Fabrication of single-crystalline Co$_3$O$_4$ nanorods via a low-temperature solvothermal process

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Abstract

Co$_3$O$_4$ nanorods with average diameter and length of ~50 nm and 1 μm were successfully prepared via a simple surfactant-assisted solvothermal method at 160 °C for 12 h. The formation of Co$_3$O$_4$ nanorods is attributed to alcoholysis of cobalt ions dispersed in ethanol in the presence of a capping agent—CTAB. The composition and purity of the sample were characterized by X-ray diffraction (XRD). Transmission and scanning electron microscopy images show that the particles are homogenous and have the shape of rods. The mechanism of forming Co$_3$O$_4$ nanorods is also discussed.

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1. Introduction

In the past few years, one-dimensional (1D) nanomaterials have attracted considerable attention due to their unique optical, electrical and magnetic properties and potential applications in nanodevices [1–3]. Intensive work has been directed towards the synthesis of 1D nanomaterials, such as nanorods, nanowires and nanotubes. Co$_3$O$_4$, a mixed valence compound with a normal spinel structure, is the stabllest phase in the Co–O system and one of the most important transitional metal oxides that has a gas-sensing behavior and solar energy reflecting properties [4,5]. Due to its function in the reduction of SO$_3$ with CO [6,7], ammonia oxidation [8] and the reduction of NO with methane [9], cobalt oxide can also be used as an effective catalyst in environmental protection and chemical engineering process. Furthermore, it is also a traditional precursor of an anode material in Li-ion rechargeable battery [10].

Various methods have been developed to prepare Co$_3$O$_4$, such as sol–gel route, reduction–oxidation route, gel hydrothermal oxidation, homogeneous precipitation, chemical spray pyrolysis, chemical vapor deposition and cobalt salt decomposition [11–17]. However, most of the attention has been focused on the synthesis of cobalt oxide nanoparticles. Because the properties and applications of Co$_3$O$_4$ are greatly influenced by its size, shape and size distribution, preparation of cobalt oxide...
of different sizes and morphologies including tubes, rods, films, hollow spheres and cubic single crystals in nanoscale was also intensively conducted [18–23]. However, reports of 1D cobalt oxide are relatively few [19,20]. Furthermore, high temperature and complex steps are often needed in their synthesis. Then it will be of great significance if temperature could be decreased and steps be simplified. Heath and LeGoues pioneered the use of solvothermal synthesis for generating semiconductor nanowires [24]. This method was later exploited by Qian et al. to process a rich variety of materials [25]. In this letter, a moderate temperature solvothermal strategy was applied for the growth of single-crystalline Co$_3$O$_4$ nanorods with the assistance of surfactants.

2. Experimental

All chemicals used in this work were of analytical reagent grade, obtained from the commercial market and used without further purification. X-ray diffraction patterns were measured using a Rigaku D/max-IIIB X-ray diffractometer at a scanning rate of 4° per minute with 2θ ranging from 10 to 90°, using Cu Kα radiation (λ=1.5418 Å). Photomicrographs were obtained using a JEM-2010 transmission electron microscope (TEM), working at 160 kV and a JEOL JSM-840 scanning electron microscope (SEM) working at 20 kV.

The experimental process is very simple. In a typical process, 1.1 g, 1.2 g, 1.3 g, 1.4 g and 1.5 g of Co(NO$_3$)$_2$·6H$_2$O were dissolved in 10 ml absolute ethanol respectively, then 1.0 g of CTAB was added to the solutions. The mixture was magnetically stirred until it became homogenous. Then they were transferred into 18 ml autoclaves, sealed and kept at 160 °C for 24 h. After that, the autoclaves were allowed to cool to room temperature naturally. The obtained precipitation was then filtered, washed with absolute ethanol to remove ions and possibly remaining surfactant in the final products, and dried at 80 °C in air for 6 h. Control experiment was done similarly by varying the amount of CTAB at 0 g, 0.5 g and 1.0 g.

3. Results and discussion

Fig. 1 shows the XRD pattern of Co$_3$O$_4$ nanorods. All the diffraction peaks can be indexed to a cubic phase with lattice constant of $a=8.0722$ Å. No impurity peaks are observed.

Fig. 2 is a typical SEM image of Co$_3$O$_4$ nanorods. As can be seen, the sample was composed of uniform rod-like structures with diameter of 50 nm and length of 1 μm. JEM-2010 transmission electron microscope at 160 kV was also employed to examine the morphology of the nanorods. Samples were prepared by placing drops of diluted ethanol dispersed on the nanocrystalline surface of cooper grids, which were purchased commercially. Fig. 3a gives the TEM image of the sample, clearly confirming that the products consist of uniform rod-like Co$_3$O$_4$ particles and the diameter and length of the nanorods are in good agreement with those observed in SEM. SAED pattern (Fig. 3b) obtained by focusing the electron beam on an individual nanorod indicates its single crystal nature.

As is known some oxygen can be dissolved in water, it is in charge of the oxidation of Co(II). Keeping the amount of ethanol and CTAB at

![Fig. 2. SEM image of Co$_3$O$_4$ nanorods.](image1)

![Fig. 3. a. TEM image of Co$_3$O$_4$ nanorods. b. SAED pattern of Co$_3$O$_4$ from a single nanorod.](image2)
10 ml and 1.0 g, different amounts of Co(NO$_3$)$_2$·6H$_2$O were added to the reactant system, and if the amount of Co(NO$_3$)$_2$·6H$_2$O is above 1.3 g, mixtures of Co$_3$O$_4$ and Co(OH)$_2$ could be obtained which were identified by XRD (not shown). At the same time, the oxidation speed is an important factor when synthesizing nanorods. The oxidation ability of oxygen in the autoclave is appropriate for the oxidation of Co (II) to Co$_3$O$_4$. If a little amount of an extra oxidant such as H$_2$O$_2$ was added to the autoclave, only Co$_3$O$_4$ particles with irregular shapes were obtained. Moreover, the sample was poorly-crystallized as characterized by XRD. This could be explained by H$_2$O$_2$ being a strong oxidant that could accelerate the speed of oxidation, and under such conditions only a poorly-crystallized sample with irregular shapes could grow. Choosing ethanol rather than water as the reaction solvent also aims to slow down the speed of crystal growth. Moreover, ethanol is a suitable solvent for the intermediate cobalt hydroxide transformation to Co$_3$O$_4$ through dehydration and oxidation.

Control experiments were performed to examine the function of CTAB. The experiments without surfactant cannot produce 1D nanostructure, indicating that the surfactant in the experiments was indispensable for the formation of 1D morphologies of the final products (Fig. 4a). With an increasing amount of CTAB, the percentage of Co$_3$O$_4$ nanorods would increase (Fig. 4b). CTAB has been successfully used as the morphology-directing agent for the synthesis of one-dimensional nanostructures, such as CuO, Cu$_2$O, Cu, PbO$_2$ and Pb$_3$O$_4$ nanorods [26,27]. In their synthesis, due to electrostatic interactions, inorganic precursor and cation surfactant CTAB can form different conformational inorganic–surfactant composite templates. While in our synthetic system, CTAB was used as a capping agent. We speculate that micelles are hard to form in ethanol in solvothermal conditions. Thus the shape of Co$_3$O$_4$ could be considered in terms of growth kinetics, by which the fastest growing planes should disappear to leave behind the slowest growing planes as the facets of the product. This implies that the final shape of Co$_3$O$_4$ could be controlled by introducing CTAB to change the free energies of the various crystallographic surfaces and thus to alter their growth rates. Interestingly, if the as-prepared sample was observed by TEM without ultrasonic cleaning, many broom-like structures could be observed (Fig. 5). It seemed that it was the ultrasonic that made the nanorods separate from each other.

4. Conclusion

In summary, uniform single-crystalline Co$_3$O$_4$ nanorods were successfully prepared via a surfactant-assisted solvothermal reaction at 160 °C for 20 h. CTAB was proved to be responsible for the growth of the nanorods. This method may prove to be applicable for the synthesis of other kinds of metal oxide.

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References