Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1643–1647

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of flower-like 3D ZnO microstructures and their size-dependent ethanol sensing properties

Xintai Su [a], Hua Zhao [a], Feng Xiao [a,*], Jikang Jian [b], Jide Wang [a]

[a] Ministry Key Laboratory of Oil and Gas Fine Chemicals, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China
[b] College of Physics Science and Technology, Xinjiang University, Urumqi 830046, China

Received 18 March 2011; received in revised form 29 August 2011; accepted 28 September 2011
Available online 5 October 2011

Abstract

Flower-like 3D ZnO microstructures constructed from nanorods of different sizes were prepared by a microwave hydrothermal (MH) process in the presence of *o*-, *m*- and *p*-nitrobenzoic acid, respectively. Well-crystallized flower-like ZnO microstructures were obtained after 10 min MH treatment. The X-ray powder diffraction (XRD) test indicated that all the products were consistent with the hexagonal ZnO phase, and scanning electron microscopy (SEM) investigation revealed that the flower-like 3D ZnO microstructures were built with sword-like nanorods 60–100 nm in width and several micrometers in length. The formation mechanism of these flower-like 3D ZnO microstructures is discussed briefly. The gas sensitivity of the as-prepared ZnO microstructures to ethanol at different operation temperatures and concentrations was also studied. The results indicated that the gas sensitivity of the ZnO microstructures was influenced by the particle size and microcosmic configuration, the larger particles with crowded nanorods having higher gas sensitivity.

Keywords: A. Powders: chemical preparation; D. ZnO; E. Sensors

1. Introduction

Gas sensors based on metal–oxide semiconductors can be used in a wide variety of applications such as gas monitoring and alarms [1,2]. As one of the earliest discovered and well-established gas sensing oxides, ZnO has been extensively studied for the detection of many types of gases such as C_2H_5OH, CO and NO_x [3–6]. It has been reported that the gas response increases abruptly when the particle size decreases or surface area increases [7,8]. Because of the high specific area, well-aligned microstructure and less agglomerated configuration, flower-like ZnO microstructures assembled from 1D nanorods may have the ability to promote the gas sensing property or catalytic property [9–12].

Flower-like 3D ZnO microstructures composed of nanorods are usually prepared with hydrothermal or solvent-thermal methods, in which some polymers and surfactants are used as the structure-directing agents [13–18]. For example, the flower-like ZnO, MnO_2, Bi_2S_3 and $La(OH)_3$ assemblies composed of nanorods were fabricated with PEG as the structure-directing agent [13]. Zhang and Ge [14,15] obtained flower-like ZnO constructed from nanorods through a very simple hydrothermal method in the presence of cetyltrimethylammonium bromide (CTAB). Wang and co-workers [16] synthesized flower-like ZnO architectures with nanorods by a thiourea-assisted aqueous solution route. Although some work on assembling flower-like 3D ZnO microstructures with nanorods has been performed, the sizes and morphologies of the flower-like 3D microstructures and their corresponding gas sensing properties are seldom reported.

Recently, we found that some organic acids such as *p*-nitrobenzoic acid, citric acid and tartaric acid play an important role in the formation of metal oxide nanocrystals [19–21]. In our experiment, *o*- (*m*- or *p*-) nitrobenzoic acid was used as the assistant agent to synthesize the flower-like 3D ZnO microstructures, and it was found that *o*- (*m*- or *p*-) nitrobenzoic acid can be used to change the morphologies of ZnO particles under MH conditions. Subsequently, the corresponding size-dependent ethanol sensing properties of the flower-like 3D ZnO microstructures were investigated.

* Corresponding author. Tel.: +86 991 8581018; fax: +86 991 8582807.
E-mail address: 19085006@qq.com (F. Xiao).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.09.055

2. Experimental

2.1. Sample preparation

All reagents were analytical pure and were used as received without further purification. In a typical procedure, $Zn(CH_3COO)_2{\cdot}2H_2O$ (2.0 g, 9.20 mmol) was dissolved in deionized water (20 mL). *O*- (*m*- or *p*)-nitrobenzoic acid (0.5 g, 0.75 mmol) was added to the above solution under continuous stirring (they are labeled as *o*-ZnO, *m*-ZnO and *p*-ZnO, respectively). After 5 min, aqueous NaOH (2.0 M, 60 mL) was added and a transparent solution was obtained, which was then pretreated under an ultrasonic water bath and transferred into a 100 mL Teflon container with 66% capacity. The MH experiments were carried out in a Milestone ETHOS microwave system where reactants were treated in Teflon liners. Under the radiation (2.45 GHz in frequency) of the microwave system, the reactants were heated to a previously set temperature and maintained at that value, which was monitored by a thermocouple, for 10 min so as to allow the crystal to grow. After the reaction, the resulting solid products were centrifuged, washed with distilled water and ethanol several times, and finally dried in air at 60 °C. To examine the effect of assistant agent, the control experiment without assistants was performed and the sample was named after *Blank*-ZnO.

2.2. Characterization

The obtained samples were characterized with a X-ray diffractometer (XRD) (Rigaku D/max-ga X-ray diffractometer) at a scanning rate of 2° min^{-1} and scanning range of 2θ from 10° to 80° with Cu Kα radiation (λ = 1.54178 Å). The scanning electron microscopy (SEM) images were obtained on LEO1450VP. The specific surface areas of the as-prepared products were measured on JW–BK Brunauer–Emmett–Teller (BET) equipment by using adsorption data over the relative pressure ranging from 0.05 to 0.35. The samples were degassed at 105 °C for 2 h to remove physisorbed gases prior to the measurement. Gas sensing measurements were carried out on a computer-controlled WS-30A system (Zhengzhou, China).

2.3. Sensors fabrication

The method and instruments of the gas-sensor test were similar to those in the reported literature [6]. The mixture of about 36 mg of the as-prepared flower-like ZnO microstructures and 0.1 mL of terpinol was completely ground into paste. Then the paste was daubed onto the ceramic tube of the sensor body, which was then annealed in a muffle stove at 400 °C for 3 h. To improve stability and repeatability, the as-fabricated sensors were fixed onto the gas-sensing apparatus and aged for 24 h at 300 °C prior to use. The sensor-settled chamber was kept under a continuous flow of dry air for 30 min before analysis. A certain amount of alcohol was injected into a heating-device part of the apparatus and gasified quickly.

3. Results and discussion

Fig. 1(a)–(c) shows the XRD patterns of the samples prepared by the MH method for 10 min. All the diffraction peaks can be indexed as the hexagonal ZnO with lattice constants of $a = 3.250$ Å and $c = 5.207$ Å, which match the values of the standard card (JCPDS 36-1451). No peaks of impurities were detected from this pattern, which implies that pure ZnO can be obtained under the current synthetic route. The formation of ZnO phase within 10 min shows the advantage of the MH method over the conventional hydrothermal process. One apparent reason for the extremely rapid crystallization is the generation of localized high temperatures in the presence of microwaves.

The morphologies of ZnO microstructures synthesized with different assistant agents are shown in Fig. 2(a)–(c). It can be seen that all the flowerlike products consist of sword-like ZnO nanorods which were 60–100 nm in width and several micrometers in length. It is apparent that the products have a similar morphology but different sizes and amounts of nanorods. When *o*-nitrobenzoic acid was used as the structure-directing agent, the sphere organization of ZnO microstructures with uniform diameters of about 4 μm was obtained (Fig. 2(a)). When *m*- and *p*-nitrobenzoic acids were used in the reaction system, the diameters of the ZnO flowers were increased to about 6 and 8 μm, respectively (Fig. 2(b)–(c)). We also note that the ZnO microstructures with a smaller size have scattered nanorods.

The organic acid plays an important role during the formation of the flower-like ZnO microstructures under MH conditions. The flower-like ZnO microstructures are formed probably through a capping molecular mechanism similar to those proposed by Zhang et al. [14]. In this mechanism, the organic acid plays the role of selective adsorption agent, controlling the growth rate of various faces of ZnO through adsorption on these surfaces from different directions. Under basic condition and microwave irradiation, the dehydration reaction finishes in a short time. The nitro group stands on

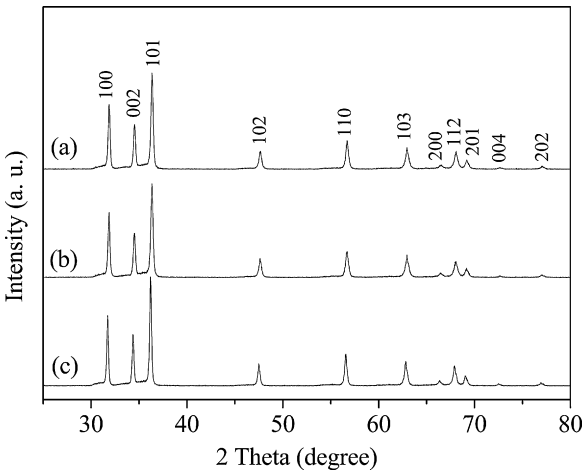

Fig. 1. Powder XRD patterns of flower-like ZnO microstructures prepared by MH method in the presence of (a) *o*-nitrobenzoic acid, (b) *m*-nitrobenzoic acid and (c) *p*-nitrobenzoic acid.

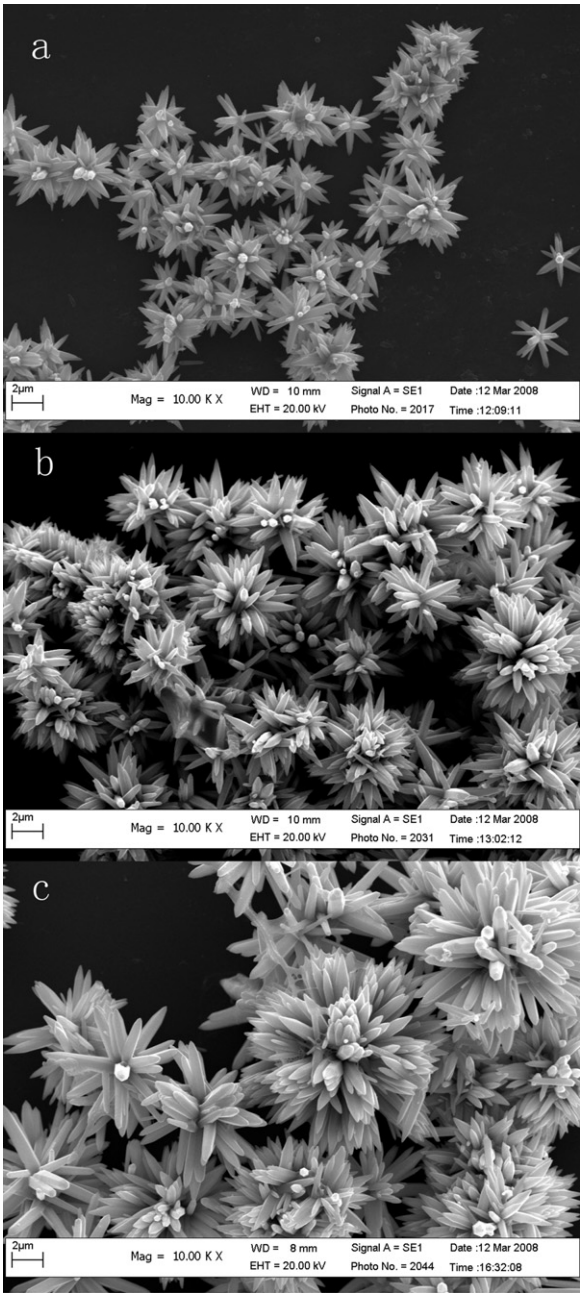

Fig. 2. SEM images of the samples prepared by MH method in the presence of (a) *o*-nitrobenzoic acid, (b) *m*-nitrobenzoic acid and (c) *p*-nitrobenzoic acid.

different positions of benzoic acid, which may influence the growth of ZnO microstructures because of different space steric hindrance effects, in which the space steric hindrance of ortho position is the biggest, the meta position is second and the para position is the smallest. As a result, all the products show a similar flower-like morphology but with different sizes and amounts of nanorods. According to Fig. 2, the size and the amount of nanorods of the three ZnO samples are in the order of *p*-ZnO > *m*-ZnO > *o*-ZnO. To substantially understand the effect of nitrobenzoic acids, the experiment of MH process without any assistant agent was carried out. Only submicrorods were obtained as shown in Fig. 3. The diameters of ZnO

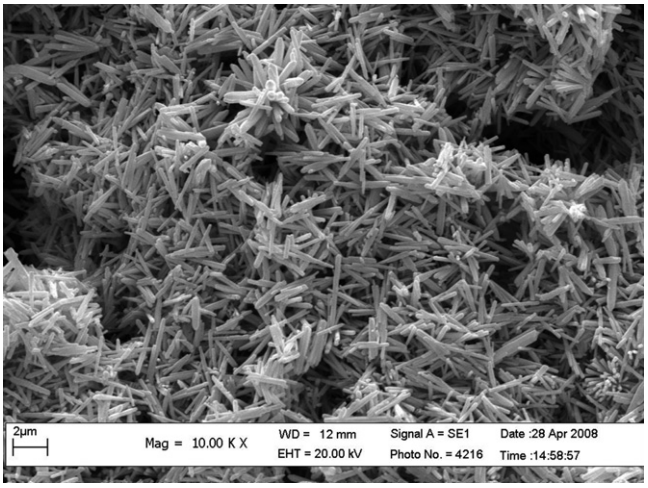

Fig. 3. SEM image of ZnO microrods obtained by the MH process without any assistant agent.

rods are about of 200 nm and length of up to 4 μm. The result exclusively indicates the function of nitrobenzoic acids for the formation of the flower-like ZnO 3D microstructures in the present MH process. However, the detailed mechanism for the formation of flower-like ZnO microstructures still needs to be investigated further.

To test the gas sensitivity of the products, we studied the ethanol sensing property of the as-prepared ZnO microstructures. Fig. 4 shows the response values to 100 ppm ethanol of the four kinds of sensors based on *Blank*-ZnO, *o*-ZnO, *m*-ZnO and *p*-ZnO at different operating temperatures. According to the results, the optimum working temperatures of all the sensors are the same (420 °C).

Also from Fig. 4, we can find that the sensor response of the four samples was in the order of *p*-ZnO > *m*-ZnO > *o*-ZnO > *Blank*-ZnO. The obtained results can be addressed by the bigger surface-to-volume ratio of *p*-ZnO (24.9 m^2/g) over that of *m*-ZnO (22.6 m^2/g), *o*-ZnO (19.3 m^2/g) and *Blank*-ZnO (16.6 m^2/g), as the sensing process of ZnO is generally

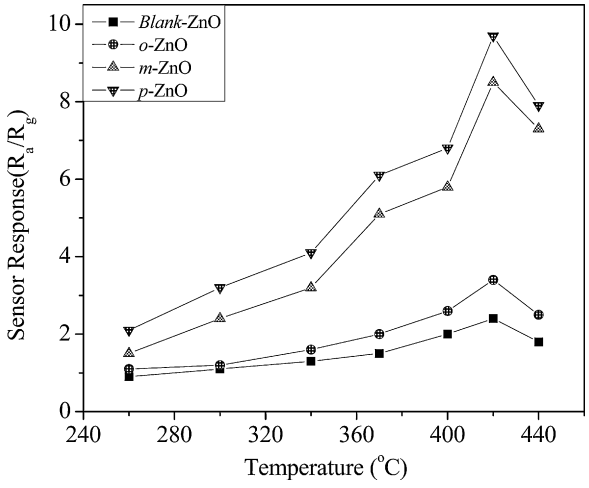

Fig. 4. Relationship between working temperature and sensor response of sensors made from *o*-ZnO, *m*-ZnO, *p*-ZnO and *Blank*-ZnO to 100 ppm ethanol.

considered as a surface controlled process [22,23]. The change of the resistance, which is responsible for the sensitivity, is mainly caused by the reaction between the test gases and the oxygen species such as O_2^-, O^-, O^{2-} on the sensor surface. These oxygen species are usually formed by the reaction of the oxygen molecules that are adsorbed on the sensor surface with electrons from the conductance band of the semiconductor sensor. Once the reaction between ethanol and active oxygen species occurs, electrons captured by the negative charged oxygen species will enter into the ZnO microstructures, resulting in a decrease in resistance of sensing materials, which means a corresponding increase of sensor response.

In order to further clarify the sensing characteristics of the flower-like 3D microstructures, the gas concentration dependences of the three sensors were tested. Fig. 5 shows the signal voltage versus time curves of *o*-ZnO, *m*-ZnO and *p*-ZnO to ethanol with different concentrations at 420 °C. It is clearly shown that the sensor response is enhanced with the increase of ethanol concentration for *o*-ZnO, *m*-ZnO and *p*-ZnO, respectively. Also, by comparing the three curves in Fig. 5, we find that there is a big difference between the responses of the three sensors. When ethanol with the same concentration was introduced into the test chamber, the signal voltage of *p*-ZnO changed to a new state with the highest voltage value, followed by *m*-ZnO and *o*-ZnO. The above phenomenon indicate that sensor *p*-ZnO had a comparatively high sensitivity to ethanol over *m*-ZnO and *o*-ZnO, which may be explained by the larger contact surface areas of *p*-ZnO compared to *m*-ZnO and *o*-ZnO. Furthermore, we find that the sensitivity of the sensors is influenced by the size and the amount of nanorods. Therefore, controlling the morphology and the size of the ZnO microstructures is important to their gas sensitivity.

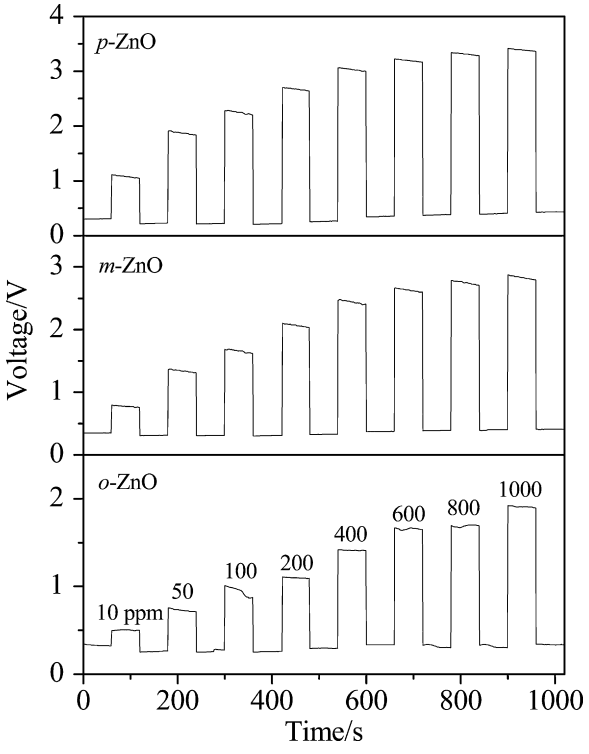

Fig. 5. Curves of signal voltage versus time of sensors made from *o*-ZnO, *m*-ZnO and *p*-ZnO at 420 °C with different ethanol concentrations.

4. Conclusions

In conclusion, flower-like ZnO microstructures with different sizes have been successfully prepared through a rapid MH route. The shape and size of the obtained microstructures are influenced by the *o* (*m*- or *p*)-nitrobenzoic acid. When *o*, *m* and *p*-nitrobenzoic acid are used as the structure-directing agent, the diameters of ZnO flowers are 4, 6 and 8 micrometer, respectively. This method provides a rapid, facile and efficient way to obtain unique flower-like ZnO microstructures. The gas sensitivity of the flower-like ZnO microstructures has a size dependent effect, which may be due to their different contact surface areas and special space configurations.

Acknowledgements

We appreciate the financial support of the High-Tech Project of Xinjiang Province (No. 200915124).

References

[1] D.E. Williams, Semiconducting oxides as gas-sensing resistors, Sens. Actuators B 57 (1999) 1–16.
[2] K. Potje-Kamloth, Semiconductor junction gas sensors, Chem. Rev. 108 (2008) 367–399.
[3] Z.P. Sun, L. Liu, L. Zhang, D.Z. Jia, Rapid synthesis of ZnO nano-rods by one-step, room-temperature, solid-state reaction and their gas-sensing properties, Nanotechnology 17 (2006) 2266–2270.
[4] T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani, A new detector for gaseous components using semiconductive thin films, Anal. Chem. 34 (1962) 1502–1503.
[5] H.W. Ryu, B.S. Park, S.A. Akbar, W.S. Lee, K.J. Hong, Y.J. Seo, D.C. Shin, J.S. Park, G.P. Choi, ZnO sol–gel derived porous film for CO gas sensing, Sens. Actuators B 96 (2003) 717–722.
[6] D. Gruber, F. Kraus, J. Müller, A novel gas sensor design based on $CH_4/H_2/H_2O$ plasma etched ZnO thin films, Sens. Actuators B 92 (2003) 81–89.
[7] J.H. Lee, Gas sensors using hierarchical and hollow oxide nanostructures: overview, Sens. Actuators B 140 (2009) 319–336.
[8] L. Liao, H.B. Lu, J.C. Li, H. He, D.F. Wang, D.J. Fu, Size dependence of gas sensitivity of ZnO nanorods, J. Phys. Chem. C 111 (2007) 1900–1903.
[9] F. Lu, W.P. Cai, Y.G. Zhang, ZnO hierarchical micro/nanoarchitectures: solvothermal synthesis and structurally enhanced photocatalytic performance, Adv. Funct. Mater. 18 (2008) 1047–1056.
[10] S. Ashoka, G. Nagaraju, C.N. Tharamani, G.T. Chandrappa, Ethylene glycol assisted hydrothermal synthesis of flower like ZnO architectures, Mater. Lett. 63 (2009) 873–876.
[11] L. Jiang, G.C. Li, Q.M. Ji, H.R. Peng, Morphological control of flower-like ZnO nanostructures, Mater. Lett. 61 (2007) 1964–1967.
[12] N.F. Hamedani, A.R. Mahjoub, A.A. Khodadadi, Y. Mortazavi, Microwave assisted fast synthesis of various ZnO morphologies for selective detection of CO, CH_4 and ethanol, Sens. Actuators B 156 (2011) 737–742.
[13] X.F. Zhou, S.Y. Chen, D.Y. Zhang, X.F. Guo, W.P. Ding, Y. Chen, Microsphere organization of nanorods directed by PEG linear polymer, Langmuir 22 (2006) 1383–1387.
[14] H. Zhang, D.R. Yang, Y.J. Ji, X.Y. Ma, J. Xu, D.L. Que, Low temperature synthesis of flowerlike ZnO nanostructures by cetyltrimethylammonium bromide-assisted hydrothermal process, J. Phys. Chem. B 108 (2004) 3955–3958.
[15] J.C. Ge, B. Tang, L.H. Zhuo, Z.Q. Shi, A rapid hydrothermal route to sisal-like 3D ZnO nanostructures via the assembly of CTA^+ and

$Zn(OH)_4^{2-}$: growth mechanism and photoluminescence properties, Nanotechnology 17 (2006) 1316–1322.

[16] Z. Wang, X.F. Qian, J. Yin, Z.K. Zhu, Large-scale fabrication of tower-like, flower-like, and tube-like ZnO arrays by a simple chemical solution route, Langmuir 20 (2004) 3441–3448.

[17] S. Li, G.A. Gross, P.M. Günther, J.M. Köhler, Hydrothermal micro continuous-flow synthesis of spherical, cylinder-, star- and flower-like ZnO microparticles, Chem. Eng. J. 167 (2011) 681–687.

[18] K. Zou, Y.S. Wu, J.B. Zhao, L.L. Wu, Ethylene glycol assisted hydrothermal synthesis of flower-like and sphere-like ZnO, Adv. Mater. Res. 148–149 (148) (2011) 849–850.

[19] X.T. Su, Y.N. Li, J.K. Jian, J.D. Wang, In-situ etched WO_3 nanoplates: hydrothermal synthesis, photoluminescence and gas sensor properties, Mater. Res. Bull. 45 (2010) 1960–1963.

[20] X.T. Su, F. Xiao, Y.N. Li, J.K. Jian, Q.J. Sun, J.D. Wang, Synthesis of uniform WO_3 square nanoplates via an organic acid-assisted hydrothermal process, Mater. Lett. 64 (2010) 1232–1234.

[21] Q.J. Sun, J.M. Luo, Z.F. Xie, J.D. Wang, X.T. Su, Synthesis of monodisperse $WO_3 \cdot 2H_2O$ nanospheres by microwave hydrothermal process with L (+) tartaric acid as a protective agent, Mater. Lett. 62 (2008) 2992–2994.

[22] J.Q. Xu, Y.P. Chen, D.Y. Chen, J.N. Shen, Hydrothermal synthesis and gas sensing characters of ZnO nanorods, Sens. Actuators B 113 (2006) 526–531.

[23] Y.L. Cao, P.F. Hu, W.Y. Pan, Y.D. Huang, D.Z. Jia, Methanal and xylene sensors based on ZnO nanoparticles and nanorods prepared by room-temperature solid-state chemical reaction, Sens. Actuators B 134 (2008) 462–466.