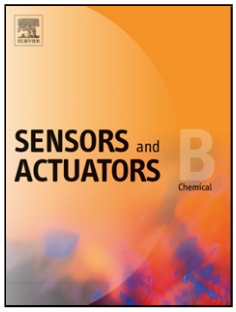

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High humidity enhanced surface acoustic wave (SAW) H_2S sensors based on sol–gel CuO films

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Highlights

- The sensor can detect H_2S gas with a concentration as low as 0.5 ppm.
- The frequency shift of sensor is derived from the change of mass loading on films.
- The responses became much faster and stronger with the increase of RH.

Abstract

Surface acoustic wave (SAW) sensors based on sol–gel processed porous and nanoparticulate CuO films were explored for H_2S detection operated at room temperature. The SAW sensor showed a negative frequency shift when exposed to H_2S gas, due to the mass loading effect on the sensitive CuO film. It has a high sensitivity of H_2S, a detection limit of 500 ppb and a good selectivity to H_2S gas compared with H_2, C_2H_5OH, acetone, NH_3, CO, NO, NO_2 gases. Relative humidity (RH) was identified to have a critical influence on the sensing performance of the sensor. The responses became much faster and stronger with the increase of RH. The significant enhancement in the sensing performance is attributed to that the chemical reaction between H_2S and CuO is hindered and the physical adsorption of CuO to H_2S is enhanced.

Key words: SAW sensors, H_2S, CuO, physical adsorption, RH.

1. Introduction

Precision detection of hazardous gases (such as NH_3, NO, NO_2, CO, H_2S) has become crucial in recent years due to wide applications of explosives, combustible, flammable and toxic gases in industry, military and daily activities [1-5]. Among these toxic gases, hydrogen sulfide (H_2S), a colorless gas with foul odor like rotten eggs, is generally produced in decomposition of organic matters, human and animal's wastes, food processing, cooking stove, craft paper mills, tanneries, oil refineries and other industrial activities [6-10]. It is one of the most highly toxic gases, which can irritate eyes, skin and mucous membranes, as well as damage nervous systems of human-beings even at low concentrations [11, 12]. Therefore, the detection and monitoring of very low concentrations of H_2S in environment is highly crucial and required.

Compared to other commonly used H_2S gas sensors such as semiconductor and electrochemical sensors, surface acoustic wave (SAW) sensors have advantages of high sensitivity, good stabilization, high selectivity and low cost, as well as wireless control [13]. A typical SAW gas sensor is essentially an oscillator consisted of an amplifier and a resonator coated with a sensitive film [14, 15]. The wave energy is mainly concentrated on the surface of SAW devices within one or two wavelengths, therefore, any perturbations or changes on sensitive film, such as mass loading, conductivity, temperature and pressure, etc., will have significant impact on the propagation of waves, thus leading to frequency shift of SAW sensors. Therefore, sensitive films are the essential component of SAW sensors.

Previous studies have shown that cupric oxide (CuO) is an excellent candidate for H_2S sensing [17-19]. For example, Sonia et al. fabricated a H_2S semiconductor sensor based on CuO thin films, which has a response of 37.7 to 10 ppm H_2S [20]. Hu al. fabricated an H_2S semiconductor sensor based on Pd-doped CuO nano-flowers, which had a response of 63.8 to 1 ppm H_2S [21]. Owing to its extraordinary adsorptive capability to H_2S [22-24], CuO has ability to capture H_2S molecules from ambient environment (e.g., through physical adsorption) and then further react with these molecules (through chemical reactions). These reactions generate CuS or Cu_2S on the surface of CuO particles [25]. Both these two generated phases may change physical and chemical properties of CuO, such as its mass, elastic modulus and electrical conductivity, thus the CuO film sensing layer is suitable for SAW H_2S gas sensors.

In this study, the porous CuO films are prepared using a sol-gel method for H_2S gas sensing. In addition, ambient relative humidity (RH) is found to have a significant impact on the sensing performance of sensors and the mechanisms are investigated.

2. Experimental details

The SAW resonator was fabricated on a ST-cut ($42^{\circ}\ 75'$) quartz substrate, consisted of input and output interdigital transducers (IDTs, 30 pairs each other) and 100 pairs of reflection gratings. The IDTs with a periodicity of 16 μm were formed using a conventional lift-off method with a sputtered 200 nm aluminum layer. The aperture of the IDTs was 3 mm.

CuO sensitive films were prepared using a sol-gel process. Following the procedure [26], copper acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$) was dissolved into 2-methoxyethanol–monoethanolamine (MEA) solutions with a concentration of 0.25 mol/L. The molar ratio of the MEA to Cu was 2:1. The resultant solutions were stirred at room temperature for half an hour to yield homogeneous sols, which were then aged for 12 hours. After that, the sols were coated onto the entire surface of the SAW resonators at a speed of 8000 rpm/min for 25s. The coated SAW resonators were immediately heated at 250 ^{o}C for 5 min. After repeating this procedure for several times, the SAW resonators were annealed at a temperature of 400 ^{o}C for 2 hours.

The coated SAW resonator was connected to the oscillator circuits to form a SAW sensor as shown in Fig. 1. The sensor was mounted inside a testing chamber with a volume of 20 L in an ambient environment at room temperature. The concentration of H_2S in the chamber was controlled by injecting diluted H_2S gas with different concentrations through a high-precision syringe. The frequency shift, which indicated the responses of sensors, was measured using a frequency counter (Agilent 53210A). Electrical measurements for sensing films were conducted using a source

meter (Keithley 2400). A Bruker D8 X-ray diffractometer was employed to characterize the crystallinity of the prepared CuO films. Micro-Raman spectra of the CuO film were measured using a WITec Raman Spectrometer. A field-emission scanning electron microscopy (FEI Inspect F) was used to characterize the morphology of the sensitive films.

3. Results and discussion

3.1 Structural characterization

X-ray diffraction (XRD) result of CuO powders is shown in Fig. 2. The patterns were recorded with a Bruke D8 Advance powder X-ray diffractometer with Cu Kα (λ = 0.15406 nm). The powders were obtained by drying the CuO sols for 2 hours at 400 ^{o}C, and then put on glass for XRD analysis. The XRD pattern of the CuO was identified as monoclinic CuO (C2/c space group, JCPDS #48-1548). The peaks at lattice planes (110), (11-1)/(002), (111)/(200), (11-2), (20-2), (112), (020), (021), (202), (11-3), (022), (31-1)/(311), (113)/(220), (311), (004)/(22-2) are located at 2θ = 32.5 ^{o}, 35.5^{o}, 38.7^{o}, 46.2^{o}, 48.7^{o}, 51.3^{o}, 53.5^{o}, 56.7 ^{o}, 58.1^{o}, 61.6^{o}, 65.8 ^{o}, 66.4^{o}, 67.9^{o}, 72.4^{o}, 75.0^{o}, respectively. No other obvious peaks for impurity were found, indicating the high purity of the sensitive film. Estimated based on the Debye-Scherrer's formula, the average size of CuO particles is about 23.6 nm.

The top view and cross-section SEM images of sensitive film are shown in Fig. 3. The film is uniform and continuous with an average film thickness of 53.91 nm but with a porous surface. The average size of nanoparticles of the film is about 25 nm, which was consistent with the value estimated from XRD result.

Raman spectra of the sensitive films before and after exposure to H_2S are shown in Fig. 4, in which the peaks at 292 cm^{-1}, 339 cm^{-1} and 626 cm^{-1} are corresponding to A_g (296 cm^{-1}), $B_g^{(1)}$ (346 cm^{-1}), and $B_g^{(2)}$ (636cm^{-1}) modes of CuO crystals [27], respectively. The results in Fig. 4a, 4b and 4d demonstrate that the films before and after, exposure to 0.5 ppm H_2S at RH = 30% and 50 ppm H_2S at RH = 75% are all

consisted of pure CuO. In Fig. 4c, a sharp peak at 474 cm^{-1} can be observed, which is assigned to the spectroscopic feature of CuS [28-32] and there are no CuO peaks observed in this spectrum, indicating that CuO has changed to CuS through the chemical reaction between H_2S and CuO when the sensitive film was exposed to 50 ppm H_2S at RH = 30%.

3.2 **H_2S gas sensing performance**

Responses of the SAW sensor to 50 ppm H_2S tested under RH = 30% at 25 °C are shown in Fig. 5. The sensor exhibits a negative frequency shift, which could be attributed to the mass loading effect, elastic loading effect and electric loading effect since the temperature and pressure are kept at constant values [16]. Mass loading, elastic loading and electric effect refer to the change in mass, elasticity and resistance of the sensitive film respectively. From the previous studies [33-34], CuO can capture H_2S molecules from ambient environment (through physical adsorption), owing to extraordinary adsorptive capability of CuO to H_2S and chemical reaction between them will generate CuS on the surface of CuO particles (through chemical reaction shown in equation 1). Both the physical adsorption and chemical reaction can increase mass loading effect on the sensitive film of CuO since CuS is heavier than CuO Chemical reaction can also lead to the change in resistance of the sensitive film. Therefore, the frequency shift may be caused by both mass loading and electric loading.

$$H_2S(ads) + CuO \rightarrow CuS + H_2O \quad (1)$$

The mass loading on the film can change the central frequency (Δf) of a SAW sensor as follows [35],

$$\Delta f = (\kappa_1 + \kappa_2)\, f_0^{\,2} \Delta m \tag{2}$$

where $\kappa_1 = -8.7 \times 10^{-8}$ $m^2 s\ kg^{-1}$ and $\kappa_2 = -3.9 \times 10^{-9}$ $m^2 s\ kg^{-1}$ are material constants of the substrate S-T cut quartz; $f_0 = 198.98$ MHz is the central frequency of SAW resonators; Δm is the mass loading on the SAW device. Due to the fact that both κ_1 and κ_2 values are negative, the increasing mass loading will cause a negative frequency shift.

The relationship between the shift of central frequency (Δf) versus the surface conductivity (σ_s) of the film can be described as follows [36];

$$\frac{\Delta f}{f_0} = \frac{\Delta v}{v_0} \approx -\frac{K^2}{2} \frac{\sigma_s^2}{\sigma_s^2 + v_0^2 C_s^2} \tag{3}$$

where $C_s = 0.5$ pF cm^{-1}, $K^2 = 0.0011$, $v_0 = 3158$ m s^{-1} and $\sigma_s = 1/\rho$ are the surface capacitance values per unit length, the electromechanical coefficient, the undisturbed SAW velocity of quartz substrate and the sheet conductivity of the films in air, respectively. Here the central frequency of SAW resonators is $f_0 = 198.98$ MHz is, $\sigma_s = 3.0 \times 10^{-6}$ S m^{-1} was measured by a four probe method using Keithley 2400. The acoustoelectric parameter ($\xi = \sigma_s \cdot (v_0 C_s)^{-1}$) of sensitive film can be calculated and the data of frequency shift vs the acoustoelectric parameters obtained from Eq. (3) for coated SAW devices are shown in Fig. 6. The original acoustoelectric parameter (the original condition) is located at point 1, where $\Delta f_1 / f_0 = -5.4848 \times 10^{-4}$. After the film exposed to 50 ppm H_2S, the sheet conductivity of the film is decreased. As a result, the acoustoelectric parameter is shifted to point 2, where $\Delta f_2 / f_0 = -5.4763 \times 10^{-4}$.

Thus, the frequency shift caused by electric loading was calculated to be $\Delta f = (\Delta f_2 - \Delta f_1) = -(5.4763\times10^{-4} - 5.4862\times10^{-4})\times f_0 = -197.0$ Hz, which is much lower than the measured frequency shift. It indicates that the frequency shift was mainly contributed by the increased mass loading caused by the physical adsorption and the chemical reaction.

To further verify how these two effects contribute to the negative frequency shift under different circumstance, the sensor was tested with 0.5-50 ppm H_2S with RH = 30% at 25 °C. As shown in Fig. 7a and Fig. 7b, the frequency shift was -1200 Hz when the concentration of H_2S was 500 ppb and became much larger with the increase of the concentration of H_2S. With the concentration of H_2S up to 20 ppm, the frequency shift was ~ -15 kHz. The response and recovery times with error bars are shown in Fig. 7c. The response and recovery times are relatively shorter at lower concentrations but increased with the increase of H_2S concentration. It should be noted that the sensor can't be fully recovered with the concentration of H_2S, higher than 10 ppm. The increasing responses and recovery times at higher H_2S concentrations indicates that the sensing mechanism of CuO to H_2S with different concentrations may be different. Fig. 7d shows the response (frequency shift) over the concentration, together with error bars. The graph is not close to a linear curve. Besides, Raman spectra of the sensitive film (see Section 3.1) reveal that (1) no apparent CuS was obtained on the sensitive film after exposure to H_2S at low concentrations; while (2) CuS was clearly presented at higher concentrations. Therefore, it can be concluded that; (1) reaction 1 can only happen at high

concentrations and the responses of the sensor to H_2S with low concentrations are mainly caused by physical adsorption, 2) response caused by physical adsorption is much faster than that caused by chemical reaction. Based on this analysis result, it can be proposed that it is possible to accelerate the response and recovery of the sensor by enhancing the physical adsorption and hindering the chemical reaction at the same time.

In order to prove this assumption, we have performed experiments, where the response of sensor was tested under different environments with different RH values. The reason can be explained in proceeding context; i.e. If the water is the product of reaction (1), the value of RH will have a significant impact on the sensing property of the SAW sensor. We can see that with a high RH value, chemical reaction (1) may be hindered even the concentration of H_2S is high, since there is excess H_2O on the surface of CuO.

Fig. 8 shows the experimental results, indicating the response becomes obviously stronger and faster with the increase of the RH. Moreover, Raman spectrum analysis was also performed and the results revealed that no CuS was produced on the sensitive film at a high RH level, even if the film was exposed to 50 ppm H_2S, based on these results, it can be concluded that; (1) reaction 1 was hindered at higher RH value; and (2) physical adsorption was enhanced at a higher RH value. From literature, the adsorption capacity of CuO to H_2S is stronger than that of CuS [24, 37-39]. Besides, the CuS on the surface of the CuO particles will act as a barrier and reduce the direct contact between H_2S gas and CuO particles. With less CuS on the film (less

chance of chemical reaction occurrance), more CuO particles are able to contact the H_2S gas and the adsorption capacity of the CuO film to H_2S is stronger.

The SAW sensor was tested with 0.5 ppm-10 ppm H_2S with RH= 75 % at 25 °C and the result was shown in Fig. 9a. The response and recovery time are gradually increased with the increase of H_2S concentration. Compared with the response values obtained at RH = 30%, those at 75% RH are much stronger, the response and recovery times at RH = 75% are much shorter. Fig. 9c shows the response (frequency shift) over the concentration, together with error bars. The image is very close to a linear curve. These results confirm further, the influence of RH on the response. As a result, the SAW sensor based on CuO has a stronger and faster response to H_2S at a high RH, indicating that this sensor is promising for the application of detection of H_2S at a high RH.

The selectivity of the sensor was also investigated by exposing the sensor in the chamber with RH = 75% at 25 °C and then injected with 50 ppm of H_2, C_2H_5OH, acetone, NH_3, CO, NO, NO_2 and ethyl-mercaptan and 10 ppm of H_2S successively into the chamber. The whole results are shown in Fig. 10a and its magnification is shown in Fig. 10b. It is obvious that the response to H_2, C_2H_5OH, acetone, NH_3, CO, NO, NO_2 and ethyl-mercaptan are much weaker compared to that of H_2S, signifying its excellent selectivity. This excellent selectivity is attributed to the extraordinary adsorptive capability of CuO to H_2S.

The stability of the SAW sensor was tested with exposure to 2 ppm H_2S in the environment with 75% RH for 4 successive cycles. As shown in Fig. 11, the sensor

shows similar responses in four successive cycles, demonstrating that the sensors have a good stability. The response time and recovery time are slightly different, which is attributed to the operating error. In order to see the shifts of base lines and magnitudes, we did 15 consecutive experiments of 2 ppm and 10 ppm at RH=75%. The results are shown in Fig.12. The fluctuations of base line are smaller than 300 Hz. The fluctuation of frequency shift is less than 5% for the fifteen consecutive tests, indicating good reproducibility.

3. Conclusions

In this work, we investigated a SAW H_2S gas sensor based on porous CuO films, prepared using sol–gel method at room temperature. The CuO films have a porous surface composed of a lot of nanoparticles having an average size of about 25 nm. The SAW sensor showed negative frequency shifts toward H_2S gas, caused by the increase of mass loading. The SAW sensor exhibited better sensing performance in the environment with a higher RH, since the chemical reaction between H_2S and CuO is hindered. The sensor showed a good selectivity towards H_2S at higher RH values at room temperature.

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Figure caption

Fig. 1. (a) Schematic diagram of a SAW sensor; (b) Top view of the SAW sensor sample.

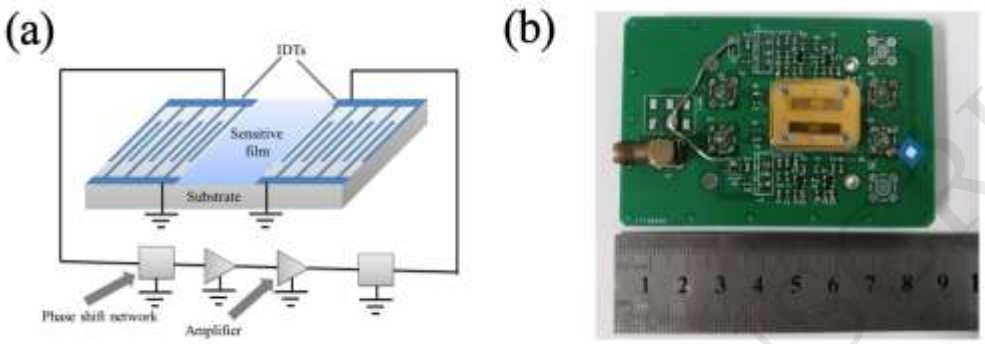


Fig. 2. XRD patterns of as-prepared CuO powders.

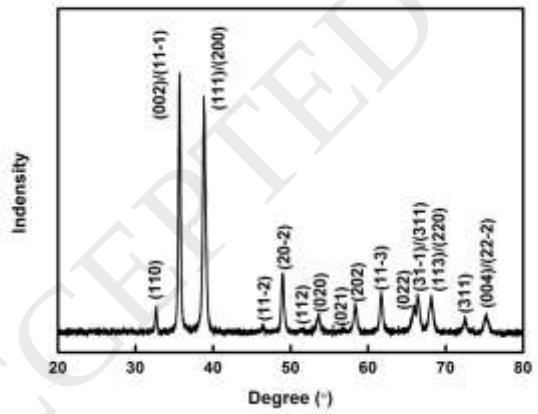


Fig. 3. SEM image of top-view and cross-section view of as-synthesized CuO film.

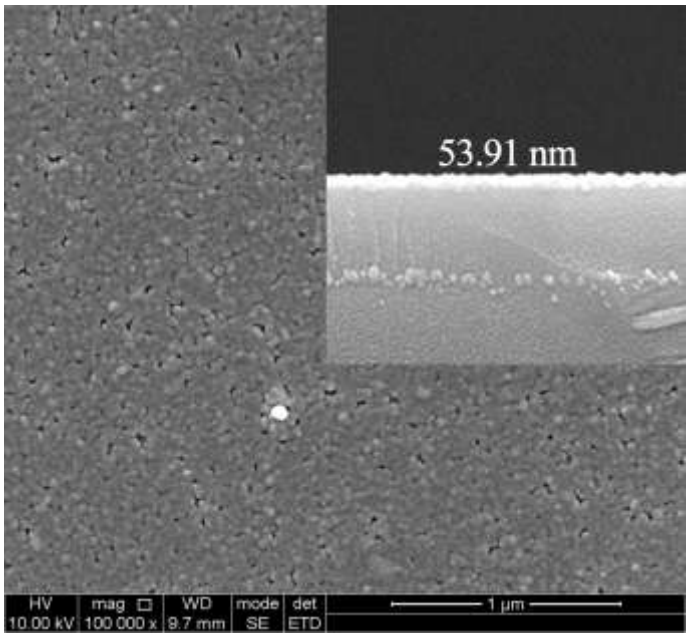


Fig. 4. Raman spectra of CuO sensitive film: (a) the original CuO film; (b) film surface exposed to 0.5 ppm H_2S at RH = 30%; (c) film surface exposed to 50 ppm H_2S at RH = 30%; (d) film surface exposed to 50 ppm H_2S at RH = 75%.

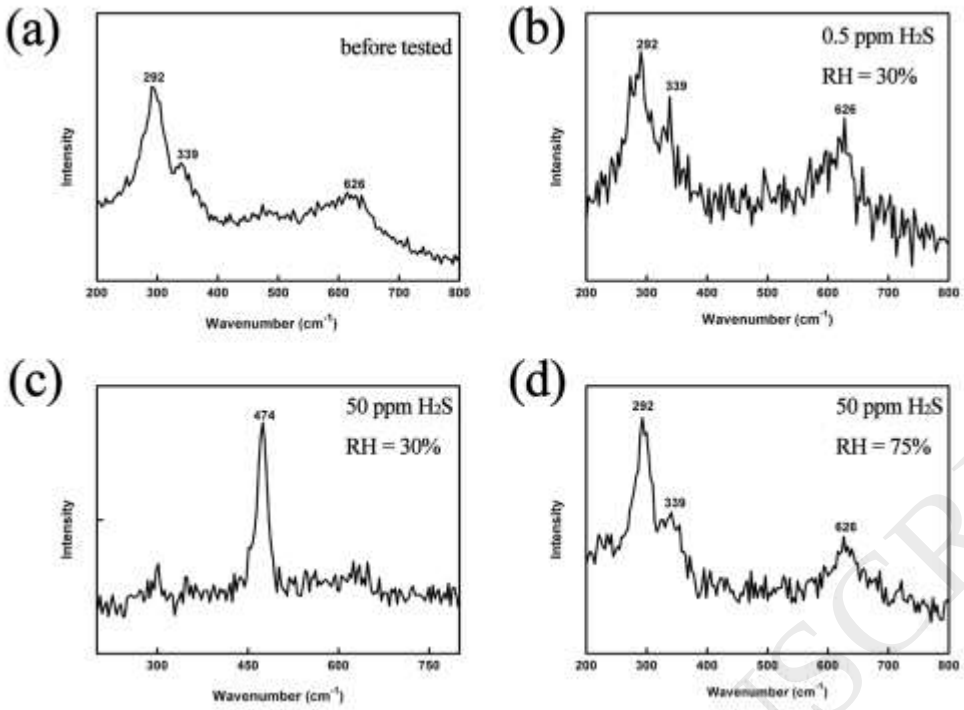


Fig. 5. Responses of the SAW sensor to 50 ppm H_2S with RH = 30% at 25 °C.

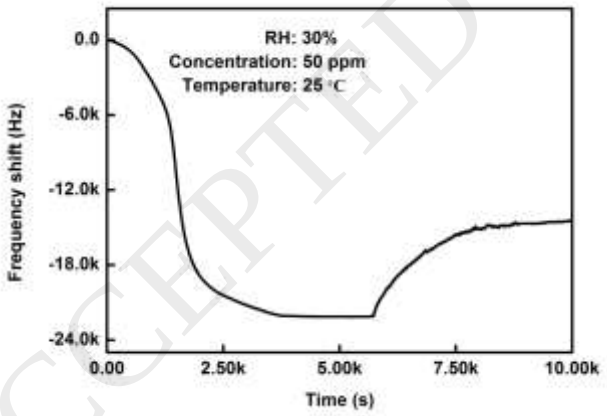


Fig. 6. Plot of frequency changes versus acoustoelectric parameter ($\xi = \sigma_s \cdot (v_0 C_s)^{-1}$).

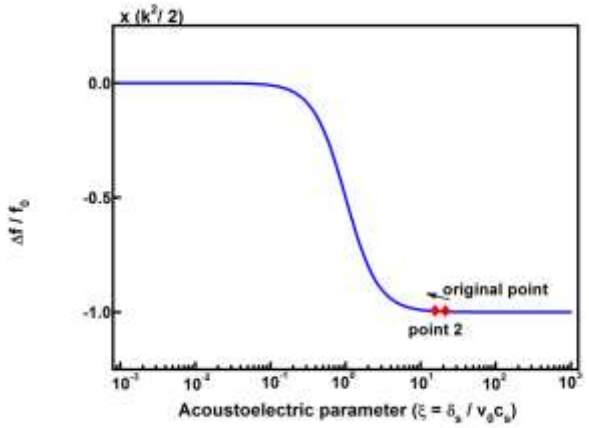


Fig. 7. (a) Dynamic responses of the sensor to 0.5-10 ppm H_2S with RH = 30% at 25 °C; (b) The responses of the sensor to 20 ppm and 50 ppm H_2S; (c) the response and recovery time versus the H_2S concentration.

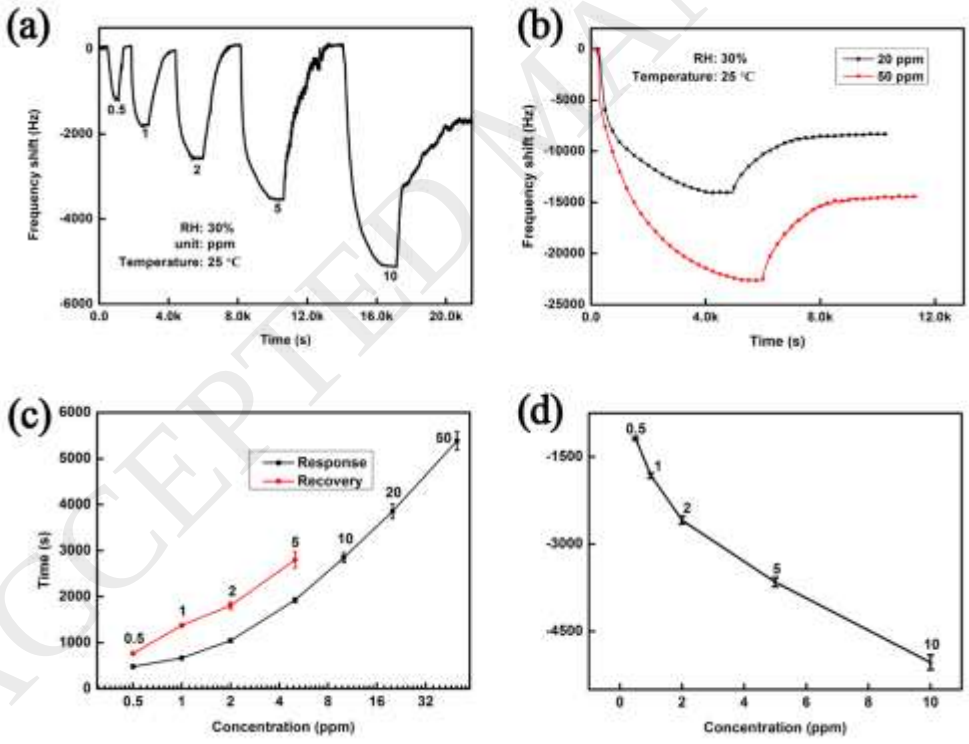


Fig. 8. (a) Dynamic response of the sensor to 10 ppm H_2S with various RH at 25 °C; (b) the response and recovery time versus the RH.

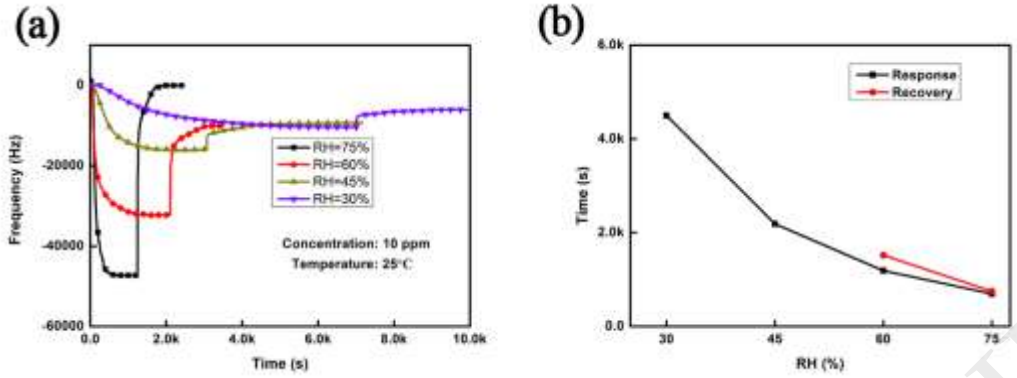


Fig.9. (a) Dynamic response of the sensor to H_2S of various concentrations with RH = 75% at 25 °C; (b) the response and recovery time versus the concentration.

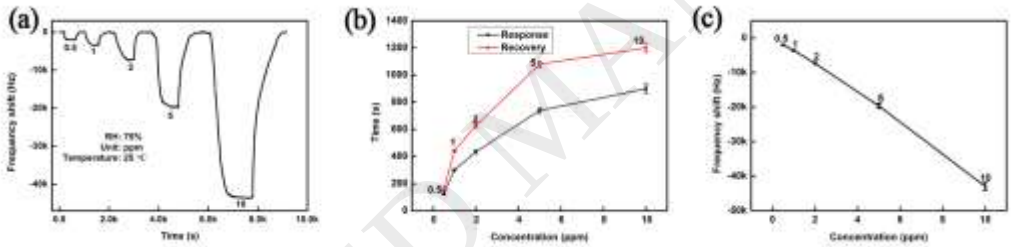


Fig. 10. (a) Response under different gas with RH=75% at 25 °C; (b) the magnification of (a).

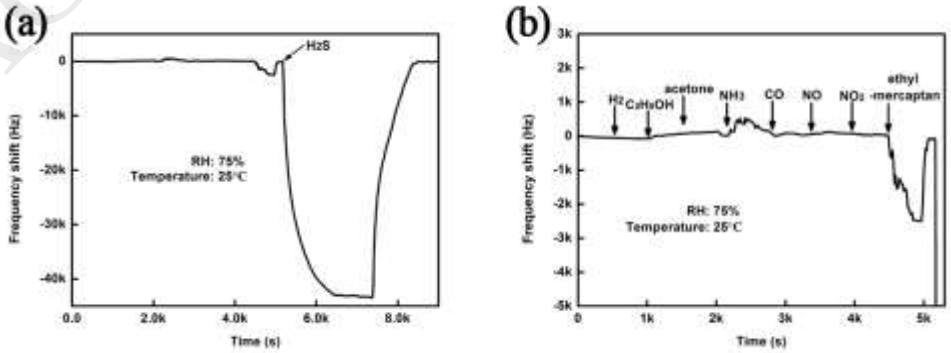


Fig. 11. Short term stability testing by exposing the sensors to 2 ppm H_2S with RH=75% at 25 °C for a few cycles.

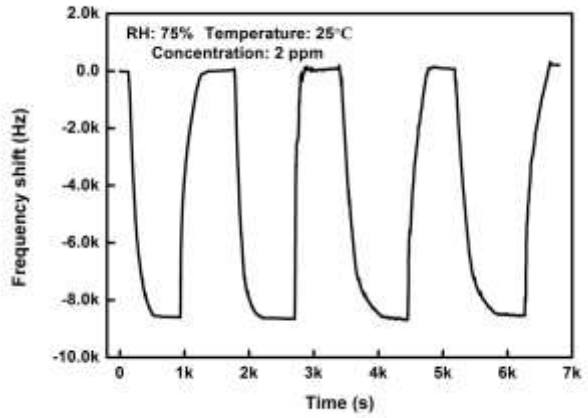
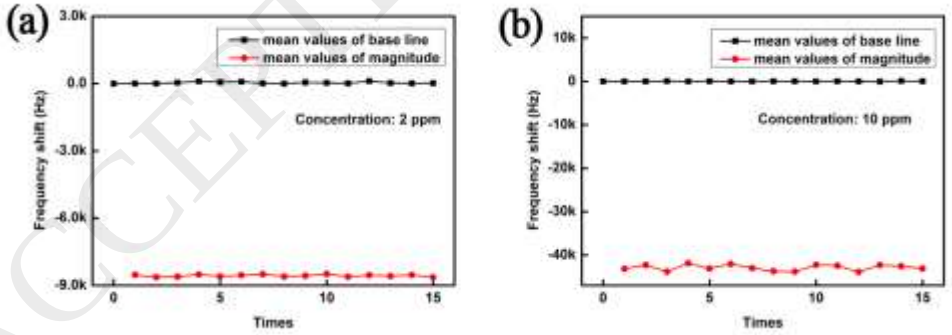


Fig. 12. The frequency shifts of base line and magnitude in 15 consecutive experiments of (a) 2 ppm and (b) 10 ppm at RH=75%



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