



## ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> composites for chloroform detection



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### ABSTRACT

In this work, ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> composites were prepared via a simple coprecipitation and a hydrothermal method followed by a calcination process. The as-prepared composites were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), Inductively Coupled Plasma (ICP), X-ray photoelectron spectroscopy (XPS) etc. Moreover, gas sensors based on ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> were fabricated. It revealed that the sensor with certain metal ratio exhibited a fast and remarkable response to chloroform and was able to detect low concentration of chloroform down to 1 ppm in 20 s. The gas sensing mechanism was also discussed.

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### 1. Introduction

Chloroform, a kind of chlorinated hydrocarbon, is a sweet-smelling, colorless, specific smell and volatile liquid. It is mainly introduced to the environment from its use as solvent in paints, adhesives, color-removers, degreasers and so on [1]. It is worth noting that inhaling or absorbing chloroform can cause acute poisoning and damage to livers. Moreover, when it comes into oxygen under lights, it will produce highly toxic phosgene and HCl. Therefore, the task to detect chloroform as quickly and accurately as possible, especially in very low concentrations, to alert people to the extent of out-door and in-door inhalation of noxious pollutants is of great importance. For now, most techniques for the determination of chloroform are instrumental methods, such as laser-induced fluorescence [2,3], solid phase micro-extraction [4] and mid-infrared sensor technology [5], whereas they all detect chloroform in solution and there is relatively less reports in gas detection. Furthermore, the above instruments are often expensive and are not portable. For solving this problem, the portable gas sensors have emerged for the routine examination of toxic or harmful gases. Among the gas sensing candidates, metal oxide materials such as ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, In<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, have been widely fabricated into sensors and studied in gas-sensing application due to

their simple processing, low cost and convenient testing, etc. This kind of gas sensors is chemiresistor one, which gives the resistance change curve when meeting with different gases. As one of the earliest discovered and most widely applied metal oxide sensors materials, zinc oxide with a wide band gap of 3.37 eV and a large binding energy has become widely used in various forms of sensors, which has been proved to detect many gases, such as ethanol, benzene and toluene and so on [6].

However, every semiconductor gas sensor not only has merits but also has some demerits, such as long response time, poor selectivity and the high requirement of operating temperature [7]. Among the methods [6–18] to improve the performances of chemical sensors, the functionalization of metal oxides with catalysts shows great potential in improving gas response selectivity which is attributed to the synergistic effects that produced by different gas sensing components [7,12–17]. So far there are many reports about compounds containing catalyst that have been applied to the gas sensitive fields [7,12,13,16,18]. For example, it has been proved that even there is only a very small amount of P-type CuO, it could obviously promote the activity of ZnO [19]. According to previous reports [7,12,13], the strong affinity of CuO–H<sub>2</sub>S changes the P–N heterojunction, constructed by N-type M<sub>x</sub>O and P-type CuO, and enhances the gas response of M<sub>x</sub>O to H<sub>2</sub>S or other gas considerably. But this material has relatively poor stability when contacting the target gas. Al<sub>2</sub>O<sub>3</sub>, a very good carrier, has frequently been used to carry other metal or transition metal for catalytic application, which also plays as a dispersion agent. Moreover, Kocemba found that an addition of Al<sub>2</sub>O<sub>3</sub> could improve the sensing properties of sensors, which may be strongly connected with the increased

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adsorption of oxygen and gas [20]. Therefore, a thought that using  $\text{Al}_2\text{O}_3$  and  $\text{CuO}$  together might improve the sensing properties of  $\text{ZnO}$  comes into beings. Also based on the fact that there is relatively less report about metal–oxide semiconductor sensors for the detection of chloroform directly, composite materials of  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  have been prepared in our work by a simple co-precipitation plus hydrothermal method and followed by a calcination process. Here the presence of  $\text{CuO}$  has been applied to increase the gas response of  $\text{ZnO}$ . Along with the  $\text{Al}_2\text{O}_3$  carrier which increased the adsorbed oxygen, the  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  composite shows better gas sensing properties than the single oxide, such as  $\text{ZnO}$ ,  $\text{CuO}$  and  $\text{Al}_2\text{O}_3$ . The element ratio among the metals has been further studied in terms of chloroform sensing, it turns out that the metal ratio ( $\text{Zn}:\text{Cu}:\text{Al}$ ) of the best chloroform sensor is 1:0.7:0.6.

## 2. Experimental

### 2.1. Materials

The starting materials were  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.0% purity from Xi long Chemical Co., Ltd),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99.0% purity from Beijing chemical plant),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.0% purity from Beijing chemical plant),  $\text{NaOH}$  (96.0% purity from Beijing chemical plant) and  $\text{Na}_2\text{CO}_3$  (99.8% purity from Beijing chemical plant).

### 2.2. Preparation of $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$ composites

The precursor was prepared by a classical co-precipitation method [21] and followed by a hydrothermal treatment. Solution A was prepared with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (5.95 g, 0.02 mol),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (9.66 g, 0.04 mol),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (7.50 g, 0.02 mol) and deionized water. Solution B was prepared with  $\text{NaOH}$  (6.40 g, 0.16 mol),  $\text{Na}_2\text{CO}_3$  (1.06 g, 0.01 mol) and deionized water. Afterwards, the two solutions were added dropwise into a four-necked flask containing moderate deionized water at  $25^\circ\text{C}$  with a rotor stirring constantly. This B solution was applied here to keep the pH value of the reaction at  $8.0 \pm 0.5$ . Then the uniformity solution was transferred into Teflon-lined autoclaves and crystallized at  $100^\circ\text{C}$  for 12 h, which was further centrifuged, washed and dried at  $60^\circ\text{C}$  for 12 h. The resulting precursor was placed into the muffle furnace and calcined separately at  $500^\circ\text{C}$  for 5 h in air. Accordingly, these contrastive samples with different metal ratio were named as  $\text{ZnAl}_{1.2}\text{-500}$ ,  $\text{ZnCu}_{0.9}\text{-500}$ ,  $\text{ZnCu}_{0.2}\text{Al}_{0.5}\text{-500}$ ,  $\text{ZnCu}_{0.1}\text{Al}_{0.4}\text{-500}$  and  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  on the basis of ICP results.

### 2.3. Characterization

The crystalline structures of the composites were characterized using Rigaku XRD-6000 diffractometer at 40 kV and 30 mA in the  $2\theta$  range of  $3\text{--}70^\circ$ , and the morphologies of the composites were also observed using a Zeiss SUPRA 55 at 20 kV, with the surface coated with a thin platinum layer in order to avoid the charging effect. The lattice fringes and crystal boundaries of the samples was examined by HRTEM on a JEOLJ-2100. Elemental analyses were performed using the Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer. The samples' specific surface areas were tested using BET (Quantachrome)-AUTOSORB-1. The chemical surface's valence states of elements and Cu LMM Auger spectra were performed using Thermo VGESCALAB 250 X-ray photoelectron spectroscopy with all of the binding energy corrected by contaminant carbon ( $\text{C } 1s = 284.6 \text{ eV}$ ).

### 2.4. Gas sensing measurements

The gas sensing test of  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  composites were conducted on the test system of Chemical Gas Sensing-8 (CGS-8) in

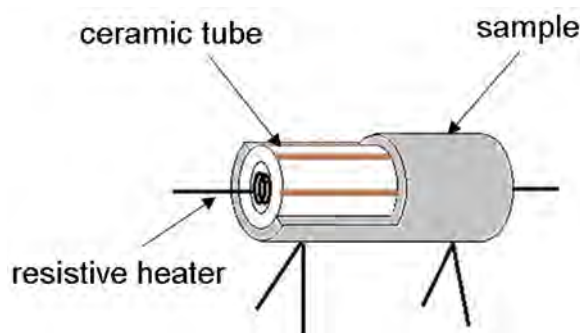


Fig. 1. Profile image of the gas sensor.

ELITE TECH, China, and the customized chemiresistor sensor device is widely used for gas sensing test [22,23]. Fig. 1 presents the profile image of the gas sensor. First, the sample was milled with a little water into paste in an agate mortar, and the paste was painted on an alumina ceramic tube with a pair of Pt electrodes for resistance measure. A small Ni–Cr alloy coil was further placed through the tube as a heater, which was used to vary the working temperature by adjusting the heating current [22].

The sensing properties of  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  sensors were tested at varied operation temperatures by recording the sensor's resistance variation while changing its ambient atmosphere from air to a certain target gas. The gas response is designated as  $S = R_a/R_g$ , where  $R_a$  is the sensor resistance in air (base resistance) and  $R_g$  is the one in the target gas. The response time is defined as the time of the sensor resistance from  $R_a$  to  $R_a - 90\% \times (R_a - R_g)$  after the target gas is introduced into the chamber with the sensor inside, and the time taken from  $R_g$  to  $R_g + 90\% \times (R_a - R_g)$  after the atmosphere is replaced by air is recovery time. The target gas of chloroform was prepared by injecting the liquid chloroform into a container inside the chamber and evaporating it with a heater.

## 3. Results and discussion

### 3.1. Characterization of the composite oxides

The crystalline structures of the contrastive samples calcinated at  $500^\circ\text{C}$  with varied metals ratio were characterized with X-ray diffractometer. Fig. 2 shows the X-ray diffraction (XRD) patterns of the contrastive samples calcinated in  $500^\circ\text{C}$  with varied ratio of elements. All the contrastive samples show  $\text{ZnO}$  or  $\text{CuO}$  diffraction peaks which depends on their compositions. From the XRD pattern

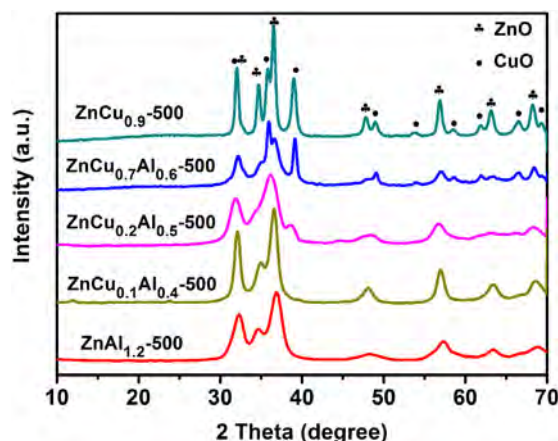


Fig. 2. The XRD patterns of contrastive samples calcinated at  $500^\circ\text{C}$  with varied metals ratio.

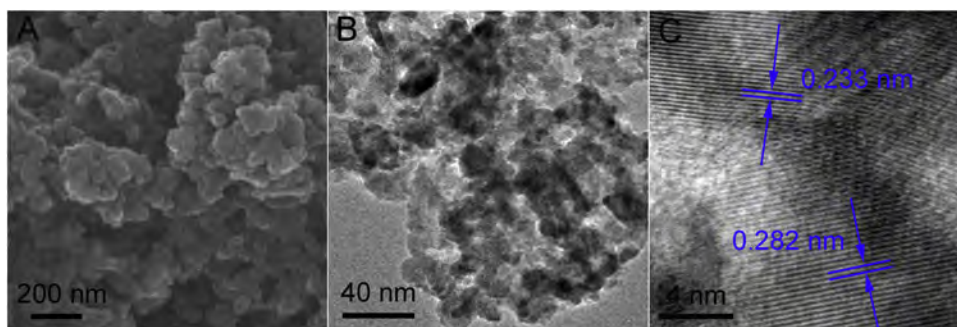


Fig. 3. (A) SEM image, (B) TEM and (C) HRTEM of  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ .

of  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  composites,  $\text{ZnCu}_{0.2}\text{Al}_{0.5}\text{-500}$ ,  $\text{ZnCu}_{0.1}\text{Al}_{0.4}\text{-500}$  and  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ , we can see the main diffraction peaks which are marked with symbols can be indexed to  $\text{CuO}$  and  $\text{ZnO}$ . Additionally, all the reflection peaks are quite broad, which demonstrates the nanometric-grained nature of the composite. As the ratio of  $\text{Cu}:\text{Zn}$  increases, the peaks of  $\text{CuO}$  gradually separated with the ones of  $\text{ZnO}$ . And no significant diffractions of  $\text{Al}_2\text{O}_3$  are observed in all the composites which contain aluminum from the ICP results.

The morphologies of the contrastive composites  $\text{ZnO}/\text{CuO}/\text{Al}_2\text{O}_3$  are similar to  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ . Herein, we take  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  as an example to illustrate the morphologies of the composites. From Fig. 3(A) it can be observed that the composite oxide  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  is constructed of many nearly uniform particles with similar shape, which diameters are about 40 nm, and there are no big blocks observed. As shown in the TEM image (Fig. 3B and C), the lattice fringes of 0.282 nm and 0.232 nm are corresponding to 100 plane of hexagonal  $\text{ZnO}$  and 111 plane of Monoclinic  $\text{CuO}$  respectively, which are in agreement with XRD analysis ( $\text{ZnO}$ : PDF#36-1451;  $\text{CuO}$ : PDF#48-1548). And the lattice fringe of  $\text{Al}_2\text{O}_3$  could not be found in TEM image, which is consistent with the above XRD result. It indicates the composite material is comprised of at least two types of gas-sensing materials,  $\text{ZnO}$  and  $\text{CuO}$ , which have similar morphologies and overlapped each other with the diameter of 40 nm around.  $\text{Al}_2\text{O}_3$  might present as an amorphous state.

### 3.2. Chloroform sensing mechanism and response properties

It is generally known that, there exists an optimum working temperature for every sensor to obtain maximal response [22] and suitable response/recovery time. Therefore, the first experiment is to find the optimal working temperature of the specific material. The responses to 50 ppm chloroform of  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  and the contrastive samples with varied ratio of elements at the temperature range of 150–300 °C are presented in Fig. 4. Take  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  for example to illustrate, it shows increased gas response with the temperature rising. When the heating temperature is about 200 °C,  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  has the highest gas response (8.5) to 50 ppm chloroform. However, when the temperature keeps on rising, the gas response decreases. It can be explained as that with the increase of temperature, the chemical adsorption of oxygen molecules gradually plays a leading role, resulting in the increase of the adsorption amount of oxygen species on the material's surface. As the temperature increases above the optimal temperature, for example here is 200 °C for  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ , the oxygen species reduces and the gas response decreases accordingly. It is likely that the distribution and concentration of oxygen vacancies are relatively fixed while the carrier mobility decreases with increasing temperature [24]. Due to  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  has the highest gas response to chloroform, further experiments were put on this sample and the optimal operation temperature was chosen as 200 °C.

By comparing their chloroform responses of the samples calculated at 500 °C with varied ratio of metal elements,  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  shows the best gas response among the five;  $\text{ZnCu}_{0.2}\text{Al}_{0.5}\text{-500}$  comes the second and  $\text{ZnCu}_{0.1}\text{Al}_{0.4}\text{-500}$  takes the third place as shown in Fig. 4. Meanwhile, the samples with only two kinds of metal elements,  $\text{ZnAl}_{1.2}\text{-500}$  and  $\text{ZnCu}_{0.9}\text{-500}$ , exhibit poor sensing properties, which are similar to  $\text{ZnCu}_{0.1}\text{Al}_{0.4}\text{-500}$ . With the addition of  $\text{CuO}$  and  $\text{Al}_2\text{O}_3$ , as in  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  and  $\text{ZnCu}_{0.2}\text{Al}_{0.5}\text{-500}$ , the gas response of chloroform sensing increases. It could be attributed to the acceleration of  $\text{CuO}$  and the effective particle dispersion by  $\text{Al}_2\text{O}_3$ . It can be also speculated that  $\text{ZnO}$ ,  $\text{CuO}$  and  $\text{Al}_2\text{O}_3$  might have synergistic effect on contributing the chloroform sensing properties of the composite with three metal oxides. In  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ ,  $\text{ZnCu}_{0.2}\text{Al}_{0.5}\text{-500}$  and  $\text{ZnCu}_{0.1}\text{Al}_{0.4}\text{-500}$ , the ratio of  $\text{Cu}:\text{Al}$  is 1.1, 0.4 and 0.25 respectively. From the chloroform response of the above three composites, it can be seen that the gas response of chloroform sensing is proportional to copper content in the samples. The possible sensing mechanism will be discussed later in this paper. Again,  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$ , which possesses the highest amount of copper and shows the highest gas response to chloroform, was selected for further studies regarding its long term stability and selectivity etc.

Sensing response characteristics of  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  to chloroform at different concentrations were investigated at 200 °C, which are shown in Fig. 5. As we know,  $\text{ZnO}$  is an N-type semiconductor whereas  $\text{CuO}$  is a P-type one considering their sensing behaviors [25–28]. When the N-type semiconductor is put from air into reducing gas atmosphere, its resistance reduces; however, when it is put into oxidizing gas, its resistance increases. Here in our results, the  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  composite, which has N-type semiconductor and P-type  $\text{CuO}$  overlapped together as shown in TEM image,

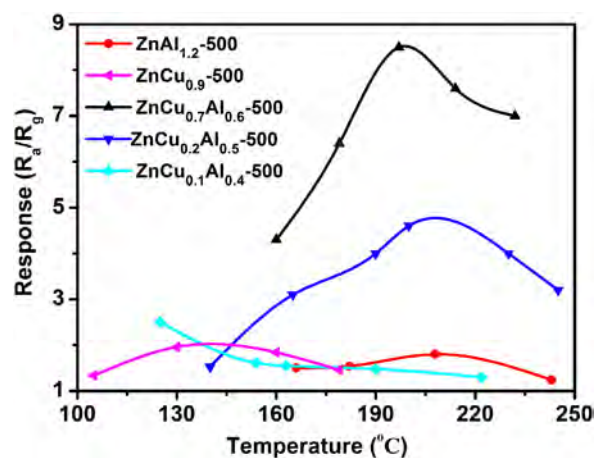


Fig. 4. The responses to 50 ppm chloroform of all the contrastive samples with varied ratio of metal elements at the working temperature range of 150–300 °C.

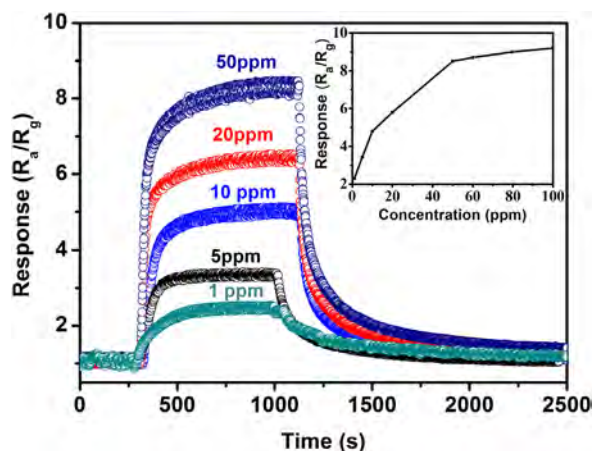


Fig. 5. The response curves of  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  versus 1–50 ppm chloroform at working temperature of 200 °C, the inset Fig. is its maximum gas response values versus to the chloroform's concentrations (1–100 ppm).

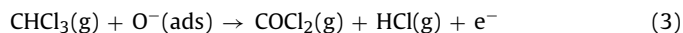
exhibits the same sensing behavior as the N-type semiconductor ZnO has. Furthermore, to different concentration of chloroform,  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  shows similar response and recovery curve. Along with the concentration increase, the gas response ( $R_a/R_g$ ) increases gradually. However, it is not a straight or linear growth in all with the increase of chloroform's concentration, which is shown in the inset picture of Fig. 5. It can be seen that the gas response ( $R_a/R_g$ ) of  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  increases drastically at the range of 1–10 ppm. And at the range of 10–50 ppm, it still shows linear growth but becomes slower. When the increase of chloroform concentration continues,  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  shows more slow growth in response. It can be explained that: a certain specific surface area restricts a finite list of active sites and the amount of adsorbed oxygen species. When the gas concentration exceeds a certain value, most of the active sites are occupied and the amount of adsorbed oxygen species becomes saturated, which results in the slow rise in response with the concentration increase. It also can be calculated that the sample response time to chloroform at 50 ppm is about

15 s in Fig. 5. The recovery time is a bit long, which may be caused by the strong binding force between the sample and chloroform. Moreover, it is worth noting that  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  can detect low concentration of chloroform in 20 s even the concentration is as low as 1 ppm, and its gas response is about 2.5, which is quite satisfactory by going through the references.

Volkenstein has ever proposed an interesting theoretical model for gas adsorption about semiconductors, taking into account the influence of the adsorbed gas species and electronic coupling between semiconductors. Gas species adsorption process includes two consecutive steps: 'weak or neutral chemisorption' and 'strong or ionized chemisorption' [27–29]. Bejaoui et al. accordingly proposed that sensor response is controlled primarily by the conduction mechanism and the chemical interactions between the sensor and the ambient gas [30]. Based on their research, gas sensing mechanism to chloroform in our work is shown in Fig. 6. The chloroform sensing mechanism can be proposed as follow: when  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  is heated in air by modulating current, the oxygen molecules trap electrons and dissociate into oxygen atoms O and  $\text{O}^-$ ,



The adsorbed oxygen species play a vitally important role in chloroform sensing. When the  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  is exposed to chloroform, the chloroform vapor reacts with  $\text{O}^-$  on the surface, resulting in a decrease of adsorbed oxygen species and an increase in the electron concentration on the surface of composite, as shown in Fig. 6. The reactions take place as below:



Moreover, during chloroform gas sensing, the chloroform gas removes the adsorbed oxygen species on ZnO or  $\text{Al}_2\text{O}_3$  and reacts with CuO on the surface of composite to convert into metallic CuCl according to Eq. (4), which increases the release of electrons back to the composite, thus the decreased resistance. That is why  $\text{ZnCu}_{0.7}\text{Al}_{0.6}\text{-500}$  behaves a significant decrease in the sensor resistance when the sensor is exposed to chloroform and thus

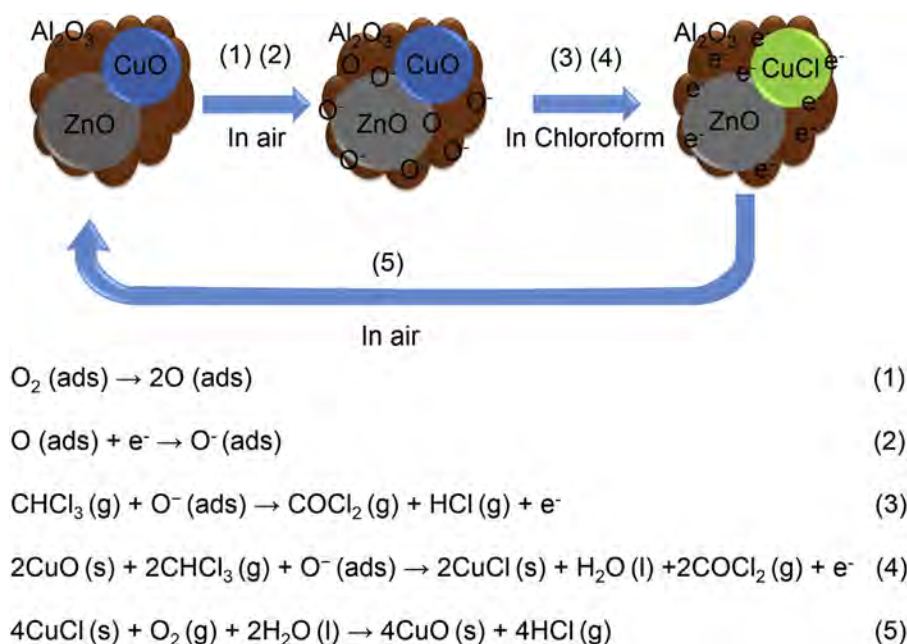


Fig. 6. The possible gas sensing processes of the composite to chloroform.

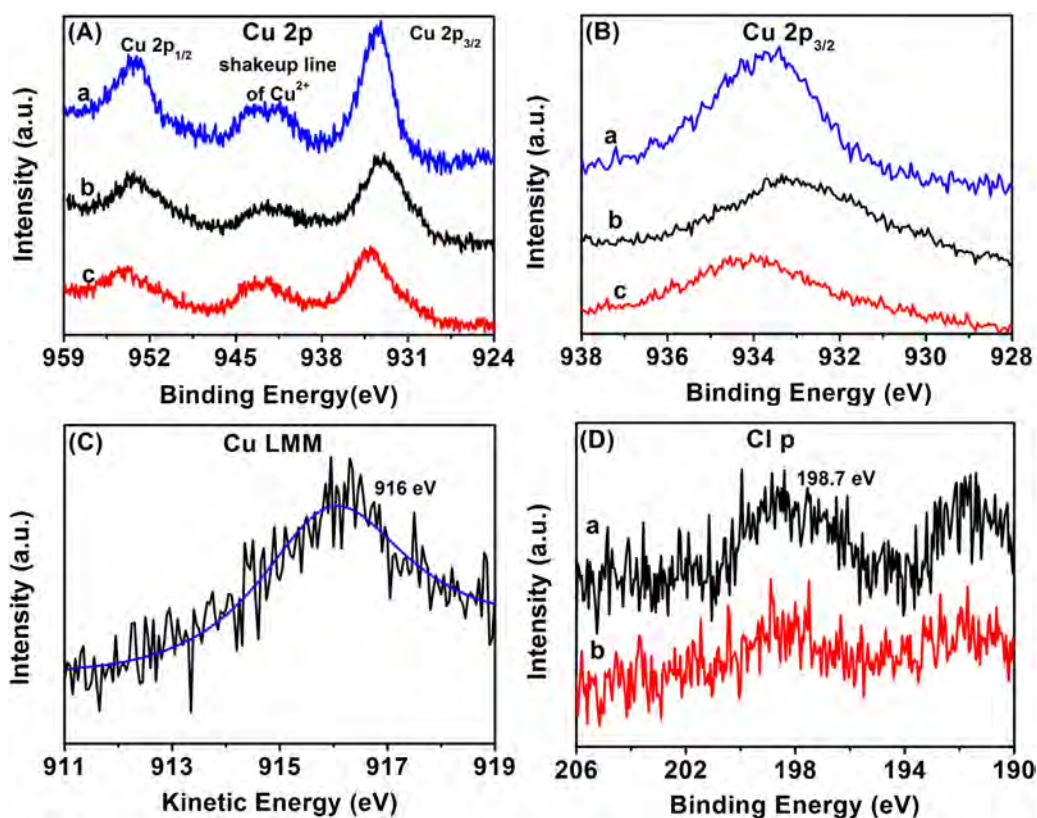
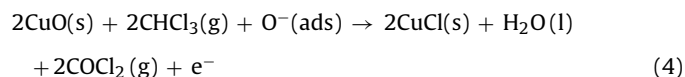


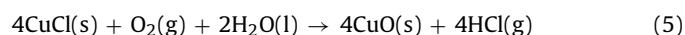
Fig. 7. (A) Cu 2p XPS of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 in air (a), in chloroform (b) and recovered in air(c); (B) the enlarged Cu 2p<sub>3/2</sub> XPS peak in (A); (C) Cu LMM Auger spectrum of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 after chloroform exposure; (D) the Cl p XPS spectra of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 after being exposed in chloroform (a) and recovered in air (b).

the increase in gas response ( $R_a/R_g$ ) as observed in Fig. 5.



Obviously, compare to ZnAl<sub>1.2</sub>-500, the addition of CuO in the composite has improved the gas response. We calculated the Gibbs free energy of Eq. (4) in light of Gibbs formula. No matter what the temperature is, Gibbs free energy of this equation is always negative, suggesting that the above reaction is thermodynamically favored. Therefore, the mechanism reaction we proposed here is feasible.

However, CuCl is easily oxidized when it contacts air. Therefore, when the sensor has been put back into air ambient, the sensing material would return to its initial states as shown in the reaction (5).



In order to verify our assumption that CuO changes to CuCl during the sensing process, the chemical surface's valence states of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 after being exposed in air (a), in chloroform (b) and recovered in air(c) were investigated by Cu and Cl XPS characterizations. The Cu XPS spectra of the ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 have been shown in Fig. 7(A and B). As shown in Fig. 7A(a), the Cu 2p binding energies are 933 eV (Cu 2p<sub>3/2</sub>) and 953.2 eV (Cu 2p<sub>3/1</sub>), which both correspond to the binding energies of the Cu 2p of CuO [13,31,32]. The peak around 943 eV is attributed to the shakeup line of CuO. After being exposed in chloroform, as shown in Fig. 7A(b), the binding energies of Cu 2p<sub>3/2</sub> and Cu 2p<sub>3/1</sub> is broadened and shifted to lower binding energy. The shakeup line at 943 eV almost disappears, showing that the chemical state of Cu changes [13]. In addition, there appears a shoulder peak around 932 eV, which

suggests the generation of low valence states of copper. From the enlarged Cu XPS spectra (Fig. 7B), which indicates that the chemical state of Cu ions changes and the possible presence of either Cu<sup>0</sup> or Cu<sup>1+</sup>. In order to verify the low valence state of copper, the Cu LMM Auger spectrum has been shown in Fig. 7C, from which the peak positioned at approximately 916–917 eV is corresponding as Cu<sup>+</sup>[13], the low valence state of copper. Furthermore, when the sensor was put back into air atmosphere, the Cu 2p peak positions were shifted back to those of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500, which were observed before sensing, and the shakeup peak that had disappeared now reappeared. The shoulder peak at 931.8 eV almost disappeared (Fig. 7A(c) and B(c)), which further specifies the Cu<sup>+</sup> had changed back to Cu<sup>2+</sup>. The Cl p spectra of the composite have been done after being exposed in chloroform (Fig. 7D(a)) and recovered in air (Fig. 7D(b)). After chloroform exposure, the Cl p peak at 198.7 eV appeared significantly, which indicates the composite has Cl element on its surface. However, the Cl p peaks decreased after air purging as shown in Fig. 7D(c), which further supports that CuCl generated during gas sensing in chloroform and changed back to CuO in air. CuO in the composite plays as a reactant in the sensing process by converting to CuCl and recovering back to CuO. During the generation of CuCl, the electrons have been released into the composite, which aggravates the resistance decrease of the sensor and thus the high gas response of  $R_a/R_g$  to Chloroform.

The stability and life span as the fundamental characteristics of gas sensor were also tested in the atmosphere with 5 ppm chloroform at its optimal operation temperature. Fig. 8 shows the response of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 in 5 ppm chloroform. Once the sensor contacts with chloroform, it responds rapidly. Even after five cycles, the sensor still shows good reproducibility and nearly parallel results (Fig. 8), which is a good characteristic for gas sensor.

Due to the selectivity to certain gas is equally important as the fundamental characteristic of gas sensor, the sensor based

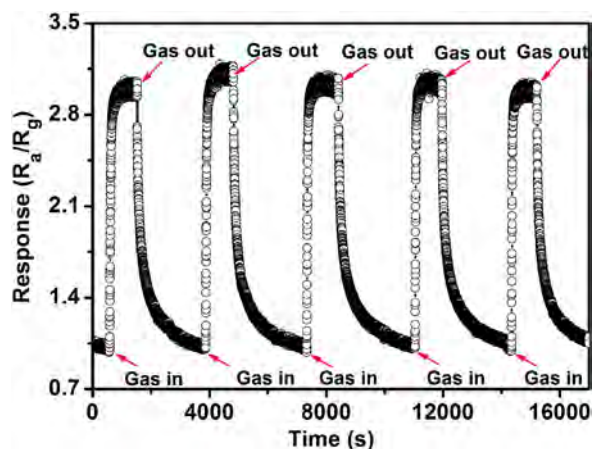


Fig. 8. Repeatability and stability of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 to 5 ppm chloroform at operation temperature of 200 °C.

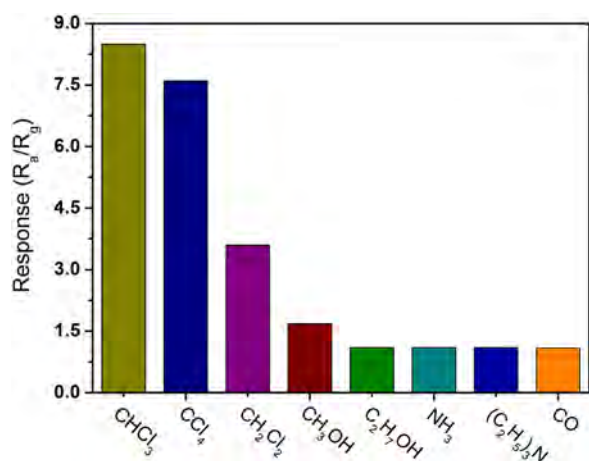


Fig. 9. Selectivity of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 to 50 ppm gas vapors at operation temperature of 200 °C.

on ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 was further test regarding its gas responses to a series of typical volatile gases at its optimal operation temperature. It can be found in Fig. 9 that ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 exhibits similar high response to other chlorohydrocarbon besides chloroform, while shows low response to other common hazardous gas such as methanol, ethanol, ammonia, triethylamine and CO in the same concentration of 50 ppm, which indicates that ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 has relatively good selectivity to chlorohydrocarbon especially to chloroform.

#### 4. Conclusions

This paper reported a kind of chloroform sensing composite based on ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> composites. It was prepared by a simple coprecipitation and hydrothermal method followed by a calcination approach. The composites have good sensing behaviors to chlorohydrocarbon, especially to chloroform. It can be observed that the addition of CuO and Al<sub>2</sub>O<sub>3</sub> is necessary and the ratio between them also has important effect on the composite's gas sensing properties. By tuning the ratio of Cu:Al, the composite of ZnCu<sub>0.7</sub>Al<sub>0.6</sub>-500 was obtained with highest gas response to chloroform and can detect chloroform in 20 s even at the concentration of 1 ppm. It can be also speculated that ZnO, CuO and Al<sub>2</sub>O<sub>3</sub> have synergistic effect on contributing the chloroform sensing properties of the composite with three metal oxides. The preparation of ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> composites provides a train of thought for

detection chloroform, which might have the potential to monitor chloroform in industrial production in the future.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.12.099>.

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