

Superstructures of self-assembled cobalt nanocrystals

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Uniform three-dimensional superstructures of spherical cobalt nanocrystals are produced by the interplay between dipolar interaction and applied magnetic field. An anomalous low-temperature magnetic behavior is observed, indicating that uncompensated surface spins become ordered below 10 K, as evidenced by the presence of two magnetic phases that superimpose in hysteresis loops as compared to measurements at 20 K. The approach discussed here provides a framework for applications such as high-performance mesomagnets, microelectronic and magnetic devices fabrication, and can be extended to other nanocomposite materials fabrication if cobalt particles can act as carriers for other nanoparticles. © 2004 American Institute of Physics.

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Engineering nanocrystal NC materials are of vital interest in fundamental and technological studies in the field of condensed matter.^{1–4} A variety of lithography techniques and chemical synthesis have been utilized to produce nanocrystals with controlled size and composition as building blocks of these materials. The combination of chemical synthesis and self-assembly is the most attractive technique among them because it produces small structure units at scales beyond the spatial limits of other techniques, and precisely engineers structures on the nanometer scale over large regions. Interest in this technique is increasing by virtue of its potential for the fabrication of microelectronic and magnetic devices, which require very uniform two- (2D) or three-dimensional (3D) organization of NCs. Motivated by ultrahigh-density magnetic recording, high quality magnetic NCs^{5–10} have been successfully synthesized by solution-phase metal salt reduction. However, due to the long-range dipolar interaction combined with localized interactions, such as van der Waals attraction and steric repulsion, organizing 3D superstructures of magnetic NCs is very challenging.¹¹ In this letter, we demonstrate the self-assembly behavior of superparamagnetic cobalt NCs in applied magnetic fields, and thereafter produce uniform grain-like superstructures by depositing the NCs in a magnetic field. The findings suggest that it may be possible to prepare mesomagnets and magnetic quantum devices by self-assembly of NCs.

Cobalt NCs are synthesized by rapid pyrolysis of cobalt

carbonyl in an inert atmosphere. Details of the preparation have been described.^{11,12} The size distribution and particle shape are controlled by varying the surfactant, its concentration and the reaction temperature. From an observation of high resolution transmission electron microscopy (TEM), it is found that the crystal structure of spherical particles is ϵ -Co, a metastable cubic structure isomorphous with β -Mn, while the structure of the disk-like particles is hcp-Co. A surfactant coating layer (~ 2 nm in thickness) separates particles and passivates them against oxidation. Figure 1 shows typical 2D self-assembled patterns of cobalt NCs with differ-

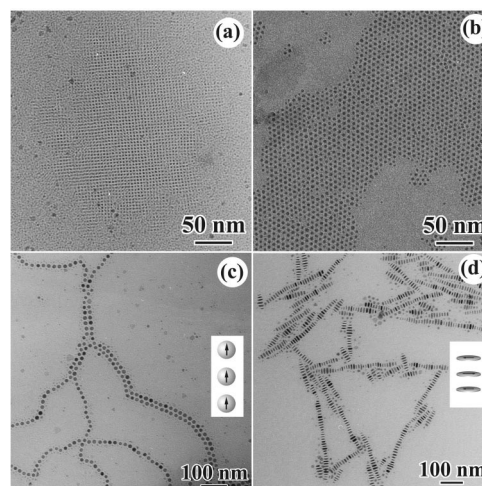


FIG. 1. Two-dimensional self-assembled arrays of monodispersed cobalt nanocrystals: (a)–(c) 3, 6, and 17 nm spherical particles, respectively; (d) 5×20 nm nano-disks.

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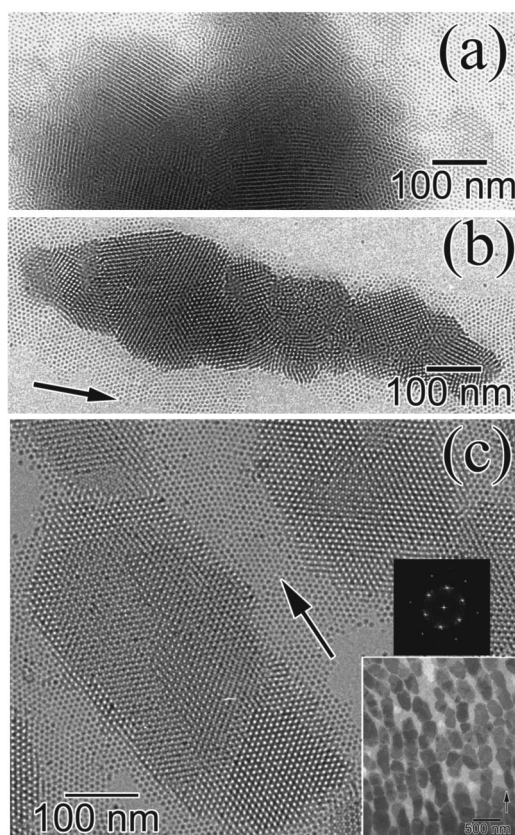


FIG. 2. Three-dimensional superstructures of 6 nm ϵ -cobalt nanocrystals, deposited with an external magnetic field: (a)–(c) 0.0 Oe, 1.0 kOe and 5.0 kOe, respectively. An extensive existence of such uniform superstructures is shown in the inset of (c). The arrows represent the directions of the applied magnetic field.

ent sizes and shapes deposited by simply evaporating the solvent from dispersion. The spherical NCs of 3 and 6 nm are superparamagnetic at room temperature, and tend to self-assemble into periodic patterns [square and hexagonal close-packed superlattices as shown in Figs. 1(a) and 1(b)]. However, the spheres of 17 nm and nano-disks of 5×20 nm (an in-plane easy axis was found) are blocked, and arrange into chains of spheres and rows of nano-disks by the strong dipolar interaction [Figs. 1(c) and 1(d)]. Each nano-disk row consisting of 7–30 particles minimizes interaction energy by aligning parallel to each other. The difference in the arrangements between big spheres and disks indicates two ground states of systems dominated by magnetic dipolar interaction, the so-called ferromagnetic longitudinal (FL) and the antiferromagnetic transverse configurations¹³ as sketched in the insets, respectively. In this letter, we choose to study 6 nm superparamagnetic cobalt NCs because the colloidal dispersions of small particles have long term stability attributed to the weak dipolar interaction. This stability is indispensable to producing uniform superstructures on larger scales.

A monodispersion of 6 nm NCs is diluted to 10% by toluene, and then deposited on carbon-coated TEM grids at room temperature. A magnetic field ranging from 0.0 to 5.0 kOe is applied during solvent evaporation. The evaporating time is over 30 min. TEM images of 3D self-assembled arrays are shown in Fig. 2. One obviously sees that the array deposited without magnetic field consists of short-ranged stacking ordered regions, which are randomly oriented and

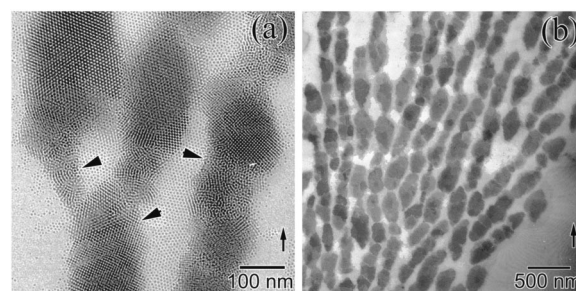


FIG. 3. Three-dimensional superstructures of 6 nm ϵ -cobalt nanocrystals doped with 10 nm nanocrystals (marked by the short arrows) at a concentration ratio of 20:1. The external field is 5.0 kOe, and the direction is given by the black arrow. (b) Indicates an extended area of superstructures.

form a polycrystalline-like superstructure with a round shape [Fig. 2(a)]. In the presence of an external magnetic field, however, elongated grain-like superstructures are produced [Figs. 2(b) and 2(c)]. The long axis of each grain is parallel to the direction of the magnetic field. A Fourier transform of Fig. 2(c) (as shown in the inset) indicates that the arrays deposited at 5.0 kOe have uniform hexagonal stacking order, extending over a very large area [inset of Fig. 2(c)], while those deposited at 1.0 kOe have a great deal of stacking faults. The field of 5.0 kOe is strong enough to saturate the colloidal dispersion at room temperature, where effects of the thermal fluctuations and the local interactions on the assembly behavior are negligible. Therefore, according to Hayter and Pynn,¹⁴ the colloidal dispersion has an anisotropic liquid structure factor $S(\mathbf{q})$ determined by the interplay between dipolar field and the external field. In the direction of the magnetic field, a series of neighbors on either side of a given particle are present, while such long-ranged arrangement is unfavorable along the directions perpendicular to the field. The anisotropy of the structure factor determines the elongated ellipsoidal shape of the superstructure, with the long axes parallel to the field. At low magnetic field, however, thermal fluctuations are no longer negligible. The random flipping of magnetic moments induced by the thermal fluctuations greatly affects the order of the stacking layers and therefore produces many stacking faults as shown in Fig. 2(b). Increasing the particle size to about 10 nm results in a great enhancement of the length/width ratio of grain-like superstructures. It means, for the big particle dispersions, that the FL dipolar interaction increases the nearest-neighbor contacts along the direction parallel to the field and almost suppresses those contacts along the perpendicular directions.

The dipolar interaction can be adjusted by doping with particles of different size. The superstructures are then readily tailored to meet the requirements of technological applications. As an initial attempt, we mixed the diluted dispersions (10% by toluene) of 6 and 10 nm NCs at a concentration ratio of 20:1, and subsequently deposited them on TEM grids. The evaporation process is the same as above, and the magnetic field is fixed at 5.0 kOe. As shown in Fig. 3, although the grain-like superstructure still appears extensively over large regions [Fig. 3(b)], the grain shape is no longer as uniform as those produced by monodispersion. The details of the arrangements can be seen in Fig. 3(a). The 10 nm particles mainly appear at grain boundaries as connections between the grain-like superstructures of 6 nm NCs,

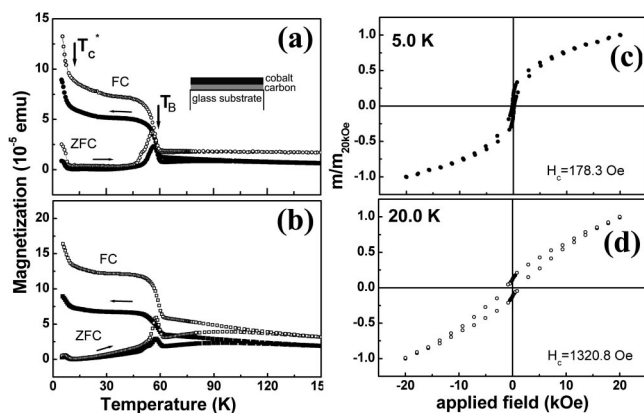


FIG. 4. ZFC and FC curves of the samples deposited with field (open) and without field (solid). (a) Monodispersions of 6 nm particles; (b), doped samples. T_c^* is the transition temperature and T_B is the blocking temperature; (c) and (d) are hysteresis loops of the monodisperse sample deposited with field, which are measured at 5 and 20 K. Samples were prepared by depositing the cobalt nanocrystals on glass substrates with a buffer layer of amorphous carbon (~ 20 nm in thickness) as sketched in the inset.

providing ideal systems to study spin-dependent electron transport and other magnetic behaviors. Some of them appearing in the arrays of the small particles result in a few of stacking faults.

The magnetic moment versus temperature under a field of 10 Oe is measured after zero-field cooling (ZFC) and after field cooling (FC), as shown in Figs. 4(a) and 4(b). The measurements are carried out along the direction of deposition field. It is found that all ZFC curves peak at the blocking temperature of the 6 nm NCs, $T_B \approx 57$ K. Note that the peaks of the samples deposited in magnetic field are sharper than those deposited in zero field, indicating a uniform spatial distribution of easy axes in addition to a narrow size distribution (standard deviation is less than 5%). The 10 nm particles in the doped samples, which have higher T_B , result in a slight increase in the magnetic moment at elevated temperature. Their large magnetic moments enhance the dipolar interaction and broaden the peaks in the ZFC curves [Fig. 4(b)]. The temperature, T_c^* , marked by the arrow in Fig. 4(a) where a steep step appears in the FC curve, reflects a transformation of magnetic phase in the 3D superstructures. It is also found that a small ZFC peak appears near this temperature. Attributed to the reduced symmetry of atom environment on the particle surface, a strong surface anisotropy is induced and results in disorder of surface spins.^{15,16} The existence of disordered surface spins is displayed by nonsaturation character of the magnetization as shown in Fig. 4(d). At low enough temperature, however, the surface spins become ordered because the exchange interaction in each particle is dominative. In present study, we associate the ZFC peak at

T_c^* (about 10 K) and the rapid increase of magnetization in FC curve with the “freezing” of disordered surface spins. Such variation of surface spins increases the net magnetic moment of NC and enhances the dipolar interaction as well. A notable reduction of coercivity at low temperature [178.3 Oe at 5 K, but 1320.8 Oe at 20 K as shown in Figs. 4(c) and 4(d)] is then obtained, which may be caused by a collective reversal process. Doping 10 nm NCs enhances the transformation temperature by about 10 K because of change of the ratio of surface/volume and the dipolar interactions, while deposition in applied field does not change it obviously.

We have fabricated uniform 3D superstructures of Co NCs by magnetic deposition, which can be readily tailored by the NC size and magnetic field strength. Our method shows great potential for future applications in high-density magnetic recording and high-performance mesomagnets. Furthermore, it can be extended to other NC systems, providing both a model for studying the fundamentals of dipolar interactions and a practical route to fabricate functional nanosized electronic and magnetic devices.

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