nanocrystals. It is attributed to the difference in hardness of the magnetic materials (see Chapter 10, cobalt nanocrystals constitute a hard magnetic material while maghemite is a soft one) as well as to van der Waals interactions between the magnetic materials (see Chapter 3, the Hamaker constant of metallic cobalt is higher than that of oxide nanocrystals). The strength of the applied field and evaporation rate control the mesoscopic structure. Figure 1.34 shows that whatever the strength of the applied field, maghemite nanocrystals are aligned along the direction of the magnetic field in tubelike structures. However, the average width of the cylinders and the compacity increase with the strength of the applied field [15, 24]. Similar results are obtained with cobalt nanocrystals: the roughness decreases and the average distance between two adjacent stripes decreases linearly with the strength of the applied magnetic field [13]. The organization in the absence and presence of a magnetic field differs with the evaporation rate [13]. This is illustrated with cobalt nanocrystals coated with dodecanoic acid (Figs. 1.6 and 1.35). When evaporation takes place in air and in the absence of a magnetic field, a 3D film with high roughness is obtained (Fig. 1.35 A).



Fig. 1.33 SEM images of spherical γ -Fe₂O₃ nanocrystals, deposited in the absence (A–D) and in the presence (E–H) of a magnetic field. Nanocrystals are surface-passivated with octanoic acid (A, E), decanoic (B, F), dodecanoic acid (C, G), and citrate ions (D, H).

High magnification (Fig. 1.35 E) shows that cobalt nanocrystals tend to aggregate in 70-nm-diameter spherical shapes. The application of a magnetic field induces formation of a linear structure (Fig. 1.35 B) made of these 70-nm spherical aggregates (Fig. 1.35 F). Under hexane vapor, such aggregates are not observed and a homogeneous film, with cracks, is observed without an applied field (Fig. 1.35 C and G); in its presence, long stripes corresponding to a highly compact film are seen (Fig. 1.35D and H). Hence, these changes in morphologies are related to eva-



Fig. 1.34 SEM images obtained at various magnifications for spherical citrate-coated γ -Fe₂O₃ nanocrystals, deposited in various magnetic field strengths: (A, B) 0.01 T; (C, D) 0.05 T, and (E, F) 0.59 T.

poration rate and again to nanocrystal interactions. A rapid evaporation favors the close approach between nanocrystals and attractive van der Waals and dipolar interactions between nanocrystals increase, inducing spherical aggregation. In a slow evaporation, the nanocrystals freely diffuse in solution leading to formation of homogeneous structures.

The anisotropy shape of nanocrystals also plays a role in the mesoscopic structure. Chainlike structures are obtained with cigar-shaped maghemite nanocrystals coated with citrate ions [80] and having an average length, width, and aspect ratio of 325, 49, and 6.7 nm, respectively. Figure 1.36A shows nanocrystals randomly deposited without an external magnetic field during evaporation. With a magnetic field (1.8 T), the nanocrystals are aligned with their long axis along the field direction (Fig. 1.36C). The applied field assembles the nanocrystals in chains and aligns their easy axes with their magnetic moments during evaporation. By in-



Fig. 1.35 SEM images of 3D films made of spherical cobalt nanocrystals, deposited in the absence (A, C, E, G) and in the presence (B, D, F, H) of a magnetic field. The evaporation takes place in air in 45 min (A, B, E, F) and under a saturated hexane atmosphere in 12 h (C, D, G, H).

creasing the amount of material deposited, similar morphologies are obtained. With no applied magnetic field, a thin magnetic film is obtained and the nanocrystals are randomly oriented (Fig. 1.36 B). The application of a magnetic field during evaporation induces the organization of the nanocrystals into ribbons (Fig. 1.36 D). The nanocrystals are mainly oriented with their long axis along the direction of the applied field.



Fig. 1.36 TEM (A, C) and SEM (B, D) images of cigar-shaped γ -Fe₂O₃ nanocrystals deposited in the absence (A, B) and in the presence (C, D) of a magnetic field.

From these data it is concluded that the mesoscopic structures markedly differ with the nanocrystal coating agent and the nature of the material, and are influenced by the strength of the magnetic field, the evaporation rate, and the extent of the nanocrystal anisotropy.

1.5.2.2 Applied Field Perpendicular to the Substrate

Recently in our laboratory, solid mesostructures, such as columns or labyrinths of cobalt nanocrystals coated with dodecanoic acid, were produced by applying a magnetic field during the evaporation of the fluid containing magnetic nanocrystals dispersed in a nonpolar solvent. A transition from columns to labyrinths is shown in Fig. 1.37. However, a thick film of cobalt nanocrystals underneath such "supra" structures was observed. In this case, the applied magnetic field is rather high and is located in the nonlinear regime.

By improving the synthesis mode of cobalt nanocrystals, the underlying layer disappeared with more or less similar structures remaining [16]. A theory is developed to understand the formation of these patterns (see Chapter 3). Taking into account the radius, the height of the cylinders, the magnetic phase to the total volume ratio, and the center-to-center distance between cylinders, and by using the model developed in ref. [105], the estimated interfacial tension deduced by the minimization of the total free energy is 5×10^{-5} N m⁻¹. From this it is concluded that the formation of structures takes place in a concentrated solution of nanocrys-



Fig. 1.37 SEM images obtained by evaporating a concentrated solution of cobalt nanocrystals deposited in a magnetic field perpendicular to the HOPG substrate.The evaporation time is 12 h. The strength of the applied field is (A) 0.01 T; (B) 0.27 T; (C) 0.45 T; (D) 0.60 T, and (E) 0.78 T.

tals induced by a liquid–gas phase transition and not via a Rosenweig instability [89]. This is confirmed by a video recorded during the evaporation process. Dots appear 7 hours after the evaporation starts (Fig. 1.38 A). Figure 1.38 shows that the number of dots increases progressively and then they migrate in the solution to form a hexagonal array (Fig. 1.38 D). At the end of the evaporation a wave due to capillary forces induces the collapse of the columns (Fig. 1.38 E and F). This is confirmed by the SEM image recorded at the end of the evaporation process (Fig. 1.39).

At this point a question arises: what process controls the formation of columns and/or labyrinths? To answer this we have to take into account the size distribution of nanocrystals with mainly the same average nanocrystal size. The SEM image shown in Fig. 1.40 (see page 43) is produced with nanocrystals having 5.7-nm average diameter and 13% size distribution. Well-defined structures are produced with formation of dots (insert A, Fig. 1.40), collapsed columns (insert B, Fig. 1.40), and very few labyrinths. On replacing HOPG by TEM substrate, the columns are well defined (insert C, Fig. 1.40), and their ends are highly organized in fcc structures (insert D, Fig. 1.40). By increasing the size distribution to 18% and keeping a similar average diameter (5.9 nm), the SEM pattern markedly differs with the appearance of labyrinths and flowerlike patterns (Fig. 1.41). Inserts a and b show that the flowerlike patterns are in fact the ends of fused columns and that they tend to form wormlike patterns and labyrinths, as shown in Fig. 1.41. By using the same procedure as that described above, the TEM image shows that the columns are not well defined (insert C) and their



Fig. 1.38 Video microscopy image (A) obtained during the evaporation of a cobalt nanocrystal solution in a 0.25-T magnetic field at the instant when the columns appear. A silicon substrate is used. The ring in (B) encloses the columns, the arrows in (C) indicate the direction of column diffusion. (E, F) Images obtained at the end of the evaporation of a cobalt nanocrystal solution; the arrow indicates the direction of the wave created by the capillarity forces.

extremities are totally disordered (insert D). A careful examination of the labyrinthine structures shows that they are made of fused columns having more or less the same height (Fig. 1.42).

From these data and those reported in refs. [17, 18, 106–108] we have quite good knowledge of the mechanism of production of mesostructures when magnetic nanocrystals are subjected to a rather large vertical applied field. It is concluded that the column growth in the concentrated liquid phase of cobalt nanocrystals is induced by a phase transition. They migrate inside the solution to self-



Fig. 1.39 SEM image obtained at the end of the evaporation process.



Fig. 1.40 SEM image of mesostructures made of 5.7-nm cobalt nanocrystals with 13% size distribution The vertical magnetic field strength applied during the evaporation process is 0.25 T. Inserts (A) and (B) are magnifications of the SEM image; (C) and (D) are TEM images at two different magnifications, obtained with the same experimental procedure.

organize in a hexagonal network. Waves induced by capillary forces induce the collapse of most of these columns. Their rigidity is controlled by the ability of nanocrystals to self-organize in fcc structures. They can thus retain their integrity. Conversely, the disorder inside and at the edges of the columns, mainly due to the large size distribution of the nanocrystals, induces their fusion. However because the columns are formed in the solution, those having a similar size tend to attract



Fig. 1.41 SEM images of mesostructures made of 5.9-nm cobalt nanocrystals with 18% size distribution. The vertical magnetic field strength applied during the evaporation process is 0.25 T; silicon is used as substrate. Inserts (A) and (B) are magnifications of the structures in the SEM image. Inserts (C) and (D) are TEM images at two different magnifications, obtained with the same experimental procedure.



Fig. 1.42 SEM image of labyrinthine structures showing that they are made of fused columns.

each other by van der Waals interactions and to fuse. This makes it possible to produce rather homogenous wormlike structures or labyrinths. Furthermore, these mesostructures are independent of the strength of the applied field in the range of 0.1 to 0.8 T, because the experiments are carried out where there is non-linear behavior of the magnetic field.

1.6 Conclusion

The last few years have seen extremely rapid advances in the preparation of very narrow size distributions of various types of nanomaterials. These advances have enabled many groups to prepare 2D and 3D nanoparticle superlattices. In the same way, organizations of nanoparticles in mesoscopic patterns such as rings, chains, and ribbons have also been developed. Some of these patterns require the presence of external forces to be formed. These various systems constitute an open research field and many exciting phenomena remain to be discovered. Such new materials could have a significant impact on future electronic, optics, and magnetic storage devices. Nevertheless, the optimization of their fabrication is still needed in order to obtain very regular and well-defined patterns. In this chapter, we have shown that many parameters are involved in the formation of these organizations.

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