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Synthesis of Co submicrospheres self-assembled by Co nanosheets via a complexant-assisted hydrothermal approach

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ABSTRACT

Co submicrospheres with the typical diameter of ca. 500 nm, and possessing beautiful morphologies composed of dense Co nanosheets ca. 10 nm thick, were synthesized by a facile and low-cost complexant-assisted hydrothermal approach. Magnetic measurement at room temperature indicated the coercivity of the submicrospheres reached 268 Oe, which was much higher than that of bulk Co and of some microstructure cobalt materials reported previously. Hexagonal close-packed (hcp) and face-centered cubic (fcc) cobalt phases in the materials were identified by X-ray diffractometer (XRD). It was revealed that the addition of the complexant sodium tartrate played a crucial role in the formation of the hierarchical architectures of the Co submicrospheres. We believe that the high coercivity of the synthesized submicrospheres may result from their special nano-micro structure, and we suggest that this low-cost and facile synthesis approach can be used for large-scale production of Co magnetic materials with special structures and morphologies, as well as excellent magnetic properties.

1. Introduction

Magnetic nanostructures represent a particularly interesting class of materials for both fundamental scientific research and potential technological applications [1–3]. In recent years, controlling the morphologies and structures of magnetic nanomaterials has become the focus of intensive research, because the electronic, optical, catalytic, and magnetic properties of magnetic materials depend considerably on their size, shapes, and dimensionality [4–7]. As some of the most important magnetic materials, Co nanostructures have been of particular interest for their high saturation magnetization and magnetic coercivity, as well as their excellent catalytic properties [8–10]. In the past few years, much attention in this area has been paid to assembling low-dimensional Co nanostructures into three dimensional (3D) complex architectures, as a possible way to improve the magnetic anisotropy of the materials. To date, a number of 3D Co hierarchical architectures composed of nanosized subunits have been successfully fabricated by various methods [11–23]. Recently, Zhang et al. reported the synthesis of Co chains self-assembled by Co submicrospheres with the assistance of PVP in ethylene glycol solution [15]. Liu et al. demonstrated the fabrication of hierarchical Co nanoflowers composed of nanorods, through a solvothermal synthesis in polyol using Ru as the heterogeneous nucleation agent and hexadecylamine as the structure-directing agent [18]. Yang et al. prepared hexagonal Co microspheres composed of nanoflakes via a two-step process, in which cobalt bis (4-pyridine carboxylate) tetrahydrate was used as precursor of Co [19]. Obviously, noble metals, a considerable amount of surfactants, or some uncommonly used reagents are indispensable in most of these approaches, which makes the synthetic process less attractive because large-scale production of these microstructures will be costly.

In this study, we report the synthesis of Co submicrospheres with a typical diameter of ca. 500 nm, composed of Co nanosheets ca. 10 nm thick. The method was facile and low-cost, employing the complexant sodium tartrate (ST) to assist in the formation of hierarchical architectures. The prepared Co submicrospheres were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), and superconducting quantum interference device (SQUID) magnetometry. The effects of the complexant on the morphology of the final products, and the role of ST in the synthesis process, were also investigated.

2. Experimental section

All reagents were of analytic grade and double-distilled water was used throughout the experiment. In a typical synthetic

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process, 6 mmol $CoCl_2 \cdot 6H_2O$ and 12 mmol ST were dissolved in 102 mL H_2O, followed by dropping 30 mL NaOH solution (5 M) and 16 mL hydrazine hydrate solution (50%) into the above solution under intense stirring. The total volume of the solution was ca. 150 mL and the final concentrations of $CoCl_2$, ST, NaOH, and hydrazine hydrate were 0.04, 0.08, 1, and 1 M, respectively. Afterwards, the solution was transferred into a Teflon-lined stainless steel autoclave, which was kept in an air oven at 393 K for 8 h. After the reaction, the solid precipitate in the bottom of Teflon cup was collected and washed with double-distilled water and acetone, then dried in a vacuum oven at 333 K for 12 h.

X-ray diffraction patterns were recorded using a Shimadzu XD-3A X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology and elements of the sample were studied using a Hitachi 4800 field emission scanning electron microscope (FE-SEM) equipped with X-ray energy-dispersive spectroscopy. The M/H hysteresis loop was recorded with a Quantum Design MPMS XL-7 superconducting quantum interference device magnetometer.

3. Results and discussion

The morphology and sizes of the samples were examined by FE-SEM. Fig. 1a, shows a low-magnification SEM image of the synthesized materials, in which the spherical particles can be clearly observed. It is important and interesting that the spherical particles are neither dense nor simply porous, but have a beautiful morphology and plentiful hierarchical architectures, as shown in Fig. 1b; the particles resemble peony flowers, and are composed of compact Co nanosheets ca. 10 nm thick.

The XRD pattern of the Co microspheres in Fig. 1c shows five peaks at $2\theta = 41.6^\circ$, 44.3°, 47.4°, 51.5°, and 75.9°, suggesting the coexistence of hexagonal close-packed (hcp) and face-centered cubic (fcc) phases of Co in the samples [24]. The hcp and fcc phases of Co are close in energy because they differ only in the stacking sequence of the atomic planes in the cubic (111) direction; mixtures of these two phases have often been observed in samples prepared by wet-chemical methods [25,26]. The EDS pattern in Fig. 1d indicates that the sample is essentially pure Co. A small amount of oxygen (1.2 wt%) was also detected, which may

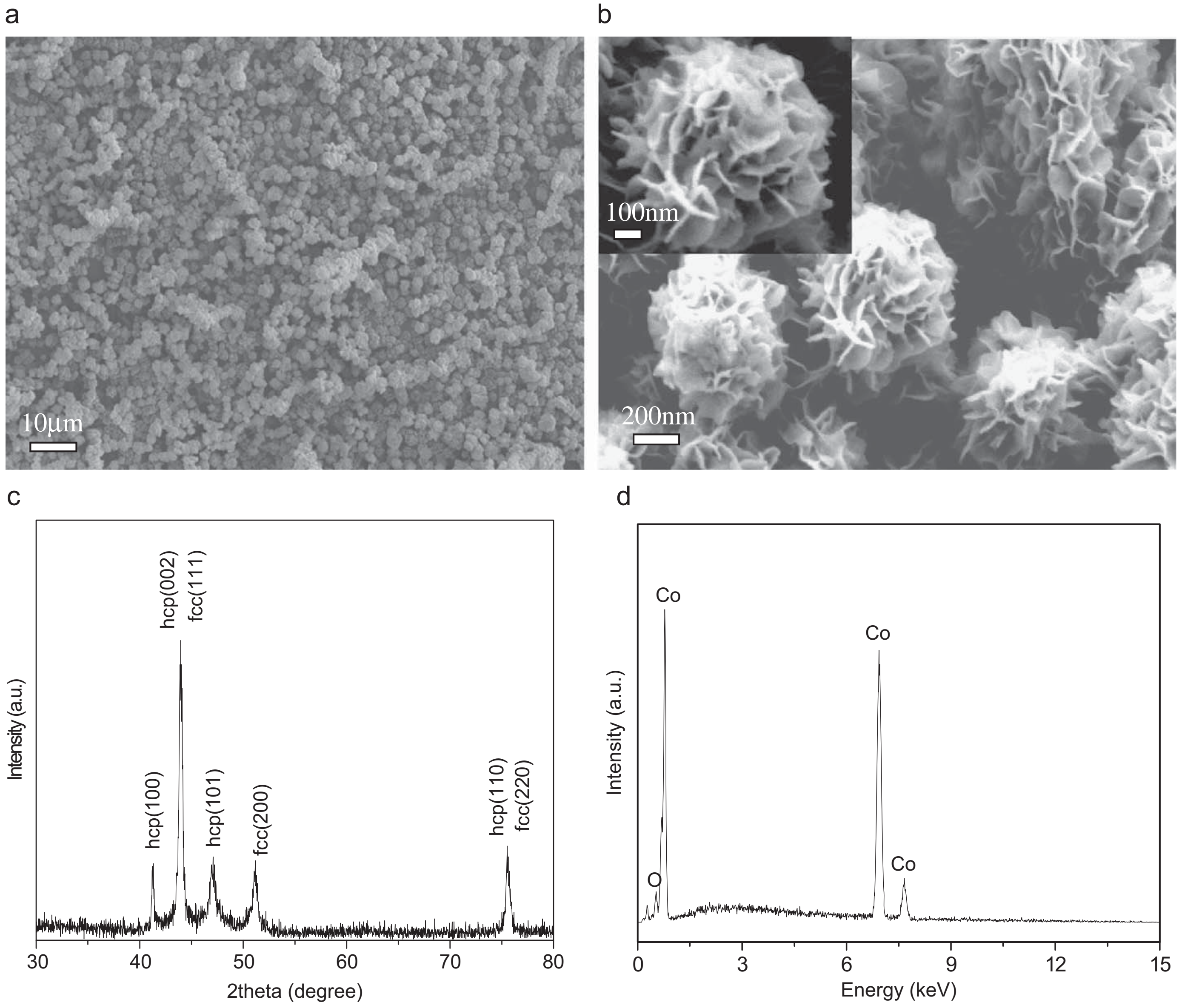

Fig. 1. SEM images (a), (b), XRD and EDS patterns (c), (d) of the Co sample.