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Synthesis of hierarchical ZnO nanostructure assembled by nanorods and their performance for gas sensing

X.H. Jiang, S.Y. Ma*, W.Q. Li, T.T. Wang, W.X. Jin, J. Luo, L. Cheng, Y.Z. Mao, M. Zhang

Key Laboratory of Atomic and Molecular Physics & Functional Materials of Gansu Province, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China

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ABSTRACT

Dumbbell-shaped and flower-like zinc oxide architectures were fabricated by adding different surfactants under a simple hydrothermal route. Their morphologies and gas-sensing properties were mainly studied. The different morphology was attributed to the different surfactants. The polyethylene glycol (PEG) played a key role in the formation of the single-crystalline nanoflower. Among all of above samples, the sensor based on nanoflower showed the highest response, shortest response/recovery time and the most excellent selectivity to acetone under the optimal working temperature of 370 °C. The enhancement in acetone sensing properties was owed to flower-like hierarchical structure which could provide more gas diffusion ways. These results demonstrated that the ZnO nanoflower with PEG-assisted could be a good candidate for fabricating effective acetone sensors. In addition, a possible formation mechanism of nanoflowers and gas sensing mechanism were proposed, too.

1. Introduction

There has been received extensive researches about gas sensors based on metal oxide semiconductors, such as SnO_2, ZnO, TiO_2, Fe_2O_3, WO_3 and In_2O_3, which are used for detection of toxic, inflammable and corrosive gases [1]. As a potential candidate for gas sensors, ZnO becomes one of the most representative materials due to direct wide band gap of 3.37 eV and large binding energy of 60 meV [2]. Generally, the gas response is based on the adsorption or reaction of gas molecules on the surface [3]. Hence, the morphology of the sensing materials is regarded as a key factor to enhance the gas sensing performance [1–3]. Some workers have pointed out flower-like architectures show many superior advantages such as better selectivity, stability and excellent repeatability [4]. Herein, in this paper, the characteristic of gas sensitive of ZnO nanoflower by PEG-assisted is mainly studied. The sensor based on nanoflower exhibits the better performance to acetone at 370 °C. Moreover, the formation processes of ZnO nanoflower is also primarily discussed.

2. Experimental

The typical ZnO nanoflower sample was obtained as follows: 1.8 g $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 g PEG4000 were first dissolved into 20 ml distilled water. Then the mixed solution was stirred at 25 °C for 30 min. During this process, ammonia water ($NH_3 \cdot H_2O$) was added drop by drop for adjusting the pH value. Afterwards, the solution was transferred into 50 ml Teflon-lined stainless steel autoclave, the autoclave was heated to 120 °C for 24 h in an oven and then cooled down to room temperature naturally. The product was washed with distilled water and absolute ethanol several times and then dried at 80 °C for 2 h. Finally, the ZnO nanoflowers were obtained by annealing in a furnace at 450 °C for 2 h. It is noteworthy that the PEG could be replaced with the Polyvinyl Pyrrolidone (PVP) or Cetyltrimethyl Ammonium Bromide (CTAB), while keeping other conditions intact in order to obtain different samples for a clear comparison.

Microstructures were characterized by X-ray diffraction (XRD, D/Max-2000), scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, USA FEI TEVNAI G^2 TF20). The gas sensing performance was measured by WS-60A gas sensing measurement system (Wei Sheng Electronics Science and Technology Co. Ltd. China). The response (R) was defined as R_a/R_g, where R_a and R_g were the resistance of the sensor in air and test gas, respectively [5].

3. Results and discussion

Fig. 1(a) displays the XRD patterns, which indicate that all the ZnO samples present a hexagonal wurtzite structure and all diffraction peaks are in accordance with JCPDS card (No. 36-1451). No

* Corresponding author. Tel.: +86 18393718240; fax: +86 9317971503.
E-mail address: 18393718240@163.com (S.Y. Ma).

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other peaks of impurity are observed, which indicate the high purity of the ZnO hexagonal phase of these products. Thus, the result shows that the as-prepared products are signal phase hexagonal ZnO. The EDX spectroscopy of ZnO nanoflower (Fig. 1(b)) indicates that it is composed of Zn and O elements (the presence of signals of Cu and C can be ascribe to the Cu and C grid).

The surface morphologies of as-prepared ZnO samples are dowsed by SEM technique. Fig. 2(a–c) show dumbbell-shaped, where it can be seen the sample's size is more and more smaller with different surfactants of none, PVP or CTAB, respectively. However, the unique flower-like associate with the numerous nanorods also turn up in the sample with the PEG (Fig. 2(d)).

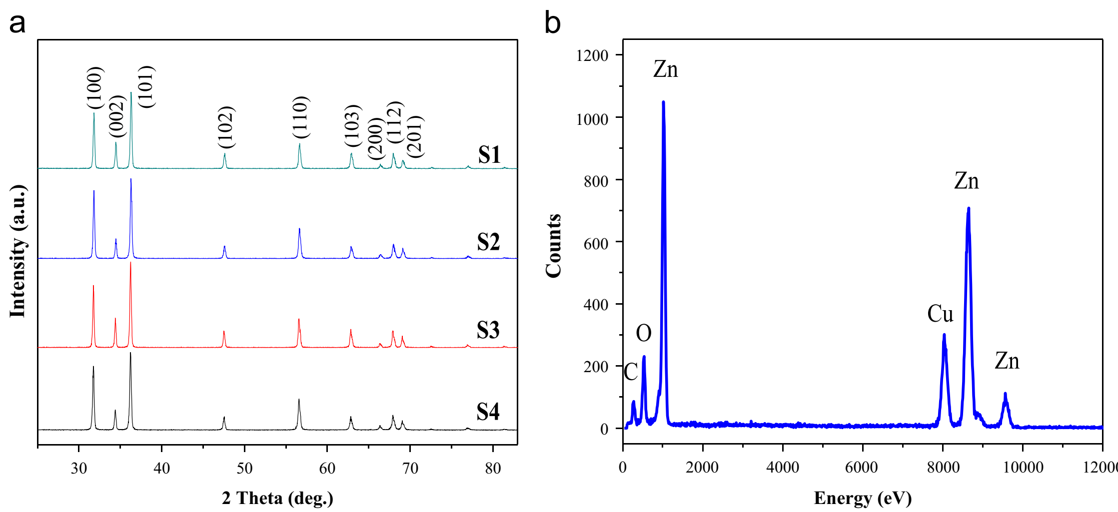

Fig. 1. (a) XRD patterns of S1 (without surfactant), S2 (with PVP), S3 (with CTAB) and S4 (with PEG) samples. (b) EDX pattern of ZnO nanoflower.

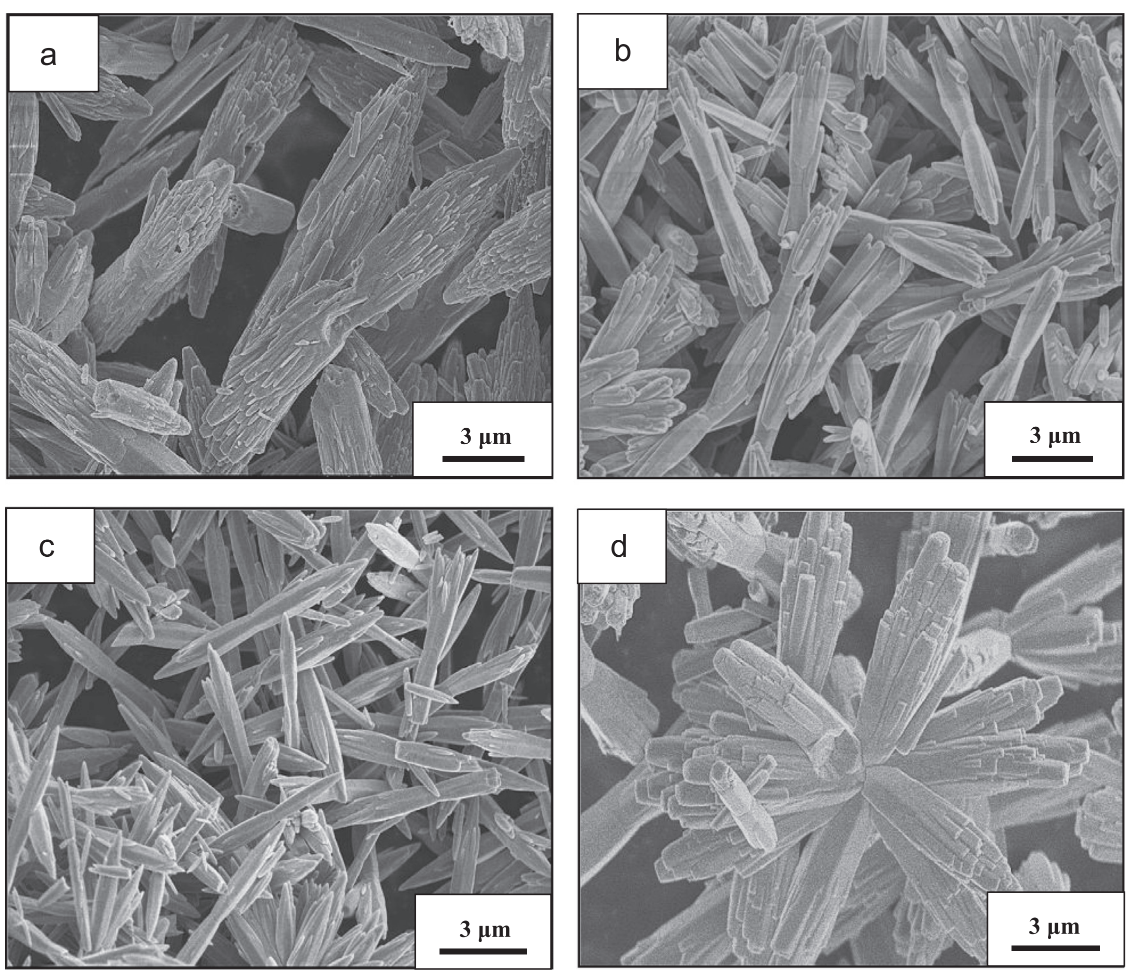

Fig. 2. SEM images of the sample (a) S1, (b) S2, (c) S3 and (d) S4.