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Preparation of large Co nanosheets with enhanced coercivity by a magnetic-field-assisted solvothermal approach free of surfactants, complexants or templates

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ABSTRACT

We presented a magnetic-field-assisted solvothermal route to prepare hexagonal close-packed (hcp) large Co nanosheets free of any surfactants, complexants or templates. Scanning electron microscope (SEM) images showed that the typical size and thickness of the Co nanosheets were several microns and ca. 50 nm, respectively. Magnetic measurement indicated the coercivity of the sample reached 317.3 Oe, which was much higher than those of bulk Co metal and previously reported Co nanoplatelets. It was found that the solvents played a crucial role in determining the morphology and the crystal structures of the Co products, and the introduction of ethanol conduced to the formation of pure hcp phase Co microcrystal. The external magnetic field was also found to be indispensable for the formation of sheet-shaped morphology.

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1. Introduction

Cobalt nanomaterials have received much attention owing to their size-dependent magnetic, electronic and catalytic properties, which are of interest for the fundamental scientific research and potential technological applications in, for example, high-density information storage, magnetic sensors, etc [1-3]. Recently, controlling the morphology of magnetic nanomaterials has become a research hotspot in view of the fact that the electronic, optical, catalytic and magnetic properties of the magnetic metals depend considerably on their shapes and the textures. It has been demonstrated that many properties of the shape-anisotropic magnetic materials with unusual and novel forms significantly differ from those of the spherical counterparts. For instance, the plate-like magnetic particles have a higher permeability and a good microwave absorption property in microwave frequency range owing to their large shape anisotropy [4]. Compared with spherical Co nanoparticles, the Co nanomaterials with special shapes often show enhanced coercivity [5,6], which is highly desirable for some applications, such as high-density magnetic recording media and permanent magnets. Up to now, a number of differently shaped Co nanocrystals and their assembly structures have been synthesized by wet chemical methods, such as Co nanorods [7], Co nanowires [8], Co nanobelts [9], Co nanoplatelets [10], Co nanobowls [11], Co nanotubes [12] and Co nanoflowers[13,14]. Obviously, the synthesis of most of these microstructures is highly related to the surfactants, complexants or templates, which play a key role in controlling the morphology of the products. However, the post-treatment of the templates is complex and the presence of organic molecules on the surface of the magnetic nanomaterials has detrimental effect on the magnetic properties, which may result in difficulties for their potential application as nanodevices [6,14,15]. Despite significant progress in the shape-controlled synthesis of metallic microstructures, it is still a challenge to synthesize shape-anisotropic Co nanomaterials without the assistance of surfactants, complexants or templates. Therefore, it is highly desirable to develop new methods to prepare the Co nanomaterials with controlled morphology without using the above-mentioned additives.

On the other hand, several groups have reported that the existence of a magnetic field could significantly influence the movement of magnetic nuclei/nanoparticles in solution during the reaction, which could grow and assemble into one-dimensional nano- or micron-sized wires/rods under an external magnetic field [16–18]. So far, there has been no report on the synthesis of multi-dimensional magnetic microcrystals under external magnetic fields yet. It is still an open question whether these magnetic nuclei or nanoparticles would inevitably

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self-assemble into one-dimensional wires or rods under an external magnetic field and whether some multi-dimensional magnetic microstructures could be obtained under an external magnetic field.

In this work, micron-sized cobalt sheets with thickness of ca. 50 nm were synthesized successfully with the assistance of an external magnetic field by solvothermal method, in which no surfactants, complexants or templates were used. Additionally, our experiment results demonstrated that besides one-dimensional Co wires/rods, multi-dimensional Co microcrystals with special morphology could also be obtained under an external magnetic field.

2. Experimental section

All reagents were of analytic grade and double-distilled water was used throughout the experiment. In a typical synthetic procedure, 6 mmol CoCl₂ · 6H₂O was dissolved in 48 mL H₂O, followed by dropping 10 mL NaOH solution (15 M) to the CoCl₂ solution under intense stirring. Then, 16 mL hydrazine hydrate solution (50%) and 75 mL ethanol were dropped in sequence to the above suspension. The volume ratio of water to ethanol in the resulting suspension with total volume of ca. 150 mL was 1:1, and the final concentrations of CoCl₂, NaOH and hydrazine hydrate were 0.04, 1 and 1 M, respectively. Afterwards, the suspension was transferred into a Teflon-lined stainless-steel autoclave that was placed in a magnetic field with the magnetic field strength of 0.1 T at the center of the Teflon vessel. The magnetic field was provided by two pieces of magnets, one was put under the bottom of the autoclave and the other was put on the top of the autoclave. Finally, the autoclave, together with the two magnets, was kept in an air oven at 160 °C for 10 h. The reaction we employed could be formulated as follows:

$$\mathrm{Co}^{2+} + 2\mathrm{OH}^{-} \to \mathrm{Co}(\mathrm{OH})_2 \tag{1}$$

$$2Co(OH)_2 + N_2H_4 \rightarrow 2Co + N_2 + 4H_2O$$
 (2)

After the reaction, the solid was collected and washed with double-distilled water and acetone, and then dried in a vacuum oven at $60 \,^{\circ}$ C for 12 h.

X-ray diffraction (XRD) patterns were recorded using a Shimadzu XD-3A X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). The morphology and elements of the sample were studied using a LEO 1530 VP field emission scanning electron microscope (FE-SEM) with an X-ray energy-dispersive spectroscopy (EDS). The *M*/*H* hysteresis loop was recorded with a Quantum Design MPMS XL-7 superconducting quantum interference device magnetometer (SQUID).

3. Results and discussion

The XRD pattern of Co sample (Fig. 1a) showed five peaks at $2\theta = 41.4^{\circ}$, 44.2° , 47.2° , 62.3° and 75.6° , which were assigned to the diffractions from the (100), (002), (101), (102) and (110) planes of hexagonal close-packed (hcp) Co (space group: P63/ mmc1(194); JCPDS: 05–0727, a = 2.503 Å, c = 4.060 Å), respectively. No diffraction peaks of impurities, such as CoO and Co(OH)₂, were observed in the XRD pattern. EDS pattern of the Co sample (Fig. 1b) indicated that the product was essentially pure metallic Co. A small amount of oxygen (0.47 wt%) was also detected, which may result from the slight surface oxidation of the Co sample. Fig. 1c was the low-magnification SEM image of cobalt sample, revealing that a large amount of micron-scale cobalt thin sheets could be obtained by this approach. Fig. 1d showed that the surface of the Co thin sheets was relatively smooth, and the inset in Fig. 1d indicated that the quite uniform thickness of the Co sheets was around ca. 50 nm.

In addition, it should be noted that this reaction was carried out under the external magnetic field, implying the Co nuclei would not necessarily grow into one-dimensional nano- or micron-sized wires/rods under an external magnetic field.

We found that the solvents played an important role in determining the morphology and crystal structures of the Co products in the present study, and the introduction of ethanol to



Fig. 1. XRD (a), EDS (b), patterns and SEM images (c) and (d) of the Co nanosheets.



Fig. 2. SEM images of Co samples prepared using different solvents: water (a) and (b), water/ethylene glycol (c) and water/glycerol mixture (d).

the reaction system was crucial for the formation of Co nanosheets. For comparison, the SEM images of the Co products prepared using water, water/ethylene glycol (1:1 in volume ratio) and water/glycerol (1:1 in volume ratio) mixture as solvents are shown in Fig. 2. When water acted as solvent, the product was three-dimensional flower-like Co microcrystals composed of Co nanorods radiating from the center. This result confirmed that it was not necessarily the case that the Co nuclei would selfassemble to wires/rods under an external magnetic field during reaction. When water/ethylene glycol was substituted for water/ ethanol as solvent, Co rods with the diameter of 5-10 µm were obtained. While, when water/glycerol was used as solvent, onedimensional Co chains, which consisted of many Co spheres with the diameter of $2-3 \,\mu\text{m}$, were produced. Compared with the XRD pattern of Co nanosheets (Fig. 1a), XRD patterns (Fig. 3) of Co samples prepared using water, water/ethylene glycol and water/ glycerol mixture as solvent showed an additional peak at 51.3°, which could be attributed to the diffraction from the (200) plane of face-centered cubic (fcc) Co, suggesting these Co samples were present as both the hcp and fcc phase [19].

It has been reported that the morphology and crystal structures of metallic nanomaterials prepared by solution-chemistry reduction route were highly related to the solvents used in the synthesis [19-21]. On the one hand, the solvents could affect the reduction rates of metal salts, thus influenced their morphology of final products [19,20]. In our previous work, it was found that the reduction rate of Co salt by N₂H₄ varied with the solvents and the introduction of ethanol could remarkably facilitate the reduction of Co salt [20]. It was possible that a relatively high reduction rate conduced to the formation of Co nanosheets in the present study. On the other hand, the viscosity of the solvents, which would determine the diffusion rate of the generated metal nuclei, would also be an important factor affecting the morphology and crystalline nature of the products. In the water/ethanol mixture, ethanol could provide a good environment for the diffusion of nuclei, which was favorable for the anisotropic growth Co nanocrystals [19]. While in the water/ethylene glycol and water/glycerol mixture, the relative high viscosity of solvents would restrain the diffusion of nuclei and thus resulted in the formation of spherical particles [19]. In these cases, when the



Fig. 3. XRD patterns of Co samples prepared using different solvents: water (a), water/ethylene glycol (b) and water/glycerol mixture (c).

magnetic field was presented, the spherical particles tend to align along the magnetic line of force and favor the formation of Co wires or rods.

In addition, we found that the external magnetic field was indispensable for the formation of Co nanosheets. For comparison, we conducted a contrast experiment in which the external magnetic field was removed while other experimental conditions were kept unchanged. Fig. 4a shows the low-magnification SEM image of the corresponding product, indicating the leaf-like structure of the Co sample with the thickness of ca. 300 nm and the size of $3-4\,\mu$ m. High-magnification SEM (Fig. 4b) showed that each leaf-like Co microcrystal was composed of a long central backbone and plenteous of secondary branches, which were parallel to each other and emerged at the same angle (ca. 60°) with respect to the central backbone. It was interesting that even without the assistance of external magnetic field the Co nuclei could grow into leaf-like Co microcrystals, which was quite



Fig. 4. SEM images with different magnifications of Co sample prepared in the absence of the external magnetic field.



Fig. 5. Magnetic hysteresis loop of the Co nanosheets measured at 300 K.

different from previous report that only aggregated Co particles were obtained when the external magnetic field was removed [17]. This suggests that there may be some other factors, such as solvents as mentioned above, controlling the shape-anisotropic growth of Co nanocrystals.

Without the assistance of the magnetic field, the Co nuclei grew into leaf-like Co microcrystals, which could be described with the diffusion-limited aggregation (DLA) model [22]. While when the magnetic field was available, the growth of the Co nuclei was not only controlled by DLA model, but also affected by the external magnetic field force. By comparing Fig. 1c and d with Fig. 4a, it was clear that the Co nanosheets prepared under the magnetic field were larger and thinner than the leaf-like Co microcrystals obtained without the magnetic field. This implied when the magnetic field was presented, the Co nanosheets tend to grow at the directions along the sheet planes. It was possible that the newly generated Co nuclei during the reaction were prone to move to the rim of the existent Co nanosheets under the magnetic field and then added themselves to the Co nanosheets, thus resulted in forming large Co nanosheets. The exact role of the external magnetic field in our synthetic route is interesting but is not well understood yet and further study is still necessary.

The *M*/*H* hysteresis loop (Fig. 5) of powdered Co nanosheets measured at room temperature showed a ferromagnetic behavior. Note that the coercivity (H_c) of the large Co nanosheets was 317.3 Oe, showing enhanced coercivity compared to the value of bulk Co (ca. tens of oersteds at room temperature [23]). The coercivity was also higher than those of the previously reported Co nanoplatelets with diameter of 120 nm and thickness of 10 nm

(109 Oe [24]), and Co nanoplatelets with diameter of 100 nm and thickness of 8 nm (218 Oe and 176 Oe in the parallel and perpendicular directions, respectively [10]). Considering the fact that the as-prepared large Co nanosheets were randomly oriented in the sample, H_c could be increased if all nanosheets could be arrayed in the same direction [10]. It is well acknowledged that the behavior of the magnetization of magnetic materials is highly dependent on the types of anisotropy, the most common of which are crystalline and shape anisotropy. The crystal anisotropic constants of hcp phase and fcc phase Co were 4.5×10^6 erg/cm³ [25] and $2.7 \times 10^6 \text{ erg/cm}^3$ [26], respectively. Thus, for Co, crystallizing as hcp phase would show higher coercivity owing to its relatively large crystal anisotropy constant. Furthermore, a nonspherical polycrystalline specimen can possess shape anisotropy and a small departure from sphericity in shape would result in significant increase in coercivity [5]. So, the high coercivity of the synthesized Co nanosheets could be attributed to the anisotropic shape of Co nanosheets and the hcp crystal structure with high crystallinity.

4. Conclusions

Large hcp phase Co nanosheets with the thickness of 50 nm were synthesized by a solvothermal route under an external magnetic field without the assistance of any surfactants, complexing agents or templates. The solvents played a crucial role in determining the morphology and the crystal structures of the Co products. Additionally, the external magnetic field was indispensable for the formation of Co nanosheets. Magnetic measurement of the Co nanosheets at room temperature indicated the coercivity of the sample came up to 317.3 Oe, which was much higher than those of bulk Co metal and previously reported Co nanoplatelet. Our experimental results implied that it was not necessarily the case that the Co nuclei would self-assemble into one-dimensional cluster under an external magnetic field during reaction. Furthermore, multi-dimensional Co microstructures could also be obtained under an external magnetic field. More importantly, this facile magnetic-field-assisted solution-phase route may provide a new method to prepare some anisotropic magnetic nanocrystals with unusual and novel morphology.

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