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Full Length Article

Low-temperature and highly enhanced NO_2 sensing performance of Au-functionalized WO_3 microspheres with a hierarchical nanostructure

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ABSTRACT

Hierarchically nanostructured WO_3 microspheres that had two types of Au functionalization modes (i.e., Au-loaded mode and Au-doped mode) were characterized in terms of their microstructure and NO_2 sensing performance. Pure, Au-loaded, and Au-doped WO_3 microspheres were synthesized using a hydrothermal method, followed by a dipping method for Au-loaded WO_3 microspheres. Microstructure characterization indicated that uniform microspheres with 3–6 μm in diameter were assembled from numerous well-defined individual WO_3 nanorods with a single crystal hexagonal structure. The morphology and size of the WO_3 microspheres were not affected by the functionalization of the Au nanoparticles, and the W, O, and Au elements were well-distributed in the WO_3 microspheres. The NO_2 sensing properties indicated that the Au nanoparticles not only improved the sensor response and reproducibility but also decreased the operating temperature at which the sensor response reached a maximum. Gas sensors based on pure, Au-loaded, and Au-doped WO_3 microspheres exhibited a linear relationship between the sensor response and NO_2 concentration. The sensing performance was significantly enhanced in the following order: pure, Au-loaded, and Au-doped WO_3 microspheres. This result is due to the modulation of the depletion layer via oxygen adsorption as well as chemical and electronic sensitization of Au nanoparticles.

1. Introduction

As the precursor of nitric and nitrous acid, NO_2 has a biting odor and is a poisonous and corrosive gas, which primarily originates from burning fuel, industrial processes, and vehicle exhaust in urban areas [1–3]. NO_2 is an important contributor to acid rain and photochemical smog, resulting in detrimental to the environment and human health. Therefore, the detection of NO_2 has recently attracted considerable attention because its poisonous, corrosive, and destructive properties. Currently, various types of gas sensors, such as optical, electrochemical, and resistive gas sensors, have been widely developed for NO_2 detection in real time [4–9]. Among these gas sensors, metal oxide semiconductors have played an important role in domestic safety, environment monitoring, and chemical process control due to their high response, outstanding selectivity, good reproducibility, and low cost [10–12].

WO_3, which is an n-type metal oxide semiconductor with a wide band gap of 3.2 eV at 300 K, has attracted much interest in gas sensing applications. Many attempts have been made to improve the gas sensing properties of WO_3 materials. One attempt involved preparing WO_3 sensing materials with a high specific surface area. It is well known that the microstructure of WO_3 materials has a significant effect on its gas sensing properties. Therefore, extensive studies have been focused on fabricating WO_3 sensing materials with various morphologies and structures, such as nanofilms, nanowires, nanosheets, nanofibers, nanoplates, microspheres, microtubes, and hollow spheres, to increase its specific surface area [13–28]. Another effective attempt for enhancing the gas sensing performance involved the addition of a noble metal to the WO_3 sensing materials. Hieu et al. [29]. investigated the NH_3 sensing properties of pure and Pd-loaded WO_3 nanorods synthesized using a hydrothermal method, followed by thermal calcination to activate surface bonding for Pd decoration. The Pd nanoparticles significantly improved the sensing properties

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and reduced its optimal operating temperature. Shen et al. [30]. reported that upon exposure to NO_2, the porous Pt-loaded WO_3 thin films prepared by reactive magnetron sputtering exhibited a nearly 90 times higher response compared to that of the unloaded one. Moreover, the peak operating temperature decreased from 200 °C for the unloaded film to 100 °C for the Pt-loaded film. Srivastava and Jain [31] investigated the NH_3 sensing performance of undoped and Pt-doped WO_3 films prepared using a sol-gel process. The results indicated that the high response was correlated to an increase in the barrier height and an increase in the air resistance in the Pt-doped WO_3 film. Li et al. [32]. synthesized Co-doped WO_3 hierarchical flower-like nanostructures assembled with nanoplates (FNPs) using a hydrothermal method and determined that the sensor response to acetone was effectively improved by Co doping. The enhanced sensing performance of Co-doped WO_3 FNPs was mainly due to the defects in the Co-doped WO_3 lattice as well as the effective catalytic activity of Co catalyst. Although many efforts have been made to improve the sensing properties of metal oxide semiconductor by adding noble metals either on the surface or in its interior, the effect of these two noble metal functionalization modes on the sensing performance and reaction mechanism is rarely discussed.

Therefore, in the current study, pure, Au-loaded, and Au-doped WO_3 microspheres with hierarchical nanorod-assembled architectures were synthesized using a facile hydrothermal method, followed by a dipping method for the Au-loaded WO_3 microspheres. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) were used to characterize the pure and Au-functionalized WO_3 microspheres. The NO_2 sensing properties and reaction mechanism of the pure and Au-functionalized WO_3 microspheres were systematically investigated.

2. Experimental

2.1. Chemicals

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, 99.5%), potassium sulfate (K_2SO_4, 98.5%), oxalic acid ($H_2C_2O_4$, 99%), citric acid ($C_6H_8O_7{\cdot}H_2O$, 99%), hydrochloric acid (HCl, 36.7%), absolute ethanol (C_2H_5OH, 99.7%), and hydrogen tetrachloroaurate ($HAuCl_4$, 99%) were purchased from the Tianjin Kemiou Chemical Reagent Co. These chemicals were analytical grade and used without further purification. Deionized water was used in all the synthesis and fabrication processes.

2.2. Synthesis of sample

Pure WO_3 microspheres were synthesized using a previously reported hydrothermal method [23,24]. In a typical procedure, 6 mmol of $Na_2WO_4{\cdot}2H_2O$ and a mixture of 6 mmol of K_2SO_4, 6 mmol of $H_2C_2O_4$, and 6 mmol of $C_6H_8O_7{\cdot}H_2O$ as the complexing surfactants were dissolved in 120 mL of deionized water with stirring to form a clear solution. Then, a 3 M HCl solution was added dropwise to the clear solution under continuous stirring until the pH value was adjusted to 1. The obtained solution was subsequently transferred to a 200 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. After naturally cooling to room temperature, the resulting precipitates were collected and washed with deionized water and absolute ethanol several times followed by drying in an electronic oven at 60 °C for 4 h. To prepare the Au-doped WO_3 microspheres, a certain amount of $HAuCl_4$ solution was simultaneously added to the previously mentioned clear solution prior to adjusting the pH value to complete synthesis process. To prepare the Au-loaded WO_3 microspheres, a certain amount of $HAuCl_4$ solution was mixed with the obtained pure WO_3 microspheres for 30 min using ultrasonic dispersion. The Au concentration in the WO_3 microspheres was estimated to be 2 wt.% by calculating the weight ratio of Au to WO_3 for both the Au-loaded and Au-doped WO_3 microspheres. The obtained pure, Au-loaded, and Au-doped WO_3 microspheres were annealed at 400 °C for 4 h in air to stabilize the structure and sensing properties. It was confirmed from FESEM images that the morphologies and structures of pure and Au-functionalized WO_3 microspheres were not changed after annealing process.

2.3. Characterization of sample

The crystallinity and phase composition of pure and Au-functionalized WO_3 microspheres were examined using an X-ray diffractometer (XRD, PANalyticalX'Pert Pro) with Cu Kα radiation (λ = 1.5406 Å) in a 2θ range from 10 to 60° at a scanning speed of 2° per minute. The operating current and voltage were 40 mA and 40 kV, respectively. The morphology and structure of the samples were investigated using a field emission scanning electron microscope (FESEM, ZEISS Ultra Plus) equipped with an energy dispersive X-ray spectrometer (EDS). The operating voltage of FESEM was 15 kV. Additional microstructure analysis of the samples was carried out using a high-resolution transmission electron microscope (HRTEM, JEOL 2100F) with an operating voltage of 200 kV. The surface analysis of the samples was investigated using X-ray photoelectron spectroscope (XPS, Thermo ESCALAB 250) with a monochromatic Al Kα X-ray excitation source (hν = 1486.6 eV). The spectra were referenced to the binding energy of C 1s at 284.6 eV. Fourier transform infrared spectroscopy (FTIR) was performed at room temperature using an infrared spectrometer (NICOLET 380) by pressing the mixture of the sample and IR grade KBr powder into a pellet with a mass ratio of 1:100.

2.4. Fabrication of gas sensor

Gas sensors based on pure and Au-functionalized WO_3 microspheres were fabricated as follows: (1) The sample powders were mixed with a certain amount of deionized water and ground in an agate mortar to form a slurry. (2) Next, several drops of terpineol were added to the slurry to improve its adhesive bond strength. (3) Then, the slurry was coated onto a pair of Au electrodes, which were previously printed on an alumina substrate, where two Pt wires were used for the resistance measurements and two additional Pt wires were connected to a heating resistor to control the operating temperature. (4) The alumina substrate was assembled onto the sensor holder to form gas sensor device after drying at room temperature for 30 min in air. (5) Finally, the gas sensor was annealed at 300 °C for 8 h in air to stabilize the sensing layer and remove the terpineol.

2.5. NO_2 sensing measurement

The NO_2 sensing measurements for the pure and Au-functionalized WO_3 microspheres were performed using a commercial static gas sensing test system (WS-30A, Weisheng Electronics Co. Ltd, PR China) in a fume hood. The operating temperature of the gas sensors was varied from room temperature (i.e., 25 °C) to 125 °C by adjusting the heating voltage. A reference resistor was placed in series with the gas sensor to form a complete measurement circuit. The electrical resistance of the gas sensors was determined by measuring the voltage when a voltage of 5 V was applied between the Au electrodes. NO_2 was injected into the test chamber using a syringe to a predefined concentration ranging