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Synthesis of three-dimensional flower-like hierarchical ZnO nanostructure and its enhanced acetone gas sensing properties

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ABSTRACT

A three-dimensional (3D) flower-like hierarchical ZnO nanostructure was successfully synthesized via a facile and efficient hydrothermal method. The sample was characterized by XRD, FESEM, Raman, UV–vis DRS and Photoluminescence (PL) techniques. The XRD pattern revealed that the sample was well-crystallized in a hexagonal wurtzite structure. FESEM images showed that the as-prepared ZnO exhibited a nanosheet-assembled hierarchical flower-like ZnO nanostructure, which was self-assembled by thin and uniform nanosheets with a thickness of approximately 30 nm. Raman spectra exhibited that the sample kept the crystal structure of the bulk ZnO and possessed more surface defects. UV–vis spectra showed that a significant blue-shift in the absorption edge for the as-prepared ZnO as compared to the commercial ZnO. PL spectra indicated that the concentration of surface oxygen vacancies in the as-prepared ZnO was much higher than that of the commercial ZnO. Furthermore, the nanosheet-assembled flower-like ZnO nanostructure exhibited excellent gas sensing properties towards acetone, indicating that the as-prepared ZnO architecture is a promising material for gas sensors.

1. Introduction

With the rapid development of industrialization and urbanization in the past few decades, environment pollution caused by the volatilization of hazardous gases has become an important issue. Acetone, as a widely used solvent in industry and laboratory, can volatilize easily and affect human health when its concentration is higher than 173 ppm [1]. Although the study on acetone sensor is necessary, the present reported acetone sensors have suffered from some disadvantages, such as poor selectivity, inadequate sensitivity [2–6]. Therefore, it is highly desirable to develop high performance sensors for rapidly selective detection of acetone.

Among various metal oxide semiconductor (MOS)-based gas sensing materials studied so far, ZnO, as a nontoxic, inexpensive and wide-band-gap II–VI compound semiconductor, has been proved to be one of the promising materials for gas sensors [7–11]. It's well known that the properties of ZnO depend highly on its nanostructures, including crystal size, orientation and morphology. As a consequence, ZnO nanocrystals with highly controlled microstructures have been investigated extensively in recent years [12–14]. Specially, ZnO hierarchical nanostructures assembled from lower dimensional nano-building blocks have attracted tremendous attention due to their exceptional physical and chemical properties [15–18].

Up to now, various hierarchical ZnO architectures, including nanowire arrays, nanohelixes, nanopropellers, urchin-like spheres, flower-like microstructure and tower-like nanocolumns have been prepared by different methods, such as thermal evaporation, chemical vapor deposition (CVD), template-assisted growth, electrochemical process, solvothermal process, electrospinning, and hydrothermal process [19–22]. However, most of hierarchical ZnO architectures were fabricated successfully with the assistance of surfactants or templates. So the self-assembly of ZnO nano-building blocks into 3D hierarchical architectures in the absence of any

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surfactants or templates is still remained a big challenge for researchers. Among all fabrication techniques, hydrothermal synthesis, as an important method of solution synthesis, is particularly attractive due to its low energy requirement, safe and environmentally friendly processing condition, sufficient crystallization and high-quality growth orientation [23].

In this paper, 3D flower-like hierarchical ZnO nanostructure assembled by ZnO nanosheets is prepared by a simple hydrothermal method in the absence of surfactant and template. The structural, optical and gas sensing properties of the as-prepared sample are investigated. In addition, the possible formation and sensing mechanism of 3D flower-like hierarchical ZnO nanostructure is discussed.

2. Experimental

2.1. Sample synthesis

All reagents were analytically pure, purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China), and used without further purification.

The 3D flower-like hierarchical ZnO nanostructure was prepared by a hydrothermal method. In a typical procedure, $Zn(NO_3)_2$ (9 mM) was dissolved in 25 ml of distilled water. Then pH of the solution was maintained around 11 by gradually adding KOH followed by vigorous stirring. The above solution was transferred into a Teflon-lined stainless steel autoclave and kept at 200 °C for 3 h. After the heating was terminated, the solution was allowed to cool down to room temperature. The product was harvested using centrifugation, washed with distilled water and ethanol for four times alternately, and dried at 60 °C in a vacuum. Finally, the 3D flower-like hierarchical ZnO nanostructure was obtained and subjected to structural and gas-sensing characterizations.

2.2. Characterization

The crystallographic structures of the samples were collected by powders X-ray diffraction (XRD, Cu Ka radiation, SmartLab 3 kW, Rigaku, Japan). The product morphology observations were carried out on Field Emission Scanning Electron Microscopy (FESEM, Su8010, Hitachi). Raman spectra were collected using a Renishaw InVia micro-Raman spectrometer in backscattering geometry with an Ar^+ laser (λ_{ex} = 532 nm). UV–vis spectra were recorded on Ultraviolet Spectrophotometer (UV-2550, Shimadzu), using $BaSO_4$ as a reference. Steady and time-resolved photoluminescence (PL) spectra were measured at room temperature on an Edinburgh FLS-920 spectrometer.

2.3. Fabrication of sensors

The gas-sensing performance of the sensors was measured through a gas-sensing characterization system (WS-30A, Weisheng Electronics Co., Ltd., China). The structure of the gas sensor belongs to the side-heated type. The preparation process is described as follows: the as-prepared sample was mixed with a suitable amount of terpineol to form a paste and then coated onto the surface of a ceramic tube where a pair of Au electrodes had been installed at each end, and a Ni–Cr heating wire going through the tube was employed as a heating filament to control the operating temperature by tuning the heating voltage. Measuring electric circuit and the structure of the gas sensor is the same as described in the literature [24]. Then the sensors were dried and aged for testing. The operating temperature was regulated automatically by the gas-sensing system and accurately controlled by adjusting the heating voltage. In the process of test, a given amount of target gas were injected into a test chamber and uniformly dispersed by a fan. The gas response was defined as the ratio of the electric resistance, namely S = Ra/Rg, where Ra and Rg is the resistance of metal oxide semiconductors in air and the target gas, respectively. The response or recovery time was estimated as the time taken for the sensor output to reach 90% of its saturation after applying or switching off the target gas in a step function.

3. Results and discussion

3.1. Structure and morphology

The analysis of the phase and crystallinity of the samples was performed by XRD. The representative XRD patterns of the as-prepared and commercial ZnO powders are shown in Fig. 1. The JCPDS data of ZnO (card No. 36-1451, green bars (in the web version)) is also included in this figure for comparison. The crystal planes (100), (002), (101), (102), (110) and (103) in the XRD patterns can be perfectly indexed to the hexagonal wurtzite structure of ZnO according to the ZnO standard JCPDS card and no diffraction peaks from any other impurities were detected. The strong and sharp diffraction peaks suggest that the product is highly crystalline. A comparison between the XRD patterns of the as-prepared and commercial ZnO powders indicates that the as-prepared ZnO displays the preferential orientation of the (002) facet. It also should be noted that, from the ZnO JCPDS file and commercial ZnO XRD pattern, the diffraction intensity ratio of the (002) polar facets and the (100) nonpolar facets are 0.77 and 0.87, respectively. However, from the XRD pattern of the as-prepared ZnO, the ratio increases to 0.99, suggesting the abundant (002) planes of the as-prepared ZnO and a large fraction exposure of polar facets [25]. In addition, it can be seen in Fig. 1 that the integrated intensity of the (101) Bragg reflections, which showed the maximum intensity in the XRD patterns and can be used as a good yardstick to evaluate the structural perfection, is larger for the as-prepared ZnO than that for commercial ZnO. This suggests that the degree of structural perfection for the as-prepared ZnO increased as compared to commercial ZnO.

The morphology and microstructure of the as-prepared product were characterized via FESEM. Fig. 2A–C shows the representative

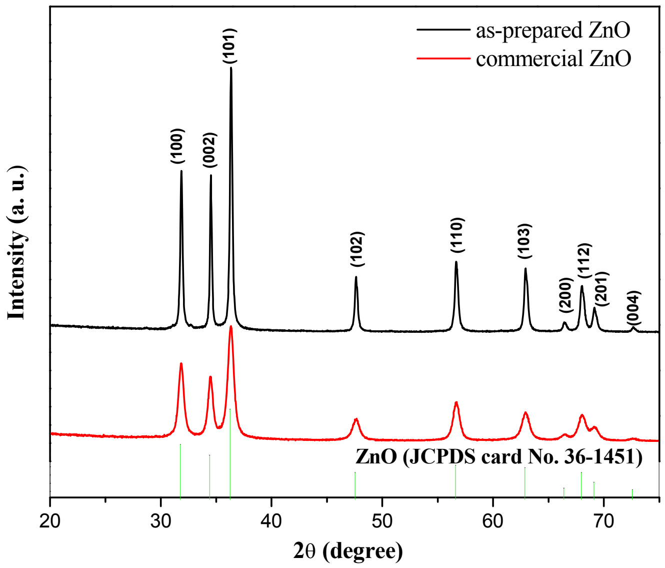

Fig. 1. XRD patterns of the as-prepared ZnO nano-architecture and commercial ZnO powders.