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Shape-controlled synthesis and self-assembly of hexagonal cobalt ultrathin nanoflakes

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ABSTRACT

Hexagonal cobalt microspheres composed of ultrathin nanoflakes were obtained via a hydrothermal reduction route by using the metal complex cobalt bis (4-pyridine carboxylate) tetrahydrate as a precursor of cobalt. The diameter of these spheres is about 2 μm. The thickness of the cobalt nanoflakes is about 10 nm along the easy magnetization axis [0 0 1], which is approximate to the critical size (12 nm) for single-domain behavior in Co. The hysteresis loop of the sample shows an interesting soft magnetic behavior with low coercivity (24.5 Oe). It is noticed that the coercivity is much lower than that of the hcp cobalt nanoflakes reported previously. The peculiar magnetic properties may result from both the anisotropy and the self-assembly manner of the nanoflakes.

1. Introduction

Anisotropic hexagonal Co nanocrystals have been paid much attention for their high saturation magnetization and magnetic coercivity [1–2]. It is found that magnetic properties of nanomaterials depend significantly on the size and morphology of materials. For instance, the spherical cobalt nanoparticles with diameters smaller than the critical size (12 nm) of single magnetic domain are usually superparamagnetic at room temperature [3], which makes these particles impractical for many applications [4]. There are two feasible ways to increase the magnetic anisotropy to overcome the problem. One is modifying the shape of the nanoparticles [5–9], and the other is assembling nanocrystals into multidimensional morphologies [10–13]. Single-crystalline hexagonal close-packed (hcp) cobalt nanoflakes with thickness of ~8 nm show a ferromagnetic behavior and an obvious magnetic anisotropy, though the thickness of the nanoflakes is smaller than that of the single magnetic domain. The coercivity values of these nanoflakes are unequal with each other when the external magnetic field is applied parallel ($H_{||}$) and perpendicular ($H_{\perp}$) to the flakes. The $H_{||}$ and $H_{\perp}$ values are 218 Oe and 176 Oe at 300 K, respectively. And the $H_{||}$ value is 772 Oe at 3 K. The predominantly exposed planes of these flakes are (0 0 1) [9]. The coercivity (Hc) value of the hexagonal cobalt spheres consisting of nanoplatelets is 590 Oe at 5 K. And the thickness of these nanoplatelets which growth orientation is [0 0 1] is about 20 nm [10]. In addition, the flowery assembly of hcp-cobalt flakelets shows the Hc value of 308 Oe at room temperature, while the Hc value is 946 Oe at a low temperature of 2 K. The flakelets are about 50–100 nm thick and their top/bottom faces are (0 0 1) [11]. Based on the Hc values at low temperatures, the coercivity of the assembly is reduced when the [0 0 1] thickness decreases. The [0 0 1] direction is the easy magnetization axis of hexagonal cobalt phase [14]. It is proposed that the thickness along the easy magnetization axis is an important factor influencing the magnetic properties of these nanostructures. This paper aims to prepare hexagonal cobalt ultrathin nanoflakes and understand the effect of self-assembly of hexagonal cobalt nanoflakes on the magnetic properties. The metal organic complex cobalt bis (4-pyridine carboxylate) tetrahydrate ($CoL_2(H_2O)_4$) was selected as a precursor to prepare hcp cobalt ultrathin nanoflakes. The $CoL_2(H_2O)_4$ molecule has a special spatial structure [15] which may control the thickness of the nanoflakes.

2. Experimental

All chemicals were of analytical grade and used without further purification. In the first step, the metal organic complex $CoL_2(H_2O)_4$ was synthesized by a hydrothermal method according to the literature [15]. In a typical synthesis of microspheres, 0.03 g of $CoL_2(H_2O)_4$ was dispersed in 20 mL 85 wt% hydrazine hydrate ($N_2H_4{\cdot}H_2O$). A stable orange solution was formed after vigorous magnetic stirring for 30 min. Then 10 mL NaOH aqueous solution (10 mol L^{-1}) was added dropwise with constant stirring and the solution turned blue. The final mixture was transferred into a 60 mL Teflon-lined stainless steel autoclave, which was closed tight and maintained at 160 °C for 36 h. After the autoclave cooled to room temperature, the black powder settled at the bottom of the autoclave and was collected by a mag-

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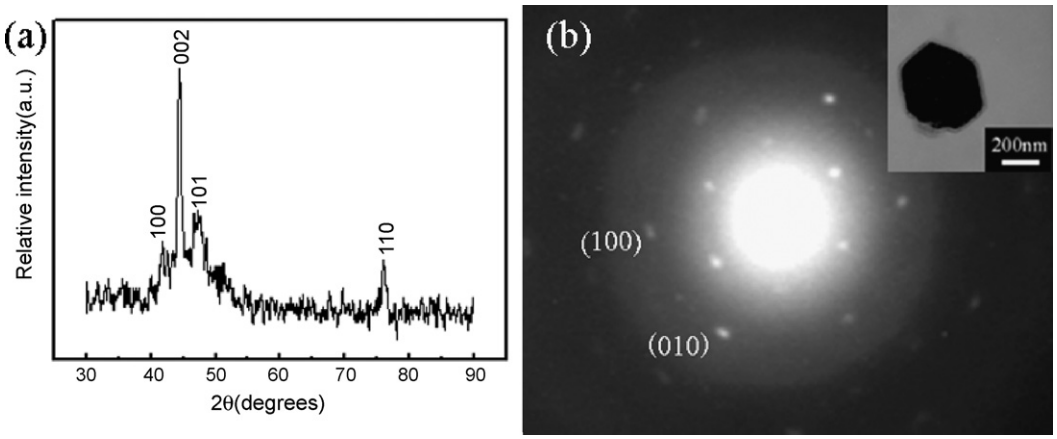

Fig. 1. (a) XRD pattern of as-prepared sample; (b) SAED pattern of an isolated nanoflake.

net. Then the solid product was rinsed with distilled water and absolute ethanol several times respectively and finally dried in air at room temperature.

3. Characterization

The X-ray diffraction data of as-obtained products were collected by a Rigaku (Japan) D/max-γA X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). The SEM images were taken by a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). The selected area electron diffraction (SAED) pattern was obtained with a Hitachi H-800 electron microscope and high-resolution transmission electron microscope (HRTEM) images were recorded with a JEOL-2010 transmission electron microscope. A superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL-7) was used to measure the magnetic properties of as-prepared samples.

4. Results and discussion

The chemical composition and the phase of as-obtained product were determined by X-ray diffraction. The XRD pattern of a representative sample is presented in Fig. 1a. It can be identified as hexagonal cobalt, in which no other phases can be detected

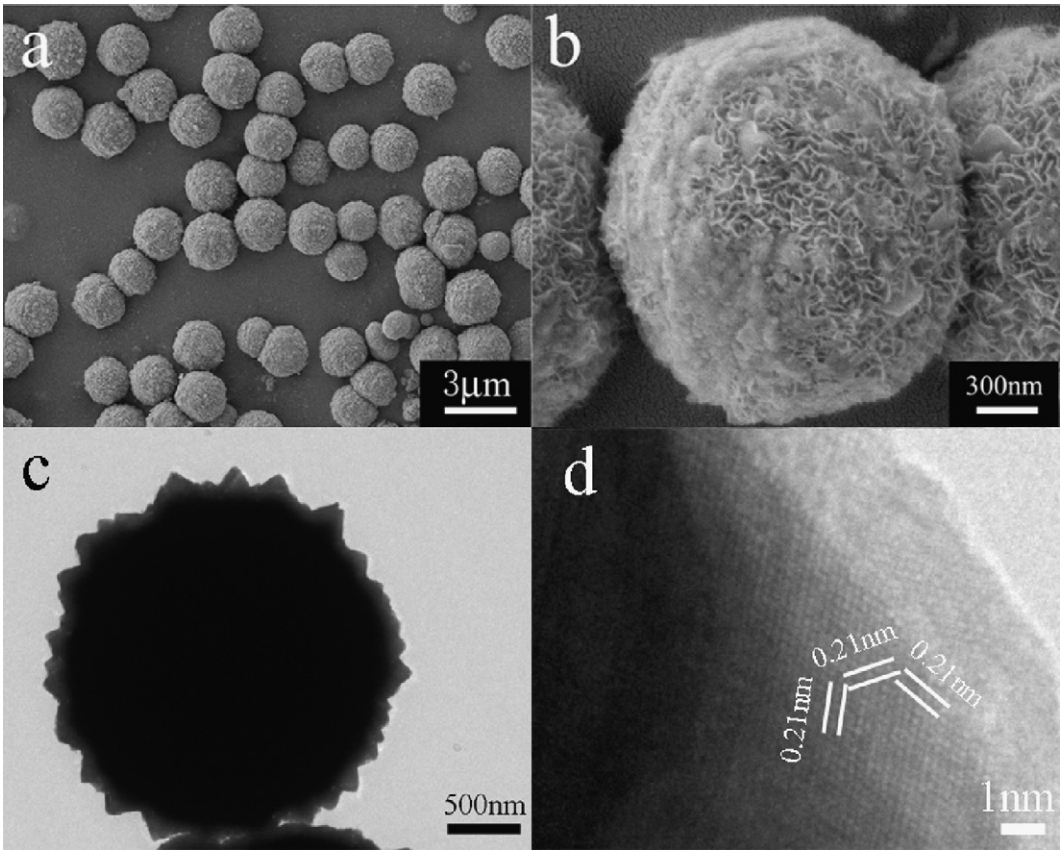

Fig. 2. SEM images at low magnification (a) and high magnification (b) and TEM images at low resolution (c) and high resolution (d) of the microspheres composed of nanoflakes.