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Au modified single crystalline and polycrystalline composite tin oxide for enhanced n-butanol sensing performance

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ABSTRACT

A SnO_2 hierarchical structure was prepared by the calcination of precursor that was synthesized by a hydrothermal method that used carbon fiber as the template. In particular, the SnO_2 hierarchical structures were assembled from polycrystalline micro-tubes and single crystalline nanorods. Au nanoparticles were modified on the surface of SnO_2 hierarchical structures with a facile chemical reduction method. The gas sensing performances of SnO_2 and Au decorated SnO_2 hierarchical structures were examined. Test results showed that the Au decorated SnO_2 hierarchical structures had a better gas sensing performance than pure SnO_2 toward n-butanol. The response of 100 ppm n-butanol was 382 at 260 °C. The response and recovery time was 7 s and 2 s. The Au decorated SnO_2 hierarchical architectures exhibited excellent selectivity toward n-butanol. The properties of the sample were attributed to the unique crystal structures of SnO_2 and the catalysis of Au nanoparticles.

1. Introduction

Because of the advantages of high response, low cost, fast response, and quick recovery rate, there is significant research interest within metal oxides based gas sensors within applications such as environmental detection, disease diagnosis, public security and industrial manufacturing [1–6]. Tin oxide is a typical n-type semiconductor that had been used to detect various gases including hydrogen, carbon monoxide, ethanol, and acetone [7–9]. Although SnO_2 based sensors have been studied and used in various areas, there is a desire to enhance its sensing performance for a wider applicability. This includes high sensor response, good selectivity, fast response and recovery speed [1].

There have been many proposed methods that would enhance the sensing properties of SnO_2 based gas sensors. For example, Li and co-workers fabricated SnO_2 porous hierarchical structures by using grapefruit exocarp as a template. The sensor response of the unique SnO_2 structure based sensor was 50 toward 10 ppm formaldehyde [10]. Zhang reported porous SnO_2 multi-tube arrays by using the bristles on the wings of butterfly as bio-template. This exhibited highly sensitivity to H_2S at room temperature [11]. Ma and co-workers prepared porous SnO_2 flower-like architectures using a hydrothermal process. This method exhibited a high sensor response to ethanol [12]. The combination of these research results indicate that the gas sensing performance of SnO_2 could be improved through designing a microstructure. This would be attributed to the unique microstructure that could provide a majority of the active sites that are used for sensing the reaction and a large number of passageways in gas diffusion.

Surface modification is another effective method used to improve the sensing performance of SnO_2 sensor. For example, Zhang and co-workers prepared Au modified porous SnO_2 spheres. These Au/SnO_2 samples displayed excellent sensing performance for ethanol and acetone [13]. Xu et al. reported Au modified SnO_2 micron rods. The gas sensing test results indicated that the Au sensitization could improve the sensitivity and selectivity of SnO_2 [14]. Our previous research used fabricated porous SnO_2 and Au decorated SnO_2 spheres. Test results showed that Au/SnO_2 had a higher response to CO and H_2 than the pure SnO_2 [15]. These research results indicate that surface modification by Au nanoparticles is an efficient method that improves the sensing performance of the SnO_2 nanostructure. In a majority of the published work, three dimensional polycrystalline SnO_2 was used for the matrix. Until now, the polycrystalline and single crystalline combined SnO_2 is seldom reported for gas sensor. In fact, the electronic excitation and transmission speed of the single crystalline SnO_2 were much higher than the polycrystalline [16]. Therefore, it would be expected that the sensing performance would be enhanced by using single crystalline and three dimensional polycrystalline combined SnO_2 matrixes for decoration.

The following study used fabricated Au nanoparticles decorated SnO_2 hierarchical structures. The SnO_2 hierarchical matrix was assembled with porous SnO_2 polycrystalline micro-tubes and SnO_2 single crystalline nanorods. The Au decorated SnO_2 sensors had superior gas sensing properties for n-butanol than the pure SnO_2 and reported SnO_2 sensors. This included a high sensor response, fast response and recovery speed, low detection limit, and excellent selectivity. The

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enhanced sensing property was ascribed to the composite crystal structure of the SnO_2 matrix and the catalysis of Au nanoparticles.

2. Experimental and methods

2.1. Materials

Tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), Sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$), Urea ($CO(NH_2)_2$), and Carbon fiber were all purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were analytical grade and were unaltered.

2.2. Synthesis of Au decorated SnO_2 micro-tubes

The long carbon fiber was cut into short fibers about 2 mm in size. The SEM images of carbon fiber were shown in Fig. S1. The short carbons were then immersed into concentrated nitric acid for about 5 min to remove impurities. The short carbon fibers were washed with deionized water several times. The carbon fibers were dried in an oven at 70 °C. 0.1 g of short carbon fibers were added in the 60 ml deionized water and ethanol mixed solution (the volume ratio of deionized water and ethanol was 1:1.67) where they subjected to ultrasonic dispersion for 30 min. A 1.8 g urea and 0.228 g sodium stannate trihydrate were added to the above solution where they were magnetically stirred for 10 min. The mixture was decanted into a 100 ml reaction still and was heated for 3 h at 180 °C. A precipitate was obtained from the solution, which was washed with ethanol and deionized water. The SnO_2 micro-tube was prepared via the calcination of as-prepared precipitate at 800 °C for 2 h with a heating rate of 2 °C/min. The decoration of Au nanoparticles was carried out according to a previous report and the experimental details are provided in the supporting information [15].

2.3. Characterizations and sensing properties measurements

X-ray powder diffraction (XRD) patterns were obtained with a Rigaku Dmax-rc X-ray diffractometer using Ni filtered Cu Kα radiation ($V = 40$ kV, $I = 50$ mA) with a scanning rate of 4° min^{-1}. The morphology and microstructure of the Au decorated SnO_2 was characterized with a field emission scanning electron microscope (SEM JSM-6700F) at an accelerating voltage of 20 kV and electric current of 1.0×10^{-10} A. A JEOL JEM-2100 high-resolution transmission electron microscope (HR-TEM) operated at 200 kV was used as well. The X-ray photoelectron spectra were obtained with a Kratos Analytical X-ray photoelectron spectrometer (XPS) using Al Kα ($hv = 1486.6$ eV) radiation for the excitation source under an anode voltage of 12 kV and an emission current of 10 mA.

2.4. Gas sensing performance test

The gas sensor was fabricated according the following method. The obtained Au decorated SnO_2 sample was mixed with deionized water at a mass ratio of 3:1 to form the sizing agent. The sizing agent was coated on a 3 mm Al_2O_3 square planar electrode that was purchased from Zhengzhou Winsen Electronics Co., Ltd., Henan, China. The square planar electrode was connected with a pedestal. The gas sensors were aged at 200 °C for 7 days before gas sensing test. The sensing performances test was carried out on a WS-30A gas sensing instrument (Zhengzhou Winsen Electronics Co., Ltd., Henan, China). The temperature was about 26 °C with a relative humidity of around 40–50%. The sensor responses in this work were calculated using R_a/R_g, where R_a and R_g were the resistance of sensor exposed to air and detect gas. The response and recovery time were defined as the time required for the change of resistance to reach 90% of the equilibrium value after injection and the detected gas was removed.

3. Results and discussion

3.1. Characterizations of Au decorated SnO_2 hierarchical structures

Fig. 1 shows the XRD patterns of the as-prepared SnO_2 and the Au decorated SnO_2 hierarchical structures. The diffraction peaks were indexed with tetragonal structure of SnO_2 (JCPDS 41–1445) for the pure SnO_2 hierarchical structure sample (Fig. 1a). This featured a space group of *P42/mnm* and lattice parameters of a = b = 4.738 Å and c = 3.187 Å. After the decoration of Au nanoparticles (Fig. 1b), most of the diffraction peak were indexed with the tetragonal SnO_2. The other diffraction peaks were indexed to the Au (220) plane. The intensity of SnO_2 (200) and (112) planes increased due to the overlap between the Au (111) and (220) diffraction peaks.

The morphology and microstructure of the as-prepared Au decorated SnO_2 hierarchical structure was studied through SEM and TEM. The SEM image (Fig. 2a) revealed that the final product have a micro-tube morphology with a diameter of about 7 μm. The SEM image of the fracture (Fig. 2b) confirmed the hollow structure of the SnO_2 micro-tube. The high magnification SEM image (Fig. 2c) revealed that the surface of the as prepared SnO_2 micro-tube was assembled from nanoparticles. This indicated the porous structure of the micro-tube. The inner structure of the micro-tube was examined by grinding the sample in an agate mortar. Fig. 2d shows numerous nanorods that grew on the inner surface of the micro-tube. The SME images showed that the SnO_2 hierarchical structures were constructed with SnO_2 micro-tubes and SnO_2 nanorods.

Fig. 3 shows the TEM images of the Au decorated SnO_2 hierarchical structure. Fig. 3a displays a representative image of the Au decorated SnO_2 sample. There were many cracks that formed on the surface of the SnO_2 micro-tubes. A mass of SnO_2 nanorods existed on the inner wall of the SnO_2 tube. Fig. 3b shows the high magnification TEM images of the SnO_2 nanorods. The length and the diameter of the nanorods were about 50 nm and 10 nm. Many nano particles observed on the surface of the nanorods that had a size of less than 10 nm. The HRTEM image of the nanorod showed that the lattice fringe spacing were 0.336 nm and 0.265 nm. These agreed with the {110} and {101} planes of SnO_2 (Fig. 3c) [17]. The distinct lattice boundary and parallel lattice fringes in the HRTEM image imply the high crystallinity of the SnO_2 nanorods. The corresponding Fourier transform pattern (FFT) result indicates the single crystalline nature of the SnO_2 nanorods (inset of Fig. 3c). The HRTEM image of the nanoparticle indicated that the interplanar distance was 0.236 nm. This was in agreement with the {111} plane of Au (Fig. 3d).

XPS analysis was carried out to demonstrate the deposition of Au particles on SnO_2 hierarchical structures. As shown in Fig. 4a, the energy

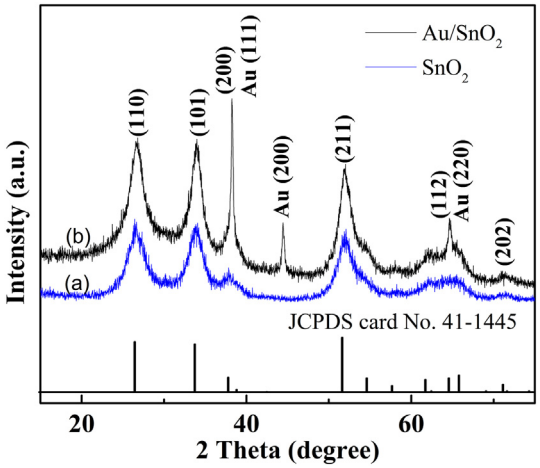

Fig. 1. XRD patterns of SnO_2 (a) and Au decorated SnO_2 (b) hierarchical structures.