Assembly of Centimeter Long Silica Coated FePt Colloid Crystals with Tailored Interstices by Magnetic Crystallization

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Recent development in controlling chemistry on a nanometer-scale (nanochemistry) has enabled the preparation of high-quality nanocrystals in solution with controlled size and shape.[1,2] The self-assembly of these nanocrystals into large colloid crystals in such a way that manipulation of the secondary structures of nanocrystals can be carried out in order to harness the size-dependent properties of individual nanocrystals while providing the possibility of tuning collective properties due to interactions between the subunits is an exciting new direction.[3] As a result, progress has been made to fabricate nanoparticles as three-dimensional (3D) regular structures, as these crystals have potential uses in optical filters, switches, sensors, and waveguides.[4] Several techniques have been developed for creating such materials, including colloidal self-assembly, 3D holography using laser beams and photolithography,[5] and so forth. However, there is very little work that has been devoted to exploiting magnetic nanoparticle assemblies as 3D porous crystals, which could be useful for molecular separation based on the magnetic chromatography concept.[6] Magnetic nanoparticles have been used as nanovehicles in separation.[7–9] The anticipated assembled porous superparamagnetic colloidal crystals could provide even stronger, more controllable local magnetic field of the colloids which, when combined with the flow characteristics over the tailored molecular porosity, would allow the species of interest to have strong interactions (under external magnetic flux) leading to their more controlled elution in magnetic separation. Thus, new superparamagnetic porous colloid crystals are required for the separation of chemical or biochemical species (no coercivity upon removal of external magnetic field). Nevertheless, there remained several challenges that limited its first development until this present work. First, typical procedures used for synthesis of nanoparticle entities generally use organic ligands that make the resulting colloid crystals hydrophobic. This is problematic for the application of valuable, mostly water-soluble paramagnetic biological species such as proteins and antibodies. Also, the organic ligands as spacer groups may not be able to provide sufficiently large and rigid interstices in the resulting colloid crystals for chemical/biological species of interests to percolate. Second, colloidal crystallization is expected to be difficult and challenging as only colloids with size distributions less than 5% can form three-dimensional (3D) periodic colloidal crystals. There exists a limited set of materials such as silica, zirconia, and some polymer colloids which can be routinely prepared with size distributions narrow enough for forming monolithic high-quality colloidal crystals.[10] Unfortunately, these colloids do not exhibit the required magnetic properties.

Here, we demonstrate a bottom-up approach for the *first* synthesis of centimeter long magnetic colloidal crystals, which have adjustable internal interstices for potential use in magnetic gradient separation of chemical or biochemical entities. The large colloidal crystals are composed of three-dimensional regular arrays of superparamagnetic FePt nanoparticle encapsulated in a protective hydrophilic silica shell with controllable thickness.

Primary silica encapsulated iron–platinum nanoparticle was synthesized based on our previous procedures, the encapsulated FePt was in chemically disordered face centered cubic (fcc) structure which shows superparamagnetic properties before heat treatment.[11] Particle size distribution was evaluated via the TEM imaging of the sample. The result indicated that a majority of the particles was in the range of 31–35 nm, but there were particles in smaller and larger dimensions (Supporting Information). Such size range did not allow self-assembling of the particles into colloid crystals. In view of this, a new magnetic induced crystallization technique was attempted. This was similar to the recent report by Gu et al. who demonstrated the concept of controlled aggegation of magnetic nanoparticles by exposing to varied

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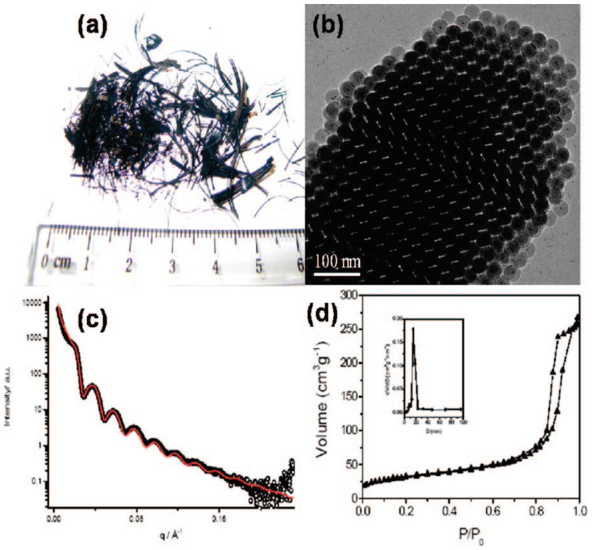

Figure 1. (a) Acicular, centimeter-sized core−shell colloidal crystals of 3 nm FePt core in 33 nm silica sphere. (b) TEM image showing a hcp arrangement of the encapsulated nanoparticles inside the crystal. (c) Small angle X-ray scattering (SAXS) data (black line) which were modeled (red line) with a best fit of a hcp crystal composed of monodisperse ellipsoids of $a = 2 \times 165$ Å, $b = 2 \times 165$ Å, $c = 2 \times 0.8 \times 165$ Å. (d) BET data showing a large surface area of the crystals and a pore size ∼15 nm (inset) which matches with the expected dimension of the windows accessing to octahedral pores in the 33 nm hcp colloids.

magnetic field.[12] First, the powder sample was washed four times in pure ethanol to remove impurities. It was then placed in an ultrasonic bath for 1 h with 100 mL of ethanol in a 150 mL beaker at 55 °C for controlled crystallization. This time, crystallization parameters were carefully tuned including a slow but gradual evaporation of the solvent with an external magnetic field (field direction pointing downward) applied underneath the beaker (a permanent magnet of ∼6000 G). No further heat treatment was carried out. A scheme in the Supporting Information illustrates the growth of the three-dimensional arrays of SiO_2-encapsulated FePt nanoparticles as supercrystals.

As seen from Figure 1, needle-shape crystals were collected via the controlled crystallization technique with the influence of external magnetic field, many of them reached centimeter in length (Figure 1a). The high resolution TEM confirmed (Figure 1b) the three-dimensional stacking of nanoparticles into crystals. It is interesting to find from the figure that the size distribution of individual assembled core−shell magnetic FePt (3 nm in diameter) in silica (33 nm in diameter) nanoparticles within a selected colloidal crystal is much smaller than 5%. This clearly implies that the controlled crystallization aided by the use of magnetic flux is a size selective process which collects the magnetic particles of same dimension for crystallization. The stacking of the nanoparticles appears to be in the form of hexagonal close packing (hcp) with occasional stacking fault lines (mismatches) clearly visible from the TEM image. The corresponding electron diffraction pattern results also suggested self-assembling of monodispersed core−shell magnetic nanoparticles into the macroscopic hcp colloidal crystals (Supporting Information). Small angle X-ray scattering (SAXS) experiments were carried out on beamline ID02 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A wavelength λ of 1 Å was used together with a CCD camera to collect data. The sample−detector distance was fixed to 2 m. The SAXS data were corrected to allow for sample transmission, background scattering, and detector response. The corrected data was then normalized to absolute units. The data from the two-dimensional area detector were finally converted to one-dimensional form using different integration masks. The obtained intensity $I(q)$ ($q = 4\pi(\sin\theta/\lambda)$, where 2θ is the scattering angle) was then plotted as a function of q (Figure 1c). The best fitting obtained to the SAXS data in Figure 1c corresponds to a 3D structure representing a hcp crystal order, such that the structural objects are monodisperse ellipsoids with full-length axis $a = b = 33$ nm, $c = 26.4$ nm, and anisometry $\nu = 33/26.4 = 1.3$ (the deviation from spherical shape was probably due to a slight deformation of soft particles along the stacking c-axis, as evidenced by the TEM image, see Supporting Information). Similar observation was also made in the SAXS study of monodisperse 6.2 nm spherical CdSe colloid crystals which actually gave an ellipsoidal packing with $\nu = 1.2$.[13] The primary dimension for the individual nanoparticles confirmed by TEM and SAXS (∼33 nm in diameter) is rather large, and thus one would expect that a large interstitial spacing exists within this macroscopic crystal. It is indeed shown in the BET/pore size measurement data (Figure 1d) which clearly suggests a high surface area (110.6 $m^2\ g^{-1}$) and porous nature of this material (a sharp pore size of 15 nm which appears to be comparable with theoretical pore dimensions).

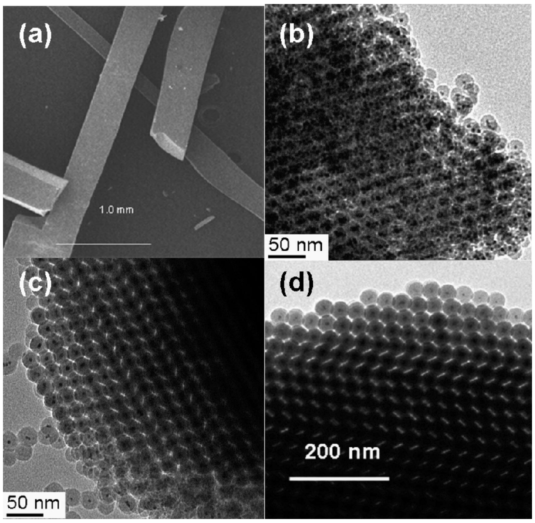

Figure 2. (a) Image captured by environmental scanning electron microscopy (ESEM) showing the morphology of self-assembled, three-dimensional colloidal crystals of SiO_2 encapsulated FePt (SiO_2@FePt) nanoparticles with sharp crystal edges. (b−d): TEM images showing hcp arrangement of silica encapsulated FePt nanoparticles of different silica thicknesses, 20 (gelation time = 18 h), 26 (40 h), 33 nm (48 h), respectively (hence different sizes of interstices).

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SEM (Figure 2a) also indicated a good crystallinity of the material (sharp edges), which was revealed at a higher magnification by TEM to be composed of stacking of nanoparticles (Figure 2b). It was evident that the thickness of the silica shell can be altered by changing the gelation time. As a result, engineering the porosity of these colloid crystals is made possible (Figure 2b). As stated, it is rather challenging to assemble nanoparticles into large, high quality colloid crystals unless the individual particles share almost identical size, shape, and surface features. Undoubtedly, our colloid crystal products consist of monodisperse silica encapsulated FePt particles arranged in a hcp structure with well-defined interstitial sites. It is thus believed that fabricating encapsulated particles as colloid crystals would be easier than those of bare particles since the silica encapsulation may reduce irregularities (faceted) of the core, hence, facilitating their arrangement into regular 3D assemblies. Vibration saturation magnetization curves of the core−shell magnetic nanoparticles before (powder) and after being aligned (3-D crystal) were compared. The results clearly indicate that the magnetically aligned supercrystals display much higher superparamagnetic magnetic response than corresponding particles without the prealignment (see Supporting Information).

To summarize, we show that the ability to assemble silica coated magnetic nanoparticles into high quality colloid crystals from the bottom-up construction approach through magnetic crystallization which could enable exploitation of the exciting idea of magnetic molecular differentiation within the single crystal. This approach could open up a new avenue for preparing new porous magnetic crystals with high surface area for potential separation of chemicals or biochemicals of a wide range of interests.

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Supporting Information Available: Detailed procedures for the sample preparation, characterization, and magnetic crystallization are included (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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