



# Ultra-fast and low detection limit of H<sub>2</sub>S sensor based on hydrothermal synthesized Cu<sub>7</sub>S<sub>4</sub>-CuO microflowers

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## ABSTRACT

In this work, Cu<sub>7</sub>S<sub>4</sub>-CuO microflowers were successfully synthesized through a simple hydrothermal route. The influence of S doping amount on the corresponding microstructures and gas sensing properties of the composites are investigated. In the comparative gas sensing test, the sensor fabricated from Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%) microflowers exhibited the highest response (156–50 ppm) to hydrogen sulfide with a fast response and recovery time. Furthermore, Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%) microflowers gas sensor not only showed superior hydrogen sulfide selectivity compared with other gases, but also ppb-level detection limit (100 ppb–16.2) at 225 °C, even lower detection limit (50 ppb–1.8). The synergistic effects between CuO and Cu<sub>7</sub>S<sub>4</sub>, more surface adsorbed oxygen, and active sites were regarded as the main reasons for the ultrasensitive and selective hydrogen sulfide detection.

## 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is a neurotoxic gas that is extremely irritating and can cause suffocation. Its toxicity is approximately equal to cyanide. In addition to acting on the nervous system and respiratory system, H<sub>2</sub>S can also cause organ damage. It is relatively easy to be released from the industrial production of oil, coal, and natural gas. In addition, H<sub>2</sub>S is also produced at the site of organic matter spoilage and often tends to accumulate in poorly ventilated municipal sewer pipes, other types of fermenters and vegetables. When people are exposed to H<sub>2</sub>S environment for a long time, it will pose a huge threat and harm to human health and safety. The threshold limit value (TLV) of H<sub>2</sub>S for 8 h exposure is 10 ppm [1], which is established by the American Conference of Governmental Industrial Hygienists. Therefore, early and efficient real-time monitoring of H<sub>2</sub>S gas is essential for humans to stay away from disease. Among the many sensors [2], Gas sensors based on metal oxide semiconductors [3–6] have attracted great attention because of its low cost, excellent stability, high sensitivity, fast response, simplicity in fabrication, and compatibility with smart devices [7,8]. SnO<sub>2</sub> [9], ZnO [10], CuO [11], WO<sub>3</sub> [12], Fe<sub>2</sub>O<sub>3</sub> [13] are typical semiconductor sensing materials. Most of them have been used to detect hydrogen sulfide. Although ZnO nanorods [14], flower-like CuO [15], and CuO nanosheets [16] were reported to detect H<sub>2</sub>S at room temperature in recent

years, their response and recovery time were not less than 200 and 1000 s, respectively. Particularly, the recovery time of the ZnO nanorods was even up to 3592 s. These drawbacks of the reported sensing materials, for example, low detection limit [17,18] and slow response-recovery time [19], prevent the practical application in detecting ppb-level H<sub>2</sub>S. Therefore, the development of sensing materials for the ultra-fast response-recovery time of hydrogen sulfide gas under the optimal condition remains challenging. For the abundant two-dimensional (2D) layered promoter Cu<sub>7</sub>S<sub>4</sub> (Cu<sub>1.75</sub>S) on the earth [20–22], it has excellent catalytic activity and a simple preparation method. Notably, as the most stable structure in the Cu<sub>x</sub>S<sub>y</sub> system, Cu<sub>7</sub>S<sub>4</sub> has good stability. Meanwhile, as a non-stoichiometric p-type semiconductor (bandgap 1.2–2.4 eV) with unique optical, electric, and thermal properties [23,24], copper sulfide is a material with prospective applications in photocatalytic properties [25], gas sensors [26], and lithium-ion batteries [27]. At present, there are relatively few and imperfect studies on the application of copper sulfide material in gas sensors. As previously reported in the literature, Galdikas et al., have conducted ammonia sensor based on solid-state Cu<sub>x</sub>S films [28], and Fu et al., made a CuS doped CuO sensor to detect H<sub>2</sub>S and NH<sub>3</sub> [29].

Therefore, this article makes full use of the unique advantages of Cu<sub>7</sub>S<sub>4</sub> nanoparticles to construct unique 2D-3D Cu<sub>7</sub>S<sub>4</sub>-CuO microstructures, and realizes efficient synergy to improve gas sensitivity and

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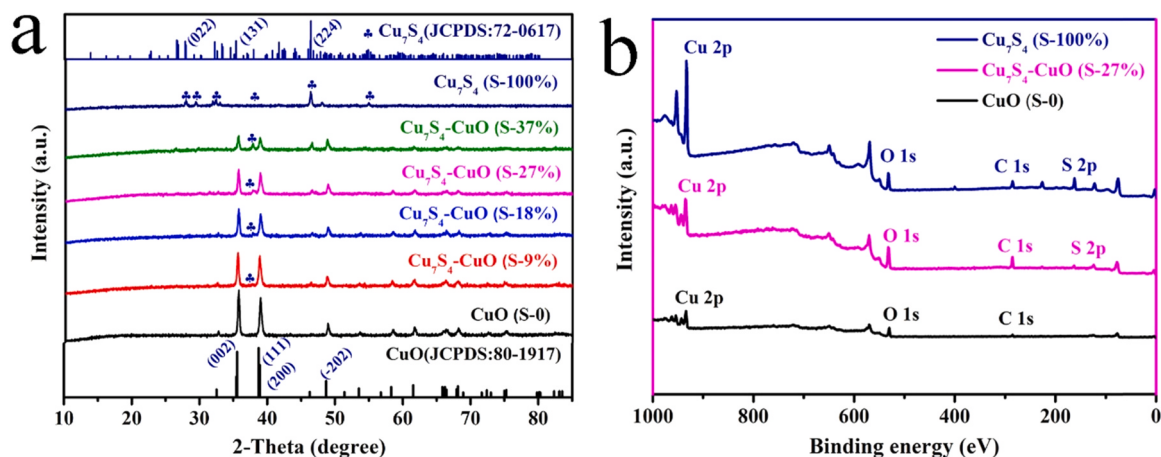
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**Fig. 1.** (a) XRD patterns of the obtained samples: pure  $\text{CuO}$ ,  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S/Cu = 9, 18, 27, and 37 mol%) composites and pure  $\text{Cu}_7\text{S}_4$ . (b) X-ray photoelectron spectra (XPS) survey scan of the obtained samples:  $\text{CuO}$ ,  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S/Cu = 27 mol%) composites and pure  $\text{Cu}_7\text{S}_4$ .

sensing efficiency. In this work,  $\text{Cu}_7\text{S}_4\text{-CuO}$  microflowlers were obtained and used to fabricate  $\text{H}_2\text{S}$  gas sensors. And the sensor based on  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S/Cu = 27 mol%) microflowlers exhibited a low ppb-level detection limit and excellent selectivity to  $\text{H}_2\text{S}$  gas.

## 2. Experimental

### 2.1. Preparation of the $\text{CuO}$ and $\text{Cu}_7\text{S}_4\text{-CuO}$ samples

Cupric Acetate Anhydrous ( $\geq 99\%$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ), Sodium hydroxide ( $\geq 97\%$ ,  $\text{NaOH}$ ) were purchased from Aladin Industry corporation. Ammonium hydroxide ( $\geq 25\%$ ,  $\text{NH}_3\cdot\text{H}_2\text{O}$ ) and Thioacetamide (TAA,  $\geq 98\%$ ,  $\text{CH}_3\text{CSNH}_2$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemical reagents used in this experiment were analytical grade from a commercial supplier and used without further purification. The synthesis details are as follows: First, 5.3 mmol of  $\text{Cu}(\text{CH}_3\text{COO})_2$  and 20 mL of deionized water were mixed and stirred for 10 min. Next, 6.82 mL of  $\text{NH}_3\cdot\text{H}_2\text{O}$  was added and kept stirring for 15 min. Then, 0, 0.5, 1.0, 1.5, and 2.0 mmol of TAA were added and the mixed solutions were kept for 0.5 h. Finally, 0.02 mol of  $\text{NaOH}$  was added and stirred for 30 min. Next, the uniformly mixed solutions were respectively transferred to the 50 mL Teflon-lined stainless-steel autoclaves, which were then sealed and put into a hot oven with a constant temperature of  $180^\circ\text{C}$  for 24 h. When the stainless-steel autoclaves cooled to room temperature, centrifuge the resulting precipitates five times with ethanol and deionized water alternately, then dry the products at  $80^\circ\text{C}$  for 12 h in an oven. The final black-precipitated materials with S/Cu ratios of 0, 9, 18, 27, and 37 mol% were obtained. The desired products with S concentrations of 0, 9, 18, 27, and 37 mol% were sequentially labeled as S-0, S-9%, S-18%, S-27%, and S-37%. In our experiment, pure  $\text{Cu}_7\text{S}_4$  sample, as contrastive materials, was also synthesized by the similar hydrothermal routes, as shown in [supporting information](#). And the pure  $\text{Cu}_7\text{S}_4$  sample was labeled as S-100%.

### 2.2. Characterization of materials

The phase and crystallization information of the samples were characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 V diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ ). The morphology and internal structure of the as-prepared samples were observed by scanning electron microscopy (SEM, JSM-7500F JEOL), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) with an operating voltage of 200 kV (JEM-2200FS JEOL), and selected area electron diffraction (SAED). The analyses of energy-dispersive X-ray spectroscopic (EDS) were obtained with the

help of TEM attachment. The X-ray photoelectron spectra (XPS) were performed by an ESCALAB 250 Analytical XPS spectrometer with a monochromatic X-ray source ( $\text{Al K}\alpha$ ,  $h\nu = 1486.6\text{ eV}$ ). The binding energy values were corrected for specimen charging by referencing the C 1s line to  $284.6\text{ eV}$ . The BET surface areas and the pore size distribution were obtained by the Brunauer-Emmet-Teller (BET) and the Barrett-Joyner-Halenda (BJH) measurements. The thermal stability of the sample was carried out on a Thermal Gravimetric Analyzer (Netzsch, STA 449 F3 Jupiter) from  $25$  to  $800^\circ\text{C}$ . The UV/vis spectrophotometer (SHIMADZU, UV-2500) was used to determine the bandgap of the samples.

### 2.3. Fabrication and measurement of gas sensor

For device fabrication, a series of samples with different proportions of S content as sensing materials were respectively dissolved with the deionized water in an agate mortar to form a slurry (weight rate of samples and DI water is 1:4) and then coated uniformly onto the ceramic tube substrate which consists of a pair of Au electrodes and four Pt wires, to form a sensing film. The length, outer and inner diameter of the ceramic tube substrate are approximately 4, 1.2, and 0.8 mm, respectively. The coating was calcined at  $100^\circ\text{C}$  for 2 h in the muffle furnace to make the sensing materials and the ceramic tube substrate closer. Then, a Ni-Cr alloy coil heater used to control the working temperature was inserted through the well-coated ceramic tube. Welding the well-coated and sintered ceramic tube on a hexagon base. The gas sensor was aged at  $100^\circ\text{C}$  for 48 h. The main purpose of this procedure is obtaining a stable gas sensor. [Fig. S1](#) shows the schematic diagram of the gas sensor device. Then, the performance of the as-prepared sensors was through the RQ-2 series Intelligent Test Meter (Qingdao, China) at a laboratory condition ( $25^\circ\text{C}$ , 35%–40% relative humidity). The sensing measurement of the sensors was carried out by a static system [30], as shown in [Fig. S2](#). The resistance of sensing material was continuously recorded by digital multimeter and the sensing response (S) was defined as the percentage of relative variation in resistance ( $\Delta R/R_a \times 100\%$ ), where  $\Delta R$  represents the variation of resistance before and after contacting with target gases, while  $R_a$  represents the resistance of the gas sensor in the initial state. The response/recovery time is defined as the time required for the resistance to reach 90% of the total resistance variation relative to the former equilibrium value after exposure to/removal from target gases.

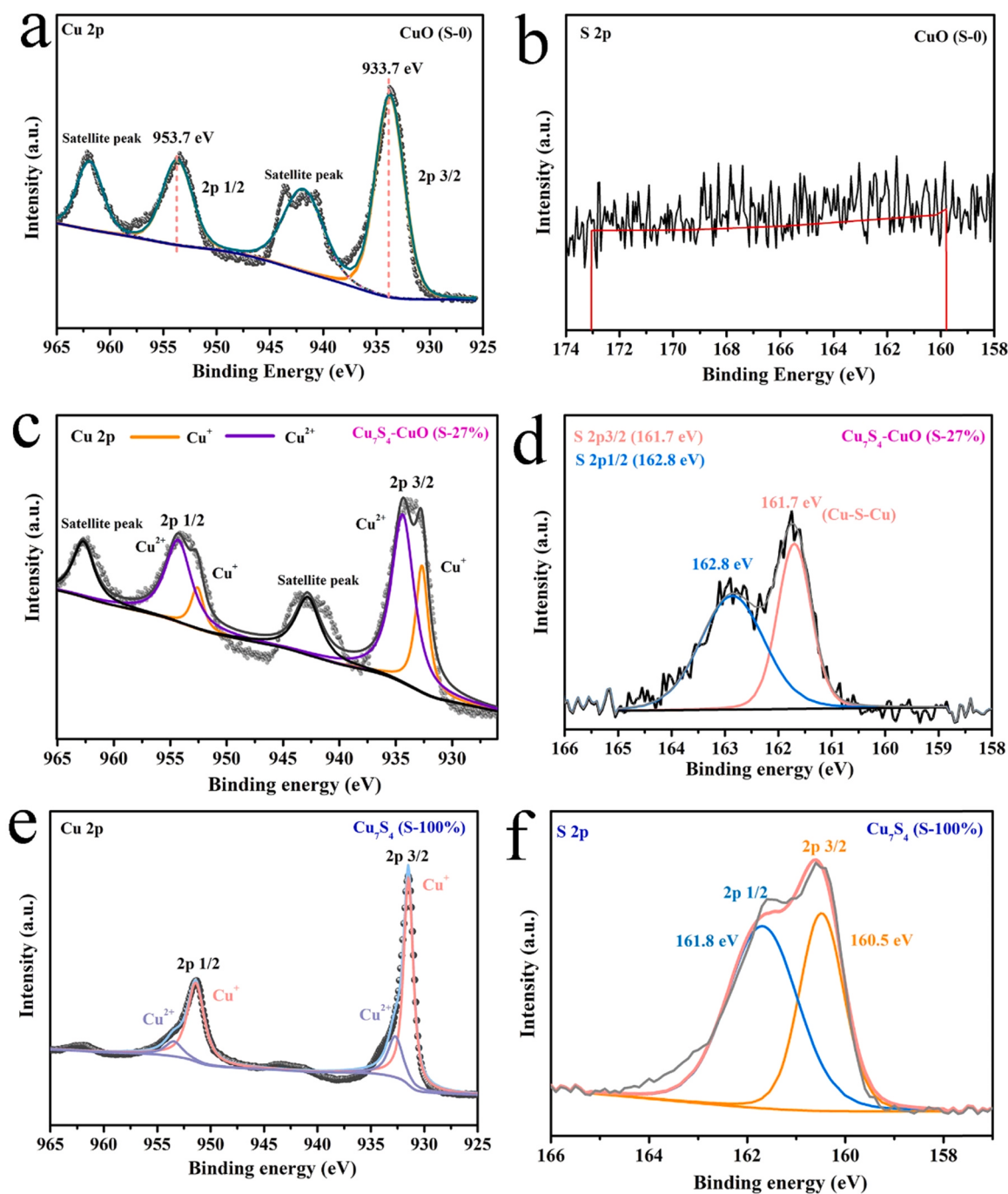


Fig. 2. (a, c, e) Cu 2p and (b, d, f) S 2p XPS spectra of the obtained samples: CuO, Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%) composites and pure Cu<sub>7</sub>S<sub>4</sub>.

### 3. Results and discussion

#### 3.1. Structural and morphological characteristics

XRD patterns of the as-prepared samples with different S /Cu ratios of 0–37 mol% and pure Cu<sub>7</sub>S<sub>4</sub> samples are shown in Fig. 1a. Two phases of Cu<sub>7</sub>S<sub>4</sub> and CuO were observed in Cu<sub>7</sub>S<sub>4</sub>-CuO structures (S-9% ~ S-37%) and the Cu<sub>7</sub>S<sub>4</sub> peaks were enhanced with the increasing S /Cu ratios (0–37 mol%). Besides, the Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 9, 18, 27, and 37 mol%) samples matched well with the standard CuO (Cc (9), JCPDS No. 80-1917) and Cu<sub>7</sub>S<sub>4</sub> (Pnma (62), JCPDS No. 72-0617) patterns, and no other phase peaks were detected. And the sharp and intensive diffraction peaks of the samples indicated its good crystalline quality [31]. Thus, the as-obtained Cu<sub>7</sub>S<sub>4</sub>-CuO materials were proved to be composited by

Cu<sub>7</sub>S<sub>4</sub> and CuO phases through the XRD analyses. To further confirm the chemical compositions of the obtained materials, XPS analyses were employed to characterize the samples (pure CuO, the Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%), and pure Cu<sub>7</sub>S<sub>4</sub>) as well, it could be noticed from the XPS survey spectrum that the signals of O, S, and Cu elements were observed in the Cu<sub>7</sub>S<sub>4</sub>-CuO microflowlers with S/Cu ratios of 27 mol% and pure Cu<sub>7</sub>S<sub>4</sub> sample (Fig. 1b). The signal of S was not found in the pure CuO sample.

Furthermore, Fig. 2 displays the high-resolution spectra of Cu 2p and S 2p species in pure CuO, the Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%), and pure Cu<sub>7</sub>S<sub>4</sub>. The Cu 2p spectra (Fig. 2a) of the pure CuO, the main peaks located around 933.7 eV with satellites (941.9 eV) and 953 eV with satellites (961.9 eV) were assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> of Cu<sup>2+</sup>, respectively. The S 2p spectrum of pure CuO does not detect the presence of the S element, as shown in Fig. 2b, which is consistent with the

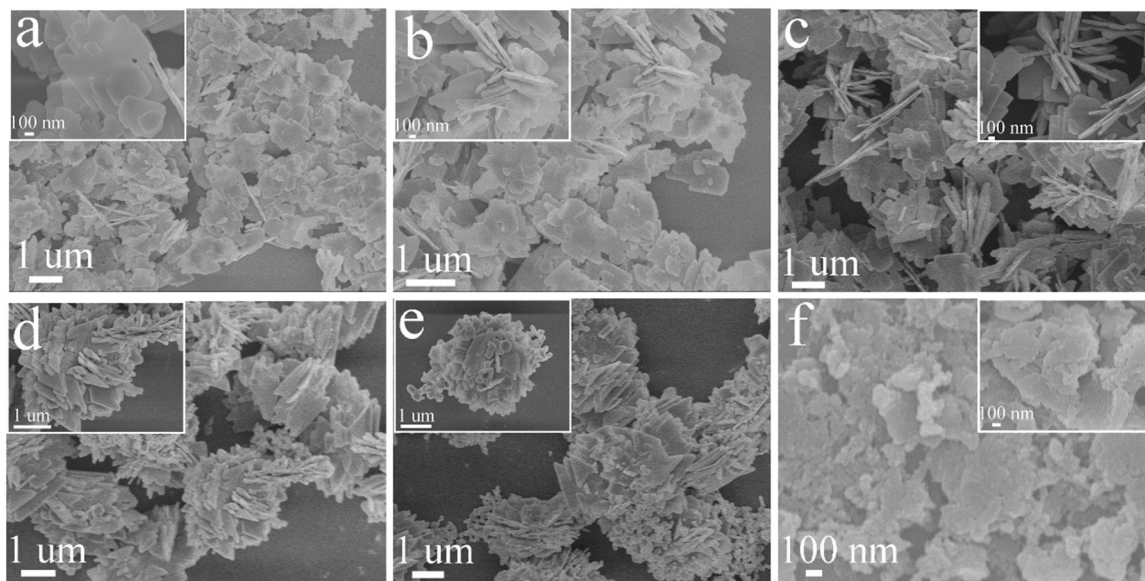


Fig. 3. FESEM images of (a) S-0, (b) S-9%, (c) S-18%, (d) S-27%, S-37% and pure Cu<sub>7</sub>S<sub>4</sub> (S-100%).

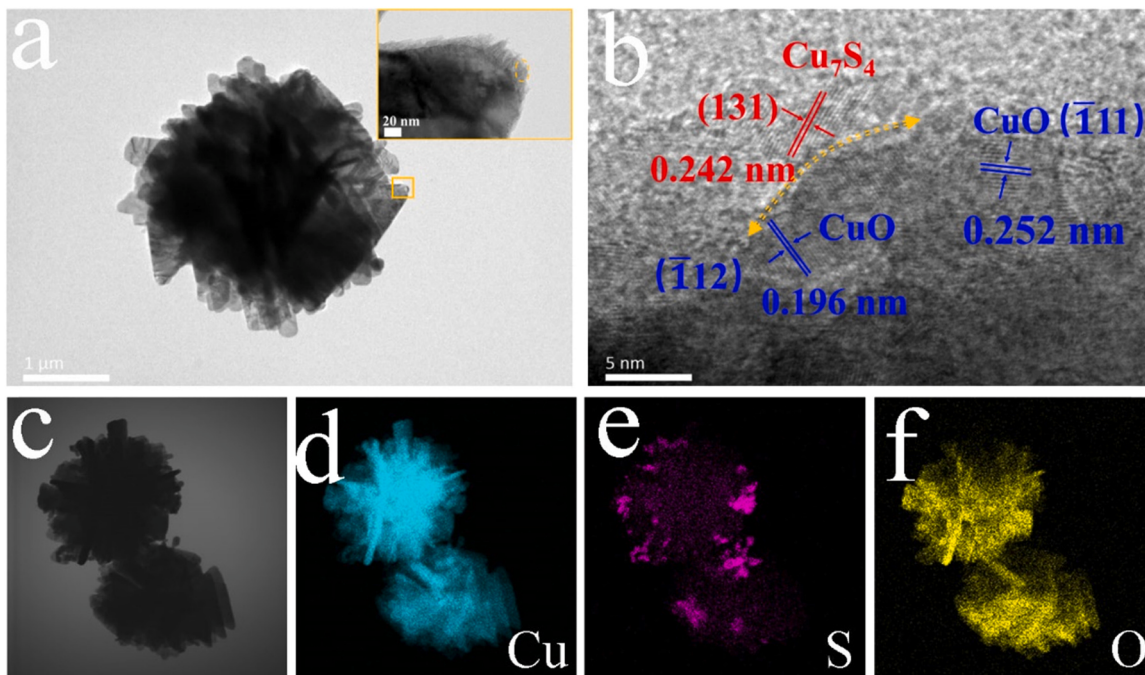
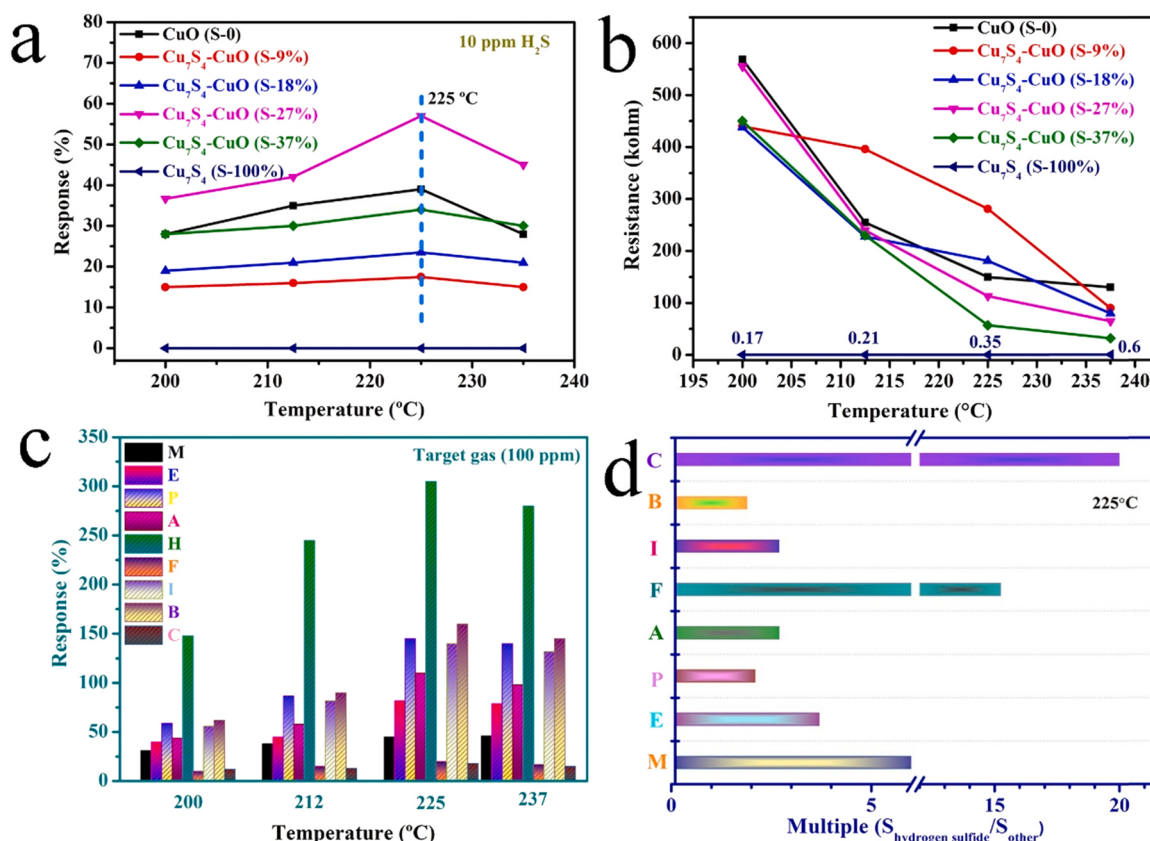


Fig. 4. (a) TEM image of S-27% (the inset is high-magnification image of S-27%), (b) HRTEM images of labeled areas and (c, d, e, f) EDS element mapping images of S-27%.

XRD results. Fig. 2c is the Cu 2p spectra of the Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%), The Cu 2p peaks could be deconvoluted into six peaks, the peaks located around 932.7/934.4 eV with their satellite (942.8 eV) and 952.6/954.3 eV with their satellite (962.7 eV) were assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> of Cu<sup>+</sup> and Cu<sup>2+</sup>, respectively. Additionally, from the S 2p spectra shown in Fig. 2d, the main peaks located at around 161.7 and 162.8 eV were assigned to the S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> orbitals of divalent sulfide ions (S<sup>2-</sup>), respectively, which correspond to the sulfides in Cu<sub>7</sub>S<sub>4</sub>. Therefore, it indicates the presence of Cu<sub>7</sub>S<sub>4</sub> in the Cu<sub>7</sub>S<sub>4</sub>-CuO (S/Cu = 27 mol%) sample. From Fig. 2e-f, the Cu 2p and S 2p spectra of pure Cu<sub>7</sub>S<sub>4</sub>, the high-resolution XPS spectrum in Fig. 2(e) showed that the main peaks at 931.5 and 951.4 eV were Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively, which confirmed the presence of Cu<sup>+</sup> in pure Cu<sub>7</sub>S<sub>4</sub>.

Furthermore, the presence of Cu<sup>2+</sup> in pure Cu<sub>7</sub>S<sub>4</sub> was demonstrated from the peaks at 932.5 and 953.7 eV. In the XPS spectrum of S 2p in Fig. 2 f, the peak located at around 160.5 and 161.8 eV corresponded to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub>, respectively, which indicated that the chemical state of S was -2. Therefore, the XPS results further confirmed the existence of Cu<sub>7</sub>S<sub>4</sub> and CuO phases, indicating the formation of pure samples and Cu<sub>7</sub>S<sub>4</sub>-CuO composites in this work.

The morphology and microstructure of samples were obtained by SEM and TEM. Fig. 3a-f show the low magnification and high magnification SEM images (insets) of S/Cu ratios of 0, 9, 18, 27, 37 mol%, and pure Cu<sub>7</sub>S<sub>4</sub> samples. It can be observed from SEM images that their morphology gradually changed with the increase of sulfur content. The pure CuO (S-0) sample was 2D dispersed nanosheets structure with a



**Fig. 5.** (a, b) Response-temperature, Resistance-temperature of the sensors based on the Cu<sub>7</sub>S<sub>4</sub>-CuO composites with different S/Cu ratios of 0–37 mol% and pure Cu<sub>7</sub>S<sub>4</sub> sample. (c) Responses of the S-27% to 100 ppm different test gases (M: methanol, E: ethanol, P: n-propanol, A: acetone, H: hydrogen sulfide, F: formaldehyde, I: isopropanol, B: n-butanol C: carbon monoxide) at different working temperature; (d) The response ratios of the S-27% sensor to hydrogen sulfide (100 ppm) versus other gases (100 ppm).

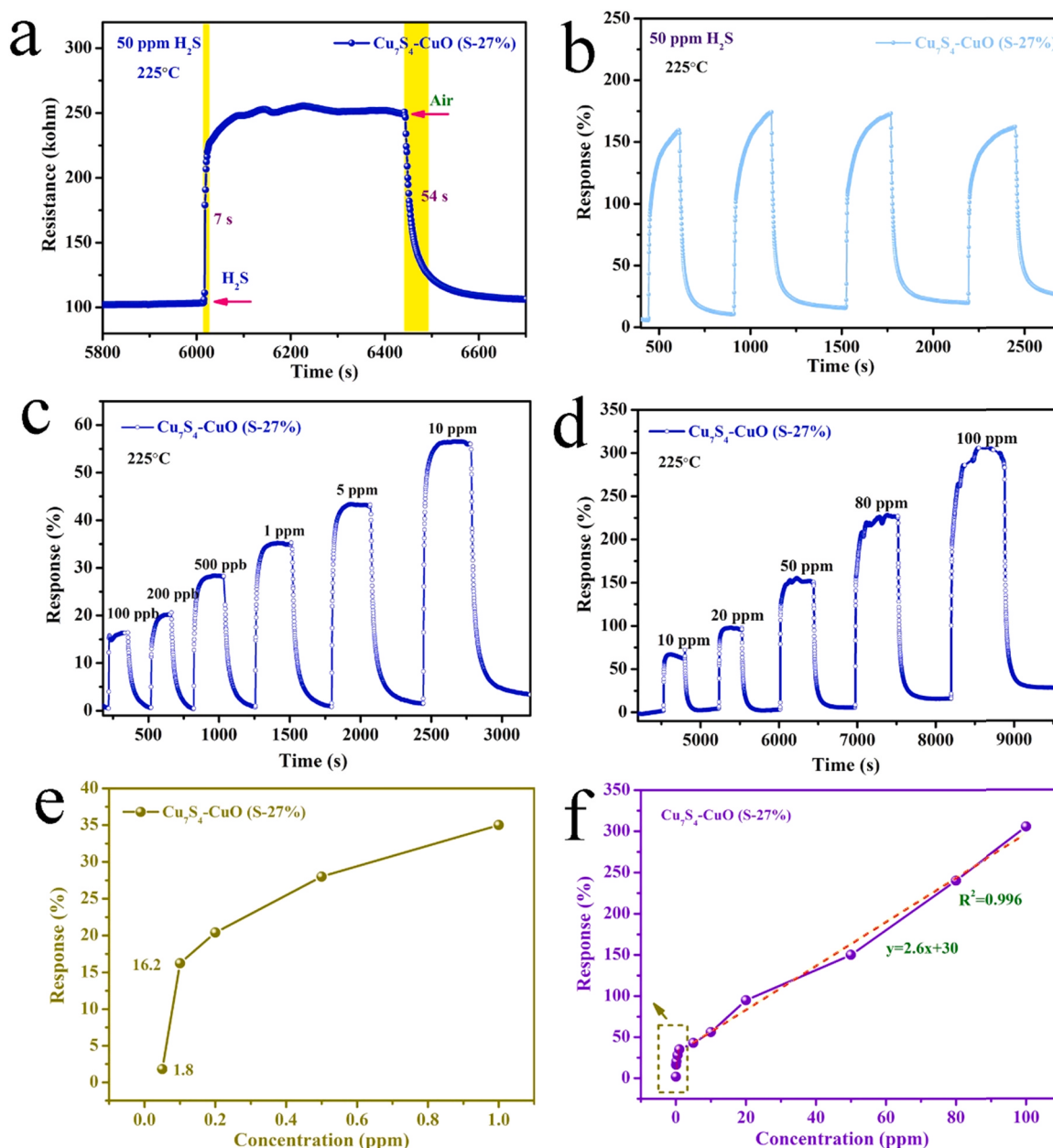
thickness of about 75 nm, and its shape was similar to that of oats, as shown in Fig. 3a. While the S-9%, S-18%, and S-27% samples were gradually assembled into microflowers with the increase of S element, which was assembled from 2D nanosheets (as shown in Fig. 3b-d). The diameter of the microflowers was about 2.6 μm. Moreover, the assembling 2D nanosheets became more tightly with S doping. For S-37%, the sample was a block composed of many small nanoparticles. Microflowers structure almost do not exist (as shown in Fig. 3e). Therefore, S doping greatly affects the micromorphology and the grain growth of CuO. However, for the pure Cu<sub>7</sub>S<sub>4</sub> sample (Fig. 3f), it was composed of agglomerates of many nanoparticles. Fig. 4a shows the TEM images of the S-27 mol% sample. The microflowers assembled from two-dimensional nanosheets can be clearly seen. The size of the S-27 mol% microflowers was about 2.6 μm, which was consistent with its SEM images. The inset in Fig. 4a was the local magnified image and high-resolution TEM (HRTEM) images (Fig. 4b) in the designated region. Clearly, two kinds (marked yellow dotted line) of lattice fringes with spacing of 0.196 (marked blue) and 0.242 nm (marked red) were clearly found in Fig. 4b, which were attributed to the CuO and Cu<sub>7</sub>S<sub>4</sub> (131) lattice planes, respectively. And these findings are consistent with the XRD results presented in Fig. 1a. Besides, the S-27 mol% composite was also investigated by STEM and elemental mapping, as shown in Fig. 4c-f. The three elements (Cu, O and S) were detected. It may be found that the signal of S element is weaker than the signals of the other two elements, which implies that the content of sulfur is less. And most signals of S were distributed in the edge area, which may be due to the accumulation of some nano-fragments. Therefore, the results obtained from the above TEM analysis further shows that the composite is composed of CuO and Cu<sub>7</sub>S<sub>4</sub>.

### 3.2. Gas-sensing performance

For the metal oxide semiconductor, the operating temperature will affect the carrier concentration, the adsorption, the desorption of gas molecules, the change of the material resistance and the gas response value [32–35]. Therefore, the first thing to do is to determine the optimal operating temperature of the gas sensor. We have studied and compared the gas sensitivity characteristics of S-0, S-9%, S-18%, S-27%, S-37%, and pure Cu<sub>7</sub>S<sub>4</sub> samples to obtain excellent gas sensors, and discussed the role of the Cu<sub>7</sub>S<sub>4</sub> in improving sensing performance.

Their response values to 10 ppm H<sub>2</sub>S are shown in Fig. 5a. It can be clearly seen that each response curve varies with temperature had a peak value, which has two phases: rising phase and falling phase. Except for the S-100%, the maximum response value of each sensor appeared at 225 °C. Among them, S-27% had the highest response value to H<sub>2</sub>S. We all know that sulfur compounds are unstable at certain temperatures. To more clearly identify the phase of the samples, we performed thermogravimetric analysis on the S-27% and pure Cu<sub>7</sub>S<sub>4</sub> samples. We found that the samples were stable at the working temperature of 225 °C, and no phase change was found. And it is worth mentioning that copper sulfide did not undergo oxidation and decomposition under the entire test conditions, which can be observed from the TG diagram, as shown in Fig. S3a-b. At the same time, we calcined the pure Cu<sub>7</sub>S<sub>4</sub> sample in air atmosphere of 225 °C for 2 h. According to the XRD characterization results, the diffraction peak of the Cu<sub>7</sub>S<sub>4</sub> phase was also observed in Fig. S3c. We can further accurately identify the pure Cu<sub>7</sub>S<sub>4</sub> sample has no phase change.

Therefore, all subsequent test temperatures were performed at 225 °C. In addition, the response values of S-0, S-9%, S-18%, S-27%, S-37% and S-100% to 10 ppm H<sub>2</sub>S gas were 39, 17.5, 23.5, 57, 34 and 0,



**Fig. 6.** (a) Dynamic response-recovery curve of the S-27% sensor to 50 ppm hydrogen sulfide. (b) the cycle curves of response to 50 ppm hydrogen sulfide at 225 °C. (c-d) the dynamic responses of S-27% sensor. (e-f) The relationship between the responses of the S-27% sensor and hydrogen sulfide concentrations (50 ppb-100 ppm).

respectively, as shown in Fig. 5a. Obviously, except for the  $\text{Cu}_7\text{S}_4$  sensor, all sensors based on  $\text{Cu}_7\text{S}_4\text{-CuO}$  had a higher response to 10 ppm hydrogen sulfide. Among them, the response value of the S-27% sensor was 1.5 times higher than that of the S-0 sensor, and it had high selectivity. In addition, except for the S-100% sensor, it can be observed from Fig. 5b that the resistance of all sensors decreased as the operating temperature increased. Because thermal excitation energy induced more carriers to the conduction band, thus leading to high conductivity and low resistance.

In practical applications, it is vital and essential for gas sensors to have good selectivity. Fig. 5c shows the responses of the S-27% sensor to 100 ppm nine target gases (methanol, ethanol, n-propanol, acetone, hydrogen sulfide, formaldehyde, isopropanol, n-butanol, carbon monoxide) at different working temperature (200–237 °C). In particular, the S-27% had the greatest response to all test gases at 225 °C. For clarity, as shown in Fig. 5d, in order to evaluate and confirm the selectivity of the

gas sensing device, we used the ratio ( $S_{\text{hydrogen sulfide}}/S_{\text{other}}$ ) of the response to  $\text{H}_2\text{S}$  ( $S_{\text{hydrogen sulfide}}$ ) and the response to a specific gas ( $S_{\text{other}}$ ). The larger the ratio, the better the selectivity of the sensor. Therefore, all the ratios are between 2 and 20 for the S-27%, and the results shows that it has good selectivity. The important parameter for evaluating sensor performance is response time and recovery time, which is defined as the time consumed to achieve 90% resistance change. Fig. 6a shows the individual response and recovery curves of S-27% to 50 ppm  $\text{H}_2\text{S}$ . It can be observed that the response-recovery time of S-27% was only 7 and 54 s, respectively, and the sensor can continue to recover to the initial resistance stable value after being removed from the test. At the same time, we found that under low-concentration (5 ppm) hydrogen sulfide gas atmosphere, the response recovery time of the S-27% was 7 and 40 s (Fig. S4), indicating that S-27% had good response-recovery characteristics. It can be explained as follows:  $\text{H}_2\text{S}$  gas molecules are easy to detect, but as the concentration increases, the

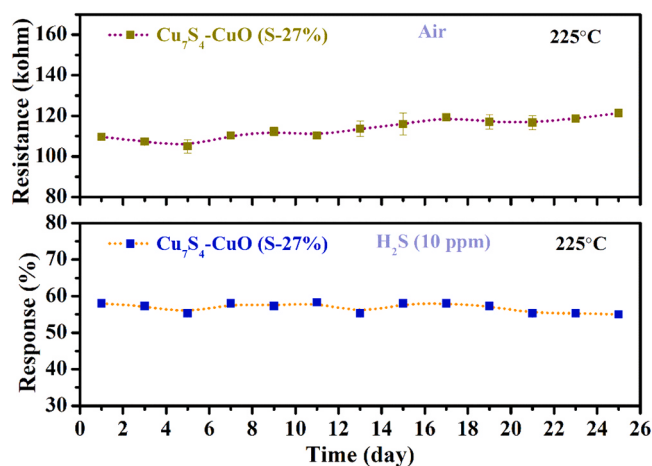


Fig. 7. Initial resistances in fresh air and responses to 10 ppm hydrogen sulfide of the S-27% sensor as a function of 25 days.

release of gas molecules becomes more difficult. It is not difficult to understand that a higher concentration of  $\text{H}_2\text{S}$  gas will accelerate the diffusion rate of gas molecules in the sensing material, but the recovery time includes the adsorption, dissociation, and ionization of oxygen molecules. Transient resistance of S-27% sensor to 50 ppm  $\text{H}_2\text{S}$  was measured repeatedly at 225 °C. As depicted in Fig. 6b, the S-27% sensor exhibited fast response and good repeatability. Therefore, from the analysis of the above results, it can be observed that the presence of an appropriate amount of copper sulfide ( $\text{Cu}_7\text{S}_4$ ) is indeed beneficial to improve and accelerate the sensing characteristics. The presence of the copper sulfide ( $\text{Cu}_7\text{S}_4$ ) improves the conductivity of the composite and facilitates the reaction with hydrogen sulfide [36,37]. And it can accelerate the reaction between active oxygen and gas molecules and improve the reaction efficiency.

The dynamic response curves of S-27% and S-0 sensors to different concentrations of  $\text{H}_2\text{S}$  gas at 225 °C are shown in Fig. 6c-d and Fig. S5a. Obviously, the response of the S-27% sensor linearly increased with the  $\text{H}_2\text{S}$  concentration throughout the measurement range and showed good response-recovery performance even in the sub-ppm-level  $\text{H}_2\text{S}$  gas. More importantly, we observed that the S-27% sensor had a wide detection range (100 ppb–100 ppm) and a lower detection limit (100 ppb–16.2), even lower detection limit (50 ppb–1.8), as shown in Fig. 6e. Notably, with the increasing concentration of  $\text{H}_2\text{S}$ , the gas responses of the S-27% sensor increased in a good linear relationship ( $R^2=0.996$ ,  $y=2.6x+30$ ) for a concentration range from 1 to 100 ppm, as shown in Fig. 6f. However, for the S-0 sensor (Fig. S5a), its gas detection range was narrower (5–100 ppm) than that of the S-27%. The S-0 sensor had poor restorability and could not recover to the initial resistance state. And the  $\text{Cu}_7\text{S}_4$  sensor does not have any response value to  $\text{H}_2\text{S}$ , as shown in Fig. S5b. For other sensors, including S-9% (5–100 ppm), S-18% (2–100 ppm), and S-37% (1–100 ppm), their detection range was narrower than that of the S-27% sensor (50 ppb–100 ppm), as shown in Fig. S5c. The results further verifies that the existence of a certain amount of the low resistance/high conductivity  $\text{Cu}_7\text{S}_4$  can promote more gas molecules to react with absorbed surface oxygen and greatly improve the sensing performance of CuO to  $\text{H}_2\text{S}$ .

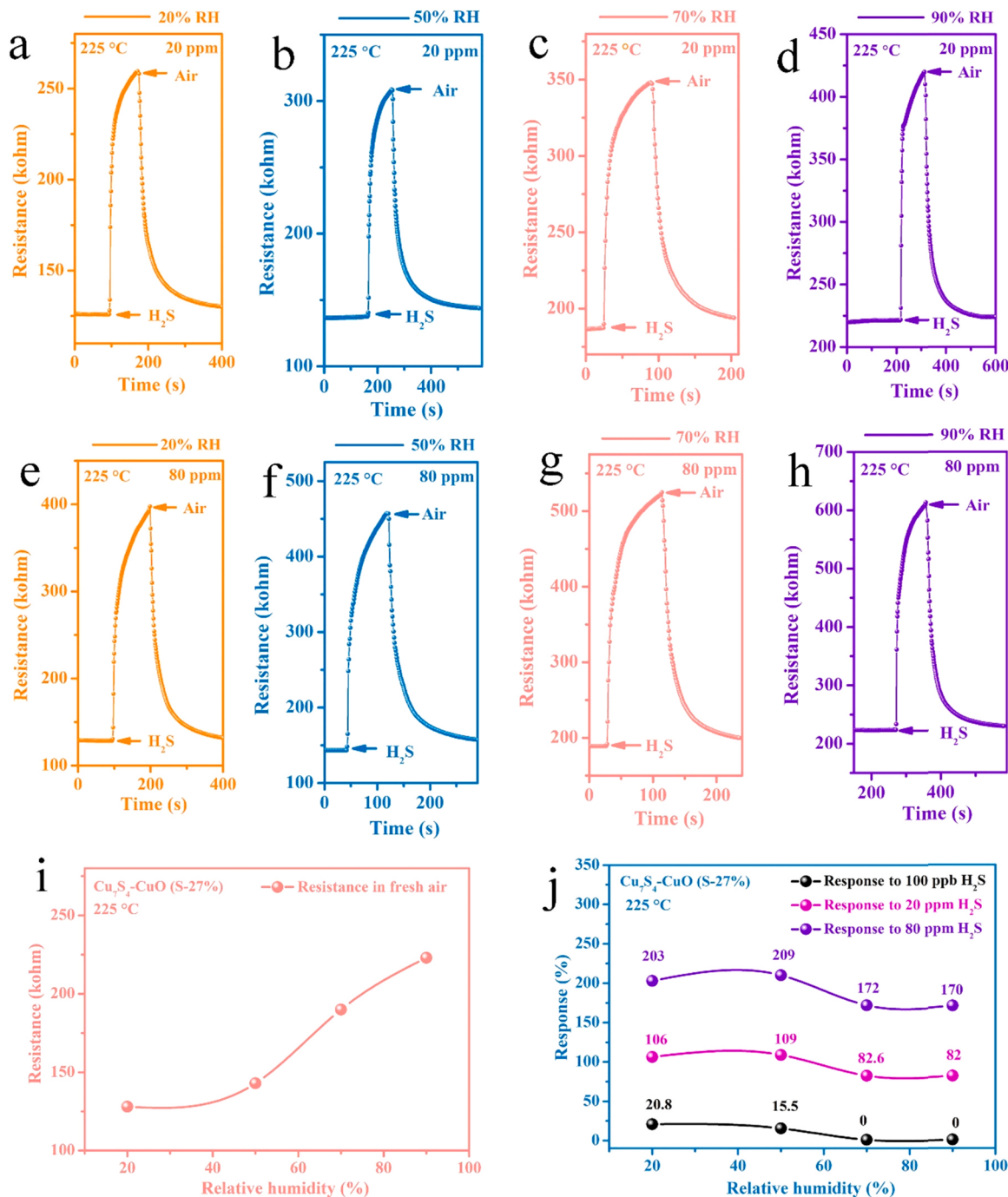
In order to further prove the stability of the gas sensor, the influence of its long-term work on the sensor must be carried out. The response to 10 ppm hydrogen sulfide and the resistance (in fresh air) value of the S-27% sensor for 25 consecutive days were measured in the laboratory condition, as shown in Fig. 7. Notably, the gas response value of the S-27% sensor fluctuated around 56 with a variation range of no more than 5.3%. It indicates that the sensor exhibits good stability. Based on the above test results,  $\text{Cu}_7\text{S}_4$ -CuO (S-27%) sensor exhibits excellent sensing performance toward  $\text{H}_2\text{S}$ .

Furthermore, for the practical application of semiconductor metal oxides, the influence of humidity on the sensing characteristics cannot be ignored. The performance test of the S-27% sensor to different concentrations of  $\text{H}_2\text{S}$  under relative humidity (RH) of 20, 50, 70, and 90 was investigated, respectively (Fig. 8a-j and Fig. S6). The schematic diagram of the humidity test device is shown in the supporting information (Fig. S7). Clearly, all dynamic response-recovery curves showed similar changes, that is, the resistance increased sharply after exposure to hydrogen sulfide, and then quickly returned to the baseline resistance again in fresh air, even at high humidity 90%. When the relative humidity (RH) was 20% and 50%, the response value of the S-27% sensor fluctuated little. However, when the relative humidity reached more than 70%, the response value of the S-27% sensor decreased. Moreover, as the humidity increased, the initial resistance of the S-27% sensor gradually increased in fresh air (Fig. 8i). This phenomenon can be explained by the pre-adsorbed oxygen species competition between the target gas and water vapor [38–41]. Although the response value of the sensor decreases as the humidity increases, it is acceptable in practical applications.

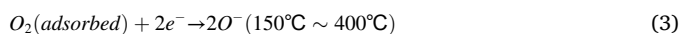
### 3.3. Gas-sensing mechanism

For metal oxide semiconductor gas sensors, the sensitive mechanism involves complex physical and chemical processes such as surface reaction, carrier transport in polycrystalline, and sensitive body utilization. It highly depends on the composition, micro-nano structure and surface interface state of the sensitive material [6,42,43]. The excellent sensing characteristics and selectivity of the S-27% sensor can be explained as follows. First of all, the theoretical basis of the gas sensor principle is that the oxygen ions adsorbed on the surface of the sensitive material undergo an oxidation-reduction reaction with the target gas molecule, which changes the sensor resistance [32,34]. At the same working temperature, the narrow band-gap semiconductor sensitive material has more thermally excited carriers and surface adsorption of oxygen [44]. According to previous theoretical research reported [45, 46] and the results obtained in this work, the band gaps of CuO and  $\text{Cu}_7\text{S}_4$ -CuO (S-27%) were about 1.98 and 1.92 eV, respectively (Fig. 9). Therefore, the surface of the  $\text{Cu}_7\text{S}_4$ -CuO (S-27%) composites has more adsorbed oxygen and target gas molecules to participate in the reaction, which improves the gas sensitivity characteristics. Furthermore, CuO and  $\text{Cu}_7\text{S}_4$  are p-type semiconductors, and the pure  $\text{Cu}_7\text{S}_4$  has higher conductivity, its resistance at 225 °C ( $\sim 0.35 \text{ K}\Omega$ ) was much lower than that of CuO material ( $\sim 150 \text{ K}\Omega$ ) as well as the resistances of the p-p heterojunctions (seen in TEM analyses) between  $\text{Cu}_7\text{S}_4$ -CuO (S-27%) composites ( $\sim 113 \text{ K}\Omega$ ). Therefore, in this two-phase tightly mixed composite material, the charge transfer between  $\text{Cu}_7\text{S}_4$  grains is selected as the main conductive channel owing to the  $\text{Cu}_7\text{S}_4$  resistance is much lower. Therefore, the proper  $\text{Cu}_7\text{S}_4$  can improve the conductivity, increase active sites of the sensing materials, and further reduce the barrier and resistance of the sensor. It is not difficult to understand that highly conductive  $\text{Cu}_7\text{S}_4$  in the composite is beneficial to shorten the response time of the sensor to ppm-level hydrogen sulfide.

When the sensor is exposed to fresh air, most oxygen molecules are adsorbed on the surface of the  $\text{Cu}_7\text{S}_4$ -CuO (S-27%) microflowers and capture the electrons out from the surface conduction band of sensitive material. At this time, the thick hole accumulation layer (HAL) was formed around the surface of the p-type  $\text{Cu}_7\text{S}_4$ , and the HAL shell acts as a main conduction channel due to its higher conductivity than the inner core (Fig. 10a) [6]. In addition, the hole depletion layer (HDL) is formed near the surface of the  $\text{Cu}_7\text{S}_4$  under the CuO particles, which acts a contrary effect on the carrier concentration from hole accumulation layer, and the resistance of sensing material decreases. In this situation, active oxygen species such as  $\text{O}_2^-$ ,  $\text{O}^-$ , and  $\text{O}^{2-}$  relying on the working temperature are produced. These procedures can be expressed by Eqs. (1–4).



**Fig. 8.** (a-h) Dynamic response curves of the  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S/Cu = 27 mol%) sensor to different concentrations of hydrogen sulfide at various humidity and their resistance relations in fresh air and (j) corresponding response value at 225 °C.



In the environment of hydrogen sulfide at 225 °C, the oxygen species were reduced to  $\text{O}^-$  species (Eq. (3)), the hydrogen sulfide gas molecules can easily react with the active oxygen species ( $\text{O}^-$ ) adsorbed on the surface of the  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S-27%) microflowlers, which releases the trapped electrons back to the conduction band of  $\text{Cu}_7\text{S}_4\text{-CuO}$ . As a result,

the hole concentration is reduced, and the conduction channel becomes thinner, especially in the area under the widened hole depletion layer (HDL), the transfer of conduction carriers is impeded in some way, which increased resistance of  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S-27%) [47,48]. That is, the narrow conduction channel in the hydrogen sulfide gas will contribute a huge change in the resistance of the  $\text{Cu}_7\text{S}_4\text{-CuO}$  (S-27%) composite material, which can explain the material's ultra-sensitive gas detection (high performance and low detection limit). These reactions are influenced by many factors including structural parameters, distribution of oxygen components, defects [49], etc. The above physical and chemical reaction processes are simply described in Eqs. (5–7) and Fig. 10b.



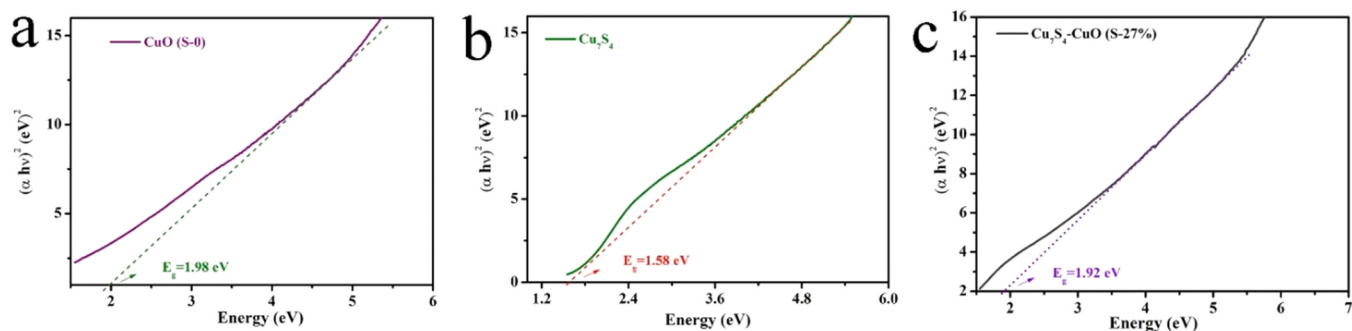


Fig. 9. (a-c) The estimated band gap energy of the pure CuO (S-0), pure Cu<sub>7</sub>S<sub>4</sub> (S-100%) and Cu<sub>7</sub>S<sub>4</sub>-CuO (S-27%), respectively.

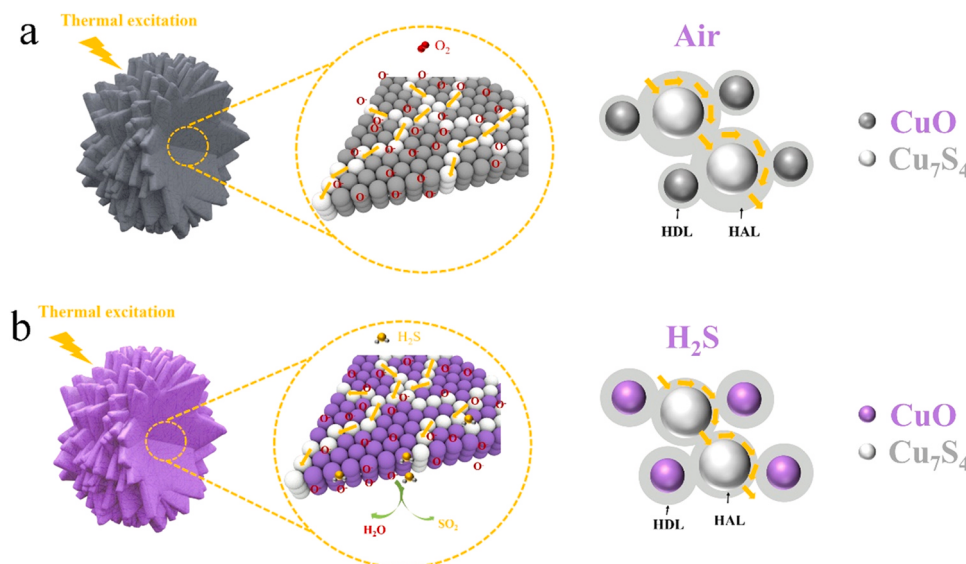


Fig. 10. Schematic illustration of electron transfer process in the sensing reaction.

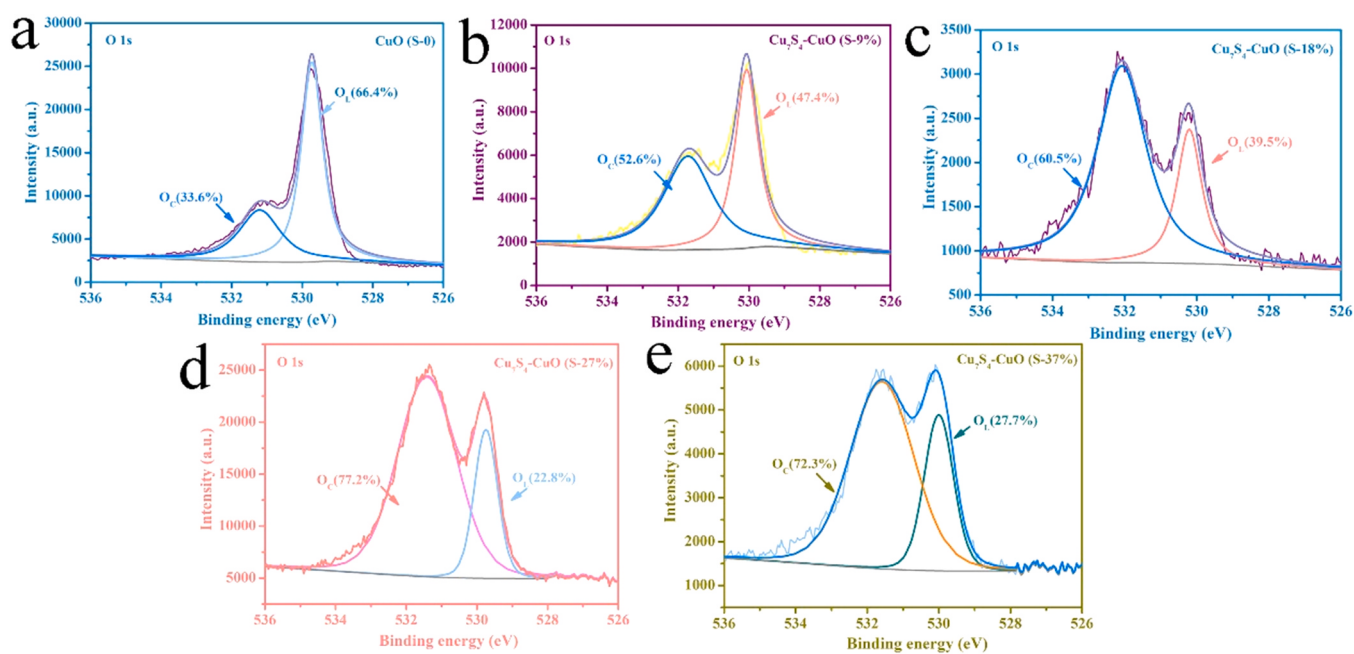


Fig. 11. (a-e) The XPS spectra of O 1s of the samples (S-0, S-9%, S-18%, S-27% and S-37%).

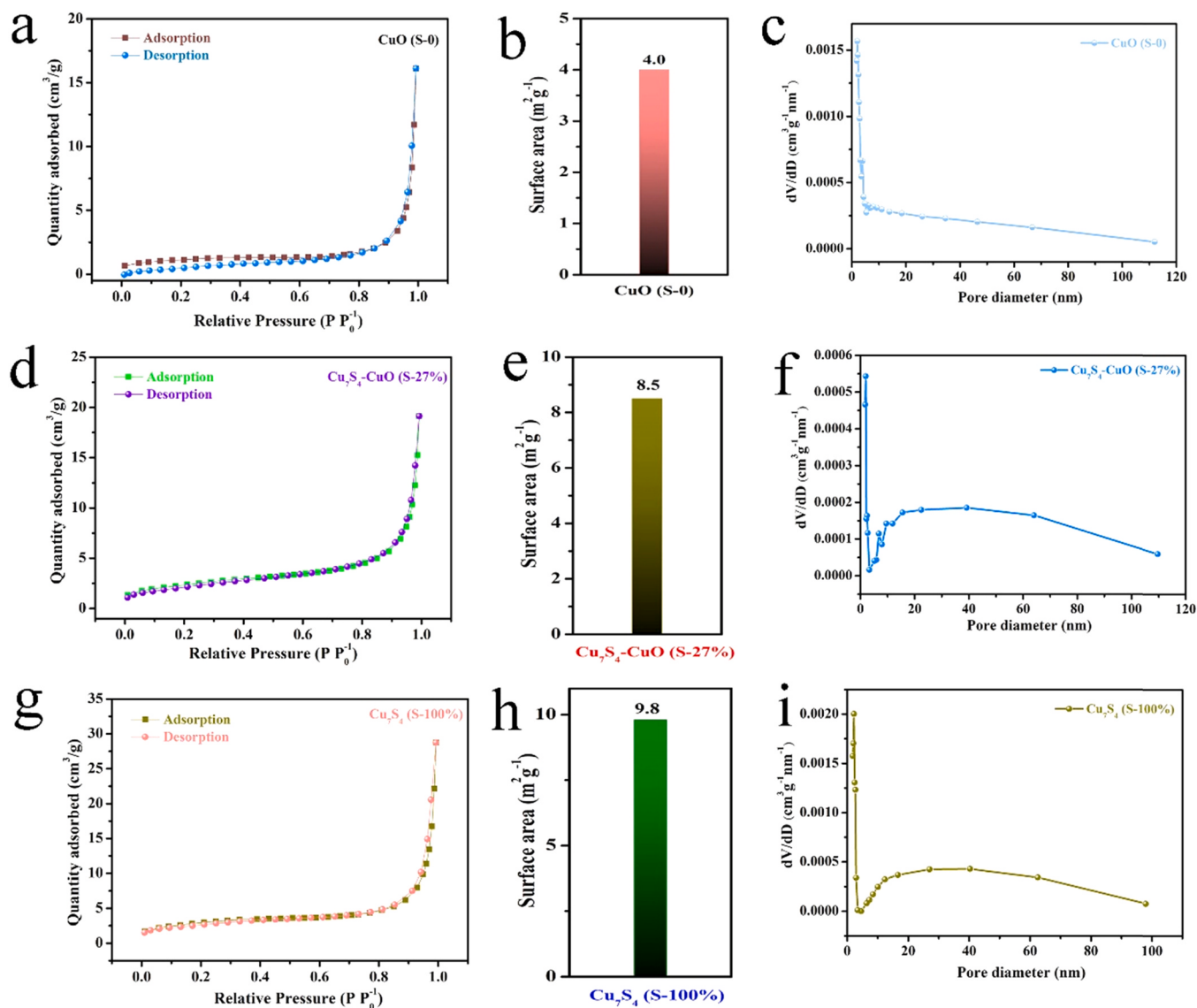
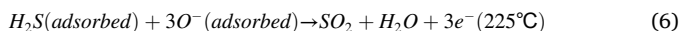


Fig. 12. N<sub>2</sub> adsorption-desorption isotherms, BET surface area and pore size distribution curve value of the S-0 (a-c), S-27% (d-f) and S-100% (g-i).



Additionally, the O 1 s peak of all samples is displayed in Fig. 11 a–e, respectively. The asymmetric O 1 s peaks of the S-27% can be coherently decomposed into lattice oxygen species (O<sub>L</sub>) and chemisorbed oxygen (O<sub>C</sub>) with binding energies about  $529.7 \pm 0.1$  and  $531.5 \pm 0.1$  eV, respectively [50]. The amount of chemisorbed oxygen of the S-0, S-9%, S-18%, S-27% and S-37% were 33.6%, 52.6%, 60.5%, 77.2% and 72.3%, respectively. It can be observed that as the content of Cu<sub>7</sub>S<sub>4</sub> increased, the content of adsorbed oxygen on the surface of the sensing material increased, and the S-27% sensor had the largest surface adsorbed oxygen (77.2%). It can be explained again that the presence of an appropriate amount of low resistance Cu<sub>7</sub>S<sub>4</sub> can improved the gas sensitivity of the material and effectively shorten the response time. And it meant that more active sites were available for more gas reactions to occur in the S-27% at the same time. Therefore, the change of oxygen composition caused by Cu<sub>7</sub>S<sub>4</sub> can greatly promote the H<sub>2</sub>S sensing performance of the material. The synergistic catalysis between p-type semiconductor CuO and non-stoichiometric p-type semiconductor Cu<sub>7</sub>S<sub>4</sub> (Cu<sub>1.75</sub>S) promotes specific sensing reactions [51]. This is due to the p-p heterojunction

formed by Cu<sub>7</sub>S<sub>4</sub> and CuO, which can increase the adsorbed oxygen and active sites on the surface.

Additionally, the S-27% sample itself had special structural advantages. N<sub>2</sub> adsorption-desorption curves and pore size distributions of the S-0%, S-9%, S-18%, S-27%, S-37%, and pure Cu<sub>7</sub>S<sub>4</sub>, are shown in Figs. 12 and S8. As shown in Fig. 12 a–i, it can be observed that all the samples were mesoporous structure. The mesoporous structure with a large surface area also has a positive effect on the sensing performance [52]. The larger specific surface area ( $8.5 \text{ m}^2 \text{ g}^{-1}$ ) was founded in the S-27% materials, which was much higher than those of the S-0 ( $4.0 \text{ m}^2 \text{ g}^{-1}$ ). This structure can provide sufficient active sites to promote the adsorption of oxygen and the interaction between the oxygen species and the target gas [53]. The above results are consistent with the morphological evolution of the sample. From the analysis of the SEM results, the microflowers assembled from 2D nanosheets can avoid agglomeration and increase the specific surface area. Both the large surface area and morphology of sensing material have positive effects on the gas reaction and highly enhanced the sensing performance of the S-27% sample in some way.

## 4. Conclusions

In this paper, the Cu<sub>7</sub>S<sub>4</sub>-CuO composites were synthesized by hydrothermal method, and a series of characterization and gas sensing performance tests were carried out. The gas sensing test revealed that the sensor based on Cu<sub>7</sub>S<sub>4</sub>-CuO (S-27%) microstructure showed enhanced selectivity and sensitivity to H<sub>2</sub>S at the operating temperature of 225 °C. More importantly, the ppb-level detection limit (100 ppb-16.2) indicated the potential application on the trace hydrogen sulfide detection. Such behaviors could be attributed to the existence of p-p heterojunctions, the large BET surface areas, and the synergistic combination between Cu<sub>7</sub>S<sub>4</sub> and CuO. In addition, the sensor showed reliable long-term stability. The gas sensor fabricated in this work provides an efficient and viable strategy for building gas sensors with high performance.

## CRediT authorship contribution statement

**Na Wang**, Conception, Design, Analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Rongrong Jin**, Analysis, Writing – review & editing. **Yue Zhou**, Methodology, Writing – review & editing. **Liupeng Zhao**, Methodology, Supervision, Writing – review & editing. **Tianshuang Wang**, Methodology, Writing – review & editing. **Lianjing Zhao**, Methodology, Writing – review & editing. **Fangmeng Liu**, Methodology, Writing – review & editing. **Xu Yan**, Methodology, Writing – review & editing. **Chenguang Wang**, Methodology, Writing – review & editing. **Peng Sun**, Conception, Analysis, Methodology, Supervision, Writing – review & editing. **Geyu Lu**, Conception, Analysis, Methodology, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2021.130847](https://doi.org/10.1016/j.snb.2021.130847).

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