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Enhanced triethylamine sensing properties by designing Au@SnO_2/MoS_2 nanostructure directly on alumina tubes

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ABSTRACT

Two dimensional semiconductors are promising gas sensing materials due to their large surface-to-volume ratio. However, some drawbacks just like low response, long recovery time, and insufficient selectivity limits the development of two dimensional semiconductors gas sensors. In order to optimize the gas sensing properties of MoS_2 sensors, tri-material compound nanostructure of sensing materials is designed and synthesized by depositing Au and SnO_2 nanoparticles on the surface of MoS_2 nanoflowers. Comparing with the pristine MoS_2 sensor, the Au@SnO_2/MoS_2 sensor exhibits better sensing properties to triethylamine, such as higher sensitivity and faster response/recovery speed. The enhanced sensing properties of Au@SnO_2/MoS_2 sensor are discussed from the points of Au@SnO_2 Schottky contact and SnO_2/MoS_2 N-N heterojunction on the basic of depletion layer model. Moreover, MoS_2 nanoflowers are directly grew on Al_2O_3 tubes via a facile and cost-effective hydrothermal method. And the construction of Au nanoparticles decorated SnO_2/MoS_2 nanoflowers heterostructure were built by employing the pulsed laser deposition and DC-sputtering methods.

1. Introduction

Triethylamine (TEA) is one of the toxic volatile organic compounds (VOCs) with a strong fishy malodor, which has caused a serious threat to environment and human beings. Naturally, TEA is given off from the dead fishes and seashells, whose concentration is markedly dependent on the fish kind and freshness [1,2]. It would damage human health, causing including skin burns, headaches, nausea, eye irritation, and respiratory difficulty with results of pulmonary edema and even death [3]. Long term exposure to TEA could result in abnormal embryos as well [4]. Some reports reveal that wastewater containing TEA have serious damage on environment, especially for aquatic ecology [4]. Unfortunately, due to the extensively use in the polymerization reactions, solvents, and corrosion inhibitors, TEA has become the intense pollutant in industrial and manufacturing areas [5]. According to the standard by Occupational Safety and Health Administration (OSHA), the TEA concentration should not exceed 10 ppm on a volumetric basis (ppmV) in the air [6]. Therefore, it is necessary to develop a simple and portable TEA sensor with excellent sensing performances in order to monitor the real environment.

Nowadays, two-dimension (2D) semiconducting materials are considered as the most promising alternative candidates for the next-generation gas sensing devices [7–9]. Recently, molybdenum disulfide (MoS_2), as one of the typical n-type 2D semiconductor materials, has already been applied in the field of gas sensors [10–14]. Unlike graphene which lacks a band gap and needs to open a gap, MoS_2 possesses an alterable band gap determined by the layer numbers, which is in the range of 1.3–1.9 eV [15]. MoS_2 turns into an promising gas sensing material, mainly due to its special characters, such as various active sites (sulfur defect, vacancy, and edge site), high surface-to-volume ratios, and high yield preparation of the materials [14,16,17]. Therefore, MoS_2 sensors exhibit the outstanding sensing performances to various gases, for instance, NO_2 [18], NH_3 [19], O_2 [20], H_2 [21], and even VOCs, like ethanol [22] and eugenol [12]. Currently, the works are mostly focused on the researches of layer-like MoS_2 gas devices. However, the gas sensors based on MoS_2 with special morphologies are rarely studied, for example, the flower-like. The special morphologies relatively enlarged the surface area of MoS_2 providing more adsorption sites for the gas molecules. In addition, it has been found that the single-

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layer MoS_2 gas sensors were not stable enough during sensing response [23]. Therefore, it is meaningful to develop stable MoS_2 gas sensors.

In order to get preferable sensing performances, not only stable response, but also high sensitivity, good selectivity, and fast response/recovery speed, some strategies have been used to improve the sensing properties of semiconductors, such as the decoration of metal oxides and noble metal nanoparticles. For example, Cui et al. [13] reported a nanohybrid of SnO_2 nanocrystal-decorated crumpled MoS_2 nanosheet, which exciting air-stable property for room temperature sensing of NO_2. Yan et al. [24] prepared Au/MoS_2 sensor via a simple hydrothermal method and investigated the sensing properties to NH_3. The results showed that the Au functionalized MoS_2 hierarchical nanostructures allowed the sensors to work at low temperature. The idea of tri-material compound was proposed to reinforce the gas sensing properties. Ju et al. [25] synthesized ZnO nanorods composited with SnO_2 and Au nanoparticles, which realized the detection of TEA at low temperature. Thus it can be seen that, compositing semiconductors with the right metal oxides and noble metal nanoparticles should be an effective way to optimize gas sensing properties.

Inspired by these works, we design Au@SnO_2/MoS_2 nanostructure to improve the TEA sensing performances of pristine MoS_2 nanoflowers. The MoS_2 nanoflowers were directly synthesized onto the alumina (Al_2O_3) tubes, which simplified the fabrication process and protected the intrinsic nanostructure physical properties. As expected, the sensing properties of Au@SnO_2/MoS_2 sensor are better than that of pristine MoS_2 sensor, which is nearly 2 times higher in response and 54 s shorter in recovery times. The formations of Schottky contact and N-N heterojunction are the key to enhance sensing properties and the mechanisms is discussed in detail.

2. Experimental

2.1. Direct growth of MoS_2 nanoflowers on the Al_2O_3 tubes

All the chemical reagents were analytical graded and used without further purification. First of all, cleared Al_2O_3 tubes were immerged in MoS_2 seed layer solution to form a film of seed layer on its surface. The MoS_2 seed layer solution was obtained by ultrasonic dispersion method with adding a 1 mg/mL solution of MoS_2 powder into *N*-Methyl-2-Pyrrolidone (NMP) for 30 min. After that, the Al_2O_3 tubes covered with seed layer were placed on 80 °C flat heater to evaporate the solvent, NMP.

MoS_2 nanoflowers were synthesized via hydrothermal method. In the typical experiment, 0.245 g sodium molybdate (Na_2MoO_4), 0.347 g thiocarbamide (CH_4N_2S), and 0.215 g citric acid ($C_6H_8O_7$) were dissolved into 35 mL deionized water with continuous stirring to get a clear solution. Then the aqueous solution and the Al_2O_3 tubes covered with seed layer were transferred into a Teflon-lined stainless steel autoclave together, and maintained at 180 °C for 24 h. After reaction, the Al_2O_3 tubes were taken out form the autoclave, washed with deionized water and ethanol for several times and dried at 70 °C for 12 h. The overall fabrication process for MoS_2 nanoflowers on the Al_2O_3 tubes was schematically demonstrated in Fig. 1. The sensors prepared with pure MoS_2 nanoflowers are defined as MoS_2 sensors.

2.2. Growth of SnO_2 shell and Au nanoparticles onto MoS_2 nanoflowers

A layer of SnO_2 nanoparticles was deposited on the surface of MoS_2 flowers by pulsed laser deposition (PLD) method using SnO_2 target at room temperature. Therefore, the SnO_2/MoS_2 heterojunctions were obtained. The corresponding sensors are named as SnO_2/MoS_2 sensors. After that, Au nanoparticles were loaded onto the surface of SnO_2/MoS_2 nanoflowers by DC-sputtering with a working time of 30 s, which is described as Au@SnO_2/MoS_2 sensors.

2.3. Material characterizations and sensor properties testing

The morphology microstructure and composition of materials were measured by a field emission scanning electron microscope (FESEM, FEI QUANTA FEG250) equipped with energy dispersive X-ray spectroscopy (EDS, INCA MAX-50) and a high resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL). The surface elemental composition was checked with X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The phase of sensing materials was checked with X-ray diffraction (XRD, D8-Advance, Bruker). Fourier transform infrared spectra (FT-IR) were recorded at room temperature on a FT-IR spectrophotometer (Nicolet 380) as KBr pellets in the 4000–500 cm^{-1} region. Differential thermal analysis and thermogravimetry (TG/DTA, STA-409-EP, Netzsch) were used to study the oxidation progress of MoS_2 powder. The sensor properties were measured by a gas-sensing test system (WS-30A, Weisheng Electronics, China) in the air at a relative lower humidity of ~25%. The sensing response (S) equals to the ratio of R_a/R_g, where the R_a and R_g are the resistance of materials in the air and target gas, respectively.

3. Results and discussion

3.1. Crystal structure and morphology of the MoS_2 nanoflowers

The formation of MoS_2 nanoflowers in hydrothermal system could be concluded as follows. Firstly, the MoS_2 seed layer is important precondition for MoS_2 nanoflowers to directly grown on the Al_2O_3 tubes, which is considered as the preferential nucleation site. The similar strategies have been studied and used in the previous works of our group [26,27]. During the reaction, sodium molybdate was chosen as the precursor for molybdenum and thiocarbamide was used as the sulfur source. MoO_4^{2-} anions were reduced due to the high temperature and formed MoS_2 nanoparticles [28]. Secondly, in order to lower the high surface energy, these nanoparticles grow up into nanosheets structure through a process of oriented aggregation. On the same time, a part of nanosheets also appeared on the surface of Al_2O_3 tubes with the help of the MoS_2 seed layer. As the reaction continue, the nanosheets tend to merge together to shape MoS_2 nanoflowers by a self-assembly process [29]. After the hydrothermal process, MoS_2 nanoflowers were directly grown on Al_2O_3 tubes.

The SEM was used to characterize the morphology of MoS_2 nanoflowers in Fig. 2(a) and the inset picture. It can be clearly seen that MoS_2 nanoflowers with the uniform morphology are directly grown on the surface of Al_2O_3 bulk, which are about 300 nm in diameter. Spectrum of EDS (Fig. 2(b)) shows the peaks of O, Al, S, and Mo elements. No peaks of the impurities are observed in the samples. Panels (c) and (d) of Fig. 2 are the SEM and EDS images of SnO_2/MoS_2 nanoflowers. Obviously, a thin layer of SnO_2 is covered on the MoS_2 nanoflowers after deposited by PLD. Although the peak of Sn is not very apparent, the table of element that inset in Fig. 2(d) proved the existence of Sn element. Fig. 2(e) and (f) exhibit the SEM and EDS images of Au@SnO_2/MoS_2 nanoflowers. The Au nanoparticles are not easy to be seen even in the high-magnification of SEM image (inset panel). However, the peaks of Au can be clearly observed in the EDS images.

Furthermore, TEM were carried out to explore the nanostructure and crystallinity of the synthesized Au@SnO_2/MoS_2 nanoflowers. Fig. 3(a) is the typical TEM image of Au@SnO_2/MoS_2.