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Size-controlled synthesis, growth mechanism and magnetic properties of cobalt microspheres

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ABSTRACT

Monodispersed cobalt microspheres with remarkably uniform morphology and tunable size have been successfully synthesized via a facile and effective solvothermal route. It is found that sodium hydroxide has a great influence on the size and shape of the resulting cobalt powders. Through adjusting the molar ratio of NaOH to Co^{2+}, the size of cobalt microspheres can be precisely manipulated. In addition, the magnetic properties of the as-synthesized samples demonstrate that cobalt microspheres exhibit ferromagnetic property related to their sizes. More importantly, this study not only provides a facile and effective strategy to prepare the cobalt microspheres with tunable sizes, but also gives a reference for the synthesis of other magnetic functional materials.

1. Introduction

During the past decades, magnetic functional materials have attracted tremendous interest owing to their potential applications in the fields of magnetic sensors, catalysis, bioimaging and high-density data storage [1–4]. As one of the most significant magnetic materials, cobalt (Co) nano-/micro-particles have become a research focus in the field of materials science because of their high saturation magnetization and magnetic coercivity [5–7]. Till now, much effort has been devoted to the controllable synthesis of cobalt particles, because the magnetic properties are strongly dependent on the particle sizes, shapes and dimensionality. But owing to the complexity of crystalline structures and chemical compositions of magnetic materials, it is still a challenging and urgent task for synthetic chemists to simultaneously control over the size, morphology and monodispersity of cobalt particles. To address this problem, a deep understanding on the observed complex phenomena of crystal growth and the underlying fundamental theory and principle is of significance. Additionally, in view of the applications, cobalt nano-/micro-materials should be not only prepared in large quantity with controllable size and morphology, but also synthesized by using a mild and facile strategy. Therefore, developing a facile and more controlled approach will be highly promising for the controllable synthesis of cobalt nano-/micro-particles.

To date, some synthesis methods including electrochemical deposition [8], thermal decomposition [9], liquid-phase metal salt reduction [10] and hydrothermal methods [11] have been developed to synthesize ferromagnetic cobalt. Comparing with these approaches, the solvothermal method has been regarded as an effective and convenient strategy for the synthesis of inorganic functional materials with controllable morphologies and tunable sizes [12]. However, as far as we known, size-controllable synthesis of Co mcirospheres via solvothermal method has been rarely reported.

In this work, we report a facile solvothermal synthetic method for one-step synthesis of cobalt microspheres with tunable sizes. The possible mechanism for the formation and size control of cobalt microspheres has been proposed. In addition, the magnetic properties of these products with different particle sizes are also investigated to explore the effect of sizes on their magnetic properties.

2. Experimental procedure

All the chemicals were of analytical grade and used without further purification. In a typical synthesis process, 10 mmol $CoCl_2{\cdot}6H_2O$ was dissolved into 40 mL ethylene glycol to obtain homogeneous solution. Then, 20 mmol oxalic acid and 70 mmol NaOH were added into the above solution, respectively. After vigorous stirring for 30 min, 4 mL anhydrous ethylenediamine was dropwise added into the above mixture. The as-obtained mixture was vigorously stirring for 15 min and then transferred into a

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50 mL Teflon-stainless steel autoclave, sealed and treated at 200 °C for 12 h. After cooling down to room temperature naturally, the precipitates were washed with ethanol and deionized water several times and then dried in vacuum at 60 °C for 12 h.

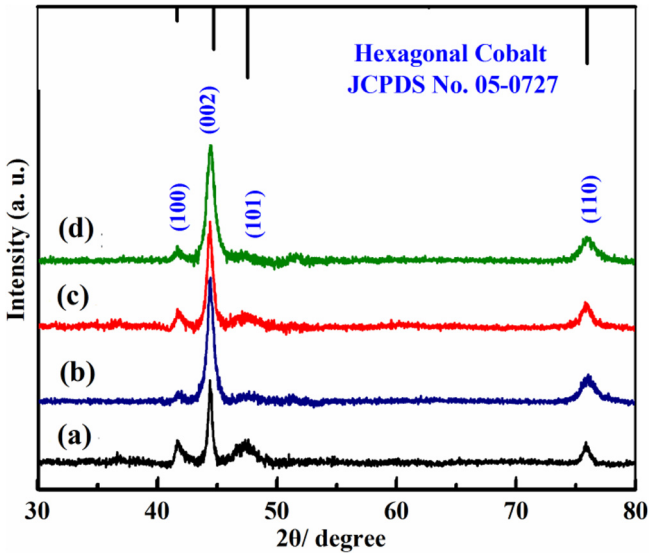

Fig. 1. XRD patterns of the cobalt samples synthesized with different molar ratios of OH^- to Co^{2+}: (a) 1, (b) 3, (c) 5, (d) 10. The standard data of hexagonal cobalt is shown as a reference.

XRD patterns were recorded on an ARL X'TRA diffractometer using Cu Kα radiation (45 kV, 40 mA, 10 °/min from 10° to 80°). SEM images were obtained using a scanning electron transmission microscopy (SEM, Hitachi, SU8010). TEM images and SAED patterns were recorded on a JEM-200CX equipped with an energy dispersive spectroscopy, operating at 200 kV. The magnetic measurements were carried out using a superconducting quantum interference device magnetometer (SQUID, MPMS, XL-7). All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 presents the XRD patterns of the cobalt samples synthesized with different molar ratios of OH^- to Co^{2+}. As shown, all the diffraction peaks (2θ = 41.7°, 44.8°, 47.6° and 62.7°) can be well indexed to the hexagonal phase of Co (JCPDS No. 05-0727). The crystal structure of hexagonal Co is determined with lattice parameters of a = 2.503 Å and c = 4.061 Å, space group $P6_3/mmc$ [13]. Obviously, no characteristic peaks for impurities are detected, indicating that pure Co samples can be obtained via solvothermal method. To provide further insight into the samples, SEM, TEM investigations and EDS analysis are also performed. The SEM images in Fig. 2a and b show that the as-synthesized sample (OH^-/Co^{2+} = 10) entirely consists of a large quantity of monodispersed microspheres with an average diameter of 0.73 μm. The uniform morphology of cobalt microparticles could also be demonstrated by TEM image presented in Fig. 2c. Moreover, the SAED pattern (inset in Fig. 2c) displays the spotty polycrystalline diffraction rings, corresponding to the (100), (101), (002) and (110) planes of

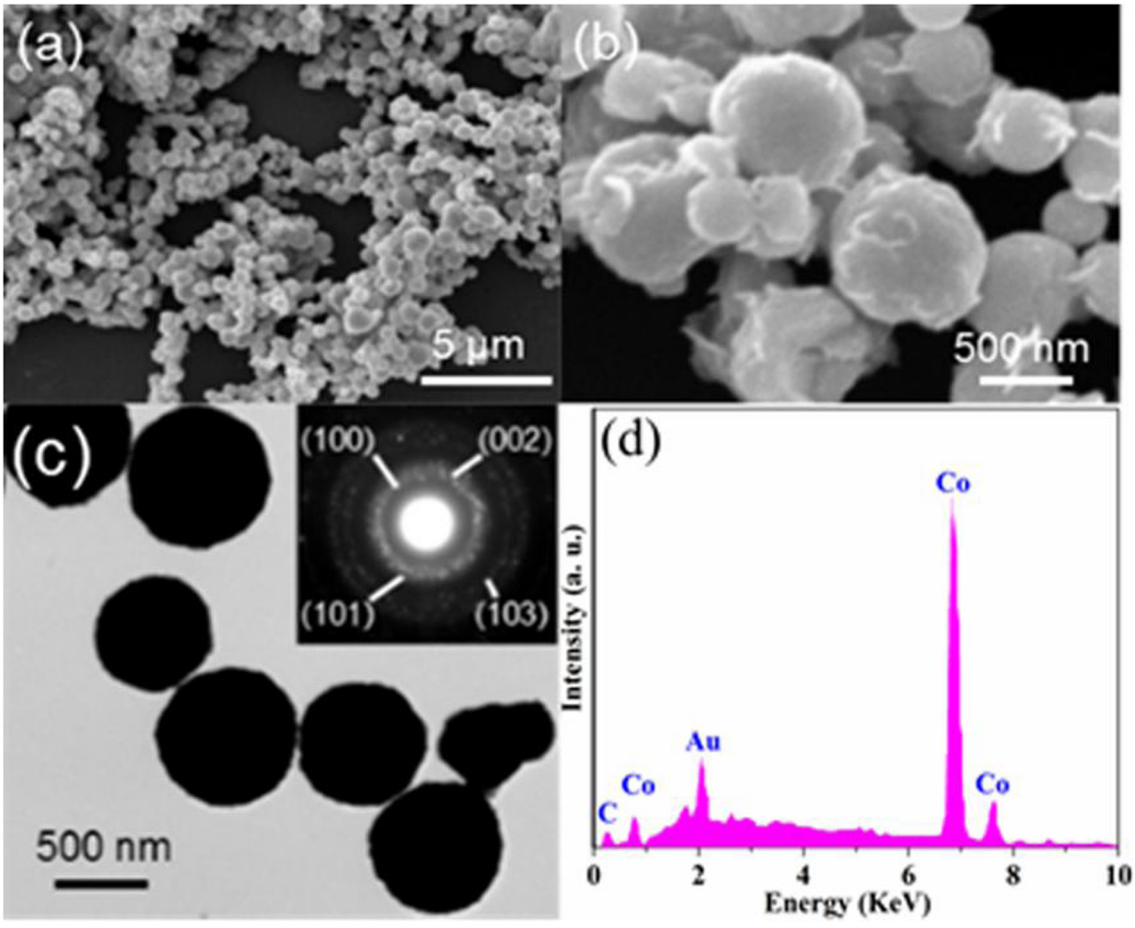

Fig. 2. FE-SEM image with low magnification (a), high magnification (b), TEM image (c) and EDS pattern (d) of cobalt microsphere (OH^-/Co^{2+} = 10).