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SYNTHESIS OF SnO_2 NANORODS BY HYDROTHERMAL METHOD FOR GAS SENSOR APPLICATION

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Abstract. *SnO_2 nanorods have been successfully prepared by hydrothermal method using tin chloride, ammonia, sodium hydroxide and cetyltrimethyl ammonium bromide (CTAB) as starting materials. Structural properties and surface morphologies of the SnO_2 nanorods were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The experimental results show that diameters of the nanorods are around 100 nm to 300 nm with length of several micrometers. In the preparation process of nanorods, the surfactant CTAB plays an important role in the formation and growth processes of SnO_2 nanorods. The gas sensitivity experiments have demonstrated that the SnO_2 nanorods exhibit a good sensitivity to alcohol vapors, which may offer potential applications in the gas sensors.*

I. INTRODUCTION

It was discovered decades ago that atoms and molecules interacting with semiconductor surfaces influence surface properties of semiconductors, such as conductivity and surface potential. Seiyama and Taguchi first applied the discovery to gas detection [1,2]. Since then, semiconductor gas sensors have been widely used as domestic and industrial gas detectors for gas-leak alarm, process control and pollution control. Semiconductor oxides have been more successfully employed as sensing materials for the detection of different gases, such as CO, CO_2, H_2, alcohol... Both n-type (such as SnO_2, TiO_2 and ZnO) and p-type semiconductor oxides (NiO) can be used as gas sensor materials [3]. Among these semiconductor oxides, tin dioxide (SnO_2) is an n-type semiconductor with a wide band gap and high chemical stability. It has been widely applied for various devices, such as gas sensor, dye-base solar cell and transparent conducting electrodes [5-8]. As the gas sensing and other properties of SnO_2 materials are strongly dependent on their size

and shape, it is obvious that the controlled synthesis of the nano/microstructure of SnO_2 materials is very important for special applications [13].

Up to now, SnO_2 materials with different morphologies have been fabricated by a few methods. For example, SnO_2 nanorods were synthesized by a vaporliquid-solid approach [9,10]. SnO_2 nanotubes have been fabricated by an infiltration technique [11]. SnO_2 nanowires have been obtained in a chemical vapor deposition (CVD) process [12]. However, these preparation methods usually require very high temperature and rigorous experimental condition. In this paper, we report the preparation of tin dioxide nanorods by a hydrothermal soft-chemical process. By this method, we can easily control a variety of parameters such as temperature, pressure, concentration of chemical species, solution concentration, pH and starting compounds. Besides, the gas sensing properties of SnO_2 nanorods were also studied.

II. EXPERIMENTAL

II.1. Preparation of SnO_2 Nanorods

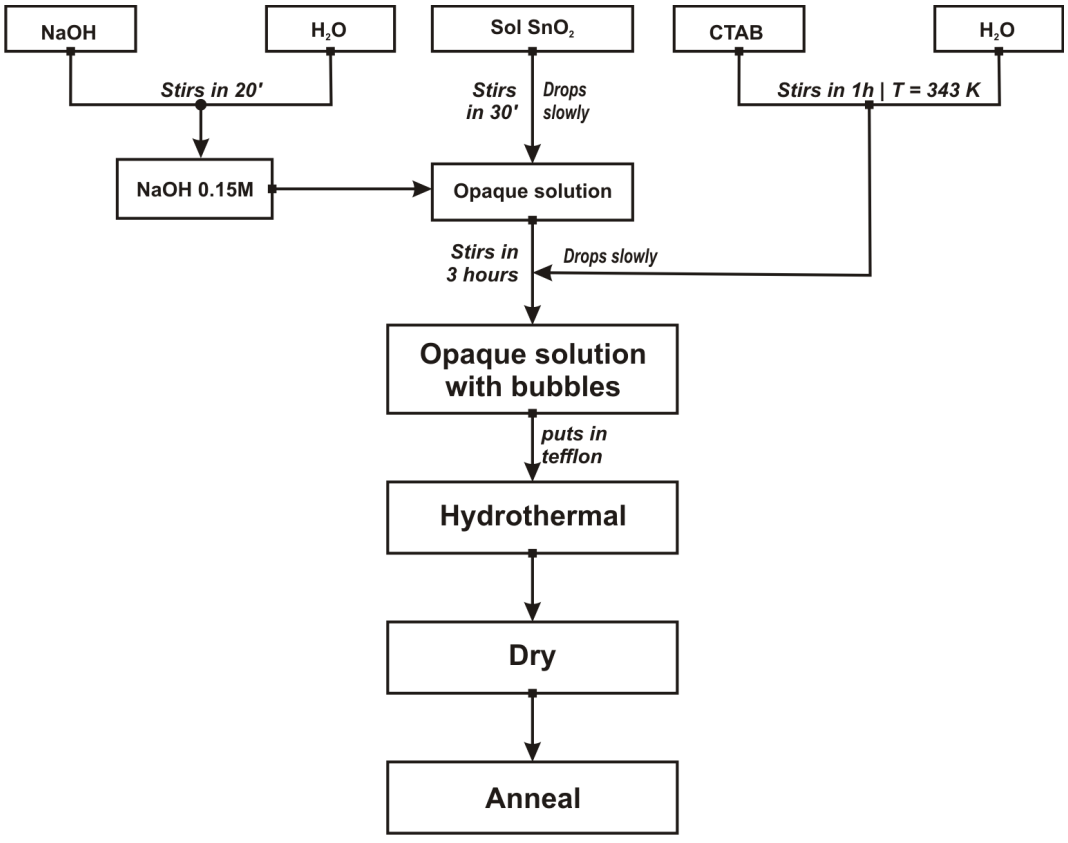

Fig. 1. Diagram of preparation of SnO_2 nanorods.

In a typical procedure, first the SnO_2 sol suspension with 6 nm in diameter was prepared by hydrothermal treatment method [4]. And then the above SnO_2 transparent sol was added to 0.15 M NaOH solution with vigorous stirring to obtain an opaque solution. After that, 2 mmol of cetyltriethyl ammonium bromide (CTAB) was added into the opaque solution, followed by heating to make CTAB dissolve completely. Then the mixture was poured into a stainless teflon-lined 200 ml autoclave and heated to 140 $^{\circ}$C for 20 hours. After cooled down to room temperature, the resulting white precipitate was collected by centrifugation, washed with ethanol for several times and annealed at 600 $^{\circ}$C for 3 hours. SnO_2 nanorods were obtained as white powder. Fig. 1 shows the preparation procedure of SnO_2 nanorods. Structural properties and surface morphologies of the SnO_2 nanorods were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

II.2. Measurement of Gas Sensing Properties

To fabricate thin-film sensor devices, the above SnO_2 nanorods were coated on a silicon substrate attached with a pair of comb-type Pt electrodes. After that, the thin films were sintered at 600 $^{\circ}$C for 30 minutes. The gas sensing properties were measured in a conventional flow apparatus with external electric furnace at temperatures in the range of 100 $-$ 400 $^{\circ}$C. The sensor response (S) was defined as the ratio of the sensor resistance in air (R_a) and in the sample gas (R_g). The apparatus for gas sensor testing is shown in Fig. 2.

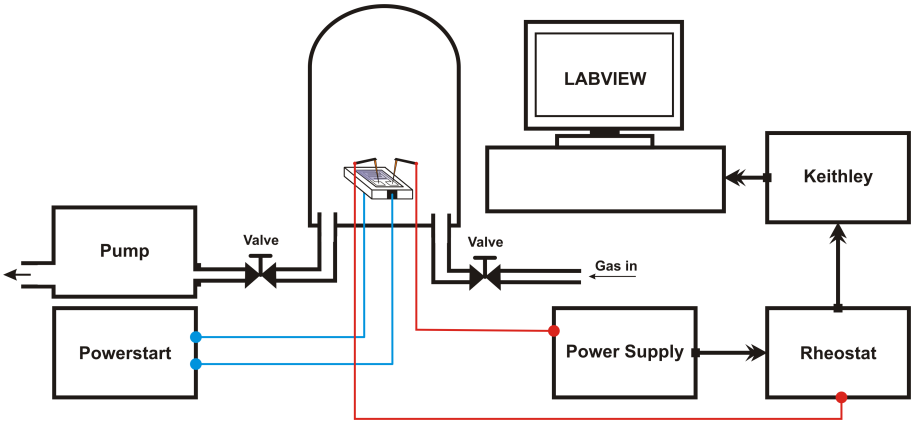

Fig. 2. Apparatus for gas-sensor testing.

III. RESULTS AND DISCUSSION

III.1. Morphology and Structure of SnO_2 Nanorods

The XRD pattern of SnO_2 nanorods after calcination at 600 $^{\circ}$C for 3 hours is shown in Fig. 3. All of the diffraction peaks can be perfectly indexed to the rutile structure of SnO_2 with tetragonal lattice parameters $a = 4.7$ Å and $c = 3.2$Å, which is consistent with the standard data file. No characteristic peaks of impurities, such as NaOH and

cetyltrimethyl ammonium bromide (CTAB), were observed. It demonstrates that the obtained SnO_2 nanorods are pure phase of rutile SnO_2.

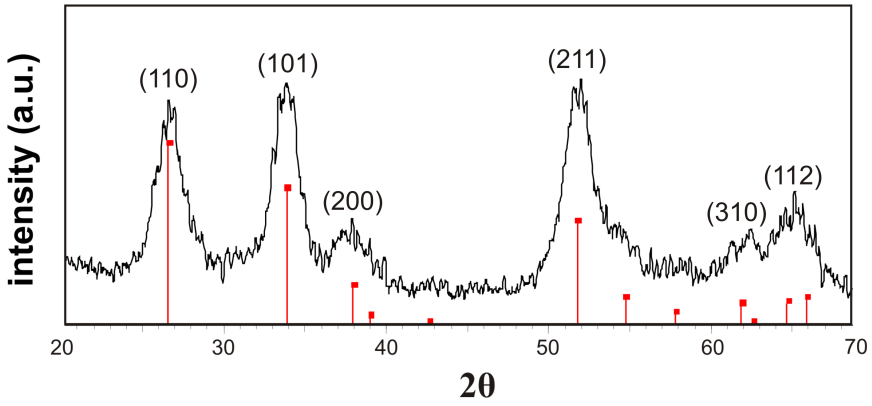

Fig. 3. XRD pattern of SnO_2 nanorods after calcination at 600°C for 3 hours.

Fig. 4a and Fig. 4b show SEM images of SnO_2 nanoparticles and nanorods after annealing at 600 °C for 3 h, respectively. The results show that the diameters of SnO_2 nanorods are in the range of $100 - 300$ nm with length of several micrometers. The morphology of nanorods is found to be dependent on the synthesis conditions. The dimensions and aspect ratio are a function of hydrothermal time, temperature and mole ratio of SnO_2/NaOH.

Thus, the SnO_2 nanorods which were prepared by hydrothermal treatment at 140 °C for 20 hours are similar to the value reported by O. Lupan and Caixin Guo [15, 6]. In that report, the results (Fig. 4c) show that the diameters of SnO_2 nanorods are in the range of $100 - 150$ nm with lengths of the order of $1 - 2$ μm.

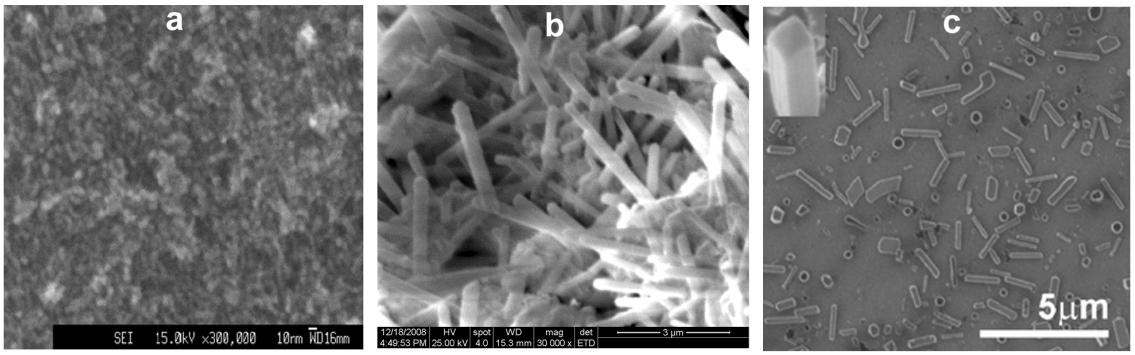

Fig. 4. a, b, SEM images of SnO_2 nanoparticles and nanorods after annealing at 600°C for 3 h; c, value reported by O. Lupan and Caixin Guo.

III.2. Gas sensing properties of the sensor devices

To investigate the gas sensing properties of the sensor devices to some target gases such as LPG, acetone, NH_3 and C_2H_5OH in air, we used thin films which were derived from SnO_2 nanorods material. We studied the dependence of the sensor response (S) on operating temperature and concentration of target gas in the air. The results are shown in Fig.5. Fig. 5a shows the dependence of the sensitivity to some target gases on operating temperature of the thin film derived from SnO_2 nanorods. It is clear that the operating temperature has an obvious influence on the response of sensor. The response increases with increasing operating temperature. The tin dioxides nanorods-based sensor exhibited the highest sensitivity to C_2H_5OH at 300 $^\circ$C. If the temperature increases over 300 $^\circ$C, the response decreases. This behavior can be explained in analogy with mechanism of gas adsorption and desorption on the surface of SnO_2 nanorods. An n-type metal-oxide can adsorb oxygen from the atmosphere both in the O^{2-} and in the O^- species. The adsorption of O^- is the most interesting process in sensor, because this oxygen ion is the more reactive and thus makes the material more sensitive to presence of reducing gases. At relatively low temperature the surface preferentially adsorbs O^{2-} and the sensitivity of the material is consequently very small. As the temperature increases, the dominant process becomes the adsorption of O^-, and then the response increases too. If the temperature increases too much, progressive adsorption of all oxygen ionic species previously adsorbed occurs and the response decreases.

Fig. 5b plots the sensor response of the SnO_2 film to some target gases at 300 $^\circ$C. The experimental results show that responses of the sensor based on SnO_2 nanorods exhibit good dependence on gas concentrations. The sensor response increases by increasing of gases content. It can be seen that the sensor exhibits very low response to acetone, NH_3, LPG, but good response to C_2H_5OH. This mean that the sensor has a good selectivity to other reducing gases, such as acetone, NH_3, LPG.

Fig. 6 shows the response and recovery curve of thin film to various concentrations of C_2H_5OH at 300 $^\circ$C. The result shows that resistance of the thin film decreased with appearance of C_2H_5OH. The transient to C_2H_5OH for sensor derived from SnO_2 nanorods was very sharp with the response time and recovery time are of 30 seconds.

IV. CONCLUSION

SnO_2 nanorods with diameters of $100 - 300$ nm and lengths of several micrometers have successfully prepared by hydrothermal method, using inexpensive chemicals such as $SnCl_4$, NaOH and NH_4OH. The XRD patterns revealed that the obtained products exhibit tetragonal rutile structure of SnO_2. The sensor fabricated from the nanorods exhibited excellent ethanol sensing properties with good response, high selectivity. The experimental results indicate the potential applications of using SnO_2 nanorods for fabricating alcohol vapor gas sensor.

ACKNOWLEDGMENTS

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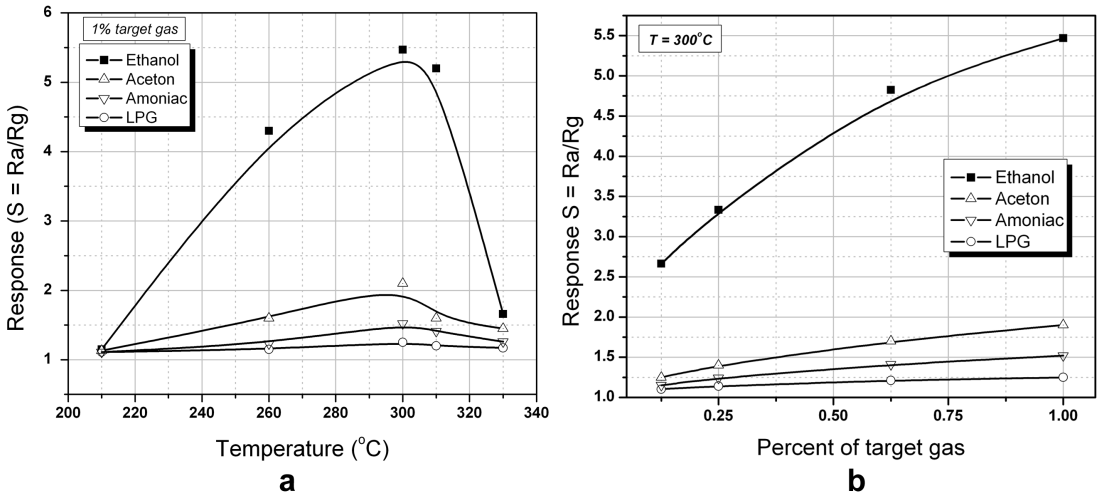

Fig. 5. a, The effects of the operating temperature on the response of sensor at 1 percent target gas; b, Variation in sensor response to different tested gases at operating temperature of 300°C.

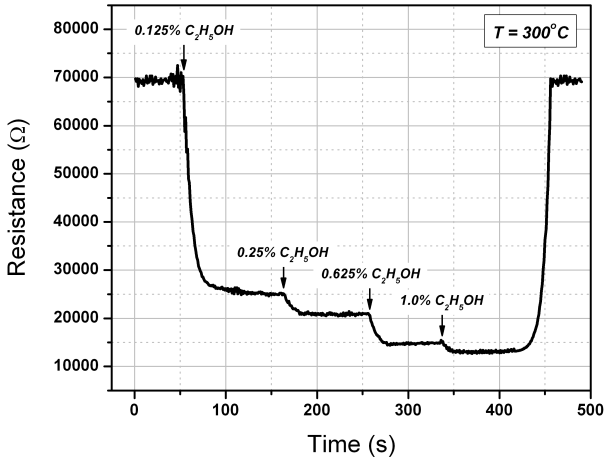

Fig. 6. Response transients to C_2H_5OH at 300°C for thin film derived from SnO_2 nanorods.

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