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ARTICLE TYPE

Improved H_2S gas sensing properties of ZnO nanorods decorated by a few nm ZnS thin layer

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To avoid the spontaneous reaction between ZnO gas-sensing materials and detected H_2S gas, a strategy of ZnO nanorods decorated with several nm ZnS thin layer was designed. The ZnS decorated layer was prepared by passivating oriented ZnO nanorods in H_2S atmosphere. The effect of passivation processes on the H_2S sensing property was investigated. It was found that ZnO nanorods decorated with 2-nm thickness of ZnS possessed a repeatable and superior response to ppm-level H_2S at room temperature. Moreover, a confinement effect was proposed to explain the improved sensing property of the decorated ZnO nanorods.

1. Introduction

Hydrogen sulphide (H_2S), often existing in living environment and factory, is a colorless and highly toxic gas. Its typical permissible exposure limit is only about 10 ppm,[1,2] above which it may cause headache, dizziness, nausea, irritation of the eyes and respiratory tract.[3-5] Human exposured to H_2S gas at the level higher than 250 ppm are likely to result in neurobehavioral toxicity and may even cause a quick death.[6,7] Hence, it has become extremely important to effectively detect such hazardous gas at the concentration as low as ppm level.

In the recent years, there have been many efforts to develop sensitive H_2S detection sensor based on metal oxides (i.e. SnO_2, In_2O_3, ZnO, WO_3 et al.).[8-14] Most of the efforts are focused on the ZnO sensing material owing to its good response for H_2S, low cost, and flexibility in fabrication. However, the present sensors for H_2S detection still suffer from some drawbacks such as poor gas-sensitive stability, high work temperature, and long response and recovery time. Zhao et al.[15] presented Cu-doped ZnO nanofibers for H_2S sensing at low concentration (1-10 ppm) with a high work temperature of 230°C. Wu et al.[16] reported ZnO nanorods-based sensor for detection of H_2S at room temperature with response of 35 to 1 ppm target gas. Unfortunately, the response time of their sensor was 20 minutes and the response curve can not recover to original baseline after release of H_2S. Thus, it is necessary to develop highly sensitive room-temperature H_2S-sensors with shorting response and recovery time.

Herein, we envision that a uniform thin layer of sulphide on metal oxides may improve the repeatability of metal oxides-based H_2S sensors because a thin sulphide layer might confine the metal oxides to react with H_2S, and allow the electrons to pass for maintaining the sensing property. To study the feasibility of this design, ZnS-confined ZnO nanrods was synthesized via passivating oriented ZnO nanorods in low concentration of H_2S. In this route, a uniform layer of sulphide was achieved by gas-solid interface reaction. This ZnS-decorated ZnO nanorods film presented a repeatable and sensitive detection of H_2S at room temperature down to ppm level. In addition, this nanostructure also displayed a satisfactory selectivity in detecting of H_2S, which advanced us toward the realization of effective detection of H_2S at room-temperature.

2. Experimental

2.1. Nanorods growth and surface passivation

Oriented ZnO nanrods were grown on flat ceramic substrates via a two-step solution approach.[17] There were five pairs of Au interdigitated electrodes (both the width and distance were 250 μm) on the ceramic plate. ZnO nanoparticles on the ceramic substrates were first prepared by dipping in a ZnO colloidal solution. Then, solution growth of oriented nanorods was carried out by suspending the ceramic substrate with ZnO seeds upside down in an equimolar (25 mM) aqueous solution of zinc nitrate hydrate and hexamethylenetetramine at 95℃ for 3 h. After drying at 60°C, the as-prepared sample was annealed at 350°C for 2 h. For the formation of ZnS passivation layer on ZnO nanorods, the ceramic substrates with oriented ZnO nanorods were exposed to different concentration of H_2S at room temperature for hundreds of seconds. The resulting products was annealed at 150°C and then stored in desiccator.

2.2. Characterization of the samples

The morphology and crystal structure of samples were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700) and transmission electron microscope (TEM, JEOL JEM-2100). Energy-dispersive spectrometry (EDS, Oxford) was used to analyze the chemical component of as-prepared sample.

2.3. Gas-sensing measurement

Gas-sensing tests were performed with a CGS-1TP intelligent gas sensitive analysis system (Beijing Alice technology co., Ltd, china) using a stationary state gas distribution method. The ceramic substrate with oriented ZnO nanorods was laid on temperature control platform without heating. Two probes were pressed on electrodes of sample by controlling the position adjustment in the analysis. Before test, the sample was aged in air at room temperature for 2 days. When the resistance of the sensor was stable, the target gas, H_2S, was injected into test chamber and mixed with the air inside by two fans. The resistance variation was recorded to characterize the sensing property of as-prepared nanorod film between interdigital electrodes. When the variation of resistance lower than 1×10^{-4} MΩ, the test was stopped and air was injected to purge the test chamber for 60 s.

The sensor response to test gas (S_r) is defined as follows:

$$S_r = \frac{R_a}{R_g}$$

Where R_a is the resistance of the sensor in air, and R_g is the resistance in a test gas.

3. Results and discussion

3.1. Morphology observation

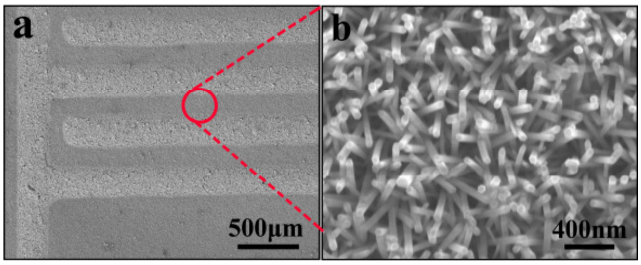

Figure 1. (a) FE-SEM image of ceramic substrate with as-grown ZnO nanorods. (b) Magnified FE-SEM image of oriented ZnO nanorods on the interdigital electrodes gap.

The morphology of as-grown sample was characterized by field-emission scanning electron microscopy and shown in figure 1. Figure 1a displays that a uniform thin film grows on the ceramic substrate between interdigital Au electrodes. From its high-magnification image (Fig. 1b), we can see that the film is composed of densely packed and oriented nanorods with diameters of 60~80 nm and average length of 0.7 μm (see supporting figure S1a). The hexagonal top-end of nanorods suggests a c-axis growth of ZnO wurtzite crystal, which is confirmed by the corresponding XRD result (see supporting figure S1b). According to its XRD pattern obtained using $Cu_{K\alpha}$ incident radiation, the oriented ZnO nanorods are pure hexagonal wurtzite phase with a preferentially c-axis orientation.

3.2. Gas sensing performance of pure ZnO nanorods

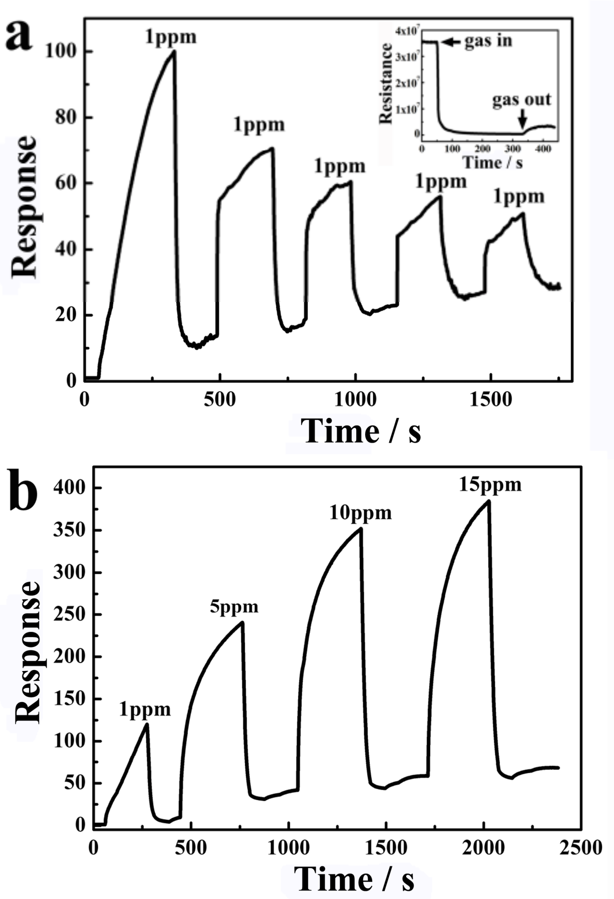

Figure 2. (a) Sensing behavior of ZnO naorods for repeatedly detection of 1ppm H_2S. The top-right inset shows resistance variation of ZnO nanorods to 1 ppm H_2S at the first cycle. (b) Response of ZnO nanorods to difference concentrations of H_2S.

Sensing behavior of pure ZnO nanorods grown on ceramic substrate with interdigitated electrodes towards H_2S was tested at room temperature. Figure 2a shows that the response of ZnO nanorods to 1 ppm H_2S is as high as 102 when the sensor is used at the first time, but the value descends gradually when the sensor is repeatedly used. It also can be found that the baseline drifts upwards and the response curve can not recover to original baseline. From the response-recovery curve shown in top-right inset of Fig. 2a, it takes about 60 s to attain a slow resisitance variation lower than 1×10^{-3} MΩ/s, but the resistance recovers 10 % of the base value in 40 s and then attains a new baseline. These results demonstrate a poor repeatability of ZnO nanorods-based sensors for H_2S detection at room temperature. When the sensor is used to detect different concentration of H_2S, similar baseline drift and response distortion take place, which is shown in Fig. 2b. The un-recovery behavior ought to be attributed to the irreversible chemical reaction between the H_2S and ZnO nanorods surface, in which process ZnS is formed on the surface of ZnO nanorods.

3.3 Gas sensing performance of ZnO-ZnS core-shell nanostructure

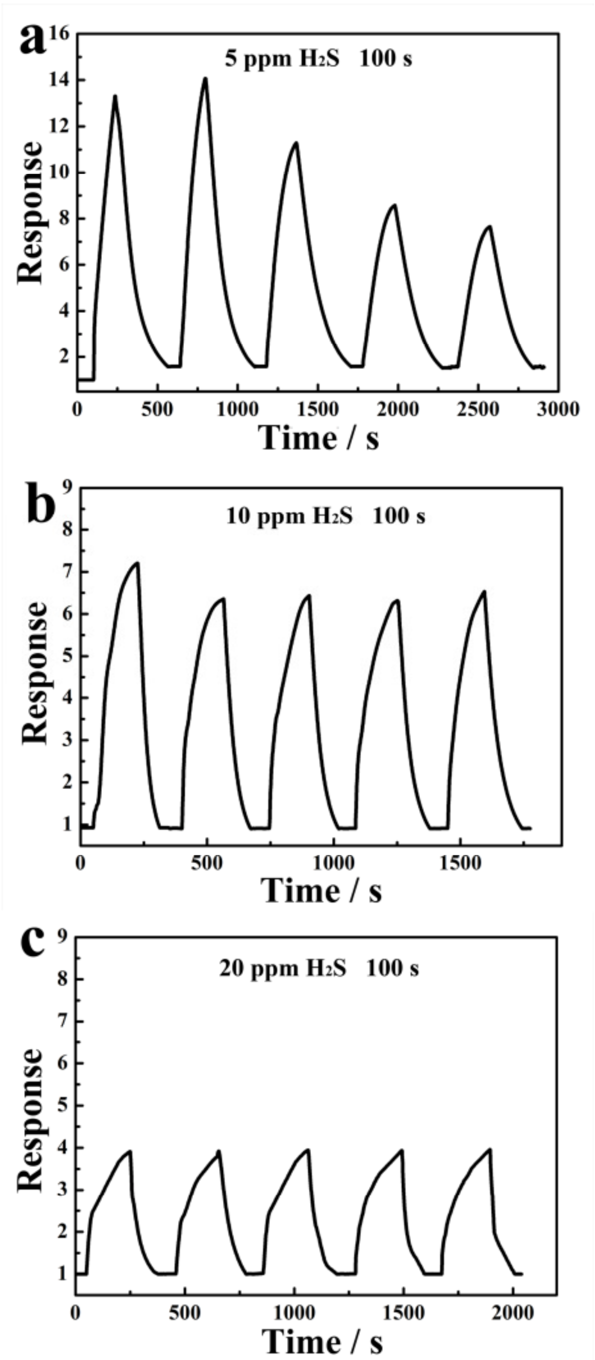

Figure 3. The repeatability of passivated ZnO nanorods in different concentration of H_2S for 100 s in monitoring 1 ppm H_2S. (a) 5 ppm; (b) 10 ppm; (c) 20 ppm.

To improve the stability of ZnO nanorods-base H_2S sensor, we passivated the as-grown ZnO nanorods in different concentration of H_2S at room temperature for the formation of a thin layer of ZnS film. After being annealed at 150°C for 2 hours, the passivated ZnO nanorods was fabricated into sensors for detection of 1 ppm H_2S. Figure 3a shows that, after storage in 5 ppm H_2S for 100s, ZnO nanorods-based sensors still displays an instability in repeatedly detecting of 1 ppm H_2S. But baseline of the sensor does not change too much, which is an evident signal of improvement of stability. When the passivation concentration is elevated to 10 ppm, the responses of passivated ZnO nanorods towards H_2S tend to be repeatable. There is only a little variation between the response of the first cycle and others, which is displayed in figure 3b. Figure 3c shows that a stable detection of 1 ppm H_2S is achieved on the ZnO nanorods passivated in 20 ppm H_2S. We can also found that the responses of passivated ZnO nanorods in 20 ppm H_2S noticeably decrease compared with that in 10 ppm passivation concentration. These results demonstrate that a passivation in H_2S is capable of improving the repeatability of ZnO nanorods-based sensor for detection of 1 ppm H_2S, but a high level of passivation concentration depresses the response of passivated ZnO nanorods.

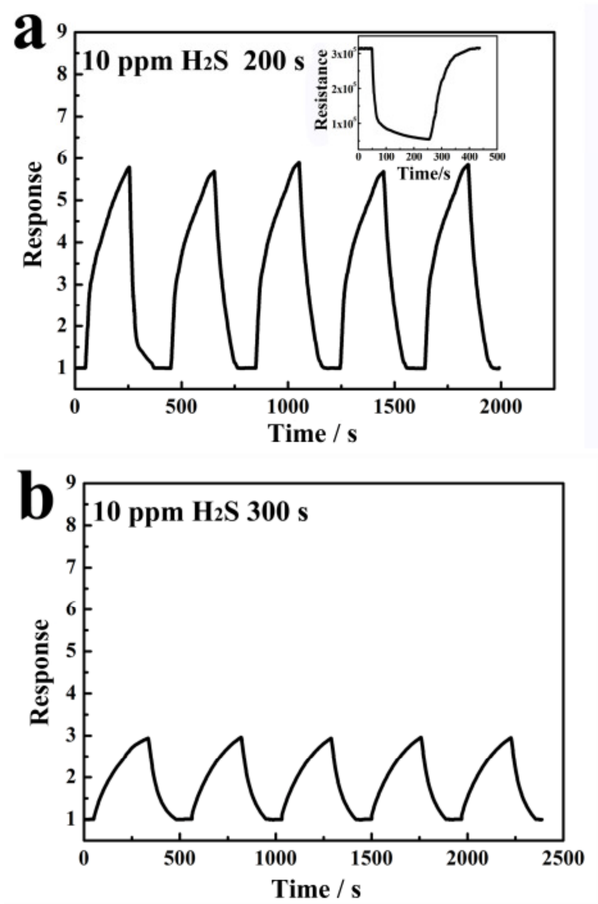

Figure 4. Repeatability of ZnO nanorods-based sensors in detection of 1 ppm H_2S after being passivated in 10 ppm H_2S for 200 s (a) and 300 s (b). Top-right inset in Fig. 4a shows corresponding resistance variation of passivated ZnO nanorods at the first cycle.

Effect of passivation times on the repeatability of ZnO nanorods-based sensor was studied by prolonging storage time in 10 ppm H_2S ambience. The test results are shown in figure 4. When the storage time increases to 200 s, the responses of passivated ZnO nanorods become stable for repeatedly detection of 1 ppm H_2S, and the values are all around 5.9 (Figure 4a). It also can be noticed that the transient response curve recovers to its baseline (in air) after releases of H_2S in the recorded five cycles. A typical resistance variation of passivated ZnO nanorods to 1 ppm H_2S is shown in inset of figure 4a. It can be seen that resistance of the sensor decreases rapidly when the target gas is injected and recovers to the original value when the gas is removed. The response time and recovery time are 70 s and 100 s, respectively. These results demonstrate that the passivated ZnO nanorods shows a reversible response-recovery characteristic to H_2S. Figure 4b displays that further prolonging the passivation time to 300s enables the sensor repeatedly detect 1 ppm H_2S, as well, but its sensitivities are only about 2.8. It means that an excess passivation time depresses the response of ZnO nanorods-base sensors. From the results mentioned above, we conclude that storage in 10 ppm H_2S for 200 s are the optimum passivation parameters of ZnO nanorods at room temperature for repeatedly detection of 1 ppm H_2S.

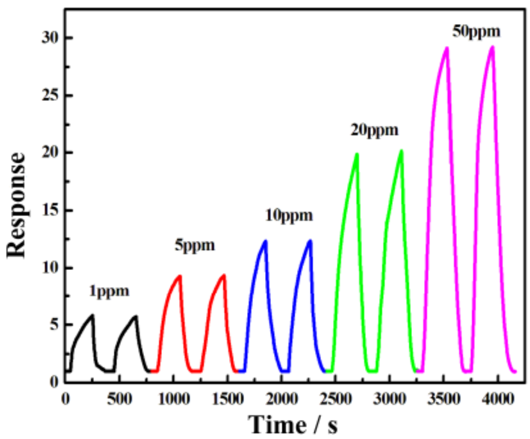

Figure 5. Repeatability test of the sensor based on passivated ZnO nanorods at optimum condition to different H_2S concentrations.

The sensing property of passivated ZnO nanorods at optimum condition to different concentrations of H_2S was also tested in our experiment. Figure 5 shows two time-cycling response of the sensor for each concentration. It can be seen that the response increases with an increase of the gas concentration from 1 ppm to 50 ppm. The sensor has almost the same sensitivities for the two cycles, and its response curve recovers to the baseline in air when test gas is released. Additionally, a stable response of the sensor was also found even in the case of repeatedly monitoring 500 ppm H_2S, seeing supporting figure S2. These results demonstrate that the passivated ZnO nanorods film has a good repeatability to detect a wide range of H_2S.

Figure 6 shows the responses of the sensor based on passivated ZnO nanorods to several reducing gas, where the working temperature is room temperature and the gas concentration is 10 ppm. It is clearly shown that the sensor displays a high response to H_2S and much smaller response to other reducing gas including formaldehyde, toluene, hydrogen, ethanol, ammonia and carbon monoxide. These results show that the sensor based on passivated ZnO nanorods possesses satisfactory selectivity for detection of H_2S.

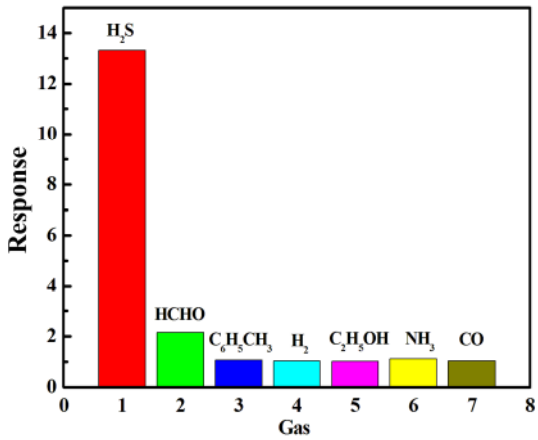

Figure 6. Selectivity of passivated ZnO nanorods at optimum condition to several reducing gases at room temperature.

3.4. Sensing mechanism

The adsorption and dissociation of H_2S on ZnO surface have been widely investigated in the present studies.[18] H_2S is decomposed to HS^- firstly and then to S^{2-} step by step:

$$ZnO + H_2S(ads) \longrightarrow ZnS + H_2O \quad (1)$$

The reaction enthalpy ΔH of this formula is negative,[19] which demonstrates the reaction between ZnO and H_2S is an unreversible and exothermic process at room temperature. The spontaneous reaction between ZnO and H_2S ought to be the main reason for the high response of pure ZnO nanorods in detecting of H_2S at the first time and the poor repeatability of it in the following cycles. Meanwhile, the spontaneous reaction affords us an opportunity to obtain a thin ZnS layer at the interface between ZnO nanorods and H_2S gas. The formation process of ZnS layer on ZnO nanorods was investigated by using transmission electron microscope (TEM), which is shown in figure 7.

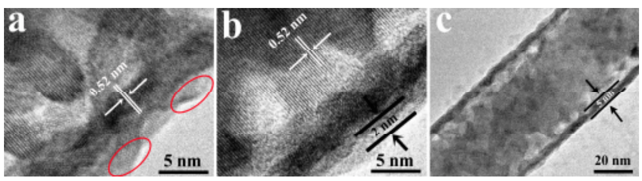

Figure 7. TEM images of ZnO nanorods passivated in 10 ppm H_2S for different times. (a) 100 s; (b) 200 s; (c) 300 s.

Figure 7 presents the morphology-evolution of the oriented ZnO nanorods in 10 ppm H_2S at room temperature for different times. The interplanar spacing of 0.52 nm in figure 7 illustrates the rod grows along a longitudinal [0001] orientation of wurtzite-structured ZnO. From figure 7a, we can see some isolated amorphous substance on the rod surface, which is marked with red elliptic circle. This result indicates only a discontinuous film is formed on ZnO nanorod passivated for 100 s. After passivaton at 10 ppm for 200 s, a continuous amorphous film is form on ZnO nanorod, whose thickness is about 2 nm (see Fig. 7b). When passivation time is prolonged to 300 s, the thickness of amorphous layer increases to ~5 nm, which is shown in figure 7c and supporting figure S3. The EDS data recorded on the samples shown in figure 7b and 7c displays an increase of atom percentage of sulfur, seeing supporting figure S4. These results demonstrate that ZnS film is formed and grows thicker on ZnO nanorods accompanying with the prolongation of passivation time.

The annealing at 150°C effectively stabilized the amorphous ZnS passivation layer. Without anneal, the passivated ZnO nanorods in 10 ppm H_2S for 200s still showed a poor repeatability in detecting of 1 ppm H_2S (see supporting figure S5), and the ZnS thin film would grow thicker which was shown above. But, a repeatable detection of H_2S was realized on the annealed sample. Two possible effects of post-thermal annealing on the stabilization of ZnS passivation layer were as follows. On the one hand, the annealing process made the amorphous ZnS passivation layer denser and more uniform by removing H_2O molecules.[20] On the other hand, some stable cubic phase might formed in the ZnS passivation layer after annealing at 150°C because the cubic phase is more stable than the hexagonal phase when the size of ZnS lower than 10 nm.[21] From the corresponding sensing property (shown in figure 4), we can see that a 2-nm-thick ZnS film on surface enables the ZnO nanorods to steadily detect H_2S. And the thicker the ZnS film, the lower the response.

Having taking into account the above results and disscusion, a confinement effect[22,23] is proposed to interpret the repeatability of ZnS-confined ZnO nanorods in detection of H_2S. On the one hand, ZnS film can confine ZnO nanorods to react with H_2S because it is chemically inert to H_2S. On the other hand, the electrons are capable of passing the ZnS film for formation of oxygen depletion layer since the thickness of ZnS is lower than the depletion layer.[24] At room temperature, the adsorbed oxygen species are mainly O_2^-. H_2S interacts with the adsorbed oxygen species at room temperature[25] and losses a large number of electrons as indicated in the following equation:

$$2H_2S_{(g)} + 3O^-_{2\,(ads)} \longrightarrow 2H_2O_{(g)} + 2SO_{2(g)} + 3e^- \quad (2)$$

When the H_2S is released, oxygen regains electron from ZnO-ZnS core-shell nanorods and forms oxygen depletion layer again. Hence, the repeatable and sensitive detection of H_2S was realized on ZnS surface-confined ZnO nanrods. In addition, other reducing gases could not react with O_2^- at room temperature, which ought to be the main reason for the selectivity of ZnS-confined ZnO nanrods in detection of H_2S. Although response of ZnO nanorods to H_2S was depressed by surface ZnS passivation layer, the response of passivated ZnO nanorods can be improved by further decoration of Pt, Pd or Au nanoparticles without sacrifice of its repeatability for detecting H_2S.

4. Conclusions

We have demonstrated a strategy of ZnO nanorods decorated with several nm ZnS thin layer for improving H_2S sensing property. Under optimum condition, the sensor based on the decorated ZnO nanorods gives a satisfactory repeatability in detecting different concentrations of H_2S relative to the undecorated ones, and has still a sensitive response and rapid recover with a response of about 5 even in the case of 1 ppm H_2S, which is especially useful for low-concentration H_2S detection. The improvement can be explained by a confinement effect of a few nm ZnS thin layer on the surface of ZnO nanorod. Furthermore, the decoration of sulphide thin layer might be used to improve the H_2S gas-sensing properties of other metal oxides.

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Notes and references

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