Communication

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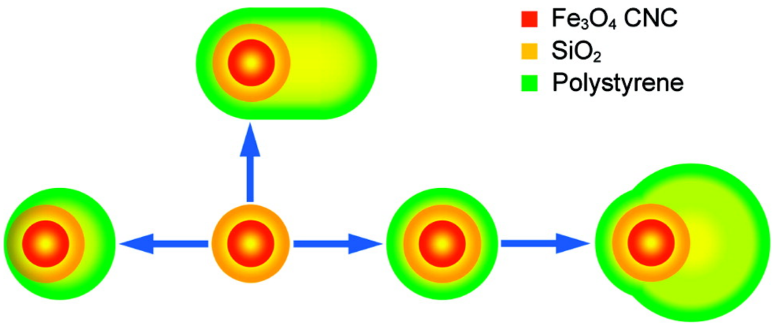

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Superparamagnetic Composite Colloids with Anisotropic Structures

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The success of “bottom up” approaches to building functional devices and materials often hinges on the availability of suitable building blocks.[1−3] Much effort has therefore focused on the preparation of monodisperse colloidal particles with complex structures, with compositional/morphological control being achieved through various means such as colloidal chemistry, mechanical stretching, swelling and phase separation, and space-confined assembly.[4] In typical syntheses, the particles produced show little deviation from isotropy in terms of composition and surface properties. The creation of monodisperse colloids with strongly anisotropic surface properties, chemical compositions, and physical properties will greatly increase the possibilities for fine-tuning interparticle interactions and eventually the structure and functionality of particle ensembles.[5]

In this paper, we report a unified set of emulsion polymerization processes for the synthesis of a series of spherical and nonspherical magnetite−polystyrene (Fe_3O_4−PS) composite colloids with the superparamagnetic cores concentrically or eccentrically positioned inside polystyrene shells (Figure 1). The uniform size, anisotropic structure/shape, and the potential for magnetic control suggest these colloids for a range of applications, for example, as active components in sensors and actuators, microelectromechanical systems, and photonic devices.[6] In particular, these particles are ideal candidates for constructing three-dimensional colloidal photonic crystals with complete and magnetically tunable bandgaps.[7]

The magnetic cores of our structures are Fe_3O_4 colloidal nanocrystal clusters (CNCs) that can be synthesized with tunable sizes from ∼30 to ∼180 nm using a high-temperature hydrolysis process.[8] Since each of them is composed of many small primary nanocrystals, the CNCs retain superparamagnetic behavior at room temperature while possessing higher saturation magnetization than individual nanodots. After coating a transition layer of silica through a modified Stöber process,[9] the particle surfaces were further functionalized with a monolayer of coupling agent [3-(methacryloyloxy)propyl]trimethoxysilane (MPS) through the siloxane linkage.[10] Each MPS molecule contains a C═C double bond which copolymerizes with monomers upon initiation, promoting the polymer growth on the particle surface.

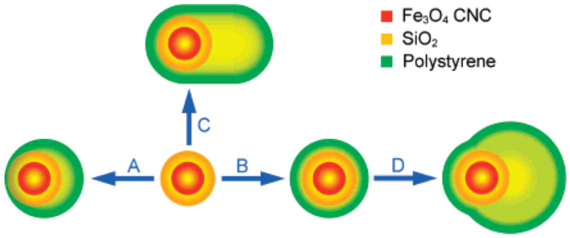

Figure 1. Synthesis scheme for $Fe_3O_4@SiO_2@PS$ composite colloids through seeded emulsion polymerization. The morphologies of the final products are controlled by (A) interfacial tension, (B) crosslinking, and (C) single and (D) separated steps of swelling and phase separation.

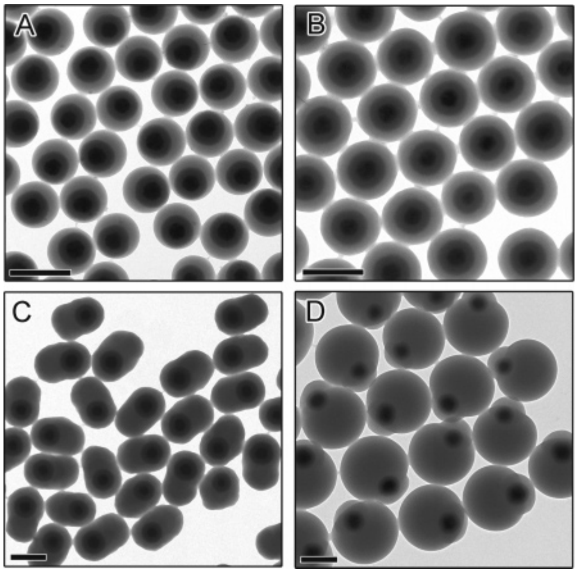

Figure 2. TEM images of a series of $Fe_3O_4@SiO_2@PS$ composite colloids with complex structures/shapes produced by emulsion polymerization of styrene using MPS grafted Fe_3O_4/SiO_2 particles as seeds: (A, B) Spherical colloids produced in one-step emulsion polymerization (A) without and (B) with DVB as crosslinker; (C) Ellipsoids formed by swelling and phase separation in one-step emulsion polymerization; (D) Doublets produced by separated steps of swelling and phase separation. All scale bars are 400 nm.

Monodisperse $Fe_3O_4@SiO_2@PS$ core−shell spherical colloids were produced through one-step emulsion polymerization of styrene using MPS grafted $Fe_3O_4@SiO_2$ as seeds and sodium dodecyl sulfate as a surfactant. Figure 2A shows a typical TEM image of the resulting colloids with clearly distinguishable three-layer structures including a Fe_3O_4 core, a silica layer, and a polystyrene shell. Interestingly, each $Fe_3O_4@SiO_2$ core is eccentrically positioned inside the polystyrene sphere. The formation of such eccentric structure is due to the interfacial tension between the hydrophilic seed particle and the hydrophobic monomer.[11] At the initial stage of polymerization, a thin layer of polystyrene shell is deposited in the form of small particles on the silica surface through copolymerization with the surface double bonds. After absorbing hydrophobic monomers, the polystyrene shell tends to contract and reduce the surface area as a result of interfacial tension, leading to asymmetric distribution of polymer around the seeds. Modification with MPS provides the silica surfaces considerable compatibility with the swollen polymer shell so that the final products still maintain an overall spherical shape with the major part of the inorganic core engulfed in the polymer phase.[11]

Besides the interfacial tension, the degree of contraction also depends on the viscosity of the monomer-swollen shell polymers.[11] The viscosity of linear polymer is relatively low so that its contraction leads to the eccentric location of core particles after the completion of polymerization. A high viscosity of the monomer-swollen shell, achieved by introducing a crosslinker-divinylbenzene (DVB) during the polymerization, limits the degree of contraction

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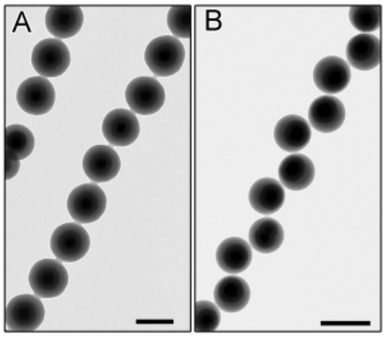

Figure 3. TEM images of self-assembled chainlike structures of (A) concentric and (B) eccentric spherical colloids under an external magnetic field. Both scale bars are 400 nm.

and leads to the formation of a concentric core−shell structure of Fe_3O_4@SiO_2@PS (Figure 2B).

The spherical symmetry of the external interface can be broken as a result of phase separation when the monomer concentration is increased, forming ellipsoidal colloids with the magnetic core eccentrically located at one end. Figure 2C shows a TEM image of uniform ellipsoids synthesized using 50% more monomers than the case in Figure 2B. Considerable effects of swelling and phase separation are responsible for the ellipsoidal shape of the colloids. At the early stage of polymerization, the particles have the spherical and concentric morphology similar to that in Figure 2B. As the thickness of shell polymer increases, more excessive styrene monomers are absorbed in the crosslinked polymer networks. In the final stage, the elastic stress driven by the entropy change of the swollen networks causes phase separation of the monomer from the network and eventually forms additional bulges attached to the original particles. When the starting monomer concentration is low, phase separation is negligible so that the final products have a spherical shape. Further increasing the concentration of monomers induces phase separation and forms ellipsoidal particles.

The swelling and phase separation processes can be further performed in two separated steps to produce nonspherical colloids with more peculiar morphologies.[5,12] In the first step, Fe_3O_4@SiO_2 particles were coated with a concentric shell of crosslinked polystyrene using a process similar to that in Figure 2B. Additional monomers were added to the system at room temperature to swell the shell polymer network. The solution containing the swollen particles and excessive monomers was then heated to initiate the polymerization of the monomers absorbed in the polymer network. Phase separation occurs at the elevated temperature so that most of the monomers form a new bulb that is attached to the original colloid. As shown in Figure 2D, the final particles are doublets consisting of two bulbs: one bulb contains most of the original particle including the Fe_3O_4@SiO_2 particle and the other mostly contains the newly polymerized material. The relative size of the two parts of the doublets can be tuned by changing the monomer/polymer swelling ratio, the degree of crosslinking of the original colloids, and the polymerization temperature.[12] When swelling is performed prior to polymerization at room temperature, a high monomer/polymer swelling ratio can be achieved, making it possible to form doublets with significantly asymmetric structures (Figure 2D). In this case, the participation of excessive monomers in the second-step polymerization also contributes to the final structure of the products.[11b]

The combination of anisotropic shape/structure and magnetic properties make these composite colloids new types of building blocks for constructing secondary structures with interesting and possibly tunable configurations. As a simple demonstration, we show in Figure 3 that the composite spheres with concentric and eccentric superparamagnetic cores display distinct assembly behaviors when they are subjected to an external magnetic field: the concentric composite particles form simple linear chains which are expected for building blocks with simple isotropic configurations, while more complicated zigzag chains have been observed when the eccentric composite particles were assembled under similar conditions. The zigzag configuration is the direct result of the eccentric structure of the composite particles: the strong magnetic dipole interactions pull the magnetic cores in the neighboring colloids to the closest positions.

In summary, we have demonstrated the synthesis of a family of composite colloids with superparamagnetic cores concentrically or eccentrically located in the polystyrene shells. The uniform size, complex shapes and structures, and superparamagnetic properties make these colloidal particles ideal building blocks for the fabrication of novel functional devices and materials.

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Supporting Information Available: Experimental procedures, magnetic property measurements, TEM images of Fe_3O_4 CNCs, Fe_3O_4@SiO_2 particles, and additional ellipsoids and doublets. This material is available free of charge via the Internet at http://pubs.acs.org.

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