

Preparation of Macroporous Semiconductive Materials for the Sensing of Sulfur Compounds

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In this study, macroporous SnO₂ was prepared for the sensing of sulfur compounds, which are used as odorants to improve the safety of natural gas. Macropores in the semiconducting SnO₂ were formed using polystyrene nanobeads as a template. The mixing ratio of the polystyrene colloid and tin chloride solution used as the precursors was controlled to form an ordered array of macropores. The chemical sensing properties of the macroporous SnO₂ were investigated by injecting sulfur compounds into the sensing chamber using an *I–V* source meter. The macroporous SnO₂ materials were highly sensitive to sulfur compounds.

1. Introduction

Semiconducting tin oxide exhibits good chemical gas sensing properties towards a range of gases.⁽¹⁾ One of the most common ways to tune the sensitivity and selectivity of these materials is to dope them with various noble metals.⁽²⁾ The gas sensing performance of various sensing materials can simply be enhanced by controlling their morphological features during chemical synthesis. In particular, the generation of highly specific surface areas and uniform systems of large pores increases the probability of a gas interacting with a semiconductor, which is likely to increase the sensitivity of the material. The concept of utilizing self-assembled arrays of amphiphiles to synthesize well-ordered mesoporous materials⁽³⁾ has recently been applied to tin oxide (SnO₂). SnO₂ is the most widely used n-type semiconductor in gas-sensing devices because of its ability to detect combustible gases, such as CH₄, C₂H₅OH, CO, and H₂. The SnO₂-based sensor is generally operated at 250–500 °C in air. SnO₂ adsorbs oxygen from the atmosphere, forming an electron-depleted zone. Reducing gases react with the adsorbed oxygen, increasing the electron concentration in the material and decreasing the electrical resistance.

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Recently, a coal gasification process, which produces a synthetic gas (syn-gas), has been developed for electrical power generation and coal-to-liquid oil processes. However, sulfur compounds of 5000 ppmv are contained in the syn-gas produced in the coal gasification process, and cause the corrosiveness problems of the facilities and catalyst in the electrical power generation and catalytic chemical conversion processes. Therefore, sulfur compounds must be removed for a stable energy process. Thus, the detection of sulfur compounds contained in syn-gas is very important. Various SnO₂-based gas sensors were developed for the detection of hydrogen sulfide.⁽⁶⁻⁹⁾ The metal-doped SnO₂ and SnO₂-transition metal oxide composite materials were synthesized in order to enhance the sensitivity of a gas sensor. The calcination temperature for the synthesis of SnO₂ was controlled for high-crystallinity SnO₂.^(10,11) In this study, macroporous SnO₂ was prepared and used as a gas-sensing material for the detection of small-content H₂S in the syn-gas purified in the sulfur removing process. Although the sensitivity of a SnO₂-based sensor increases with increasing H₂S content, it decreases at a low H₂S content. Therefore, the increases in contact area over the sensor and gas diffusion rate were carried out with the synthesis of macroporous SnO₂ in this study.

In this study, macroporous SnO₂ was prepared using a polystyrene (PS) nanobead template in order to provide an effective pathway for the sensing of sulfur compounds, such as H₂S. It could be expected that the macroporous SnO₂ has better sensing properties than nonporous SnO₂ because the macroporous SnO₂ has a larger surface area and an interconnected macroporous structure enhances gas diffusion. The macroporous SnO₂ was prepared by the addition of polystyrene nanobeads as a template. Polystyrene nanobeads were synthesized by the suspension polymerization method. The sensing properties of the macroporous SnO₂ were compared with those of the nonporous SnO₂, which was prepared by a precipitation method.

2. Materials and Methods

2.1 Synthesis of polystyrene nanobeads

A polystyrene colloid was used as a template additive for the formation of pores in the semiconducting materials and synthesized as spherical particles by the polymerization of a styrene monomer (Sigma-Aldrich, C₆H₅CH = CH₂, MW = 104.15). The polystyrene nanobeads were prepared in an experimental setup equipped with a 500 ml jacketed glass vessel, a magnetic stirrer, a condenser, a vacuum system, a nitrogen flow system, and a thermocouple by the suspension polymerization method. The temperature was controlled using a PID controller and kept within ±0.1 °C. The narrowly dispersed latex was prepared by the surfactant-free emulsion polymerization of styrene. Millipore water (468 ml) and styrene (0.11 mol) were charged in the reactor. The reactor was purged with alternate cycles of nitrogen and evacuation, and finally left under a nitrogen atmosphere. After heating the reaction mixture to 70 °C with constant stirring at 400 rpm, the initial solution (0.42 g, 1.5 mmol of KPS in 10 ml of water) was injected into the reactor through a syringe. The reaction was allowed to proceed under these conditions for 12 h.

2.2 Synthesis of macroporous SnO₂

The synthesis of macroporous SnO₂ was carried out in a rotary vacuum evaporator. A mixture solution (100 ml), consisting of a 0.05 M SnCl₄ solution and a polystyrene colloid (50 ml), was placed in a 500 ml round flask. The volumetric ratio of SnCl₄ and the polystyrene colloidal solution was fixed to 1/1. The glass substrate was placed at the bottom of a glass container. The water in the mixture solution was removed by vacuum evaporation at 50 °C. After evaporation, the resulting solid mixture, which consisted of polystyrene spherical nanobeads and SnCl₄, was calcined at 600 °C for 4 h on an alumina substrate to thermally decompose the polystyrene used as the template. The physical properties of the macroporous SnO₂, such as surface area, crystal structure and surface morphology, prepared in this study were also examined by the nitrogen adsorption method, X-ray diffraction (XRD) and scanning electric microscopy (SEM). The alumina substrate, 10 × 10 mm² in size and coated with a platinum thin layer, was used as the electrode material for the fixation of macroporous SnO₂, as shown in Fig. 1. The macroporous SnO₂ powder was prepared as a slurry phase using isopropyl alcohol as a dispersant. The macroporous SnO₂ in the slurry phase was deposited over the alumina substrate.

2.3 Measurement of sensing properties of macroporous SnO₂

The electrical properties of the macroporous SnO₂ used as the chemical gas-sensing material were examined using an *I-V* meter (SourceMeter 2635A, Keithley) and the electrical current of the macroporous SnO₂ at 200 °C was measured by allowing a source voltage of 10 V to pass through a platinum electrode on the substrate. The alumina substrate of the gas sensor was patterned onto a platinum electrode. The electrical properties of the macroporous SnO₂-based chemical sensor were analyzed by the adsorption and desorption of H₂S in the experimental setup, and the electric resistance was measured over the macroporous SnO₂. The experimental setup for the sensing of H₂S consisted of a mass flow controller (MFC) to control the gas composition, an electrical oven to control the sensing temperature, a sensing chamber to allow contact between the H₂S and macroporous SnO₂ coated on the sensor device, and an *I-V* source

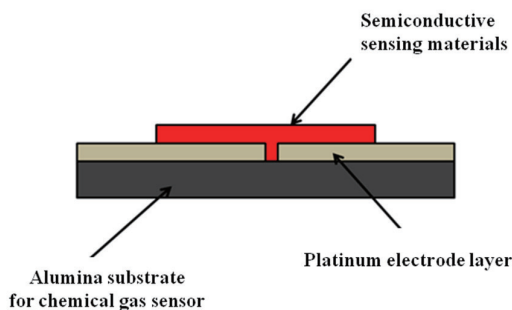


Fig. 1. (Color online) Schematic diagram of the chemical gas sensor.

meter to measure the electric resistance, as shown in Fig. 2. The sensing temperature was fixed to 200 °C to examine the response of the macroporous SnO₂ used as a chemical sensor, and the H₂S content was fixed at 50.9 ppmv. The H₂S adsorption and desorption steps were repeated for three cycles under all experimental conditions and the adsorption step was carried out at the maximum current. The measured currents were used as the data for analyzing the response with the injection of H₂S.

3. Results and Discussion

3.1 Analysis of the physical properties of macroporous SnO₂

Spherical polystyrene nanobeads were synthesized by the suspension polymerization method, and their size was approximately 300 nm, as shown in Fig. 3. The size of the polystyrene nanobeads was controlled by the concentration of styrene monomer used in the polymerization process. Ordered macroporous materials were synthesized with polystyrene nanobeads owing to their homogeneous spherical size.

The macrosized pores formed over the surface of the SnO₂ layer prepared in this study were examined, as shown in Fig. 4. Macropores were formed in the SnO₂ bulk

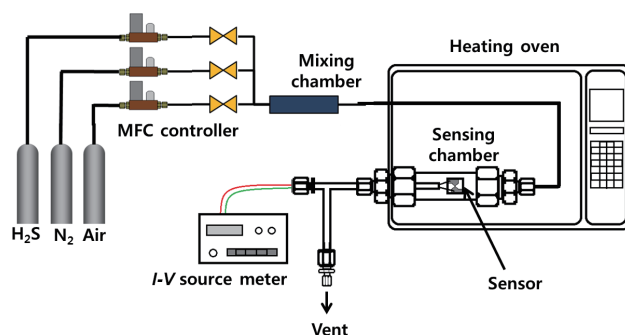


Fig. 2. (Color online) Schematic diagram of the experimental apparatus for measuring the responses of the chemical gas sensor.

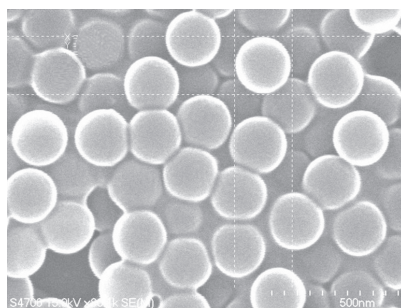


Fig. 3. SEM image of the polystyrene nanobeads synthesized by the suspension polymerization method.

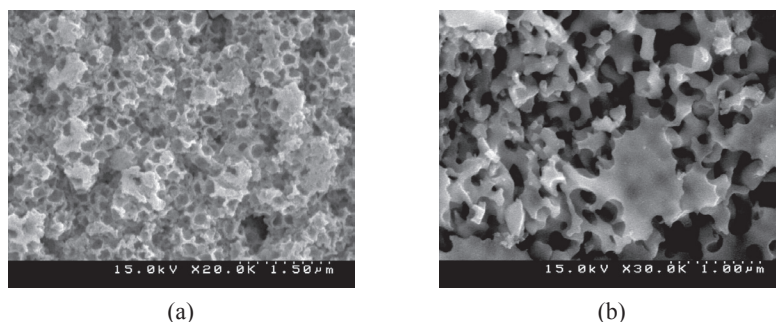


Fig. 4. SEM images of the macroporous SnO₂ prepared with the polystyrene nanobeads: (a) $\times 20000$ and (b) $\times 30000$.

powder. The size of the pores matched that of the polystyrene nanobeads used as the template for the formation of macropores in SnO₂. The ordered macropores formed in SnO₂ were spherical. These spherical macropores were interconnected in the SnO₂ bulk and dispersed homogeneously, as shown in Fig. 4(b). Therefore, the SnO₂-based chemical gas sensor showed a strong response because the gases diffused well into the SnO₂ bulk layer.

The surface areas of the macroporous SnO₂ and nonporous SnO₂, which were prepared by a precipitation method, were measured by the nitrogen adsorption method. The two SnO₂ samples showed substantially different surface areas. The surface area of SnO₂ prepared by the precipitation method was approximately 17 m²/g and that of macroporous SnO₂ was approximately 54 m²/g. SnO₂ is a nonporous material, but it is highly sensitive to many types of gases. The isotherm curves obtained by nitrogen adsorption and desorption exhibited a typical low pore volume, as shown in Fig. 5(a). On the other hand, the pore size distribution (PSD) curve measured by nitrogen adsorption and Hg porosimetry confirmed that macroporous SnO₂ has meso and macropore sizes of approximately 33 and 130 nm, as shown in Figs. 5(b) and 6.

XRD showed that the macroporous SnO₂ had high crystallinity with a tetragonal structure, as shown in Fig. 7(a). The XRD peak pattern of the macroporous SnO₂ revealed the same structure as the common SnO₂ prepared by the precipitation method, as shown in Fig. 7(b). Therefore, the effects of the surface area and gas diffusion on chemical gas sensitivity can be determined with the formation of macropores in the SnO₂ bulk. The peaks of 28, 41, and 51° of 2θ , as shown in Fig. 7(a), agreed with the XRD pattern of KCl, which was formulated from potassium in the initiator (KPS) and chlorine in the precursor (SnCl₂).

3.2 Response of macroporous SnO₂ for H₂S

In this study, the changing electric current of the macroporous SnO₂ deposited on the chemical sensor was examined by the addition of hydrogen sulfide or air into the sensing chamber. Hydrogen sulfide and air were introduced alternately into the sensing chamber, and these experiments were performed repeatedly for 3 cycles. Air was used as the purge gas for the desorption of hydrogen sulfide adsorbed over the macroporous SnO₂, and the

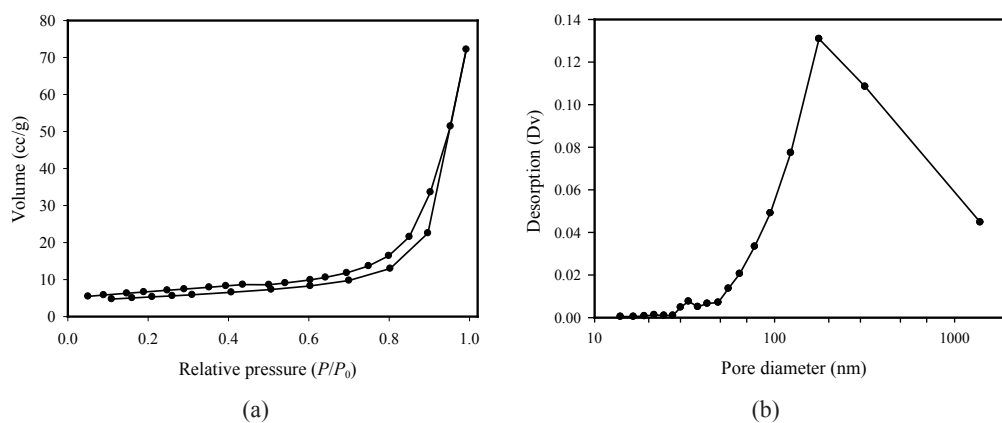


Fig. 5. (a) Isotherm and (b) pore size distribution curves of macroporous SnO_2 measured by nitrogen adsorption and desorption.

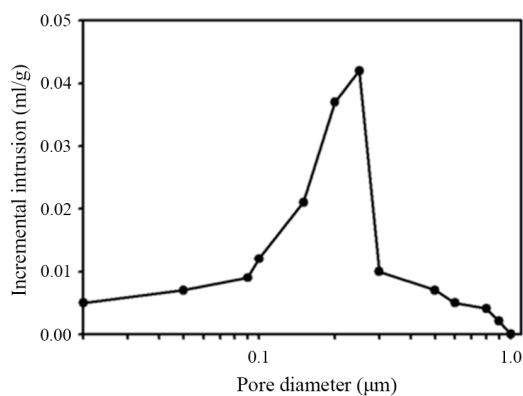


Fig. 6. Pore size distribution curve of macroporous SnO_2 measured by Hg porosimetry.

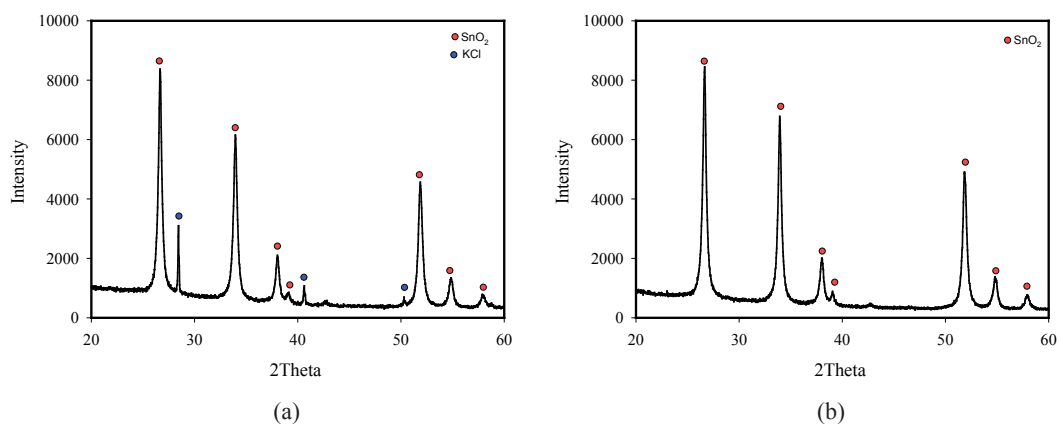


Fig. 7. (Color online) XRD patterns of (a) macroporous SnO_2 and (b) nonporous SnO_2 .

oxygen contained in the air was used as a regeneration gas for the reoxidation of S-doped SnO₂ formulated by a gas–solid reaction between hydrogen sulfide and SnO₂. Figure 8 shows the response signals obtained with 50.9 ppmv hydrogen sulfide at 200 °C. When H₂S was flowed into the sensing chamber, the electric current increased from 20 to 235 μA during the first cycle, from 15 to 240 μA during the second cycle, and from 10 to 253 μA during the third cycle. The consumption times reached by the maximum currents were approximately 250, 350, and 490 at the first, second, and third cycles, respectively. The response time increased with increasing number of cycles and the maximum electric current increased. The current decreased rapidly when the sensing chamber was purged with air and recovered within 50 s. Moreover, the response time for H₂S in the macroporous SnO₂ was increased about 2 times with only 3 cycles. It was concluded that the response time increased, because the concentration of hydrogen sulfide was reduced by mixing air and hydrogen sulfide in the gas mixing chamber at the injection times of the second and third cycles. The gas mixing chamber was located in front of the sensing chamber for the control of H₂S concentration.

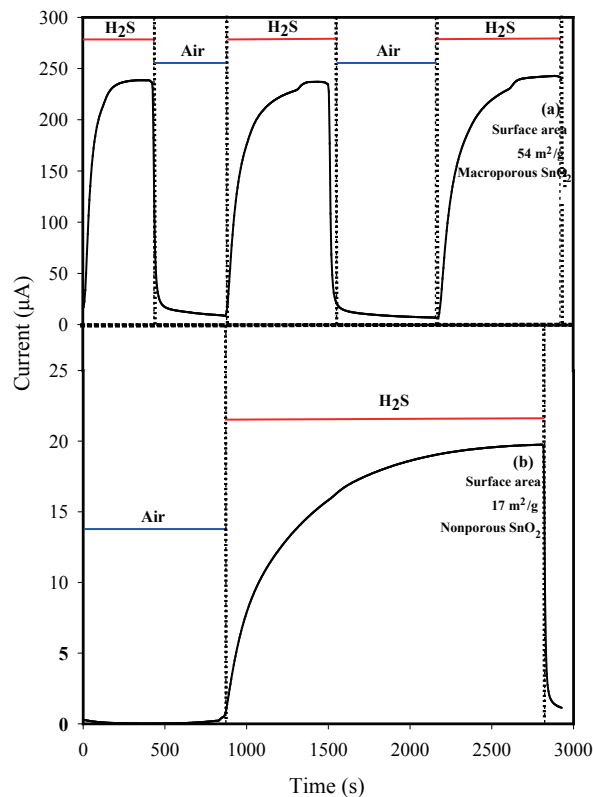


Fig. 8. (Color online) Electric currents measured over (a) macroporous SnO₂ and (b) nonporous SnO₂-based chemical sensors with 50.9 ppmv H₂S at 200 °C using an I - V source meter, alternately inputting H₂S and air.

When nonporous SnO₂ was used as the sensing material, the electric current increased slowly with the injection of hydrogen sulfide and reached a maximum value of 20 μA at approximately 1700 s. The sensing response of the nonporous SnO₂ was both lower and slower than that of the macroporous SnO₂. Gas diffusion was enhanced by the macrosized pores in the SnO₂ bulk because the difference in sensing property for hydrogen sulfide depends on the surface area and morphology of the sensitive materials.

4. Conclusions

In this study, macroporous SnO₂ was prepared by the addition of polystyrene nanobeads used as the template. These nanobeads were synthesized by the suspension polymerization method. Macroporous SnO₂ has a higher surface area than nonporous SnO₂. The macropores interconnected in the SnO₂ bulk enhance gas diffusion in the sensing materials. Therefore, high sensitivity can be obtained with the formation of macropores in the SnO₂ bulk due to the effects of the surface area and gas diffusion.

Acknowledgements

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