



## Morphology Control of $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Co}_3\text{O}_4$ Microspheres<sup>†</sup>

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$\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres composed of nanorods were firstly prepared through a microwave-assisted homogeneous precipitation reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as a morphology control agent. Then,  $\text{Co}_3\text{O}_4$  microspheres were successfully obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres at 300 °C for 2 h, which preferably preserve the morphology of precursor. The products are characterized by X-ray diffraction, field-emission scanning electron microscopy and UV-visible absorption spectrum.  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres are comprised of numerous short nanorods with diameters of 30-60 nm and lengths of 400-800 nm. A single  $\text{Co}_3\text{O}_4$  microsphere is constructed by nanoparticle-based nanorods and the minimum building block is  $\text{Co}_3\text{O}_4$  nanoparticles with diameters of 20-30 nm. The growth mechanism is simply discussed.

**Key Words:** Microspheres,  $\text{Co}_3\text{O}_4$ , Nanomaterials, Microwave.

### INTRODUCTION

As an important *p*-type semiconductor, cobalt oxide ( $\text{Co}_3\text{O}_4$ ) has potential applications in many fields, such as solid-state sensors<sup>1</sup>, solar energy absorbers<sup>2</sup>, heterogeneous catalysts<sup>3</sup> and lithium-ion batteries<sup>4</sup>. In recent years, various  $\text{Co}_3\text{O}_4$  materials with particular morphology have been synthesized, including nanorods<sup>5</sup>, nanowires<sup>6</sup>, nanocubes<sup>7</sup>, nanotubes<sup>8</sup>, nanospheres<sup>9</sup>, etc. Microwave heating has many advantages, such as rapid volumetric heating, fast reaction rate, short reaction time and energy saving, which has been used as a promising synthetic technology to prepare inorganic nanomaterials. Herein, a convenient and eco-friendly microwave-assisted chemical process was applied to prepare  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}_3\text{O}_4$  microspheres. As a morphology-directed agent,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  successfully controlled the growth of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}_3\text{O}_4$  microspheres. The products are characterized by X-ray diffraction and field-emission scanning electron microscopy. Two band gaps of the prepared  $\text{Co}_3\text{O}_4$  microspheres are estimated to be 1.75 and 2.1 eV according to its optical absorption spectrum.

### EXPERIMENTAL

0.2910 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 40 mL deionized water in a 100 mL beaker. 0.5 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and 20 mL aqueous solution containing 0.2842 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  were successively

added into the above solution under stirring and continue stirring for 15-20 min. Then, the reaction mixture was put into a domestic microwave oven and heated for 10 min at low power grade. After cooling down to room temperature, the obtained light pink precipitate was washed with deionized water for several times and then finally dried in a vacuum at 60 °C for 8 h. The collected powders were signed as sample A. 0.2 g  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres were put into a 30 mL crucible and then transferred into a resistance furnace and heated to 300 °C in air with a ramping rate of 5 °C/min, then calcined at 300 °C for 2 h under ambient pressure. The collected calcined products were signed as sample B.

Microwave-heating was performed by a domestic microwave oven [Galanz D80D23N1P-T7(B0)]. The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Philips X'Pert PRO SUPER X-ray diffractometer. Field-emission scanning electron microscope (FESEM, JSM-6700F) was used to investigate the morphology and microstructure of the obtained products. UV-visible spectrum was studied using a UV-vis spectrophotometer (TU-1800PC).

### RESULTS AND DISCUSSION

Fig. 1 shows typical XRD patterns of sample A and sample B. All the diffraction peaks of the sample A can be indexed to  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  (JCPDS card No. 37-0534). The

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diffraction peaks of the sample B are well indicated to the cubic phase  $\text{Co}_3\text{O}_4$  crystal (JCPDS card No. 42-1467). No diffraction peaks for other impurities are detected, indicating a complete decomposition of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  precursors into pure phase of  $\text{Co}_3\text{O}_4$  after calcination.

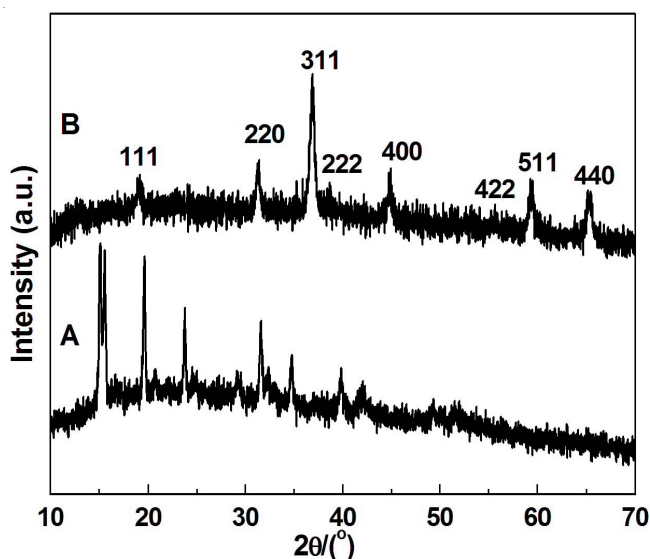


Fig. 1. Typical XRD pattern of Sample A and Sample B

Fig. 2(a) and (b) are the pictures of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  products prepared by a microwave-assisted homogeneous precipitation reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as morphology control agent. The overview field-emission scanning electron microscopy image in Fig. 2(a) reveals that the as-synthesized  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  products are mainly composed of uniformly sphere-like microstructure with diameters ranging from 3  $\mu\text{m}$  to 6  $\mu\text{m}$ . The high-magnification field-emission scanning electron microscopy image in Fig. 2(b) display that these microspheres are rough and loose, self-aggregated by unordered 1D nanostructures. Detailed view on the exterior surface of an individual microsphere (inset in Fig. 2(a)) reveals that the obtained  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres are comprized of numerous short nanorods with diameters of 30-60 nm and lengths of 400-800 nm. The surfaces of these nanorods are relatively smooth.

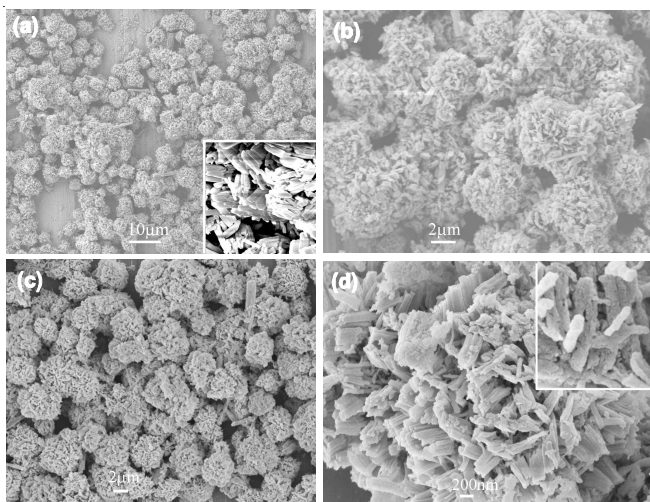


Fig. 2. (a, b)  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres, (c, d)  $\text{Co}_3\text{O}_4$  microspheres

Fig. 2(c) and (d) show the morphologies of  $\text{Co}_3\text{O}_4$  products obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  precursors at 300  $^\circ\text{C}$  for 2 h in air. Fig. 2(c) showed that the prepared  $\text{Co}_3\text{O}_4$  microcrystals still basically retain the sphere-like structure and size of precursors. Fig. 2(d) exhibits a typical  $\text{Co}_3\text{O}_4$  microsphere, which shows the microspheres become more rough and loose after calcinating. According to the inset of Fig. 2(d), we can see that the  $\text{Co}_3\text{O}_4$  microsphere is actually constructed by nanoparticle-based nanorods. The minimum building block is  $\text{Co}_3\text{O}_4$  nanoparticles with diameters of 20-30 nm.

During the process of heat treatment, the morphology and structure of  $\text{Co}_3\text{O}_4$  crystals were greatly affected by calcinated temperature. Fig. 3(a) and 3(b) are the field-emission scanning electron microscopy images of  $\text{Co}_3\text{O}_4$  products obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres at 500  $^\circ\text{C}$  for 2 h in air and simultaneously keeping other conditions unchanged, which indicate that the products are mainly irregular aggregates assembled by nanoparticle-based nanorods. It is suggested that the structure of microspheres is seriously destroyed at higher temperature. In addition, we found that the morphology of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}_3\text{O}_4$  products are greatly affected by the dosage of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . Fig. 3(c) give the picture of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  obtained in 2.0 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  reaction solution, which shows that there are plentiful thick submicrorods with the diameters of 0.2-1.0  $\mu\text{m}$  and not any microspheres are found in the products. The corresponding calcinating  $\text{Co}_3\text{O}_4$  products of Fig. 3(c) at 300  $^\circ\text{C}$  for 2 h are also thick submicrorods [See Fig. 3(d)].

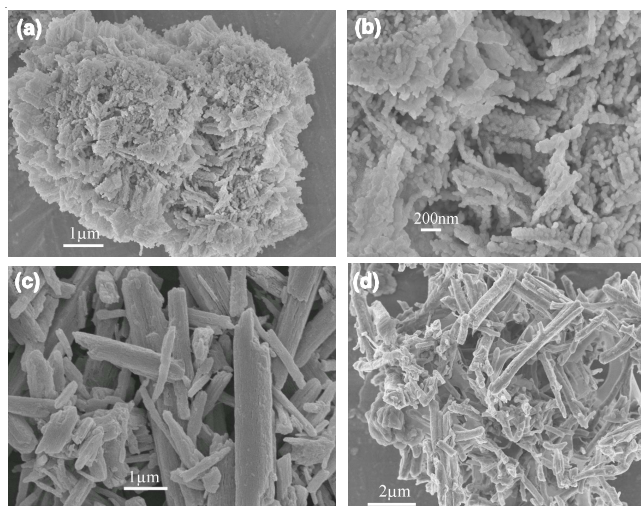
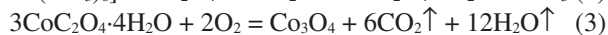


Fig. 3. (a, b)  $\text{Co}_3\text{O}_4$  products obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres at 500  $^\circ\text{C}$  for 2 h, (c, d)  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  obtained using 2.0 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and its corresponding calcinating  $\text{Co}_3\text{O}_4$  product at 300  $^\circ\text{C}$  for 2 h

In the present system, as a morphology control agent, aqueous ammonia was introduced into the reaction system of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . At a proper concentration of aqueous ammonia,  $\text{Co}^{2+}$  react with  $\text{NH}_3$  to form  $[\text{Co}(\text{NH}_3)_6]^{2+}$  complexes.  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  primary nuclei are produced and rapidly developed into nanorods under microwave irradiating. Then, orientated aggregation growth of nanorods along the special lattice face may lead to the formation of  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$

microspheres. Finally,  $\text{Co}_3\text{O}_4$  microspheres are successfully obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres. The related chemical reaction process can be described as follows:



The optical property of  $\text{Co}_3\text{O}_4$  microspheres was detected by UV-VIS absorption spectrum, which is shown in Fig. 4. Three strong peaks located at 275, 481 and 778 nm are clearly observed [Fig. 4(a)], which may be attributed the band gap absorption of the  $\text{Co}_3\text{O}_4$  products. The optical band gap  $E_g$  can be determined by the equation:  $(\alpha h\nu)^n = A(h\nu - E_g)$ , where A is the edge-width parameter,  $h\nu$  is the photon energy and n is 2 for  $\text{Co}_3\text{O}_4$  having a direct band gap<sup>10,11</sup>. Fig. 4(b) is the  $(\alpha h\nu)^n - h\nu$  curve of  $\text{Co}_3\text{O}_4$  microspheres. Two band gaps of the prepared  $\text{Co}_3\text{O}_4$  microspheres are estimated to be 1.75 and 2.1 eV by plotting and extrapolating to zero.

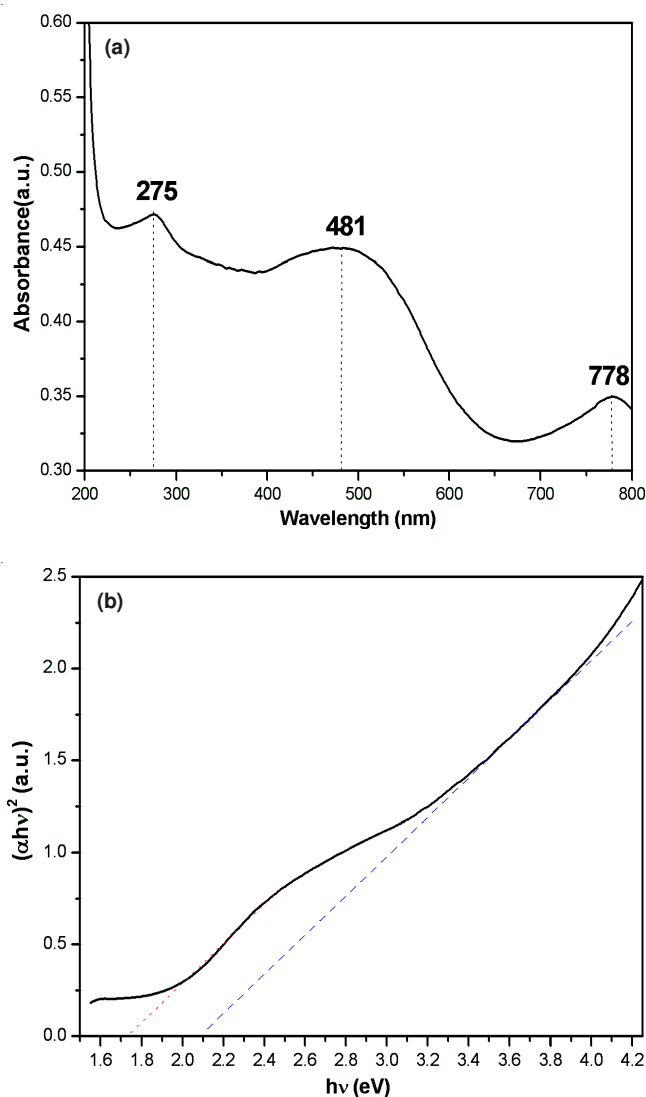


Fig. 4. Optical absorption spectrum (a) and  $(\alpha h\nu)^n - h\nu$  curve (b) of  $\text{Co}_3\text{O}_4$  microspheres

## Conclusion

In summary, a simple and environmental-friendly chemical process has been used to synthesize the  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{Co}_3\text{O}_4$  microspheres. As a morphology-directed agent,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  successfully controlled the growth of microspheres.  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres are comprised of numerous short nanorods with diameters of 30-60 nm and lengths of 400-800 nm.  $\text{Co}_3\text{O}_4$  microspheres were obtained by calcinating  $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  microspheres at 300 °C for 2 h in air. Two band gaps of the prepared  $\text{Co}_3\text{O}_4$  microspheres are estimated to be 1.75 and 2.1 eV according to its optical absorption spectrum.

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