**Ultra-sensitive room-temperature H2S sensor using Ag-In2O3 nanorod composites**

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**Abstract**

Ultra-sensitive H2S sensors operated at room temperature were fabricated using Ag-In2O3 nanorod composites synthesized using sol-hydrothermal method followed by NaBH4 reduction process. TEM proved that the In2O3 was nanorod structures of ~110 nm in length and ~35 nm in diameter. Ag nanoparticles with diameters from 10 to 15 nm homogeneously decorated on the surfaces of the In2O3 naonorods. XRD and XPS analysis proved that the Ag elements are existed as zero-valent metallic silver on the surface of the In2O3 nanorods. Ag nanoparticles could enhance the formation of chemisorbed oxygen species and interactions between H2S molecules and oxygen species due to spill-over effect, and the electron transfer between Ag and In2O3 nanorods also enhanced the sensing properties. Therefore, the H2S sensors based on the Ag-In2O3 nanorod composites showed significantly improved sensing performance than those based on the pure In2O3 nanorods. The optimized content of Ag nanoparticles is 13.6 wt%. Operated at room temperature, the H2S sensors made of 13.6 wt% Ag-In2O3 nanorod composites exhibited an ultra-highly response of 93719 to 20 ppm H2S and a superior detection limit of 0.005 ppm. The sensor also showed good reversibility, good selectivity, excellent reproducibility and stability for detection of H2S gas.

*Keywords:* In2O3, Ag, Nanorods, Composite, H2S, Gas sensors

**1 Introduction**

Hydrogen sulfide (H2S) is widely used as a raw chemical material in many industrial processes, and it is also commonly released from natural gases or biodegradation of organic matters. However, it is one of the most dangerous and toxic gases, which can significantly affect human health, even with extremely low concentrations. Therefore, developing a highly sensitive H2S sensor is of great importance [1]. Metal oxide semiconductors materials are often reported as promising candidates of sensing materials for H2S sensors, and these include SnO2 [2,3], ZnO [4], Fe2O3[5,6], TiO2 [7], CuO [8] and In2O3 [9]. However, many reported H2S gas sensors only show good sensitivities at a higher working temperature [2−9], and at room temperature, most these H2S sensors often show low responses. Another common problem for many reported H2S gas sensors is the difficulty to quickly recover to their initial state after finishing the H2S detection process. Incomplete recovery often occurs, and a long recovery time or even irreversibility of sensing performance are commonly existed. A room temperature H2S gas sensor with a high response and an excellent reversibility is urgently required.

Among many different types of metal oxides, In2O3 has been reported to have good sensing performance to many hazardous gases [10,11]. In particular, because of its high response to H2S, the In2O3 based H2S sensors have been attracted much attention in recent years. Various nanostructures of In2O3 have been synthesized to detect H2S gas, such as nanoparticles [12], nanowhiskers [13], nanobelt [14], nanotubes [15], nanofiber [16,17], and nano-films [18], etc. However, we needs to point out that the response and reversibility of all the above mentioned nanostructures of In2O3 to H2S at room temperature are still far from satisfied. Nanorods of In2O3 with their large ratios of surface area-to-volume are a promising gas sensing material, which have been used to detect formaldehyde [10], NO2 [11], ethanol [19, 20] and acetone [21] at high working temperature above 100 ℃, but its H2S gas sensing properties at room temperature have not been explored extensively so far. In2O3 nanorods have been prepared using magnetron sputtering [19], template [10], sol-gel [22], electrochemical deposition [23], evaporation deposition [24], and hydrothermal method [20]. Among these, the hydrothermal method is facile and effective. However, surfactant or urea is generally needed to prepare In2O3 nanorods [11, 20, 21]. In this paper, the In2O3 nanorods were synthesized in aqueous alkali using sol-hydrothermal method without urea or surfactant.

Due to their effectiveness in improving chemical sensitization and electronic sensitization, noble metals have often been used for surface modification of sensing materials in gas sensing applications. These noble materials include Pt [25,26], Au [27,28] and Ag [29-35]. Among them, Ag is an excellent and active catalyst. If the Ag nanoparticles can be decorated onto nanostructured In2O3 surfaces, fast chemical adsorption of oxygen molecules can be obtained to produce lots of oxygen species on the surface on the surface of sensing materials due to spill-over effect. The interaction between chemisorbed oxygen and target gas molecules such as H2S can be significantly enhanced, thus resulting in a significantly improved sensing performance. However, as far as we have searched in the literature, there was no previous reports for the room-temperature operated H2S gas sensor using Ag-In2O3 composite nanostructures.

Therefore, in this paper, we will aim to explore H2S gas sensing performance of a new types of nanocomposite, i.e., Ag nanoparticle decorated In2O3 nanorods. In2O3 nanorods were synthesized using sol-hydrothermal method without surfactant and their surface were further decorated with Ag nanoparticles through NaBH4 reduction process. H2S sensors operated at room temperature were fabricated using these Ag nanoparticles/In2O3 nanorods composites. At room temperature, the sensor exhibited an excellent reversibility, ultra-highly responses and a superior detection limit to H2S gas. The enhanced gas sensing mechanisms using this nanocomposites design were systematically investigated.

**2 Experimental**

**2.1 Preparation of In2O3 nanorods**

In2O3 nanorods were prepared using sol-hydrothermal and calcination process. Firstly, 20 ml of NaOH aqueous solution (0.75 mol/L) was added into 20 ml of InCl3ˑ4H2O ethanol solution (0.075 mol/L) under a vigorous stirring. Then, this mixed solution was stirred for another hour to form a sol, which was transferred into a 50 ml Teflon-lined autoclave. The solution was kept at 180 oC in an oven for hydrothermal reactions for 12 hrs. After that, the white precipitates from the autoclave were washed by a mixture of deionized water and ethanol for three times using centrifuge and dried at 80 oC for 6 hrs to obtain white In(OH)3 powers. Finally, the white In(OH)3 powers were further calcined at 500 oC in air for 2 hrs to obtained yellow In2O3 powders.

**2.2 Decoration of Ag nanoparticles on In2O3 nanorods**

An aqueous solution of 1 ml citric acid (with a concentration of 0.02 mol/L) were mixed with an aqueous solution of 100 ml AgNO3 with a concentration of 0.2 mmol/L. In2O3 powders of 40 mg were added into the above mixed solution and stirred for 30 min. Then, 3 ml NaBH4 with a concentration of 7 mmol/L was added into the above liquid drop-by-drop within 10 min under an ultra-sonication process and maintained for 2 hrs. Finally, the black suspension liquid was centrifuged and then washed by a mixture of deionized water and ethanol for three times and dried at 60 oC for 6 hrs to obtain the composites.

**2.3 Characterization**

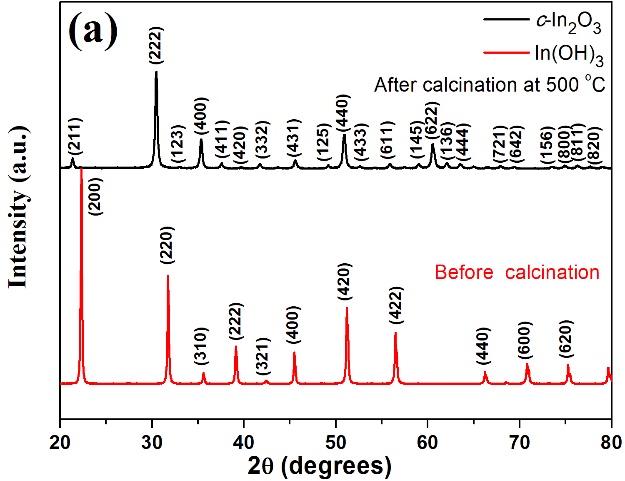
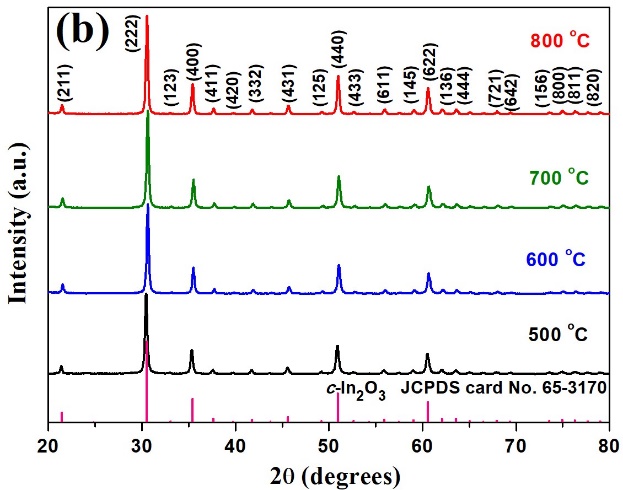
Microstructures of the Ag-In2O3 nanorod composites were characterized using a transmission electron microscope (TEM, JEM-2100F, 200 kV), attached with an energy dispersive X-ray (EDX) analyzer. The powder X-ray diffraction (XRD, D/MAX-2500, Cu Kα radiation, Dandong Co.) was employed to analyze the crystalline structures of the samples. The Brunauer-Emmett-Teller (BET) surface areas of samples were estimated using a N2 physisorption testing method (JW-BK122W, JWGB SCI. TECH.). X-ray photoelectron spectroscope (XPS, Kratos Axis-Ultra DLD apparatus, Al Kα radiation) was used to analyze chemical states and element composition. The concentrations of Ag element in the samples were measured using Inductive Coupled Plasma (ICP) Emission Spectrometer of AtomScan 16 (ICP, TJA, USA).

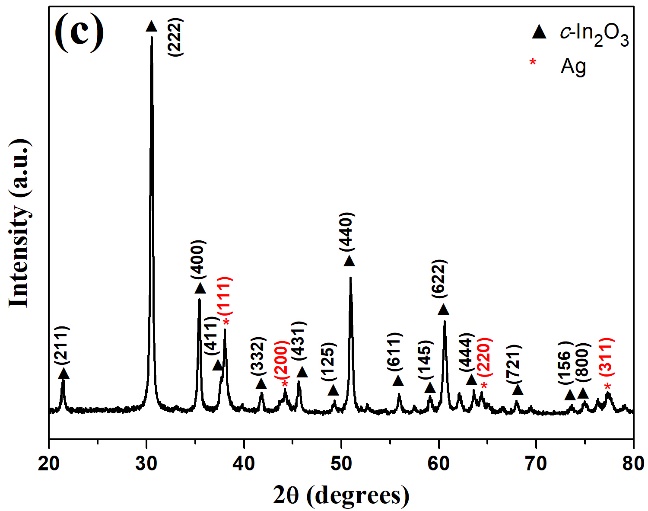
**2.4 Sensor fabrication and measurement**

An aluminum oxide ceramic tube (with a length of 4 mm and a diameter of 1 mm) was used as the substrate of the sensor. Two gold electrodes were made on its surface at both ends, which were connected using Pt wires (with the sensor’s photo shown in the sensor’s photo in Fig. S1 in the Supplementary Material). The sensing materials of In2O3 or Ag-In2O3 nanoconposites were uniformly dispersed in alcohol ultrasonically for 5 minutes. Then a thick film was dip-coated onto the ceramic tube to form a thick film. The ceramic tube with the film of sensing materials was then dried at 100 oC for 1 hr to remove the alcohol. The Pt wires on the ceramic tube were connected to a Keithley 2400 digital source-meter in order to measure the electrical resistance of the sensing film between the two gold electrodes. To precisely control the working temperature, a Ni–Cr alloy resistive heater was placed inside the ceramic tube to heat the film of sensing materials. The gas response of the sensors (R) is defined as Ra/Rg, where Ra is the baseline electrical resistance in air, and Rg is the electrical resistance in the target gas of H2S, respectively. The relative humidity in the testing process is 30%.

**3 Results and discussion**

**3.1 Microstructure analysis of samples**

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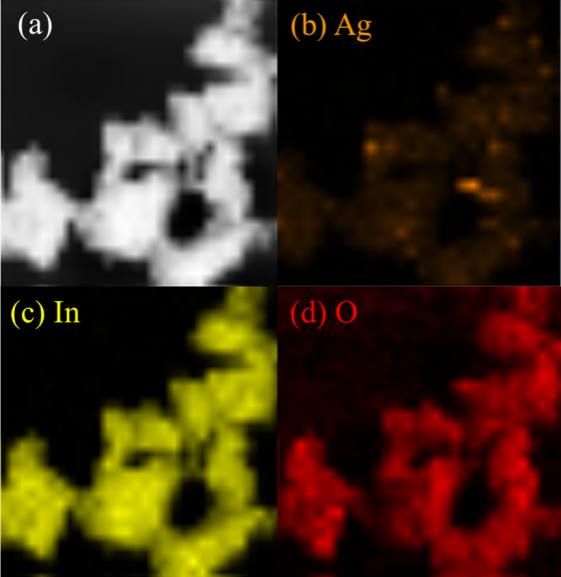
**Figure** **1** XRD patterns of **a** samples before and after calcination at 500 oC for 2 hrs, **b** In2O3 after calcination at different temperatures for 2 hrs, **c** 13.6 wt% Ag-In2O3 nanorod composites.

The XRD patterns of the samples obtained from the hydrothermal process before and after calcination are shown in Fig. 1a. It can be seen that the product after the hydrothermal reaction is crystalline In(OH)3 (JCPDScard No. 16-0161). After it has been calcinated at 500 oC for 2 hrs, the XRD diffraction peaks shown in Fig. 1a are corresponding to the crystal planes of cubic In2O3 crystallites (JCPDS card No. 65-3170). There are no other phases observed, meaning that the In(OH)3 have completely transformed into In2O3 crystallites after calcination. To investigate the effect of calcination to the crystallinity of In2O3, the In2O3 have been calcinated at 600 oC, 700 oC and 800 oC for 2 hrs respectively, and the corresponding XRD patterns are shown in Fig. 1b. As the calcination temperature rises, the increase of intensity of all XRD diffraction peaks is very small, meaning that the crystallinity of In2O3 is stable at the calcining temperature from 500 oC to 800 oC. After the Ag nanoparticles were decorated onto the nanorods, some extra-diffraction peaks at 38.1o, 44.3o, 64.4o and 77.5o appear in the XRD pattern of the Ag-In2O3 nanorod composites (see Fig. 1c), which are corresponding to those of (111), (200), (220) and (311) of the metallic Ag (JCPDS card No. 04-0783), indicating that the Ag elements are existed as metallic silver with zero valence.



**Figure** 2 **a** TEM and **b** HR-TEM image of 13.6 wt% Ag-decorated In2O3 nanorods.

Fig. 2 presents TEM and HR-TEM images of Ag-In2O3 nanorod composites. The In2O3 shows nanorods of ~110 nm in length and ~35 nm in diameter. Surfaces of the In2O3 naonorods are decorated by many Ag nanoparticles, whose diameters are ranged between 10 and 15 nm. Fig. 2b shows a typical HR-TEM image of Ag-In2O3 nanorod composites. The aligned interplanar spacing of 0.293 nm is in a good agreement with the (222) lattice planes of In2O3, and the interplanar spacing of 0.236 nm of the nanoparticle is corresponding to the (111) lattice plane of sliver. EDX pattern (shown in Fig. S2 in the Supplementary Material) also proves that there are Ag elements in the sample. Modification of the In2O3 nanorods by Ag nanoparticles can decrease the contact potential barriers of Ag and In2O3 and thus facilitate the efficient electronic transport between noble metal Ag nanoparticles and In2O3.

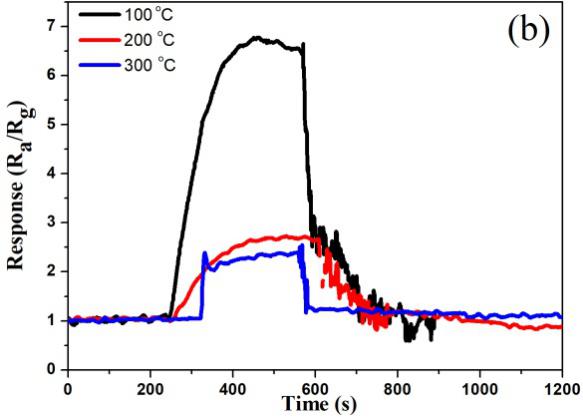
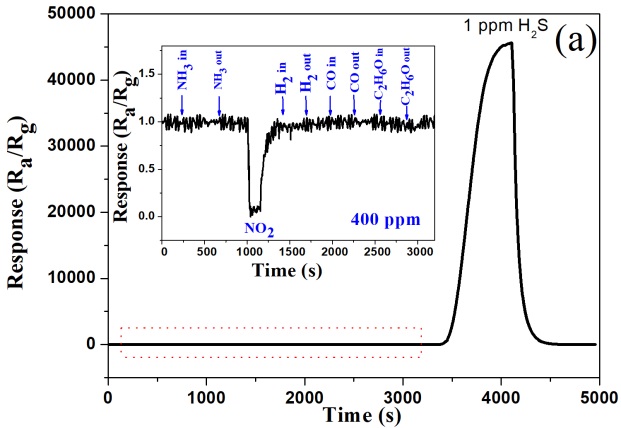
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**Figure** **3** EDX elemental color mapping images of 13.6 wt% Ag-In2O3 nanorod composites. **a** TEM, **b** Ag, **c** In, **d** O.

In order to further investigate the spatial distributions of Ag, In and O elements in the Ag-In2O3 nanorod composites, EDX color mapping analysis was conducted and the images are presented in Fig. 3. The elemental mapping revealed the Ag, In and O elements are homogeneously distributed in the Ag-In2O3 nanorod composites, which confirm that the Ag nanoparticles are homogeneously decorated on the surfaces of In2O3 nanorods. ICP analysis also confirmed the presence of Ag elements in the Ag-In2O3 nanorods composites and the measured Ag weight percentage is 13.6 wt%. The specific surface areas of the pure In2O3 nanorods and Ag-In2O3 nanorod composites are 9.8 and 19.1 m2/g, respectively based on the BET nitrogen adsorption/desorption analysis. The addition of Ag nanoparticles onto the In2O3 nanorods apparently increases the surface areas of the samples, which are surely beneficial for the increase of the response of H2S gas sensing [2].

**3.2 Gas sensing properties**

The sensors made of Ag-In2O3 nanorod composites operated at different operation temperatures from 25 oC to 300 oC (as shown in I-V characteristic curves in Fig. S3 in the Supplementary Material) all show good linear behaviors, indicating a good ohmic contact of Ag-In2O3 nanorod composites with the Au electrodes. Furthermore, the measured electrical resistance is 52.6 MΩ at the room temperature of 25 oC and it decreases with the increase of temperature, a characteristic of the standard semiconductor materials.

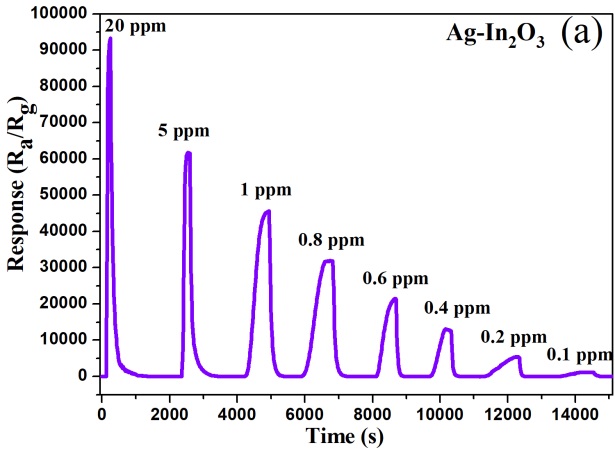
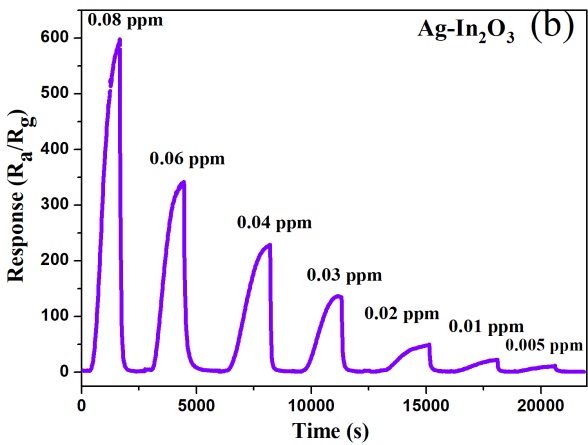


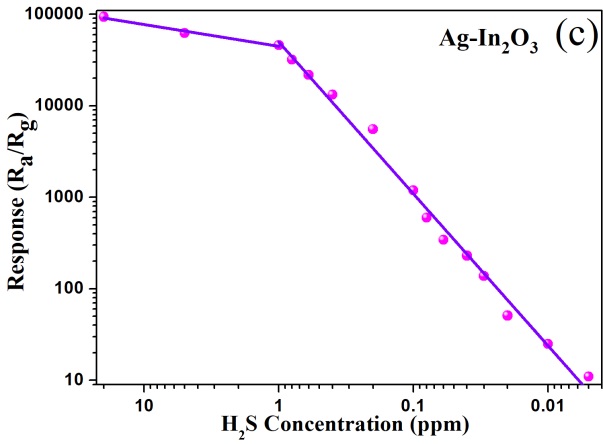
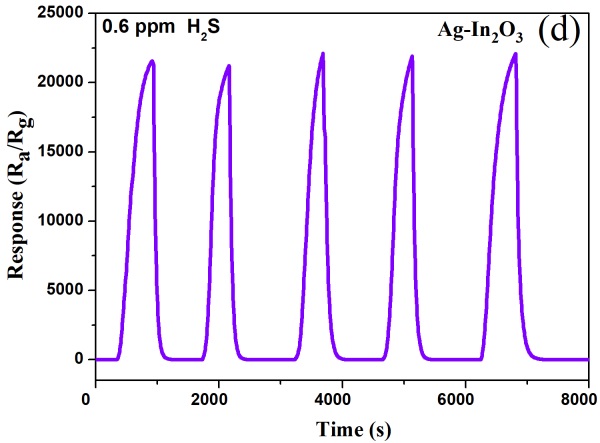
**Figure 4** **a** Response of the sensors based on 13.6 wt% Ag-In2O3 nanorod composites for 1 ppm H2S and other gases of 400 ppm (NH3, H2, CO, NO2, alcohol) at room temperature of 25 oC, **b** Response of the sensors for 1 ppm H2S at different working temperatures from 100 oC to 300 oC.

To investigate sensing selectivity of the sensors, the response of the sensors based on Ag-In2O3 nanorod composites to 1 ppm H2S and other gases of 400 ppm (NH3, H2, CO, NO2 and alcohol) at room temperature of 25 oC were obtained and the results are shown in Fig. 4a. It can be seen that the sensors have an ultra-high response value of 45627 to 1 ppm H2S. Results also showed that the responses of the sensors to other gases of 400 ppm are negligible, such as NH3, H2, CO and alcohol. Only for 400 ppm NO2 gas, there was an obviously response. Because the NO2 is an oxidizing gas, the electrical resistance of the sensor based on the n-type sensing material of Ag-In2O3 nanorod composites has been increased after injecting of the NO2 gas. However, the response value of the sensor to NO2 gas of 400 ppm is only 0.06, which is far lower than that of H2S of 1 ppm (i.e., 45627). Therefore, the above results clearly indicate that the sensors based on Ag-In2O3 nanorod composites have a very good selectivity towards H2S compared with the other gases.

To investigate the effect of working temperature on responses of the sensors to H2S, the sensor was tested at different working temperatures. Fig. 4b shows the responses of the sensors based on Ag-In2O3 nanorod composites to 1 ppm H2S with testing temperatures from 100 oC to 300 oC. Compared to the response value of the sensors of 45627 at room temperature of 25 oC, those response values obtained at working temperatures of 100 oC, 200 oC and 300 oC are 6.8, 2.7, and 2.3, respectively. Clearly, the responses of the sensors based on Ag-In2O3 nanorod composites decrease significantly with the increase of working temperature. The largest H2S sensing response was obtained at room temperature.

Figs. 5a and 5b show the dynamic response/recovery curves of the sensors based on Ag-In2O3 nanorod composites to H2S gas with different concentrations from 20 ppm to 0.005 ppm measured at room temperature. The sensors have a steady baseline of electric resistance in air at room temperature. When the H2S gas was injected into the testing chamber, the electric resistance of sensors was decreased instantly. After the H2S was released, the electric resistance of sensors was quickly recovered to its original baseline before the injection. This means that the sensors have a good reversibility for the H2S gas sensing at room temperature. Furthermore, it was found that the sensors have ultra-high changes of electric resistance values before and after their exposures to the H2S gas.

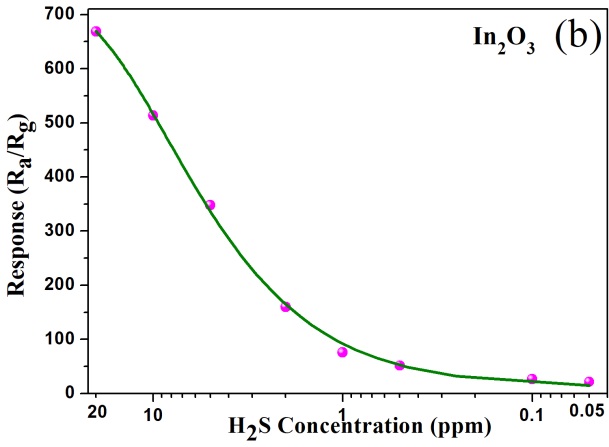
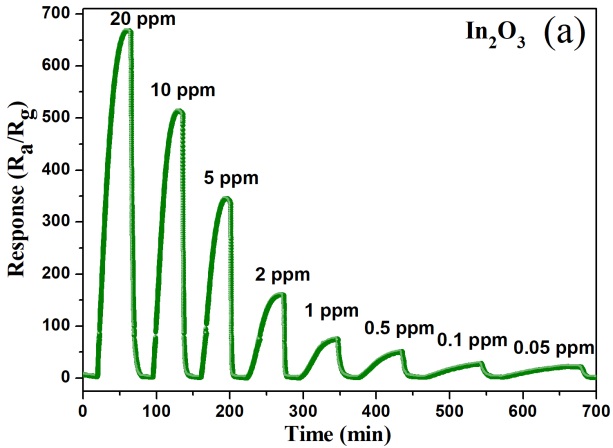
 

**Figure 5** Response/recovery curves of the sensors based on 13.6 wt% Ag-In2O3 nanorod composites to H2S gas with different concentrations at room temperature **a** from 20 ppm to 0.100 ppm and **b** from 0.080 ppm to 0.005 ppm, **c** The response values of the sensors to different concentrations of H2S gas, **d** The response/recovery curves by successively testing the sensors to 0.600 ppm of H2S gas for five times.

Fig. 5c shows the corresponding response values of the sensors to different concentrations of H2S gas. The response value is 93719 to 20 ppm of H2S. When exposed to sub-ppm concentration of H2S, it still has a high response value. For example, for 0.005 ppm of the H2S gas, the sensor exhibited a high response value of 11, meaning that the sensor has a superior detection limit in detecting the H2S, and the response values of the sensor are dependent on the H2S concentration. The response values of the sensor are linearly increased with the increase of H2S concentration, meaning that the responses have good linearity characteristics with the H2S concentration (R2= 0.9675). However, with the concentrations of H2S above 1 ppm, the rate of increase of response values becomes smaller, which is mainly because the adsorption of H2S on the surface of Ag-In2O3 nanorod composites tends to be gradually saturated.

To investigate the reproducibility of the H2S sensors based on Ag-In2O3 nanorod composites, the sensor was successively tested in 0.600 ppm of H2S gas for five times and the response/recovery curves are shown in Fig. 5d. For these five tests, the response/recovery curves are reproducible with the successive injection and releasing of the H2S gas. When the sensor was exposed to 0.600 ppm of H2S gas, the response signals were increased to the highest values with almost the same response value of 21689, and after the H2S gas was replaced by the air, the curves were all returned to the baseline, indicating a good reproducibility.

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**Figure** **6** **a** Response/recovery curves and **b** the response values of the sensors based on pure In2O3 nanorods to H2S gas with different concentrations from 20 ppm to 0.05 ppm at room temperature.

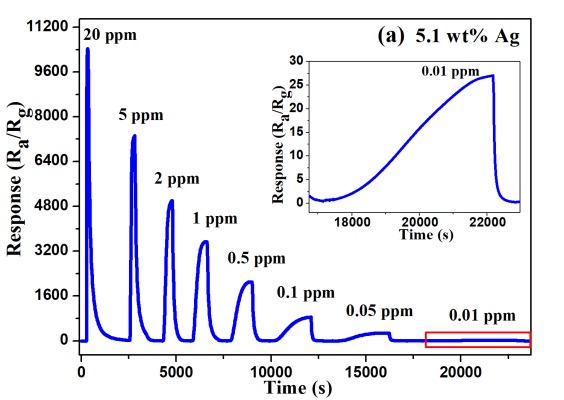
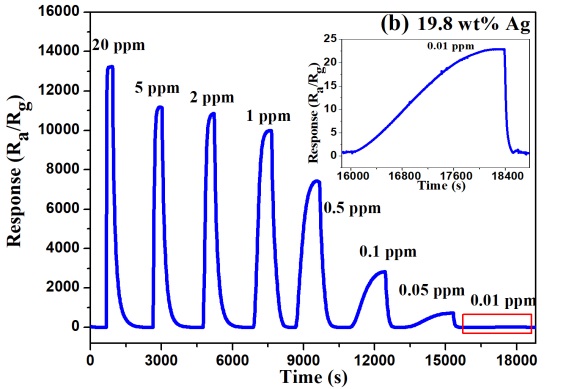
As a comparison to the sensor based on Ag-In2O3 nanorod composites, the H2S sensing properties of the sensors made of pure In2O3 nanorod have also been studied. Fig. 6a shows the dynamic response/recovery curves of the sensors based on pure In2O3 nanorods to H2S gas with different concentrations at room temperature, and the corresponding response values of the sensors to different concentrations of H2S gas are shown in Fig. 6b. Similar to those of the Ag-In2O3 nanorod composites, the responses of sensors based on pure In2O3 nanorods increase with the increase of H2S concentration. However, it was found that the response values of the pure In2O3 nanorods based sensors are far lower than these based on the Ag-In2O3 nanorod composites. For example, the response value of the pure In2O3 nanorods based sensors was 668.4 to 20 ppm H2S, whereas it was 93719 for the sensor based on the Ag-In2O3 nanorod composites. The detection limit of the pure In2O3 nanorods based sensors is 0.050 ppm, which is much higher than that of 0.005 ppm of the Ag-In2O3 nanorod composites based sensors. Obviously, a significant improvement of the H2S response (approximately 140 times of increase) and a decrease of H2S detection limit were obtained by decorating the surface of the In2O3 nanorods with Ag nanoparticles.

The response and recovery times were calculated based on the times for the sensor to achieve 90% of the resistance changes in the processes of response and recovery, respectively. All the response time and the recovery time of the Ag-In2O3 nanorod composites based sensors to H2S gas with different concentrations at room temperature are apparently shorter than those of the pure In2O3 nanorods based sensors (as shown in the histogram of the response/recovery times of the sensors in Fig. S4 in the Supplementary Material). For example, the response/recovery times to 20 ppm of H2S for the Ag-In2O3 nanorod composites based sensors are 84s/186s at room temperature, whereas those are 1512 s/318 s for the pure In2O3 nanorods based sensors.

Table 1. Summary of sensing properties of various H2S sensors made of various metal oxides operated at room-temperature

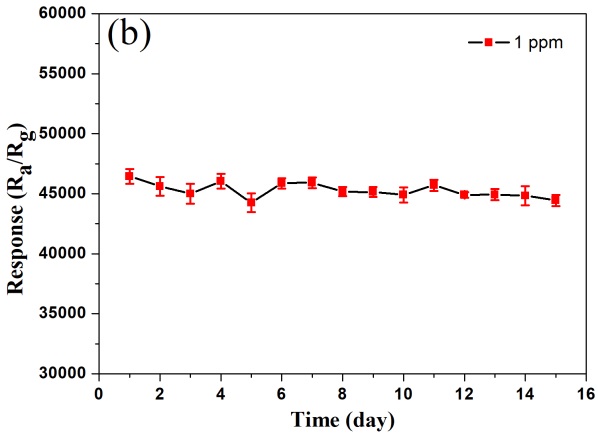
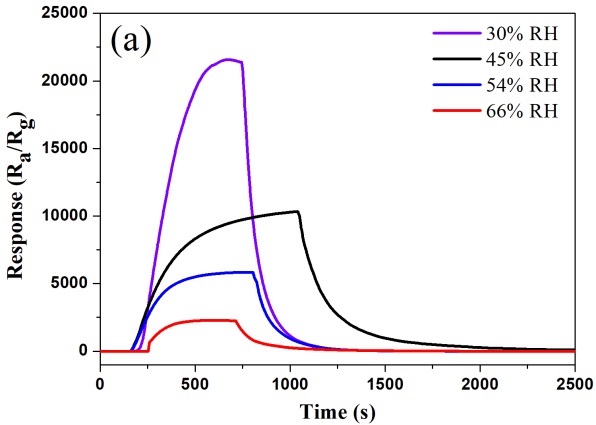
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| --- | --- | --- | --- | --- | --- |
| Material | Structures | Response (concentration) | Response  /recovery time (s) | Detection limit (ppm) | Ref. |
| In2O3 | Nanotubes | 167 (20 ppm) | 250/500 | 1 | [36] |
| In2O3 | Nanowires | 1.4 (1 ppm) | 48/56 | 1 | [37] |
| In2O3 | Nanocrystals | 25 (1 ppm) | 1500/300 | 0.030 | [38] |
| PVA-In2O3 | Films | 1.9 (1 ppm) | 300/1860 | 0.500 | [39] |
| In2O3 | Toruloid nanotubes | 320.14 (50ppm) | 45/127 | 1 | [15] |
| CeO2 | Nanowires | 1.98 (100 ppm) | 100/260 | 0.050 | [40] |
| ZnO | Flower-like structures | 581 (5 ppm) | 500/6000 | 0.500 | [41] |
| ZnO | Comb-like | 4 (1 ppm) | 48/540 | 0.100 | [42] |
| ZnO | Nanobelt | 8 (10 ppm) | 2000/No recovery | 0.500 | [43] |
| ZnO | Quantum dots | 113.5 (50 ppm) | 16/820 | 10 | [44] |
| CuO | Porous nanosheets | 5.01 (0.2 ppm) | 336/543 | 0.010 | [45] |
| SnO2:NiO | Thin films | 440 (10 ppm) | 800/6000 | 0.100 | [46] |
| Sb-SnO2 | Nanoribbons | 1.6 (0.1 ppm) | 320/450 | 0.100 | [47] |
| α-Fe2O3 | Porous nanoparticles | 38.4 (100 ppm) | 100/3750 | 0.050 | [48] |
| Ag-In2O3 | Nanorods | 93719 (20 ppm) | 84/186 | 0.005 | This work |

As noble metal catalysts, the Ag nanoparticles accelerate the absorption of oxygen molecules and desorption of H2S molecules. Therefore, the Ag-In2O3 nanorod composites based sensors have much better sensing properties than the pure In2O3 nanorods based sensor. It can be concluded that the addition of Ag nanoparticles in In2O3 can remarkably increase the H2S sensing properties at room temperature. So far, there are many reports of the room-temperature H2S gas sensors based on various metal oxides, such as In2O3 [15,36-39], CeO2 [40], ZnO [41-44], CuO [45], SnO2 [46,47] and Fe2O3 [48], and most of them were all reported to detect sub-ppm H2S as listed in the Table 1. However, compared with the room-temperature H2S sensors based on Ag-In2O3 nanorod composites in this study, the responses of these H2S gas sensors values are much lower, and the detection limit was much higher than 0.005 ppm. Also the recovery times of those reported room-temperature H2S gas sensors in Table 1 were generally very long, sometimes there was incomplete recovery observed. Therefore, the room-temperature H2S sensors based on Ag-In2O3 nanorod composites in this study have obviously better sensing properties.

**Figure** **7** Room temperature response/recovery curves to different concentrations H2S gas of the sensors based on Ag-In2O3 nanorod composites with different Ag contents: **a** 5.1 wt% and **b** 19.8 wt%.

To investigate the effect of Ag contents on the sensing properties of H2S gas sensors, In2O3 nanorods decorated with two other Ag concentrations of 5.1 wt% and 19.8 wt% were also prepared and then were used to make the H2S sensor. Their room temperature response/recovery curves to different concentrations of H2S gas are shown in Fig. 7. It can be found that these Ag-In2O3 nanorod composites with different Ag contents all have higher responses than those based on the pure In2O3 nanorods, but they are obviously lower than that of the 13.6 wt% of Ag-In2O3 nanorod composites. Therefore, we can conclude that the optimized content of Ag nanoparticles in this study is around 13.6 wt%.



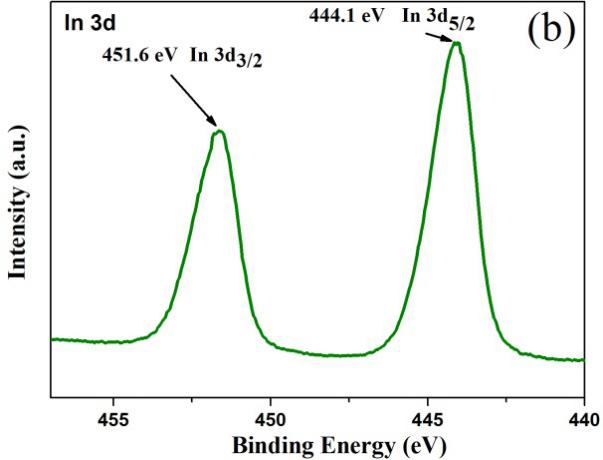
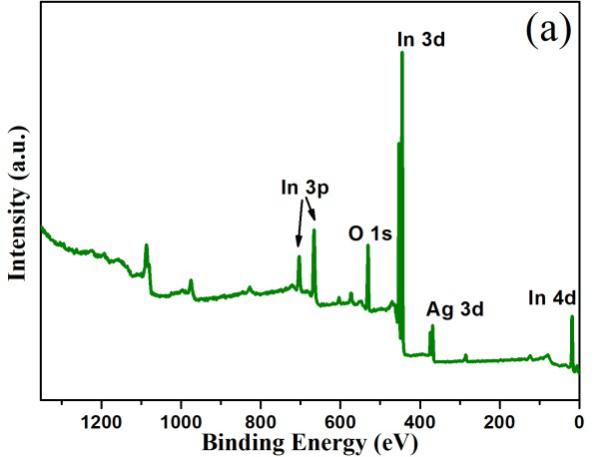
**Figure** **8** **a** Dynamic response/recovery curves of the sensor based on 13.6 wt% Ag-In2O3 nanorod composites to 0.6 ppm of H2S gas under different relative humidity at room temperature, **b** Stability of the sensor based on 13.6 wt% Ag-In2O3 nanorod composites to 1 ppm of H2S gas at room temperature and 30% RH for 15 days.

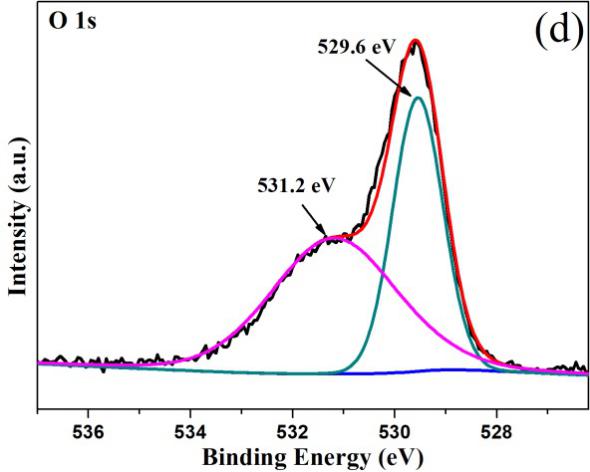
The humidity have been reported that could influence the sensing properties of gas sensors [49]. Therefore, the sensing properties of the sensor based on 13.6 wt% Ag-In2O3 nanorod composites to 0.6 ppm of H2S gas under different relative humidity at room temperature were measured, and the dynamic response/recovery curves are shown in Fig. 8a. When the relative humidity is higher than 45%, the response and recovery speeds are enhanced. However, the response values of the H2S sensor decrease with the increase of relative humidity from 30% to 70%. Stability of the sensors based on 13.6 wt% Ag-In2O3 nanorod composites to 1 ppm of H2S gas at room temperature and 30% RH was measured and the response values in 15 days are shown in Fig. 8b. It can be found that the response values are stability in the testing process, and the deviation of gas response values is less than 3%, which means that the sensor based on 13.6 wt% Ag-In2O3 nanorod composites has a good stability.

**3.3 Enhanced gas sensing mechanism of Ag-In2O3 nanorod composites.**

Sensing properties of the gas sensors are strongly affected by the chemical states of the surface of sensing materials [50]. In order to obtain the information of the chemical states of the chemical elements in the Ag-In2O3 nanorod composites, XPS analysis was performed and the obtained XPS spectra are shown in Fig. 9. Based on the XPS survey spectrum shown in Fig. 9a, the sample is comprised of In, O and Ag elements. The relative contents of all elements on the surface were calculated and the ratio of the surface atoms of O, In and Ag is 61.7:32.75:5.55. The binding energies at 451.6 and 444.1 eV in Fig. 9b of the high resolution XPS spectrum are corresponding to the In 3d3/2 and In 3d5/2 of In3+ in the Ag-In2O3 nanorod composites [51].

As shown in the XPS spectrum of Ag 3d (Fig. 9c), the peaks at the binding energies of 373.6 and 367.6 eV are attributed to the Ag 3d3/2 and Ag 3d5/2 of metallic Ag [52], which indicates that the Ag elements are existed as zero-valent silver in the composites. This result are consistent with the XRD analysis. Compared with the standard binding energy of metallic Ag (374.2 eV and 368.2 for Ag3d3/2 and Ag 3d5/2, respectively.), an obvious shift to lower binding energy side can be observed, meaning that there are electron transfers from Ag nanoparticles to In2O3 at their interfaces [52] This indicates that there are strong interactions of Ag with In2O3. Two obvious peaks at 529.6 and 531.2 eV can be observed in the O 1s spectrum in Fig. 9d. The former binding energy of 529.6 eV is assigned to the O2– ions in the crystal lattice of In2O3, and the latter of 531.2 eV can be attributed to the surface chemisorbed oxygen ions [34].The content of chemisorbed oxygen ions is as high as 57 % in total oxygen content, based on the calculation from integral proportion in XPS spectrum of O1s. Therefore, the content of chemisorbed oxygen ions is very high on the surface. The plenty of surface chemisorbed oxygen ions on the surface of In2O3 nanorods is beneficial to the increase of response of the sensors [53].

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**Figure** **9** **a** XPS survey spectrum of Ag-In2O3 nanorod composites and high-resolution spectra of **b** In 3d, **c** Ag 3d, **d** O 1s.

In2O3 is an n-type semiconductor material. The gas-sensing mechanism of In2O3 based sensors is based on the conductivity changes of the In2O3 sensing materials, which is mainly resulted from the reaction of the target gases with the chemisorbed oxygen ions on the surface of In2O3. In air, oxygen molecules are easily absorbed onto the surface of In2O3 nanorods, and then form chemisorbed oxygen ions (O2−, O−, O2−) by trapping electrons from the conduction band of In2O3 nanorods. At room temperature, the chemisorbed oxygen species is O2− [54]. As a result, the formation of chemisorbed oxygen ions leads to the formation of a depletion layer on the surface of the In2O3 nanorods and eventually results in an increase of electrical resistance of the sensor [5].The Ag nanoparticles can act as highly active catalysts on the surfaces of In2O3 nanorods to create more specifically active sites, and thus enhance the absorption of oxygen molecules and formation of chemisorbed oxygen ions on the surface of Ag by trapping more electrons from In2O3. This will result in an increase of width of the electron depletion layers of In2O3 sensing materials. In addition, due to the spill-over effect [55], the chemisorbed oxygen ions will be spilled over to the surface of In2O3 to increase the quantity chemisorbed oxygen ions on the surfaces of In2O3 nanorods.

When the sensor based on Ag-In2O3 nanorod composites is exposed to H2S gas, H2S molecules will be absorbed on the surface of In2O3, and then react with the surface chemisorbed O2− ions. At the same time, the Ag nanoparticles also absorb the H2S molecules, which are diffused into the surfaces of In2O3 through the spill-over effect [31,33,55]. Thus, more H2S molecules will be absorbed and then react with the chemisorbed oxygen ions. Finally, the H2S molecules will be oxidized into SO2 and H2O, which then releases many electrons based on the following reaction formula [54]:

H2S + 3/2O2− → SO2 + H2O + 3/2e− (1)

The released electrons will be transferred to the electron deletion layer on the surfaces of the In2O3 nanorods, thus reducing its thickness, and finally result in the decrease of the electric resistance of the sensor. Because the Ag nanoparticles are strongly decorated on the surfaces of In2O3 nanorods, apart from the chemical sensitization by the spillover effect explained before, the electronic sensitization also affects the sensing property of the sensors by accelerating the electron transfer between H2S and the sensors [33]. Therefore, because of the combined chemical sensitization and electronic sensitization, there are significant changes in the resistance of film of the Ag-In2O3 nanorod composites than those of the pure In2O3 nanorods, thus resulting in much higher responses. Furthermore, the detection limit to the H2S will also be much lower and the response/recovery times will be significantly reduced.

**4 Conclusion**

The Ag-In2O3 nanorod composites were successfully synthesized to be used to detect the H2S at room temperature. Compared with pure In2O3 nanorods based sensors, the Ag-In2O3 nanorod composites based H2S sensors showed much better sensing properties. At room temperature, it exhibited an ultra-highly response, good sensing selectivity, excellent reversibility and low detection limit. The enhanced sensing performance of the Ag-In2O3 nanorod composites was attributed to be the chemical sensitization and electronic sensitization. Therefore, the H2S sensor based on Ag-In2O3 nanorod composites is promising in H2S detection at room temperature.

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**Appendix A. Supplementary material**

Photo of the room temperature H2S sensors based on Ag-In2O3 nanorod composites. EDX pattern of Ag-In2O3 nanorod composites. I–V curves of the sensors based on Ag-In2O3 nanorod composites at different operation temperatures. The histogram of the response/recovery times of the sensors to H2S gas with different concentrations at room temperature.

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