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Coaxial electrospinning heterojunction SnO_2/Au-doped In_2O_3 core-shell nanofibers for acetone gas sensor

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ABSTRACT

SnO_2/Au-doped In_2O_3 core-shell (CS) nanofibers (NFs) were designed and synthesized through a facile coaxial electrospinning method. To investigate its potential application, commercial gas sensor was fabricated and its gas sensing properties were tested. The SnO_2/Au-doped In_2O_3 CS NFs sensor showed enhanced acetone gas sensing properties compared to the Au-doped In_2O_3 single NFs sensor counterpart. The SnO_2/Au-doped In_2O_3 CS NFs sensor exhibited a high response to acetone at 300 °C, whereas Au-doped In_2O_3 NFs sensor showed a relative low response to acetone at 300 °C. Furthermore, the former sensors also showed a fast response speed and a good selectivity to acetone. In addition, the underlying mechanism for the enhanced acetone sensing properties of SnO_2/Au-doped In_2O_3 CS NFs sensor could be attributed to the catalytic activity of Au and the CS structure. The approach and results proposed in this study may contribute to the realization of more sensitive CS structure NFs sensors.

1. Introduction

Gas sensors based on micro/nanomaterials are well known to be intensively applied in portable electronics and revealed important applications in environmental pollution, personal safety, transportation industries, and in biology and medicine [1–3]. Nowadays, the developments of gas sensors based on semiconducting metal oxides (SMOX) focus on high response to target gas with a low concentration, fast response/recovery speed, and excellent selectivity because all of the three sensing properties above are the most important gas sensing properties [4,5]. Considering that the gas sensors based on SOMX are the resistance-type sensors, the sensing mechanism is summarized as the changes in conductivity of the sensing film caused by interaction with the target gas-molecules [6]. The oxygen in air which are adsorbed on the surface of SMOX to form chemisorbed oxygen species [7] and the chemisorbed oxygen species play key roles in the interaction with the target gas-molecules. Therefore, to enhance the gas sensing properties of the sensors based on SMOX, noble metals such as Au, Ag, Pt and Pd are frequently used to improve their gas sensing properties due to the catalytic properties [8,9] and spillover effect [10,11]. According to many reported results, it is an effective method to enhance the gas sensing properties of the sensors based on SMOX by using doping or loading of noble metals. However, there still remain some shortcomings, such as a poor selectivity to the target gas [9,12,13], that need to be solved.

Over the past few years, more structures and morphologies, such as functionalized surface [14], binary transmission metal oxide [15], CS structures [16] and hierarchical heterostructures [17], were developed and used to enhance the gas sensing properties of the sensors based on SMOX. Among these techniques and methods, fabrication of CS structure has attracted a great deal of attention and was applied in many fields; including super capacitors [18], photo catalyst [19], biosensor [14], electrochemical energy storage [20], solar cell [21] and gas sensors [22]. For the gas sensors based on SOMX, a heterojunction is created at the interface between the core and shell and can play a role in enhancing the sensing capability, making it better than those of single-structure counterparts [23–25]. For this reason, various kinds of gas sensors based on SMOX with CS structures have been fabricated. For instance, Singh et al. fabricated gas sensors based on In_2O_3-ZnO CS nanowires, and the sensors exhibited good selectivity and a high sensitivity to ethanol [26]. Moreover, the sensing mechanism of the sensors with a CS structure has been investigated and results indicated that the sensors exhibited the best sensing properties when shell thickness is equivalent to the Debye length of the shell material [27].

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However, there is still a little investigation of gas sensors based on CS NFs.

In our previous investigation, SnO_2-In_2O_3 CS NFs were synthesized and observed to be efficient in detecting acetone [28]. However, the sensor based on SnO_2-In_2O_3 CS NFs exhibited a quite long recovery time. More detailed acetone s ensing properties of sensor based on SnO_2-In_2O_3 CS are introduced in the supporting information Fig. S1. In this work, by doping noble metals and fabrication of CS structures, SnO_2/Au-doped In_2O_3 CS NFs were synthesized by a coaxial electrospinning method. The sensors based on the CS NFs were fabricated and the gas sensing properties were investigated. The results indicated that the sensors exhibited high sensitivity and good selectivity to acetone and rapid response/recovery processes.

2. Experimental section

2.1. Materials

Chloride dehydrate ($SnCl_2{\cdot}2H_2O$) was purchased from Beijing Yili Fine Chemical Co. Ltd., China. Poly (vinyl pyrrolidone) (PVP) (K_{90}), $HAuCl_4{\cdot}4H_2O$ and Indium nitrate ($In(NO_3)_3{\cdot}9/2H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ethanol (C_2H_5OH) was purchased from Beijing Chemical Works. Dimethylformamide (DMF) was purchased from Tianjin Tiantai Fine Chemical Co. Ltd. All the chemical reagents above were all of analytical grade.

2.2. Synthesis of material

Two precursors were prepared to synthesize SnO_2/Au-doped In_2O_3 CS NFs by using a coaxial electrospinning method. First of all, 0.6 g $SnCl_2{\cdot}2H_2O$ were dissolved in the mixture of 4.8 mL of DMF and 1.2 mL of C_2H_5OH. After stirring for 10 min, 0.8 g PVP were added into the solution to form the $SnCl_2$/PVP precursor as the inner fluid. As for the outer fluid, 1.0 g $In(NO_3)_3{\cdot}9/2H_2O$ were dissolved in the 6 mL of C_2H_5OH to form solution A. $HAuCl_4{\cdot}4H_2O$ were dissolved in DMF to form solution B and the concentration of $HAuCl_4$ in the solution B is 0.0004 g/mL. The ratio of the amount of substance of Au and In is 0.1%, so 2.2 mL of solution B and 1.8 mL of DMF was added into the solution A. After stirring for 10 min, 1.5 g PVP was added and the outer fluid was prepared.

The process of coaxial electrospinning is similar to our previous work [28]. The feeding rates of inner and outer fluid were 0.5 and 0.6 mL h^{-1}, respectively. A voltage of 16 kV was offered. The distance between the nozzle and the collector was 15 cm. The samples were able to be collected after spinning for 15 min. The samples were annealed at 550 °C for 1.5 h with a heating rate of 1 °C min^{-1}. Cooling naturally, the final products were obtained. Au-doped In_2O_3 NFs were prepared through a same process above by only using the outer fluid.

2.3. Characterizations

X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ=0.15418 nm) in the range of 10–70° (2θ) at a scanning rate of 5° min^{-1}. Field emission scanning electron microscopy (FESEM) images were performed on a JEOL JEM-6700F microscopy operating at 15 kV. The energy dispersive X-ray (EDX) analysis was also performed during field emission scanning electron microscopy (FESEM) measurements. The transmission electron microscopy (TEM) micrographs were taken with a Tecnai G2 20S-Twin transmission electron microscope operating at an accelerating voltage of 120 kV. The N_2 adsorption-desorption isotherm measurements were performed on a JW-BK 132F volumetric adsorption analyzer at 77 K.

2.4. Fabrication and measurement of the gas sensor

For the fabrication of the typical gas sensors, the products were mixed with ethanol and deionized water (1:1 in volume) in a mortar to form a paste. As shown in Fig. 1a, there are two gold electrodes which were printed at the end of the ceramic tube. For each gold electrode, a pair of Pt wires was pasted by sintering. The gas sensors were made by coating the ceramic tube with prepared paste to form the sensing film [29]. A photo of the fabricated sensor was shown in Fig. 1b and a theoretic diagram of the gas sensing test circuit was showed in Fig. 2c.

The electrical properties of the gas sensor were measured by a CGS-8 intelligent test meter (China). The sensor response was defined as $S = R_0/R_g$, in which R_0 is the sensor resistance in the air, and R_g is the sensor resistance of the sensors in target gas. The response and recovery times were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively [17]. The operating temperature of the sensor was varied between 200 and 320 °C.

3. Results and discussion

3.1. Structural and morphological characteristics

The XRD patterns shown in Fig. 2 revealed the crystal structures of as-prepared products: SnO_2/Au-doped In_2O_3 CS NFs (Fig. 2a) and Au-doped In_2O_3 NFs (Fig. 2b). The intense peaks marked with circle can be indexed to tetragonal SnO_2 (JCPDS card no. 41-1445). As for the intense peaks marked with diamond can be indexed to cubic In_2O_3 (JCPDS card no. 06-0416). Moreover, no obvious Au peaks in the pattern were observed due to the low contents of Au. In addition, no other impurities peaks were observed by XRD. The existence of Au components in SnO_2/Au-doped In_2O_3 CS NFs was confirmed by EDX elemental mapping analysis.

The morphology and structure of SnO_2/Au-doped In_2O_3 CS NFs and Au-doped In_2O_3 NFs were characterized by FESEM and TEM. The FESEM images Fig. 3a and b depicted that the SnO_2/Au-doped In_2O_3 CS NFs possessed a high length-diameter ratio and a relatively smooth surface with about 220 nm in diameter. Fig. 3c presented the TEM image of SnO_2/Au-doped In_2O_3 CS NFs. The TEM image indicated that the density of the NFs and the contrast of the TEM images changed obviously. This result characterized that the NFs had a CS structure. Besides, EDX elemental mapping (Fig. 3d–f) revealed the different distributions of Sn, In and Au elements in the CS structure. It can be seen that the distribution of Sn is smaller than those of In and Au. So, the EDX elemental mapping exhibited that the NFs had a SnO_2 core and Au-doped In_2O_3 shell. This result characterized that the NFs had a CS structure. Besides, EDX elemental mapping (Fig. 3d–f) revealed the different distribution of Sn, In and Au elements in the CS structure. In contrast, the FESEM and TEM images of Au-doped In_2O_3 NFs were shown in Fig. 3(g–i). In Fig. 3g and h, the results characterized that the sample was made of NFs with a diameter of about 100 nm. To explore the microstructures of Au-doped In_2O_3 NFs, the sample was investigated by TEM (Fig. 3i) and the result indicated that the microstructure was uniform and no core shell structure was found.

Moreover, the BET specific surface area and the porosity (BJH pore size) of the SnO_2/Au-In_2O_3 CS NFs (Fig. 4a) and Au-doped In_2O_3 NFs (Fig. 4b) were evaluated by the Nitrogen adsorption-desorption measurements. The Nitrogen adsorption-desorption isotherm (inset) and corresponding BJH pore size distribution are given in Fig. 4(a, b). According to the reported literatures (the IUPAC