



# Hydrothermal synthesis of cobalt particles with hierarchy structure and physicochemical properties



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## ABSTRACT

Microsphere, micro-net-sphere, hexagon plate and sandwich-like cobalt particle were successfully synthesized via a facile, environmentally friendly and one-step solvothermal method. Subtle control over the reaction conditions could easily achieve these different morphologies with certain crystal structures. Solvothermal method utilized here is pollution free, without surface-active agent and facile to perform. The effects of alkali and  $\text{Co}^{2+}$  content as well as the reaction temperature on the size, morphology and microstructure were investigated individually. Moreover, the catalytic properties concerning the catalytic thermal decomposition of ammonium perchlorate (AP) and magnetic properties of these selected samples were evaluated. It finds that the alteration trend of related properties correspond well with the variation of these samples' microstructure and morphology. In addition, comparing with the other morphology, Co particles with the morphology of hexagon sheet exhibits outstanding catalytic performance, implying significant practical application in the development of energy-efficient rocket solid propellant recipes.

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## 1. Introduction

Investigations of magnetic metal materials in nano-size is of significant importance owing to their novel properties and applications in bio-sensing [1], ultra high density data storage devices [2], targeted drug delivery [3,4], magnetic resonance imaging contrast enhancement (MRI) [5], ferro-fluids [6], and catalysis [7]. Fabrication of nanoscale and microscale crystals with different structures, sizes as well as morphologies recently has attracted much attention from researchers, because these above factors significantly influence material's physical and chemical properties, even their technological applications [8,9]. There have been many efforts to prepare magnetic nanomaterials especially cobalt, because their properties are closely relevant with their phase, shape and size [10,11]. The pure cobalt possess special significance in both theory and technology because it can crystallize in three different phase structures: the hexagonal-close-packed (HCP), the face centered cubic (FCC) and the epsilon phase [9]. As for the size and morphology, by now various morphologies of ferromagnetic cobalt crystals such as wires, rods,

disks, chains, rings and spheres in nanoscale and sub-micronscales have been successfully fabricated [12–15].

In order to synthesize cobalt crystals with various morphologies in different sizes and structures, multitudinous methods of fabrications have been exploited. Among these synthesizing approaches, solvothermal method demonstrates its superiority in controlling shapes of target product [16]. A lot of research papers report that the solvothermal method were often involved into employing some kinds of surface active agents for the sake of controlling morphology. But these agents are usually adsorbed onto the surface of the formed product and are difficult to eliminate, which may deteriorate the properties and limit the applications of the final products [17]. The precise modulation of the phase and morphology of cobalt crystals by controlling the reaction process without surfactant remains a challenge. Herein, we demonstrate a facile and surfactant-free solvothermal route to synthesize Co microcrystals possessing a variety of special morphologies such as microparticle, micro-net-sphere structures, hexagonal plate as well as sandwich-like hexagonal stack. Via regulation of the content of reagent and temperature, the evolution mechanism of morphology and crystallinity were explored. Furthermore, the influences of different morphology and crystallinity of Co particles on catalytic and magnetic properties were investigated.

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## 2. Experimental details

All chemicals, ethylene glycol ( $C_2H_6O_2$ ), sodium hydroxide (NaOH) and cobalt chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ ), ammonium perchlorate (AP) were commercial products with analytical grade without further purification. In a typical procedure for preparing metal Co hexagonal plates, 3 mmol of  $CoCl_2 \cdot 6H_2O$  was dissolved into 20 ml of ethylene glycol (EG) to form a homogeneous solution. And then, 20 ml of NaOH (1.32 g)-EG solution was added cautiously into cobalt salt EG solution while the solution was stirred continuously. The reaction mixture was stirred vigorously for 30 min and consequently put into a 50 ml Teflon-lined stainless steel autoclave. The sealed autoclave was heated to  $200^\circ C$  and held for 10 h, and then was cooled to room temperature naturally. The resultant black product was collected by centrifugation, washed with deionized water and anhydrous ethanol alternately for five times. Finally, the sample was dried in an oven at  $60^\circ C$  for 4 h to remove the solvent remained in the final product. To investigate the crystal growth mechanism and morphology evolution process, control experiments were carried out by varying the content of NaOH and cobalt salt, the reaction temperatures and reaction time, while keeping the other synthetic conditions constant.

The structure and phase of the samples were examined by X-ray diffraction (XRD, D8/ADVANCE diffractometer,  $Cu K\alpha \lambda = 1.5418 \text{ \AA}$ ). The microstructure was observed on the field emission scanning electron microscope (SEM, LEO-1530, Oberkochen, Germany, LEO-1530) and transmission electron microscope (TEM, JEM-2100F). The catalytic properties of samples concerning the thermal decomposition of AP were tested through Thermo Gravimetric Analyzer (N33-TG 209 F3), in which the mass percentage of selected metal cobalt samples is 4%. Magnetic properties of as-obtained products were measured at room temperature using a vibrating sample magnetometer (VSM, BHV-50HTI) at room temperature.

## 3. Results and discussion

Powder XRD measurements were performed to identify the crystal phase of the as-obtained products. Fig. 1 shows the XRD pattern of the sample prepared with 3 mmol of  $CoCl_2 \cdot 6H_2O$  and 1.32 g of NaOH, where H and F denote the HCP and FCC structures of cobalt respectively. Though the HCP structure is the most stable phase for bulk Co at room temperature, the coexistence of HCP and FCC phases in the same cobalt sample are relative stable phases, as reported previously [18]. The HCP and FCC phases of cobalt are close-packed structures that differ only in the stacking sequence of

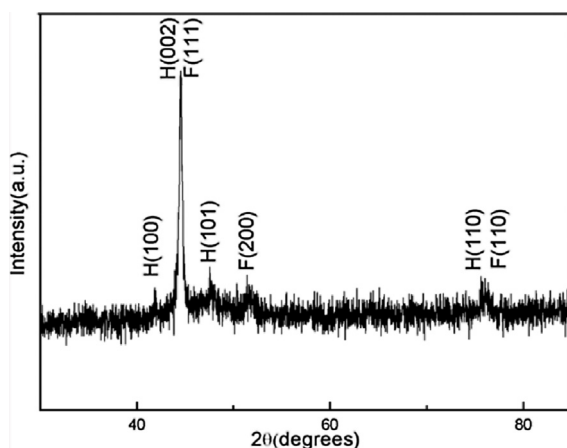


Fig. 1. XRD pattern of the sample synthesized in a typical procedure at  $200^\circ C$  for 10 h.

atomic dense planes: ABCABCABC for fcc and ABABAB for hcp. Low stacking faults energy could easily lead to the formation of both phases in the same sample [18].

When the content of  $Co^{2+}$ , reaction temperature and time were kept constant (3 mmol,  $200^\circ C$ , 10 h), the crystal orientation and morphology were closely related with the variation of NaOH content. Fig. 2 shows the XRD patterns of the products obtained with various NaOH content. It could be evidently observed that the crystal orientation of the samples are all along the direction of H (002) and F(111). However, the crystallization degree shows an interesting variation trend. When NaOH content increased from 0.6 g to 1.32 g, the degree of crystallinity became better. But when NaOH content further increased to 3.75 g even higher, yet it got reduced. Therefore, the highest degree of crystallinity was achieved with NaOH of 1.32 g.

Fig. 3 shows SEM images of the products, indicating the influence of NaOH on the morphology of obtained product. The samples synthesized with low NaOH content (Fig. 3a) were composed of micro-sphere particles with the diameter of  $1 \sim 2 \mu m$ , this kind of micro-sphere particles were covered with irregular nanoparticles. However, the micro-net-sphere particle which surface was attached with networks weaved with nanowires was obtained with 0.75 g NaOH shown in Fig. 3b. When the content of NaOH was increased to 1.32 g, samples were mostly made up of single-layer hexagon plate (Fig. 3c) and the diameter was about  $3 \mu m$  with thickness of 100 nm. At the same time, there existed a small amount of spherical particles with diameter of  $\sim 1 \mu m$ . With slight increase in content of NaOH (1.44 g), hexagon plates presented a double layer structure with a little increase in thickness as well as the ratio of irregular particles. As for 1.86 g of NaOH, three-tier hexagonal plate stacked into sandwich-like shape and monolayer tent to be thicker. Some of these kind of particles present rough fluey sketch, as shown in Fig. 3e. Cobalt chains composed of micro-balloon particles with an average length of  $50 \mu m$  could be easily found in Fig. 3f. They were almost made up of in homogeneous micrometer spheres. There also were lots of single spheres with the diameter of about  $2 \mu m$ . Relying on the XRD results and SEM images, it could readily conclude that: the crystallographic orientation of the samples positively correlates with the proportion of hexagonal sheets in the products; if the content of NaOH was appropriate (about 1.32 g), hexagonal plates take up the most part of obtained product and the orientation crystallization is better than that of the other samples shown in SEM images.

The effect of  $Co^{2+}$  content on the morphology and crystalline state of the products was also investigated while the content of NaOH, reaction temperature and time were kept constant (1.32 g,  $200^\circ C$  and 10 h, respectively). Fig. 4 shows the XRD patterns of the

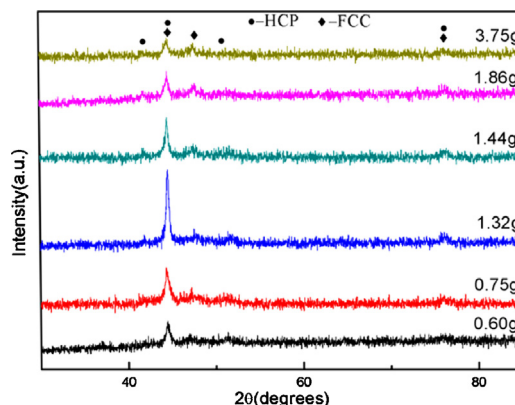


Fig. 2. XRD patterns of the samples obtained with different NaOH content.

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