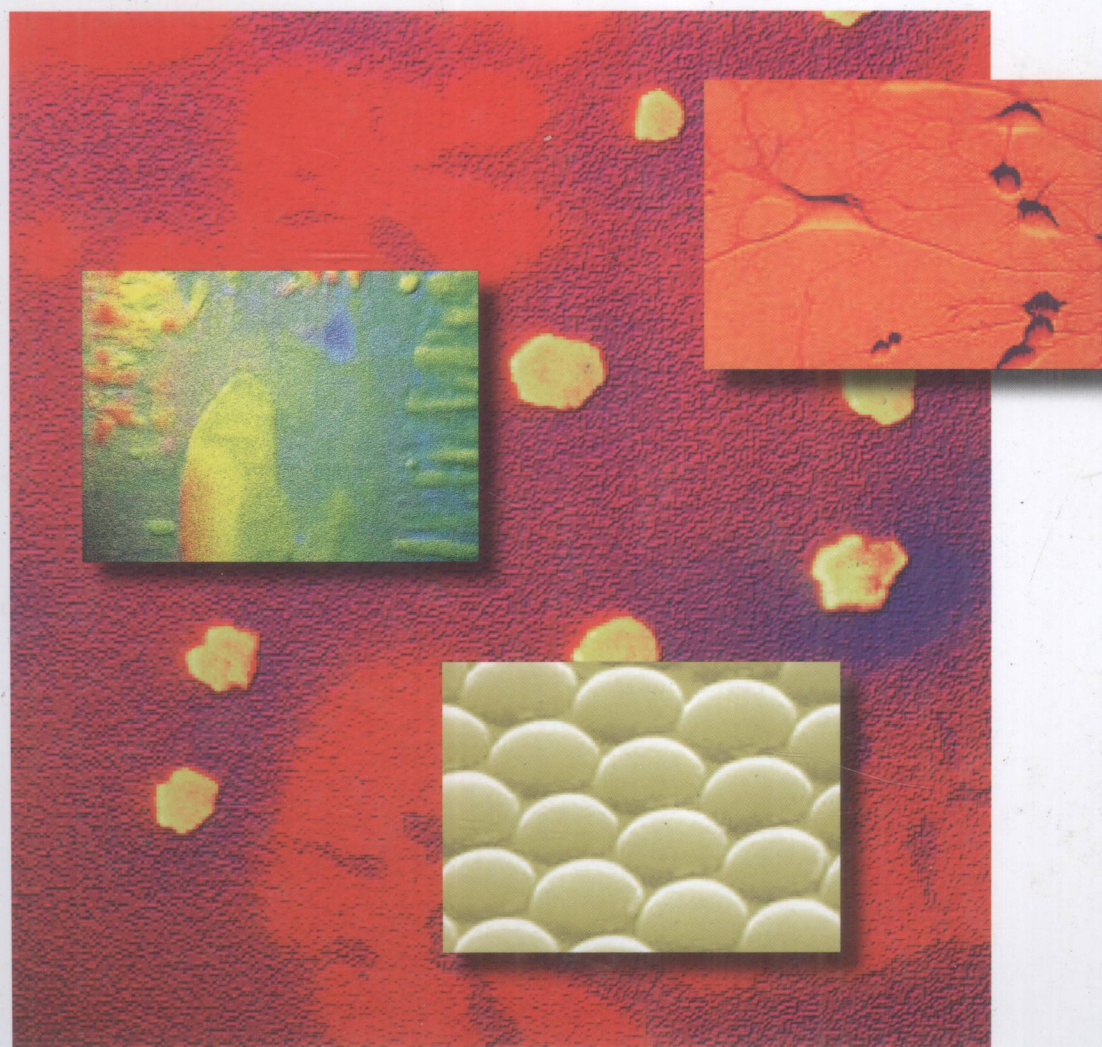


Edited by Marie-Paule Pileni

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# Nanocrystals Forming Mesoscopic Structures



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*Edited by*  
*Marie-Paule Pileni*



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## 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



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 ( $\text{Ag}_2\text{S}$ ,  $\text{CdSe}$ ,  $\text{PbSe}$ ) [8, 19, 33, 34], metals ( $\text{Ag}$  [20, 21, 27, 29, 35–46],  $\text{Au}$  [47–62],  $\text{Pd}$  and  $\text{Pt}$  [63, 64],  $\text{Co}$  [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 mesoscopic 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-