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水浴法制备蝴蝶状的微结构 CuO

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摘要:以硝酸铜为铜源,六次甲基四胺为有机碱,去离子水为溶剂,采用简捷水浴加热技术控制合成了由三角纳米片组成的蝴蝶状微结构 CuO。产品的组成和形貌用 XRD、EDX、场发射扫描电镜(FESEM)、TEM、HRTEM 和选区电子衍射(SAED)进行了表征。结果表明 CuO 的形貌主要受六次甲基四胺用量的影响。随着其用量的增加,CuO 的形貌经历了飞鱼状–蝴蝶状–牡丹状的递变。并对蝴蝶状 CuO 微结构的形成机制及形貌的演变进行了探讨。

关键词:氧化铜;微结构;晶体生长;水浴技术

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Preparation of Butterfly-Like CuO Microstructure via Water Bath Method

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Abstract: Butterfly-like CuO microstructures composed of triangular nanosheets were controllably synthesized via a water bath heating technique using copper nitrate ($Cu(NO_3)_2$) as copper source, hexamethylene tetramine ($C_6H_{12}N_4$) as organic base and deionized water as solvent. The crystal structure, composition and morphology of the as-prepared products were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDX), field-emission scanning electron microscopy (FESEM), transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM) and selected area electronic diffraction (SAED). The results show that the morphology of CuO crystals is greatly affected by the dosage of $C_6H_{12}N_4$. With the increase in the concentration of $C_6H_{12}N_4$, the morphology of CuO is changed from flyingfish-like, via butterfly-like, to peony-like microstructure. The formation mechanism of butterfly-like CuO microstructure and the evolution of morphology are discussed.

Key words: copper oxide; microstructure; crystal growth; water bath technique

0 Introduction

Recently, many efforts have been focused on controlled organization of primary building units into organized and designed hierarchical structures because of their novel and useful physical properties different from bulk or discrete counterparts[1-3]. Therefore, it is of great interest for chemists and material scientists to

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controllably prepare hierarchical microstructures with specific morphology[4-6].

As an important p-type transition-metal-oxide semiconductor with a narrow band gap (1.2 eV), CuO has attracted a great deal of attention owing to their important applications, such as gas sensors[7], magnetic storage media[8], heterogeneous catalysts[9], superconductors[10], lithium ion electrode materials[11]. Many approaches have been developed to prepare CuO nanomaterials with various morphologies. Ren et al.[12] prepared pricky star-like CuO by the hydrothermal route in the presence of cationic gemini surfactant. Wang et al.[13] synthesized CuO hollow microspheres through hydrothermal method in the presence of CTAB. Heng et al.[14] prepared CuO with various morphologies (rod-shaped, spherical, shuttle-shaped and starfruit-like) using sonochemical and microwave-hydrothermal technique. Li et al.[15] synthesized well-aligned CuO nanostructured arrays via a conveninent one-step route by adjusting the reaction temperature. Yin et al.[16] prepared 1D CuO nanorods by the coupling microemulsion method with homogeneous precipitation. Li et al.[17] fabricated urchin-like CuO core-shell structure through a PEG-assisted hydrothermal route. Chen et al.[18] synthesized mesoporous CuO via thermal decomposition of CuC_2O_4 precursors. Liu et al.[19] prepared CuO nanofibers by decomposing $Cu(OH)_2$ using a dielectric-barrier discharge plasma. Deng et al.[20] synthesized cocoon shaped CuO hollow nanostructure by a green and facile microwave-assisted aqueous process. Allam et al.[21] obtained various CuO nanostructures by electrochemical technique. Even though the reported synthetic methods have been proven to be the successful ways to fabricate CuO with controlled morphologies, complicated synthetic procedures are still involved, such as special equipment, high temperature, and post removal of the surfactants. Therefore, further development of a facile, low temperature and template-free synthetic method is quite necessary.

Herein, a facile water bath heating route was developed to fabricate butterfly-like CuO microstructures composed of triangular nanosheets on a large scale. This method is simple and green, it does not need high reaction temperature and long reaction time. The morphology of CuO crystals are greatly affected by the dosage of $C_6H_{12}N_4$. With the increase in the concentration of $C_6H_{12}N_4$, the morphology of CuO is changed from flyingfish-like, via butterfly-like, to peony-like microstructure.

1 Experimental

1.1 Preparation of the butterfly-like CuO microstructures

All chemicals (A.R.) were purchased from Shanghai Chemical Reagents Co. and used without further purification.

In a typical procedure, 6.302 3 g (30 mmol) hexamethylenetetramine ($C_6H_{12}N_4$) was first dissolved into 50 mL deionized water in a 100 mL conical flask, and then 10 mL of 0.1 mol·L^{-1} Cu $(NO_3)_2$ aqueous solution was added. The molar ratio of $C_6H_{12}N_4$ to $Cu(NO_3)_2$ was 30. The mixture was magnet stirred for 20 min and subsequently water bath treated at 80 ℃ for 1 h. The resulting black powder was collected, washed with anhydrous ethanol and deionized water for several times and then finally dried in a vacuum at 50 ℃ for 6 h.

1.2 Chracterization

The phase purity of the as-synthesized products was examined by XRD using a Philips X′ Pert PRO SUPER X-ray diffractometer (40 kV, 40 mA) equipped with graphite monochromatized Cu $K\alpha$ radiation (λ = 0.154 06 nm) and solid state X′ cellerator. The incident light divergent slit size is 0.5°. The diffracted beam anti-scatter slit size and receiving slit size is 2° and 0.1 mm, respectively. The scan rate of 0.02°·s^{-1} was applied and the patterns were recorded in the 2θ range of 20°~70°. Field-emission scanning electron microscope (FESEM) images of the sample were taken on a field-emission microscope (FEI Sirion 200, 15 kV) attached with an energy dispersive X-ray spectrometer (EDX). The transmission electron microscope (TEM) images of the samples were taken on a H7650 transmission electron microscope with an accelerating voltage of 100 kV. The high resolution transmission electron microscope (HRTEM) and selected area

electronic diffraction (SAED) were recorded on a high-resolution transmission electron microscope (JEOL JEM-2010) with an accelerating voltage of 200 kV.

2 Results and discussion

2.1 Characterization of the butterfly-like CuO microstructures

Fig.1 (a) shows the XRD pattern of the as-synthesized sample. All diffraction peaks can be assigned to the crystalline CuO with monoclinic structure (PDF, No.05-0661, a=0.468 4 nm, b=0.342 5 nm, c=0.512 9 nm). No peak from impurities can be observed in the XRD pattern of the obtained sample. The strong and sharp reflection peaks suggest that the products are of highly crystalline ones. The purity and composition of the as-prepared sample by EDX analysis are shown in Fig.1(b). The result exhibits only the presence of Cu and O elements in products. The molar ratio of Cu∶O obtained from the peak areas is 0.98∶1.03, which is in agreement with stoichiometry of CuO. A peak assigned to Al is due to background from the aluminum foil.

The morphologies of the as-prepared CuO products are shown in Fig.2. Fig.2 (a) and (b) indicates that the products are mainly composed of uniform elegant butterfly-like microstructures with sizes of 2~4 μm. The enlarged image (inset in Fig.2(a)) clearly demonstrates an individual butterfly-like microstructure. Fig.2 (c) gives the picture of two butterfly-like particles with

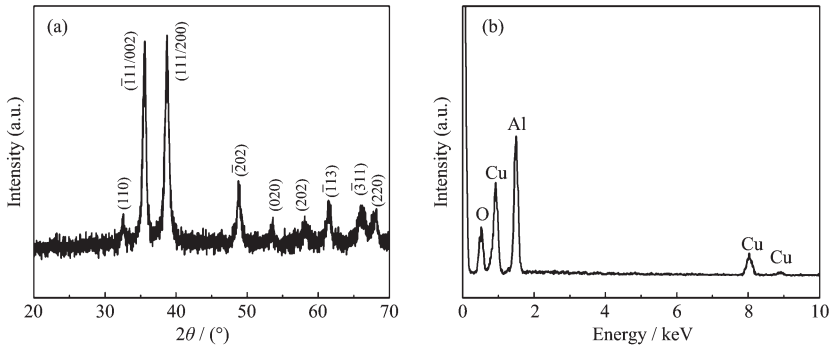
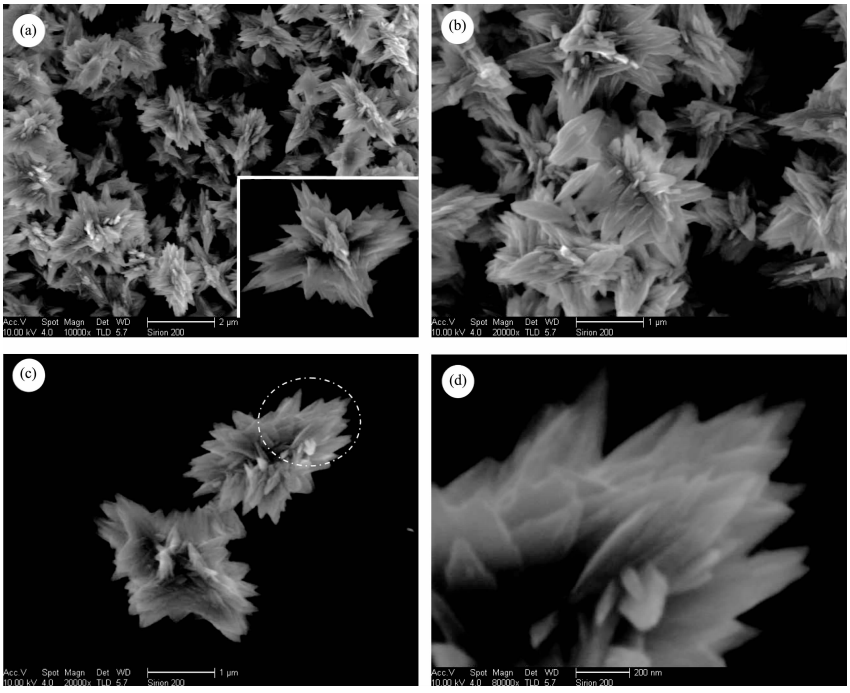


Fig.1 XRD pattern (a) and EDX result (b) of the as-prepared sample



(a, b) Overview images, (c) Two butterfly-like particles, (d) Enlarged imgage taken from the area marked by a circle in Fig.2(c)

Fig.2 FESEM images for CuO butterfly-like microcrystals

almost the same size, which interestingly shows us the backside and abdomen of a butterfly, respectively. One can see that these butterfly-like structures consist of many triangular shaped nanosheets with cuspate tip. The length of the body is 3 μm and the width of the wing is 1 μm. Fig.2 (d) is a high-magnification image recorded from the area marked by a circle in Fig.2(c), which reveals that the width of each nanosheet gradually decreases from the bottom towards its tip. The average thickness of these nanosheets is 15 nm.

Fig.3 (a) and (b) show the typical TEM images of the as-synthesized CuO sample. The butterfly-like microstructures mainly preserve their shapes during the ultrasonic treatment. Fig.3 (b) is a high-magnification image recorded from an individual CuO microstructure, which further confirms that the as-prepared butterfly-like CuO microstructures are constructed by triangular nanosheets, agreeing with the FESEM results. Fig.3(c) shows a typical HRTEM image obtained from an individual nanosheet. The average distance between the neighbouring fringes is 0.252 nm, corresponding well to interlayer spacing of the (002) planes of monoclinic CuO. The inset is SAED pattern recorded on a piece of nanosheet, revealing its single crystalline nature.

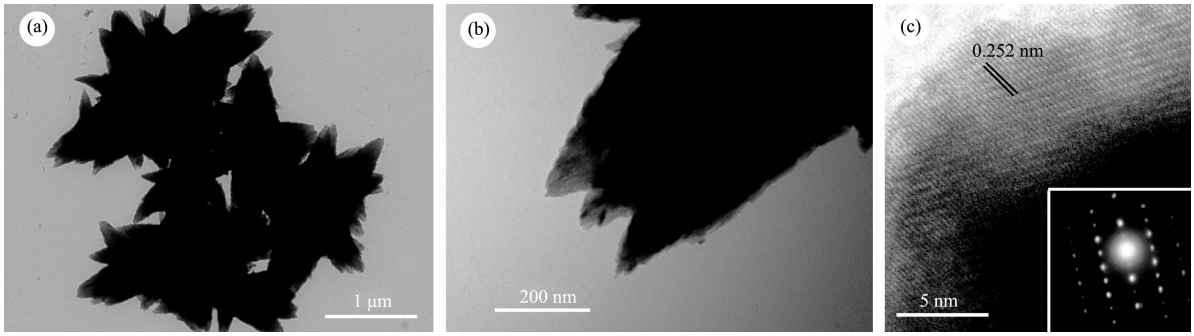


Fig.3 TEM and HRTEM images for CuO butterfly-like microcrystals

2.2 Growth mechanism and influencing factor

In the present reaction system, hexamethylene tetramine ($C_6H_{12}N_4$), a nontoxic, water-soluble, nonionic tetradentate cyclic tertiary amine[22], may not only act as an organic base but also as a good complexing reagent to coordinate with metal ions. First, $C_6H_{12}N_4$ coordinates with metal Cu^{2+} to form $[Cu(C_6H_{12}N_4)_2]^{2+}$ complexing cations at room temperature[23]. Second, under the condition of water bath heating, the preformed complexes decompose to release dissociative metal Cu^{2+} ion, and at the same time, $C_6H_{12}N_4$ hydrolyzes in aqueous solution and generates hydroxide anions (OH^-). Third, Cu^{2+} in the solution reacts with OH^- to form copper hydroxide $Cu(OH)_2$ or tetrahydroxocuprate(Ⅱ) anions $Cu(OH)_4^{2-}$ (In high concentration of $C_6H_{12}N_4$ solution, $Cu(OH)_4^{2-}$ may be produced)[24]. Finally, the newly-produced $Cu(OH)_2$ or $Cu(OH)_4^{2-}$ will dehydrolyze quickly to generate CuO products. The whole reaction process can be described as follows:

$$2C_6H_{12}N_4+Cu^{2+} \rightleftharpoons [Cu(C_6H_{12}N_4)_2]^{2+} \quad (1)$$

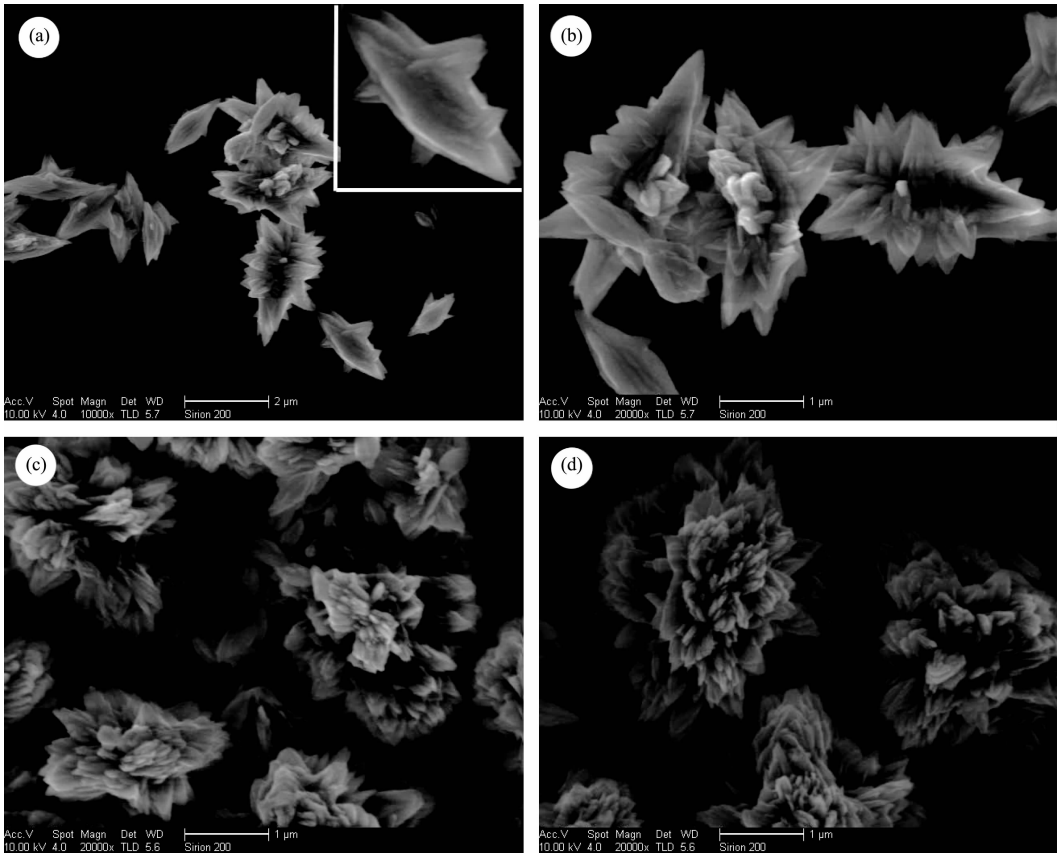
$$C_6H_{12}N_4+6H_2O=4NH_3+6HCHO \quad (2)$$

$$NH_3+H_2O=NH_4^++OH^- \quad (3)$$

$$Cu^{2+}+2OH^- \text{ (or } 4OH^-)=Cu(OH)_2 \text{ (or } Cu(OH)_4^{2-}) \quad (4)$$

$$Cu(OH)_2 \text{ (or } Cu(OH)_4^{2-})= CuO+H_2O \text{ (or } CuO+H_2O+2OH^-) \quad (5)$$

To evaluate the effect of organic base concentration, a series of parallel experiments were performed by only changing the dose of hexamethylene tetramine ($C_6H_{12}N_4$) and keeping other conditions unchanged, which was checked with FESEM as shown in Fig.4. The growth process of butterfly-like CuO and its subsequent transformation into peony-like microstructure has been observed with the increase in concentration of $C_6H_{12}N_4$. When the amount of $C_6H_{12}N_4$ is reduced to 5 mmol, flyingfish-like microcrystals as well as some underdevelopment butterfly-like microstructure are produced (Fig. 4(a)). The inset in Fig.4(a) is a single magnifying flyingfish-like microcrystal. It shows that the body is made up of several shuttle-like nanoparticles through overlaping with each other and the film is comprised of triangular shaped nanosheets. The obtained CuO products take on underdevelopment butterfly-like



(a) 5 mmol, (b) 15 mmol, (c) 45 mmol, (d) 60 mmol

Fig.4　FESEM images of CuO products obtained using different dosages of $C_6H_{12}N_4$

morphology when the adding amount of $C_6H_{12}N_4$ is 15 mmol (Fig.4 (b)). Fig.4 (c) gives the picture of CuO products when the adding amount of $C_6H_{12}N_4$ is up to 45 mmol, indictating that irregular microflowers are obtained. When the adding amount of $C_6H_{12}N_4$ is increased to 60 mmol, large quantities of beautiful peony-like CuO microstructures consisting of triangular petals are found in the products (Fig.4(d)). It should be noted that these peonies are not spherical but actually ellipsoidal.

A formation mechanism for CuO butterfly microstructure and its succeeding evolution influenced by the concentration of organic base solution is described as follows (Fig.5). First, at lower concentration of organic base solution (5 mmol $C_6H_{12}N_4$), CuO primary nuclei are produced by decomposing $Cu(OH)_2$ and rapidly developed into shuttle-like monomers under water bath heating. In order to decrease the high specific surface energy, some preformed nanoshuttles tend to pile up plane by plane through oriented-overlaping to form the body of flying fish. Due to existing high active sites at the lateral part of nanoshuttle aggregates, secondary nucleation and growth of triangular shaped films would take place on these active sites to form flyingfish-like microcrystal. Then, increasing the concentration of organic base (15 mmol $C_6H_{12}N_4$), much more CuO substances are produced by the decomposition of $Cu(OH)_2$ or $Cu(OH)_4^{2-}$, which would lead to second nucleation , and epitaxial growth not only proceeds at the lateral part but also at the top and bottom surface of nanoshuttle aggregates. So, at a proper concentration of organic base solution (30 mmol $C_6H_{12}N_4$), perfect butterfly-like CuO microstructures are formed. Finally, at higher concentration of organic base (60 mmol $C_6H_{12}N_4$), much more uncoordinated $C_6H_{12}N_4$ exsiting in the solution hydrolyzes to produce too much OH^- anions and a supersaturated solution of $Cu(OH)_4^{2-}$ might be generated, thus, excessive CuO products are created rapidly. The pre-obtained flyingfish-like microstructures quickly develop into

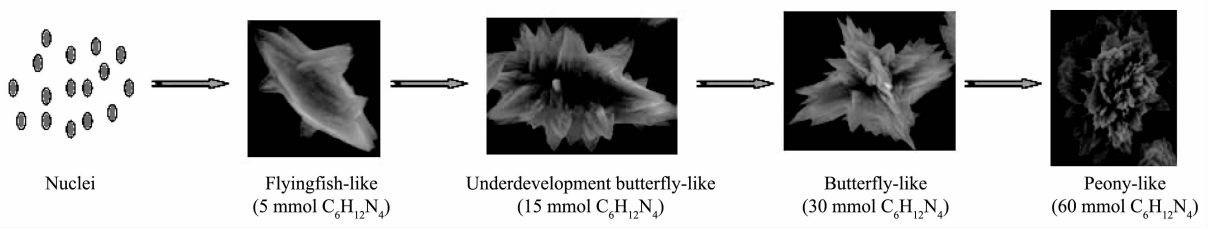


Fig.5 Schematic illustration of the formation process for CuO butterfly-like microstructrue and its evolution with the increase of dosage of $C_6H_{12}N_4$

peony-like clusters of radiating sheet-like nanocrystals because the second growth may be too rapid to be separated from the second nucleation.

3 Conclusions

In summary, elegant butterfly-like CuO microstructures have been fabricated via a water bath heating technique. FESEM and TEM images show that the size of as-prepared CuO butterfly-like microstructures is 2~4 μm and the microstructures are composed of triangular nanosheets with thickness of 15 nm. The growth process of butterfly-like CuO microstructure and the evolution of morphology influenced by the dosage of organic base were investigated in detail. The synthetic route is convenient and environment-friendly.

References:

[1] Chatterjee T, Jackson A, Krishnamoorti R, et al. *J. Am. Chem. Soc.*, **2008**,**130**:6934-6935

[2] Raula M, Rashid M H, Paira T K, et al. *Langmuir*, **2010**,**26**: 8769-8782

[3] FENG Yi(冯怡), MA Tian-Yi(马天翼), LIU Lei(刘蕾), et al. *Sci. China B*(*Zhongguo Kexue B*), **2009**,**39**(9):864-886

[4] Bai P, Wu P P, Yan Z F, et al. *J. Phys. Chem. C*, **2007**,**111**: 9729-9733

[5] Portehault D, Cassaignon S, Baudrin E, et al. *Cryst. Growth Des.*, **2009**,**9**:2562-2565

[6] Wang C, Han X J, Zhang X L, et al. *J. Phys. Chem. C*, **2010**, **114**:14826-14830

[7] Tamaki J, Shimanoe K, Yamada Y, et al. *Sensors Actuators B*, **1998**,**49**:121-125

[8] Kumar R V, Diamant Y, Gedanken A. *Chem. Mater.*, **2000**,**12**: 2301-2305

[9] Switzer J A, Kothari H M, Poizot P, et al. *Nature*, **2003**,**425**: 490-493

[10]Schon J H, Dorget M, Beuran F C, et al. *Nature*, **2001**,**414**: 434-436

[11]Gao X P, Bao J L, Pan G L, et al. *J. Phys. Chem. B*, **2004**,**108**: 5547-5551

[12]REN Chong-Gui(任崇桂), XU Jian(徐建), JIA Yan-Jin(贾晏金), et al. *Acta Chim. Sinica*(*Huaxue Xuebao*), **2007**,**65**(5): 459-464

[13]Wang S L, Xu H, Qian L Q, et al. *J. Solid State Chem.*, **2009**, **182**:1088-1093

[14]HENG Qiu-Li(衡秋丽), XIAO Feng(肖峰), LUO Jian-Min(骆建敏), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2009**,**25**(2):359-363

[15]LI Ben-Xia(李本侠), WANG Yuan-Yuan(王媛媛), WANG Yan-Fen(王艳芬). *Acta Phys. Chim. Sin.* (*Wuli Huaxue Xuebao*), **2009**,**25**(11):2366-2372

[16]YIN Yi-Dong(尹贻东), LI Cheng-Fa(李成发), HOU Hai-Ge(侯海鸽), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2010**,**26**(2):293-299

[17]Li J Y, Xiong S L, Pan J, et al. *J. Phys. Chem. C*, **2010**,**114**: 9645-9650

[18]Cheng L, Shao M W, Chen D Y, et al. *Mater. Res. Bull.*, **2010**,**45**:235-239

[19]Li Y, Kuai P Y, Huo P P, et al. *Mater. Lett.*, **2009**,**63**:188-190

[20]Deng C H, Hu H M, Zhu W L, et al. *Mater. Lett.*, **2011**,**65**: 575-578

[21]Allam N K, Grimes C A. *Mater. Lett.*, **2011**,**65**:1949-1955

[22]Vayssieres L, Keis K, Hagfeldt A, et al. *Chem. Mater.*, **2001**, **13**:4395-4398

[23]Zhang Y G, Wang S T, Qian Y T, et al. *Solid State Sci.*, **2006**, **8**:462-466

[24]Ni Y H, Li H, Jin L N, et al. *Cryst. Growth Des.*, **2009**,**9**:3868-3873