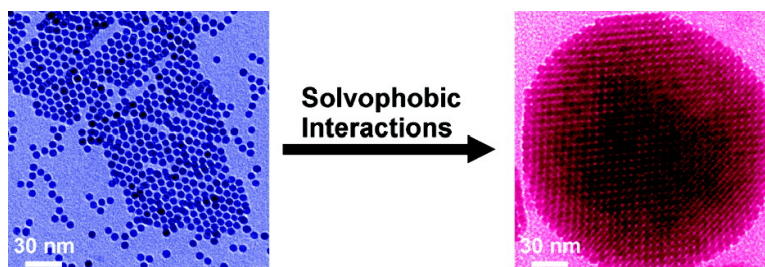


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Supercrystalline Colloidal Particles from Artificial Atoms

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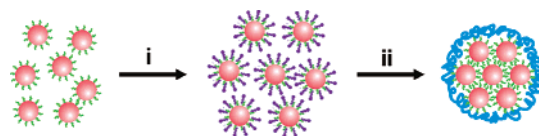
Because of their unique physical properties, nanoparticles are often described as “artificial atoms”.^{1,2} The ability to assemble these artificial atoms into desired and higher-ordered architectures (e.g., nanoparticle superlattices) may open a new way to fabricate functional materials of interest for applications such as biomedical diagnosis,^{3,4} catalysis,⁵ plasmonics,⁶ and high-density data storage.⁷ To date, methods have been developed for the preparation of nanoparticle thin films and colloidal crystals with a variety of superlattice structures,^{7,8} from which new collective properties have been discovered.⁹ However, a major challenge still remains, the inability to prepare nanoparticle superlattices with well-defined size and shape (i.e., supercrystalline collections of artificial atoms in the form of “superparticles”).

Previous approaches for controlling the size and shape of nanoparticle assemblies include spray drying,¹⁰ emulsion polymerization,¹¹ DNA-induced assembly,³ small-molecule or polymer mediator-induced assembly,¹² and Debye screening.¹³ However, nanoparticle assemblies made by these approaches either lack long-range ordering or have poor size or shape distributions.^{3,10–13} Herein, we report a new approach for using solvophobic interactions to control the formation of nanoparticle assemblies. On the basis of this approach, we have synthesized high-quality colloidal superparticles (SPs) from nonpolar-solvent-dispersible Fe₃O₄ nanoparticles. These colloidal SPs are spherical and have relatively narrow size distributions, and they also exhibit a nearly perfect superlattice structure with nanometer-scale lattice spacing. In addition, these SPs can be further assembled into close-packed solid structures, demonstrating their role as a new type of building block in nanoscience.

Our synthesis approach utilizes water-soluble Fe₃O₄ nanoparticle-micelles as precursors for the synthesis of supercrystalline colloidal SPs (Scheme 1). The formation of nanoparticle-micelles was driven by the hydrophobic van der Waals interactions between the hydrocarbon chain of the Fe₃O₄ nanoparticle ligands (i.e., oleic acid) and the hydrocarbon chain of the surfactant (i.e., dodecyltrimethylammonium bromide, DTAB).¹⁴ After the nanoparticle-micelles were introduced into an ethylene glycol solution, the van der Waals interactions between nanoparticle ligands and surfactants were weakened,^{15a} and then, nanoparticle-micelles decomposed due to the loss of DTAB molecules in the solution. As a result, a solvophobic interaction between nanoparticle ligands and ethylene glycol solution was induced,¹⁵ leading to nanoparticle aggregation and the formation of SPs (Scheme 1).

In a typical experiment, a chloroform solution of oleic-acid-functionalized Fe₃O₄ nanoparticles (5.8 ± 0.3 nm in diameter, 28 μM, 1.0 mL) was mixed with an aqueous DTAB solution (65 mM, 1.0 mL), and a clear nanoparticle-micelle aqueous solution was obtained by evaporating the chloroform. Under vigorous stirring, the nanoparticle-micelle solution was injected into a poly(vinyl pyrrolidone) (PVP, MW = 55000) ethylene glycol solution (2.0 mM, 5.0 mL), and the mixture solution was heated to 80 °C at 10 °C/min. The temperature was maintained for 6 h, and then, the

Scheme 1. The Synthesis of SP: (i) Nanoparticle-Micelle Formation and (ii) the Formation of SP



reaction solution was cooled to room temperature. Colloidal SPs were precipitated from the reaction solution by centrifugation, with a typical yield of about 70%.¹⁶

The resulting SPs are highly dispersible in polar solvents (e.g., ethanol and water) and form stable colloids. Transmission electron microscope (TEM) and scanning electron microscope (SEM) images show that the SPs are spheres with a diameter of 190 nm and a relative standard deviation of 15% (Figure 1a and b). The repulsive solvophobic interaction between ethylene glycol and Fe₃O₄ nanoparticles is likely the reason that the SPs adopted a spherical shape, in which they can have the minimum surface energy.^{15a} In addition, these colloidal particles can be easily assembled into multilayered, close-packed particle films (Figure 1c). Moreover, these SPs are superparamagnetic, and thus, they can be further assembled into parallel-line-like structures under an external magnetic field (Figure 1d).¹⁶ The spacing between the particle lines is due to repulsion between in-plane dipole moments induced by the external field.¹⁷

The supercrystalline structure of these SPs was further determined by TEM and selected-area small-angle electron diffraction (SAED) studies (Figure 2). TEM clearly shows that these particles exhibit on-axis superlattice fringe patterns that are related to a face-centered cubic (fcc) superlattice structure with a lattice constant of 11.7 ± 0.2 nm.¹⁶ The [001] image shows the perpendicular cross fringes projected from the {200}_{SL} and {220}_{SL} planes of the superlattice (Figure 2 a). The cross fringes in the [011] projection image exhibit an angle of 70.5° (Figure 2c), which is consistent with the theoretically expected value of 70.53° between the (1̄11)_{SL} and (1̄11)_{SL} planes.¹⁸ The [111] projection image shows the characteristic hexagonal cross fringes with an interdot spacing of 4.7 nm (Figure 2e), which is much smaller than the size of the artificial atoms (5.8 nm Fe₃O₄) but precisely related to the spacing of 4.1 nm between the {022}_{SL} planes in the superlattice.¹⁶

These TEM data indicate that the superlattice fringes are not direct images of the nanoparticle artificial atoms but just provide their superlattice spacing information.¹⁹ This fact suggests that the origin of these superlattice fringes is from electron-phase contrast due to the interference among the incident beam and small-angle diffraction beams through these supercrystalline SPs.¹⁹ Please note that the results herein have provided the first identification of superlattice fringes of nanoparticle superlattices, which is of fundamental importance to understand the three-dimensional (3D) structure of nanoparticle assemblies.

The interplanar spacing and angles obtained from the low-resolution TEM images are precisely consistent with the corresponding SAED patterns.¹⁶ These SAED patterns show sharp-spot

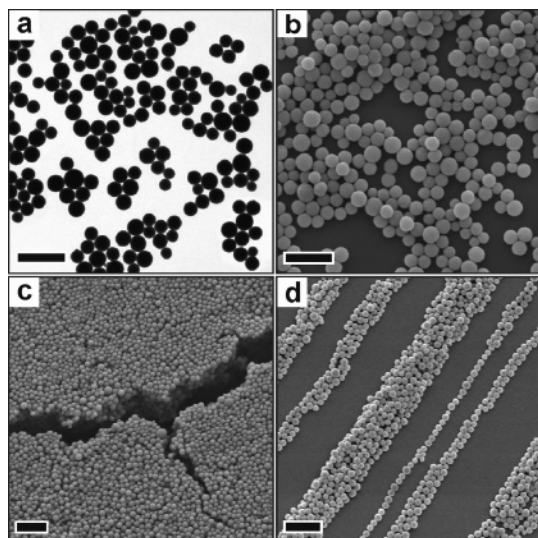


Figure 1. TEM image (a) and SEM image (b) of SPs with 190 nm diameters; SEM images of the multilayered assemblies of these SPs (c), and SP assembly under an external magnetic field (d). The scale bars: a, b, 500 nm; c, d, 1 μ m.

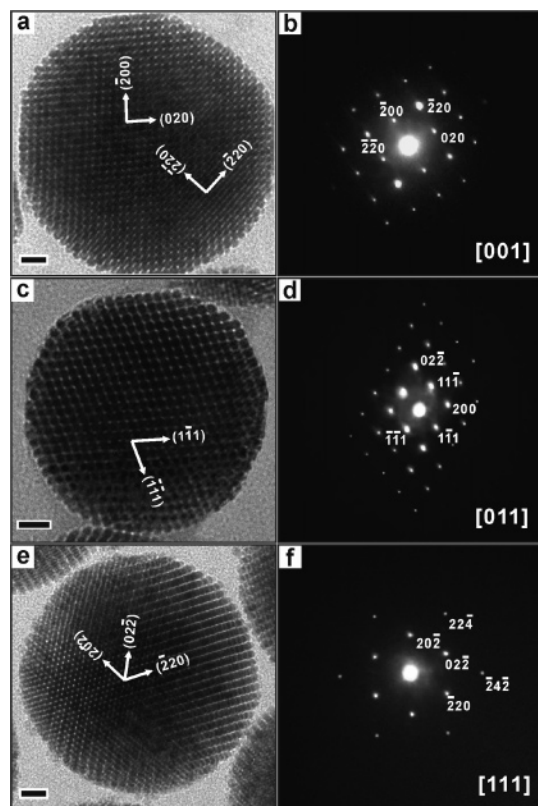


Figure 2. (a) TEM image of a SP viewed along the [001] zone axis and (b) the SAED pattern taken from this SP; (c) TEM image of a SP viewed along the [011] zone axis and (d) the SAED pattern taken from this SP; (e) TEM image of a SP viewed along the [111] zone axis and (f) the SAED pattern taken from this SP. The scale bars: a, c, e, 20 nm.

arrays (Figures 2 b, 2d and 2f), which are single-crystal-like ED patterns,¹⁹ demonstrating the 3D perfection of the superlattice.^{8b} Taken together, these results show that the colloidal SPs possess a “single-supercrystal” structure, where all of the 5.8 nm Fe_3O_4 nanoparticle artificial atoms occupy the lattice points in the fcc superlattice. More interestingly, similar to those single crystalline nanocrystals made of atoms,²⁰ these single supercrystalline SPs also

exhibit stacking faults. TEM studies indeed show that a few of these particles did have clear stacking faults along the (111)_{SL} planes of the fcc superlattice.¹⁶ However, selected-area, wide-angle electron diffraction studies of these SPs show the ring patterns of polycrystalline Fe_3O_4 , indicating that the SPs do not exhibit a long-range atomic order.¹⁶

In conclusion, we have demonstrated the first evidence that one can use solvophobic interactions to make supercrystalline colloidal SPs from nonpolar-solvent-dispersible nanoparticle artificial atoms. These SPs exhibit superlattice fringes under a low-resolution TEM, providing an interesting analogue to the lattice fringes of colloidal nanocrystals under a high-resolution TEM. Second, because of their excellent stability in polar solvents, these colloidal SPs can be further assembled into more complex and hierarchically ordered materials in which new properties may occur. Third, the synthesis approach could be readily generalized for making supercrystalline colloidal SPs from nonpolar-solvent-dispersible nanoparticles with other sizes and chemical compositions such as metals, metal oxides, and semiconductors. Finally, if one builds upon the analogy between a nanoparticle and an artificial atom, these supercrystalline SPs are the equivalent of well-defined “nanoclusters” of artificial atoms.

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Supporting Information Available: Detailed synthetic procedure, SAED patterns, SEM, and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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