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Self assembly of inorganic nanocrystals in 3D supra crystals: Intrinsic properties

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ABSTRACT

Here we describe how arrangements of nanocrystals can self-organize in 3D arrays called supra crystals. The 3D arrays can fall into the familiar categories of face centered cubic (fcc), hexagonal compact packing (hcp) crystals, and body centered (bcc) crystals. Intrinsic collective properties of these 3D arrangements are different from the properties of individual nanoparticles and from particles in bulk.

We demonstrate by two various processes and with two types of nanocrystals (silver and cobalt) that when nanocrystals are self ordered in 3D superlattices, they exhibit a coherent breathing mode vibration of the supra crystal, analogous to a breathing mode vibration of atoms in a nanocrystal.

Comparison between the approaches to saturation of the magnetic curve for supra crystals and disordered aggregates produced from the same batch of nanocrystals is similar to that observed with films or nanoparticles either highly crystallized or amorphous.

1. Introduction

The first self assembly of nanocrystals having diameters the order of a few nanometers (<10 nm) was discovered more than a decade ago [1,2]. Later, several groups demonstrated that a rather large number of nanocrystals were locally ordered [3]. The 3D superlattices were made up of a few nanocrystal layers. To be able to find new physical properties due to the ordering, the same batch of nanocrystals has to be either ordered or disordered at the mesoscopic scale (several hundred micrometers). Very few groups have been able to make 3D superlattices made of several thousand layers called supra crystals. These have been produced for silver [4,5], CdSe [2,6], cobalt [7,8] and gold [9,10] nanocrystals.

When nanocrystals are ordered in 2D superlattices, each influences the physical properties of the assembly. Hence, they are neither those of the isolated nanocrystals nor those of the corresponding bulk phase. They could depend on the shape of the nanocrystal ordering at the mesoscopic scale. Collective optical [3,11,12,15] and magnetic [3,12–14] properties due to dipolar interactions are observed when the nanocrystals are organized in 2D superlattices [3]: The optical properties of 5 nm silver nanocrystals organized in hexagonal networks give rise to several plasmon resonance modes attributed to the film anisotropy. In the magnetic properties, the hysteresis loop of nanocrystals self ordered in 2D superlattices is squarer than that of isolated nanocrystals. The calculated and experimental hysteresis loops for a chain-like structure are squarer than that of a well-ordered array of nanocrystals. Also, the linear chains of nanocrystals behave as homogeneous nanowires [16,17].

Here, we demonstrate that the ordering of nanocrystals at the mesoscopic scale is not simply an aesthetic arrangement but in fact a new generation of materials with intrinsic properties (optical, magnetic, crystal growth, etc...).

2. Self-organization of inorganic nanocrystals

The nanocrystals, coated with surfactant molecules, described below are made in water-in-oil droplets stabilized by a surfactant and called reverse micelles [18]. After washing, the coated nanocrystals are dispersed in a given solvent and a drop is deposited on a substrate. The size distribution (<13%), particle–particle and particle–substrate interactions play an important role in nanocrystal ordering in close packed hexagonal network. Note that other types of the ordering as rings of nanocrystals governed by Marangoni instabilities is produced by inducing temperature gradient during the evaporation process and is the fingerprint of the solvent [19].

In most cases, when nanocrystals are able to self-organize in compact hexagonal network over a long distance, the regular periodic arrangement of nanocrystals in 3D superlattices, called supra crystals, with more than a thousand layers of organized nanocrystals occurs. Previous studies show that the main factor determining the preferred crystal structure of a nanocrystal superlattice is the softness of the nanocrystals. This encompasses its compressibility, deformability and the nature and the range of the nanocrystal interactions [20–24]. It is also well known that colloids as micelles and/or copolymers are able to form supra aggregates characterized by a crystalline phase.

Here we demonstrate [25] that various crystal structures of the supra crystal such as hexagonal compact packing (hcp), face centered cubic (fcc) and body centered cubic (bcc), are produced

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in thermodynamic equilibrium. By controlling the substrate temperature two crystalline structures are produced as in the classical phase diagram of bulk material of atoms [26,27].

Silver nanocrystals (5 nm) coated with decanethiol and dodecanthiol [$Ag(C_{10})$, · $Ag(C_{12})$] and dissolved in decane. For 15 °C substrate temperature deposition, the obtained small angle X-ray diffraction (SAXRD) pattern (Fig. 1A) shows two strong reflections (numbered 1 and 1' in Fig. 1A) normal to the substrate. The width of the first order Bragg reflection is nearly resolution-limited indicating long-range ordering of the nanocrystals perpendicular to the surface. Other less intense spots are also observed in this pattern revealing a three-dimensional, long-range ordering within supra crystalline domains. The corresponding simulated diffraction pattern is shown in the Fig. 1A inset and gives unambiguous evidence for hcp packing. The experimental and calculated diffraction spot coordinates fit very well and enable indexing of the diffraction pattern. On increasing the substrate temperature to 25 °C, the diffraction pattern is typical of silver nanocrystal fcc packing with the (1 1 1) plane lying parallel to the substrate. A further increase in the substrate temperature to 50 °C improves the crystallinity of supra crystals with a marked decrease in the defects (Fig. 1B and its inset). There is an increase in the supra crystal crystallinity with temperature and, if it is slow enough, the structure does not depend on the evaporation rate.

We know that to be bounded to the nanocrystals surface the alkyl chains used as coating agent have to be rather long. Simultaneously to form a compact network the nanocrystals coated with surfactant molecules have to act as hard spheres. This can be obtained when the alkyl chains as rather short. Hence a very subtil compromise between these two parameters has to be found to be able to produce hcp and fcc supra crystals at thermodynamic equilibrium. Hence, with the same batch of nanocrystals dispersed in a given solvent, the two structures (hcp/fcc), with a very small difference in the free energy, can be produced as in the bulk metallic phase. By using $Ag(C_{12})$ instead of $Ag(C_{10})$, i.e., a change of the chain length of the coating agent by two carbon atoms and by keeping the same solvent (decane) the diffraction pattern observed when the substrate temperature is 15 °C during the evaporation process shows a halo larger than the experimental resolution indicating that disordered aggregates are produced (Fig. 1C). On increasing the substrate temperature between 25 °C and 35 °C, the diffraction patterns display several diffraction spots typical of a compact structure corresponding to hcp with more or fewer defects. On further increasing the substrate temperature to 50 °C, the diffraction pattern markedly changes and displays diffraction spots typical of a bcc arrangement (Fig. 1D). This is confirmed by the corresponding simulated diffraction pattern in the Fig. 1D inset. As with $Ag(C_{10})$ it is possible to obtain again two crystalline structures such as hcp containing more or fewer defects, bcc supra crystals and also disordered assemblies. Again these structures are in thermodynamic state. Thus, silver nanocrystals, characterized by a given coating agent and dispersed in decane, grow into supra crystals having various structures. The change in the structure is tuned by changing either the substrate temperature and/or the

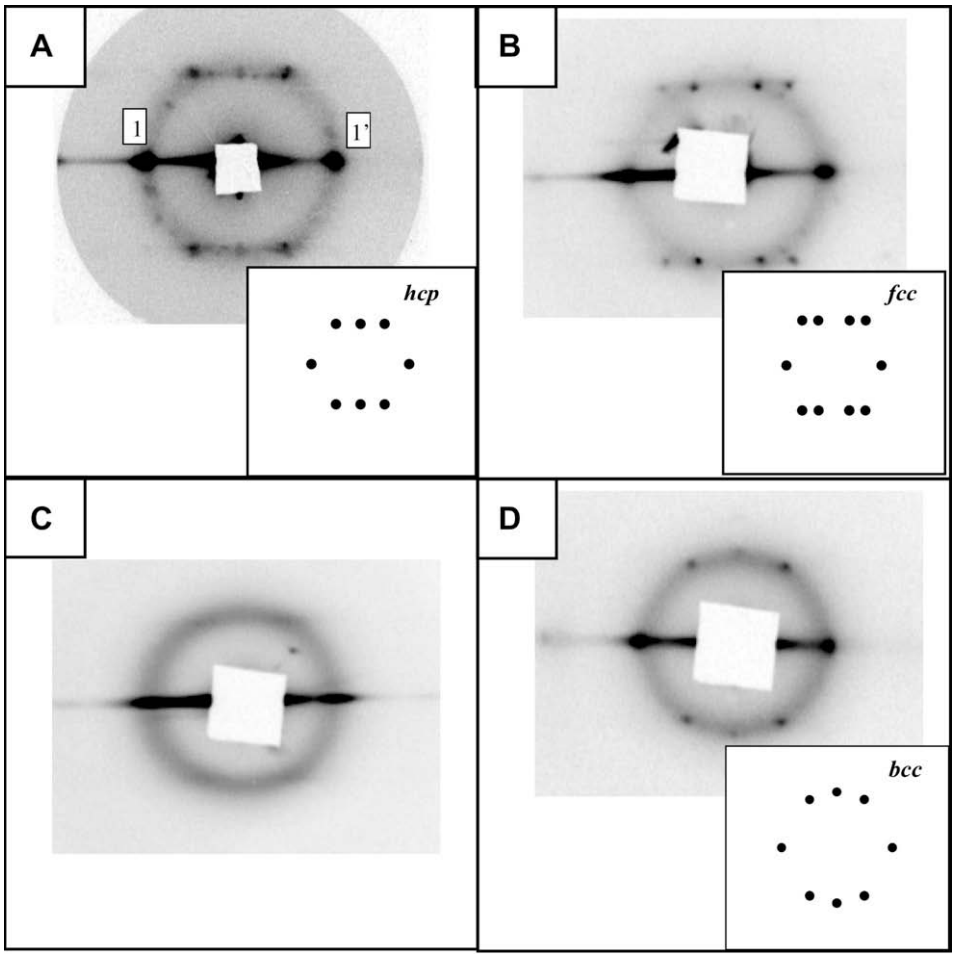

Fig. 1. Small angle X-ray diffraction patterns corresponding to Ag-C10 nanocrystals initially dispersed in decane, evaporated at 15 °C (a), 50 °C (b) and to Ag-C12 nanocrystals initially dispersed in decane evaporated at 15 °C (c), 50 °C (d). The insets are the corresponding simulated diffraction patterns.