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Gold-nanoparticle-decorated Tin Oxide of a Gas Sensor Material for Detecting Low Concentrations of Hydrogen Sulfide

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Hydrogen sulfide (H_2S) is an offensive-smelling, colorless, and toxic gas that can cause poisoning even in small quantities. In this study, we proposed a sensor that can detect H_2S with a low composition using SnO_2 and Au nanoparticles as a catalyst. We investigated the structure formed in the thin layer of a sensing material and determined whether it can absorb the tested gas well and produce a high sensing response. We also determined the optimal operating temperature and showed that it has excellent response and recovery times. Pure SnO_2 was synthesized by a simple thermal decomposition method. In the next step, the wet chemical method was used to dissolve the SnO_2 and Au nanoparticles before a viscous liquid compound was deposited onto the electrode by the drop-casting method. The sensor's performance for H_2S gas detection was tested at low concentrations with four concentrations of Au nanoparticles on SnO_2-based materials. The results showed that the structure formed in the thin layer is an agglomeration of hollow grains, which allows the gas to be absorbed properly. The result indicated that 40 µl of Au nanoparticles was the optimum concentration for a H_2S gas sensor, with responses of 65.12% at 0.2 ppm and 87.34% at 1 ppm. The response time was 8 s, whereas the recovery time was 31 s. Moreover, the optimal operating temperature for the reaction was 200 °C. The findings of this experiment demonstrated that depositing Au-nanoparticle-decorated SnO_2 by the drop-casting method produced a structure with superior gas-sensing performance.

1. Introduction

H_2S, which is a colorless gas that is highly poisonous and corrosive, is produced as a by-product of activities such as coke extraction, coal oil extraction, and natural gas production.(1) Low H_2S levels can harm the sense of smell, whereas significant H_2S levels can numb the olfactory nerve.(2) In a case study, a 20-month-old baby who lived around a coal mine that emitted 0.6 ppm H_2S was exposed for a long time, causing illness resembling subacute necrotizing encephalopathy.(3) Therefore, an early warning device is needed to detect H_2S at low concentrations.

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Metal oxide semiconductors (MOSs) as chemically resistant gas sensors have gained popularity in recent years for use in environmental sensors, automotive emission sensors, and food safety measurements owing to their low production cost, high sensitivity, and ease of application, as well as their ability to detect various gases.[4] The existing MOSs that are widely used for gas sensors are ZnO for H_2 gas sensors,[5] SnO_2 for the detection of ammonia,[6] CuO for the detection of target gases such as volatile organic compounds (VOCs), hydrogen sulfide, carbon monoxide, carbon dioxide, hydrogen, and nitrogen oxide,[7] TiO_2 for the detection of SO_2,[8] Fe_2O_3 for the detection of NO_2,[9] WO_3 for the detection of some VOCs,[10] α-Fe_2O_3 for the detection of hydrogen,[11] and NiO for the detection of ethanol.[12] One of the metals described, SnO_2, is of interest in this study because it has many advantages, including low cost and high and long-term stability.[13] It has a direct band gap of 3.37 eV and a large excitation binding energy of 60 meV.[14] In addition, SnO_2 can be used to detect gases at the ppm level, and its detection limit is at the ppb level.[14]

To enhance the sensitivity and selectivity of a sensor, additional metals such as Au, Pd, and Pt are used as catalysts or sensitizers in the sensing process.[15,16] In this research, Au was chosen as the catalyst. Au contributes significantly to the increase in the sensing response of WS_2 and SnO–WS_2.[17] Because the presence of Au nanoparticles sufficiently contributes to electrical sensitization and chemical sensitization, an increase in the amount of Au nanoparticles causes an increase in the response.[18] Au + SnO_2 can reduce the operating temperature to 70 °C and increase the sensing response fourfold.[19]

Various methods are utilized to apply nanomaterials to sensor electrodes, including inkjet printing, laser scribing, electrochemical deposition, electrospinning deposition, and drop-casting. Among the deposition methods, the drop-casting method was used in this study because of its simplicity, low cost, and relatively low precipitation temperature.[20] The drop-casting method became well known for creating semiconductors with an excellent crystallite structure, thus enhancing device performance.[21]

In this study, SnO_2 was used as a base material, and Au nanoparticles were used as a catalyst to enhance the sensing response. SnO_2 was synthesized by the thermal decomposition method,[22] and the drop-casting method was used for sensor fabrication.[23] H_2S was the gas to be detected and had a concentration of 1 ppm and below.

2. Materials and Methods

Pure SnO_2 nanoparticles were obtained by heating 1.35 g of SnO powder and 13.5 ml of oleic acid in a three-neck flask under argon ambient at 310 °C with stirring at 500 rpm. After 1 h, 12 ml of tri-n-octylamine was injected into a round bottom flask with three necks; the temperature was increased to 340 °C for 2 h with stirring at 500 rpm. The viscous liquid in the flask was finally cooled to room temperature and cleaned ten times with ethanol and hexane.

The sensor device was prepared by the drop-casting method.[24] We dissolved 0.01 g of SnO_2 powder with four different volumes of 50 mM $HAuCl_4{\cdot}3H_2O$ (0, 20, 30, and 40 μl) in 10 ml of deionized water with ultrasonication. Then, we dropped 4 μl of viscous liquid of Au + SnO_2 onto the Pt electrode shown in Fig. 1. We placed this electrode in an oven at 50 °C and held it

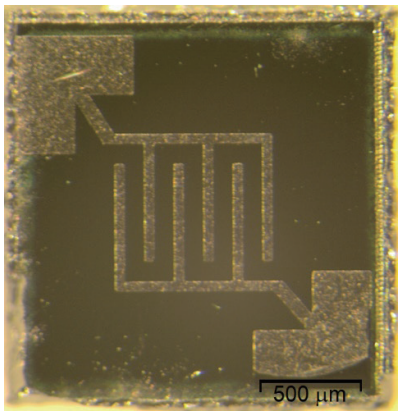


Fig. 1. (Color online) Pt electrode.

overnight, followed by annealing at 500 °C for 1 h. Sensing response testing was performed by injecting H_2S of 0.2, 0.4, 0.6, 0.8, and 1.0 ppm concentrations in a measurement gas sensor chamber. The sensing response is expressed as

$$R = \frac{I_x - I_y}{I_y} \times 100\%. \quad (1)$$

I_x is the current when the sensor is exposed to H_2S and I_y is the current when the sensor is exposed to oxygen. The crystallographic structure, morphology, and microstructure were observed by transmission electron microscopy (TEM), X-ray diffraction (XRD), and scanning electron microscopy (SEM), respectively.

3. Experimental Results

The XRD pattern analyses of four variations of Au-nanoparticle-decorated SnO_2 showed that the intensities of the Au peaks (111), (200), and (220) increased with the Au concentration, as marked by the boxes in Fig. 2. The XRD Au peaks in the graph correspond to the Au JCPDS 04-784 structure.

The drop-casting method used to deposit materials causes the agglomeration of SnO_2 and Au nanoparticle grains. This method also induces a high porosity in the thin layer of the sensor material. Grain aggregation and porosity are uniformly distributed across the sensor material surface. This surface structure is advantageous for absorbing the target gases being detected, as depicted in Fig. 3(a). As indicated in Fig. 3(b), the average diameter of the particles is 34.20 nm.

SEM and TEM images of the surface of pure SnO_2 nanoparticles are shown in Figs. 3(a) and 4, respectively; the diameter of the granules is 4–76 nm.

Small grains are evenly distributed among the large grains on the surface and are Au nanoparticles, as shown in the TEM image in Fig. 5(a). For the Au nanoparticles to increase the sensing response, their diameter must be small; the diameter of the Au nanoparticles in the

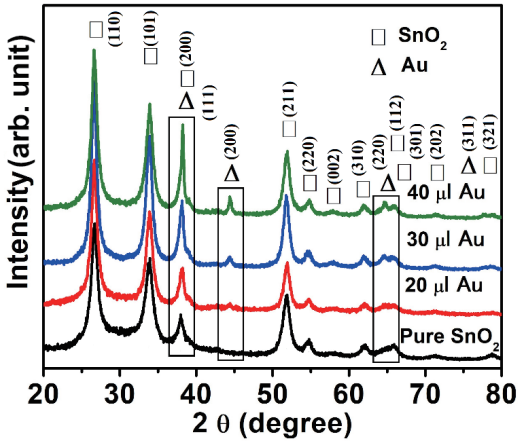
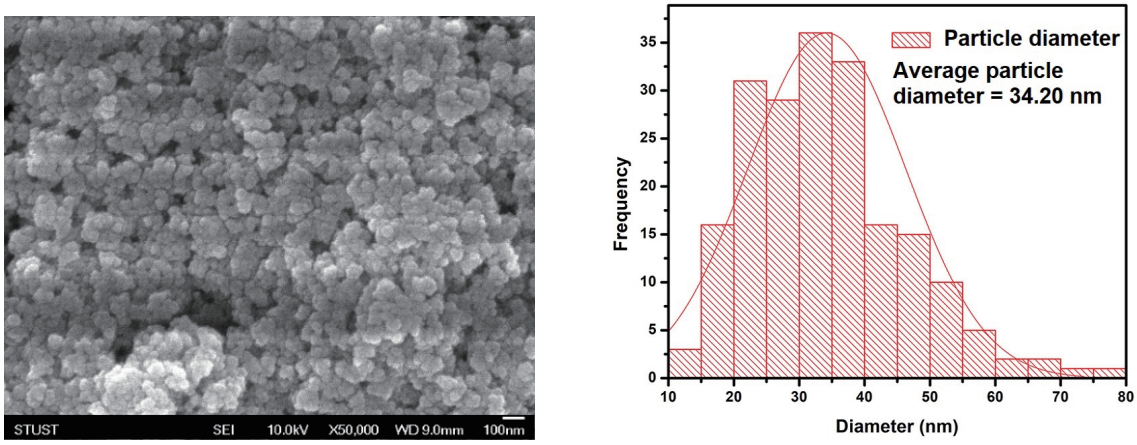


Fig. 2. (Color online) XRD pattern analyses of pure SnO_2 and Au-nanoparticle-decorated SnO_2.



(a) (b)

Fig. 3. (Color online) (a) SEM image of surface of Au-nanoparticle-decorated SnO_2 and (b) histogram curve of diameter distribution of SnO_2 particles.

image is 2–3 nm. Porosity and particle diameter have substantial effects on gas response.[25] The element analyses of Au-nanoparticle-decorated SnO_2 showed that Sn is 49.70 wt%, O is 40.72 wt%, and Au is 1.16 wt%, as presented in Fig. 5(b).

As mentioned previously, the sensing response was measured with four Au nanoparticle concentrations. It was observed that the sensing response increased with the concentrations of H_2S and Au nanoparticles, as shown in Fig. 6.

At a H_2S concentration of 0.2 ppm, the sensing responses at the four Au nanoparticle concentrations were 11.00, 49.63, 68.05, and 65.12%, respectively. Moreover, at a H_2S concentration of 1 ppm, the sensing responses were 51.27, 67.14, 81.05, and 87.34%, respectively. From the above results, it was found that adding Au nanoparticles as a catalyst can increase the

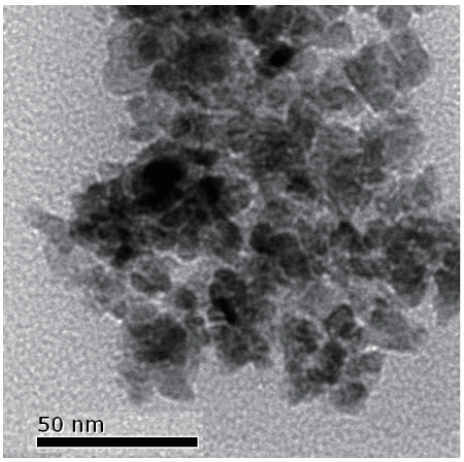
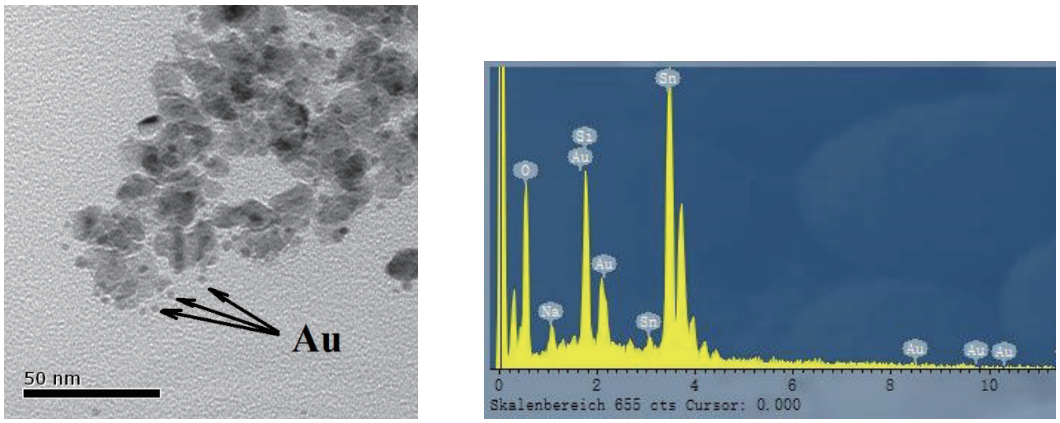


Fig. 4. TEM image of surface of pure SnO_2 nanoparticles.



(a) (b)

Fig. 5. (Color online) (a) TEM image of surface and (b) results of element analyses of Au-nanoparticle-decorated SnO_2.

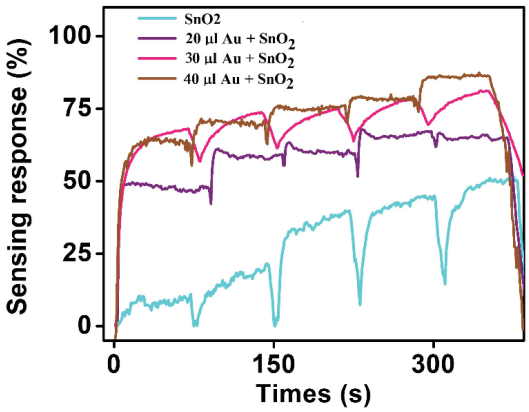


Fig. 6. (Color online) Sensing response with four Au nanoparticle concentrations.

sensing response. In contrast, adding Au nanoparticles reduces the operating temperature. The optimal operating temperatures were 250, 250, 150, and 200 °C, respectively, as shown in Fig. 7.

Three tests were carried out to determine the optimal operating temperature. At 150 °C, the sensing response was poor and tended to diminish over time. When the sensor was operated at 200 °C, its sensing response improved; the response tended to stabilize and create a horizontal line. When the sensor was operated at 250 °C, the sensing response became unstable. Therefore, adding 40 µl of Au nanoparticles to SnO_2 resulted in the optimal operating temperature of 200 °C, which decreased by 50 °C compared with the operating temperature of pure SnO_2, as shown in Fig. 8.

Adding Au nanoparticles will speed up the response; on the other hand, it will slow down the recovery, as shown in Figs. 9(a) and 9(b). The time differences for response and recovery after adding Au nanoparticles were 9 and 18 s, respectively.

The mechanism of a semiconductor gas sensor relies on the absorption and release of gas molecules, as shown in Fig. 10. When a gas sensor is exposed to clean air, oxygen molecules are adsorbed on the surface and react with free electrons to generate oxygen ions, as shown by Eqs. (2)–(5).[26]

$$O_{2(g)} + e^- \rightarrow O_2^-{}_{(ad)} \tag{2}$$

$$O_{2(ad)} + e^- \rightarrow O_2^-{}_{(ad)} \tag{3}$$

$$O_2^-{}_{(ad)} + e^- \rightarrow 2O^-{}_{(ad)} \tag{4}$$

$$O^-{}_{(ad)} + e^- \rightarrow O^{2-}{}_{(ad)} \tag{5}$$

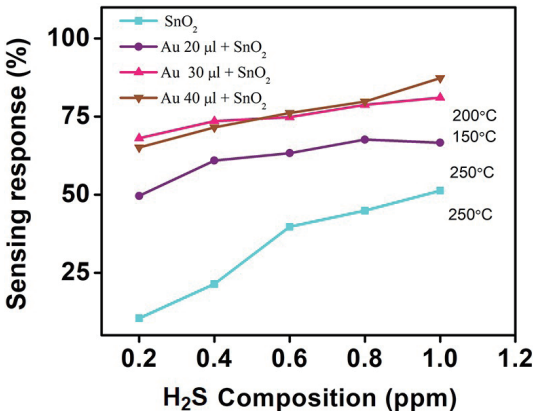


Fig. 7. (Color online) Increase in sensing response with specific H_2S gas concentration and optimal operating temperature for each Au nanoparticle concentration.

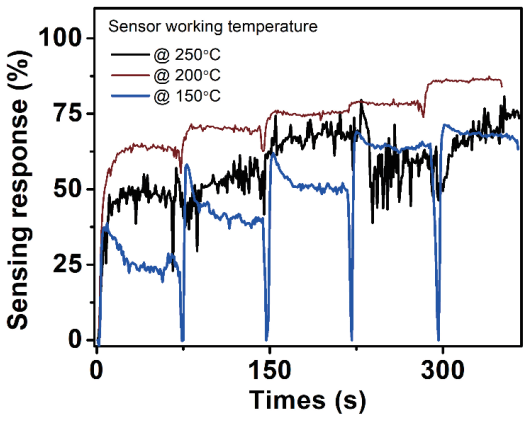


Fig. 8. (Color online) Optimal operating temperature of Au-nanoparticle-decorated SnO_2 with 40 µl of Au nanoparticles.

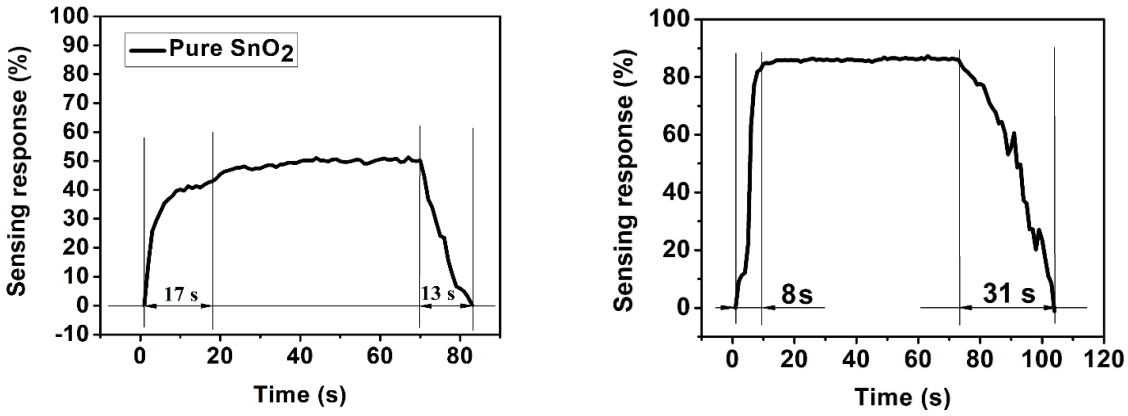


Fig. 9. Response and recovery times of (a) pure SnO_2 and (b) Au-nanoparticle-decorated SnO_2.

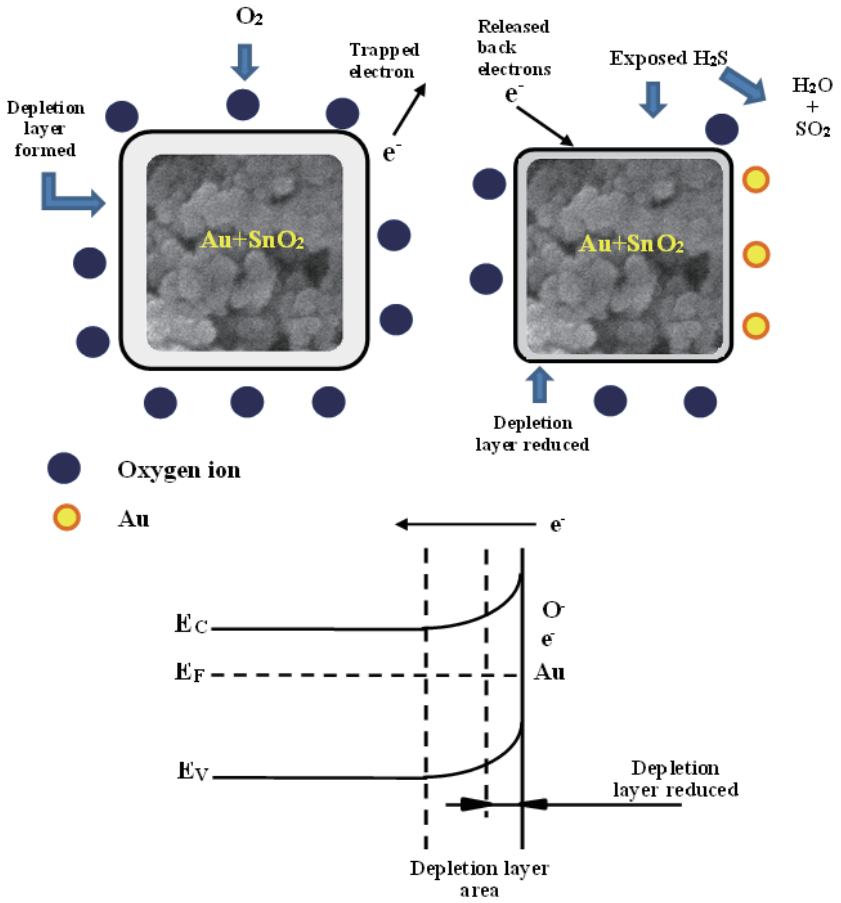


Fig. 10. (Color online) Schematic of sensor mechanism.

When the sensor is exposed to H_2S gas, the trapped electrons are returned to the bulk, and the response of H_2S and oxygen can be described by Eq. (6).[27]

$$H_2S + 3O^{2-}{}_{(ads)} \rightarrow H_2O_{(g)} + SO_{2(g)} + 6e^- \quad (6)$$

The improvement in the sensitivity of the sensing response is dependent on at least two factors: electronic sensitization and chemical sensitization. In the electronic sensitization mechanism, the electrons generated by SnO_2 will move to the electron noble metal (this occurs owing to the dissimilarity in work function) so that the noble metal will be electron-rich. Then, there is an increase in the depletion in the electron oxide film. As a result, SnO_2 decorated with Au, Pt, and Ag becomes more susceptible to the environment because of the increasing potential barrier among bordering grains. The chemical sensitization mechanism of Au, Pt, and Ag is also called the spillover effect, where the catalytic process occurs from a metal-assisted catalyst. In this process, the oxygen molecules and the target gas to be adopted have more sites from noble metals than from SnO_2 particles, which results in the adsorption and dissociation of the molecules due to the high catalytic and conductive properties of metal particles. In air, metal particles will absorb ionic oxygen species and increase the depletion region of the adjacent SnO_2 particle surface. When the sensor is in operation, the metal nanoparticles adopt the target gas and are also directly oxidized by ionic oxygen species near the surface of the adjacent metal particles. The spillover effect of these metal particles increases the amount and speed of electron transfer.[15,28]

4. Conclusions

The intensities of the Au peaks (111), (200), and (220) increased with the Au nanoparticle concentration. When the drop-casting method was used, the materials deposited on the electrode, grain agglomeration, and the presence of many pores in the thin film of the sensor made it easy for the gas to be absorbed. The SnO_2 particle diameter was 4–80 nm, whereas the Au nanoparticle diameter was 2–3 nm. These diameters are suitable for enhancing the effectiveness of the gas sensor. The sensing response increased with the concentrations of H_2S and Au nanoparticles; however, the optimal operating temperature decreased when Au nanoparticles were added. The operating temperature of SnO_2 with 40 µl of Au nanoparticles was improved to 200 °C. At that temperature, the created line in the graph was stable and horizontally linear. The response time was 8 s and the recovery time was 31 s, which are both good results. Applying the drop-casting method of SnO_2 decorated with Au nanoparticles is recommended because it is easy to produce a thin layer with many pores around the surface, which can lead to good sensor performance.

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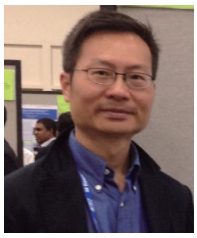

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