



## Gas sensing characteristics of composite NiO/Al<sub>2</sub>O<sub>3</sub> for 2-chloroethanol at low temperature



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### ABSTRACT

Composite NiO/Al<sub>2</sub>O<sub>3</sub> was prepared by calcination of Ni/Al hydrotalcite for gas sensing materials. Methods of XRD, SEM, TEM, EDS and BET were used to analyze the structure, composition and morphology of the composite oxide. It was found that the sample was composed of crystal NiO and amorphous Al<sub>2</sub>O<sub>3</sub>. Furthermore, the composite NiO/Al<sub>2</sub>O<sub>3</sub> has smaller grain size and larger surface area than that of pure NiO obtained by the same process. In the gas sensing experiments, the sensor based on NiO/Al<sub>2</sub>O<sub>3</sub> showed superior gas sensing response and selectivity to 2-chloroethanol at low temperature. The response (R<sub>g</sub>/R<sub>a</sub>) of NiO/Al<sub>2</sub>O<sub>3</sub> was 6.8–20 ppm 2-chloroethanol at 160 °C. The role of Al<sub>2</sub>O<sub>3</sub> in the composite was also discussed.

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### 1. Introduction

2-Chloroethanol, one of the typical volatile organic compounds (VOCs), is an important chemical raw material for preparation of synthetic fiber, medicines, dyes and paper. Another use of 2-chloroethanol is to be a solvent for acetate, resins, paints, etc.; however, this substance is very hazardous. It was found that repeated or long-term exposure to 2-chloroethanol can cause acute damage on the human central nervous system, liver, kidneys and upper respiratory tract [1]. In addition, 2-chloroethanol is the main residue as one of the breakdown products of ethylene oxide which is now used to disinfect foods in many countries. It has been reported the residue may bring cancer risks to human [2].

Practical methods should be found to match the requirements of detecting 2-chloroethanol gas. Up to now, gas chromatography is the main method to detect 2-chloroethanol, however, it has complex operations with expensive equipments. In recent years, a wide range of studies revealed that semiconductor oxides showed good performance on detecting gases. For example, nickel oxide (NiO), as one of the p-type semiconductors with a wide band gap (3.6–4.0 eV) [3], has been reported to have attractive responses to HCHO [4], H<sub>2</sub> [5], ethanol [6], etc. More recently, much attention has been focused

on combining NiO with other components to achieve more desirable gas sensing performance of nickel oxide. It was reported that the composites, accompanied by the introducing of other phases, presented multi-functional properties (e.g., mechanical, chemical, thermal and electrical properties) which were different from that of the individuals [7].

For example, Liu et al. [8] investigated the gas sensing performance of one p-NiO/n-ZnO heterostructure for detection of acetone and found that the composite showed much better properties than that of pure NiO and ZnO. They attributed the superior performance of the composite to the formation of p-n heterojunctions in the NiO/ZnO composites. Arshak et al. [9] prepared NiO/Fe<sub>2</sub>O<sub>3</sub> thick film with different molecular percentages and measured their gas sensing properties to six kinds of organic vapors (methanol, toluene and propanol, etc.). The series of composites showed high responses to toluene and propanol. The response/recovery times of the sensor with 75/25 M wt.% of NiO to Fe<sub>2</sub>O<sub>3</sub> was 30/45 s to propanol and 40/48 s to toluene, respectively. Moreover, these sensors could be used without a heating element, which may be suited to industry applications particularly. Lin et al. [10] prepared tungsten doped chrysanthemum-like NiO composite via a hydrothermal process and found that the WO<sub>3</sub>-0.33H<sub>2</sub>O-NiO sensors exhibited higher response to ethanol than that of pure NiO and WO<sub>3</sub>-0.33H<sub>2</sub>O. It was believed that the doping of WO<sub>3</sub> resulted in the special structure of nickel oxide and the excellent performance of the composites. The studies above show that hybridization of different elements

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can result in synergic effects among these components [11] which may promote the performance of the gas sensing materials.

In this work, we combined NiO and  $\text{Al}_2\text{O}_3$  into one system and investigated the gas sensing properties of the composite. The motivation of choosing  $\text{Al}_2\text{O}_3$  as additive was that  $\text{Al}_2\text{O}_3$  is a very important adsorbent in catalysis. The activity species ( $\text{Al}^{3+}$ ,  $\text{O}^{2-}$ , dissociated group  $\text{OH}^-$  and proton defects) on its surface are centers of adsorption for different gases [12]. Therefore, in the process of detecting gases,  $\text{Al}_2\text{O}_3$  may increase the adsorption quantity of oxygen and tested gases [13]. Moreover, transition metal oxides deposited on the surface of alumina always possess high dispersion form.

Among the methods of preparing composite oxides, which are varied from sol-gel [7] to impregnation [14] or homogeneous precipitation [15] and so on, we considered that calcination of hydrotalcite like compounds (HTlc) was the effective one [16]. HTlcs are composed of brucite-like layers which contain bivalent and trivalent cations as well as interlayer anions and water [17]. The multinuclear NMR spectroscopy study showed that metal cations were fully ordered in the HTlcs layers [18] and further thermal decomposition of HTlcs could produce composite oxides with high thermal stability, homogeneous elements distribution, large surface area and unique functional properties [11].

Herein, we prepared NiO/ $\text{Al}_2\text{O}_3$  composite oxide by thermal treatment of Ni/Al hydrotalcite precursor. Considering that the general molar ratio of the two metal ions in hydrotalcite  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3]\cdot 4\text{H}_2\text{O}$  is 3:1, we set the molar ratio of Ni/Al as 3:1 as well. In the gas sensing measurements, the composite showed high response to 2-chloroethanol. And to the best of our knowledge, only a few papers have reported the gas response of semiconductor oxides to 2-chloroethanol till now [19,20].

## 2. Experiment

### 2.1. Preparation and characterization

The precursor, a Ni/Al hydrotalcite like compound (the molar ratio of Ni:Al is 3:1) was synthesized by the co-precipitation method. The typical process is described as follows: Maintaining the pH constant ( $9.5 \pm 0.1$ ), an aqueous solution containing NaOH and  $\text{Na}_2\text{CO}_3$  (the molar ratio is 3:1) was added dropwise into a metal nitrates solution containing  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$  under constant stirring. The obtained suspension was aged for 24 h at  $60^\circ\text{C}$  in a water bath. Thereafter, the precipitate was filtered, thoroughly washed with distilled water until the pH value of the filtrate equals to 7. The resulted filter mass was dried at  $80^\circ\text{C}$  for 24 h to obtain Ni/Al-HTlc precursor. By means of grinding Ni/Al-HTlc into powder and then calcining it at  $600^\circ\text{C}$  for 2 h, the composite oxide was obtained and named as NiO/ $\text{Al}_2\text{O}_3$ . For comparison, pure NiO was prepared



Fig. 1. Photograph of a blank gas sensor.

by precipitation of  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ , followed with the same calcination process.

The phases of the as-synthesized samples were characterized by X-ray diffraction (XRD, D8-Advance using  $\text{CuK}\alpha$  radiation, Bruker). Plots of reflection intensities versus  $2\theta$  were smoothed digitally to show the peak features without background and noise. Their morphologies and composition were investigated by scanning electron microscope (SEM, HITACHI S-2500), transmission electron microscopy (TEM, TECNAI G2 TF20, FEI) and energy dispersive X-ray spectroscopy (EDX, INCA MAX-50). BET surface areas and pore size distributions of the samples were analyzed using Micromeritics ASAP 2020 instrument by  $\text{N}_2$  adsorption-desorption isotherm at  $-196^\circ\text{C}$ .

### 2.2. Fabrication and measurement of thick-film sensors

The powder of the obtained sample was mixed with a suitable amount of deionized water and ground into paste. Then the paste was coated onto small ceramic tubes with a thickness of about  $10\ \mu\text{m}$  to form a thick-film gas sensor. The ceramic tubes were mounted with Au electrodes and Pt lead wires at both ends. Ni-Cr alloy wires as coil heating were inserted in the tubes to control the operating temperature. Fig. 1 shows the photographs of the fabricated sensors in the experiments. The gas sensing performances of the sensors were measured by CGS-8 intelligent gas sensing

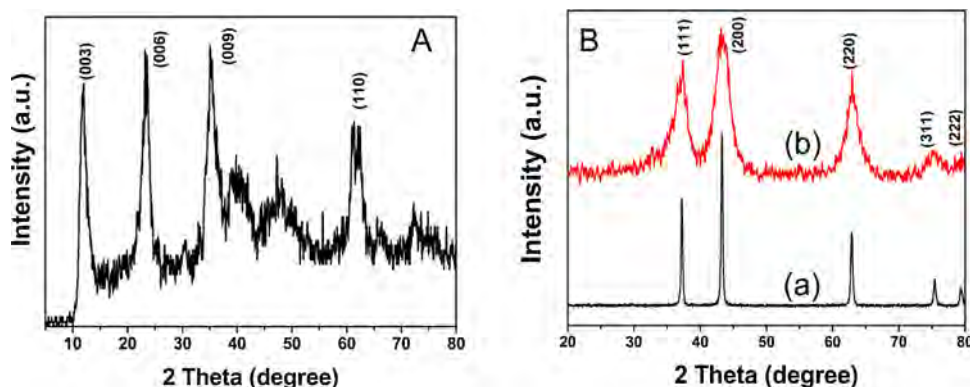


Fig. 2. XRD patterns of (A) Ni/Al-HTlc precursor and (B) calcined oxides ((a) pure NiO and (b) NiO/ $\text{Al}_2\text{O}_3$ ).

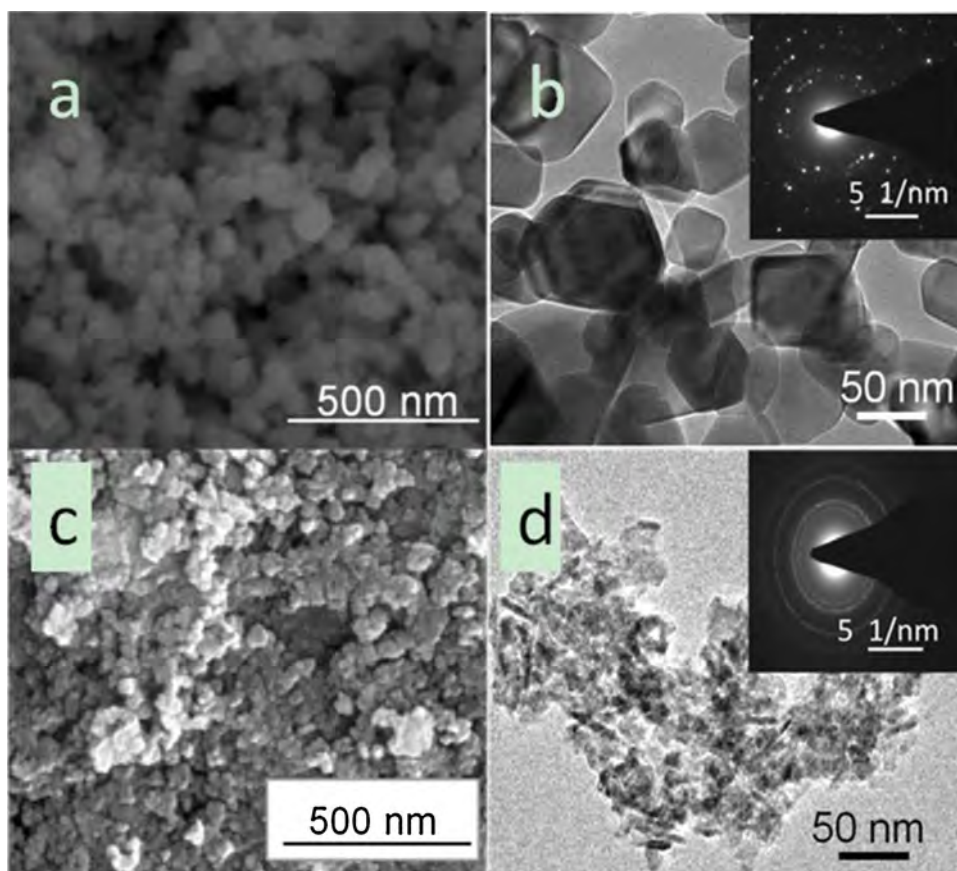


Fig. 3. SEM images of (a) pure NiO and (c) NiO/Al<sub>2</sub>O<sub>3</sub>; TEM and SAED images (inset) of (b) pure NiO and (d) NiO/Al<sub>2</sub>O<sub>3</sub>.

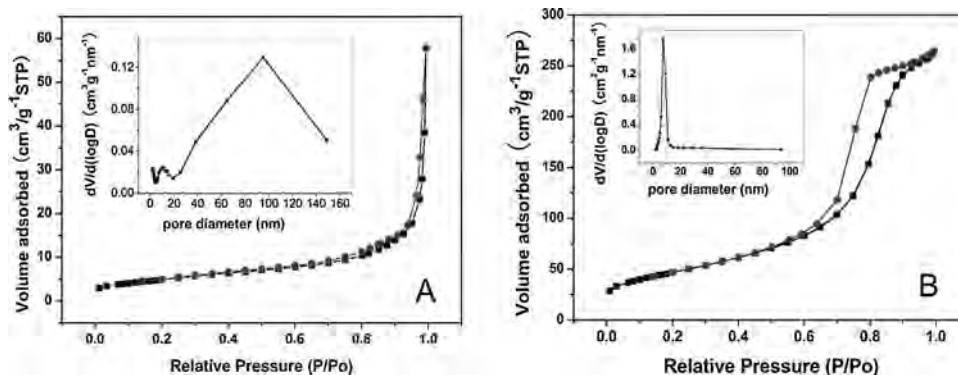


Fig. 4. N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution curves (inset) of (A) pure NiO and (B) NiO/Al<sub>2</sub>O<sub>3</sub>.

analysis system (Beijing Elite Tech Co., Ltd., China). The vapor samples are all analytically pure and CO<sub>2</sub> is 99.99% pure.

The prepared sensors were first dried for 24 h in air at room temperature and then pre-heated at different operating temperatures for about 60 min before gas sensing tests. Fresh air (relative humidity was about 25–30% at room temperature) was used as carrier gas. When the sensors' resistance in air was stable, a suitable amount of test gas was injected into the test chamber (20 L in volume). Mean values were obtained from the results of 5 different sensors and each test repeated three times.

The gas response in the experiments was defined as  $R_{\text{gas}}/R_{\text{air}}$ , where  $R_{\text{air}}$  is the sensor's resistance in air, while  $R_{\text{gas}}$  is that in a sample gas. The response and recovery times were defined as the times taken by the sensors to achieve 80% of the total resistance change after the ambience was changed.

### 3. Results and discussion

#### 3.1. Structures and morphologies

The XRD image of Ni/Al-HTlc is given in Fig. 2(A). The precursor shows main peaks at  $2\theta = 11^\circ, 23.7^\circ, 37.7^\circ$  and  $62.2^\circ$  in the pattern which are attributed to HTlc structure (JCPDS file No. 38–0715). XRD patterns of pure NiO and NiO/Al<sub>2</sub>O<sub>3</sub> are shown Fig. 2(B). Both of them show three dominant Bragg peaks at  $2\theta = 37^\circ, 43^\circ$ , and  $62.9^\circ$  which are ascribed to (111), (200) and (220) crystal facets of cubic nickel oxide (JCPDS 44–1159). Obviously, the reflection peaks of NiO/Al<sub>2</sub>O<sub>3</sub> broaden remarkably than that of pure NiO, suggesting a significant decrease in the average crystal particle size of the composite. This is in good agreement with the results calculated using Scherrer Equation: the crystallite size of NiO/Al<sub>2</sub>O<sub>3</sub> is about 14 nm

**Table 1**  
EDX analysis data of NiO/Al<sub>2</sub>O<sub>3</sub>.

Element	O	Al	Ni
wt%	28.10	9.84	62.06
at%	55.27	11.47	33.26

while that of pure NiO is about 43 nm. Furthermore, it is worth noting that no significant diffraction peaks of Al<sub>2</sub>O<sub>3</sub> are observed in the XRD pattern of NiO/Al<sub>2</sub>O<sub>3</sub>. Considering that in the process of calcinations in air at 600 °C, Al<sub>2</sub>O<sub>3</sub> should have been formed in the material [21]. Thus we concluded that the phase of Al<sub>2</sub>O<sub>3</sub> is amorphous in the composite. This conclusion is consistent with the earlier studies which also revealed the presence of amorphous phase in the same case from the XRD pattern [16,21,22].

The morphologies and microstructures of the samples were studied by SEM and TEM. As shown in Fig. 3, both of the powders are nanoparticles with nearly nanocube shape and porous nature. Particularly, the TEM results show that, comparing to the pure NiO, NiO/Al<sub>2</sub>O<sub>3</sub> has more homogenous distribution of crystallites, smaller average particle size and smaller pores. As shown in Fig. 3(d), the composite particle size is smaller by an order of magnitude than that of pure NiO. It is generally accepted that smaller particle size and homogenous distribution can lead to larger surface area and more crystal defects of the crystalline NiO which results in more adsorption sites on the surface or grain boundaries of the crystallite NiO.

Inset figures in Fig. 3(b) and (d) show the corresponding selected area electron diffraction (SAED) pattern of the two samples. The pure NiO shows the spot type pattern which verifies the presence of single crystallite particles, while NiO/Al<sub>2</sub>O<sub>3</sub> shows electron diffraction rings which indicates their poly-crystalline structure. The results above are correlated well with the XRD results.

The elements component content in the composite NiO/Al<sub>2</sub>O<sub>3</sub> was detected by EDS spectrum. As shown in Table 1, the atomic ratio of Ni and Al in the sample is about 3:1, which is close to the original dose-stoichiometry of the sample preparation.

Further analysis was performed by nitrogen adsorption and desorption measurements to learning more surface properties of the two samples. Fig. 4 depicts the N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution curves of pure NiO (A) and NiO/Al<sub>2</sub>O<sub>3</sub> (B). From the figure, one can see that the pore size distribution of pure NiO (A) is wide and the main pore size is as large as more than 50 nm; on the contrary, the pore size distribution of NiO/Al<sub>2</sub>O<sub>3</sub> is narrow and the main pore size is about 10 nm meaning a mesoporous characteristic of the composite. What's more, the average surface area of sample NiO/Al<sub>2</sub>O<sub>3</sub> is 168.91 m<sup>2</sup>/g, which is almost an order of magnitude larger than that of NiO (17.89 m<sup>2</sup>/g). The larger effective surface and porosity for NiO/Al<sub>2</sub>O<sub>3</sub> composite may create favorable conditions for a gas sensing process because the process is taken place on the surface or interface of the materials.

### 3.2. Gas sensing measurements

The resistance values of the sensor based on NiO/Al<sub>2</sub>O<sub>3</sub> in air at elevated temperatures were measured and shown in Fig. 5. As can be seen, the resistance of the sample was decreased with the increasing temperature in air, which conforms to the intrinsic feature of semiconductors.

Fig. 6 shows the responses of the sensors based on NiO/Al<sub>2</sub>O<sub>3</sub> and pure NiO to 50 ppm 2-chloroethanol as a function of operating temperature. It can be seen that both of NiO/Al<sub>2</sub>O<sub>3</sub> and pure NiO show responses to 2-chloroethanol. The mechanism of this process can be explained as follows. There are large amounts of oxygen in air which can be adsorbed on the surface and grain boundaries of nickel oxide. The adsorbed oxygen can be changed into various

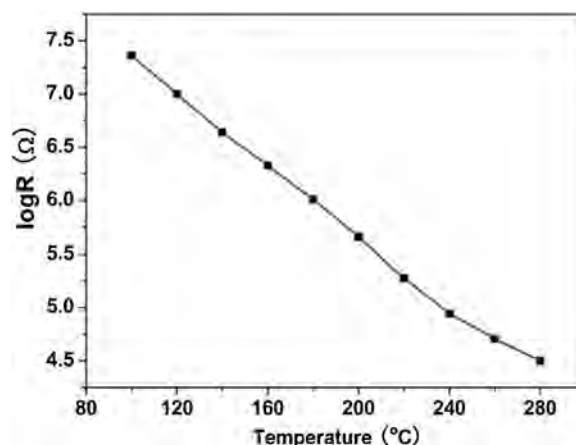


Fig. 5. Temperature dependence of the resistance for NiO/Al<sub>2</sub>O<sub>3</sub> sensor in air.

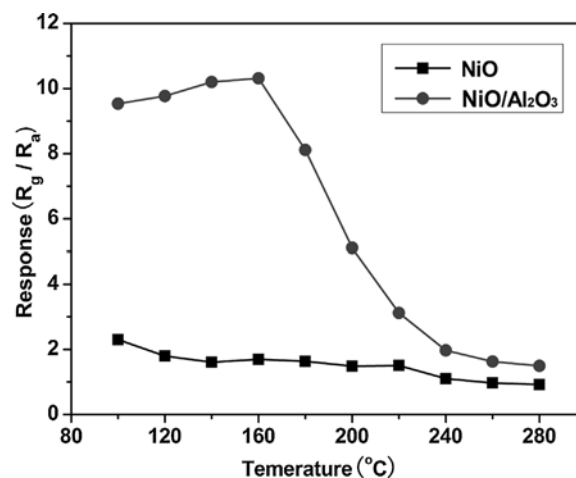
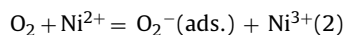
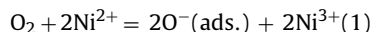
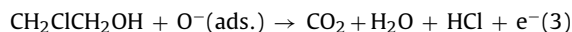


Fig. 6. Temperature dependence of the response for pure NiO and NiO/Al<sub>2</sub>O<sub>3</sub> to 50 ppm 2-chloroethanol.

chemical adsorptive states carrying negative charge by trapping electrons from Ni<sup>2+</sup> on the surface of the semiconductor [23]. The reactions are shown below:



As a p-type semiconductor, the main carriers of NiO are electric holes. The concentration of the holes is deep related to the generation of Ni<sup>3+</sup> in the materials. The equilibria process above will increase the concentration of electric holes and decrease the barrier height for a hole to transport which eventually leads to a low resistance. As the reducing 2-chloroethanol gas is introduced, the electrons trapped by the adsorptive states of oxygen will be released due to the chemical interaction between 2-chloroethanol molecules and the oxide anions, for example:



Ni<sup>3+</sup> will then converted into Ni<sup>2+</sup> by trapping the released electron. Then the barrier height increases with the decreasing of the holes concentration accordingly. Thus, the value of the sensor resistance increases, i.e., the sensor shows response behavior to the test gas.

Looking at Fig. 6 more closely, we can also see that the sensor based on pure NiO shows low responses in the whole temperature range with a little decrease upon the rise of the operating temperature. The best response of NiO is only about 1.7–50 ppm

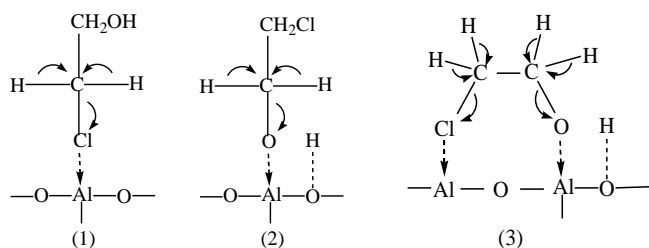


Fig. 7. Three modes of chemisorption of 2-chloroethanol on  $\text{Al}_2\text{O}_3$  surface and the influence of inductive effect of  $\text{Al}^{3+}$  on 2-chloroethanol.

2-chloroethanol gas at  $160^\circ\text{C}$ . However, the responses of the sensor  $\text{NiO}/\text{Al}_2\text{O}_3$  change dramatically with the increasing temperature. Particularly, the sensor shows excellent response in the temperature range of  $140\text{--}180^\circ\text{C}$ . The best response reaches  $10.0\text{--}50$  ppm 2-chloroethanol at  $160^\circ\text{C}$ , which is much higher than that of the pure  $\text{NiO}$ . After that, with the temperature increasing, the response decreased gradually to a value around 1.5. Therefore, the optimal operating temperature of the composite to 2-chloroethanol was about  $160^\circ\text{C}$  and this operating temperature is really low for gas sensing semiconductor materials.

The reason for the variation in the two samples' responses was discussed as follows. First, in the thermal treatment process of HTLC precursor, aluminum atom may replace Ni centers in  $\text{NiO}$  crystallites. In this way, more crystal defects are generated which results in more reaction sites on the surface or grain boundaries of the crystallite  $\text{NiO}$ . Second, amorphous  $\text{Al}_2\text{O}_3$  in the composite may serve as a "diluent" [13] of  $\text{NiO}$  crystallites. It could separate  $\text{NiO}$  crystallites and thus restrain the growth of the crystallites which result in great changes for  $\text{NiO}$  in the textural properties (particle size, surface or inner surface area, pore diameter, etc.) as shown in the results of XRD, SEM, TEM and BET. These changed texture structures can provide enough domains for  $\text{NiO}$  to adsorb gases (oxygen or the detected gas) and thus changes the electronic properties of the composite greatly. At last, it is well known that  $\text{Al}_2\text{O}_3$  is a very important adsorbent and it can physisorb or chemisorb 2-chloroethanol molecular on the surface of the composite in the temperature range  $140\text{--}180^\circ\text{C}$  for that Al atom is Lewis acid site whereas molecular 2-chloroethanol has two basic sites (Cl and O). Three chemisorption modes (see Fig. 7) may be considered on the surface of  $\text{Al}_2\text{O}_3$ : (1) on the surface Al ion with Cl-down (2-chloroethanol), (2) on the surface Al ion with O-down (2-chloroethanol), (3) on the surface Al ion with Cl and O atoms (2-chloroethanol) together down to the adsorbed sites. For mode (2) and (3), the dissociative hydrogen atom down to the surface O ion and forms hydroxyl group which can desorb in the form of  $\text{H}_2\text{O}$ .

The role of chemisorption with regard to the enhancement of the sensing response using  $\text{Al}_2\text{O}_3$  was discussed as follows. For mode (1), Al ion can accept a pair of electrons from Cl atom incompletely as a Lewis acid. Accordingly, the positive charge on the carbon adjacent to atom Cl should increase along with the  $\text{H}\text{--}\text{C}$  bonds and  $\text{C}\text{--}\text{Cl}$  bond weakened due to the inductive effect. In this case, molecular 2-chloroethanol with the weakened bonds should react with oxygen anions ( $\text{O}^-$ ,  $\text{O}^{2-}$ ) on the surface of  $\text{NiO}$  near alumina facilely. So, the role of chemisorption of 2-chloroethanol on  $\text{Al}_2\text{O}_3$  is that  $\text{Al}_2\text{O}_3$  can serve as dehydration and cracking catalyst owing to the Lewis acid sites [24]. For mode (2) and (3), the roles of  $\text{Al}_2\text{O}_3$  can be explained similarly to mode (1).

Considering the amorphous characteristic of  $\text{Al}_2\text{O}_3$ , we speculate that there may be rich of 2-chloroethanol molecular which can be adsorbed on the composite surface in this temperature range. So, in some extent, the condensed 2-chloroethanol with weakened bonds helps improving the response of  $\text{NiO}/\text{Al}_2\text{O}_3$ . However, when the temperature increases sequentially, it is difficult

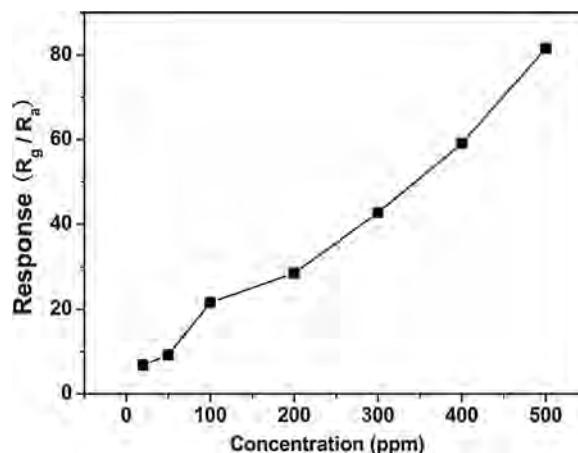


Fig. 8. Concentration dependence of the response for  $\text{NiO}/\text{Al}_2\text{O}_3$  to 2-chloroethanol at  $160^\circ\text{C}$ .

for 2-chloroethanol to be adsorbed on the surface of the composite and the sensors response decreases accordingly. In short, the role of  $\text{Al}_2\text{O}_3$  of the composite in improving the response to 2-chloroethanol may be that it can significantly enlarge the material surface area, form more crystal defects, adsorb more 2-chloroethanol molecular and help cracking the molecular on the composite surface.

In order to understand the concentration dependence of response for the sensor based of  $\text{NiO}/\text{Al}_2\text{O}_3$  composite oxide, the sensors were further exposed to various concentrations of 2-chloroethanol at  $160^\circ\text{C}$ . As can be seen in Fig. 8, there is a nearly good linearity of the composite response on gas concentrations. It is also noted that the response of  $\text{NiO}/\text{Al}_2\text{O}_3$  reach as high as  $6.8\text{--}20$  ppm 2-chloroethanol and  $83.0\text{--}500$  ppm 2-chloroethanol, respectively. Comparing to the previously reported gas sensing materials ( $\text{In}_2\text{O}_3$  microbundles and porous  $\text{SnO}_2$  nanospheres) which exhibited a superior sensing performance toward 2-chloroethanol at  $300^\circ\text{C}$  and  $260^\circ\text{C}$ , respectively [19,20],  $\text{NiO}/\text{Al}_2\text{O}_3$  in our work showed higher response to 2-chloroethanol at much lower operating temperature ( $160^\circ\text{C}$ ). With such significantly high response to 2-chloroethanol at low operating temperature,  $\text{NiO}/\text{Al}_2\text{O}_3$  may have the potentiality in the application of detecting 2-chloroethanol.

Selectivity is another important gas-sensing character of a gas sensor. To observing the response of  $\text{NiO}/\text{Al}_2\text{O}_3$  to other gases, the measurements of the sensor to acetonitrile, ethanol, *n*-hexane and  $\text{CO}_2$  were carried out at the optimal operation temperature and the results were compared with 2-chloroethanol. As shown in Fig. 9, the response of sensor  $\text{NiO}/\text{Al}_2\text{O}_3$  to 2-chloroethanol is higher than to the other four gases at  $160^\circ\text{C}$ .

The response diversity to the five gases for the composite may be caused by the gases' different reactive nature, different molecular polarity and molecular deformation, different adsorption temperature and so on. In addition, our sensor showed low response to  $\text{CO}_2$  which is in consistent with the results reported in Ref. [25,26] in which the work function of materials with NiO varied on exposure to  $\text{CO}_2$ . For the stable chemical property of  $\text{CO}_2$ , the sensing mechanism of  $\text{CO}_2$  is not yet clear. The formation of carbon trioxide complexes was suggested to be one of the origins of  $\text{CO}_2$  sensing mechanisms for some samples such as  $\text{CuO}\text{--}\text{BaTiO}_3$  [27],  $\text{LaOCl}$  [28], and  $\text{LaFeO}_3$  [29]. As for  $\text{NiO}$ , Gordon and Lambert [30] and Matsumoto et al. [31] have studied the adsorption of  $\text{CO}_2$  on  $\text{NiO}$  respectively by He II UP spectra, O (1s), C (1s) XP spectra and IR spectra and demonstrated that  $\text{CO}_3^{\delta-}$  was formed on the surface of  $\text{NiO}$ . Species of carbon trioxide complexes such as  $\text{CO}_3^{2-}$ , which are produced by the reaction of  $\text{CO}_2$  with oxygen atoms on the

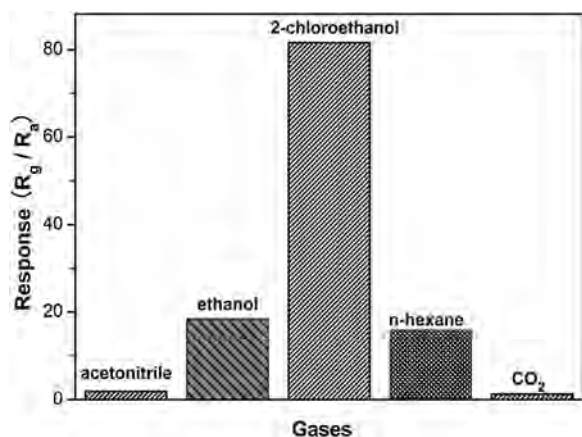


Fig. 9. Responses of NiO/Al<sub>2</sub>O<sub>3</sub> at 160 °C to different gases: 500 ppm of acetonitrile, ethanol, 2-chloroethanol, *n*-hexane and 5000 ppm of CO<sub>2</sub>.

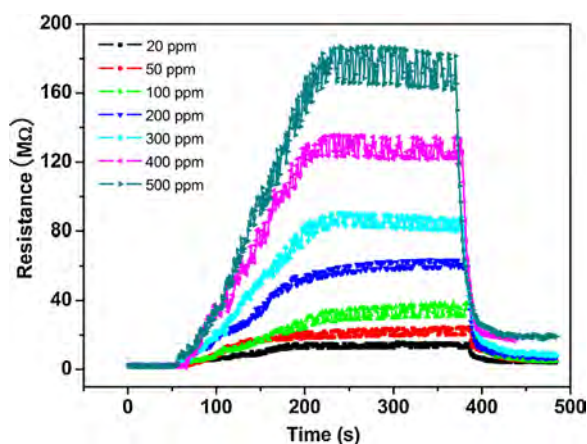


Fig. 10. Response and recovery curves of NiO/Al<sub>2</sub>O<sub>3</sub> to 20–500 ppm 2-chloroethanol at 160 °C.

surface of the material, are considered to be associated with O<sup>−</sup> and anion vacancies [30]. So the carbonation may modify the potential barrier height of p-type semiconductor oxides and thus lead to the resistance increase [27]. This may be also the reason of our sensor for the response to CO<sub>2</sub>. Anyway, the sensor based on NiO/Al<sub>2</sub>O<sub>3</sub> showed good selectivity to 2-chloroethanol at this temperature.

The response and recovery time could determine the operational applicability of a sensor in the practice of detecting gases. The concerned experiments were carried out as follows: In a fume cupboard, the sensor was set at temperature 160 °C in air. When the sensor's resistance reached a stable value, a suitable amount of 2-chloroethanol was injected in the gas chamber. After the resistance reached another stable value, the chamber was opened to expose the sensor in air again.

Fig. 10 shows the survey of the responses and recovery behaviors for the sample to 20–500 ppm 2-chloroethanol at 160 °C. It can be seen that the resistance curve rises dramatically upon the injection of the tested gas and decreases to the initial value rapidly with the remove of the tested gas. These results also confirm that our sample had a typical behavior of a p-type semiconductor. As shown in Fig. 10, the sensor shows good response-recovery characteristic when detecting various concentrations of 2-chloroethanol. For example, the response and recovery time was about 3 min and 20 s to 100 ppm 2-chloroethanol, respectively.

Stability is also an important factor that can seriously influence the practicability of a gas sensor. To examine the stability of the composite, the sensors were retained in dryer and tested for

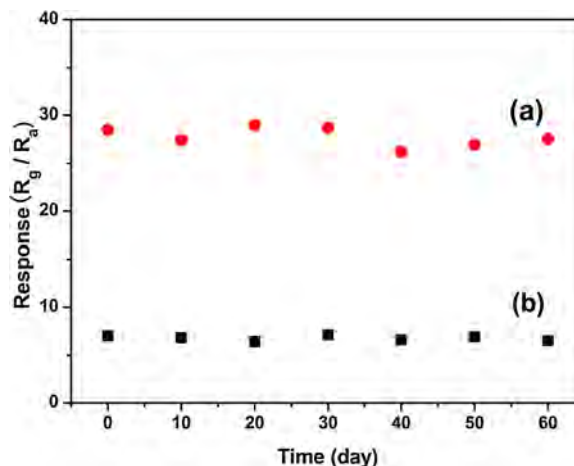


Fig. 11. Response stability of the gas sensors based on NiO/Al<sub>2</sub>O<sub>3</sub> at 160 °C to (a) 200 ppm 2-chloroethanol and (b) 20 ppm 2-chloroethanol.

2-chloroethanol in air with 25% humidity at 160 °C every ten days in two months period. As shown in Fig. 11, the sensor responses were stable except a small variation. It is generally accepted that nanoparticles of small dimensions often grows up due to their coalescence at high operating temperatures over time [32,33]. The coarsening crystal grain [34] may have strong effect on sensors' electrophysical properties because grain size is often regard as an important factor in gas sensing [35]. So we presume that the good stability of NiO/Al<sub>2</sub>O<sub>3</sub> may attribute to the low operating temperature in the tests. As for the small drifts, they are more likely to be induced by the small changes in the ambient humidity or the seasonal fluctuation of temperature in the surroundings [32]. The results above indicated that the sensors based on the NiO/Al<sub>2</sub>O<sub>3</sub> material were stable.

Based on the results above, it can be seen that, sample NiO/Al<sub>2</sub>O<sub>3</sub> showed superior gas sensing response and selectivity to 2-chloroethanol at low temperature than pure NiO and the additive of Al<sub>2</sub>O<sub>3</sub> must play an important role in the process. However, due to the insulating nature of Al<sub>2</sub>O<sub>3</sub>, the resistance value of our sensor based on NiO/Al<sub>2</sub>O<sub>3</sub> in 2-chloroethanol seems somewhat high, which may hinder its practical application to some extent. Therefore, the use of Al<sub>2</sub>O<sub>3</sub> in our sample is a double-edged sword. Even so, there are still some important implications in the practice of detecting 2-chloroethanol in our study.

In our next work, the ratio of NiO/Al<sub>2</sub>O<sub>3</sub> will be varied within the HTlc precursors to decrease the resistance value of the sensor in order to prepare the optimal sensor material which should have more desirable practicability in detecting 2-chloroethanol.

#### 4. Conclusions

Composite NiO/Al<sub>2</sub>O<sub>3</sub> was prepared using a simple co-precipitation method followed by a calcination process at 600 °C. In the XRD pattern, the composite NiO/Al<sub>2</sub>O<sub>3</sub> shows a typical phase of cubic nickel oxide with an amorphous phase of Al<sub>2</sub>O<sub>3</sub>. Moreover, the composite has smaller grain size with smaller pores than pure NiO as indicated in the SEM and TEM photographs. The BET surface area analyses show that NiO/Al<sub>2</sub>O<sub>3</sub> has much larger surface area and smaller pore size than pure NiO. Furthermore, the addition of Al<sub>2</sub>O<sub>3</sub> to NiO could obtain excellent gas sensing performance to 2-chloroethanol at low temperature. The highest response of the composite NiO/Al<sub>2</sub>O<sub>3</sub> could reach about 6.8–20 ppm 2-chloroethanol at 160 °C. The response and recovery time of the sensor based on NiO/Al<sub>2</sub>O<sub>3</sub> was about 3 min and 20 s to 100 ppm 2-chloroethanol, respectively. The sensor based on

composite NiO/Al<sub>2</sub>O<sub>3</sub> also showed good selectivity and response stability to 2-chloroethanol at low temperature.

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