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A facile method to fabricate porous Co_3O_4 hierarchical microspheres

J.P. Cheng, X. Chen, R. Ma, F. Liu, X.B. Zhang*

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

Flower-like Co_3O_4 hierarchical microspheres composed of self-assembled porous nanoplates have been prepared by a two-step method without employing templates. The first step involves the synthesis of flower-like $Co(OH)_2$ microspheres by a solution route at low temperatures. The second step includes the calcination of the as-prepared $Co(OH)_2$ microspheres at 200 °C for 1 h, causing their decomposition to form porous Co_3O_4 microspheres without destruction of their original morphology. The samples were characterized by scanning electron microscope, transmission electron microscope, X-ray diffractormeter and Fourier transform infrared spectroscope. Some experimental factors including solution temperature and surfactant on the morphologies of the final products have been investigated. The magnetic properties of Co_3O_4 microspheres were also investigated.

1. Introduction

Porous inorganic materials have attracted much interest because of their potential applications in various fields, such as ion exchange, catalysis, and lithium-ion batteries [1,2]. Porous structure of metal oxide with a high surface area has been required for application in many fields. Specially, Co_3O_4 is an interesting transition-metal oxide that has cubic spinel-type structure and is a p-type semiconductor. Porous Co_3O_4 has been proved to be a promising material that exhibits a wide range of applications including gas sensors [3,4], catalyst [5], battery materials [6–8].

Co_3O_4 structures with different morphologies have been prepared in literatures using various methods, such as thermal decomposition [6], polyol process [4], microwave irradiation [8,9], hydrothermal [10–14] and solvothermal [3,15] methods. Wu and co-workers employed microwave method to prepare $Co(OH)_2$ and subsequently calcined it at 450 °C to obtain porous Co_3O_4 platelets [8]. Chu et al. applied hydrothermal method to fabricate Co_3O_4 nanoplates at 160 °C for 24 h [10]. Ma et al. applied solvothermal process to prepare Co_3O_4 nanocrystals using commercial Co_2O_3 powder as precursor at 160 °C for 6–24 h [16]. These methods usually involve either unfavorably high processing temperature or long reaction time. Low-density porous Co_3O_4 structures by template-assisted method have also been synthesized [17–21]. However, the preparation of templates and the contamination by the residues of templates are inevitable. Due to the influence of size and morphology on the property of materials, it is necessary to prepare porous Co_3O_4 with control. Thus, developing a rational strategy to fabricate porous Co_3O_4 structures with tunable morphologies under moderate conditions still remains a challenge in the field of materials science.

Most reports focused on the synthesis methods of Co_3O_4 while only a few cases concerned its porous structure [8–15]. Layered cobalt hydroxide is an ideal precursor to prepare porous cobalt oxide by calcination [13]. In this work, we firstly prepared flower-like $Co(OH)_2$ hierarchical structures by solution route at low temperature and then obtained porous Co_3O_4 microspheres through subsequent calcination. After heat treatment at 200 °C for 1 h in the air, the layered cobalt hydroxide was completely converted into cobalt oxide which kept the structure of their precursor and presented porous framework.

* *Corresponding author*. Tel./fax: +86 571 87951411.
E-mail address: chengjp@zju.edu.cn (J.P. Cheng).

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2. Experimental

In our cases, cobalt hydrated acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), sodium oleate (SOA), ammonia solution ($NH_3 \cdot H_2O$, 25–28%) and hydrogen peroxide (H_2O_2, 30%) were used as raw materials. In a typical procedure, $Co(CH_3COO)_2$ (0.01 Mol) and SOA (0.0002 Mol) were added to 40 mL distilled water with stirring. Then 10 mL of $NH_3 \cdot H_2O$ was dropped into the solution under continuous stirring. When the solution was heated to 70 °C, 2 mL of H_2O_2 was added dropwise into the solution under ultrasonic irradiation. The final mixture was further kept at 70 °C for 1 h under stirring. After the reaction, it was cooled naturally to room temperature. The $Co(OH)_2$ precipitate was collected by centrifuge and washed with distilled water and ethanol, respectively, then desiccated at 120 °C. For comparison, parallel experiments were carried out at different solution temperatures (50 and 90 °C) under identical other conditions. Subsequently, Co_3O_4 product was obtained after the as-prepared $Co(OH)_2$ was directly calcined at 200 °C for 1 h.

The phase and crystallinity of the products were characterized by X-ray diffractometer (XRD, X'Pert PRO) with Cu Kα radiation. The morphology and structure of the samples were examined by scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, Philips CM200). Fourier transform infrared (FTIR) spectra were recorded with wavenumber range 400–4000 cm^{-1}. The step length was 4 cm^{-1}. Nitrogen adsorption–desorption measurement was performed with a Micromeritics ASAP2020 instrument at −196 °C using Brunauer–Emmett–Teller (BET) calculations for surface area and Barrett–Joyner–Halenda (BJH) calculations for pore size distribution. $Co(OH)_2$ and Co_3O_4 were degassed at 100 °C and 200 °C, respectively, under high vacuum. A vibrating sample magnetometer (VSM, Lakeshore 7407) was used to investigate the magnetic properties of the product at room temperature.

3. Results and Discussion

Fig. 1a shows the XRD pattern of the precursor prepared at 70 °C, in which all the diffraction peaks can be assigned to hexagonal $Co(OH)_2$, in agreement with standard diffraction file (PDF card 74-1057). No impurity peaks were detected here, indicating the pure phase of the sample. Fig. 1c shows the representative XRD pattern of Co_3O_4 which was achieved by calcining the precursor at 200 °C for 1 h. All the peaks in Fig. 1c can be indexed to F-center cubic cell of Co_3O_4 (PDF card 78-1970). Based on XRD analyses, it suggests that pure Co_3O_4 crystals can be obtained by calcining $Co(OH)_2$ precursor.

The morphology of the product was investigated by SEM. Fig. 2 shows SEM micrographs of the as-prepared $Co(OH)_2$ precursor at 70 °C and the corresponding Co_3O_4 product after calcination. The as-prepared precursor is composed of microspheres with a narrow size distribution, approximately 10 μm in diameter (in Fig. 2a). The detailed morphology of the $Co(OH)_2$ microspheres is shown in Fig. 2b, which clearly reveals that these flower-like microspheres are composed of self-assembled nanoplates with smooth surface. These nanoplates are *ca.* 30 nm thick and about 5 μm wide. Fig. 2c and d is SEM images of the flower-like Co_3O_4 microspheres after calcination at 200 °C. It is found that most of the microspheres well maintain their original shape. From Fig. 2d, it can be seen that there is no significant morphology changes or collapse even though the crystal transformed from $Co(OH)_2$ to Co_3O_4. The energy-disperse X-ray spectroscopic analysis of the microspheres indicated the existence of cobalt and oxygen.

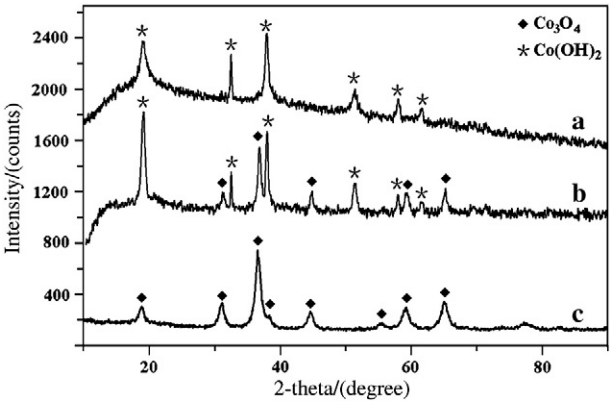

Fig. 1 – Typical XRD patterns of samples. (a) precursor prepared at 70 °C; (b) precursor prepared at 90 °C; (c) Co_3O_4 obtained from the precursor prepared at 70 °C after calcination at 200 °C for 1 h.

The as-prepared Co_3O_4 microspheres can be easily destroyed by grinding. The representative TEM images of Co_3O_4 nanoplates are shown in Fig. 3. From Fig. 3a, a large plate with size about 1.2 μm can be found with a homogenous thickness. A high magnification TEM image in Fig. 3b reveals that the nanoplate consists of a large number of nanocrystallites less than 5 nm in size. A porous structure is formed by the random connection of nanocrystallites [22]. The corresponding selected-area electron diffraction pattern (in Fig. 3b insert) confirms that the as-prepared plate-like structure is polycrystalline Co_3O_4. After heat treatment, each nanoplate in the flower-like microspheres has been transformed into porous structure. The formation of the porous structure is ascribed to the release of water vapor due to the decomposition of $Co(OH)_2$. Therefore, the hierarchical structure of Co_3O_4 microspheres can be briefly formulated as following. $Co(OH)_2$ nanoplates are formed firstly during solution synthesis and they are subsequently transformed into Co_3O_4 porous nanoplates after calcination.

The FTIR spectra of $Co(OH)_2$ and Co_3O_4 in the range of 4000–400 cm^{-1} are depicted in Fig. 4. Fig. 4a is the spectrum of $Co(OH)_2$ prepared at 70 °C. The broad band at 486 cm^{-1} corresponds to the bending vibration mode of the free Co–OH groups in the β-$Co(OH)_2$[23]. The peak strength of 3630 cm^{-1} due to the O–H stretching is very intensive, indicating the presence of $Co(OH)_2$. Two characteristic bands at 2921, 2851 cm^{-1} of C–H vibrations and the bands at 1532, 1429 cm^{-1} of COO^- stretching can corroborate the attachment of oleate on $Co(OH)_2$ microspheres [24]. The broad band centered at 3430 cm^{-1} can be assigned to hydrogen banded –OH stretching vibration arising from surface hydroxyl groups on the microspheres and absorbed water [25]. The curve *b* in