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Full Length Article

Ultrasensitive ppb-level NO_2 gas sensor based on WO_3 hollow nanospheres doped with Fe

Ziyue Zhang [a], Mahmood haq [a], Zhen Wen [a,b], Zhizhen Ye [a], Liping Zhu [a,*]

[a] State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Cyrus Tang Center for Sensor Materials and Applications, Zhejiang University, Hangzhou, 310027, China

[b] Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China

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ABSTRACT

WO_3 mesoporous hollow nanospheres doped with Fe synthesized by a facile method have mesoporous hollow nanospherical like morphology, small grain size (10 nm), high crystalline quality and ultrahigh surface area (165 m^2/g). XRD spectra and Raman spectra indicate the Fe doping leading to the smaller cell parameters as compared to pure WO_3, and the slight distortion in the crystal lattice produces a number of defects, making it a better candidate for gas sensing. XPS analysis shows that Fe-doped WO_3 mesoporous hollow nanospheres have more oxygen vacancies than pure WO_3, which is beneficial to the adsorption of oxygen and NO_2 and its surface reaction. The gas sensor based on Fe-WO_3 exhibited excellent low ppb-level (10 ppb) NO_2 detecting performance and outstanding selectivity.

1. Introduction

The rapid economic development and environmental pollution are like two sides of a coin, particularly in the nowadays. Environmental issues, such as, global warming, ozone depletion and air pollution, are very critical, particularly for developing countries. NO_x ($NO + NO_2$) coming from the combustion of fossil fuels and automobile exhaust is one of the main factors leading to the acid rain, photochemical smog and air pollution and increasing the risk of respiratory diseases to human beings[1]. In the air, most NO is oxidized to NO_2. The monitoring of extremely low concentrations of ground-level NO_2 (0–150 ppb) becomes important to check air quality. According to reported, the gas sensor used for NO_2 detecting could successfully adapted to air quality sensor that automatically blocked the influx of outdoor air into automotive cabins when the NO_2 concentration outside is high (>5 ppm) [2]. The detection and the emission control of NO_2 are crucial to reduce their noxious effects on environmental and human beings. On the other hand, NO is contained in the exhaled breath of human beings because of the metabolic process. However, compared with healthy people, there is more NO (>30 ppb) in the exhaled breath of asthma patients[3]. After emission, NO is diluted with ambient air and oxidized to NO_2 in the ambient atmosphere. Therefore, detecting of trace concentration of NO_2 from the exhaled breath of human beings can be used to diagnose asthma. The use of NO_2 sensors in environmental monitoring or for asthma diagnosis from exhaled breath requires a sensitive response to low-ppb level NO_2.

Due to the great danger of NO_2, considerable research efforts have been devoted to the research of sensors for NO_2 detection [4–7]. The rapid, sensitive and accurate analysis of NO_2 in air and in human breath is a key technique for effective environmental atmosphere monitoring and noninvasive diagnosis of diabetes. The traditional detecting apparatus is expensive and requires special knowledge for operation, which is not suitable for real-time measurements [8]. The semiconductor gas sensors work by changing resistance of active material due to the surface adsorption and desorption of gas molecules and the related space charge effects, which have great potential to be used as air quality sensor and respiration sensor. Liu et al. synthesized the WO_3 nanorods and microspheres by hydrothermal to detect 20 ppm NO_2 at 350 °C [9]. ZnO films were prepared by Min et al. by DC magnetron reactive sputtering for 5 ppm NO_2 detection at 300 °C [10]. Cho et al. synthe-

* Corresponding author.
E-mail address: zlp1@zju.edu.cn (L. Zhu).

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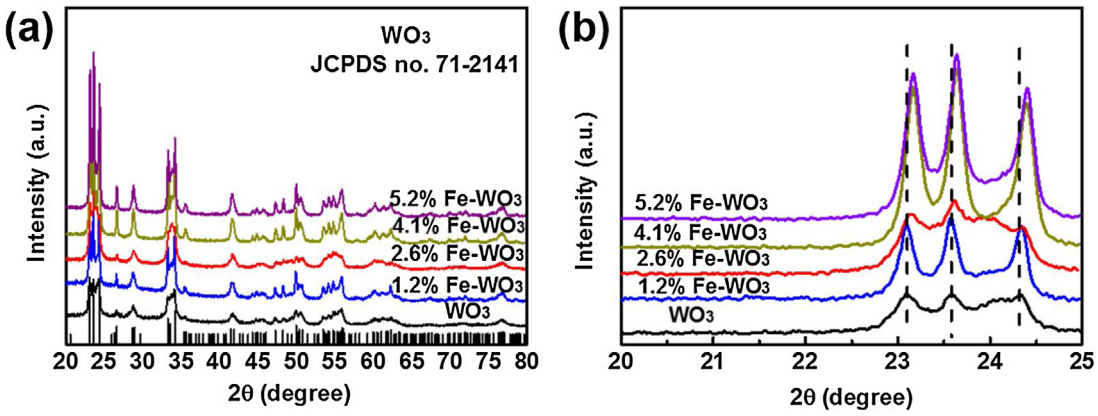

Fig. 1. (a) XRD patterns and (b) magnified peaks in the 2θ range from 20° to 25° of as-prepared samples.

sized the Pd-doped TiO_2 nanofibers by calcination of electrospun PVP/TiO_2/Pd composites to detect 0.8–2.8 ppm NO_2 at 180 °C [11]. WO_3/TiO_2 mixture prepared by screen printing were used to sensing 0–300 ppm NO_2 at 180 °C [12]. According to the most reported data, WO_3 is demonstrated as the most promising metal oxide for NO_2 gas sensing due to its inherent electrical resistivity, excellent sensitivity and selectivity. However, as for any other metal oxide based gas sensor, pure WO_3 operates efficiently usually in the temperature range 200–500 °C, which prevents the extensive use of WO_3 based gas sensors [13]. Therefore, it is obligatory to realize the optimal low concentration NO_2 sensing performance of WO_3 at low temperature. Enhanced sensing performance can be achieved by modifying the physical and chemical properties including grain size, wall thickness, porous structure, crystallinity, dopants and defects [7,14–16]. Doping is important for the formation of defects and modification of the electronic structure of metal oxides [14]. Defects such as oxygen vacancies are inherent in metal oxides and create a space charge layer depleted of electrons and negatively charged oxygen ions on the surface [7]. Doping of metal elements, especially noble metals, such as Pd, Au and Pt, has been used to functionalize the semiconducting metal oxides (e.g. ZnO, SnO_2, Fe_2O_3, WO_3, and NiO) for enhanced gas detection performance [17–20]. However, the high cost of noble metals reduces the potential applications of this strategy. The doping of other metal elements for metal oxide gas sensors is also of advantage for their gas-sensing enhancement, which makes it possible to obtain an ideal gas sensor with outstanding sensitivity, good selectivity, and low cost [21–24]. In addition, diffusion of gas molecules, recognition by the reactive surface and transducing by the sensing layer are three important aspects to be involved in the response of gas sensors [5]. Hence, enhancing the effective adsorption and diffusion of target gas and carrier mobility would be a good way to improve the sensing properties of sensors. The WO_3 with small grain size, mesoporous structure and large specific surface area is perspective nanostructures for enhancing gas sensing performances, which provides improved surface sensing activities and allows more gas exposure and easy gas sensing.

In this work, we prepared Fe doped WO_3 hollow nanospheres with different concentrations (0–5.2% by molar ratio) with the assistance of carbon colloidal nanospheres and following annealing. As-prepared samples have hollow nanospherical like morphology, small grain size, high crystalline quality, and ultrahigh surface area (165 m^2/g). In gas sensing application, it is found that doping of the WO_3 hollow nanospheres with 5.2% Fe exhibited the best NO_2 gas sensing performance at 120 °C in the concentration range 10–1000 ppb, compared with pure WO_3. In addition, it also exhibited outstanding selectivity, high response rate and good stability.

2. Experiments

2.1. Sample preparation

The carbon spheres were hydrothermally synthesized using the method reported [25]. 1.5 g WCl_6 and a certain proportion of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 200 mL of *N*,*N*-dimethylformamide to synthesize the Fe doped WO_3 nanostructures. Adding the carbon spheres (160 mg) into the above solution and sonicating for 30 min, and then stirring the as-obtained mixture solution at room temperature for 12 h. The precipitate was filtered, rinsed with distilled water and ethanol, and dried in an oven in air at 80 °C for 6 h. After annealing the products in air at 450 °C for 10 h, the Fe doped WO_3 nanostructures were obtained. Though controlling the ratio of WCl_6 and $Fe(NO_3)_3{\cdot}9H_2O$ (1:0, 8:3, 7:3, 3:2, 1:1) in the solution, the WO_3 with different amount of Fe dopant were prepared. The contents of Fe in WO_3 were 0, 1.2, 2.6, 4.1 and 5.2% by molar ratio. The corresponding products were marked as S1, S2, S3, S4 and S5, respectively.

2.2. Fe-WO3 hollow nanospheres characterization

The crystal phase identification were investigated by XRD (Bede D1) system with Cu-Kα1 radiation over the 2θ range of 20–80°. The microstructures and morphologies of Fe-WO_3 nanostructure were examined by SEM (Hitachi, S-4800) with an accelerating voltage of 5 kV. TEM and HRTEM images were taken by a HRTEM analyser (HRTEM, FEI F20) with an accelerating voltage of 200 kV to identify the crystal structure of the samples. Raman measurements were performed using a Renishaw inVia Raman spectrometer to determine the chemical and physical states of the samples. A Renishaw frequency doubled NdYAG laser excitation source of wavelength 532 nm was used. Raman shifts between the wavenumbers 200 and 1100 cm^{-1} were measured. To avoid local heating of the samples, a low power of about 5 mW was applied on the samples. The XPS spectra were recorded on a Thermo ESCALAB- 250 spectrometer with a monochromatic Al Kα radiation source (1486.6 eV) and the binding energies determined by XPS were corrected with reference to the adventitious carbon peak (284.8 eV) for each sample. Specific surface areas were computed from the results of N2 adsorption–desorption isotherms at 77 K (Micromeritics ASAP 3020) by using Brunauer–Emmet–Teller (BET).

2.3. Fabrication of gas sensor

The as-obtained samples were mixed with anhydrous ethanol and ground in a mortar over time to form a paste. Coating the paste on a polycrystalline alumina ceramic plate (8 mm × 4 mm, 0.5 mm