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Ben Niu

University of Jinan China

Liyang Man

University of Jinan, Jinan

Jieqiang Wang

jjew@uow.edu.au

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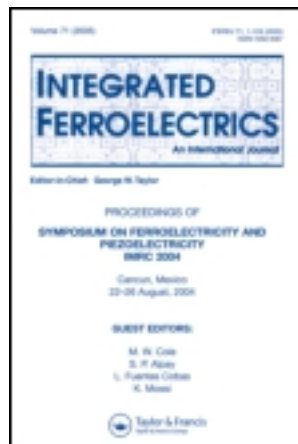
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Ben Niu^a, Liying Man^a & Jieqiang Wang^{a, b}

^a School of Materials Science and Engineering, University of Jinan, Jinan, 250022, P.R. China

^b Institute for Superconducting and Electronic Materials, University of Wollongong, NSW, 2522, Australia

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Microwave Hydrothermal Synthesis of Nano Co_3O_4 with Various Morphologies

BEN NIU,¹ LIYING MAN,¹ AND JIEQIANG WANG^{1,2,*}

¹School of Materials Science and Engineering, University of Jinan, Jinan 250022, P.R. China

²Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

The precursors with various morphologies including nanowires, nanosheets, and hexagonal nanoplatelets were synthesized under different conditions by the microwave hydrothermal method. The precursors are transformed into Co_3O_4 with various nanostructures through thermal decomposition. It is very important to synthesize the precursors controlling the microwave hydrothermal conditions, such as the mineralizer, the reaction temperature, and the reaction time. The microwave assisted hydrothermal approach presented here opens a potential avenue to explore the synthesis of various other metal oxides with different nanomorphologies.

Keywords Co_3O_4 ; morphology; nanostructure; microwave hydrothermal synthesis

1. Introduction

Co_3O_4 has a wide range of applications in varistor ceramics, catalysts, sensors, electrochemical materials, and magnetic materials, and the particle size and morphology of Co_3O_4 have a significant effect on the physical and chemical properties [1–2]. Recently, more and more attention has been paid to the control of the morphologies and microstructures of nanomaterials. So a variety of methods [3–5], such as chemical spray pyrolysis, liquid-control-precipitation, and sol–gel method, etc, have been used to prepare special morphology of nanosized Co_3O_4 , to enhance surface area and electrochemical reactivity. Therefore, the electrochemical performance of Co_3O_4 with small particle size and special textural characteristics, especially, one-dimensional (1-D), such as porous Co_3O_4 nanotubes [6, 7], and nanowires/nanorods [8, 9], etc., has recently been widely explored using various template-synthesis methods.

We present here a novel microwave-assisted hydrothermal synthesis approach that offers nanosized Co_3O_4 . The methods take advantage of both the microwave irradiation and the hydrothermal effect to offer products with controlled shapes, sizes, and structures within a short reaction time. That is, we not only prepare one-dimensional (1-D) Co_3O_4 nanowires, but also two-dimensional (2-D) Co_3O_4 macroporous nanosheets and hexagonal nanoplatelets were obtained.

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*Corresponding author. E-mail: mse_wangjq@ujn.edu.cn

2. Experiments

2.1. Materials Preparation

All of the chemical reagents were of analytical grade and used without further purification. The experimental details are as follows: 0.021 mol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 ml distilled water under stirring, and 0.168 mol $\text{CO}(\text{NH}_2)_2$ was introduced into the above-mentioned solution. Then, 10 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 ml distilled water under stirring, and 2 M KOH solution was introduced into the above-mentioned solution at a rate of $2 \text{ mL} \cdot \text{min}^{-1}$, until the pH value of the solution reached 11. The above milky solution was stirring after 30 min, respectively, then, transferred into a double-walled vessel. The vessel was sealed and maintained in a Microwave Accelerated Reaction System (MARS-5, CEM Corporation, USA) at 110°C for 1 h, 140°C for 3 h, and 140°C for 3 h, respectively. After the reaction finished, the resultant black precipitates were centrifuged, washed with distilled water and then ethanol to minimize the extra ions in the final products, and dried at 80°C in air. Finally, the powders were calcinated at 350°C and 500°C in air for 2 h, respectively.

2.2 Materials Characterization

The morphology and structure of the as-prepared samples were characterized by powder X-ray diffraction (XRD, GBC MMA, Cu $K\alpha$ radiation, 40 kV, 25 mA), field emission scanning electron microscopy (FESEM, JEOL JSM7500FA, 15 kV), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) (JEOL 2011F, 200 kV).

3. Results And Discussion

XRD pattern in Fig. 1 shows that the precursor processed by microwave irradiation consists of cobalt-basic-carbonate compounds and cobalt(II) hydroxide. In these precipitations, a sudden burst of nuclei occurred when the temperature was raised and the nuclei subsequently were grown into larger crystallites by an aggregation mechanism. The XRD pattern show characteristics of the cobalt-basic-carbonate phase, which is agreement with the reported compound, $\text{Co}(\text{OH})_{1.0}(\text{CO}_3)_{0.5} \cdot 0.11\text{H}_2\text{O}$, with lattice constants $a = 8.79 \text{ \AA}$, $b = 10.15 \text{ \AA}$, and $c = 4.43 \text{ \AA}$ (JCPDS card No. 48-0083) [10–12], and the brucite-like $\beta\text{-Co}(\text{OH})_2$ (JCPDS card No. 30-0443, hexagonal crystal, space group: P-3m1, $a = 3.183 \text{ \AA}$, $c = 4.652 \text{ \AA}$) was the predominant phase. The other possible precipitates, such as CoCO_3 , $\text{Co}(\text{OH})_x(\text{NO})_{2-x} \cdot n\text{H}_2\text{O}$, etc, were not detected (verified by XRD analysis).

Figure 2 shows the XRD patterns of the samples, and the peaks in the XRD spectra are identical and can be perfectly indexed as cubic spinel Co_3O_4 phase. All reflection peaks at (111), (220), (311), etc., can be indexed to the peaks of the Co_3O_4 phase, which are consistent with the values in the standard card (JCPDS Card No. 42-1467), agree very well with the literature data [13]. No peaks from other phases have been detected, indicating that the products are of high purity.

From Fig. 3 (a), it can be seen that a large quantity of nanorods with a diameter of 60–100 nm and an edge length beyond $1 \mu\text{m}$ were obtained. The wire-like precursor was synthesized due to the domination of CO_3^{2-} anion at 110°C for 1 h under microwave irradiation. The incorporated carbonate anions change the crystal structure and morphology of generated basic compounds. During the growth of compound, the carbonate anions may

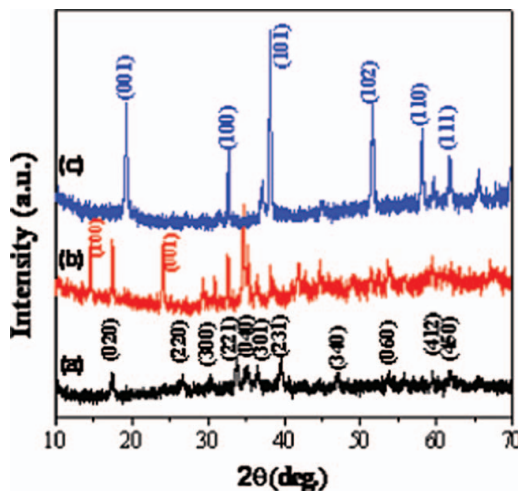


Figure 1. XRD patterns of precursor generated under different microwave irradiation conditions: (a) at 110°C for 1 h, using urea as mineralizer; (b) at 140°C for 3 h, using urea as mineralizer; (c) at 140°C for 3 h, using potassium hydroxide as mineralizer.

also act as an inhibitor that selectively decreases the rates of crystal growth along one direction, resulting in the long nanorods. Moreover, it can be seen that the size and shape of the Co_3O_4 nanowires are similar to those of the cobalt-basic-carbonate precursors. From Fig. 3 (b) and (c), we can see that many nanoparticles are selfassembled into nanochains and then the nanochains are assembled into a bundle of the uniform thin wires-like Co_3O_4 . Furthermore, the Co_3O_4 nanowires calcined at 500°C for 2 h developed perfectly.

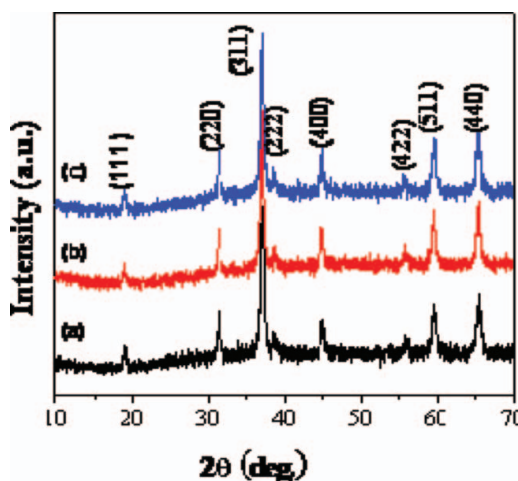


Figure 2. XRD patterns of Co_3O_4 samples calcined at 350°C for 2 h from precursors generated under different microwave irradiation conditions: (a) at 110°C for 1 h, using urea as mineralizer; (b) at 140°C for 3 h, using urea as mineralizer; (c) at 140°C for 3 h, using potassium hydroxide as mineralizer.

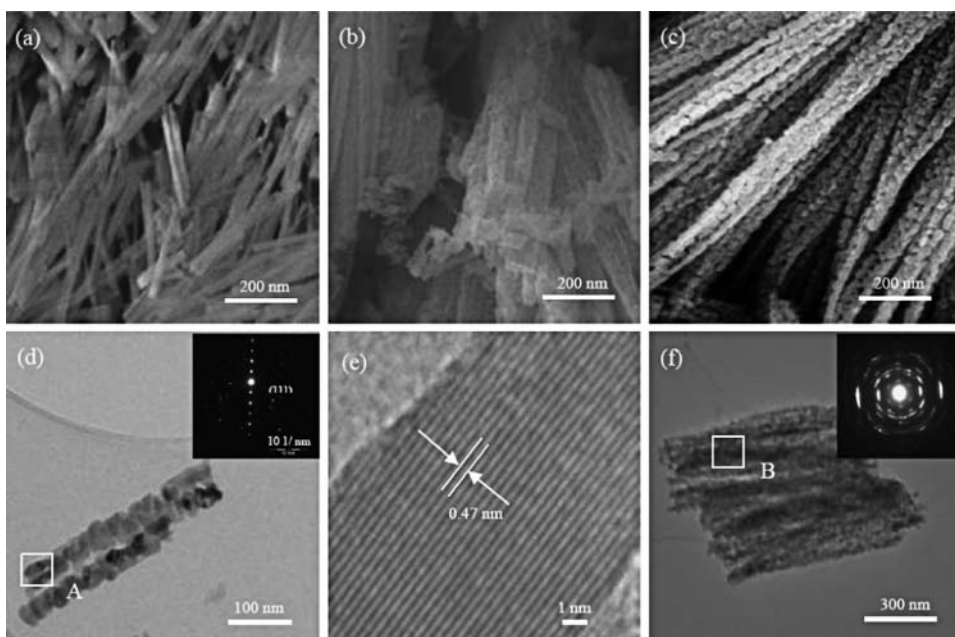


Figure 3. Morphological and structural characterizations of cobalt-basic-carbonate compounds generated under at 110°C for 1 h using urea as mineralizer, and Co_3O_4 nanowires by subsequent calcination: (a) FESEM image of precursor; (b) FESEM images of Co_3O_4 at 350°C for 2 h; (c) FESEM images of Co_3O_4 at 500°C for 2 h; (d) TEM image of nanowire array, inset is corresponding SAED patterns of A; (e) HRTEM image of a typical individual Co_3O_4 nanocrystal of site A; (f) TEM image of nanowire array, inset is corresponding SAED pattern.

Figure 3(d) and (e) are typical TEM images of Co_3O_4 nanowire at relatively high magnification, and Fig. 3(f) is at relatively low magnification. The inset in Fig. 3(d) is the SAED patterns (Selected Area Electron Diffraction Pattern) of the sample. The HRTEM image (Fig. 3(e)) indicates a highly crystalline character with a lattice spacing of 4.7 Å, corresponding to the value of the (111) plane of the Co_3O_4 phase. We select an area as shown

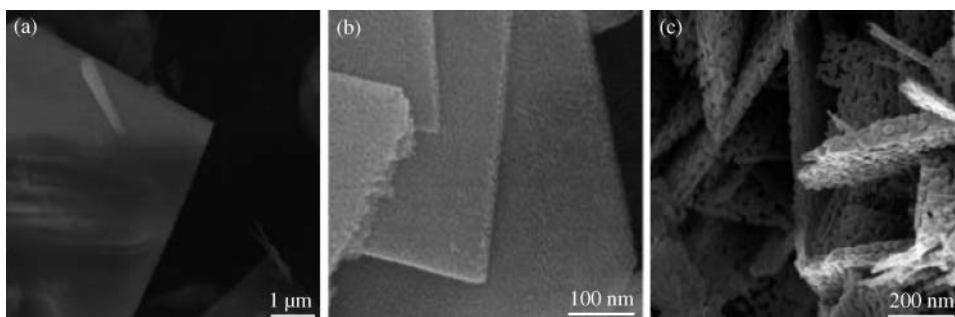


Figure 4. Morphological and structural characterizations of cobalt-basic-carbonate compounds generated under at 140°C for 3 h using urea as mineralizer, and Co_3O_4 nanowires by subsequent calcination: (a) FESEM image of precursor; (b) FESEM image of Co_3O_4 at 350°C for 2 h, (c) FESEM images of Co_3O_4 at 500°C for 2 h.

in Fig. 3 (f), the SAED patterns prove that the Co_3O_4 nanowires is crystal texture. Co_3O_4 nanowires are composed of numerous nanoparticles, with a diameter about 10–20 nm. The porous nature of the Co_3O_4 nanowires is also further confirmed by TEM, which differs from that of the precursors and may greatly increase the surface area of Co_3O_4 nanowires.

From Fig. 4(a), We can see that the precursors are typical nanosheets. The platelet-like precursor was synthesized due to the domination of OH^{-1-} anion at 140°C for 3 h under microwave irradiation. With increasing reaction temperature and time, the urea hydrolysis improved rapidly the pH value of the solution is increased, and then the carbonate anions in the compound are partially substituted by hydroxyl groups [14]. The orientational growing

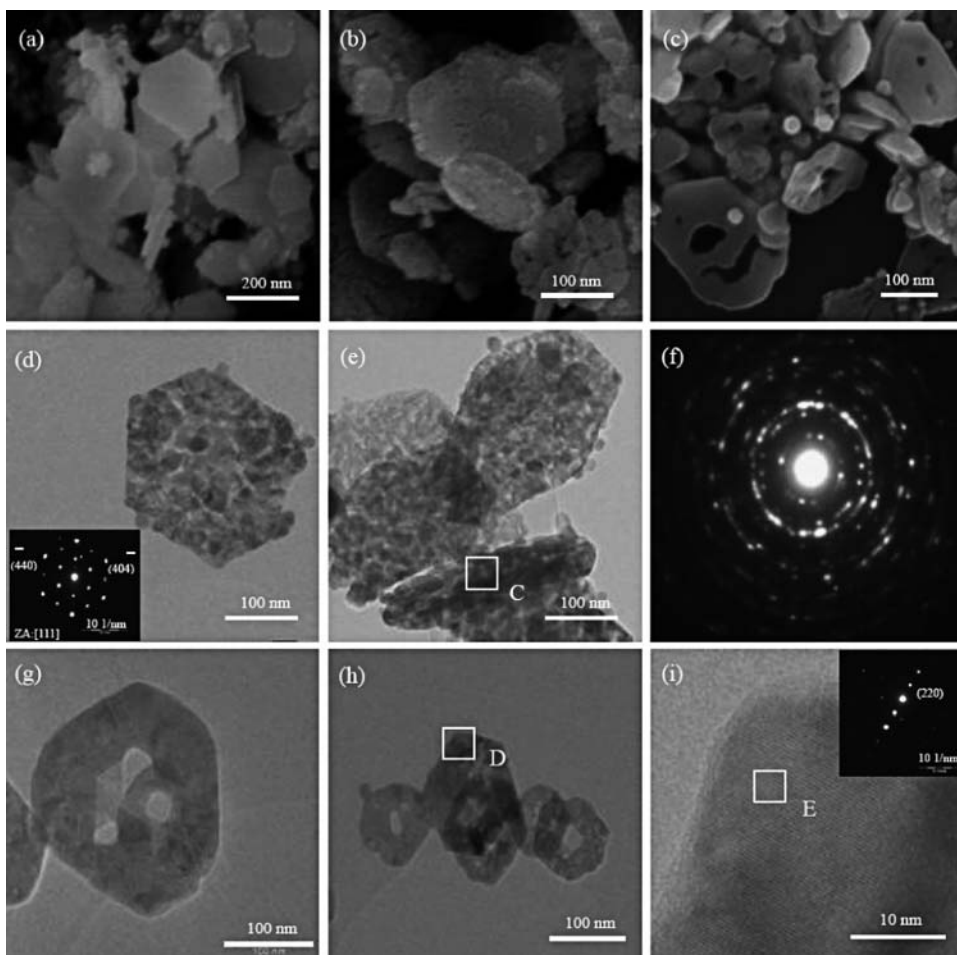


Figure 5. Morphological and structural characterizations of $\beta\text{-Co(OH)}_2$ nanoplatelets generated under 140°C for 3h using potassium hydroxide as mineralizer, and Co_3O_4 nanoplates by subsequent calcination: (a) FESEM image of precursor; (b) FESEM image of Co_3O_4 at 350°C for 2 h, (c) FESEM image of Co_3O_4 at 500°C for 2 h; (d) TEM image of a typical individual hexagonal nanoplatelet, inset is corresponding SAED patterns; (e) TEM image of Co_3O_4 nano nanoplatelets; (f) image of SAED pattern of C; (g) TEM image of a typical individual hexagonal nanoring; (h) TEM image of Co_3O_4 nano nanorings; (i) HRTEM image of Co_3O_4 nanocrystal of corner D, inset is corresponding SAED pattern of E.

tendency of the compound dominated by carbonate anions is weakened at 140°C for 3 h under microwave irradiation, so the initial nanowires aggregate side-by-side and finally form a large platelet. So we can see that, the morphologies of the precursor have a dramatic change with the temperature elevated. Furthermore, compared to Fig. 4 (b) and (c), the Co₃O₄ nanoplatelets calcined at 350°C have relatively small nanoparticles, however the Co₃O₄ nanoplatelets have big nanoparticles when they are calcined at 500°C. Above all, it is very important to synthesize the precursors with some experimental parameters, such as the reaction temperature and the calcination temperature.

From Fig. 5 (a), We can see that most platelets have an approximately hexagonal morphology, which structure enhanced due to high basicity. It is well known that the brucite-like β -Co(OH)₂ has a layered structure comprised of sheets of hexagonally close-packed OH ions with Co(II) bonded to the six OH. The sheets are parallel to the (001) plane. These Co(OH)₂ sheets are bonded to one-another by weak OH-OH dipole interactions. Therefore, brucite crystals have the tendency to grow into thin hexagonal nanoplatelets [15–16]. From Fig. 5 (b) and (c), the Co₃O₄ resultants after the calcinations with a thickness of 20–30 nm and an edge length between 100–200 nm are similar to those of the β -Co(OH)₂ precursor. With increasing the calcination temperature from 350°C to 500°C, the porous Co₃O₄ from hexagonal platelets and then to Co₃O₄ rings.

Figure 5 (d) is a typical hexagonal nanoplatelets, inset it is a SAED pattern, exhibiting the hexagonal structures of brucite-like β -cobalt hydroxides. Figure 5(f) exhibits SAED pattern of C, the Co₃O₄ nanoplatelets have a tendency to polycrystalline in nature. It can be seen from Fig. 5 (d) and (g), the porous vary in size associated with different calcination temperature. The inset in Fig. 5(i) is the corresponding electron diffraction (ED) pattern of the Co₃O₄ platelet. The HRTEM image confirms the Co₃O₄ rings structure with a lattice spacing of 2.8 Å, in accordance with the (220) plane of many Co₃O₄ single nanocrystals. This further reveals that the nanoplatelets grow in an oriented manner to form an integrated porous architecture with interesting combined properties of porosity and quasi-single-crystallinity. The β -Co(OH)₂-to-Co₃O₄ transition is known as a toptactic transformation [17–19]. The hollow nature of the Co₃O₄ ring might be caused by the Kirkendall effect, in which an inward flow of vacancies, balancing the outward transport of fast-moving cations, can condense into voids at the centre of the ring.

4. Conclusions

In summary, we have demonstrated a simple microwave-assisted homogeneous precipitation approach to synthesize cobalt-basic-carbonate compounds and cobalt(II) hydroxide. Furthermore, the dimension and morphology of the synthesized precursor compounds can be tailored due to the change of the incorporated anions (CO₃²⁻ and OH⁻¹) by controlling the temperature and time under microwave irradiation.

With increasing the calcination temperature from 350°C to 500°C, the precursor compounds are transformed into porous samples, such as, the morphology and fabric of samples changes from rods-like precursor to Co₃O₄ nanowires, platelet-like precursor to Co₃O₄ macroporous nanosheets, hexagonal platelet-like precursor to Co₃O₄ porous platelet then to rings.

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