Materials Letters 202 (2017) 44–47

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Controllable synthesis of zinc oxide hierarchical architectures and their excellent formaldehyde gas sensing performances

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ARTICLE INFO

Article history:
Received 27 April 2017
Received in revised form 15 May 2017
Accepted 17 May 2017
Available online 17 May 2017

Keywords:
Semiconductors
Zinc oxide
Formaldehyde
Sensors

ABSTRACT

Two kinds of ZnO hierarchical architectures are skillfully designed and successfully fabricated by facile room temperature solution routes followed by subsequent annealing treatments. SEM and XRD characterizations reveal that as-prepared ZnO products both present typical flowerlike morphologies but are assembled by abundant porous nanosheets and smooth nanosheets, respectively. Such hierarchical architectures are developed for formaldehyde (HCHO) detection. The gas sensing results indicate that porous-nanosheet assembled ZnO hierarchical architectures based sensors exhibit better HCHO gas sensing properties in terms of high sensitivity, good selectivity and rapid response/recovery time compared with smooth-nanosheet assembled ZnO architectures. Such excellent formaldehyde gas sensing performances are predominantly attributed to unique porous-nanosheet constructed three dimensional hierarchical structures, providing beneficial conditions for gas diffusion/adsorption, surface reaction and electron transfer.

1. Introduction

Zinc oxide (ZnO), serving as an important n-type semiconductor functional material, has attracted extensive interest due to its abundant potential applications in lithium-ion batteries [1], photodetectors [2], solar cells [3] and especially for remarkable gas sensing performances in detecting volatile organic compounds (VOCs) [4–6]. It is well-known that gas sensing characteristics of oxide semiconductors based gas sensors are greatly dependent on their morphologies, structures and compositions. Thus, controllable synthesis of ZnO nanomaterials with specific structure and desired composition is of important scientific and practical significance for the promotion of gas sensing performances and the development of gas sensors. Among various structures, three dimensional hierarchical architectures assembled by much low dimensional building blocks (such as nanoparticles, nanowires, nanorods, etc.) can provide substantial performance boosts for gas sensors owing to loose gas diffusion channels, high stability and large specific surface area [7,8].

Formaldehyde (HCHO), as one of the most serious pollutants and carcinogenic volatile organic compounds, commonly exists in indoor decorative materials and is a major cause of many diseases. Hence, the efficient detection of HCHO is of great importance and much needed for both human health and environmental protection.

In this paper, porous-nanosheet and smooth-nanosheet assembled flowerlike ZnO hierarchical architectures are skillfully designed and are successfully synthesized by facile routes. The gas sensors based on porous-nanosheet assembled ZnO hierarchical architectures exhibit better gas sensing performances, which are attributed to unique porous-nanosheet constructed three dimensional hierarchical structures.

2. Experiments

All reagents were analytical-grade purity and were used as purchased without further purification. The whole experiments included the controllable synthesis of precursors and the annealing treatment of precursors.

The precursors of porous-nanosheet assembled ZnO hierarchical architectures were fabricated as follows. 0.1 g zinc chloride and 0.14 g oxalic acid was dissolved in 10 mL and 50 mL absolute ethanol under stirring, respectively. Subsequently, zinc chloride ethanol solution was added into oxalic acid ethanol solution. After stirring for 1.5 h, white precipitates were collected by centrifuging, washed with absolute ethanol and dried in air at 60 °C for 5 h.

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http://dx.doi.org/10.1016/j.matlet.2017.05.076
0167-577X/

The precursors of smooth-nanosheet assembled ZnO hierarchical architectures were synthesized as follows. 0.3 g sodium hydrate and 0.3 g zinc acetate was dissolved in 10 mL and 50 mL deionized water with stirring, respectively. Subsequently, sodium hydrate aqueous solution was added dropwise into zinc acetate aqueous solution. After stirring for 5 min, 50 mL ethanol was slowly added into above mixed solution. After being stirred for another 5 min, white precipitates were collected by centrifuging, washed with deionized water and ethanol and dried in air at 60 °C for 5 h.

The ZnO hierarchical architectures were obtained by calcining white precipitates at 500 °C for 2 h.

The morphologies of the as-prepared ZnO products were examined using a Hitachi SU8010 scanning electron microscope. The phase structures of samples were characterized by a Bruker D8A X-ray diffractometer. The detail of the sensor fabrication was similar to our previous report [9]. The gas sensing properties were tested on a CGS-8 gas sensing analysis system. The response was defined as $S = R_a/R_g$. Here, R_a and R_g was the resistance of the gas sensor in the air and target gas, respectively. The response time and recovery time was defined as the time taken by the sensor to reach 90% of the total resistance variation in the case of adsorption and desorption, respectively.

3. Results and discussion

Fig. 1a and c shows the low magnification FESEM image of porous-nanosheet assembled and smooth-nanosheet assembled ZnO hierarchical architectures, respectively. The as-prepared products both exhibit well dispersion and approximately uniform flower-like contour. The diameters of porous-nanosheet and smooth-nanosheet assembled ZnO architectures are about 3–4 μm and 2–3 μm, respectively. The details from high magnification SEM images (Fig. 1b and d) indicate that ZnO hierarchical architectures are assembled by abundant porous nanosheets and smooth nanosheets, respectively. The nanosheets intersect each other and form radial three dimensional hierarchical structures, which can effectively prevent nanosheets aggregation and maintain the long-standing existence of the hierarchical architecture.

Fig. 2 presents FESEM image of precursors of as-synthesized ZnO hierarchical architectures. Precursors of both ZnO products show flowerlike morphologies. Combining Fig. 1, it can be concluded that flowerlike shapes are not destroyed during the annealing treatment. Meanwhile, it is interesting to find that precursors of porous-nanosheet assembled ZnO are constructed by much smooth nanosheets, indicating the dehydration of precursors results in building blocks conversion from smooth nanosheets to porous nanosheets.

The crystal phases of both ZnO hierarchical architectures are characterized by XRD. As shown in Fig. 3, all of the diffraction peaks can be indexed to the standard ZnO with the hexagonal structure (JCPDS No. 80-0075). No diffraction peaks from any other impurities are observed, indicating the high purity of ZnO products.

Fig. 4a shows responses of porous-nanosheet and smooth-nanosheet assembled ZnO hierarchical architectures based sensors to 100 ppm HCHO at different operating temperatures. Obviously,

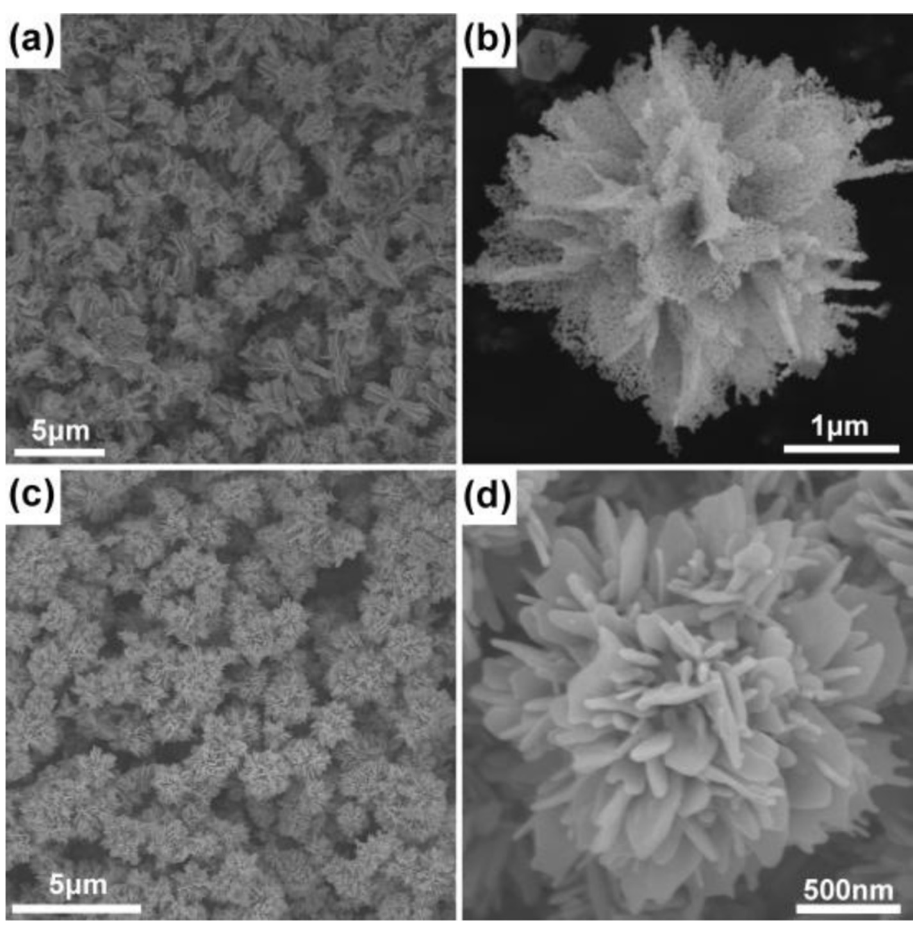

Fig. 1. FESEM images of porous-nanosheet assembled ZnO (a, b) and smooth-nanosheet assembled ZnO (c, d) hierarchical architectures.