



## Ultrafast-response stabilized zirconia-based mixed potential type triethylamine sensor utilizing $\text{CoMoO}_4$ sensing electrode



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### ABSTRACT

An ultrafast-response yttria stabilized zirconia (YSZ)-based mixed potential type gas sensor utilizing molybdate  $\text{CoMoO}_4$  sensing electrode was developed to realize the effective detection of triethylamine (TEA) at 600 °C. The gas sensing characteristic of the fabricated sensor was optimized by changing the calcination temperature of  $\text{CoMoO}_4$  sensing material and results indicated that the device attached with  $\text{CoMoO}_4$ -SE sintered at 1000 °C exhibited the highest response value (−102 mV) to 100 ppm TEA and low detection limit of 100 ppb at 600 °C. Interestingly, the response and recovery times of the present sensor to 100 ppm TEA were 1 s and 10 s, which signified the ultra-fast response rate. The response value of fabricated sensor displayed the piecewise linear function to logarithm of TEA concentrations and the sensitivities were −14 mV/decade (0.1–5 ppm) and −53 mV/decade (5–200 ppm), respectively. More importantly, the present sensor also exhibited good repeatability, selectivity, slight effect of humidity and long-term stability of 20 days, indicating a great candidate for use in detection of TEA. Furthermore, the device based on mixed potential mechanism was proposed and further verified using polarization curve.

### 1. Introduction

Triethylamine (TEA) is one of the most important volatile organic amines with the characteristics of colorless transparent, flammable, explosive, toxic and strong pungent odor and has been widely used to industrial production process, including organic solvent, polymerization inhibitor, antiseptic, catalyst and synthetic dye *etc* [1–5]. Meanwhile, TEA can also be engendered in the deterioration process of dead fish and marine creatures, and the gas concentration evidently increased along with the degree of anabatic deterioration [6]. Especially, it can cause multiple deleterious health effects, from eye irritation to respiratory problem with pulmonary edema, and even death [7,8]. On the basis of Occupational Safety and Health Administration (OSHA) standards, the concentration threshold limit of TEA should not exceed 10 ppm [2,9]. Accordingly, the development of real-time, rapid and low detection limit gas sensor with high sensitivity, selectivity and stability for detection of TEA is an inevitable necessary and urgent issue.

To date, metal oxide semiconductor (MOS) type TEA sensors based on  $\text{SnO}_2$  [10],  $\text{ZnO}$  [11],  $\alpha\text{-Fe}_2\text{O}_3$  [12],  $\alpha\text{-MoO}_3$  [13],  $\text{Zn}_2\text{SnO}_4$  [14] and  $\text{NiFe}_2\text{O}_4$  [15] have been extensively developed due to low fabrication

costs, portability and good sensing characteristics with high sensitivity. However, most of MOS gas sensors have the disadvantages of relatively insufficient response or recovery kinetics and selectivity. In contrast, solid state electrolyte type gas sensors have been paid great attention due to the excellent sensing properties to various hazardous, flammable and explosive gases. Among them, the mixed potential type gas sensor based on yttria stabilized zirconia (YSZ) electrolyte is found to be the most potential candidate because of its better environmental stability and the excellent selectivity. Up to now, the various YSZ-based gas sensors have been fabricated and were used to detect  $\text{NO}_2$  [16–20],  $\text{NH}_3$  [21,22],  $\text{SO}_2$  [23],  $\text{H}_2\text{S}$  [24], VOCs [25–27] and hydrocarbon [28,29] in literatures. However, to the best of our knowledge, YSZ-based gas sensor based on mixed potential model for detecting TEA has not been reported.

For the mixed potential type gas sensor, the sensing characteristics of developed device were closely attributed to the electrochemical catalytic activity of the sensing electrode material. The Binary metal oxides, such as  $\text{SmFeO}_3$  [30],  $\text{La}_2\text{NiO}_4$  [31] and  $\text{ZnFe}_2\text{O}_4$  [32] have displayed outstanding catalytic activity toward electrochemical reaction processes in YSZ-based gas sensor based on mixed potential

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mechanism. Molybdate  $\text{CoMoO}_4$  has been reported to show a higher catalytic activity and stability in catalysis [33], non-aqueous batteries [34], supercapacitors [35], but the electrochemical catalytic capability and durability of  $\text{CoMoO}_4$  in solid electrolyte gas sensor have not been reported. Its potential as a sensing electrode material in YSZ-based gas sensor is worthy of exploration.

Herein, for the first time, the  $\text{CoMoO}_4$  prepared by a facile hydrothermal method was used as the sensing electrode of YSZ-based mixed potential type gas sensor for detection of TEA. The effect of calcination temperature of  $\text{CoMoO}_4$  and operating temperature on sensing properties was determined. Additionally, the detailed gas sensing performance and sensing mechanism of the fabricated sensor to TEA were investigated and discussed.

## 2. Experimental

The  $\text{CoMoO}_4$  material was synthesized via a facile hydrothermal method, as described in Supporting Information [34]. The structural characteristic of  $\text{CoMoO}_4$  was investigated with Rigaku wide-angle X-ray diffractometer (D/max rA, using  $\text{Cu K}\alpha$  radiation at wave length = 0.1541 nm). Raman spectroscopy of the sensing material was performed using LabRAM HR Evolution spectrometer with a laser wavelength of 532 nm. Field-emission scanning electron microscopy (FESEM) measurement of the  $\text{CoMoO}_4$ -SE surface morphology was performed using a JEOL JSM-7500 F microscope with an accelerating voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) of the sample was measured using a Thermo ESCALAB250 spectrometer equipped with an  $\text{Al-K}\alpha$  ray source.

The sensor was fabricated using the YSZ plate (8 mol%  $\text{Y}_2\text{O}_3$ -doped, 2 mm  $\times$  2 mm square, 0.2 mm thickness, provided by Anpeisheng Corp., China) and shown in Fig. 1 [23,27]. The gas sensing properties of the fabricated sensors were measured by a conventional static method [19,26,31]. The polarization curves of the sensor were measured via the potentiodynamic method (CHI650C, Instrument corporation of Shanghai, China) using a two-electrode configuration in air and the different concentrations of TEA gases at 600 °C. The complex impedance measurements of the sensor in air and 100 ppm of various deleterious gases were performed using an impedance analyzer (Solartron 1260 and Solartron 1287) in the frequency range of 0.1 Hz–1 MHz at 600 °C. The amplitude of the AC potential signal was fixed at 300 mV in all measurements.

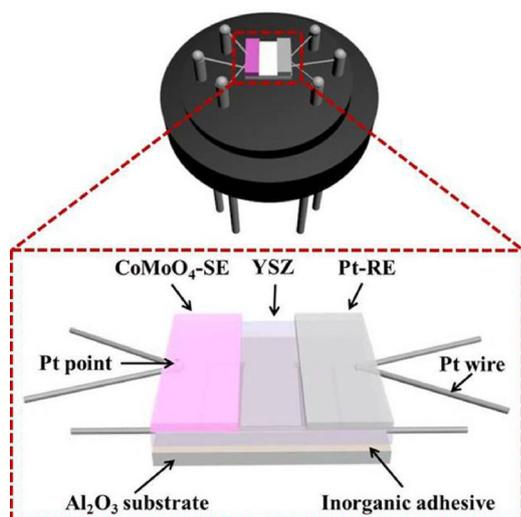


Fig. 1. Schematic diagram of the fabricated sensing device.

## 3. Results and discussion

X-ray diffraction (XRD) was measured to investigate the crystalline nature of the synthesized sensing material. The XRD pattern of  $\text{CoMoO}_4$  composite oxide material sintered at 1000 °C is indicated in Fig. 2(a). The diffraction peaks of  $\text{CoMoO}_4$  are readily indexed to  $\text{CoMoO}_4$  oxide standard XRD patterns (JCPDS#14-587). The sharp diffraction peaks demonstrated the good crystallinity of the prepared  $\text{CoMoO}_4$  sensing material. Raman spectroscopy was applied to further investigate the structure characteristic in bonding related to  $\text{CoMoO}_4$  composite material (Fig. 2(b)). The Raman peak position at 335, 364, 695, 812, 878 and 934  $\text{cm}^{-1}$  between 200 and 1200  $\text{cm}^{-1}$  can be assigned to the stretching and bending vibration model in  $\text{CoMoO}_4$ . These results are in accordance with those previously reported [34,36,37].

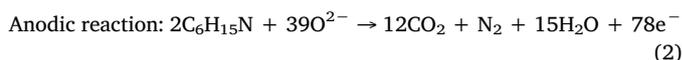
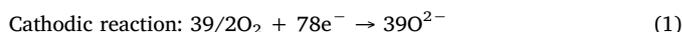
To further determine the compositions and chemical states of the prepared  $\text{CoMoO}_4$  sensing material, XPS measurement was conducted. The survey spectrum (Fig. 3(a)) demonstrates the presence of Co, Mo and O elements in the obtained material sintered at 1000 °C. For the XPS spectrum of Co 2p (Fig. 3(b)), the two major peaks located at 797.5 and 781.4 eV are characteristic of Co 2p<sub>1/2</sub> and Co 2p<sub>3/2</sub>, and the shakeup-type satellite peaks (marked as Sat.) are observed, corresponding to  $\text{Co}^{2+}$  [34,38]. The XPS spectrum in Fig. 3(c) reveals two obvious peaks at 235.3 and 232.2 eV, which are attributed to Mo 3d<sub>3/2</sub> and Mo 3d<sub>5/2</sub>, respectively. The binding energy width of Mo 3d is equal to 3.1 eV, indicating the presence of only  $\text{Mo}^{6+}$  [39]. As shown in the O 1s spectrum, the binding energy centered at 531.7 and 530.2 eV could be related to chemisorbed oxygen species and lattice oxygen in the surface of  $\text{CoMoO}_4$  material, respectively (Fig. 3(d)) [40].

In order to optimize the sensing performances of the developed sensor, the  $\text{CoMoO}_4$  sensing electrode material was sintered at different temperatures. The response values of sensors utilizing  $\text{CoMoO}_4$ -SE sintered at different temperatures (800, 1000 and 1100 °C) to 100 ppm TEA at 600 °C were measured and shown in Fig. 4. The sensor attached with  $\text{CoMoO}_4$ -SE calcinated at 1000 °C exhibited the highest response value to 100 ppm TEA at 600 °C. The sensing characteristics of the present sensors based on the mixed-potential mechanism, which has been demonstrated by some research groups [41–43]. According to this result, the sensor can be described by the following electrochemical cells:

In air:  $\text{O}_2, \text{CoMoO}_4/\text{YSZ}/\text{Pt}, \text{O}_2$

In sample gas:  $\text{C}_6\text{H}_{15}\text{N} + \text{O}_2, \text{CoMoO}_4/\text{YSZ}/\text{Pt}, \text{C}_6\text{H}_{15}\text{N} + \text{O}_2$

When the fabricated device was placed in the TEA gas atmosphere, the electrochemical reactions of cathodic (1) and anodic (2) occur simultaneously at the TPB (triple phase boundary, the interface of  $\text{CoMoO}_4$ , TEA and YSZ solid state electrolyte) of  $\text{CoMoO}_4$ -SE and form a local cell. The electrode potential is called the mixed potential when the rates of two electrochemical reactions reach the dynamic equilibrium. The potential difference between the SE and RE is the sensing response signal.



The sensing response signal for the mixed potential type gas device relies on the electrochemical reaction active sites of TPB at SE. The larger porous channels decreased the consumption of TEA in the process of diffusion in  $\text{CoMoO}_4$  electrode layer and facilitated more TEA gas to arrive at the TPB, which participated in electrochemical reaction (Observed in Fig. S1 and S2). The particles of  $\text{CoMoO}_4$  became too large with the further increase of calcination temperature and resulted in the reduction of TPB area. In this case, the electrochemical reaction active sites decreased, thus, the sensitivity of the sensor to TEA decreased obviously with the further increase of calcination temperature (1100 °C). Additionally, the  $\text{CoMoO}_4$  composite material showed the remarkable catalytic property and the good crystallization, which may

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