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Flower-like hierarchical zinc oxide architectures: Synthesis and gas sensing properties

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ABSTRACT

The unique flower-like hierarchical zinc oxide architectures were successfully synthesized from a mixture of zinc nitrate dehydrate and hydrazine hydrate by a facile hydrothermal method. The as-synthesized samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). Based on the experimental results, a possible formation mechanism of the three-dimensional ZnO hierarchical nanostructures was proposed. In addition, the gas sensing properties of as-prepared products were investigated. It was found that the sensor based on flower-like ZnO nanostructure exhibited high response, and good selectivity to hydrogen sulfide at 150 °C.

1. Introduction

There has been extensive research on metal oxide semiconductor based gas sensors, such as SnO_2 [1], ZnO [2], TiO_2 [3], Fe_2O_3 [4], WO_3 [5] and In_2O_3 [6], due to their industrial and domestic applications in toxic and flammable gas detection. It has been found that the gas sensing properties of devices are strongly dependent on the morphology of the sensing materials. Therefore, the morphological study of different materials makes a great sense to the research and application of gas sensors. Recently, zinc oxide (ZnO), which is widely known as a kind of wide-band gap semiconductors, has been proved to be an excellent gas sensing material for both oxidative and reductive gasses at the parts per million (ppm) levels and above [7]. Many exciting results on ZnO based gas sensors have been reported [8,9]. However, it remains to be a challenge for the development of more highly sensitive and selective gas sensors.

In this study, we present a facile hydrothermal method for the synthesis of the hierarchical flower-like ZnO. The as-prepared products were investigated in terms of the crystallinity, morphology, and structure. Moreover, the dependence of the morphology evolution on different reaction times has been investigated, and a possible formation mechanism was proposed. Finally, the gas sensing properties of the sensors based on the flower-like ZnO nanostructure to hydrogen sulfide had been investigated.

2. Experimental

In a typical synthesis process, 1.0975 g (5 mmol) $Zn(Ac)_2 \cdot 2H_2O$ was dissolved in 30 ml deionized water in a glass beaker and stirred for 5 min. Then 2 ml $N_2H_4 \cdot H_2O$ was slowly added dropwise in the above solution with stirring. The resulting suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave and sealed tightly. Hydrothermal treatments were then carried out at 150 °C for 24 h. After slowly being cooled to room temperature, white-colored solid powders were collected by centrifugation and washed with deionized water and absolute ethanol for several times prior to dry in air at 80 °C.

3. Results and discussion

3.1. Structural and morphological characteristics of the prepared ZnO

X-ray powder diffraction (XRD) analysis was performed to investigate the crystal phase of the flower-like hierarchical ZnO (Fig. 1a). All peaks of the sample could be indexed to hexagonal wurtzite ZnO (JCPDS card no. 36-1451). No characteristic peaks from any other impurities were detected. Furthermore, the strong and sharp diffraction peaks suggested that the products were of high crystallinity.

The morphologies and microstructures of the obtained ZnO products were characterized by FESEM observations. A panoramic FESEM image of the flower-like hierarchical ZnO architecture obtained after hydrothermal treatment is shown in Fig. 1b. We could see that each nanostructure was assembled from the homocentrically growing uniform branches. From the enlarged FESEM images of Fig. 1c and d, it could be observed that each branch of the flower-like morphology

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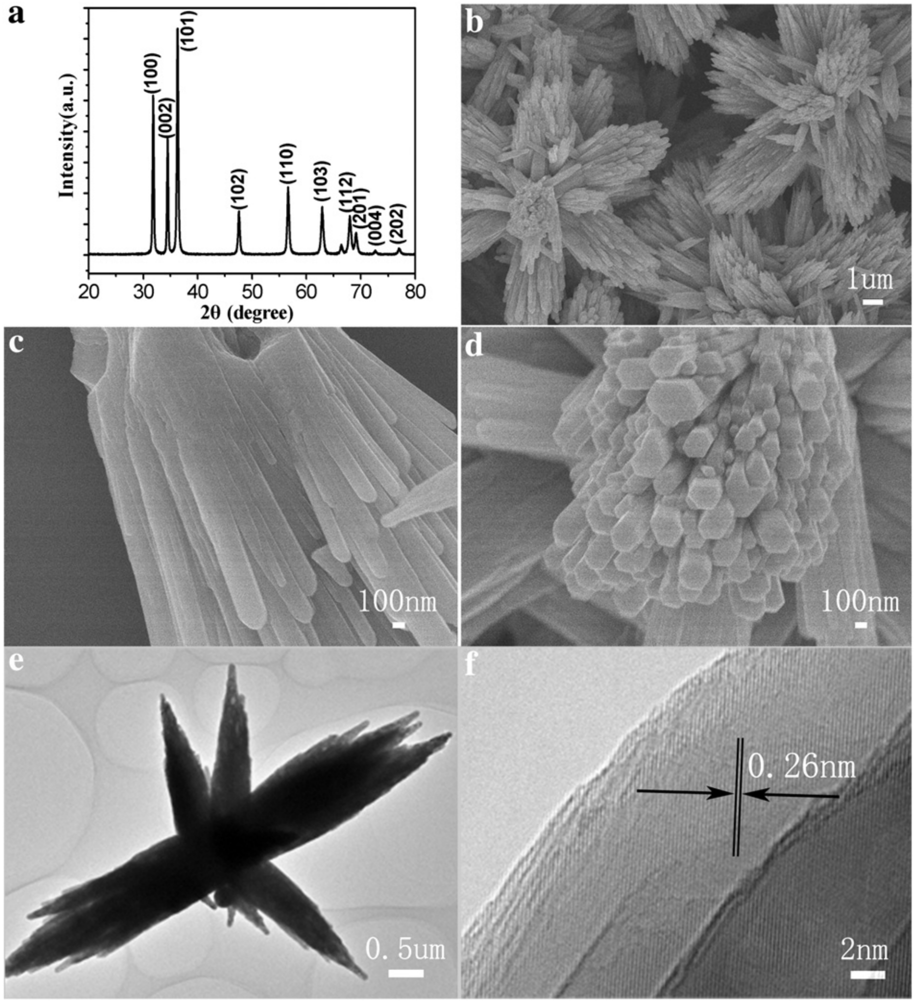

Fig. 1. (a) XRD patterns of the as-prepared ZnO sample, (b) low-magnification SEM image of the as-prepared ZnO sample, (c and d) are high-magnification SEM images of different locations, (e) TEM image result of the as-prepared ZnO sample, (f) HRTEM image of the nanorod.

was built from one-dimensional hexagonal nanorods with the diameters about 300 nm and the lengths about 5 μm. The typical TEM image in Fig. 1e shows that the hierarchical nanostructures were built from many one-dimensional nanorods, which was in accordance with the FESEM images. The corresponding HRTEM image (Fig. 1f) confirmed that the nanorod was single crystalline in structure and the spacing between two lattice planes was 0.26 nm, which was consistent with the (0 0 0 2) plane of wurtzite ZnO phase.

3.2. Growth process and mechanism of the flower-like ZnO

To understand the formation process of flower-like ZnO structure and possible growth mechanism, the evolutional morphology of the intermediates obtained at different reaction time had been investigated in detail and the results are shown in Fig. 2. The FESEM image of the sample synthesized after stirring without hydrothermal process is shown in Fig. 2a. It could be observed that the sample consisted of some irregularly polyhedra. The XRD pattern of the sample (the inset in Fig. 2a) indicated that the majority of the diffraction peaks could be clearly indexed as $Zn(OH)_2$ and matched well with the reported values from the Joint Committee on Powder Diffraction Standards card (JCPDS file no. 89-138). We could conclude that $Zn(OH)_2$ was formed at early stage before hydrothermal treatment. When the hydrothermal time was increased to 30 min, a flower-like morphology, accompanied with some aggregations, was formed (Fig. 2b). As the hydrothermal process was prolonged to 24 h, the hierarchical flower-like ZnO nanostructures were fully developed and no aggregations could be observed in the product (Fig. 1b).

The schematic illustration of growth mechanism for flower-like hierarchical ZnO architectures under hydrothermal condition is shown in Fig. 2c. In the initial stage of hydrothermal reaction, the complex $Zn(OH)_4^{2-}$ decomposed quickly and massive ZnO nuclei were created, resulting in immediate solution supersaturation due to the low solubility of ZnO [10,11], and the reactions are as follows.

$$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-} \tag{1}$$

$$N_2H_4 \cdot H_2O = N_2\uparrow + 2H_2\uparrow + H_2O \tag{2}$$

$$Z_n(OH)_4^{2-} = ZnO\downarrow + H_2O + 2OH^- \tag{3}$$

As $N_2H_4 \cdot H_2O$ could provide hydroxide anions very quickly due to its strong basicity, a large amount of growth units ($Zn(OH)_4^{2-}$ complexes) could be generated [10]. Therefore, more growth units around the ZnO nuclei might lead to a faster growth kinetics, which caused sheet defects on initial ZnO crystal [10,11]. The initial ZnO crystal had many polar (0001) surfaces due to many deviations from the idealized fourling structures of ZnO [12]. Second, ZnO crystals grew preferentially along the [0001] direction and formed a flower-like

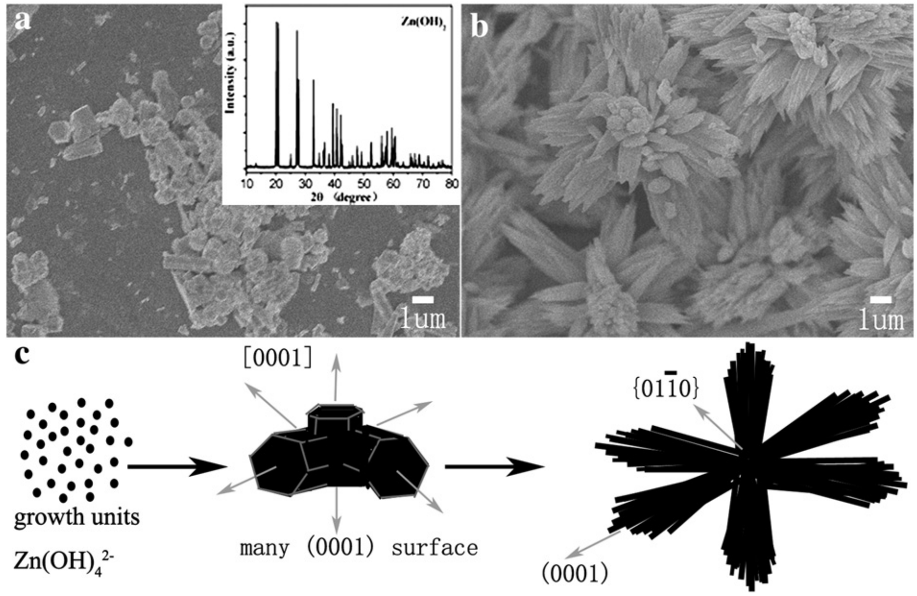

Fig. 2. SEM images of morphology evolution of samples prepared with different time: (a) 0 min and (b) 30 min. The inset of (a) shows the XRD pattern of the as-synthesized sample without hydrothermal process, (c) schematic illustration of the formation process of flowerlike hierarchical ZnO nanostructures.

shape due to the higher growth rate along the [0001] direction [12,13]. Formation of flower-shaped ZnO could also be dependent on the experimental conditions (pH value, Zn^{2+} concentration, time and temperature) [11,14].

3.3. Gas-sensing properties

The gas sensing properties of the sensor using hierarchical ZnO were investigated. Since selectivity is an important parameter of gas sensors for its practical application, the selectivity of the sensor was firstly measured. Fig. 3a shows the response of sensors using hierarchical ZnO to various target gasses, such as C_2H_9, CH_4, H_2, NO_2, CO, toluene, acetone, ethanol, Cl_2, NH_3 and H_2S. All of the gasses were tested at an operating temperature of 150 °C with a concentration of 100 ppm. It could be seen clearly that the sensor exhibited the highest response to H_2S and negligible responses to C_2H_9, CH_4, H_2, NO_2, CO, toluene, acetone, ethanol, Cl_2 and NH_3. The results indicated that the as-prepared hierarchical flower-like ZnO nanostructure displayed superior selectivity to H_2S against the other interference gasses and was very suitable for sensing H_2S at the operation temperature of 150 °C.

The relationship between response and H_2S concentrations for the sensor at operating temperature of 150 °C is depicted in Fig. 3b. From the curve, it was found that the response increased with the increase of H_2S concentration from 10 to 3000 ppm. Especially, the sensor using ZnO nanoflowers was found to exhibit high responses to H_2S gas even at low concentrations, e.g., the response to 10 ppm H_2S was 20. When the H_2S concentrations reached higher levels (2000 ppm), the response almost tended to saturation.

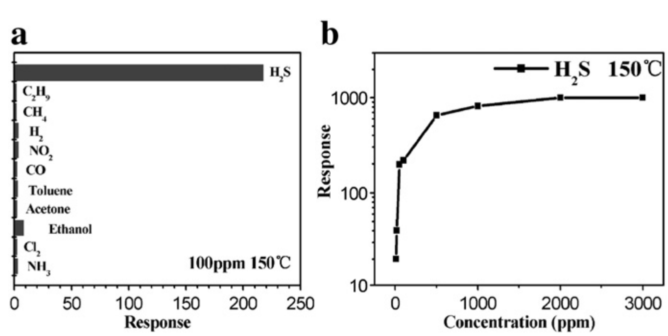

Fig. 3. (a) Response of the sensor to various test gasses at 150 °C, (b) response of the sensor versus the hydrogen sulfide concentrations.

4. Conclusions

In summary, flower-like hierarchical ZnO architectures have been successfully synthesized by a hydrothermal method. FESEM and TEM results revealed that these hierarchical nanostructures were built from one-dimensional nanorods with the diameters of 300 nm and the lengths of 5 μm. According to the experimental results, a possible formation mechanism of the three-dimensional ZnO hierarchical nanostructures was proposed. Moreover, the gas sensing properties of as-prepared products were investigated. It was found that the sensor based on flower-like ZnO nanostructure exhibited high response and good selectivity to hydrogen sulfide at 150 °C.

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