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Soft-templated formation of double-shelled ZnO hollow microspheres for acetone gas sensing at low concentration/near room temperature

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ABSTRACT

The synthesis of well-defined and complex porous hollow structures *via* a simple method is still a major challenge. In this work, a unique double-shelled ZnO hollow microsphere with a porous surface is successfully synthesized by a facile soft-templated solvothermal method followed by calcination. The presence of ethylene glycol (EG) as soft template leads to the formation of initial single-layered hollow microspheres and then a time-dependent evolution transforms them into uniform ZnO hollow microspheres with tunable shell numbers and void space. When used as sensing materials for detecting acetone, the double-shelled ZnO hollow microsphere sensor exhibits high response toward 100 ppm acetone (101.1) and achieves a rapid response rate and recovery process (within 1/7 s) at 300 °C, which are superior over those for ZnO microparticle and single shelled ZnO hollow microsphere. In addition, this sensor exhibits low detection limit (0.5 ppm), low operating temperature (40 °C), high selectivity to acetone, and long term stability, suggesting their potential applications as advanced gas sensing materials. Such outstanding gas sensing properties of double-shelled ZnO hollow microsphere is due to the larger Brunauer-Emmett-Teller (BET) surface area (76.11 $m^2 g^{-1}$), porous and double-shelled hollow structure, and excellent capabilities of surface adsorbed oxygen.

1. Introduction

Hollow structures with versatile size, morphology and interior architectures have recently been subjected to extensive research because of their unique characteristics, such as low density, high surface area, and large interior space, and their potential applications in various fields, such as gas sensors [1], energy storage [2], solar cells [3], catalysis [4], and so forth. More recently, intensive efforts have been devoted to the design and fabrication of porous hollow structures with multi-shelled architectures [5], which combine or integrate the advantages of both hollow microspheres and porous shell architectures. Such porous hollow structures with multi-shelled architectures are expected to realize their optimized physical/chemical properties for specific applications [6]. To date, several different synthesis approaches have been developed to synthesize multi-shelled hollow structures such as hard-templating method (templating silica, carbon, *etc.*) [7], soft-templating method (templating vesicles, emulsions, micelles, *etc.*) [8], and template free method (utilizing self-assembly) [9]. Among these methods, the hard-templating method is one of the most universal and effective approaches for the preparation of multi-shelled hollow structures with highly uniform morphology and size [10]. However, this synthetic method is challenging, since the multi-step deposition and template removal procedures are tedious, time-consuming, and uneconomic [11]. Thus, researchers have transferred their focus to no-templated or soft-templated strategies in recent years on the fabrication of multi-shelled hollow structures with high quality [12]. Although great progress has been made, the development of a facile soft-templated strategy for controlled synthesis of hollow microspheres with multiple shells is still a challenge [13].

Acetone is a common reagent frequently utilized in industries and laboratories [14]. Due to its volatile and deleterious characteristics, acetone may cause damage to eyes, noses, and central nervous system with concentration over 450 mg/m^3 (173 ppm) [15]. Besides, as reported by the medical research, acetone concentration (equal to or greater than 1.8 ppm) exhaled from diabetes patients is higher than that exhaled from healthy people (lower than 0.8 ppm) [16]. From the perspectives of environmental protection, safety and health conditions, it is urgently required to detect acetone concentration effectively [17]. On the other hand, as mentioned above, acetone detection limit lower than 1.8 ppm is an important parameter for the sensor aimed at the

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diagnosis of diabetes [18]. Therefore, it is urgent to pursue novel materials to improve acetone sensing properties with respect to low detection limit, low operating temperature, high response, and fast response/recovery rate.

As a promising acetone sensing material, zinc oxide (ZnO) has been intensively researched due to its relatively high sensitivity, ease of fabrication, absence of toxicity, and low cost [19]. Morphological control of nanostructure has important influence on gas sensing performances [20]. Various nanostructures of ZnO, such as nanorods, nanotubes and nanosheets, have been synthesized to improve the properties of acetone sensors [21]. These ZnO nanostructures exhibit the potential advantages for acetone sensor application [22]. Though some improvements had been obtained, there still existed many shortcomings, such as the detection limit of acetone did not reach the ppb magnitude required for the diagnosis of diabetes [23]. In addition, there was still considerable room for improvement in the time of response/recovery. As ZnO acetone sensor belongs to surface resistance control sensors, its sensitivity depends greatly on the surface microstructure, high surface area and permeable shell structure are thought to be good for electron depletion and effective gas diffusion [24], therefore, porous ZnO hollow materials with multi-shelled structures could be exceptionally desirable for acetone sensing applications.

Herein, this work reports a new double-shelled ZnO hollow microsphere based on a facile soft-template solvothermal method followed by a calcination step. Importantly, the number of shells of the as-prepared ZnO hollow microspheres can be easily tuned by varying the reaction temperature during the solvothermal process. When used as sensing materials for detection acetone, the double-shelled ZnO hollow microspheres demonstrate a great enhancement than those of ZnO microparticles and single-shelled ZnO hollow microspheres, and show fast response kinetics, low operating temperature (40 °C), low detection limit (0.5 ppm), high selectivity and long term stability to acetone. The possible origin of the enhanced gas sensing characteristics based on double-shelled ZnO hollow microspheres is discussed.

2. Experimental and method

2.1. Materials

Ethylene glycol (EG), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), ethanol and acetone were purchased from Sinopharm.

2.2. Preparation of ZnO hollow microspheres with tunable shell numbers

ZnO hollow microspheres with tunable shell numbers were synthesized by a solvothermal procedure. Typically, 3 mL EG and 40 mL ethanol were mixed. Then $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.35 g) was added the above mixture and stirred for 30 min, followed by a solvothermal treatment at 100 °C in a 50 mL Teflon-lined autoclave for t hours (t = 2 h, 6 h, 12 h and 24 h). The treated powder was washed thoroughly with ethanol followed by filtration and drying processes. Thermal annealing at 400 °C for 1 h led to production of ZnO hollow microspheres with tunable shell numbers. The samples were named as ZnO-t according to the solvothermal time (t). A reference sample (ZnO-ethanol-12) was synthesized with pure ethanol as solvent and solvothermal time of 12 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded with a Bruke D8 Advance powder X-ray diffractometer with Cu $K\alpha_1$ (λ = 0.15406 nm). Scanning electron microscopy (SEM) was performed with a FEI NanoSEM 450 instrument with an energy-dispersive X-ray spectroscopy (EDS). High resolution transmission electron microscopy (HRTEM) images were carried out with a JOEL JEM 2100F microscope. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method using the measurement instrument (Micromeritics, ASAP2020).

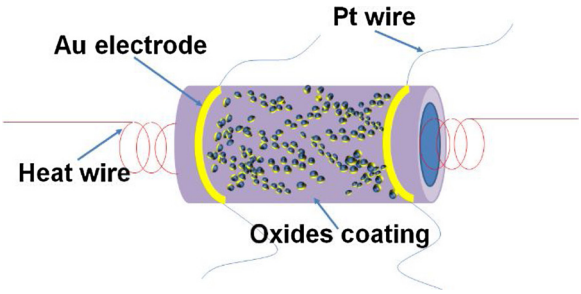

Fig. 1. Schematic of the acetone gas sensor.

2.4. Sensing tests

The gas sensing properties of as prepared ZnO hollow microspheres were tested on a WS-30A gas sensing instrument (WeiSheng Electronics Co., Ltd., Henan, China). The fabrication and testing principle of gas sensors referred to previous works [25]. Fig. 1 shows the schematic of the sensor structure based on ZnO samples. By mixing the as-obtained ZnO samples with deionized water, a homogeneous paste could be formed. The paste served as the sensitive body was coated on a ceramic tube, which was installed with platinum wires and two gold electrodes. A heat wire (Ni-Cr alloy), used as a resistor, was placed in the ceramic tube. The sensor response was defined as the ratio in sensing layer resistance (R_a/R_g), where R_a and R_g are the electrical resistance of the sensor in air and in the presence of the test gas mixed in air, respectively.

3. Results and discussion

3.1. Formation of double-shelled hollow microspheres

Since the gas sensing performance is mainly based on the surface activity, the surface morphology and uniformity both play important roles in providing more surface active sites for redox reactions. Fig. 2a–c shows the typical SEM images of ZnO-12. Fig. 2a shows that a high yield of uniform monodisperse ZnO microspheres (with an outer diameter of 3 μm). Moreover, a cracked microsphere near the center of Fig. 2b show two-layer shells, and the interior sphere is also hollow inside, indicating that the synthesized ZnO has double-shelled hollow architecture. A closer observation in Fig. 2c exhibits that the surface of the double-shelled hollow ZnO microsphere is rough, which consists of abundant nanoparticle building blocks. These nanoparticles aggregated together to constitute the thin shell of the ZnO products. In addition, the double-shelled ZnO hollow microspheres are investigated by TEM. The TEM image (Fig. 2d) shows a clear gap between the outer shell and inner shell and further confirms the unique double-shelled structure. The thickness of the inner shell is about 80 nm, whereas the outer shell is relatively thick, with around 100 nm. Furthermore, it is evident that the dense shell is accumulated by a large amount of small particles, which is consistent with the SEM observation. Fig. 2e displays the HRTEM image of the area marked by a square in Fig. 2d; the clearly resolved lattice fringes with a lattice spacing of 0.265 nm are consistent with the (002) plane of wurtzite ZnO [26]. Moreover, the solvothermal product without calcination also exhibits double-shelled hollow structures (Fig. S1), indicating this specific structure is formed during solvothermal treatment and stable even at high-temperature calcination. On the contrary, the ZnO-ethanol-12 synthesized in pure ethanol contains the irregular particles without any double-shelled or hollow structures (Fig. S2), indicating the critical role of EG in the formation of double-shelled hollow structures.