Synthesis and Electrocatalytic Properties of Co_3O_4 Nanocrystallites with Various Morphologies

L. Pan · M. Xu · Z. D. Zhang

Received: 19 November 2009 / Published online: 4 March 2010

© The Author(s) 2010. This article is published with open access at Springerlink.com

Abstract Co_3O_4 crystallites with particle, plate-, tube-, rod- and sheet-like morphologies were successfully prepared by the calcination of the corresponding precursors synthesized via a precipitation or hydrothermal procedure. The morphologies of the precursors and Co_3O_4 nano-tubes were detected by field emission scanning electron microscopy (FE-SEM). The as-obtained Co_3O_4 samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and special surface area measurement (BET). The electrocatalytic activity of *p*-nitrophenol reduction with the Co_3O_4 products decorated on a glassy carbon electrode (GCE) was tested, respectively, using cyclic voltammetry (CV) in a basic solution. The results indicated that *p*-nitrophenol was reduced with higher current density but almost at a constant potential on the Co_3O_4 /GCE in contrast with that on a bare GCE at the same conditions. The highly catalytic activity of the as-prepared Co_3O_4 in a basic solution suggested their wide applications in environmental treatment or organic synthesis.

Keywords Co_3O_4 · A glassy carbon electrode · Electrocatalysis · *p*-Nitrophenol

L. Pan · Z. D. Zhang (✉)

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

e-mail: zhazude@163.com

L. Pan · M. Xu

Department of Chemistry and Chemical Engineering, Huainan Normal University, Huainan, Anhui 232001, China

Introduction

Nanosized transition metal oxides often exhibit enhanced physical, chemical, thermal, electrical, optical, or magnetic properties, which lead to the extensive for applications in electrochemistry, biomedical device and other fields [1–5]. Among these oxides, tricobalt tetraoxide (Co_3O_4), which is described by a formula unit AB_2O_4 ($\text{A} \rightarrow \text{Co}^{2+}$, $\text{B} \rightarrow \text{Co}^{3+}$) and exhibits a normal spinel crystal structure with occupation of tetrahedral A sites by Co^{2+} and octahedral B sites by Co^{3+} [6], is an important material. With an intrinsic *p*-type semiconductor (direct optical bandgaps at 1.48 and 2.19 eV) [7], Co_3O_4 has been investigated extensively as a promising material in gas-sensing and solar energy absorption, and as an effective catalyst in environmental purification and chemical engineering. In addition, Co_3O_4 has been widely studied for its application as lithium-ion battery electrodes [8], catalysts [9, 10], field-emission materials [7] and magnetic material [11].

It is well known that the behavior of nanomaterials is predominantly dependent on the size and morphology of the particles, which is thus a crucial factor to their ultimate performance and application. For recent decades, quite a few routes have been designed to fabricate spinel Co_3O_4 with various morphologies. Co_3O_4 nanorods have been prepared by improving traditional molten salt synthesis [6] or an easily controlled hydrothermal procedure [12]. Zhang et al. used an mild and inexpensive method to prepare Co_3O_4 microsphere in mass production, and the product with a large pore volume can serve as anode material for lithium-ion batteries [13]. However, although the reports on a single morphology synthesis of Co_3O_4 crystallites are obtained easily, the ones on the multi-morphology synthesis of Co_3O_4 crystallites are scarce. Herein, we present our work involving the multi-morphology synthesis of Co_3O_4 crystallites at different conditions.

As an important electrode material, Co_3O_4 is a traditional precursor of anode in Li-ion rechargeable battery, whose electrochemical properties have been extensively studied. To our best of knowledge, the reports on the electrocatalytic activities of Co_3O_4 with various morphologies modified directly on a glassy carbon electrode (GCE) are scarce.

In the present paper, we have successfully fabricated multi-morphology Co_3O_4 products via easily controlled procedures under wild conditions. The electrocatalytic performances of the Co_3O_4 samples decorated on the GCE were investigated for *p*-nitrophenol reduction in a basic solution. The $\text{Co}_3\text{O}_4/\text{GCE}$ revealed the excellent catalytic performances for *p*-nitrophenol reduction, which indicated that the $\text{Co}_3\text{O}_4/\text{GCE}$ would have potential applications in the electrocatalytic synthesis for organic materials.

Experimental

All the reagents used in the experiments were analytical grade and were purchased from Chinese Shanghai Chemical Reagent Company and were used directly without further purification.

Preparation of Co₃O₄ Samples

Co₃O₄ with various morphologies were prepared via two methods, precipitation and hydrothermal procedures. In a typical precipitation synthesis for Co₃O₄ nanoplates, 10 mmol CoCl₂·6H₂O was dissolved in 20 mL of distilled water in a beaker, then 40 mL of aqueous solution containing 15 mmol NH₄HCO₃ and 20 mmol (CH₂)₆N₄ was added to the beaker by dropwise under vigorous stirring. As the addition of precipitation reagent was finished, the beaker was placed in 80 °C water bath for 6 h. As the system cooled to room temperature, the pink precipitation was filtered off and washed several times with first distilled water then absolute ethanol. The as-obtained precipitation was dried in an oven at 105 °C for 6 h. The final black Co₃O₄ products were synthesized by the calcination of the dried precursor at 350–500 °C for 3 h according to the TG analysis. For the preparation of Co₃O₄ nanoparticles, additional 1.0 g polyethylene-glycol (PEG 6000) was added to the CoCl₂ solution before addition of precipitation reagent, furthermore the precipitation reagent was replaced by (NH₄)₂CO₃ (15 mmol). The following preparation procedures were the same as the preparation of Co₃O₄ nanoplates. In a typically hydrothermal synthesis, 2.5 mmol CoCl₂·6H₂O, 5 mmol sodium tartrate and 10 mmol urea were dissolved in 40 mL distilled water, and a certain amount of surfactant, e.g. 0.5 g polyvinylrrolidone (PVP) or 0.5 g PEG 6000 was added subsequently. The resultant mixture was transferred into a 60 mL Teflon-lined autoclave, which was sealed and maintained at 180 °C for 24 h (for preparation of nanotubes or nanorods). For preparation of Co₃O₄ nanosheets, 2.5 mmol freshly cobalt oxalate precipitation was dispersed in 40 mL distilled water, and 1.3 mL of cyclohexylamine was added under vigorous stirring. The resultant mixture was transferred into a 60 mL Teflon-lined autoclave, which was sealed and maintained at 120 °C for 14 h. As the autoclave cooled to room temperature, the precipitates were separated from the solutions by filtering, washed with first distilled water then absolute ethanol repeatedly, and dried at 60 °C in a vacuum. Finally, the as-prepared precursor was calcinated at 400 °C for 3 h in air to prepare Co₃O₄ products. Some reaction conditions and corresponding products were listed in Table 1. The as-obtained Co₃O₄ samples were numbered as S-1–S-8.

Sample Characterization

Thermogravimetry analysis (TGA and DTA) was performed on a Shimadzu TA-50WS analyzer in N₂ gas in the temperature range from room temperature to 800 °C. Morphologies of the precursors were observed by the FE-SEM (JSM-6700F field emission scanning electron microanalyzer, with an accelerating voltage of 10 kV). Phase identification was carried out by X-ray diffraction on a Philips X'Pert SUPER powder X-ray diffraction with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The transmission electron microscopy (TEM) images were taken on Hitachi model H-800 transmission electron microscope with tungsten filament using an acceleration voltage of 200 kV. N₂ adsorption of the as-prepared samples was determined by BET measurements using a NOVA-1000e surface analyzer.

Table 1 Co_3O_4 samples prepared under different conditions and decorated on GC electrode for electrochemical determination

Sample	Reagents	Preparation method	Reaction conditions	Morphology
S-1	$\text{CoCl}_2 + \text{NH}_4\text{HCO}_3 + (\text{CH}_3)_4\text{N}_4$	Precipitation	80° for 6 h	Nanoparticles
S-2	$\text{CoCl}_2 + (\text{NH}_4)_2\text{CO}_3 + \text{PEG}(6000)$	Precipitation	80° for 6 h	Nanoparticles
S-3	$\text{CoCl}_2 + \text{tartrate} + \text{PVP}$	Hydrothermal	180° for 24 h	Nanorods
S-4	$\text{CoCl}_2 + \text{tartrate} + \text{PEG}(6000)$	Hydrothermal	180° for 24 h	Nanotubes
S-5	$\text{CoCl}_2 + \text{tartrate}$ hydrothermal	180° for 24 h	Nanorods	
S-6	$\text{CoCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{C}_6\text{-amine}$	Hydrothermal	120° for 14 h	Nanosheets
S-7	$\text{CoCl}_2 + \text{C}_6\text{-amine}$	Hydrothermal	120° for 14 h	Nanosheets
S-8	$\text{CoCl}_2 + (\text{C}_2\text{H}_5)_3\text{N}$	Hydrothermal	120° for 14 h	Nanosheets

Note: The tartrate was sodium tartrate; $\text{C}_6\text{-amine}$ is cyclohexylamine. The corresponding sample is obtained by the calcination of each precursor at 400 °C for 3 h

Electrochemical Property Measurement

The electrochemical property measurements of the bare GCE and $\text{Co}_3\text{O}_4/\text{GCE}$ in basic solutions were performed on LK 98 microcomputer-based electrochemical system (Tianjin Lanlike Chemical and Electron High Technology Co., Ltd., Tianjin, China). A three-electrode single compartment cell was used for cyclic voltammetry. A GCE (3.7 mm diameter) and a platinum plate were used as working and counter electrode, respectively, and a Ag/AgCl electrode was used as reference electrode. Prior to each measurement, the surface of the GCE was carefully polished on an abrasive paper first, then was further polished with 0.3 and 0.05 μm $\alpha\text{-Al}_2\text{O}_3$ paste in turn, finally was rinsed thoroughly with 1:1 (V:V) HNO_3 aqueous solution, acetone and doubly distilled water and dried in the air. 20 mg Co_3O_4 sample was dispersed in 4 mL doubly distilled water under ultrasonication conditions to obtain a black suspension solution. Of the suspension solution, 50 μL was taken out and trickled on the carbon surface of the GCE. After dried in air, the GCE modified with Co_3O_4 sample ($\text{Co}_3\text{O}_4/\text{GCE}$) was prepared and used directly for electrochemical measurements.

Results and Discussions

Figure 1a shows the TGA-DTA curves of the sample S-1 precursor. According to the TAG-DTA curves, there was an obvious weight loss at the temperature range of 200–310 °C, and a strong endothermic peak was observed at 275.3 °C. When the heating temperature exceeded 310 °C, the weight loss did not occur, indicating that the target product (Co_3O_4) could be obtained by the calcination of the precursor at more than 310 °C for a certain time. Figure 1b shows the TGA curves of the sample S-6 precursor (TGA-1) and sample S-4 precursor (TGA-2). From Fig. 1b, by increasing the heating temperature to 260 °C (TGA-1) or 390 °C (TGA-2), the

Fig. 1 The representative TG-DTA curves of precursors of S-1 sample (a), S-4 sample (b TGA-1) and S-6 sample (b TGA-2)

Fig. 2 SEM images of the representative precursors of S-1 sample (a), S-3 sample (b), S-4 sample (c), S-5 sample (d), and S-6 sample (e)

weight loss did not continue, which suggested the corresponding sample S-6 and S-4 could be prepared when the heating temperature was over 400 °C.

Figure 2 shows the morphologies of the precursors of the samples S-1 and S-3–S-6. From Fig. 2, the morphologies of the precursors prepared via different synthesis methods differed greatly. The precursor of sample S-1 was particles with a mean size of ~200 nm, as shown in Fig. 2a. The experiments revealed that the precursor of sample S-2 (not presented) had a similar morphology to the one of the precursor of sample S-1. The morphologies of the precursors of sample S-3 and S-4 (shown in Fig. 2b, c, respectively) demonstrated uniform rods with approximate 250 nm in

diameter and 3 μm in length. The precursor of sample S-5 (shown in Fig. 2d) revealed irregular short rods with about 200–380 nm in diameter and 0.4–4 μm in lengths. The precursor of sample S-6 was composed of numerous sheets piled up together (Fig. 2e). According to Fig. 2b–d, the precursors show rod-like, which suggested that addition of sodium tartrate was favorable to yield one-dimensional (1-D) materials. With the addition of cyclohexylamine into cobalt oxalate precipitation, a plate-like (2-D) precursor was inclined to be form via a hydrothermal process. The morphologies of the precursors suggest the shapes of the resultant Co_3O_4 samples might displayed plate-like shape.

Figure 3 shows the XRD patterns of sample S-1 (Fig. 3a), S-2 (Fig. 3b), S-5 (Fig. 3c), S-6 (Fig. 3d), S-7 (Fig. 3e) and S-8 (Fig. 3f) obtained by calcining each precursor at 400 $^{\circ}\text{C}$ for 3 h. All the diffraction peaks were in good agreement with the JCPDS file of cubic spinel Co_3O_4 (JCPDS Card No: no. 43-1003). No characteristic peaks of other impure phase like CoOOH , CoO or Co_2O_3 could be detected, indicating that the products were of high purity. The XRD patterns of sample S-3 and S-4 (not given) were similar to the one of sample S-5, which indicated that the addition of the surfactants had no influence on the phase of Co_3O_4 product. The XRD patterns further verified that the pure Co_3O_4 products could be prepared when the heating temperature was no less than 400 $^{\circ}\text{C}$.

Figure 4 demonstrates the TEM images of Co_3O_4 samples prepared by the calcination of the precursor of sample S-1 at 350 $^{\circ}\text{C}$ (Fig. 4a), 400 $^{\circ}\text{C}$ (Fig. 4b), 450 $^{\circ}\text{C}$ (Fig. 4c) and 500 $^{\circ}\text{C}$ (Fig. 4d) for 3 h, respectively. From Fig. 4, it can be observed that the calcination temperature and addition of $(\text{CH}_2)_6\text{N}_4$ played

Fig. 3 XRD patterns of S-1 sample (a), S-2 sample (b), S-5 sample (c), S-6 sample (d), S-7 sample (e) and S-8 sample (f)

Fig. 4 TEM images of S-1 sample prepared by the calcination of the precursors, which were obtained via a precipitation procedure with $\text{NH}_4\text{HCO}_3 + (\text{CH}_2)_6\text{N}_4$ (a–d) but with NH_4HCO_3 only (e), at 350 °C (a), 400 °C (b), 450 °C (c), 500 °C (d) and 500 °C (e) for 3 h, respectively

significant roles on the morphological controlling of final Co_3O_4 products. The samples prepared by calcining the precursor at 350 and 400 °C for 3 h were nanoparticles with a size in the range of about 15–30 nm. Furthermore, little nanoplates could be detected when the calcination temperature was fixed at 400 °C (Fig. 4b). Further increasing the heating temperature, almost 90% (450 °C) and over 95% (500 °C) Co_3O_4 products were nanoplates. Without addition of $(\text{CH}_2)_6\text{N}_4$ into the synthesis system, almost no nanoplates were observed even the precursor was calcinated at 500 °C for 3 h (Fig. 4e). Our previous work showed that the addition of $(\text{CH}_2)_6\text{N}_4$ was inclined to synthesize plate-like materials [14].

Figure 5 demonstrates the TEM images of Co_3O_4 samples prepared by the calcination of the precursor of sample S-2 at 300 °C (Fig. 5a), 400 °C (Fig. 5b, c) and 500 °C (Fig. 5d) for 3 h. As can be seen clearly from Fig. 5, Co_3O_4 samples exhibited nano-array arrangements. By increasing the heating temperature in the

Fig. 5 TEM images of sample S-2 prepared by the calcination of the precursor of S-2 at **a** 300 °C, **b** 400 °C and **d** 500 °C for 3 h. The image of **c** is the lowly magnified one prepared by the calcination of the precursor of S-2 sample at 400 °C for 3 h

range of 300–500 °C, the Co_3O_4 array arrangements were more regular. It also can be observed from Fig. 5 that each array was formed by numerous Co_3O_4 nanoparticles with a size range of 10–20 nm. Li et al. reported that Co_3O_4 nanoarrays were prepared by calcining its precursor synthesized by a hydrothermal procedure [15]. According to the work performed by Li et al., the products are composed of small particles, and a single nanoarray with 250 nm wide in the middle and about 2.5 μm in length is provided. In our work, the precursor was synthesized by a precipitation method, which was easily controlled. Furthermore the Co_3O_4 products arranged with arrays were in a large scale. In addition, the sizes of Co_3O_4 nanoparticles increased with increasing the heating temperature. As the precursor was calcined at a lower temperature (e.g. 300 °C, Fig. 5a), Co_3O_4 nanoparticles were easily to aggregate, but the aggregation action weakened at higher heating temperature (e.g. 400 and 500 °C, showing in Fig. 5b, d, respectively).

To obtain one- or two-dimensional Co_3O_4 products, a novel route was designed. In the work, sodium tartrate was used as ligand to cobalt ion to form a cobalt complex, and the complex was treated via a hydrothermal procedure at 180 °C for 24 h. The resultant pink precursor was calcined at 400 °C for 3 h according to the corresponding TG analysis of precursor (Fig. 1b). Co_3O_4 nanorods or nanotubes could be prepared by calcination of the precursor. If 0.5 g PVP (Fig. 6a) or no surfactant (Fig. 6d) was added to the reaction system, nanorods can be obtained, however the Co_3O_4 rods prepared with addition of PVP were rather regular. It was also found from Fig. 6a that there were many short rods (sample S-3) between the longer ones. Without addition of any surfactant, the as-prepared sample was the non-uniform short rods (sample S-5) (Fig. 6d). If the PVP was substituted by equal amount of PEG 6000, the resultant Co_3O_4 possessed tube-like shape (sample S-4) (Fig. 6b, c). Generally, PEG was used to hinder the aggregation of nanoparticles via absorption on the products. In the present work, the addition of PEG was advantageous for forming tube-like Co_3O_4 samples. In addition, if freshly precipitated cobalt oxalate mixed with a certain volume of cyclohexylamine was treated via a hydrothermal procedure at 120 °C for 14 h, a gray precursor of Co_3O_4 was produced, and sheet-like shape Co_3O_4 (sample S-6) was synthesized by the calcination of the as-prepared precursor at 400 °C for 3 h (Fig. 6d). From Fig. 6d, it can be observed that the contiguous small sheets connected together to form large sheets. If the precursor was calcined at 500 °C for the same time (3 h), the large sheets shrunk and even disappeared finally (Fig. 6e).

Figure 7 displays the TEM images of samples S-7 and S-8. For the synthesis of the S-7 and S-8, $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and sodium tartrate were not added, and only cyclohexylamine (S-7) or trimethylamine (S-8) was used. From Fig. 7, the samples all represented hexagonal nano-sheets. It was obvious that the organic amine played an important role on the sample size controlling, and the diagonal line of the hexagonal nano-sheet of sample S-7 was about 500 nm but the one of the hexagonal nano-sheet of sample S-8 was 200 nm or so. The structure and size of organic amine would have significant effects on the final size of Co_3O_4 samples. Clearly, the nano-sheets were composed of many Co_3O_4 nanoparticles. The formation mechanism of Co_3O_4 hexagonal nano-sheets needs to be investigated in the next work.

Fig. 6 TEM images of S-3 sample (a), S-4 sample (b), S-5 sample (d) and S-6 sample (e) prepared by the calcination of the corresponding precursors at 400 °C for 3 h, respectively. FE-SEM image of sample S-4 (c) prepared by the calcination of the corresponding precursors at 400 °C for 3 h. TEM image of f is Co_3O_4 nanosheets by the calcination of the precursor of sample S-6 at 500 °C for 3 h

The electrocatalytic activities for *p*-nitrophenol reduction using the GCE modified with sample S-1–S-8, respectively, were investigated. The cyclic voltammogram curves of the bare GCE and the GCE modified with sample S-1–S-8, respectively, in presence of *p*-nitrophenol in a basic solution are shown in Fig. 8. The I_{pc} (peak current value) versus potential for *p*-nitrophenol reduction with the GCE and the one modified with different Co_3O_4 samples is displayed in Table 2. All the samples owned reduction peak in the cyclic voltammogrammes, and almost

Fig. 7 TEM images of S-7 sample (a, b) and S-8 sample (c, d)

no cathodic peak could be found. Compared with the bare GCE, although the potential values of reduction peaks with the $\text{Co}_3\text{O}_4/\text{GCEs}$ basically kept constant, the corresponding current values were all higher than that with the bare GCE. The current values of reduction peaks with GCE modified with S-1–S-8 samples were 67.56, 114.21, 83.74, 137.69, 114.28, 68.14, 89.58 and 148.35 μA at the corresponding potentials of -0.956 , -1.032 , -1.031 , -1.010 , -1.104 , -1.014 , -1.028 and -1.028 V, respectively, while the current value of reduction peak was only 40.05 μA at a potential of -1.049 V using the bare GCE. Of these $\text{Co}_3\text{O}_4/\text{GCEs}$, two samples: S-4 and S-8, exhibited the higher electrocatalytic activity for *p*-nitrophenol reduction, because the cathodic peak current value were bigger (137.69 and 148.35 μA , respectively), which was 3.4 and 3.7 times bigger than that with the bare ECE (40.05 μA). Likewise, the GCE modified with S-2 (nanoparticles) or S-5 (nanorods) sample also exhibited better electrocatalytic activity for *p*-nitrophenol reduction. However, the GCE modified with sample S-6 (nanosheets) showed a little better electrocatalytic activity for *p*-nitrophenol reduction (I_{pc} and peak potential were 68.14 and -1.014 V, respectively).

Based on the BET measurement, the special surface area of sample S-1–S-8 was 37, 43, 28, 58, 34, 24, 36 and 73 g/m^2 , respectively. It was obvious that the sample S-8 and S-4 with the larger special surface area exhibited the higher electrocatalytic activity for *p*-nitrophenol reduction, and sample S-6 with the smallest surface area

Fig. 8 Cyclic voltammograms of bare GCE and the GCE modified with S-1–S-8 in 1.0 mol L⁻¹ sodium hydroxide +1.0 mmol L⁻¹ *p*-nitrophenol (scanning velocity 0.02 V/s)

Table 2 I_{pc} versus potential with Co₃O₄/GCEs for *p*-nitrophenol reduction in a basic solution

Sample		S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
I_{pc} (μA)	40.05	67.56	114.21	83.74	137.69	114.28	68.14	89.58	148.35
Potential (V)	−1.049	−0.956	−1.032	−1.031	−1.010	−1.104	−1.014	−1.028	−1.028

showed the lowest catalytic activity. It seems that the sample with a larger special surface area would reveal higher catalytic activity for *p*-nitrophenol reduction. Although the special surface area of sample S-1 was larger than that of sample S-5, the peak current value for *p*-nitrophenol reduction with the GCE decorated with sample S-5 was larger (114.28 μA) than that with the one modified with sample S-1 (67.56 μA), which indicated that the improvement of the catalytic activity with sample S-5 did not result from the surface area. Compared to the sample S-1 and S-5, both had different morphologies (nanoparticles and nanorods, respectively), namely their different structures would lead to the great catalysis difference.

Conclusion

Co₃O₄ nanomaterials with various morphologies were prepared successfully by calcining each precursor synthesized via a precipitation or hydrothermal procedures. The GCE modified with the sample S-1 and S-2 (nanoparticles), S-3 (nanorods), S-4 (nanotubes), S-5 (nanorods), S-6–S-8 (nanosheets), respectively, were used to electrocatalyze *p*-nitrophenol reduction in a basic solution using cyclic

voltammograms method. Compared with a bare GCE, *p*-nitrophenol was reduced with higher current value of reduction peak but at a basically unchangeable reduction peak potential with the Co₃O₄/GCEs, which demonstrated that modified GCEs exhibited excellent electrocatalytic activities for *p*-nitrophenol reduction. The Co₃O₄/GCEs have potential application in the environment treatment and organic electrochemical synthesis.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. A. P. Katsoulidis, D. E. Petrakis, G. S. Armatas, and P. J. Pomonis (2007). *J. Mater. Chem.* **17**, 1518.
2. G. Binotto, D. Larcher, A. S. Prakash, R. H. Urbina, M. S. Hegde, and J.-M. Tarascon (2007). *Chem. Mater.* **19**, 3032.
3. S. Sakurai, S. Kuroki, H. Tokoro, K. Hashimoto, and S.-I. Ohkoshi (2006). *Adv. Funct. Mater.* **17**, 2278.
4. K. Zhou, R. Wang, B. Xu, and Y. Li (2006). *Nanotechnology* **17**, 3939.
5. R. B. Waghulade, P. P. Patil, and R. Pasricha (2006). *Talanta* **72**, 594.
6. X. Ke, J. Cao, M. Zheng, Y. Chen, J. Liu, and G. Ji (2006). *Mater. Lett.* **61**, 3901.
7. B. Varghese, T. C. Hoong, Z. Yanwu, M. V. Reddy, B. V. R. Chowdari, A. T. S. Wee, T. B. C. Vincent, C. T. Lim, and C.-H. Sow (2007). *Adv. Funct. Mater.* **17**, 1932.
8. Y. Sharma, N. Sharma, G. V. SubbaRao, and B. V. R. Chowdari (2007). *J. Power Sources* **173**, 495.
9. N. R. E. Radwan, M. S. El-Shall, and H. M. A. Hassan (2007). *Appl. Catal. A Gen.* **331**, 8.
10. U. Zavyalova, P. Scholz, and B. Ondruschka (2007). *Appl. Catal. A Gen.* **323**, 226.
11. S. M. Rodulfo-Baechler, S. L. González-Cortés, J. Orozco, V. Sagredo, B. Fontal, A. J. Mora, and G. Delgado (2004). *Mater. Lett.* **58**, 2447.
12. X. Lou, J. Han, W. Chu, X. Wang, and Q. Cheng (2007). *Mater. Sci. Eng. B* **137**, 268.
13. H. Zhang, X. Chen, Z. Yang, L. Liu, Z. Li, T. Yu, and Z. Zou (2007). *J. Phys. D Appl. Phys.* **40**, 4129.
14. Y. Zhang, S. Wang, Y. Qian, and Z. Zhang (2006). *Solid State Sci.* **8**, 462.
15. B. Li, Y. Xie, C. Wu, Z. Li, and J. Zhang (2006). *Mater. Chem. Phys.* **99**, 479.