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Au nanoparticles modified MoO_3 nanosheets with their enhanced properties for gas sensing

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ABSTRACT

Two-dimensional nanostructures with controlled morphology and dimensionality make them a promising candidate for high-performance sensing materials. Meanwhile, surface modification with noble metals is considered as an effective strategy to enhance gas sensing performance of metal oxide-based gas sensors. In this work, a novel gas sensing material was synthesized by decorating Au nanoparticles on molybdenum oxide nanosheets. The morphology and structure of the samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The hexagonal MoO_3 nanosheets are about 600 nm in diameter, and the scale of Au nanoparticles are around 10–15 nm. Furthermore, owing to the composite structure, the sensor based on Au@MoO_3 nanocomposites showed superior gas sensing performance towards ethanol and it may have potential applications in the detection of ethanol vapors.

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1. Introduction

With the increasing concern over safety in residential areas and environmental protection, the effective detections of toxic and hazardous gases, as well as the degradation of organic pollutants, have become imperative [1–3]. As an important n-type semiconductor with a band gap of approximately 2.39–2.9 eV, molybdenum trioxide (MoO_3) exhibits distinctive gas sensing properties [4–8]. Nanostructured MoO_3 is generally considered a feasible candidate for use in gas sensors, such as nanorods [9], nanobelts [10], nanofilms [11], nanoflower [12], hollow spheres [13], and hierarchical structures [14] etc. However, the development of high-performance gas sensors based on nanostructured MoO_3 remains a challenge.

There are two common strategies that have been pursued in the literature to improve the properties of gas sensors. One method is controlling the growth of nanomaterials with a specially designed size, shape, and morphology because the properties of gas sensors are highly dependent on their surface to volume ratio. Among the various complex nanostructures, two-dimensional (2D) nanostructures such as nanoplates and nanosheets have recently received tremendous research interest because they can be effectively used as building blocks for constructing nanodevices with desired crystal orientation due to their anisotropic structures [15,16]. For instance, Ma et al. synthesized size and shape controllable preparation of WO_3 nanoplates through corresponding H_2WO_4 precursors. They found the enhanced ethanol sensing performance could be attributed to the plate-like morphology [17]. J.H. Zhan et al. reported the fabrication of porous ZnO nanoplates, and they found that the as-prepared ZnO nanoplates exhibited excellent gas sensing performance with high gas-sensing responses, short response and recovery times [18]. As seen from these achievements, it can be expected that 2D MoO_3 nanostructure would be a promising candidate with excellent gas-sensing characteristics. Despite considerable progress in the controlled fabrication of MoO_3 nanostructures with varied morphologies, there are few reports on the synthesis of 2D MoO_3 nanostructures.

The other method to improve the properties of gas sensors is surface modification with noble metals, including silver, platinum, and gold. In gas sensing, previous research has indicated that the incorporation of noble metals with semiconductor oxides by surface modification is an effective way to improve gas-sensing properties. The gas-sensing performance can be improved significantly because of the high catalytic activity of noble metals toward the test gases [19–22]. Therefore, a new model for a gas sensor has been proposed based on a 2D MoO_3 nanosheets and the catalysis of Au nanoparticles. Its gas sensing performance can be exploited more efficiently because more active sites of Au may be exposed on

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the MoO_3 nanosheets and gas diffusion and mass transport become more facile, suggesting superior gas sensing properties. Herein, we report a MoO_3 nanosheets loaded with Au nanoparticles for gas sensing applications. To the best of our knowledge, there are no reports on such a unique system that combines the advantages of 2D MoO_3 nanosheets and catalytic Au nanoparticles. Our results demonstrate that the synthesized Au nanoparticle modified hexagonal MoO_3 nanosheets exhibit significantly enhanced gas-sensing performance, which may provide a new pathway for the development of advanced materials of a similar type.

2. Experimental

2.1. Preparation of MoO_3, and Au@MoO_3 nanocomposites

All the chemical reagents were analytical graded and used without further purification. In a typical reaction, 2 mmol of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was dissolved in 70 mL deionized water and 9 mmol of thiocarbamide (CH_4N_2S) were added in after sodium molybdate completely dissolved. Stirring the solution for 20 min, then 2.2 mmol of citric acid ($C_6H_8O_7 \cdot H_2O$) was added into the above solution. After magnetically stirring for 30 min, transferred the solution into a 100 mL Teflon-lined stainless steel autoclave, and maintained at 200 °C for 21 h. The black precipitates were collected by centrifugation after the hydrothermal procedure, washed the precipitates three times with deionized water and absolute ethanol, respectively, and dried at 60 °C for 12 h in air. Finally, the gray samples were obtained by putting the sample in muffle furnace in calcination at 450 °C for 3 h in air with the heating rate at 5 °C/min.

The Au@MoO_3 nanocomposites were prepared by depositing Au nanoparticles onto the MoO_3 surface through chemical reduction method. First, 50 mg as-obtained MoO_3 products, 1.0 mL of 0.01 M chloroauric acid ($HAuCl_4$) and 1.0 mL of 0.01 M L-lysine solution were dispersed into 15 mL deionized water. After stirring for 30 min, 0.5 mL of 0.1 M sodium citrate (Na_3cit) solution was dropped in the above solution under continually stirring to reduce $HAuCl_4$ to the Au nanoparticles (Au: MoO_3 = 4 wt%). The precipitate was centrifuged, washed with deionized water and absolute ethanol and dried at 60 °C for 12 h. Finally, the Au@MoO_3 nanocomposites were obtained by calcining the sample at 300 °C for 30 min in air to remove lysine. The color change from yellow of pristine MoO_3 to purple indicated that Au nanoparticles were successfully decorated onto MoO_3 support.

2.2. Characterization

The phase composition and crystal structure of the samples were identified by powder X-ray diffraction (XRD, Bruker D8 Advance) using CuKα1 radiation (λ = 0.15406 nm) at 30 kV and 40 mA at a scanning rate of 2° at 2θ min^{-1}. The morphology and structure of the samples were characterized using FEI Sirion 200 field emission gun scanning electron microscope (FESEM, Hitachi S4800), and transmission electron microscopy (TEM, Hitachi H-800). More details about the structure were investigated by high resolution transmission electron microscopy (HRTEM, JEOL 2010). X-ray photoelectron spectra (XPS) were measured using a PHI 5300 X-ray photoelectron spectrometer with an Al Kα = 280.00 eV excitation source. All the binding energies were calibrated with respect to the signal adventitious carbon C 1 s peak with a binding of 284.7 eV. The fitted peaks in the XPS spectra were separated using the XPS-Peak 4.1 software.

2.3. Fabrication and measurement of gas sensors

The fabrication progress of the gas sensor was as follows [23–25]: the obtained samples were firstly mixed with distilled water to form slurry through milling, and then pasted onto a prefabricated alumina tube (7 mm in length and 1.5 mm in diameter, attached with a pair of gold electrodes and platinum wires) by a small brush to form a thick film. A Ni-Cr resistor (diameter = 0.5 mm, resistance = 35 Ω) in the inner alumina ceramic tube, as a heater, was used to provide the working temperature for the sensor device. Desired constant operating temperatures could be obtained by applying certain voltages to the heater. The working temperature was measured with an infrared thermometer (Omega OS542), which has stated manufacturer accuracies of ±2 °C of the true temperature. After dried in the air and aged at aging set for 2 days, the gas sensor was put into the test chamber in a measuring system of WS-30A (Winsen Electronics Co. Ltd., Zhengzhou, China) by a static process. A typical testing procedure was as follows: The sensors were put into a glass chamber (18 L) at the beginning. When the resistances of all the sensors were stable, the calculated amount of the target gas or liquid was injected into glass chamber by a micro-injector and mixed with air. For the target gases obtained from liquid, the concentration of target gas was calculated by the following formula,

$$C = (22.4 * \rho * d * V_1)/(M * V_2) \tag{1}$$

Where C (ppm) is the target gas concentration, ρ (g/mL) is the density of the liquid, d is the purity of the liquid, V_1 (μL) is the volume of the liquid, V_2 (L) is the volume of the glass chamber, and M (g/mol) is the molecular weight of the liquid. After the sensor resistances reached a new constant value, the test chamber was opened to recover the sensors in air. All the measurements were performed in a laboratory fume hood with a large draught capacity. The sensor resistance and response values were acquired by the analysis system automatically. The whole experiment process was performed in a super-clean room with the constant humidity and temperature. In the test process, a working voltage of 5 V ($V_{working}$) was applied. By monitoring the voltage across the reference resistor (V_{output}), the response of the sensor in air or in a test gas could be measured. The sensor response was defined as,

$$Response = R_{air}/\mathrm{R}_{\mathrm{gas}} \tag{2}$$

where R_{air} is the resistance of the sensor in air and R_{gas} is the resistance of sensor in the presence of the test gas. Then, the slope coefficient of response value to the logarithm of the concentration was defined as sensitivity. The response and recovery time was defined as the time taken by the sensors to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

3. Results and discussion

The crystal structure and phase analysis of pure MoO_3 and Au@MoO_3 composites are shown in Fig. 1. It can be observed that all the diffraction peaks of pure MoO_3 product were in good agreement with the standard JCPDS Card of MoO_3 (No. 35-0609). In the XRD pattern of the nanocomposites, the residual diffraction peaks of 2θ at 38.37°, 44.6°, 64.7°, 77.7° is related to the (111), (200), (220), (311) lattice plane of the Au nanoparticles. We can infer that the nanocomposites cover Au and MoO_3, it also indicating that Au dispersed on the surface of molybdenum oxide successfully and had not changed the lattice structure of MoO_3 [26].

In order to further determine the elements composition of the samples, we used the X-ray photoelectron spectroscopy (XPS) which is a very useful method in determination of the chemical

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