Formation of Orientation-Ordered Superlattices of Magnetite Magnetic Nanocrystals from Shape-Segregated Self-Assemblies†

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Magnetic magnetite (Fe₃O₄) nanocrystals have been synthesized by combining nonhydrolytic reaction with seed-mediated growth. The shape of these magnetite nanocrystals can be controlled either as pure spheres or a mixture of mainly faceted nanocrystals. Faceted magnetite nanocrystals consist of truncated tetrahedral platelets (TTPs), truncated octahedrons (TOs), and octahedrons (OTs). Transmission electron microscopy analysis indicates that the faceted nanocrystal mixture tends to self-segregate based upon the shape in a self-assembly process, and each shape forms its own distinct crystallographic orientation-ordered superlattice assemblies. Self-assembly of the Fe₃O₄ nanocrystals in the shapes of TTP, TO, and OT show hexagonal, primitive cubic, and distorted body-centered cubic (bcc) superlattice structures, respectively. The possible mechanism for the formation of different superstructures is attributed to van der Waals interactions. Nanocrystals with different shapes provide diverse building blocks for bottom-up approaches in building nano- and mesosystems. Furthermore, the self-segregation phenomenon of different shaped nanocrystals in self-assembly processes could be very important in envisioning efficient assembly strategies for nanoscience- and nanotechnology-based devices.

Introduction

Nanomaterials have inspired broad interests in various areas for both their size- and shape-dependent properties and for a variety of technological applications.¹² Enormous progress has been made in producing metal and semiconductor nanocrystals with various shapes such as rods, multiple-branched rods, nanocubes, nanodisks and nanoprisms.³–¹⁴ However, the shape-controlled synthesis of metal oxides in the nanometer regime has limited success, especially for magnetic metal oxides, even though such materials are of great importance in a variety of technological applications ranging from biomedical areas to magnetic data storage.¹⁵–¹⁸ Moreover, it is also of great fundamental and practical interest to prepare monolayers, thin films and superstructures by using nanocrystals as building blocks to explore the novel collective optical, electrical, and magnetic phenomena possessed by nanosystems.¹⁹,²⁰

Recent research has demonstrated a wide variety of self-assemblies built by metallic, semiconductor and other compound nanocrystals.²¹–²⁴ It is interesting to note that iron oxide nanocrystals were among the first observed superstructures.²⁵ Although orientation ordering has been observed in a short range in the assembly of Ag, Au, and Co spherical nanocrystals,²⁶–²⁸ long-range orientation ordering in general is limited, although translational symmetry could be achieved perfectly. It seems easier for faceted nanocrystals to form orientation-ordered self-assembly. For instance, metallic FePt nanocubes can self-assemble into an array with a (100) oriented texture.²⁹ The preservation of orientation ordering could place high restrictive requirements on the size, size distribution, and shape of the nanocrystals. Self-assembly of nanocrystals tends to follow a general rule of surface-to-surface, thus it is very likely that orientation ordering is easily lost if the particles are spherical.

The synthesis of magnetic iron oxide nanocrystals has long been of keen interest in magnetic data storage, biological application, drug delivery, and ferrofluids.³⁰–³³ Recent synthesis studies on magnetite nanocrystals have mainly focused on size control,³⁴–³⁷ while relatively few results on shape control have been reported.³⁸–⁴⁰ In this work, we present the synthesis of Fe₃O₄ nanocrystals with controllable size and a certain degree of shape control. Three typical shapes are reported, including truncated tetrahedral platelet (TTP), truncated octahedron (TO), and octahedron (OT). The Fe₃O₄ nanocrystals of different shapes are shape-selectively self-segregated from each other to form orientation-ordered superstructures through a self-assembly process. Fe₃O₄ nanocrystals in shapes of TTP, TO, and OT show hexagonal, primitive cubic-like, and distorted body-centered cubic (bcc) superlattice structures, respectively.

Experimental

Synthesis of Spherical Fe₃O₄ Nanocrystals as Seeds. The synthesis includes two steps: the spherical seed formation and seed-mediated growth. The reactions were taken place under N₂ protection. Ethanol, hexane, and acetone from Fisher Scientific, Inc. were used as received. Phenyl ether (99%), oleic acid (90%), oleylamine (tech. 70%), iron (III) acetylacetonate (Fe(III)(acac)₉) (97%), 1,2-hexadecandiol, and 1-octadecanol were purchased from Aldrich Chemical Co. and used without further treatment. In the seed-formation step, a mixture of 30 mL of phenyl ether, 2 mmol of Fe(III)(acac)₉, 10 mmol of 1,2-hexadecandiol, 3 mL of oleic acid, and 3 mL of oleylamine was quickly heated up to 260 °C, kept reflux for 30 min at that
Results and Discussion

The carrier solvent was hexane mixed with 0.2% (v/v) nanocrystal suspension on amorphous carbon-coated copper grids. The samples were prepared by dispersing a drop of suspension with various concentrations. A typical TEM image in Figure 1, which was produced by using a low-concentration (~0.1 mg/mL) suspension of faceted nanocrystals. The observed shapes of Fe₃O₄ nanocrystals are mainly TTP, TO, and OT. Although there is no uniform size across board due to the mixture nature of different shapes, the sizes of nanocrystals range from 12 to 14 nm and are approximately uniform for the nanocrystals with the same shape. The selected-area electron diffraction (SAED) pattern recorded from the region is inserted in Figure 1, which confirms the cubic spinel structure of the Fe₃O₄ nanocrystals. The ring features of the SAED pattern indicate the random orientations of these self-assembled nanocrystals.

With controlled evaporation of the carrier solvent from a hexane suspension of a higher nanocrystal concentration (~3 mg/mL), the resulted self-assembly of faceted nanocrystals possesses multilayer structures (Figures 2, 3, and 4). Significantly, the different shaped Fe₃O₄ nanocrystals have gone through a shape-selected self-separation process and have formed three distinct superstructures with highly crystallographic orientation-ordered textures. Each superlattice is a self-assembly of the same shaped Fe₃O₄ nanocrystals. Figure 2a is the superstructure that has been self-assembled by the TTP-shaped Fe₃O₄ nanocrystals. The inserted high-magnification image shows the building blocks taking the shape of TTP and having a uniform size distribution. The interesting result is that the SAED pattern from the self-assembled nanocrystals in Figure 2b shows the single-crystal type [111] zone-axis pattern, which clearly indicates the orientation ordering among the nanocrystals in the self-assembly. The high-resolution TEM (HRTEM) image of a single TTP nanocrystal is shown in Figure 2c. The clear lattice image indicates that the nanocrystal is well crystallized. The truncated tetrahedral shape can be easily distinguished from the dark-field image inserted in Figure 2d, which shows uniform contrast across its width, indicating uniform thickness. The model of a TTP nanocrystal is inserted between panels c and d of Figure 2: two {111} planes served as the top/bottom surfaces.

The shape control of these magnetite nanocrystals was achieved during the seed-mediated growth process by controlling the growth rate. Upon promoting a relatively faster growth rate, the discrepancy of surface energy on different facets starts to play a dominant role in shape evolution. The areas of the lowest energy surface tend to be maximized, resulting in the growth of the nanocrystals with polyhedral shapes. When a faster growth rate occurred at a relatively higher temperature, a more homogeneous growth on all crystallographic directions became favorable, which leads to the formation of spherical-like particles.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on nanocrystals of different sizes. The nanocrystals were heated with a rate of 2 °C/min in a nitrogen atmosphere. The DTA measurement was performed using a thermal analysis instrument. The TGA measurement was conducted using a thermogravimetric analyzer. The samples were heated from 30 to 800 °C, and the weight loss was recorded as a function of temperature. The weight loss curves showed a decrease in weight with increasing temperature. The weight loss was attributed to the loss of adsorbed water and other volatile compounds. The thermal stability of the nanocrystals was determined by the temperature at which the weight loss occurred. The results showed that the nanocrystals were thermally stable up to 500 °C. The thermal degradation occurred at a higher temperature than the nanocrystals with a lower size. The thermal stability of the nanocrystals was enhanced by the size of the nanocrystals. The larger nanocrystals showed a higher thermal stability than the smaller nanocrystals.

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Conclusion

The self-assembly of magnetite nanocrystals was performed by evaporating a carrier solvent of hexane from a nanocrystal suspension with various concentrations. A typical TEM image of a single nanocrystal is shown in Figure 1, which was produced by using a low-concentration (~0.1 mg/mL) suspension of faceted nanocrystals. The observed shapes of Fe₃O₄ nanocrystals are mainly TTP, TO, and OT. Although there is no uniform size across board due to the mixture nature of different shapes, the sizes of nanocrystals range from 12 to 14 nm and are approximately uniform for the nanocrystals with the same shape. The selected-area electron diffraction (SAED) pattern recorded from the region is inserted in Figure 1, which confirms the cubic spinel structure of the Fe₃O₄ nanocrystals. The ring features of the SAED pattern indicate the random orientations of these self-assembled nanocrystals.

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With controlled evaporation of the carrier solvent from a hexane suspension of a higher nanocrystal concentration (~3 mg/mL), the resulted self-assembly of faceted nanocrystals possesses multilayer structures (Figures 2, 3, and 4). Significantly, the different shaped Fe₃O₄ nanocrystals have gone through a shape-selected self-separation process and have formed three distinct superstructures with highly crystallographic orientation-ordered textures. Each superlattice is a self-assembly of the same shaped Fe₃O₄ nanocrystals. Figure 2a is the superstructure that has been self-assembled by the TTP-shaped Fe₃O₄ nanocrystals. The inserted high-magnification image shows the building blocks taking the shape of TTP and having a uniform size distribution. The interesting result is that the SAED pattern from the self-assembled nanocrystals in Figure 2b shows the single-crystal type [111] zone-axis pattern, which clearly indicates the orientation ordering among the nanocrystals in the self-assembly. The high-resolution TEM (HRTEM) image of a single TTP nanocrystal is shown in Figure 2c. The clear lattice image indicates that the nanocrystal is well crystallized. The truncated tetrahedral shape can be easily distinguished from the dark-field image inserted in Figure 2d, which shows uniform contrast across its width, indicating uniform thickness. The model of a TTP nanocrystal is inserted between panels c and d of Figure 2: two {111} planes served as the top/bottom surfaces.
and six intersected \{111\} and \{100\} planes composed the side surfaces. Using the model as a building block, the self-assembled superstructure is sketched in Figure 2d. The TTP nanocrystals in plane tend to pack as close as possible. While in the perpendicular direction, the second plane tends to overlap right on the bottom plane without translation. Consequently, the holes in the multilayer area are clearly visible, and a superlattice with a hexagonal columnar structure is formed.

The superstructure built from self-assembled Fe$_3$O$_4$ nanocrystals with a TO shape is shown in Figure 3a. A high-magnification image from the multilayer area is inserted in Figure 3a. The corresponding SAED pattern is displayed in Figure 3b. This self-assembly is also orientation-ordered along the crystallographic zone axis. The electron beam of the SAED pattern is parallel to the [001] direction. The HRTEM image of a single TO nanocrystal is shown in Figure 3c; the four edges correspond to \{220\} planes. A three-dimensional model and a two-dimensional projection of the TO Fe$_3$O$_4$ nanocrystals are illustrated in Figure 3d. The self-assembled superstructure built by the TO nanocrystals is sketched in Figure 3e. The second layer overlapped on the first layer without translation or twist, forming a simple cubic-like superstructure.

The image in Figure 4a displays the superstructure built up by the OT nanocrystals. From the inserted image, the overlap among the octahedral can be clearly observed. The SAED pattern in Figure 4b indicates that most of the building blocks take the same crystal orientation of [110]. The HRTEM image of a single nanocrystal in Figure 4c shows a well-faceted structure; the low contrast of the two horizontal corners is consistent with the projected thickness of the OT. The three-dimensional model is depicted in Figure 4d. Top-view and side-view illustrations of the self-assembled superstructure are sketched in Figure 4e,f, respectively. The self-assembly can be approximated to be a distorted bcc superstructure.

Clearly, the type of crystal structure of these observed superstructures and their specific crystallographic orientations depend upon the shapes of the Fe$_3$O$_4$ nanocrystal building blocks. Such results unambiguously demonstrate that the shape of nanocrystals plays a crucial role in self-assembly for determining both the crystal structure and the orientation of three-dimensional superstructures. There are two striking features in the formation of these superstructures. First, all self-assembled superstructures are the result of shape-selective self-segregation. Second, the contact in the packing sequence follows the face-to-face (facet-to-facet) mode between neighboring individual nanocrystals in all three types of superstructures. Certainly, it can be speculated that such oriented superstructure formation essentially originates from the energy balance between van der Waals attractive potential and repulsive potential among nanocrystals as well as between nanocrystals and the substrate. If considering nanocrystals with different shapes as “unlike molecules” and nanocrystals with the same type of shape as “like molecules”, the shape-selective self-segregation assembly of different shaped nanocrystals should be a spontaneous process, which follows the usual consequence of an effective attraction between like molecules in a multicomponent mixture, providing that the interactions are not dominated by Coulombic or H-bonding forces. In other words, such a shape-selective self-segregation process is the display in the nanomaterial regime
of the principle of the “like-dissolving-like” rule commonly encountered in molecular chemistry.

Furthermore, for faceted nanocrystals, theoretical studies have pointed out that the crystallographic orientation is mainly determined by the maximization of the van der Waals interactions between the facets of neighboring nanocrystals. The face-to-face stacking mode gives rise to stronger van der Waals interactions than those of either edge-to-edge or corner-to-corner packing. The energy of attractive van der Waals interactions for face-to-face stacking is inversely proportional to the square of the distance between two faces, whereas, for edge-to-edge stacking, such a van der Waals interaction energy is inversely proportional to the separation distance. Consequently, the face-to-face stacking sequence is favorable for maximizing the van der Waals attractive interactions among closely packed nanocrystals at shorter distances. The Fe₃O₄ nanocrystals in the studied size range are superparamagnetic and possess weak magnetic features. The possible magnetic interactions are considered to play negligible roles in these self-assembly processes.

Conclusions

Magnetite nanocrystals with TTP, TO, and OT shapes have been synthesized by a seed-mediated growth method. The growth temperature is the key factor in controlling the shape of the Fe₃O₄ nanocrystals. Highly oriented three-dimensional superstructures built from such faceted Fe₃O₄ nanocrystals have been determined to be hexagonal, primitive cubic-like, and distorted bcc. The crystallographic orientations of superstructures are strongly related to the shapes of Fe₃O₄ nanocrystals. The face-to-face stacking mode in these superstructures is considered to be the result of maximizing van der Waals interaction energy. Nanocrystals with different shapes provide diverse building blocks for bottom-up approaches in building nano- and meso-systems. Furthermore, the self-segregation phenomenon of different shaped nanocrystals in self-assembly processes could be very important in envisioning efficient assembly strategies for nanoscience- and nanotechnology-based devices.

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References and Notes