Ethylamine gas sensing properties of SnO$_2$/rGO nanocomposite materials

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Abstract. Ethylamine has been widely used in production and life, but it needs to be monitored in real-time because of its important harm to human health. In this study, an SnO$_2$/rGO nanocomposite gas sensitive material was synthesized by hydrothermal method, and the gas-sensing properties of ethylamine were tested by a self-made gas sensitivity test platform. The results show that the SnO$_2$/rGO nanocomposite materials have good gas-sensitive performance of ethylamine and low detection limit (up to 1 ppm). Finally, the mechanism of gas sensitivity is proposed.

1. Introduction
Ethylamine is easy volatile under room temperature and pressure, it is a colorless and strong smell of ammonia organic liquid, which belongs to high toxic substances. It can be used as pesticides in agricultural production, and also widely used as dye production in industrial production, antioxidant, rubber accelerator and surfactant, power fuel [1], ion exchange resin, solvents and detergents, lubricant, metallurgical processing agent, and the production of cosmetics and pharmaceuticals in daily life. It is also used as extraction agent, emulgator, medicine raw material and reagent. Ethylamine can get inside the body by inhaled, ingestion or skin contact. It can stimulate the eye, weasand, lung, excretory system and the upper respiratory tract, and damage the cornea. Ethylamine liquid splashed into people’s eyes can lead to severe eye burns; contact with skin can cause burns. Consequently, the maximum permissible concentration–time weighted average (PC-TWA) for ethylamine is 9 mg/m$^3$ (4.47 ppm); the permissible concentration–short term exposure (PC-STEL) is 18 mg/m$^3$ (8.94 ppm) in China [2]. Therefore, it is necessary to carry out real-time monitoring of this molecule.

To date, many methods have been devised for the detection of ethylamine at the ppm or ppb level, such as solvent-gas chromatography [3], headspace capillary gas chromatography [3], ion chromatography [4], and spectrophotometric method [5]. These methods have many disadvantages: gas chromatography needs derivatization processing, its operation is complicated; ion chromatography is also complex, cannot achieve real-time monitoring; spectrophotometric method contains many influence and interference factors, and its result is poor stability and reproducibility. In order to solve these problems, some new detection methods of ethylamine have been developed [6-10]. However, the materials [6-8,10] or quartz crystal microbalance (QCM) sensors [9] or optical sensor [10] used in these new detection methods are expensive and difficult to popularize. On the other hand, gas sensors based on metal oxide semiconductors, such as SnO$_2$, ZnO, and Fe$_2$O$_3$, have attracted much attention owing to
their unique features, such as low cost, high sensitivity, fast response, relative simplicity and portability [11].

It is well known that SnO$_2$ is widely used as a gas-sensing material and that graphene has very good electrical conductivity and a large surface area. Many published reports [12-22] have proved the excellent gas-sensing properties of SnO$_2$/rGO nanocomposite materials. Among them, the gases showing excellent gas sensitivity performance are NO$_2$ [12], formaldehyde [13], H$_2$ [14], methane [15], ethanol [16], C$_2$H$_2$ [17], diethyl ether [18], H$_2$S [19], trichloroethylene [20], acetone [21], NH$_3$ [22], etc.

To the best of our knowledge, there has been no published report on the sensing of ethylamine with SnO$_2$/rGO gas-sensing material, except for the sensing of ethylamine with Na[Cd(MIDC)]$_n$ [6], PPy-metal oxide semiconductor (MOS) [7], thiobarbituric-isophorone chromophore [8], etc.

In this study, a SnO$_2$/rGO gas-sensing material has been prepared by a hydrothermal method and the gas sensing properties of ethylamine vapor was tested and a gas sensitive mechanism of ethylamine was proposed.

2. Materials and methods

Graphene oxide (GO) and SnO$_2$/rGO nanocomposite powders were prepared by a modified hummer’s method and a hydrothermal method, respectively. Detailed preparation process and characterization methods can be found in our previous paper [18]. Detailed preparation process of the SnO$_2$/rGO gas sensing film and the ethylamine gas sensitivity test method can also be referred to literature [18]. The gas-sensing properties of the SnO$_2$/rGO film were investigated using a gas-sensing material screening platform [23] by testing the change of the resistances of the coating layer when the testing chamber was exposed in air and tested gases atmosphere under laboratory conditions. Gas sensitivity in this study is defined as $S = R_a/R_g$, where $R_a$ and $R_g$ are the resistances of a sensor in air and in a test gas, respectively.

3. Results and discussion

3.1. Structural characterization

Detailed characterization of GO, rGO and SnO$_2$/rGO was reported in our previous paper [18]. The research results in literature [18] showed that the specific surface area of SnO$_2$/rGO nanocomposite gas-sensitive materials synthesized by hydrothermal method reached 187m$^2$/g, larger than that in literature [22]. This large specific surface area is beneficial for the sensing properties of the SnO$_2$/rGO nanocomposite powders for ethylamine vapors.

3.2. Gas-sensing properties of SnO$_2$/rGO sensor arrays

Figure 1 shows the effect of operating temperature on the gas sensitivity of the SnO$_2$/rGO sensor to 200 ppm ethylamine. The gas sensitivity increases with increasing operating temperature, and its gas sensitivity is 39.57 at 400 °C. This phenomenon has been reported in the detection of C$_2$H$_2$ by SnO$_2$ and rGO [17] and methane by SnO$_2$ [15]. The change of physical adsorption at low temperature to chemical adsorption at high temperature of the adsorption mode of oxygen molecules is the main reason for this phenomenon [24]. As the operating temperature increases, the amount of chemically adsorbed ethylamine also increases. That is to say, the adsorbed ethylamine molecules will increase with the increase of temperature, and the adsorbed oxygen molecules are also increase, so it traps more electrons from the conduction band to form a depletion layer and causes a larger change in the resistance, increase the gas sensitivity (Figure 1). It should be pointed out that due to the power limitation of the gas-sensitive performance test circuit, on the one hand, the working temperature cannot continue to increase; on the other hand, the actual working temperature of the gas-sensitive sensor generally does not exceed 400 °C. This operating temperature of 400 °C has not yet reached the maximum gas sensitivity value, which may be related to the type of gas [25] being tested.
The following reactions may describe the adsorption of oxygen [26] and ethylamine:

\[
\begin{align*}
\text{O}_2(g) & \rightleftharpoons \text{O}_2(\text{ads}) \quad (1) \\
\text{O}_2(\text{ads}) + e^- & \rightleftharpoons \text{O}_2^-(\text{ads}) \quad (T < 100^\circ \text{C}) \quad (2) \\
\text{O}_2^-(\text{ads}) + e^- & \rightleftharpoons 2\text{O}^-(\text{ads}) \quad (100^\circ \text{C} < T < 300^\circ \text{C}) \quad (3) \\
\text{O}^-(\text{ads}) + e^- & \rightleftharpoons \text{O}_2^-(\text{ads}) \quad (T > 300^\circ \text{C}) \quad (4) \\
2\text{CH}_3\text{CH}_2\text{NH}_2(\text{ads}) + 11\text{O}_2^-(\text{ads}) & \rightarrow 7\text{H}_2\text{O} + 2\text{CO}_2 + 2\text{CN} + 22e^- \quad (5)
\end{align*}
\]

Figure 2 shows the relationship between the gas sensitivity of the SnO$_2$/rGO gas sensor and the concentration of ethylamine. As can be seen from the Figure 2, the gas sensitivity increases with the increase of the concentration of ethylamine from 1 to 200 ppm at 400 ºC. This phenomenon has also been widely reported in the literature [27]. The gas sensitivity of the SnO$_2$/rGO gas sensor was 1.03 at 1 ppm and 400 ºC, and increased to 39.57 at 200 ppm and 400 ºC. That is, the detection limit of the SnO$_2$/rGO gas sensor to ethylamine can reach 1 ppm, which meets the demand for real-time monitoring of this molecule [2].
Figure 2. Gas sensitivity of the SnO$_2$/rGO sensor vs ethylamine concentration (1–200 ppm) at 400 °C

Figure 3 shows the response and recovery times of the SnO$_2$/rGO gas sensor to 1 and 200 ppm ethylamine. As can be seen from Figure 3, these parameters were 369 and 110 s, respectively, at 1 ppm ethylamine, and 20 and 27 s, respectively, at 200 ppm ethylamine.

The high gas sensitivity of the SnO$_2$/rGO gas sensor is related to its large specific surface area (187 m$^2$/g) and the high conductivity of rGO [28]. At the operating temperature, when the negative oxygen ions are adsorbed, the SnO$_2$ surface, as an n-type semiconductor, will generate an electron depletion layer, which will cause the increase of the surface potential barrier and the resistance. When ethylamine molecules are adsorbed on the surface of SnO$_2$ gas-sensitive material, the adsorbed negative oxygen ions are consumed and free electrons are generated. In this way, the resistance of SnO$_2$ gas-sensitive material is reduced. On the contrary, when there is no adsorption of ethylamine molecules, the resistance of SnO$_2$ gas-sensitive material will recover. This change in resistance will provide a gas-sensitive detection method.

Figure 3. Response and recovery curve of the SnO$_2$/rGO sensor to 200 ppm ethylamine at 400 °C (Inset: corresponding curve at 1 ppm ethylamine).
The sensing mechanism for ethylamine based on SnO$_2$/rGO composites could be described as follows: When the SnO$_2$/rGO sensor is exposed to ethylamine, first, the ethylamine molecules will be adsorbed onto the SnO$_2$/rGO composites. Second, the adsorbed ethylamine molecules will react with the chemisorbed oxygen species (O$^2-$, O$^-$, O$^2-$) depending on the operating temperature and release the electrons to the SnO$_2$/rGO composites. Third, the electrons will flow from SnO$_2$ to rGO (Figure 4b) owing to the formation of p(rGO)-n(SnO$_2$) heterojunction [14] and the work functions of n-type SnO$_2$ and p-type rGO are about 4.55 and 4.75 eV, respectively, and results in a rapid decrease of the resistance and higher sensitivity (Figure 2).

**Figure 4.** Schematic model on gas sensing mechanism of SnO$_2$/rGO gas sensor to ethylamine

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**4. Conclusion**

An SnO$_2$/rGO ethylamine gas sensor has been successfully fabricated by a screen-printing technique based on SnO$_2$/rGO nanocomposite powders prepared by a hydrothermal method. The gas sensitivity of the obtained SnO$_2$/rGO sensor to 1 ppm and 200 ppm ethylamine reached 1.03 and 39.57 at 400 ºC, respectively.

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