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# Synthesis of $Co_3O_4$ nanostructures using a solvothermal approach

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**Abstract**

The controlled synthesis of $Co_3O_4$ nanostructures with morphologies of micro-spheres, nanobelts, and nanoplates was successfully achieved by a simple solvothermal method. Various comparison experiments showed that several experimental parameters, such as the reaction temperature and the concentration of $NH_3 \cdot H_2O$, play important roles in the morphological control of $Co_3O_4$ nanostructures. A lower temperature and a lower concentration of $NH_3 \cdot H_2O$ favor spherical products with a diameter of 1–1.5 μm, whereas a higher temperature and a higher concentration of $NH_3 \cdot H_2O$ generally lead to the formation of nanobelts with a width of 20–150 nm. In addition, $Co_3O_4$ hexagonal nanoplates with an edge length of about 200–300 nm are also obtained by adding surfactant CTAB. A rational mechanism is proposed for the selective formation of various morphologies. X-ray powder diffraction (XRD), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and field-emission scanning electron microscope (FE-SEM) were used to characterize the products.


*Keywords:* Basic cobalt carbonate; Cobalt oxide; Nanospheres; Nanobelts

## 1. Introduction

In the past few years, many different techniques have been developed for the preparation of nanomaterials, such as self-assembly [1,2], coprecipitation, sol–gel methods, microemulsions, solvothermal, and so on [3–5]. Nanomaterials have been actively studied due to both scientific interests and potential applications. Among these materials, the transition metal oxides have attracted much attention due to their electrical and magnetic properties [6]. For example, unitary spinel cobalt oxide ($Co_3O_4$) stands as an important functional material, in part because of its vast applications for use in sensors, electrochemistry, pigments, catalysis, magnetism, and energy storage [7,8]. $Co_3O_4$ nanostructures are expected to lead to even more attractive applications in conjunction with their traditional arena and nanotechnology [9–11].

Previously, $Co_3O_4$ nanostructures with various morphologies have been synthesized. He et al. synthesized monodispersed $Co_3O_4$ nanoparticles via thermal decomposition of the intermediate product $Co(NO_3)_2 \cdot 7C_6H_{13}OH$ in long-carbon-chain alcohols [12,13]. Zeng's group prepared $Co_3O_4$ nanocubes with a uniform size of ca. 47 nm in aqueous solution at 95 °C, using a nitrate-salt-mediated formation route [9,14]. In addition, Martin and his colleagues synthesized $Co_3O_4$ nanofibers by the sol–gel method combined with a template-synthesis technique [15]. The fabrication of $Co_3O_4$ nanorods was also achieved via calcinations of precursor powders, which were prepared in an inverse microemulsion [16]. Furthermore, Selke and co-workers synthesized $Co_3O_4$ nanotubes from cobalt complexes precoated onto colloidal particles [17]. The nanostructured porous $Co_3O_4$ was also synthesized by hard templating method [18]. Zhang and co-workers prepared $Co_3O_4$ nanowires by heating a pure cobalt foil in atmosphere [19]. $Co_3O_4$/ZnO nanowire array was fabricated by photochemical coating method and a mesoporous $Co_3O_4$ core/mesoporous silica shell composite was also fabricated by depositing silica on $Co_3O_4$ superlatticed particles [20,21].

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Although different morphologies of $Co_3O_4$ nanostructure were synthesized, the preparation methods need either complicated technique or rigorous conditions. Herein, we describe a simple solvothermal way to generate high-quality $Co_3O_4$ nanostructures. In our experiments, $Co_3O_4$ micro-spheres and nanobelts are acquired, respectively, at 140 °C and at 180 °C by using basic cobalt carbonate as precursor and ammonia as solvent.

## 2. Experiment

All of the chemical reagents were of analytical grade and used without further purification in this experiment. The $Co_3O_4$ nanostructures were synthesized via a hydrothermal route in the presence of ammonia. $Co_3O_4$ nanobelts were synthesized as follows: $Co_5(OH)_6(CO_3)_2 \cdot nH_2O$ was added to 60 mL $NH_3 \cdot H_2O$. This solution was stirred for 30 min to ensure that $Co_5(OH)_6(CO_3)_2 \cdot nH_2O$ dissolved completely. The mixture was transferred into a stainless Teflon-lined 80 mL capacity autoclave and kept at 180 °C for 12 h. The resulting black products were collected and washed with deionized water several times and then dried at 60 °C in air. By changing experimental parameters, such as temperature and concentration, $Co_3O_4$ micro-spheres and nanoplates of different sizes were also obtained.

The overall crystallinity and purity of the as-synthesized samples were analyzed by X-ray power diffraction with monochromatized Cu $K_\alpha$ incident radiation by SHIMADZU XRD-6000 operated at 40 kV voltage and 30 mA current. XRD patterns were recorded from 15° to 75° ($2\theta$) with a scanning step of 0.04°. The morphology and selected-area electron diffraction (SAED) patterns of the $Co_3O_4$ products were characterized by transmission electron microscopy (TEM, JEOL, Model JEM-2000, 160 kV and HRTEM, JEOL, JEM-2010F, 200 kV) and scanning electron microscopy (SEM). IR spectra were obtained on a Impact 410 FT-IR spectrometer with a resolution of 1 $cm^{-1}$.

## 3. Results and discussions

### 3.1. Characterization of $Co_3O_4$ nanostructures

Fig. 1 shows the FT-IR spectra of tricobalt tetraoxide. There are two strong bands (due to the $\nu$(Co–O) modes) at ~660 and ~578 $cm^{-1}$ in Fig. 1, which is a clear evidence for the presence of the crystalline $Co_3O_4$ [22]. The peaks at ~1600 and ~3600 $cm^{-1}$ should be assigned to $H_2O$ absorbed by the samples or KBr [23]. The peaks at ~2400 $cm^{-1}$ are obvious which should be assigned to $CO_2$ vibrant by environmental or personal. The XRD results in the next section also support this conclusion.

The phase composition and structure of as-obtained samples were examined by X-ray powder diffraction (XRD). The XRD patterns of the spherical, zonal and hexagonal plate products are shown in Fig. 2. We can see that all samples with different morphologies are $Co_3O_4$. As shown in Fig. 2, almost all of the peaks can be perfectly indexed to a pure cubic phase (space group: *Fd3m[227]*) of $Co_3O_4$ ($a = 8.084$ Å) reported in the literature (JCPDS 74-2120). But there is one peak marked with asterisk in Fig. 2, which is crystal plane (011) of $Co(OH)_2$ reported in the literature (JCPDS 74-1057).

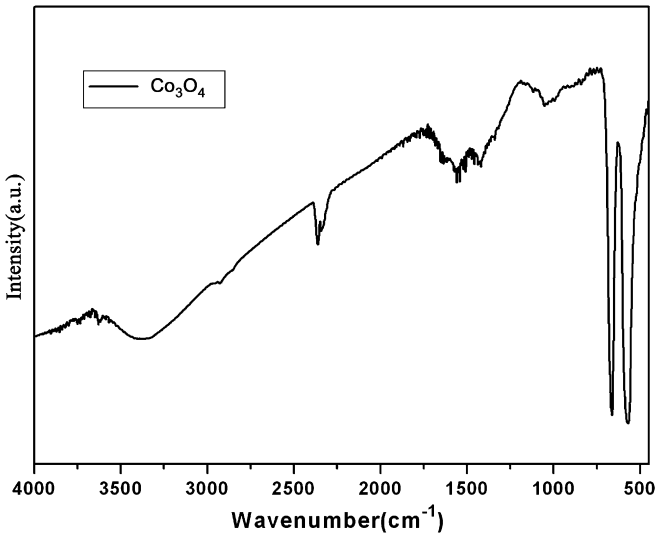


Fig. 1. FT-IR spectra of spinel cobalt oxide.

The morphology and structure of the product were further characterized by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and selected-area electron diffraction (SAED).

Fig. 3a shows a typical TEM image of $Co_3O_4$ nanobelts with width of 20–150 nm and length of 1–10 μm. Fig. 3a (inset) displays a magnified image of one nanobelt. Fig. 3b shows an HRTEM image taken from the edge of the magnified nanobelt in Fig. 3a. The nanobelt is structurally uniform with an interplanar spacing of 2.4242 Å, corresponding to the (311) lattice spacing of $Co_3O_4$. And the nanobelt grows along the [311] direction. The SAED images (Fig. 3b inset) taken from the nanobelt clearly confirm the single-crystalline nature.

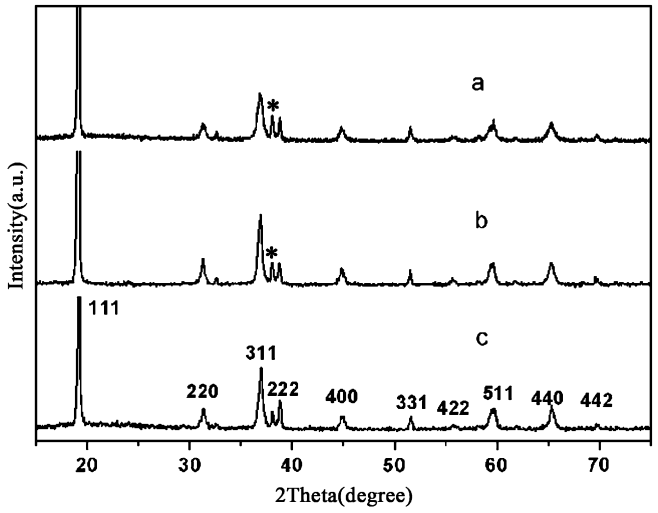


Fig. 2. XRD patterns of $Co_3O_4$ samples (a) spherical products; (b) zonal products; (c) hexagonal plates.