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Xylene gas sensor based on Au-loaded $WO_3 \cdot H_2O$ nanocubes with enhanced sensing performance

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ABSTRACT

In this work, Au was employed as an ideal dopant to obtain enhanced sensing performance of xylene gas sensor. Firstly, the as-perpared Au-doped $WO_3 \cdot H_2O$ powder was synthesized by a facile and efficient hydrothermal method. Then various techniques including X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectrometer (EDX) were employed to investigate the morphology, microstructure, crystalline nature and chemical compositions of the as-prepared Au-doped $WO_3 \cdot H_2O$ nanomaterials. The morphologies of the nanomaterials could be easily controlled by changing the atomic percentage (at%) of Au (0.15 at%, 0.30 at%, 0.45 at%) in the precursor solutions. And it have been attested that the 0.30 at% Au-doped $WO_3 \cdot H_2O$-based sensor realized higher gas response of 26.4–5 ppm xylene at 255 °C, faster response/recovery speed and stronger selectivity to target gas compared with the unloaded one. Furthermore, the detection limit could be as low as 200 ppb level. Hence, Au-loaded $WO_3 \cdot H_2O$ nanomaterial could be a promising material applied in xylene gas sensor.

Also, the mechanism involved in the improving xylene sensing properties of Au/$WO_3 \cdot H_2O$ was discussed.

1. Introduction

Gas sensors which constitute a very common and important class of electronic components are employed to trace specific pollutant or toxic gases reliably and expediently [1]. So gas sensors are needed for a wide range of applications including gauging the air pollution (e.g., greenhouse gas monitoring), supervising indoor air quality at a level for daily life (e.g., detection of alcohol and carbon monoxide) [2], monitoring toxic gas and gas composition in industrial production [3,4]. Including these gases, Volatile Organic Compounds (VOCs) accounts for a very large proportion. Around 200 types of VOCs, such as toluene, benzene, xylene, ethanol and acetone, are not only polluted the environment but also directly harmful to human's health [5]. Xylene, a colorless toxic gas, is inevitable and common in diverse coatings additives, various kinds of adhesives, refining of combustion gas fuel and production of synthetic fiber, rubber and plastic. Xylene is not only harmful to environment [6] but also considered to affect human health and security seriously [7] even in very low concentrations. Long-term exposure to xylene can cause health problems to human beings such as headache, dizzy, drowsiness, dermatitis and discomfort of the eyes which will end in cancer sometimes [6]. So it is weighs a lot to design a high performance xylene gas sensor. With continuous researches, plenty of high properties gas sensors in detecting CH_3CH_2OH [8,9], CH_3COCH_3 [10,11], H_2S [12,13], etc. have been obtained. However, researches on xylene detecting are not enough and the selective detection of this specific gas still remains a great challenge. This is due to the reactions between ionized oxygen species (O^{2-}, O^-, or O_2^-) and gases with similar physico-chemical properties such as xylene, toluene and benzene can induce similar chemoresistive changes [14–16] that result in increase of the resistance in p-type oxide semiconductors or decrease of the resistance in n-type oxide semiconductors. Therefore, great efforts are required to focus on the fabrication of reliable and practical xylene gas sensor.

It is generally known that bninary oxides such as SnO_2 [17,18], ZnO [19,20], Fe_2O_3 [21,22], Co_3O_4 [23,24], TiO_2 [25–27], NiO [28],

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etc. are typical metal oxide semiconductors (MOSs) that have been widely chosen as gas-sensing materials in recent years due to their unique electrical properties [14,15,29,30]. Sensors based on these materials show the advantages of high sensitivity, low cost, simple manufacture, fast response/recovery speed, long life, low sensitive to humidity as well as simple circuit [31]. And, these MOSs may become ideal gas sensing materials after overcoming disadvantages such as high operating temperature, poor selectivity and sharpening competitive edge by improving sensitivity and accelerating response/recovery speed [32].

Herein, we take advantage of Au-doped $WO_3 \cdot H_2O$ in this paper to detect xylene because of its special electrical properties. Various methods have been studied to synthesize this tungsten oxide compounds such as ion-exchange method [26], sol-gel [33,34], chemical vapour deposition [35,36], laser deposition [32,38,39], sputtering [33,40,41] and thermal evaporation [42,43]. However, it is common understandledge that finding out a method to resolve problems of high selectivity, fast response/recovery speed and good sensitivity at the same time is difficult in the case of gas sensors based on pure $WO_3 \cdot H_2O$. An effective route above is doping pure materials with an appropriate noble metal, which can increase the material porosity, thus increasing the specific surface area suitable for gas adsorption and consequently the sensor response [44–47]. Therefore, in this paper, the cube-like $WO_3 \cdot H_2O$ nanocrystals were successfully synthesized by a simple, effective and economical hydrothermal method at a low temperature of 120 °C for 24 h. Then Au [48–50] was introduced as a dopant to improve the properties of the sensor in this work. As it can be seen, throughout the whole process, no special equipment was employed to provide high temperature and vacuum condition which was demanded in past researches [51,52], so the device can be fabricated with low cost. Compared with the xylene gas sensor based on pure $WO_3 \cdot H_2O$, the response of Au-doped $WO_3 \cdot H_2O$ gas sensor to 5 ppm increased from 6.3 to 26.4, the response/recovery time was reduced obviously which was much faster than most reported researches [34,44,53] and selectivity was ameliorated as well. At last the possible mechanism about the improvement in the xylene sensing properties by introducing the Au dopant was discussed.

2. Experimental

2.1. Chemical reagent

In this experiment, $Na_2WO_4 \cdot 2H_2O$ (Sodium Tungstate Dihydrate) and $HAuCl_4$ (Four gold acid) were supplied by the Sinopharm Chemical Reagent Co. Ltd. $HOOC(CHOH)_2COOH$ (tartaric acid) was obtained from Beijing Chemicals Works. All the starting materials were of analytical grade and used without any further purification processes.

2.2. Synthesis process

Firstly, $WO_3 \cdot H_2O$ nanocubes were synthesized by a hydrothermal reaction [54,55] in the following sequence. In a typical process, 30 mL distilled water was used to dissolve $Na_2WO_4 \cdot 2H_2O$ (0.5 g) under magnetical stirring for 20 min at room temperature to get transparent solution. Later, 8 mL HCl aqueous solution of 3 mol/L (M) was added and the reagent was dissolved completely by stirring the solution for another 10 min. Then, different amounts of 0.01 M $HAuCl_4$ solution were added into solutions to give different doping concentration of Au. After that, 0.7 g tartaric acid was introduced. Next, the stock solution was transferred into a 50 mL Teflon-lined stainless steel autoclave to react under hydrothermal conditions at 120 °C for 24 h in sequence. Finally, the resulting product was washed several times with distilled water by the means of centrifuging to remove the ions and then dried at 60 °C in air overnight.

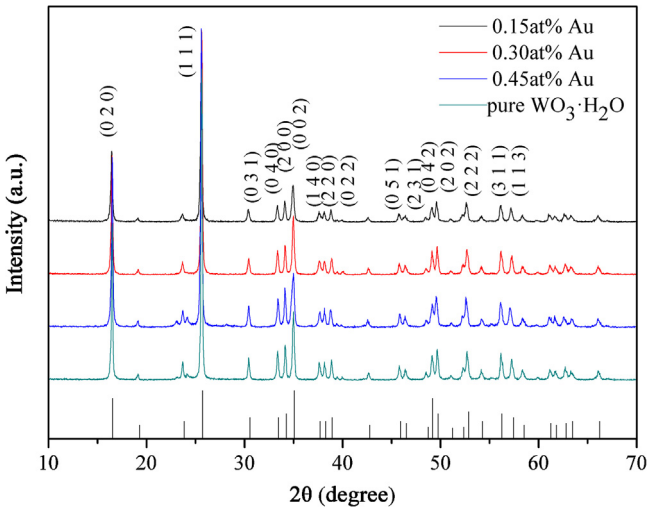

Fig. 1. XRD patterns of $WO_3 \cdot H_2O$ samples with 0 at%, 0.15 at%, 0.30 at% and 0.45 at% Au loading.

2.3. Characterization

The crystallite structures and chemical components of the samples were investigated by analyzing the wide angle X-ray Diffraction (XRD) patterns obtained with an X-ray Diffractometer (Shimadzu XRD-6000, Cu Kα radiation) and Energy Dispersive X-ray spectrogram (EDX) obtained on a JEM-ARM200F. Then a field-emission Scanning Electron Microscopy (SEM, XL30ESEM FEG) and Transmission Electron Microscope (TEM, JEOL JEM-3010) were applied to investigate the morphologies and microstructures of samples respectively.

2.4. Fabrication and measurement of sensors

The details of the sensor fabrication and the gas-sensing measurement process were similar to our previous report [37]. The as-prepared material was mixed with distilled water in a weight ratio of 4:1 evenly and then the mixture was ground in a mortar to form the corresponding paste. And the obtained paste was coated uniformly using a brush-coating method to form continuous thin film on alumina ceramic tube. On the tube, two Au electrodes were printed previously with Pt lead wires attached to both of the electrodes, and a micro-heater was inserted through the hollow centre of the ceramic tube to provide variable operating temperature of the gas sensor by tuning the heating voltage.

Next, the gas-sensing test was carried out on a CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China). And on a regular basis, the response value (S) of sensors based on n-type semiconductors is defined as $S = R_a/R_g$ for reducing gases and $S = R_g/R_a$ for oxidizing gases, where R_a is the resistance of sensors in air while R_g is the resistance in the presence of the test gas. Furthermore, the response time (τ_{res}) is defined as the duration time required for a sensor to reach 90% of the total resistance change when confront target gas (R_a to $R_a - 90\% \times (R_a - R_g)$) while the recovery time (τ_{rec}) is the time consumed to recover the resistance to 90% of the total resistance change (R_g to $R_g + 90\% \times (R_a - R_g)$) [56,57].