

## Co<sub>3</sub>O<sub>4</sub> 空心球的简易合成及其电化学性能

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**摘要:** 通过简易的水热法“一锅”制备了 Co<sub>3</sub>O<sub>4</sub> 空心球。借助 X 射线衍射仪(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和傅里叶变换红外光谱法(FTIR)等对 Co<sub>3</sub>O<sub>4</sub> 的结构和形貌进行了表征。结果表明, 产物由 Co<sub>3</sub>O<sub>4</sub> 纳米粒子构成, 并形成明显的空心多孔结构。循环伏安法(CV)测试表明, 所制备的 Co<sub>3</sub>O<sub>4</sub> 空心球呈现良好的电化学性能。本文同时对 Co<sub>3</sub>O<sub>4</sub> 空心球结构的形成过程和可能的机理进行了分析和讨论。

**关键词:** 四氧化三钴(Co<sub>3</sub>O<sub>4</sub>); 空心球; 水热法; 电化学性能

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## Simple Fabrication and Electrochemical Properties of Co<sub>3</sub>O<sub>4</sub> Hollow Spheres

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**Abstract:** Co<sub>3</sub>O<sub>4</sub> hollow spheres were hydrothermally prepared at 180 °C by the one-pot method, followed by heating to 550 °C in air. The characteristics of these Co<sub>3</sub>O<sub>4</sub> samples were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy. The results show that the as-synthesized Co<sub>3</sub>O<sub>4</sub> hollow spheres have the porous wall which consists of nanosized particles. The cyclic voltammetry (CV) measurement shows that as-prepared Co<sub>3</sub>O<sub>4</sub> hollow sphere exhibited a good pseudo-capacitance behavior. Moreover, this paper also proposes the possible formation mechanism of Co<sub>3</sub>O<sub>4</sub> hollow spheres synthesized under the one-pot method.

**Key words:** Co<sub>3</sub>O<sub>4</sub>; hollow sphere; hydrothermal; electrochemical properties

In recent years, more and more researchers have focused on hollow spherical structure materials for their potential applications in catalysis, controlled delivery, artificial cells, light fillers, low dielectric constant materials, acoustic insulation, and photonic crystals<sup>[1-4]</sup>. Some reserchers have also presented various synthesis routes to prepare inorganic materials with hollow spherical structures, such as templating method<sup>[5]</sup>, sonochemical method<sup>[6]</sup>, hydrothermal method<sup>[7]</sup> and so on. Among these hollow spherical materials, Co<sub>3</sub>O<sub>4</sub>, one

of the most important transition metal oxides, has attracted extra attention due to their broad range of applications such as magnetic materials, gas sensors, ceramic pigments, catalysts and intercalation compounds for energy storage<sup>[8-15]</sup>. Various Co<sub>3</sub>O<sub>4</sub> nanostructures including nanorods<sup>[16]</sup>, nanoplates<sup>[17]</sup>, nanoflowers<sup>[18]</sup>, nanocubes<sup>[19]</sup> and so forth, have been synthesized by different methods. However, the methods about simple fabrication of Co<sub>3</sub>O<sub>4</sub> hollow spheres are still scarce. Zhao et al.<sup>[20]</sup> have prepared Co<sub>3</sub>O<sub>4</sub> hollow spheres by

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hydrothermal synthesis with glucose as the carbon template source. However, the hydrothermal synthesis process takes too long time. Recently, many researchers pay more attention to furfural as the carbon source<sup>[21-22]</sup>. Furfural is an aromatic aldehyde, with a furan ring structure shown at right and a aldehyde, which make the chemical property of furfural extraordinary active. Another distinctive feature of furfural is its higher carbon content compared with other carbohydrates. These features make furfural an ideal carbon source.

This paper presents an one-pot method of furfural polymerization and in situ ion absorption. This method synthesized precursor microspheres at 180 °C with furfural as carbon template source and cobalt chloride as cobalt source. Co<sub>3</sub>O<sub>4</sub> hollow spheres were prepared by heating the precursor microspheres to 550 °C in air. This method is simple, convenient and of high productivity. This paper also discusses the possible formation mechanism of Co<sub>3</sub>O<sub>4</sub> hollow spheres synthesized under the one-pot method. As an example of applications, the obtained Co<sub>3</sub>O<sub>4</sub> hollow spheres as electrode material showed a good pseudo-capacitance behavior.

## 1 Experimental

### 1.1 Materials

All the chemical reagents used in our experiments were of analytical grade and were used as received without further purification. C<sub>5</sub>H<sub>4</sub>O<sub>2</sub> (furfural) and CoCl<sub>2</sub>·6H<sub>2</sub>O were purchased from Tianjin Damao Chemical Reagent Factory.

### 1.2 Synthesis of Co<sub>3</sub>O<sub>4</sub> hollow spheres

In a typical process of the synthesis of Co<sub>3</sub>O<sub>4</sub> hollow spheres, 1 g of CoCl<sub>2</sub>·6H<sub>2</sub>O was put into 30 mL distilled water to form a homogeneous solution. About 0.8 mL of furfural was added under stirring, resulting in a reddish-brown solution. Subsequently, the obtained solution was placed in 40 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 12, 18, 24 and 30 h, respectively. After that, the autoclave was allowed to cool to room temperature naturally. The products were collected by filtration, centrifuged and washed several times with water and alcohol to remove

impurities, and then dried at 80 °C for 5 h in vacuum. Finally, the products were heated to 550 °C at 2 °C · min<sup>-1</sup> for 3 h using a tube furnace in air.

### 1.3 Characterization

The X-ray powder diffraction (XRD) patterns were recorded on a MSAL-XD2 X-ray diffractometer with Cu K $\alpha$  radiation (36 kV, 20 mA,  $\lambda=0.154\,06\text{ nm}$ ). The morphology observation of the samples was examined with scanning electron microscopy (SEM, Philips XL-30) and transmission electron microscopy (TEM, Philips Tecnai-10). The Fourier transform infrared spectroscopy (FTIR) spectrum was measured by an EQUINOX 55 (Bruker) spectrometer with the KBr pellet technique ranging from 500 to 4 000 cm<sup>-1</sup>. The BET surface area of sample was measured on a Tristar 3000 (Micromeritics) instrument.

### 1.4 Electrochemical measurement

The working electrode was prepared by pressing the mixture of Co<sub>3</sub>O<sub>4</sub>, carbon black and 5% PTFE (75:15:10wt%) into a foam nickel electrode under 35 MPa. All electrochemical measurements were conducted in a standard three electrodes cell on a CHI 660B electrochemical workstation in an aqueous solution of 6 mol · L<sup>-1</sup> KOH. Different sweep rates were employed in cyclic voltammetry within the range of 0.2 to 0.6 V vs Hg/HgO.

## 2 Results and discussion

### 2.1 Phase and morphology of the as-synthesized Co<sub>3</sub>O<sub>4</sub> hollow spheres

The crystal structure of the precursor and as-synthesized product were characterized by X-ray powder diffraction (XRD) and shown in Fig.1. The broad peak, which is of low peak intensity with  $2\theta$  value of 23.5° (Fig.1a), indicates that the precursor are amorphous in nature. After calcined at 550 °C for 3 h, the product exhibits sharp diffraction peaks, shown in Fig.1b. All the diffraction peaks can be perfectly indexed to the crystalline cubic phase Co<sub>3</sub>O<sub>4</sub>. This result is in good agreement with the standard spectrum (JCPDS, No.78-1970). No characteristic peaks of other impurity phases are detected suggests that the product is of high purity.

The FTIR spectrum of the as-synthesized product

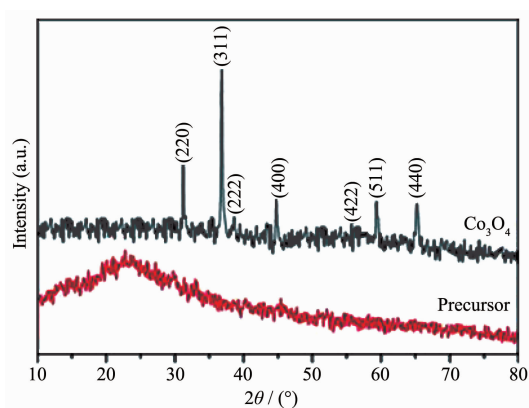


Fig.1 XRD patterns of the amorphous precursor composite (a) and the synthesized spinel  $\text{Co}_3\text{O}_4$  product (b)

is shown in Fig.2. The absorption peaks at 666 and 581  $\text{cm}^{-1}$  confirm the formation of  $\text{Co}_3\text{O}_4$  spinel oxide<sup>[23]</sup>. The broad band centered at 3 430  $\text{cm}^{-1}$  and the peak at 1 633  $\text{cm}^{-1}$  are assigned to the O-H stretching and bending modes of water<sup>[24]</sup>.

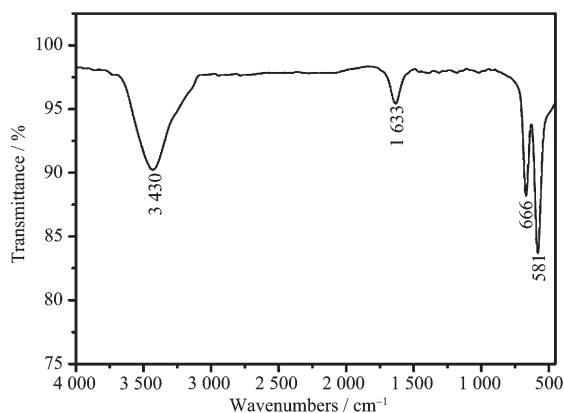


Fig.2 FTIR spectrum of the  $\text{Co}_3\text{O}_4$  product

SEM images of the as-synthesized products and their precursor composite are shown in Fig.3. The precursor is composed of a large amount of uniform microspheres with a diameter of about 5  $\mu\text{m}$ , shown in Fig.3a. The low-magnification and high-magnification SEM images, shown in Fig.3b and c, exhibit the morphologies of the as-synthesized products. Fig.3b shows the spherical morphology of the  $\text{Co}_3\text{O}_4$ , the spheres are nearly monodisperse with rough surface. Both intact and broken hollow spheres are obtained in Fig.3c. The spheres have a diameter of 1~2  $\mu\text{m}$ , which consists of nanosized particles with porous wall. In present work, a hydrothermal time of ~24 h appears to

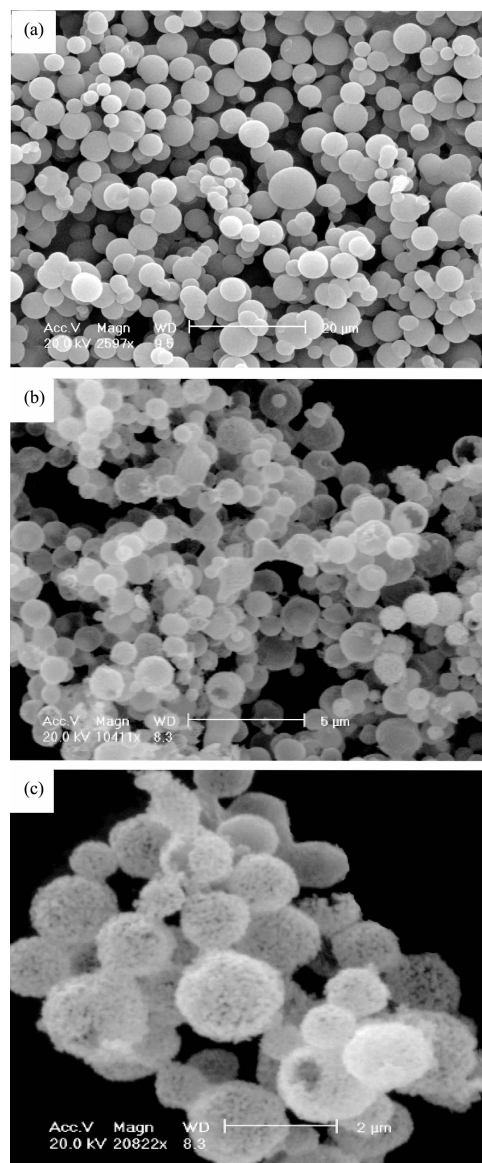
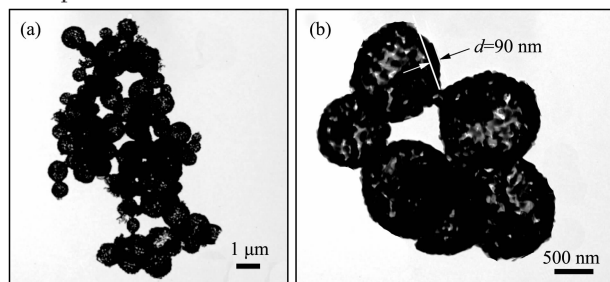


Fig.3 SEM images of the precursor microspheres (a); low-magnification image of  $\text{Co}_3\text{O}_4$  hollow spheres (b) and high-magnification of  $\text{Co}_3\text{O}_4$  hollow spheres (c)

be optimum to give a large fraction of precursor and  $\text{Co}_3\text{O}_4$  hollow spheres.

The low-magnification and high-magnification TEM images of hollow spheres are shown in Fig.4. The low-magnification TEM image, shown in Fig.4a, exhibits the overall morphology of  $\text{Co}_3\text{O}_4$  hollow spheres. The difference between the dark edges and pale centers, is noticeable by comparison of their hollow structures. The high-magnification TEM image, seen in Fig.4b, displays the morphology of hollow sphere with a wall thickness of approximate 90 nm. The

surface roughness leads to an inherent porosity and a high surface area. The BET surface area of the sample is  $57.5 \text{ m}^2 \cdot \text{g}^{-1}$  by calculating from the results of nitrogen adsorption.

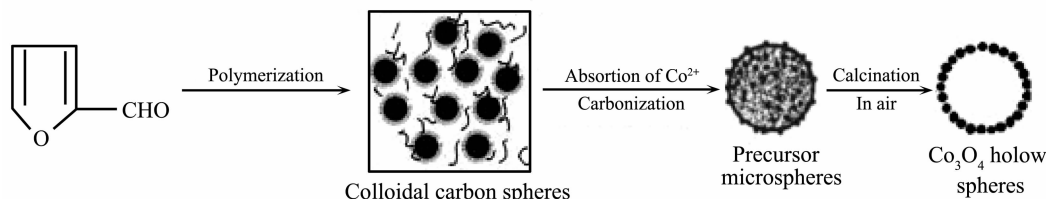


(a) Low-magnification image, (b) High-magnification image

Fig.4 TEM images of the as-obtained products showing the hollow morphology

## 2.2 Growth mechanism of the Co<sub>3</sub>O<sub>4</sub> hollow spheres

The procedure for the synthesis of Co<sub>3</sub>O<sub>4</sub> hollow spheres is illustrated in Scheme 1. The procedure can be divided into two steps: (1) the adsorption of cobalt



Scheme 1 Schematic diagram for the growth process of Co<sub>3</sub>O<sub>4</sub> hollow spheres

## 2.3 Cyclic voltammetry

The Co<sub>3</sub>O<sub>4</sub> hollow spheres sample was used as the electrode material for cyclic voltammetry (CV) measurement. Fig.6 shows the CV curves of Co<sub>3</sub>O<sub>4</sub>

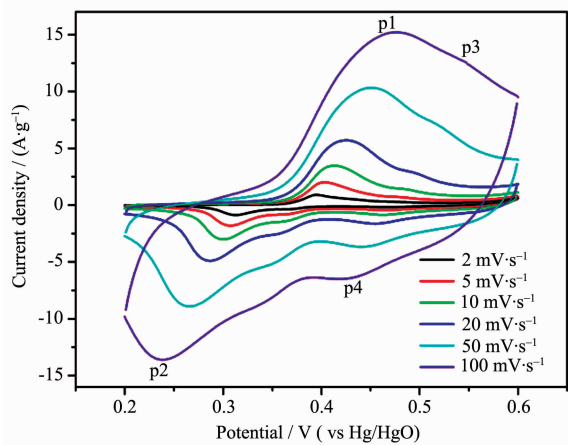


Fig.5 CVs of Co<sub>3</sub>O<sub>4</sub> in  $6 \text{ mol} \cdot \text{L}^{-1}$  KOH at room temperature and different sweep rates

ions; and (2) the growth of Co<sub>3</sub>O<sub>4</sub> hollow spheres. The possible formation mechanism of Co<sub>3</sub>O<sub>4</sub> hollow spheres can be explained as following. Firstly, furfural polymerizes to form colloidal carbon spheres with hydrophilic and reactive surface under hydrothermal condition. Subsequently, the cobalt ions are embedded into the carbon layer during the aromatization and carbonization steps<sup>[20]</sup>, and then precursor microspheres appeared. In the next calcination process, carbon cores are oxidized into CO<sub>2</sub> and gradually removed, Co<sub>3</sub>O<sub>4</sub> nanoparticles spontaneously aggregated and consequently this leads to the formation of Co<sub>3</sub>O<sub>4</sub> hollow spheres. The escaping of CO<sub>2</sub> may account for the breakage of the microspheres. The Co<sub>3</sub>O<sub>4</sub> hollow spheres are robust enough to withstand hyperthermal pretreatment, this may due to the chemical bonds formed between the opposing surfaces of atoms when structurally similar surfaces of Co<sub>3</sub>O<sub>4</sub> nanoparticles approach and imperfectly oriented attached<sup>[25-26]</sup>.

electrode measured in  $6 \text{ mol} \cdot \text{L}^{-1}$  KOH electrolyte at the scan rates of 2 to  $100 \text{ mV} \cdot \text{s}^{-1}$  (versus Hg/HgO). In the potential range of 0.2 to 0.6 V, two pairs of redox reaction peaks (p1/p2 and p3/p4) are visible in the CV curves, indicating that this process is pseudo-reversible and Co<sub>3</sub>O<sub>4</sub> electrode has good pseudo-capacitance performance.

The charge-storage mechanism of Co<sub>3</sub>O<sub>4</sub> for a pseudo-capacitor electrode in alkaline solution has been represented as an invertible oxidation-reduction, which is described by following reaction.



The peak of p1/p2 may be attributed to the redox transition of Co<sup>2+</sup>/Co<sup>3+</sup>, while peak of p3/p4 may be assigned to the redox transition of Co<sup>3+</sup>/Co<sup>4+</sup><sup>[17]</sup>. The discharge specific capacitance can be estimated from the

voltammetric charge surrounded by the CV curves according to the following formula<sup>[27]</sup>:

$$C = \frac{Q}{\Delta V \times w} = \frac{1}{2\Delta V} \int \frac{W}{vw} dI \quad (3)$$

where  $C$  is the specific capacitance of the electrode based on the mass of active materials ( $\text{F} \cdot \text{g}^{-1}$ ),  $Q$  is the sum of anodic and cathodic voltammetric charges on positive and negative sweeps ( $\text{C}$ ),  $I$  is the sample current ( $\text{A}$ ),  $w$  is the weight of active materials ( $\text{g}$ ), and  $\Delta V$  is the total potential deviation of the voltage window ( $\text{V}$ ).  $v$  is the scanning rate ( $\text{V} \cdot \text{s}^{-1}$ ) and  $w$  is the mass of active electrode materials ( $\text{g}$ ). According to formula (1), a maximum discharge specific capacitance of  $182 \text{ F} \cdot \text{g}^{-1}$  is obtained for  $\text{Co}_3\text{O}_4$  electrode at the sweep rate of  $2 \text{ mV} \cdot \text{s}^{-1}$ . Further investigations of the electrochemical properties are in progress.

### 3 Conclusions

This paper presents an one-pot method of furfural polymerization and in situ ion absorption.  $\text{Co}_3\text{O}_4$  hollow spheres were successfully prepared by the hydrothermal route. The XRD, FTIR, SEM and TEM revealed the hollow spherical structures. The results show that the as-synthesized  $\text{Co}_3\text{O}_4$  hollow spheres have the porous wall which consists of nanosized particles. The possible formation mechanism on  $\text{Co}_3\text{O}_4$  hollow spheres is also presented in this paper. This one-pot method may be extended to the preparation of various metal oxide hollow spheres. Moreover, cyclic voltammetry measurement shows that the as-prepared  $\text{Co}_3\text{O}_4$  hollow spheres electrode exhibited a good pseudo-capacitance behavior with the discharge specific capacitance of  $182 \text{ F} \cdot \text{g}^{-1}$ .

### References:

- [1] Caruso F, Caruso R A, Mhwal H. *Science*, **1998**, **282**:1111-1114
- [2] Zhong Z, Yin Y, Gates B, et al. *Adv. Mater.*, **2000**, **12**:206-209
- [3] Caruso F. *Adv. Mater.*, **2001**, **13**:11-12
- [4] HE Jun-Hui(贺军辉), CHEN Hong-Min(陈洪敏), ZHANG Lin(张林). *Prog. Chem.(Huaxue Jinzhan)*, **2007**, **19**(10):1488-1494
- [5] Caruso F. *Chem. Eur. J.*, **2000**, **6**:413-416
- [6] Zhu J J, Xu S, Wang H, et al. *Adv. Mater.*, **2003**, **15**:156-159
- [7] Wang C, Tang K, Yang Q, et al. *J. Mater. Chem.*, **2002**, **12**:2426-2429
- [8] Pal J, Chauhan P. *Mater. Charact.*, **2010**, **61**:575-579
- [9] Choia K I, Kima H R, Kima K M, et al. *Sens. Actuators B*, **2010**, **146**:183-189
- [10] Poizat P, Laruelle S, Grugeon S, et al. *Nature*, **2000**, **407**:496-499
- [11] Sugimoto T, Matijevic E. *J. Inorg. Nucl. Chem.*, **1979**, **41**:165-172
- [12] Xu R, Zeng H C. *J. Phys. Chem. B*, **2003**, **107**:926-930
- [13] Feng J, Zeng H C. *Chem. Mater.*, **2003**, **15**:2829-2835
- [14] Li W Y, Xu L N. *J. Chem. Adv. Funct. Mater.*, **2005**, **15**:851-857
- [15] Maruyama T, Arai S. *J. Electrochem. Soc.*, **1996**, **143**:1383-1386
- [16] HUANG Qing-Li(黄庆利), CHEN Hu(陈虎), ZHANG Yong-Cai(张永才). *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2010**, **26**(8):1394-1398
- [17] ZHANG Fang(张防), HAO Liang(郝亮), FU Qing-Bin(傅清宾), et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2010**, **26**(5):827-831
- [18] Zhang Y G, Chen Y C, Wang T, et al. *Microporous Mesoporous Mater.*, **2008**, **114**:257-261
- [19] HUANG Ke-Long(黄可龙), ZENG Wen-Wen(曾雯雯), YANG You-Ping(杨幼平) et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2007**, **23**(9):1555-1560
- [20] Zhao W W, Liu Y, Li H L, et al. *Mater. Lett.*, **2008**, **62**:772-774
- [21] Xing L, Qiu J S, Liang C H, et al. *J. Catal.*, **2007**, **250**:369-372
- [22] Liang X Z, Zeng M F, Qi C Z. *Carbon*, **2010**, **48**:1844-1848
- [23] Gaddsdén J A. *Infrared Spectra of Minerals and Related Inorganic Compounds*. London: Butterworth, **1975**:44
- [24] Nakamoto K, Translated by HUANG De-Ru(黄德如), WANG Ren-Qing(汪仁庆), LIAO Dai-Wei(廖代伟). *Infrared and Raman Spectra of Inorganic and Coordination Compounds(无机和配位化合物的红外和拉曼光谱)*. Beijing: Chemical Industry Press, **1991**:251
- [25] Cui Y M, Liu L, Chen Y, et al. *Solid State Sciences*, **2010**, **12**:232-237
- [26] Penn R L, Banfield J F. *Science*, **1998**, **281**:969-971
- [27] Hu C C, Tson T W. *J. Power Sources*, **2003**, **115**:179-186