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Highly sensitive NO_2 sensor based on monodispersed WO_3 nanoparticles

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Abstract

Monodispersed tungsten oxide nanoparticles were obtained by sintering the hydrothermally synthesized precursor. The size of particle can be controlled from 25 nm to 100 nm via adjustment the concentration of surfactant and annealing temperature. The thick film sensors based on as-prepared samples were fabricated and evaluated. The results manifested that the size of particle and sintered temperature had great influence on the sensing properties. The sensor had good repeatability and stability. The gas response to 40 ppb NO_2 gas, which covered environmental standard, was about 2.

Key words: Tungsten oxide, hydrothermal synthesis, gas sensor, NO_2 gas

Introduction

As the basic building block for fabrication of sintered type gas sensors, nanosized oxide semiconductor powders have been studied extensively by many researchers. Especially, the grain size effect on gas sensing properties was reported for some semiconductor oxides [1-2]. Generally speaking, the response to target gas will increase dramatically with the decreasing grain size of the sensing materials. It has been shown that the gas response increases abruptly when the particle size becomes comparable or smaller than the Debye length (33 nm for tungsten oxide) [3].

Nitrogen dioxide (NO_2) as an environmental pollutant is highly harmful. Thus, the development of NO_2 gas sensor for environmental monitoring has been urgently desired. Due to the high response to NO_2, the sensors based on WO_3 have been studied extensively [4-6]. Nanoscale WO_3 powder, which shows excellent response and selectivity in detecting NO_2, has been prepared by many methods, such as sol-gel, spray-pyrolysis, radio frequency magnetron sputtering and aqueous chemical route etc [7]. Recently, the acidification method has been used for preparing the nanozied WO_3 powder [8]. However, the grain size distribution of WO_3 synthesized with such process is in a large range even at the same synthesis condition, and when the nanoparticles are consolidated into sensing material, the aggregation between the nanoparticles becomes very strong. When the aggregates are large and dense, only the primary particles near the surface region contribute to the gas sensing reaction and the inner part remains inactive [9]. So, synthesis of monodisperse WO_3 nanoparticles is necessary to fabricate high performance NO_2 gas sensor. We synthesized stably monodisperse WO_3 nanoparticles in this work. As-prepared sample showed excellent performance to ppb level NO_2.

Experimental

All the reagents (analytical-grade purity) were purchased from Sinopharm Chemical Reagent Co., Ltd., China, and used without any further purification.

The typical synthesized process is as follows. 3 mmol $Na_2WO_4 \cdot 2H_2O$ was dissolved in 20 ml deionized water and then 2 M HCl was added dropwisely into the solution to form pale yellow precipitate. The precipitate was centrifugated and redissolved by 1 M oxalic acid solution. After that, different amounts of cetyltrimethyl ammonium bromide (CTAB) (3, 4.5, 9 mmol) were added to the solution and diluted to 40 ml. Then, it was transferred to teflon-lined stainless steel autoclave (volume 50 ml) and heated at 180 ℃ for 12 h. After the hydrothermal procedure, the autoclave cooled down to room temperature naturally. The products were collected after centrifugation and dried at 80 □ for 4 h. The as-prepared precursors were sintered to obtain final products.

The morphologies and crystal phase of the as-prepared products were observed by field emission scanning electron microscopy (SEM,

JEOL JSM-7500F, 15 kV), X-ray powder diffraction (XRD, Rigaku D/max-2550) with Cu-Kα1 radiation (λ=0.15406 nm) at 40 kV/200 mA.

In order to fabricate the thick-film sensing device, the paste prepared from the mixture of the sample and deionized water was coated onto an Al_2O_3 tube on which two gold electrodes had been formed at each end. Then, the devices were sintered at 300□ for 2 h using muffle furnace in air. A heater of Ni-Cr coil was inserted into the Al_2O_3 tube to supply the operating temperature. The electrical resistance of the sensor was measured in air and in target gas, respectively. The gas response ($S = R_g/R_a$ for oxidizing gas or R_a/R_g for reducing gas) was defined as the ratio of the electrical resistance in the target gas (R_g) to that in air (R_a). The ambient temperature was kept 25±1□ and the relative humidity was kept at 50% ± 10% RH. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response and recovery time.

Results and discussion

The XRD peaks can be assigned to monoclinic WO_3 (JCPDS 71-2141). No diffraction peaks from impurities are observed (Fig. 1). It indicates that pure WO_3 nanoparticles can be obtained through sintered the hydrothermally prepared precursor.

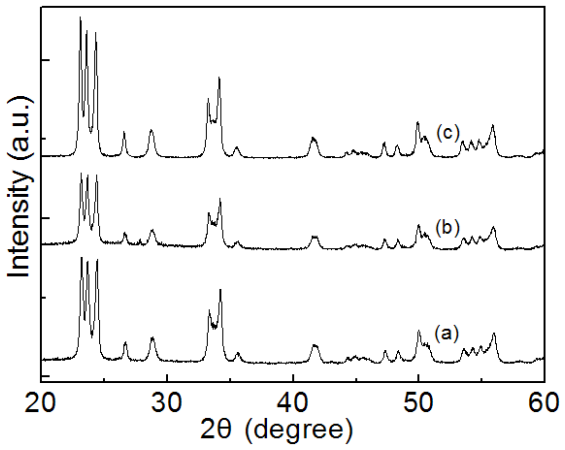

Fig. 1. XRD patterns of monodisperse nanoparticles with adding (a) 3, (b) 4.5 and (c) 9 mmol CTAB. All the samples were sintered at 500 ℃.

The SEM images of the as-prepared samples are shown in Fig. 2. The average particle sizes are estimated to be about 39, 42, 55 and 60 nm from Fig. 2a-d. It manifests that the as-prepared nanoparticles are almost monodisperse and the particle size increases with the decreasing of the CTAB concentration during the hydrothermally synthesized process (Fig. 2a-c) or the increasing of the sintered temperature (Fig. 2b and d).

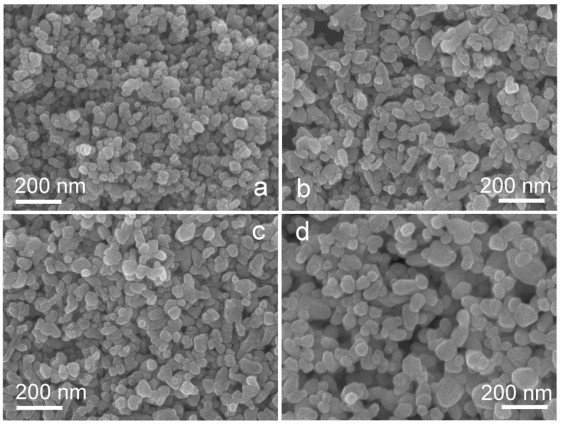

Fig. 2. SEM images of the as-prepared samples sintered at 500 ℃ with adding (a) 9, (b) 4.5 and (c) 3 mmol CTAB as well as sintered at 600 ℃ with adding (d) 4.5 mmol CTAB.

The correlation of the gas response of the sensor based on the as-prepared monodispersed WO_3 nanopaticles to 1 ppm NO_2 and the operating temperature was tested, with the result shown in Fig. 3a-b. The test results indicate that the CTAB concentration as well as sintered temperature have great effect on gas response and are slight influence on the optimal operating temperature. For the sensor fabricated from as-prepared WO_3, the response to 1 ppm NO_2 continuously increases when operating temperatures varied from 50 ℃ to 125℃, and then gradually decreases. The maximum response of the sensor operating temperature is defined as optimal operating temperature to further examine the gas sensor properties. It's clear that the sensor using WO_3 prepared by adding 4.5 mmol CTAB and sintered at 500 ℃ displays the highest gas response. The dependence of the response on the NO_2 concentration for the sensors using the samples prepared by adding different amount of CTAB as well as sintered at 500℃ and 600℃ are exhibited in Fig. 3c-d. As shown in Fig. 3c-d, the sensor response almost linearly increases with increasing the NO_2 gas concentration. The response to 40 ppb NO_2 is about 2 for the sensor based on the sample by adding 4.5 mmol CTAB and sintering at 500℃.

The dynamic response performance of the sensor was investigated at optimal operating temperature. Fig. 4 displays the response transient curve of the sensor based on the sample by adding 4.5 mmol CTAB and sintering at 500℃. The resistance of the sensor is reproducible for repeated testing cycle. The sensor shows a fast response and recovery characteristics. The time of response to 1 ppm NO_2 is about 3 min and the time of recovery is about 1.5 min.

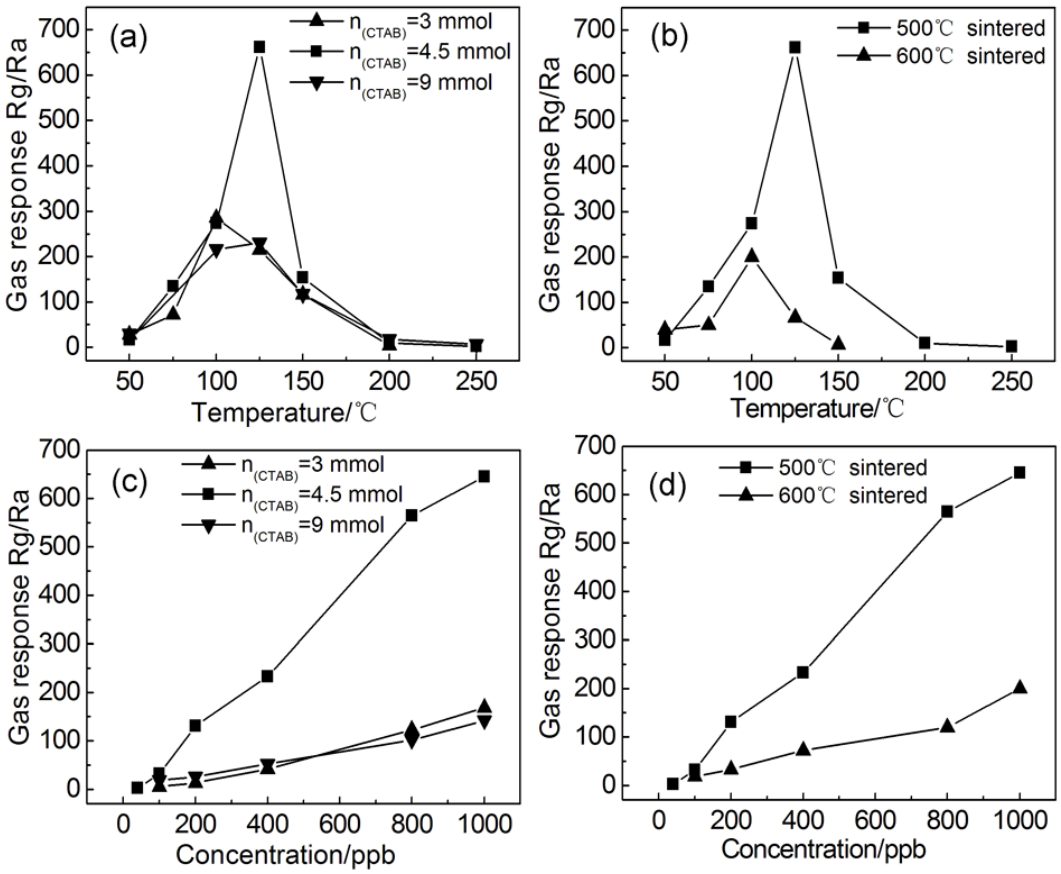

Fig. 3. (a), (b) Sensor responses as a function of operating temperatures; (c), (d) gas response versus NO_2 concentration at optimal operating temperature of the sensors prepared by adding different amount of CTAB as well as sintered at 600 ℃.

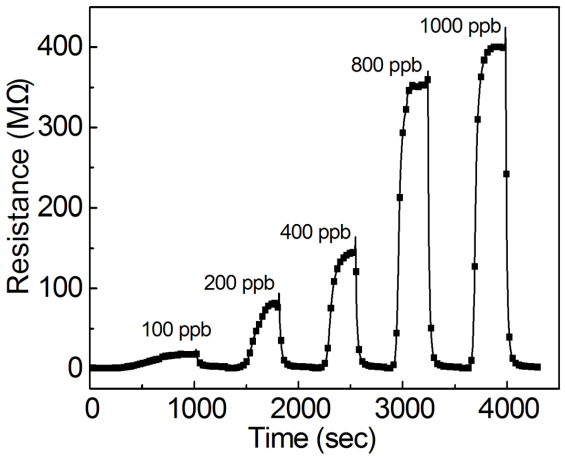

Fig. 4. Dynamic response resistance of the sensor based on WO_3 nanoparticles with adding 4.5 mmol CTAB and sintering at 500 ℃ at working temperature of 125 ℃.

For most semiconducting oxide type gas sensors, the change in resistance is primarily caused by the chemical adsorption and reaction of the gas molecules on the surface of the sensing material [10]. In air ambient, as-prepared WO_3 adsorbs the oxygen molecule on the surface to generate chemisorbed oxygen species (O_2^-, O^-, O^{2-}), and depletion region is formed on the surface area of WO_3 nanoparticles, resulting in a decrease of carrier concentration and electron mobility [11]. When the WO_3 are exposed to NO_2 gas at moderate temperature, the gas reacts at the surface of the material ($NO_{2\,(g)} + e^- \rightarrow NO_{2\,(ads)}^-$ and $NO_{2\,(g)} + e^- \rightarrow NO_{(g)} + O_{(surf)}^-$) [12], such adsorption and reaction can capture the electrons from the WO_3 and cause the increase of the depletion width and result in a decrease of the carrier concentration and electron mobility of the WO_3, which eventually decreases the conductivity of the sensor. In our sensor, the enhanced sensing properties obtained here is likely to the small grain size. The surface of the nanoparticles becomes significantly more reactive and likely to absorb oxygen and form ionized oxygen species. On the other hand, the as-synthesized product is formed by porous structures due to its monodisperse, such good porosity enhances the diffusion of NO_2 in the sensing body and makes NO_2 reach the deeper inner layer, which improves the utility of the sensing body. The more detailed reason and qualitative explanation need further study.

Conclusion

The monodisperse WO_3 nanoparticles were obtained by sintering the hydrothermally synthesized precursor. The grain size can be controlled by adjustment the concentration of surfactant and annealing temperature. As-prepared materials can be used to detect sub-ppm level NO_2.

Acknowledgements

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