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Development of sensors based on CuO-doped SnO_2 hollow spheres for ppb level H_2S gas sensing

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Abstract An effort has been made to develop a new kind of SnO_2–CuO gas sensor which could detect an extremely small amount of H_2S gas at relatively low working temperature. The sensor nanomaterials were prepared from SnO_2 hollow spheres (synthesized by employing carbon microspheres as temples) and Cu precursor by dipping method. The composition and structural characteristics of the as-prepared CuO-doped SnO_2 hollow spheres were studied by X-ray photoelectron spectroscopy, X-ray powder diffraction, scanning electron microscopy, and transmission electron microscopy. Gas-sensing properties of CuO-doped SnO_2 hollow sphere were also investigated. It was found that the sensor showed good selectivity and high sensitivity to H_2S gas. A ppb level detection limit was obtained with the sensor at the relatively low temperature of 35 °C. Such good performances are probably attributed to the hollow sphere nanostructures. Our results imply that materials with hollow sphere nanostructures are promising candidates for high-performance gas sensors.

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Introduction

Hydrogen sulfide (H_2S) is one of the typical bad-smelling and toxic gases, and is used as a process gas or generated as a by-product in laboratories and industrial areas. Detection of H_2S is of immense importance, and much attention has been paid to it. Different kinds of materials have been developed for H_2S gas sensing [1, 2]. The addition of small amounts of additives is known to provide better sensitivity [2–4]. Among the various metal oxides that have been found to impart sensitivity and selectivity to SnO_2 for the detection of H_2S, CuO is found to have an outstanding promoter action [4–12]. In the pioneering work of Maekawa and coworkers [4], CuO-doped SnO_2 thick films were first reported to have an outstanding sensitivity and selectivity to H_2S. Subsequently, various materials based on SnO_2 with CuO as a catalyst for H_2S gas sensing have been synthesized and extensively studied, such as Cu–SnO_2 bilayers and CuO–SnO_2 heterostructures [5–10], CuO-doped SnO_2 nanoribbons [11], and CuO-doped SnO_2 nanorods [12]. These SnO_2–CuO composite films are found to exhibit extraordinary sensing characteristics to H_2S gas. Their high H_2S gas-sensing mechanism has been ascribed to the formation of p–n junction between n-type SnO_2 and p-type CuO, and the strong affinity of CuO to H_2S that leads to the disruption of the p–n junction. However, most of the above papers always present the H_2S response as a function of gas concentrations ranging from 10 to 50 ppm at relatively high temperatures. The acceptable levels of H_2S in ambient environment (recommended by the Scientific Advisory Board on Toxic Air Pollutants, USA) are in the range of 20 to 100 ppb [13]; therefore, more efforts are needed to evaluate the response of SnO_2–CuO sensors to lower concentrations of H_2S.

Recently, the hollow sphere nanostructures of oxides are drawing strong research interest because of their unique structural, optical, and surface properties [14]. With such specific morphologies, the hollow sphere nanostructures are considered to be more desirable as gas sensors because of their potential for encapsulation of large quantities of guest molecules or large-sized guests within the empty core domain [15–18]. For example, Hyodo et al. [18] prepared SnO_2 hollow spheres and found that the microporous structure provided an enhancement in both active surface area and analyte diffusion throughout the film, and these films exhibited good sensitivity to H_2 and NO.

In this paper, a new kind of SnO_2–CuO sensor which is based on CuO-doped SnO_2 hollow spheres has been developed. For preparing the sensing materials, SnO_2 hollow spheres were synthesized by employing carbon microspheres as temples, and then were doped with CuO by dipping method. The composition and structural properties of the as-prepared CuO-doped SnO_2 hollow spheres were studied. The hollow sphere nanostructures were observed in the as-prepared sensing materials. The sensing performance of CuO-doped SnO_2 hollow spheres was systematically examined. The results showed that the sensor is highly selective and sensitive to H_2S, and a ppb level detection limit was obtained at 35 °C. It indicates that CuO-doped SnO_2 hollow spheres would have potential application in the detection of trace amount of H_2S gas. The comparative gas-sensing performances between CuO-doped SnO_2 hollow spheres sensor and undoped SnO_2 hollow spheres sensor to H_2S were also investigated.

Experiment

Preparation of carbon microspheres and SnO_2 hollow spheres

Carbon microspheres were prepared as described elsewhere [19]. In a typical procedure, 6 g of glucose was dissolved in 40 mL of deionized water, and then the resulting solution was transferred to a 40 mL Teflon-lined autoclave and maintained at 180 °C for 7 h. The purple-brown products were centrifuged and rinsed for several times with distilled water and ethanol, and finally dried at 60 °C for 12 h.

For the preparation of the SnO_2 hollow spheres, 0.2 g of carbon microspheres was dispersed in 35 mL ethanol by ultrasonication, and then 3.94 g of $SnCl_2 \cdot 2H_2O$ was added into the solution. After ultrasonication for 1.5 h, the solution was aged for 5 h, and then rinsed with ethanol and dried at 60 °C for 12 h. The dried powder was calcinated at 500 °C for 2 h in air, and the final products were obtained.

Preparation of CuO-doped SnO_2 hollow spheres

CuO-doped SnO_2 hollow spheres were obtained by a simple chemical method. SnO_2 hollow spheres powder (0.5 g) and 0.075 g of $Cu(NO_3)_2 \cdot 3H_2O$ were added in 10 mL ethanol. After ultrasonic treatment for 1 h, the solution was aged at room temperature for 2 h. The resulting green products were dried at 60 °C, followed by calcination at 500 °C for 8 h in air. The black products were finally obtained.

Characterization

The composition and structural properties of the obtained powder were studied by X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD; D/max 2550 V, Cu Kα radiation, wavelength 1.5418 Å), field emission scanning electron microscopy (FE-SEM; FEI, Sirion-200), and transmission electron microscopy (TEM; JEOL-2010 operated at 120 kV).

Preparation of sensor device

Sensors based on CuO-doped SnO_2 hollow spheres were prepared as follows. The mixture of SnO_2 hollow spheres powder (0.5 g) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.075 g) in ethanol was sonicated for 1 h, and then aged for 2 h at room temperature. The resulting mixture was dried at 60 °C for 1 h and then was coated on the ceramic tubes, on which interdigitated gold electrodes had been printed (the gap between electrodes: 1 mm). The as-prepared sensor component was dried at 60 °C, followed by calcination at 500 °C for 8 h in air.

Sensors based on undoped SnO_2 hollow spheres were also prepared by a method similar to the one mentioned above. SnO_2 hollow spheres without $Cu(NO_3)_2 \cdot 3H_2O$ dispersed in ethanol was applied on the ceramic tubes. The obtained sensor components were dried at 100 °C for 1 h, and then aged at 300 °C for 4 h.

Gas-sensing measurement

Gas-sensing properties are investigated by measuring the electrical resistance when exposed to target gases. Gas-sensing system and test procedure has been reported in our previous work [20]. During a typical gas-sensing test, a 20 V DC voltage was applied across the electrodes. The target gas concentration inside the testing chamber was achieved by injecting a known volume of test gas using a gas-injecting syringe. Air was allowed to pass into the testing chamber after every target gas exposure cycle. The sensor sensitivity (S), as a function of gas-sensing properties, is defined as $S\ (\%) = (R_a/R_g) \times 100 = (I_g/I_a) \times 100$,

where R_a and R_g are sensor resistances in air and H_2S–air mixtures, and I_a and I_g are the corresponding currents through it, respectively. The response times and recovery times are defined as the time to reach 90% of the total current change.

Result and discussion

Characterization of SnO_2 hollow spheres and CuO-doped SnO_2 hollow spheres

The carbon microspheres derived from hydrothermal conditions were hydrophilic with plenty of –OH and C=O groups on the surface and enabled to bind metal cations. Sn^{2+} ions were adsorbed on the surface of carbon microspheres and then were converted into SnO_2 nanoparticles during the calcination in air. Figure 1a shows a typical XRD pattern of the as-prepared SnO_2 hollow spheres. All the diffraction peaks can be indexed to the tetragonal rutile structure of SnO_2 (JCPDS Card Files, No. 71-0652). Figure 1b is the SEM image. It clearly shows that the product consists of interconnected hollow spheres. The average diameters of the hollow spheres are about 160–180 nm. TEM image of the product shown in Fig. 1c demonstrates that the walls of the hollow spheres are porous and structurally robust. SnO_2 hollow spheres are composed of numerous nanoparticles with a small size of about 15 nm, which can be calculated by Debye–Scherrer formula. The selected area electron diffraction (SAED) pattern shown in Fig. 1d suggests that as-prepared SnO_2 hollow spheres were polycrystalline.

Figure 2 is the XRD pattern of the as-prepared CuO-doped SnO_2 hollow spheres. Except for the diffraction peaks of SnO_2, the dotted peaks are indexed to CuO with tenorite crystal structures (JCPDS file No. 41-0254). Figure 3a is the low-magnification SEM image of CuO-doped SnO_2 hollow spheres. Most hollow spheres are found to have openings in the shells after calcination. A practical cave-in or a small opening on hollow spheres shell can be observed clearly in Fig. 3b. The intact hollow spheres had uniform morphology with the average diameters about 230–250 nm. Figure 3c is the TEM image of the product. Many nanoparticles were also found around the hollow spheres, which maybe result from the badly destroyed hollow spheres. As shown in Fig. 3d, the coarse shell of the hollow nanospheres is composed of dense crystallized nanocrystals. Statistical results of the image have shown that the average size of the nanoparticles is about 25 nm. Comparison with the size of nanoparticles without calcination indicates that the SnO_2 nanoparticles have grown up

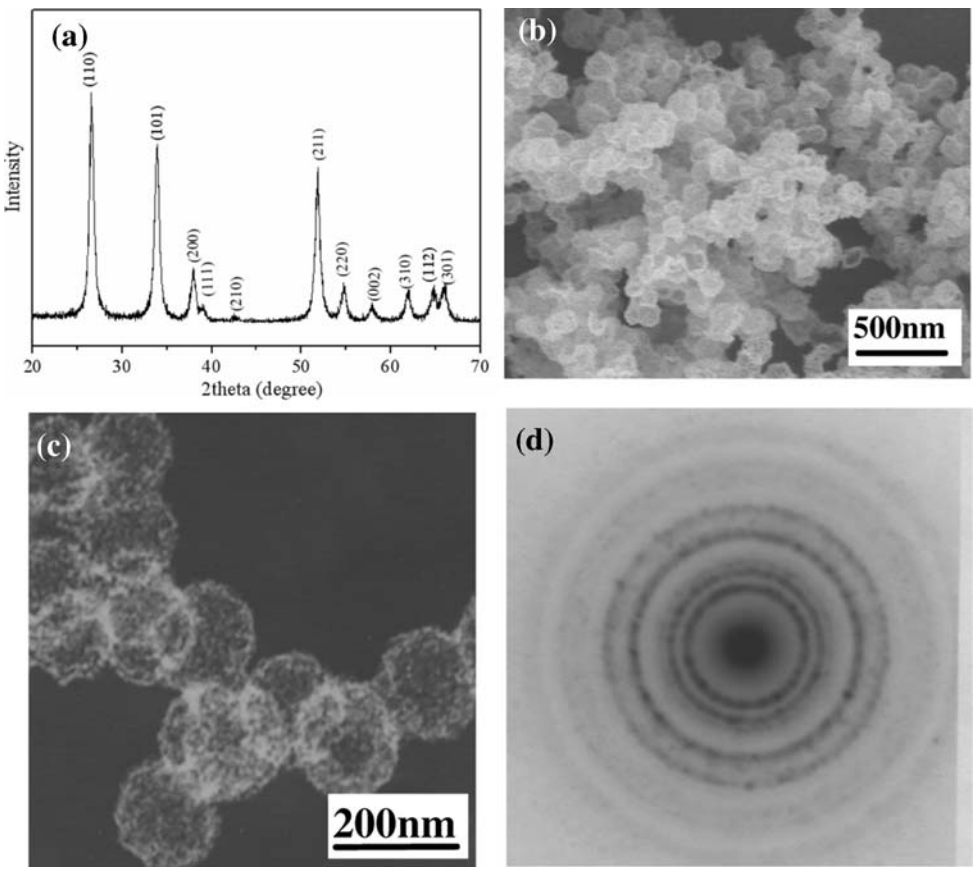

Fig. 1 **a** XRD pattern of the as-prepared SnO_2 hollow spheres. **b** SEM image of the SnO_2 hollow spheres. **c** TEM image of the SnO_2 hollow spheres. **d** Corresponding SAED pattern

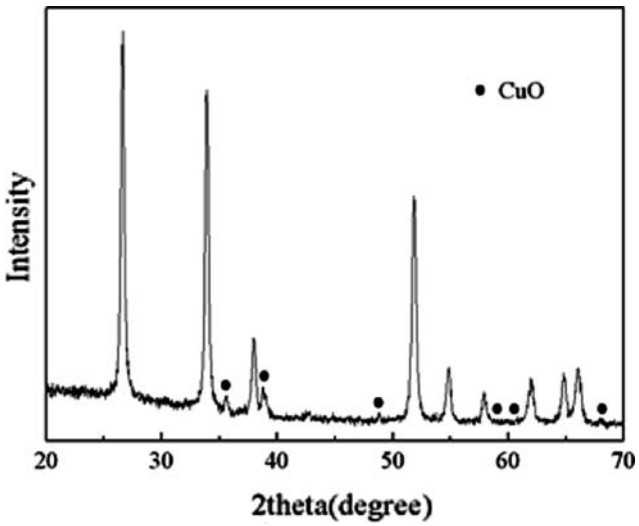

Fig. 2 XRD pattern of CuO-doped SnO_2 hollow spheres

and aggregated after the calcination. The same conclusion can also be found in Fig. 2 which shows that SnO_2 peaks become more narrowed after the calcination.

XPS was performed to illuminate the surface composition of the as-prepared CuO-doped SnO_2 hollow spheres, and the results are shown in Fig. 4. It can be seen that Sn 3d (Fig. 3a) and Cu 2p (Fig. 3b) spectra show the peaks' positions at binding energies of 486.9 and 936.5 eV, which nearly correspond to pure SnO_2 and CuO, respectively [21]. It indicates that $Cu(NO_3)_2$ has been successfully converted into CuO by calcination at 500 °C for 8 h in air.

Sensing characteristics of CuO-doped SnO_2 hollow spheres sensor

Figure 5 shows the sensitivities of CuO-doped SnO_2 hollow spheres sensor to 10 ppm H_2S. At a relatively low temperature of 18 °C, the sensitivity of the sensor can reach as high as 160,000. It can be seen that the optimum operation working temperature is at about 35 °C, and the corresponding sensitivity is the highest (5,600,000). Then sensitivity decreases with the increase in working temperature. Compared with the high working temperature of some other H_2S sensing materials from literature [1–9], it is obvious that an extremely high sensitivity at a much lower temperature (35 °C) has been achieved in this work. Detecting H_2S with high sensitivity at such low temperature is useful for chemical industries and research laboratories.

Figure 6 shows the real-time response curves of the CuO-doped SnO_2 hollow spheres sensor exposed to 10 ppm H_2S at different working temperatures. It is obvious that

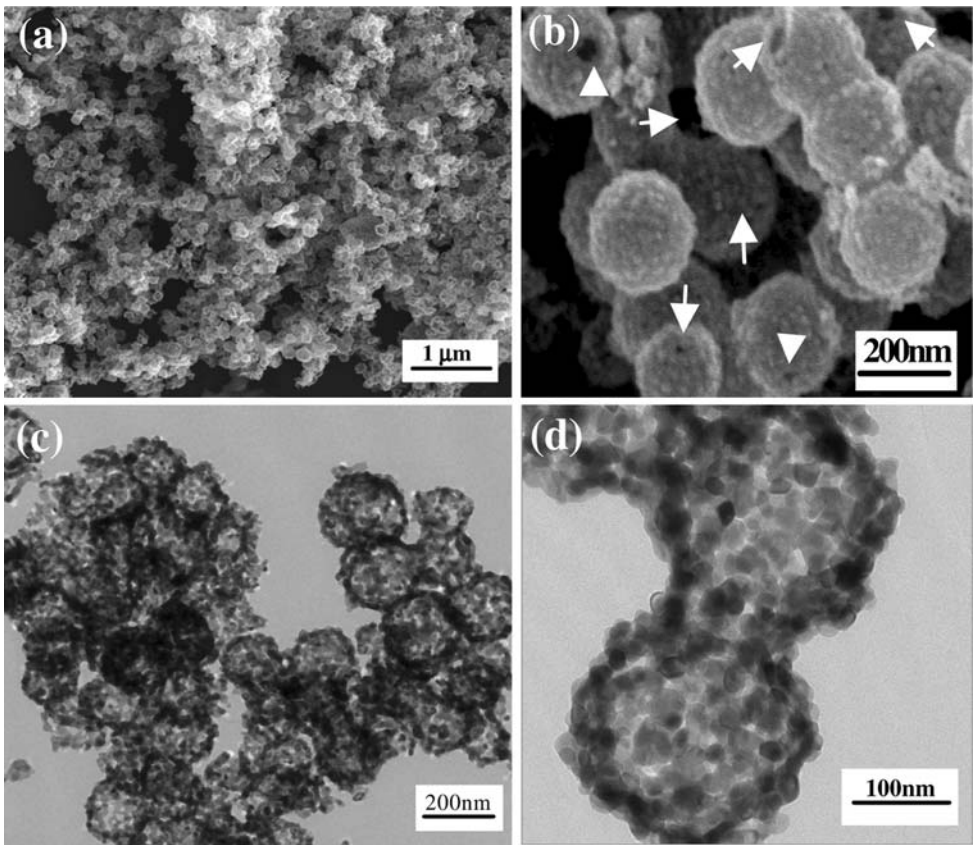

Fig. 3 SEM images of CuO-doped SnO_2 hollow spheres, (**a**) and (**b**). TEM images of CuO-doped SnO_2 hollow spheres, (**c**) and (**d**)

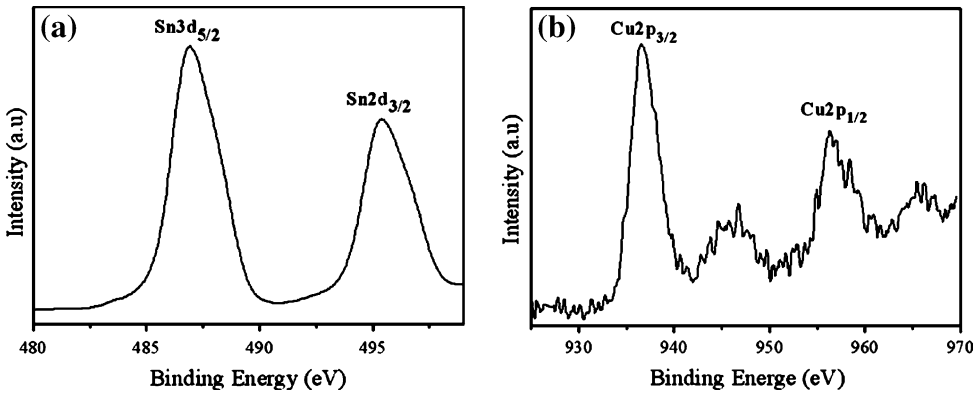

Fig. 4 **a** Sn 3d XPS spectra and **b** Cu 2p XPS spectra of CuO-doped SnO_2 hollow spheres

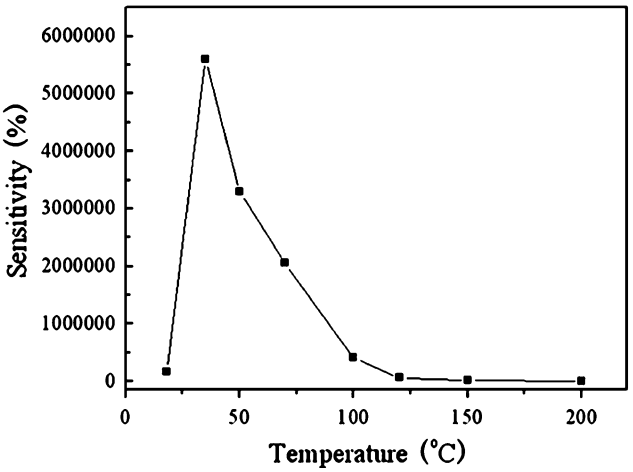

Fig. 5 The sensitivities of CuO-doped SnO_2 hollow spheres sensor to 10 ppm H_2S at various temperatures

CuO-doped SnO_2 hollow spheres sensor shows switch-like response to H_2S gas. The response time at the working temperature of 18 °C was about 5 min, and it decreased with the increase in working temperature. When the working temperature reached 35 °C, the response time was reduced to 90 s. On the other hand, the recovery time on removal of H_2S is always slow (about several tens of minutes at room temperature) but can be improved with increasing temperature.

Figure 7 is the histogram showing sensor responses of CuO-doped SnO_2 hollow spheres sensor to different concentrations of H_2S at a working temperature of 35 °C. It can be seen that the sensor showed a sensitivity of 150 to 10 ppb H_2S gas, which indicates that the lowest acceptable ambient level for H_2S (recommended by the Scientific Advisory Board on Toxic Air Pollutants, USA) can indeed be detected by CuO-doped SnO_2 hollow spheres sensor.

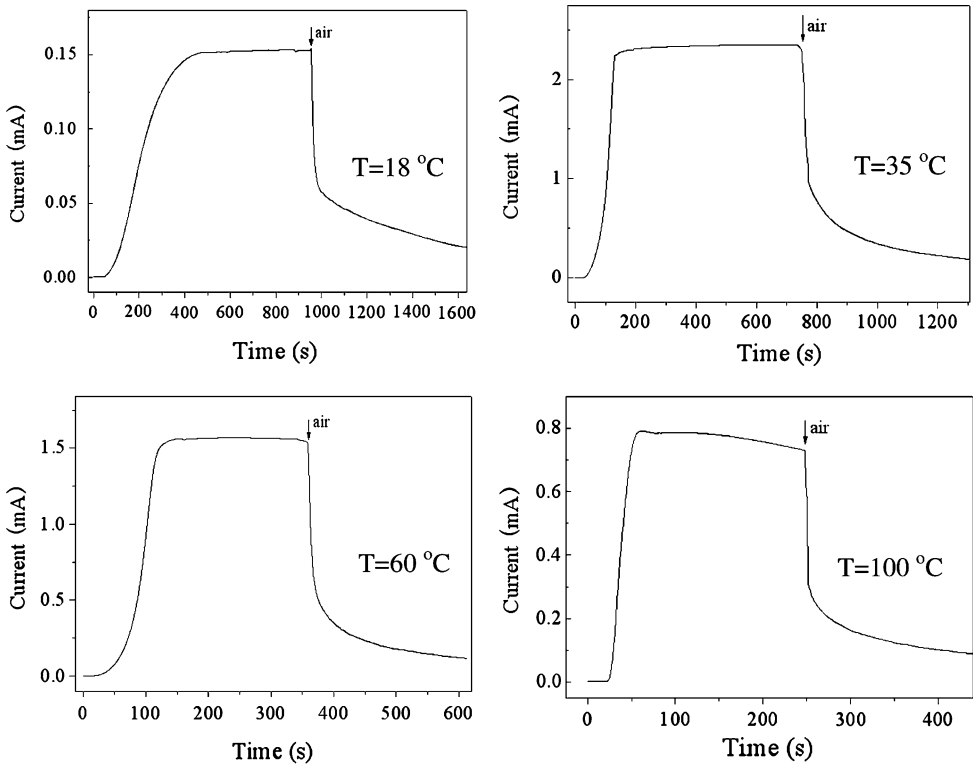

Fig. 6 Real-time curves of CuO-doped SnO_2 hollow spheres sensor upon exposure to 10 ppm H_2S at 18, 35, 60, and 100 °C

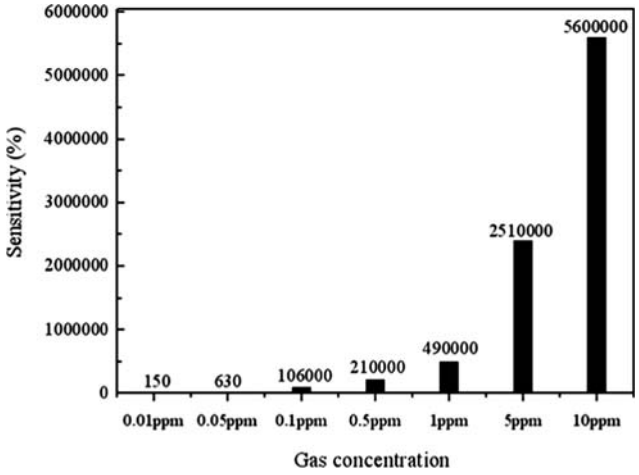

Fig. 7 Gas sensitivity of CuO-doped SnO_2 hollow spheres sensor to different concentrations of H_2S at a working temperature of 35 °C

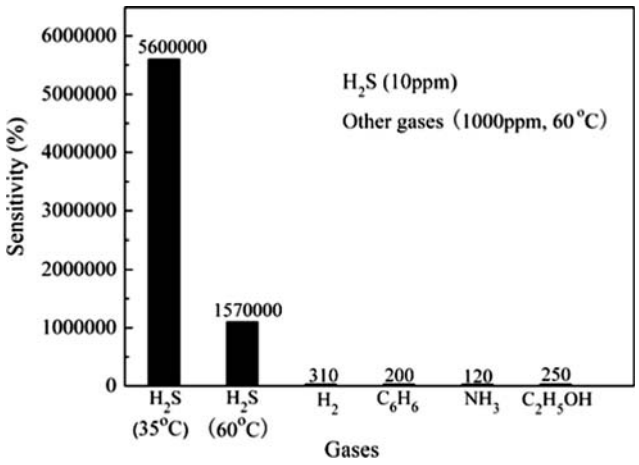

Fig. 8 Selectivity for H_2S gas from gas mixtures

Selectivity is another important parameter of a gas sensor. Sensors for application must have rather high selectivity. SnO_2 hollow spheres sensors were reported to show responses to many gases, including ethanol, H_2S, NH_3, etc. [16]. However, CuO-doped SnO_2 hollow spheres sensor has high selectivity to H_2S. Figure 8 depicts the selectivity of CuO-doped SnO_2 hollow spheres sensor to H_2S (10 ppm) at a working temperature of 35 °C and 60 °C. The sensor showed high selectivity for H_2S and could distinguish a small amount of (10 ppm) H_2S among 1000 ppm of the following gases: ethanol, NH_3, C_6H_6.

Detailed comparison of gas-sensing performances between CuO-doped SnO_2 hollow spheres sensor and undoped SnO_2 hollow spheres sensor to H_2S is illustrated in Table 1. It can be seen that the response times of CuO-doped SnO_2 hollow spheres to 10 ppm H_2S are shorter than SnO_2 hollow spheres. Note that the sensitivities of the two sensors show remarkable differences. It is obvious that

Table 1 Comparison of sensing performances between CuO-doped SnO_2 hollow spheres and undoped SnO_2 hollow spheres to 10 ppm H_2S at various working temperatures

Temperature (°C)	CuO-doped SnO_2 hollow spheres		SnO_2 hollow spheres	
	Response times (s)	Sensitivity (%)	Response times (s)	Sensitivity (%)
20	300	160000	600	6000
35	100	5.6×10^6	300	19800
120	40	63000	120	2700

CuO-doped SnO_2 hollow spheres are more sensitive to H_2S compared with the undoped SnO_2 hollow spheres. CuO can improve the sensing properties of SnO_2 hollow spheres to H_2S.

Sensing mechanism of CuO-doped SnO_2 hollow spheres

The mechanism to explain the large decrease in resistance of SnO_2–CuO thin films on exposure to H_2S gas was suggested earlier in the literature [22, 23]. On the thin film surface, p–n junctions may form between CuO and SnO_2 which are p-type and n-type semiconductors, respectively. The existence of p–n junctions causes high resistance because of their strong electronic interaction. When SnO_2–CuO thin film was exposed to H_2S gas, it was proposed that the following reaction happened:

$$CuO + H_2S \rightarrow CuS + H_2O.$$

CuO was converted to metallic CuS, and the p–n junctions were destroyed [22]. When the film sensor was removed to air, CuS can be oxidized by the oxygen reversibly and become CuO, and therefore the p–n heterojunction was recovered. The conversion of CuS to CuO is slow at low temperature, and the rate of oxidation increases with the increase in temperature. This is the reason why the recovery rate can be improved by increasing the temperature. The crystal structure of CuS is changeable at 103 °C, and when the temperature is higher than 220 °C, CuS becomes Cu_2S [24], an ionic conductor with higher resistivity. Therefore, the sensitivity of SnO_2–CuO film sensors decreases with increasing temperature.

Table 2 gives the comparison of sizes, working temperatures, and sensitivities between the H_2S sensors reported before and in this work. It can be seen that the hollow sphere nanostructured materials show high sensitivity to H_2S and can lower the working temperature. Compared with the other H_2S sensors reported so far, an extremely high sensitivity at the lowest temperature is achieved in this work.

Table 2 H_2S sensors based on SnO_2–CuO p–n junction materials reported before and in this work

Sensor materials	Size	Concentration (ppm)	Temperature (°C)	Sensitivity	References
Thick film	12 cm	100	200	7.5×10^5	[25]
Thin film	320 nm	150	140	6.5×10^6	[5]
Nanoparticles	90 nm	20	150	7.3×10^5	[26]
Nanoribbons	0.1×100 μm	3	50	2×10^4	[11]
Nanorods	10×100 nm	10	60	9.4×10^6	[12]
Hollow sphere	25 nm	10	35	5.6×10^6	This work

As mentioned above, the p–n junctions between CuO nanoparticles and SnO_2 nanoparticles play a key role for the detection of H_2S gas. In our case, the extremely high sensitivity obtained at such low temperature is probably attributed to some additional factors. It is shown that the as-prepared porous SnO_2 hollow spheres with robust surface are composed of numerous small SnO_2 nanoparticles. Even after the calcination, the SnO_2 particles are very small (about 25 nm). Compared with the bulk SnO_2 particles [5–10, 25], this special structure would enable the hollow spheres to load with CuO particles more evenly and easily. Therefore, there would be more chance to form efficient p–n junctions between CuO nanoparticles and SnO_2 nanoparticles. On the other hand, much research has proved that gas sensor with porous structures could contribute to the improved sensing performances because of enhanced active surface area and efficient gas diffusion induced by this unique structure [3, 15–18, 20, 27–30]. In our case, porous hollow sphere nanostructures are found to exist in CuO-doped SnO_2 hollow spheres. Therefore, there may be more p–n junctions that can react with H_2S gas molecules. So it is understandable that the sensitivity of CuO-doped SnO_2 hollow spheres sensor may be as high as 5.6×10^6 against 10 ppm H_2S at low working temperature. Our results imply that materials with hollow sphere nanostructures are promising candidates for high-performance gas sensors.

Conclusion

In summary, highly sensitive and selective CuO-doped SnO_2 hollow spheres sensor for H_2S detection has been developed. Compared with undoped SnO_2 hollow spheres sensor, the CuO-doped SnO_2 hollow spheres sensor is more sensitive and selective to H_2S. The sensitivity of the sensor against 10 ppm H_2S at 35 °C is up to 5.6×10^6. It is useful to detect H_2S with high sensitivity at such low temperature. A low detection limit of 10 ppb H_2S has been obtained with the sensor at the temperature of 35 °C. The good sensing performance is probably attributed to two factors. Firstly, using SnO_2 hollow spheres increases the chance of formation of p–n junctions between CuO nanoparticles and SnO_2 nanoparticles. Secondly, the existence of porous structure in the sensing materials improved the active surface area and the diffusion of gas molecules, therefore enhancing the sensing performance.

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