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2D nanosheet-assembled Pd−ZnO microflowers for acetone sensor with enhanced performances

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ABSTRACT

Hierarchical microflowers architecture assembled with 2D porous ZnO nanosheets were fabricated by a one-step solvothermal method and subsequent annealing process. A series of Pd−ZnO have been produced by injecting various volumes of $Pd(NO_3)_2{\cdot}2H_2O$ solution. The ZnO and Pd−ZnO microflowers are applied to fabricate gas sensors to investigate their sensing characteristics for various gases at different operating temperatures. The 0.05 wt% Pd−ZnO exhibit the highest selective enhancement of acetone (165%) than ammonia (0.9%), methanal (38%), methanol (71%), H_2 (35%) and CO (15%). In addition, it possesses the lower operating temperature and shorter response/recovery times (11s, 5s) toward acetone gas compared with the pure ZnO microflowers.

1. Introduction

Acetone is an important raw material for organic synthesis, the good organic solvents and the extracting agent of industry. In particular, the concentration of acetone in breath could be a vital index for diabetes mellitus [1,2]. Hence, it is urgent to find an easier, more effective solution to detect the acetone. Recently, acetone chemical sensor based on the metal-oxide semiconductors has been widely investigated for its high sensitivity, excellent selectivity and long-time stability [3,4].

Zinc oxide (ZnO), with a band gap (3.37eV), has been widely applied in photocatalysis, solar cell, transistor devices, water splitting and gas sensors [2,5–8]. Till now, diverse morphologies of ZnO, such as nanoparticle, nanowire, nanorod, and nanosheet [9–13], have been carried out by using various synthesis methods. ZnO nanosheet, for example, has been extensively used to detect chemicals such as acetone (CH_3COCH_3), ethanol (C_2H_5OH), nitrogen dioxide (NO_2), methanal (HCHO) and carbonic oxide (CO) [14–18]. In recent years, the high level 3D supercrystals evolved from low dimensional nano-architectures has caused great attention [19–21]. Due to the large specific surface areas, 3D porous architectures or hollow microspheres materials were always applied to fabricate sensors and exhibited enhanced responses for toxic gas [22,23]. However, gas sensors still meet testing requirements under some rigorous conditions like low selectivity and high operating temperature [24]. To overcome the issues, many efforts to improve the sensitivity of ZnO sensors have been made for examples, preparation of nanostructures with different morphologies [17,25], metal oxide heterostructures [20,26], and noble metals adding (such as Ag, Au, Pd, Pt) [27–29]. Pd nanoparticles (NPs) is one of the best gas sensor candidate owing to their excellent chemical stability, high surface area and low orbital energy [30–32]. Hence, Pd−ZnO materials could improve the sensing response, selectivity, response time and recovery of chemical sensors. However, only a few articles have been concerned with the synthesis of Pd−ZnO microflowers and focused on the selective enhancement to acetone vapor.

In this paper, porous nanosheet-assembled hierarchical ZnO microflowers are synthesized via a novel one-step solvothermal route and subsequently a calcination procedure. Pd nanoparticles in size of 10 nm are uniformly decorated on the surface of ZnO through injecting the solutions of $Pd(NO)_3{\cdot}2H_2O$. Sensing performance based on pristine ZnO and Pd−ZnO are systematically investigated.

2. Experimental procedure

2.1. Synthesis of ZnO microflowers

1 mmol of $ZnCl_2$ and 1 mmol of urea were dissolved into 40 mL of mixture solution which containing ethanol and deionized water with a ratio of 3:1. After the solution became homogeneous, PVP (0.2000 g) was added which acting as an surfactant to help the structure forming of ZnO precursors. The mixtures were transferred into 50 mL teflon-

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lined stainless steel autoclaves and kept at 180 °C for 4 h. The white precipitates were obtained after hydrothermal reaction and washing several times, dried at 60 °C overnight. The products were calcined in air at 500 °C to yield crystalline ZnO microstructures.

2.2. Preparation of Pd decorating ZnO microflowers

To prevent the ZnO surface structure from being affected by chemically active precursors such as nitrates, the Pd−ZnO were prepared by injecting palladium II acetate salt onto the surface of ZnO, followed by drying at 80 °C for 8 h and calcined at 300 °C for 2 h in argon atmosphere. For each series, the Pd decorating amount (wt %) was varied at 0, 0.01, 0.05, and 0.1 wt%.

2.3. Characterization

The materials crystal structures were investigated by powder X-ray diffraction (XRD) patterns on a D/max 2550 V diffractometer with monochromatized Cu Kα (λ = 1.54056 Å) incident radiation. Morphologies and sizes of the samples were characterized by field-emission scanning electron microscopy (FESEM, JSM-7001F, 10 kV) images, transmission electron microscopy (TEM, JEM-2100, operating at 200 kV), high-resolution TEM (HRTEM, 200 kV) and selected-area electron diffraction (SAED). Thermal analysis was performed by a TG/DTA instrument(TA, Q100). X-ray photoelectron spectroscopy (XPS) result was analyzed by ESCALAB-250Xi spectrometer. The specific surface area was measured using a Belsorp-Mini adsorption apparatus (Bel Japan Inc.). Gas sensing properties were carried out by WS-30A (SI). The sensor response S(S=Ra/Rg) was defined as the ratio of sensor resistance where Ra is in air and Rg is in target gas.

3. Results and discussion

XRD was firstly applied to investigate the phase structure of precursor. All the peaks match well with $Zn_5(OH)_6(CO_3)_2$ (JCPDS card No. 72-1100) in Fig. 1a. The product of $Zn_5(OH)_6(CO_3)_2$ after annealing is indexed as hexagonal wurtzite ZnO (JCPDS card No. 36-1451) shown in Fig. 1a. No peak for other impurities can be detected, indicating a complete conversion of the precursor into pure ZnO. Sharp diffraction peaks indicate the high degree crystalline of ZnO after dealing with higher temperature. To investigate the decomposition progress of the as-prepared $Zn_5(OH)_6(CO_3)_2$ precursor, TG-DTA (Fig. 1b) was performed at temperature from 25 to 1000 °C in a flowing nitrogen environment. A sharp endothermic peak centered at 252 °C is observed and the weight lose is 26%. It is in well fit with the conversion from precursor to ZnO by release of H_2O and CO_2 when elevating temperature. The decomposition can be described by the following equation (eq:1). The results display that two stages occurred during the process of $Zn_5(OH)_6(CO_3)_2$ precursor convert to crystalline ZnO. The second stage with a weight loss of 2.8% happened above 300 °C. It could be attributed to the oxidation of organic residues and evaporation of chemisorbed water.

$$Zn_5(OH)_6(CO_3)_2 \rightarrow 5ZnO + 2CO_2 + 3H_2O \quad (1)$$

FESEM images of the hydrothermally synthesized $Zn_5(OH)_6(CO_3)_2$ precursor before calcination (Fig. 2a–c). It shows that the flower-like $Zn_5(OH)_6(CO_3)_2$ with an average particle size of approximately 10 μm were successfully prepared through the one-pot hydrothermal method. As shown in Figs. 2b and 3D $Zn_5(OH)_6(CO_3)_2$ microstructures are further consisted of orderly arranged nanosheets with the average thickness of about 15 nm. Compared with smooth structure, 3D ZnO assembled with 2D porous nanosheets were obtained after annealed at 500 °C (Fig. 2d–f). It's clearly to see that the morphologies of $Zn_5(OH)_6(CO_3)_2$ are entirely retained without heavy damage, which can be attributed to loss of volatile gases such as H_2O and CO_2. These pores in different sizes may significantly improve the chemical properties or serve as transport paths for small molecules. In addition, the FESEM images of 0.01 wt%, 0.05 wt% and 0.1 wt% Pd-doping ZnO microfolwers were shown in Fig. S5. After decorating Pd nanoparticles, the morphologies of ZnO microfolwers have not been obviously changed. TEM was further used to explore the structure of the precursor in Fig. S1. It can be readily observed that smooth nanosheets of the precursor alternately connect with each other to form a flower-like surface. The HR-TEM shows the lattice fringe spacing of 0.27 nm, indexed to the (401) plane of $Zn_5(OH)_6(CO_3)_2$. The ring-like SAED pattern reveals polycrystalline of precursor.

The microstructure of porous ZnO is further investigated by the TEM images (Fig. 3a). The lattice fringe of 0.24 nm (Fig. 3b) was corresponding with the (101) plane of ZnO. The SAED image in Fig. 3c suggests the single crystal characteristic after annealed. In Fig. 3d, it is clearly observed the Pd NPs successfully decorated onto the surfaces of the nanosheets. The size of the Pd NPs is ca. 10 nm. Fig. 3e shows a HR-TEM image of the interface between Pd and ZnO, the lattice fringes with spacing of 0.24 nm corresponds to (101) crystal planes of ZnO, and the

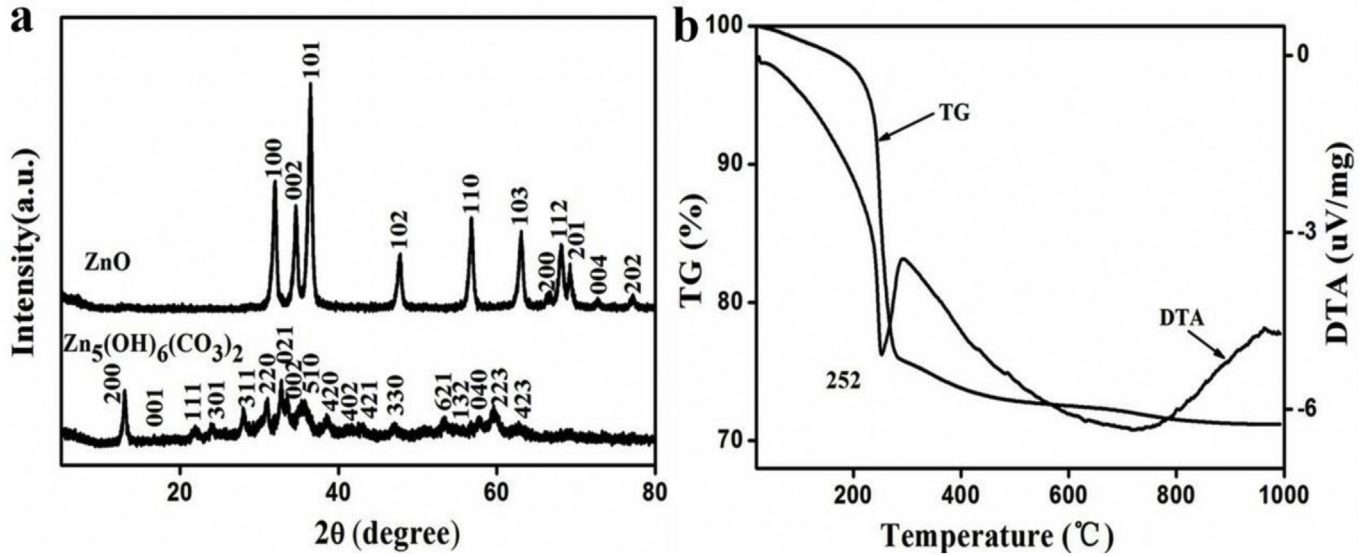

Fig. 1. (a) XRD pattern of $Zn_5(OH)_6(CO_3)_2$ precursor and crystalline ZnO microflowers annealed at 500 °C; (b) TG-DTA curves of $Zn_5(OH)_6(CO_3)_2$ precursor in range of 25–1000 °C in a nitrogen atmosphere.