

## 胶质碳球为模板制备 NiO 空心球

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**摘要:** 以胶质碳球为模板、六亚甲基四胺为沉淀剂, 在乙醇中溶剂热反应, 再经 500 °C 煅烧 6 h 制备了 NiO 空心球。通过 X 射线衍射(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)、傅里叶变换红外光谱(FTIR)和低温氮吸附-脱附, 对 NiO 的结构和形貌进行了表征。结果表明溶剂热反应时间是制备完整 NiO 空心球的关键因素, 溶剂热反应 12 h, 再经空气中煅烧, 可制得形貌均一的 NiO 空心球。所得产物是由 NiO 纳米粒子组装而成的具有多孔结构的空心球。同时, 本文对 NiO 空心球结构的形成过程和可能机理进行了分析和讨论。

**关键词:** 氧化镍(NiO); 空心球; 胶质碳球; 溶剂热

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## Synthesis of NiO Hollow Spheres Using Colloidal Carbon Spheres as Template

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**Abstract:** NiO hollow spheres were synthesized by a solvothermal reaction using colloidal carbon spheres (CCS) as sacrificial template and hexamethylenetetramine (HMT) as precipitating agent in ethanol, and then calcined at 500 °C for 6 h. The characteristics of these NiO hollow spheres samples were characterized by XRD, SEM, TEM, FTIR and low temperature nitrogen adsorption-desorption isotherms. The results show that solvothermal reaction time is crucial to the integrity of the hollow spheres. The well defined NiO hollow spheres can be synthesized through 12 h solvothermal treatment and then calcination in air. The as-synthesized NiO hollow spheres have the porous wall consisted of nanosized particles. Moreover, the formation mechanism of NiO hollow spheres is also discussed.

**Key words:** NiO; hollow spheres; colloidal carbon spheres; solvothermal

In recent years, nano- or micro-sized materials with hollow interiors have attracted increasing attention owing to their special structures and promising applications in photonic crystal, catalysis, drug delivery, chemical sensors, chromatography, and waste removal<sup>[1-4]</sup>. Several efforts have been devoted to the synthesis of hollow oxides utilizing templating method<sup>[5]</sup>, sonochemical method<sup>[6]</sup>, hydrothermal method<sup>[7]</sup> and so on. The templates can be of different types, including

silica<sup>[8]</sup>, emulsions<sup>[9]</sup>, reverse micelles<sup>[10]</sup>, biological gelatin<sup>[11]</sup>, polystyrene<sup>[12]</sup>, beeswax<sup>[13]</sup>, and even gas bubbles<sup>[14]</sup>. Among them, colloidal carbon spheres prepared by a hydrothermal method using glucose as the starting material by Li and co-workers<sup>[15]</sup> have drawn much attention as a novel template. There are hydrophilic and rich groups and micropores on the surface of those colloidal carbon spheres, which can facilitate the precipitation of metal precursors and thus

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result in the formation of hollow spheres after the removal of carbon. They can be used to synthesize hollow structures of a variety of materials, such as  $\text{TiO}_2$ <sup>[16]</sup>,  $\text{ZrO}_2$ <sup>[17]</sup>,  $\text{CeO}_2$ <sup>[18]</sup>,  $\text{Fe}_2\text{O}_3$ <sup>[19]</sup>.

NiO has received extensive attention because of its potential applications in various fields, such as catalysis<sup>[20]</sup>, battery cathodes<sup>[21]</sup>, gas sensors<sup>[22]</sup>, electrochromic films<sup>[23]</sup>, and fuel cell electrodes<sup>[24]</sup>. Various NiO nanostructures including nanoplates<sup>[25]</sup>, nanoparticles<sup>[26]</sup>, nanorods<sup>[27]</sup>, nanosheets<sup>[28]</sup>, nanowires<sup>[29]</sup>, nanotubes<sup>[21]</sup>, and hollow nanospheres<sup>[30]</sup>, have been synthesized by different methods. However, there are few reports about NiO microspheres via solvothermal method using colloidal carbon spheres as sacrificial template<sup>[31]</sup>. Herein, we report a facile method of synthesizing NiO hollow spheres with colloidal carbon spheres as template via a solvothermal route. Hexamethylenetetramine was adopted to slowly yield  $\text{OH}^-$  so as to obtain  $\text{Ni}(\text{OH})_2$  coating surrounding the spherical carbon core, and NiO hollow spheres subsequently can be gained by a calcination process.

## 1 Experimental

### 1.1 Materials

All the chemical reagents used were of analytical grade and used as received without further purification. Factory glucose,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and hexamethylenetetramine were purchased from Tianjin Damao Chemical Reagent Factory.

### 1.2 Synthesis of colloidal carbon spheres

In a typical procedure, 5 g glucose was dissolved in 30 mL water to form a clear solution, which was placed in a 50 mL Teflon lined autoclave and maintained at 180 °C for 12 h. The black or puce products were isolated by centrifugation, washed with water and absolute alcohol for three times, and then oven-dried at 80 °C for 8 h.

### 1.3 Synthesis of NiO hollow spheres

0.5 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 40 mL ethanol to form a clear solution under stirring. Then 0.2 g as-prepared colloidal carbon spheres were added and well dispersed into the above solution with the assistance of sonication for 30 min. After thorough

stirring, 0.5 g HMT was added to the solution and then transferred to a 50 mL autoclave with a Teflon seal. After maintained at 100 °C for 2~24 h, a resulting puce precipitate was centrifuged, and then washed with distilled water and alcohol respectively for three times. The composite was dried at 80 °C for 8 h, and finally calcined in air at 500 °C for 6 h.

### 1.4 Characterization

The phase structures of the products were analyzed by powder X-ray diffraction using a Bruker AXS D8 Focus X-ray diffraction (Cu target, working voltage 40 kV, working current 40 mA,  $\lambda = 0.15418$  nm, slit: 1.0 mm, scanning step length  $0.01^\circ$ , scanning speed  $4^\circ \cdot \text{min}^{-1}$ , scanning angle from  $10^\circ$  to  $90^\circ$ ). Morphologies of the products were measured by scanning electron microscopy (SEM, Philips XL-30, at an accelerating voltage of 20 kV) and transmission electron microscopy (TEM, Philips Tecnai-10, at an accelerating voltage of 100 kV). The Fourier transform infrared spectroscopy (FTIR) spectrum was measured by an EQUINOX 55 (Bruker) spectrometer with the KBr pellet technique ranging from 400 to 4000  $\text{cm}^{-1}$ . The specific surface areas and pore size distribution of NiO hollow spheres were measured by the Micromeritics TriStar 3000 Analyzer.

## 2 Results and discussion

### 2.1 Morphology and phase structure of the as-synthesized NiO hollow spheres

The XRD pattern of the colloidal carbon spheres is presented in Fig.1a. The broad peak, which is of low peak intensity with  $2\theta$  value of  $22.3^\circ$  (Fig.1a), indicates that the colloidal carbon spheres are amorphous in nature. Fig.1b shows the XRD pattern of  $\text{C@Ni}(\text{OH})_2$  sample synthesized in autoclave at 100 °C for 12 h. The broad and low intensity peaks at  $22.3^\circ$  are produced by the disordered carbon. The diffraction peaks at  $33.5^\circ$ ,  $38.4^\circ$  and  $59.8^\circ$  of  $2\theta$  are corresponding to the (100), (011) and (003) planes, respectively, which can be indexed to hexagonal  $\text{Ni}(\text{OH})_2$  phase, and these results are in agreement with the data of PDF No. 74-2075. Fig.1c shows the XRD pattern of NiO hollow spheres after calcination of  $\text{C@Ni}(\text{OH})_2$  core-shell microspheres

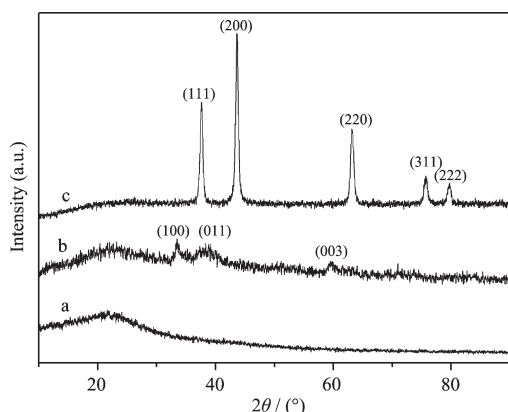


Fig.1 XRD patterns (a) colloidal carbon spheres, (b) C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in autoclave at 100 °C for 12 h, and (c) NiO hollow spheres after calcining C@Ni(OH)<sub>2</sub> core-shell microspheres (b) at 500 °C for 6 h

(synthesized in autoclave at 100 °C for 12 h) at 500 °C for 6 h. The diffraction peaks at 37.6°, 43.5°, 63.2°, 75.8° and 79.8° of  $2\theta$  are corresponding to the (111), (200), (220), (311) and (222) planes, respectively, which can be indexed perfectly to cubic NiO phase. These results are in good agreement with the data of PDF No. 78-0643. No characteristic peaks of other impurity phases are detected suggests that the product is of high purity.

The surface functional groups of the as-synthesized carbon colloidal spheres, C@Ni(OH)<sub>2</sub> core-shell microspheres, and NiO hollow spheres were examined by FTIR spectroscopy. As shown in Fig.2a, the results

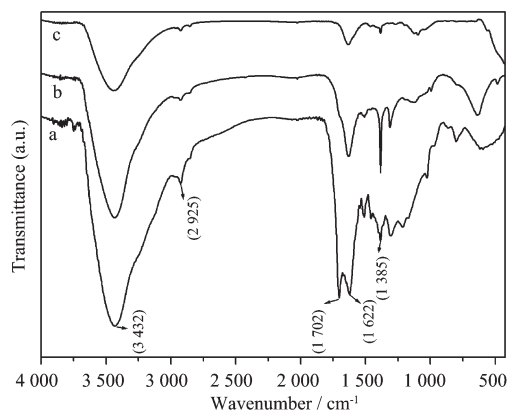


Fig.2 FTIR spectrum of (a) colloidal carbon spheres, (b) C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in autoclave at 100 °C for 12 h, and (c) NiO hollow spheres after calcining C@Ni(OH)<sub>2</sub> core-shell microspheres (b) at 500 °C for 6 h

indicate that the surface of the colloidal carbon spheres is hydrophilic and functionalized with OH and C=O groups. A stretching band of hydrogen bonded OH group is seen at 3432 cm<sup>-1</sup> from the absorbed OH groups and H<sub>2</sub>O in air. The bands at 1702 and 1622 cm<sup>-1</sup> are attributed to C=O and C=C vibrations, respectively. The bands in the range 1000~1500 cm<sup>-1</sup>, which include the C-OH stretching and OH bending vibrations, imply the existence of large numbers of residual hydroxyl groups. These functional groups provide a potential avenue to load other functional groups, molecules, ions, or nanoparticles to fabricate other core-shell or hollow structures. After the surface reaction with Ni(OH)<sub>2</sub>, the obvious change of the peaks of the C=O (shown in spectrum (b) in Fig.2) suggests that the nickel ions are coordinated with the oxygen atom from the functional groups. Additionally, the basic character of Ni(OH)<sub>2</sub> results in the adsorption of atmospheric CO<sub>2</sub>, and therefore the presence of carbonate anions on their surface could not be avoided, as suggested from the small peak (broad) at 1385 cm<sup>-1</sup>. Further calcination leads to the formation of pure NiO hollow spheres with few organic groups as seen in Fig.2 (spectrum c).

The NiO hollow spheres have the porous wall consisted of nanosized particles. Specific surface area measurement reveals that the surface area for porous NiO hollow spheres was 28 m<sup>2</sup>·g<sup>-1</sup> (Fig.3). The pore size distribution for NiO hollow spheres (inset in Fig.3)

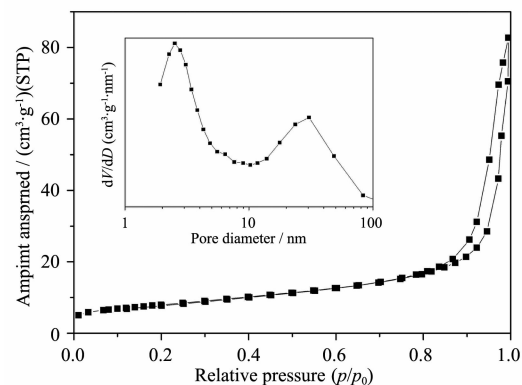


Fig.3 Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of NiO hollow spheres after calcining C@Ni(OH)<sub>2</sub> core-shell microspheres (synthesized in autoclave at 100 °C for 12 h) at 500 °C for 6 h

indicates bimodal pore size distribution in the mesoporous and macroporous region with a maximum peak pore diameter of ca. 2.5 nm.

Representative SEM and TEM images of the colloidal carbon spheres template are shown in Fig.4a and b, respectively. The as-prepared colloidal carbon spheres have an average diameter of 350~550 nm. Fig.4c~f shows SEM and TEM images of C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in autoclave at 100 °C for 12 h, which exhibits a core-shell structure clearly. After the formation of the shell, the surface of the microspheres gradually evolves from smooth one to rough one as the Ni(OH)<sub>2</sub> forms. After the formation of the shell, the spherical core-shell structure grows

larger than the bare colloidal carbon spheres. From these images, we could estimate that the core-shell microsphere diameter, the shell thickness, and the core size are about 650 nm, 75 nm, and 500 nm, respectively. Fig.5 shows some typical NiO hollow spheres after the removal of carbon templates by a calcination process. The average diameter of these hollow spheres is 400~500 nm, roughly smaller than the starting sphere due to the structural shrinkage during the removal process of the template. In addition, it is believed some shrinkage is caused by a process of the dehydration of the more loosely cross-linked shell structure ( $\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}$ ) surrounding the colloidal carbon spheres.

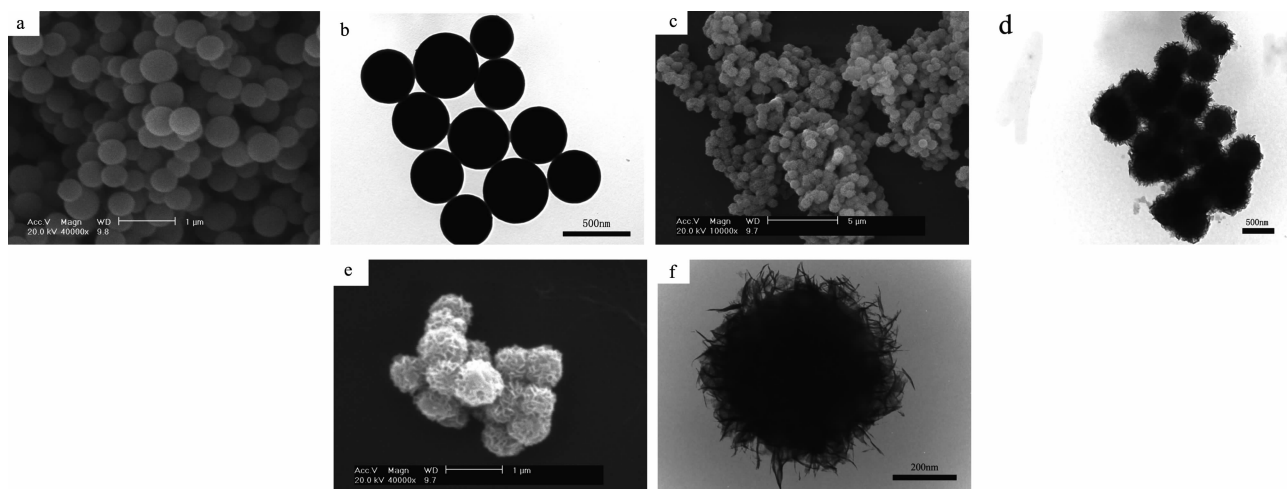


Fig.4 (a) SEM and (d) TEM image of colloidal carbon spheres template, (c,e) SEM and (d,f) TEM image of C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in autoclave at 100 °C for 12 h

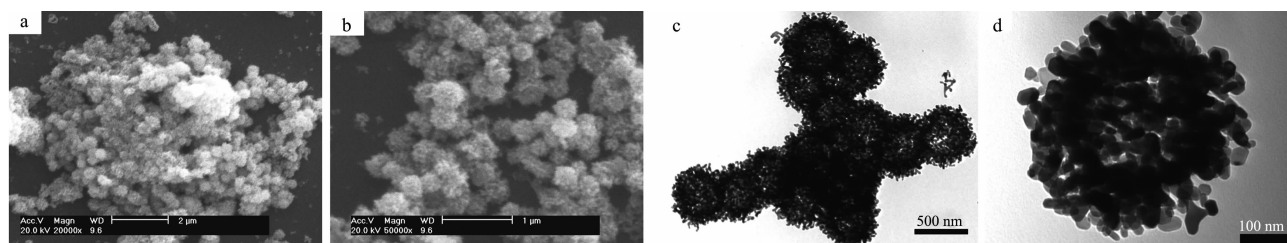


Fig.5 (a~b) SEM and (c~d) TEM image of NiO hollow spheres after calcining C@Ni(OH)<sub>2</sub> core-shell microspheres (synthesized in autoclave at 100 °C for 12 h) at 500 °C for 6 h

## 2.2 Effect of solvothermal time on the NiO hollow spheres

To investigate the influence of solvothermal time on the morphology of the NiO hollow spheres, controlled experiments were conducted. Fig.6 shows TEM images of C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in

autoclave at 100 °C for different solvothermal times and their corresponding calcined samples at 500 °C for 6 h. It can be seen that the shell thickness increases obviously with the increase of solvothermal time. The longer the solvothermal time is, the thicker of the C@Ni(OH)<sub>2</sub> core-shell microspheres is. After a calcination

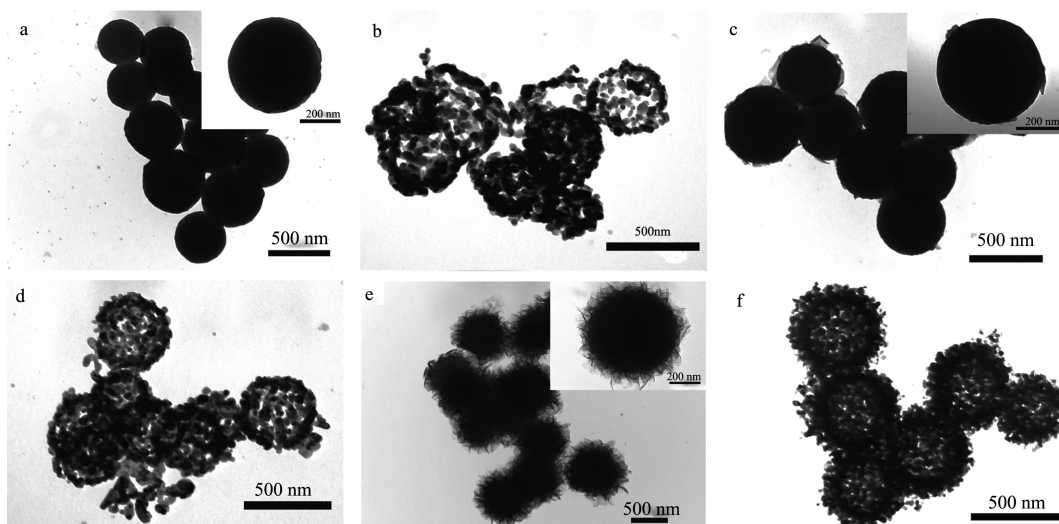


Fig.6 TEM images of C@Ni(OH)<sub>2</sub> core-shell microspheres synthesized in autoclave at 100 °C for different solvothermal times: (a) 2 h, (c) 6 h, and (e) 24 h; and their corresponding calcined samples at 500 °C for 6 h: (b) 2 h, (d) 6 h, and (f) 24 h

process, the more complete of the NiO hollow spheres is formed. When the solvothermal time is shorter than 12 h, the shell thickness of C@Ni(OH)<sub>2</sub> core-shell microspheres is very thin (Fig.6a and c), and they can not achieve uniform hollow spheres (Fig.6b and d). However, when the solvothermal time is more than 12 h, the shell walls and the size of NiO hollow spheres is no longer increases (Fig.6f). It can be concluded from the above results that the integrity of shell walls of NiO hollow spheres could be easily controlled by tuning the solvothermal time, which is a significant approach for the formation of the crystallized Ni(OH)<sub>2</sub> shell.

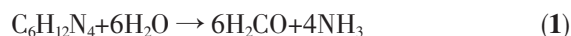
### 2.3 Growth mechanism of the NiO hollow spheres

The formation of NiO hollow spheres probably involves three steps (Scheme 1):

(1) The absorption of nickel ions from solution into the CCS's surface layer because the surface of colloidal carbon spheres is hydrophilic and contains a large amount of OH and C=O groups.

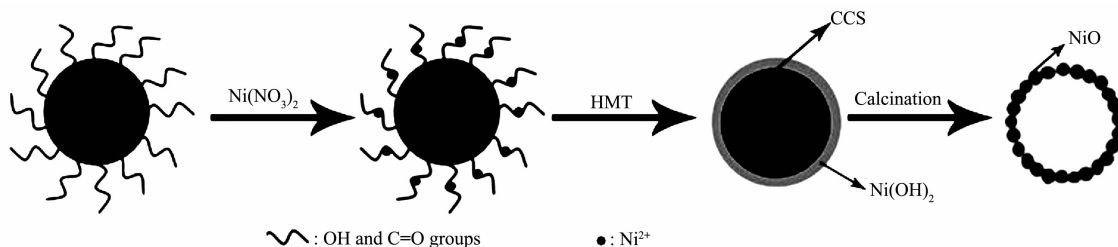
(2) During solvothermal precipitation, HMT

hydrolyzes gradually at a mild temperature (100 °C), which generates an alkaline environment. Therefore, Ni(OH)<sub>2</sub> deposits onto the surface of colloidal carbon spheres to form a condensed Ni(OH)<sub>2</sub> phase (Fig.1b, and Fig.4c~f). From these results, the possible reaction during the whole process is presented as follows:



In addition, the presence of abundant ethanol in the reaction system should reduce the polarity of the solvent, which can enhance the nickel ions to deposit on the surface of the templates and form compact Ni(OH)<sub>2</sub><sup>[19]</sup>.

(3) During the calcination step, the reaction (Ni(OH)<sub>2</sub> → NiO + H<sub>2</sub>O) occurs and results in the decomposition of amorphous Ni(OH)<sub>2</sub> layers while the carbon templates are oxidized into gaseous carbon oxides and gradually removed. The NiO primary particles grow into larger ones, aggregation or probably the epitaxial growth



Scheme 1 Schematic illustration of the formation process of NiO hollow spheres



occurs, and then leads to the interconnecting of the NiO nanoparticles to form NiO hollow spheres (Fig.1c, and Fig.5).

### 3 Conclusions

NiO hollow spheres were prepared by coating Ni(OH)<sub>2</sub> on the surface of colloidal carbon spheres via solvothermal method, followed by the calcination of the carbon spheres and dehydration of Ni(OH)<sub>2</sub> layers. The shell thickness of C@Ni(OH)<sub>2</sub> core-shell microspheres could be slightly tuned by changing the solvothermal time. By increasing the solvothermal time, the shell thickness slightly increases. To achieve uniform NiO hollow spheres, the solvothermal time has to be 12 h and the calcination temperature should be at 500 °C in air.

### References:

- [1] Zhong Z, Yin Y, Gates B, et al. *Adv. Mater.*, **2000**,**12**:206-209
- [2] Caruso F. *Adv. Mater.*, **2001**,**13**:11-12
- [3] Wu C Z, Xie Y, Lei L Y, et al. *Adv. Mater.*, **2006**,**18**:1727-1732
- [4] HE Jun-Hui(贺军辉), CHEN Hong-Min(陈洪敏), ZHANG Lin(张林). *Progress in Chemistry (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] Salgueirino-Maceira V, Spasova M, Farle M. *Adv. Funct. Mater.*, **2005**,**15**:1036-1040
- [9] Lu W, Chen M, Wu L M. *J. Colloid Interface Sci.*, **2008**,**324**:220-224
- [10] Cong Y H, Wang G L, Xiong M H, et al. *Langmuir*, **2008**,**24**:6624-6629
- [11] Huang C C, Liu T Y, Su C H, et al. *Chem. Mater.*, **2008**,**20**:3840-3848
- [12] Kondo Y, Yoshikawa H, Awaga K, et al. *Langmuir*, **2008**,**24**:547-550
- [13] Wang Z X, Chen M, Wu L M. *Chem. Mater.*, **2008**,**20**:3251-3253
- [14] Yang J H, Sasaki T. *Chem. Mater.*, **2008**,**20**:2049-2056
- [15] Sun X M, Li Y D. *Angew. Chem. Int. Ed.*, **2004**,**43**:597-601
- [16] Yu J, Wang G. *J. Phys. Chem. Solids*, **2008**,**69**:1147-1152
- [17] Guo C Y, Hu P, Yuan F L, et al. *Mater. Lett.*, **2009**,**63**:1013-1015
- [18] Li X Z, Chen F, Lu X W, et al. *J. Porous Mater.*, **2010**,**17**:297-303
- [19] Yu J G, Yu X X, Huang B B, et al. *Cryst. Growth Des.*, **2009**,**9**:1474-1480
- [20] Gondal M A, Sayeed M N. *J. Hazard. Mater.*, **2008**,**155**:83-89
- [21] Needham S A, Wang G X, Liu H K. *J. Power Sources*, **2006**,**159**:254-257
- [22] Hotovy I, Rehacek V, Siciliano P, et al. *Thin Solid Films*, **2002**,**418**:9-15
- [23] Li F, Chen H Y, Wang C M, et al. *J. Electroanal. Chem.*, **2002**,**531**:53-61
- [24] Niklasson G A, Granqvist C G. *J. Mater. Chem.*, **2007**,**17**:127-156
- [25] Wang X, Li L, Zhang Y G, et al. *Cryst. Growth Des.*, **2006**,**6**:2163-2166
- [26] Lai T L, Shu Y Y, Wang C B, et al. *J. Alloys Compd.*, **2008**,**450**:318-322
- [27] Xu C K, Xu G D, Wang G H. *J. Mater. Sci.*, **2003**,**38**:779-782
- [28] Liang Z H, Zhu Y J, Hu X L. *J. Phys. Chem. B*, **2004**,**108**:3488-3491
- [29] Wu Z Y, Liu C M, Guo L, et al. *J. Phys. Chem. B*, **2005**,**109**:2512-2515
- [30] Zhang M, Yan G J, Hou Y G, et al. *J. Solid State Chem.*, **2009**,**182**:1206-1210
- [31] Zheng J, Wu B H, Jiang Z J, et al. *Chemistry, An Asian Journal*, **2010**,**5**:1439-1444