

Facile synthesis of porous cobalt oxides through solvothermal method

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Abstract. The morphology may significantly influence the properties and applications of materials, thus the ability to tune the structure, size, and shape of inorganic materials is an important goal in obtaining nanomaterials with novel properties. A novel and facile synthesis route for the manufacture of porous Co_3O_4 is reported, utilizing cobalt nitrate as the inorganic source and triblock copolymer F127 as the morphology-directing agent by the solvothermal method. X-ray powder diffraction (XRD), N_2 -sorption and scanning electron microscopy (SEM) were used to characterize the as-prepared Co_3O_4 . The possible formation mechanism of the porous Co_3O_4 was discussed.

1. Introduction

Release of various organic pollutants including the volatile organic compounds (VOCs) such as textile dyes, phenols and aromatic amines from many industries is becoming a serious problem. There are many techniques to remove the organic pollutants. The techniques include adsorption, catalytic combustion, photocatalytic degradation and physical separation. Co_3O_4 with the normal spinel structure, where O^{2-} is cubic close packed, Co^{2+} in tetrahedral coordination and Co^{3+} in an octahedral coordination, is a magnetic semiconductor. The lowest Co-O bonds strength and the highest capability of the activation of molecule oxygen play crucial roles in the catalytic oxidation systems [1]. Due to its special physical and chemical properties, Co_3O_4 is widely used in magnetism [2], photovoltaics [3,4], sensors [5] and homogeneous catalysis [6]. Furthermore, among metal oxides, the Co_3O_4 based materials are of great interest as a photo-Fenton catalyst due to their low cost, natural abundance, visible light absorption and most importantly the good catalytic activity toward degradation of organic compounds even at neutral pH [7]. Co_3O_4 material is also regarded as promising anode for high performance Li-ion batteries (LIBs) due to its high energy density, high tap density and stable chemical property [8].

The structure (microstructure), size, and morphology may significantly influence the material properties and application, thus controlling the morphology of inorganic nanomaterials plays a important role in obtaining nanomaterials for novel properties. For the improved catalytic activity and increasing applications in various fields, the development of catalysts with desirable morphology and dimensions is a challenging task [9]. The morphology of Co_3O_4 based nanomaterials is diverse and experimentally available owing to the special spinel structure. Furthermore, Co_3O_4 is one of the most intriguing p-type semiconductors with various morphologies, which has been used in a wide range of applications such as photocatalysis [10].

The properties of the as-synthesized Co_3O_4 strongly depend on their morphologies and structure, for example, the superior electrochemical performance is attributed to the porous structures of Co_3O_4 . Hence, the synthesis of porous Co_3O_4 is of great importance. Porous Co_3O_4 has been synthesized by some methods including electrochemical method [11], Pulsed Laser Deposition (PLD) and thermal oxidation [12] and microwave-assisted method [13]. In this study, we report the facile synthesis of porous cobalt oxide (Co_3O_4) through solvothermal route in an environmentally benign alcohol-water mixture. The growth mechanism of porous cobalt oxide was also investigated.

2. Experimental Section

2.1 Materials

Triblock copolymer Pluronic F-127 (EO106PO70EO106, MW=12600, product no. P2443-250G) was purchased from Aldrich and used as received without further purification.

2.2 Synthesis of Co₃O₄

In a typical experiment, isotropic solutions were prepared by dissolving Co(NO₃)₂·6H₂O or CoCl₂·6H₂O (0.1 mol) and block copolymer F-127 (EO106PO70EO106) (0.9 g) in EtOH (23 mL), H₂O (20 mL) and 26–28% NH₃·H₂O (4.5 mL). The solution was stirred at 70 °C for 1h, then it was transferred into a Teflon-lined stainless steel autoclave and heated at 150 °C for 16 h. To remove the surfactant, the as-prepared products were washed with water, and then the sample was dried and calcined at 450 °C for 4 h (1 °C min⁻¹ under air).

2.3 Characterization

The crystalline phase and orientation of products were identified by X-ray diffraction (XRD) on a Rigaku D/MAX-Ultima III X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV, 40 mA) and a scan rate of 10 °·min⁻¹. The microstructure of the as-prepared products was characterized by a field emission scanning electron microscopy (FE-SEM, S4800, Hitachi Ltd.) with an electron accelerating voltage of 15 kV. The specific surface area of the as-prepared NiO powders was obtained on a Micromeritics TriStar 3000 instrument and the Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area.

3. Results and Discussion

Fig. 1 shows the structural characteristics of the sample prepared through the solvothermal route by using Co(NO₃)₂·6H₂O in the starting solution investigated by XRD. The diffraction peaks typical to Co₃O₄ are clearly observed, which agree with those of standard Co₃O₄ of cubic structure (JCPDS Card No. 43-1003). There are no other peaks observed in the XRD result except for the diffraction peaks of Co₃O₄, which means single-phase Co₃O₄ can be obtained route in this system through solvothermal route.

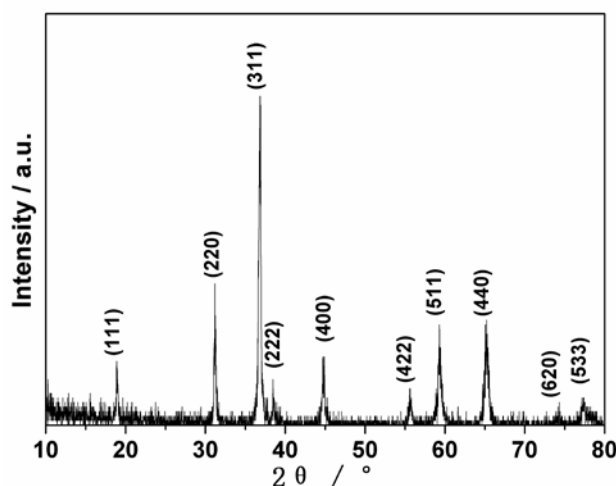


Fig. 1 XRD pattern of the product calcined at 450 °C synthesized by using Co(NO₃)₂·6H₂O as precursor.

The morphology of the as-prepared Co₃O₄ sample was characterized by FE-SEM and the images are shown in Fig. 2. From Fig. 2, the low-magnification SEM image (see Fig. 2a) of the as-prepared Co₃O₄ by using Co(NO₃)₂·6H₂O as precursor shows a uniform plate morphology. The high-magnification SEM image (see Fig. 2b) shows of the as-prepared Co₃O₄ sample has porous structure. The BET surface area of the as-prepared Co₃O₄ sample 15.09 m² g⁻¹.

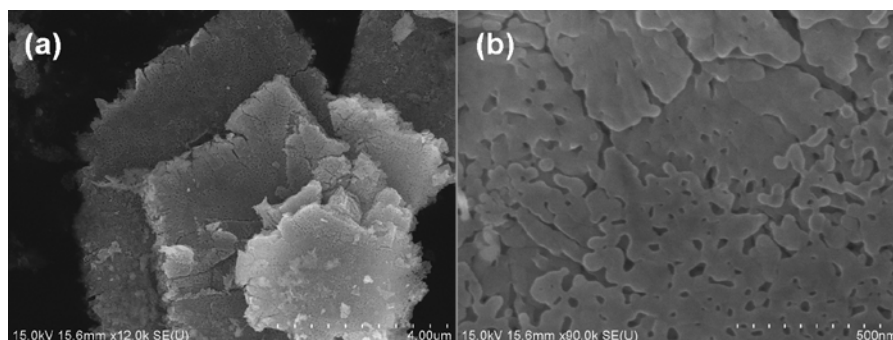


Fig. 2 SEM images of the product calcined at 450 °C synthesized by using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor.

Fig. 3 shows the low- and high magnification SEM images of the as-prepared Co_3O_4 by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the starting solution. From Fig. 3a, the low-magnification SEM image shows the Co_3O_4 particles morphology. From Fig. 3b, the high-magnification SEM image shows the morphology of the Co_3O_4 particles is polyhedron-like shape.

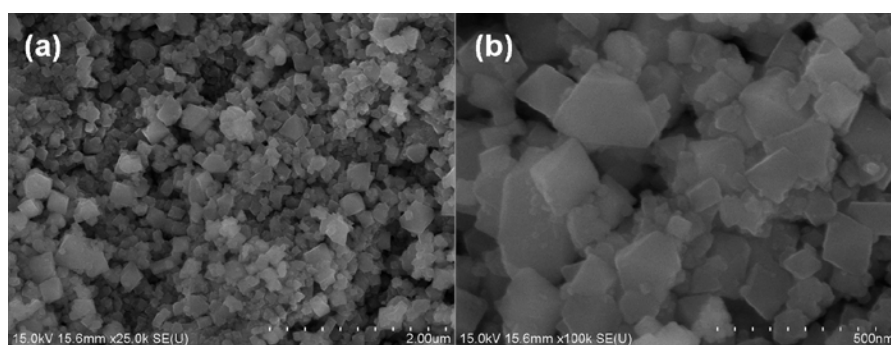


Fig. 3 SEM images of the product calcined at 450 °C synthesized by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as precursor.

In a triblock copolymer-solvent system, it is well known that block copolymers can self-assemble to a variety of lyotropic liquid crystals microstructures consisting of lamellar, hexagonal or cubic structure [14]. The very rich structural polymorphism of block copolymer in a ternary system makes it possible to synthesize various nanostructured materials. The factors which influence the synthesis of Co_3O_4 nanoparticles are supposed to exist in the following two ways: the strong gelation tendency inside the precursors when they hydrolyze; the potential disruption of the assembly of nanoparticles in process of conformation of crystal phase and the removal of template. Thus, the formation of porous Co_3O_4 can be attributed to the interaction between morphology-directing agent and hydrophilic cobalt nanoclusters and the following removal of surfactant.

4. Conclusions

In summary, porous cobalt oxide (Co_3O_4) is synthesized through solvothermal route using cobalt nitrate as the inorganic source and F127 as structure-directing agent in an environmentally benign alcohol-water mixture. The growth mechanism of porous cobalt oxide has been investigated. The formation of porous Co_3O_4 can be attributed to the interaction between morphology-directing agent and hydrophilic cobalt nanoclusters. Co_3O_4 with the porous structure may be used in many ways such as the superior electrochemical performance.

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