Self-Assembly of Co Nanoplatelets into Spheres: Synthesis and Characterization

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Uniform Co spherical assemblies were prepared via a facile hydrothermal reduction approach in the presence of surfactants with a yield of 98%. The assembled nanostructures were composed of ordered nanoplatelets with a thickness of ∼20 nm, as characterized by scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), and high-resolution TEM (HRTEM). This material exhibits ferromagnetic characteristics and has a high surface area, showing potential applications for catalysts and other related nanodevices.

Magnetic nanoscale materials have become the focus of intensive research owing to their potential applications in high-density data storage, medical diagnosis, and bioseparation.[1−3] Several methods are available for the production of magnetic nanocrystals: (1) physical routes[4] that produce essentially thin layers, (2) template methods[5] that involve the growth of nanorods or nanowires by different approaches within the channels of inorganic or track-etched organic matrixes, and (3) chemical methods[6,7] that evolve the synthesis in a solution of naonparticles. In most cases, the magnetic nanocrystals are superparamagnetic at room temperature because of their small dimensions and, thus, are not usable for many applications, such as magnetic recording. One way to increase the magnetic anisotropy of the particles is to modify their shape. This was addressed by Alivisatos's group, who synthesized cobalt nanorods.[8] However, they are thermodynamically unstable and rearrange into spherical particles. On the other hand, Chaudret and co-workers employed the decomposition of $Co_2(CO)_8$ in the presence of surfactants to produce Co nanorods.[9] Another possible way to improve the magnetic anisotropy is to assemble nanocrystals into mutlidimensional morphologies.[9,10] Mesoscale assembly of one or multidimensional building components to form ordered structures is of great interest in the area of material synthesis and device fabrication.[11−18] In addition to one-dimensional (1D) or two-dimensional (2D) assembled structures,[11] some efforts have been focused on fabricating curved structures such as spherical, tubular, and hollow structures.[11−18] These ordered nanospheres are expected to have potential applications in catalysts, drug carriers, and magnetic recording due to their dimensions and high surface areas.[11−19] The ability to synthesize uniform nanospheres with diameters ranging from nano- to microscale sizes is desirable. Generally, routes toward these ordered structures include two accesses. One is the use of various template precursors, such as droplets, silica, and block copolymers.[20−22] These methods usually require the removal of the template after the synthesis by separated techniques,

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such as acid or base etching and calcinations. Another is the control of some factors to organize the components into various curved shell structures.[23,24] For example, rodlike building blocks consisting of gold and polymer blocks domains were assembled into single-layer superstructures, including bundles, tubes, and sheets via the strong interactions between the organic polymer ends of the different rods.[25]

Co nanosized materials have extensive applications in data storage and catalysis. Several Co nanocrystals with different morphologies have been synthesized, such as monodisperse particles,[26] nanorods,[8,27] nanodisc/nanoplatelets,[28] and 2D supperlattices.[10] However, to our best knowledge, the mesoscale self-assembly of Co nanoplatelets into spheres has not been reported yet. Here we present one scheme for the fabrication of curved structures composed of nanoplatelets in a one-pot process, which is primarily based on the geometric constraints of building blocks,[24] different from either surfactants[18,19] or soft templates.[21]

Assembly and synthesis of Co nanoplatelets were performed by a one-step approach. In a typical procedure, an aqueous solution of 100 mL was first prepared by dissolving $CoCl_2 \cdot 6H_2O$ (50 mM), sodium tartrate ($Na_2C_4H_4O_6$, 0.75 M), NaOH (5 M), and sodium dodecyl benzenesulfonate (SDBS) (15 mM) in distilled water. After adding $NaH_2PO_2 \cdot H_2O$ (0.4 M), the solution was vigorously stirred and then transferred into a Teflon cup in a stainless steel-lined autoclave. The autoclave was maintained at 110 °C for 24 h and then was allowed to cool to room temperature. A black fluffy solid product was deposited on the bottom of the Teflon cup, indicating the formation of metallic Co. The final product was centrifuged, rinsed with distilled water and ethanol several times to remove any alkaline salt and surfactants that remained in the final products, and then dried in a vacuum oven at 60 °C for 4 h. The structural information on the samples was collected by powder X-ray diffraction (XRD) method. Diffraction patterns of intensity versus 2θ were recorded with a Rigaku D/Max-2000 diffractometer equipped with a Cu Kα radiation source ($\lambda = 0.154\,18$ nm) from 20° to 80° with a scanning rate of 0.2°/min. Morphologies of the samples were studied by scanning electron microscopy (SEM) (JEOL SM-6700F). Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were obtained with a HITACHI HF-2000 electron microscope. The Brunauer−Emmett−Teller (BET) surface area was obtained by N_2 adsorption/desorption isotherm data. Magnetic studies were conducted on self-assembled Co spheres by using a superconducting quantum interference device (SQUID) magnetometer.

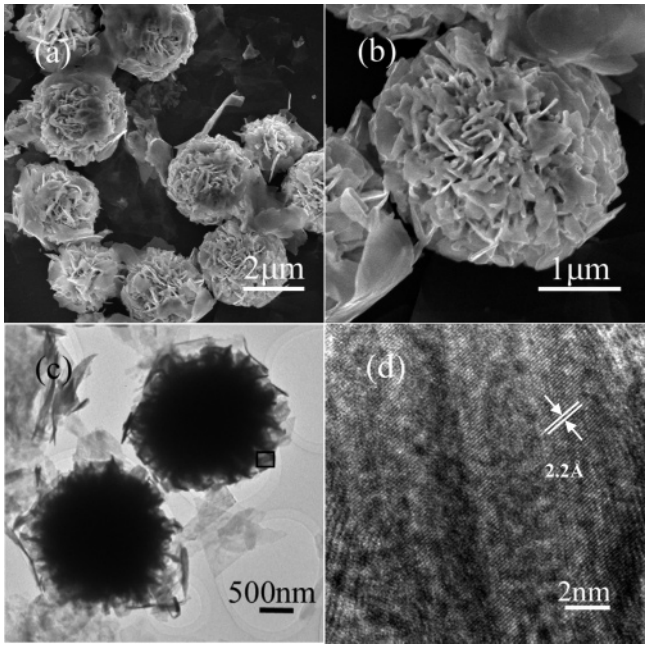

Figure 1. SEM images at a survey (a) and higher magnification (b) and TEM images at low resolution (c) and high resolution (d) of the Co spheres assembled with nanoplatelets.

From Figure 1a, one can see that the averaged diameter of spheres is about 2.8 μm, showing a relatively narrow size distribution (Supporting Information SI-1). Note that the yield of the assembled spheres is as high as 98% and remainder are cracked parts of the spheres. The enlarged image of an individual sphere is presented in Figure 1b, which indicates that the spheres are assembled by nanoplatelets with a thickness of ~20 nm. The TEM image in Figure 1c shows that spheres have solid structures with a diameter of ~2.5 μm, consistent with the size observed by SEM. The HRTEM image (Figure 1d) of the selected area in Figure 1c shows a crystalline character with a lattice spacing of 2.2 Å, which can be indexed to the (100) plane of hexagonal close-packed (hcp) Co.

The crystal structure of the product was further confirmed by X-ray diffraction (XRD). As shown in Figure 2, the recorded diffraction peaks are well-assigned to the structure of Co with hexagonal phase, indicating the formation of *hcp* Co metals (space group *P*63/*mmc*; $a = 2.5031$ Å, $c = 4.0605$ Å; JCPDS No. 5-727). Broadening of the peaks exhibited the nanocrystalline nature of the sample. No CoO peak was observed, showing the high stability of the Co nanoplatelets coated with PVP.

To investigate the influence of the surfactant, SDBS was substituted with dodecyl benzenesulfonate (DBS) and cetyltrimethylammonium bromide (CTAB). These substitutions resulted in the formation of larger Co particles without nanoplatelet components. It suggests that the use of SDBS is a prerequisite to form the assembled spheres with

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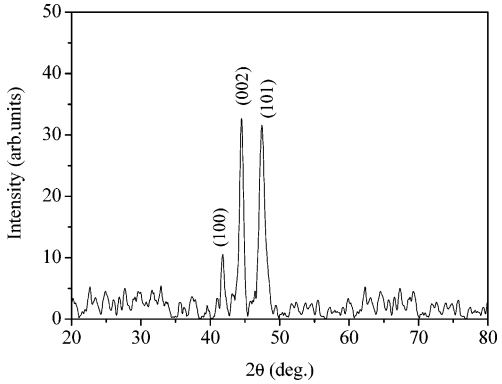

Figure 2. X-ray diffraction (XRD) pattern of the as-synthesized Co spheres assembled with nanoplatelets.

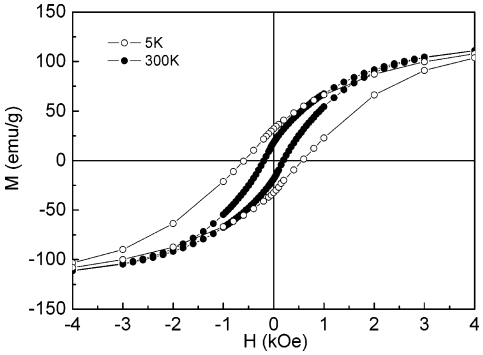

Figure 3. Hysteresis loops of the as-synthesized Co spheres assembled with nanoplatelets, measured at 5 and 300 K.

nanoplatelets. We also tested other synthetic parameters. The polyol environment does not favor the formation of platelet-assembled structures but prefers 1D structures. For example, by introducing glycerol into the present system, with the water-to-polyol ratio of 1:1 (volume), the nanorods were obtained as dominant products. However, the temperature rise does not show any additional effect on the morphology of the final products. As the product is expected to have a high surface area, we performed BET measurements. The adsorption/desorption isotherm of Co nanoplatelet spheres (Supporting Information SI-2) exhibits a characteristic behavior of plate materials such as clays,[19b] similar to γ-MnO_2. The BET surface area calculated from N_2 adsorption isotherm is about 52 m^2/g, which is a little bit smaller than the calculated one (70.8 m^2/g) for an ideal Co nanosheet with a thickness of 20 nm. This result, combined with the TEM images, suggests that each Co sphere has a core−shell structure with diverging nanoplatelets.

No evidence for obvious crack or destruction was observed, even under harsh ultrasonic dispersion, indicating a high stability of the product. We also investigated the effect of the annealing process at 300, 450, and 550 °C for 20 min under an atmospheric pressure of Ar. The Co spheres are stable up to 400 °C, as confirmed by SEM and BET. Above 400 °C, nanoplatelets are sintered into solid structures, and thin plates had changed thick and round with an increase of the annealing temperature (Supporting Information SI-3). The morphology evolution of the Co spheres indicates that the assembled nanostructures, with a high surface area, are so stable that they would have a potential application as a catalyst.

The synthesis of free-standing Co nanoplatelets has been investigated,[28] but the mechanism involved for the formation of the assembled spherical structures is still unknown. One theory suggests that when the particles are formed, the interfacial tension and the hydrophilic surfaces of Co play an important role in driving the nanoscale hexagonal flakes of Co to form spherical structures.[19b] On the basis of the proposed mechanism for the growth of 1D nanostructures under the confinement of capping reagent,[6] we herein propose that one possible function of SDBS is to kinetically control the growth rates of different faces of a Co nanocrytal through the interaction in the adsorption and desorption processes. Subsequently, the nanoplatelets assemble into spherical architectures based on their geometric structures.[23,25]

As well-known, the physical and chemical properties of nanoscale materials strongly depend on the size, size distribution, defect structures, and dimensions. The magnetic properties were investigated by the magnetization dependence of applied fields at 5 and 300 K, as shown in Figure 3. The coercivity of the sample is 590 Oe at 5 K, which is comparable with that of monodisperse hcp Co nanoclusters with a diameter of 11 nm.[26] Considering their size difference, the present product has a relatively small coercivity, even though it consists of hcp Co nanoplatelets having a high shape anisotropy. This might be partly due to the multi-domain structure and partly due to surface oxidation. The hysteresis loop at 300 K shows that the sample has a ferromagnetic character, even at room temperature.

In summary, a facile route to produce Co spheres composed of nanoplatelets is reported. The ordered spheres exhibit a high surface area and ferromagnetic character. The material can be expected to have promising applications for catalysts and other related nanodevices. Further studies will show that the synthetic route is not limited to assembled Co spheres but can be extended to various types of metal nanoparticles as well.

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Supporting Information Available: SI-1, the size distribution of the sample; SI-2, N_2 adsorption/desorption isotherms of the as-synthesized Co spheres composed of nanoplatelets; SI-3, the morphology evolution (SEM images) of Co spheres assembled with nanoplatelets, performed at different sintering process of (a) as-synthesized and annealing at (b) 300 °C, (c) 450 °C, and (d) 550 °C for 20 min. This material is available free of charge via the Internet at http://pubs.acs.org.

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