Application of Chemical Noxious Gas Test Based on Electronic Nose Technology

Ruilin Yuan
Hebi Polytechnic, Hebi 458030, China
3067349@163.com

This paper describes the development and characterization of zinc oxide nanosheet gas sensor. Such sensor is integrated in the electronic nose system to test chlorinated hydrocarbon organics and chlorobenzenes. Then it is proved weather the electronic nose system as a new test method is feasible in the industry or not. The study bears out that the prepared zinc oxide nanosheet has better sensitivity and responsiveness, its operating temperature as an optimal parameter is 220 ° C; the conversion voltage is 5V. The electronic nose has the highest sensitivity to chlorobenzenes, and the response intensity rests above 1000mV. In the test, however, the sensitivity of electronic nose to chlorinated hydrocarbon organics is relatively low. There is a clear linear relationship between the response intensity of the electronic nose and various noxious gases at the correlation coefficient of above R2=0.85. The types of the tested gases can be estimated by using a linear fitting curve and the appropriate intensity when a certain gas is tested with electronic nose.

1. Introduction

Volatile and toxic gases such as trichloroethylene, carbon tetrachloride, acetone and formaldehyde are common gaseous chemical pollutants in the air, which, if abused in the manufacture fields such as automobile, chemical industry, textile, pharmaceuticals, etc., will cause environmental pollution, especially in the case when they are misconducted after a heavy use of them, they will seriously damage the life health, for example, causing the symptoms such as fatigue and nausea in humans and animals, and can even induce cell canceration in the body (Wang et al, 2017; Dudynski, 2018). In this sense, it is of great significance for us to accurately test the above toxic gases in a timely manner (Zheng, 2011).

The traditional test method for chemical noxious gases mainly comes to the gas chromatography, which has a higher test precision. However, due to some defects such as expensive equipment, low mobility, and complicated operation it has, it fails to timely detect the environment (Shaw, 2005). Electronic nose technology, as a new method developed for testing the noxious gases in recent years (Röck et al., 2008; Baby et al., 2000; Ameer and Adeloju, 2005; Lim et al., 2009; Tang et al., 2011), has expanded its core functions such as gas sensor array and pattern recognition technologies. It features portable to move, easy to operate, and online real-time supervision (White, 2001; Hosseini et al., 2005; Krantz-Rücker et al., 2001; Hosseini and Entezami, 2001; Pietrantonio et al., 2012; Ngo, Lauque and Aguir, 2006; Jha and Hayashi, 2014). As electronic nose technology is relatively new, it is currently only used in automotive exhaust and flammable gas in the air; while for the test of volatile toxic chemicals, various types of contaminating chloralkane gases and chlorobenzenes, there are few studies on this areas (Natale et al., 2000; Dewettinck et al., 2001; Umar et al., 2012; Wilson, 2012).

In this paper, a zinc oxide nanosheet gas sensor is prepared and characterized by integrating it into the electronic nose system. Then, this integrated system is used to test chlorinated hydrocarbon organics and chlorobenzenes, and it is proved eventually that the proposed electronic nose test method is feasible in the field (Mao, 2018).
2. Integrated framework of electronic nose test system

The working principle of the electronic nose gas generator is shown in Figure 1. It consists of diffuser, thermostatic water bath and the like. When analyzing a single component gas, the generator can generate a single gas with different concentrations and directly access to the detection system; when analyzing the gases containing a plurality of component, it is used to generate an appropriate kind of gas, and after being pretreated, the gas is filled into the test system.

The electronic nose test system designed in this paper, as shown in Figure 2, mainly consists of flow controller, sample injector, chromatographic column, testing chamber, computer and so on. When it works, the gas to be tested is input into the system with the flow controller. After the gas is dried and separated, the gas enters the testing chamber. The sensor generates appropriate electrical signals after contacting with the gas, and converts them into images and data.

3. Preparation and characterization of zinc oxide nanosheet gas sensor

The electronic nose gas sensor used in this paper is self-made with zinc oxide nanosheet gas sensing materials, and the raw materials for preparing zinc oxide nanosheets include zinc acetate, urea, ethanol, distilled water and the like. The preparation process is shown in Figure 3.

The prepared zinc oxide nanosheets are characterized by XRD, see Figure 4 for characterization results. It is known from the figure that the XRD spectrum before the annealing of the raw material is the lower curve in the figure. At this time, the detected main component in the material is Zn(CO$_3$)(OH)$_6$($x$H$_2$O), and the peak intensity in the spectrum is low; after high temperature annealing at 300 °C, the XRD spectrum of the material precursor is given as the upper curve, and the typical diffraction peak of ZnO appears at 100, 101, etc. The purity of the detected ZnO is higher from the spectrum curve.
Calculate the grain size $D$ of the sample using Equation 1.

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (1)$$

$\theta$ is the diffraction angle; $\beta$ is the diffraction half-peak width; $\lambda$ is the incident wavelength. According to the calculation, the average particle diameter of the prepared zinc oxide nanosheets is 170 nm, which bears out that the prepared ZnO has a good crystallization effect.

The thermodynamic test and pore structure distribution curves of the prepared zinc oxide nanosheets are further tested, as shown in Figure 5. From the thermodynamic test curve, we can observe the presence of mesoporous pores of zinc oxide nanosheets. According to the pore structure distribution curve, the most probable pore size of ZnO is about 35 nm.

As shown in Figure 6, there is the relationship between the operating temperature of zinc oxide nanosheets and their sensitivity. It can be seen from the figure that with the increase of working temperature, the working sensitivity of ZnO first increases and then decreases, and the best sensitivity reaches 3.75S at 220 °C. It is feasible, therefore, the operating temperature of the electronic nose can be set to 220 °C, and the conversion voltage is set to 5V.

4. Test results and analysis of impact factors

The noxious gas in the environment is tested using the electronic nose system established above. As shown in Figure 7, the results come from the test on the chlorinated hydrocarbons (TCE, TCM, DCM, CT) and chlorobenzenes (1,2-DCA, toluene, ethylbenzene, 1,3-xylene) with the electronic nose system.
Figure 7: Test results of electronic nose for chlorinated hydrocarbons and chlorobenzenes

As shown in above figures, there is a big gap in the results of the test response intensity from the electronic nose on various hazardous gases. The electronic nose has a response to the TCE, and the response intensity is proportional to the concentration of the gas under test. The responses to trichloromethane (TCM) and carbon tetrachloride (CT) are relatively strong, and the response intensity grows linearly. For chlorobenzenes, the response of the electronic nose is the strongest, above 1000mV. When the concentration of the gas to be tested reaches 200μg/L, the response intensity of the electronic nose hits upon 1600mV. Based on the relevant calculation results, the electronic nose designed in this paper has 2.1mV/(μg/L) response sensitivity to chlorobenzenes.
The concentration of gas to be tested, as shown in Figure 7, and the electronic nose response intensity are fitted, and the results are as follows:

**TCE:**

\[ y = 0.22x + 27.6 \quad R^2 = 0.978 \] 

**TCM:**

\[ y = 1.08x + 84.5 \quad R^2 = 0.989 \] 

**DCM:**

\[ y = 0.34x + 71.4 \quad R^2 = 0.957 \] 

**CT:**

\[ y = 1.84x - 128.9 \quad R^2 = 0.922 \] 

**1,2-DCA:**

\[ y = 2.41x + 852.1 \quad R^2 = 0.861 \] 

**Toluene:**

\[ y = 2.78x + 1068.2 \quad R^2 = 0.958 \] 

**Ethylbenzene:**

\[ y = 1.8x + 1527.3 \quad R^2 = 0.946 \] 

**1,3-xylene:**

\[ y = 0.2x + 20.7 \quad R^2 = 0.857 \] 

From Equations 2~9, it is known that the response intensity of the electronic nose prepared in this paper has a significantly linear correlation with various noxious gases at a correlation coefficient of above \( R^2 = 0.85 \). The linear fitting curve and the corresponding intensity of the electronic nose when a certain gas is tested can be used to infer the tested gas type.

### 5. Conclusion

In this paper, a zinc oxide nanosheet gas sensor is developed and characterized, and then integrated into the electronic nose system. This system is used to test the chlorinated hydrocarbon organics and chlorobenzenes. It is also proved whether or not the proposed electronic nose system is feasible in this field. The study derives the following conclusions:

1. The zinc oxide nanosheet as prepared has a more excellent sensitivity and responsiveness, and its optimum operating temperature is 220 °C; the conversion voltage is 5V.
2. Electronic nose has the highest test sensitivity to chlorobenzene organic matter, and the response intensity is above 1000mV, but relatively low to the chlorinated hydrocarbon organic matter. There is a clear linear relationship between the response intensity of the electronic nose and various noxious gases, and the correlation coefficient is above \( R^2 = 0.85 \). The types of the tested gases can be estimated by using a linear fitting curve and the appropriate intensity of the electronic nose when a certain gas is tested with it.

### References


Dudynski M., 2018, Gasification of selected biomass waste for energy production and chemicals recovery, Chemical Engineering Transactions, 65, 391-396, DOI: 10.3303/CET1865066
Xiaoqun Mao, 2018, Design of new electrochemical sensors and detection application of chemical feedstock residues, Chemical Engineering Transactions, 65, 205-210, DOI: 10.3303/CET1865035
Shaw M.D., 2005, Toxic gas detection in the real world: practicalities and pitfalls, Synergist, 16(9), 40-42, DOI: 10.1032/0269-9321.s1597238