

A cataluminescence sensor for the detection of trichloroethylene based on PEG200/ZnO nanocomposite

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Abstract: The content of volatile organic compounds (VOCs) in the atmosphere will endanger the health and safety of human beings which makes it very important to develop a simple and rapid method for the determination of gas pollutants. Based on this, a new type of gas sensor was proposed for the detection of trichloroethylene in air. PEG200/ZnO nanocomposite were prepared by hydrothermal method. The materials were characterized by scanning electron microscope, X-ray energy spectrum and fourier infrared spectrum. The high selectivity of the materials was verified by using the cataluminescence (CTL) intensity of 9 kinds of VOCs on the surface of the materials as a reference. The results show that trichloroethylene can produce CTL response on the surface of PEG200/ZnO nanocomposite. Temperature, air flow rate and detector concentration all have certain effects on the CTL intensity. By comparing the CTL intensity under different reaction conditions, it is found that the suitable temperature and air flow rate are 120 °C, 180 mL/min and there is a good linear relationship between the relative CTL intensity and the concentration of the detected substance ($y = 28.588x - 285.56, R=0.9593$). The gas sensor has the advantage of rapid response, and trichloroethylene can produce the maximum CTL on the surface of the material within 3 ~ 5 s.

Key words: VOCs; gas sensor; detection; cataluminescence

1 Introduction

With the development of coal chemical industry, petrochemical industry and solvent manufacturing industry, as well as the increase of industrial exhaust gas and automobile exhaust gas, the content of volatile organic compounds (VOCs) in air is increasing year by year [1,2]. As an important precursor of haze and photochemical smoke, VOCs has become the main culprit of air pollution. The final result of air pollution is to endanger the health and safety of human beings [3], so it is particularly important to find a rapid detection method of VOCs in order to ensure the health of human beings.

At present, VOCs detection technology mainly includes spectrophotometry, gas chromatography, high performance liquid chromatography, etc. [4]. However, there is a disadvantage in these methods that rapid monitoring cannot be achieved. In view of this situation, we urgently need to develop a portable method which can quickly determine VOCs at very low concentration level [5]. Currently, cataluminescence (CTL)-based sensors showed significant advantages. Yu et al [6]. found that NiO with various morphologies showed different CTL capabilities to detect H₂S. Tang et al [7]. found that NaYF₄:Er had a good CTL effect on ketones. Jiao et al [8]. have studied a new alcohols sensor based on CTL on nano-CdS. These and numerous studies have shown that a method of measuring one or more VOCs based on a CTL sensor is possible [9-12].

Trichloroethylene is the most common VOCs in the air. It not only has potential carcinogenic risk to the human body [13,14], but also has great damage to the eyes and the central nervous system. Therefore, in combination with the advantages of the rapid detection method based on the CTL, it is necessary to study a method to quickly detect the trichloroethylene.

A large number of studies have shown that nanometer ZnO has excellent photocatalytic and photoluminescence properties [10,15]. Xu et al. [16] found that PEG200 can be used to improve the CTL properties of materials. In view of this, nanometer ZnO modified materials were used as sensing elements to design and construct CTL - based sensors for rapid detection of VOCs in this paper. The PEG200/ZnO nanocomposite were prepared by hydrothermal. Taking nine typical VOCs pollutants including trichloroethylene as the research object, the high CTL sensitivity nanomaterials for the detection of trichloroethylene were found.

2 Experiment

2.1 Experimental materials

All the reagents were of analytical grade and used as received without further purification. The PEG200, ZnCl₂, Na₂CO₃, carbon tetrachloride, n-hexane, chlorobenzene,

ammonia, butanone, ethanol, xylene, trichloroethylene, and acetone are all purchased from Shanghai Group Chemical Reagent Co., Ltd.

2.2 Preparation of PEG200/ZnO nanocomposite

Surfactants can affect the morphology and structure of substances and PEG200 can be used to improve the CTL properties of materials [16-18], so PEG200 was selected to modify ZnO. The preparation of materials refers to the relevant literature [19]. 2 mL PEG200 was added to 20 mL $1.0 \text{ mol}\cdot\text{L}^{-1}$ Na_2CO_3 solution and stirred for 30 min, and then the mixed solution was added to 20 mL $0.5 \text{ mol}\cdot\text{L}^{-1}$ ZnCl_2 solution ($30 \text{ }^\circ\text{C}$). Secondly, stir the reaction mixture for 30 min, and then leave it for another 30 min to completely precipitate the product. After filtered, washed and dried at $70 \text{ }^\circ\text{C}$ for 24 h, the obtained product was calcined at $550 \text{ }^\circ\text{C}$ for 3 h as resulting materials.

2.3 Characterization

The photos of field-emission scanning electron microscope (SEM) were obtained by using field-emission SEM (ARURIGA) to study the morphology of the material, and the elemental analysis of the samples was carried out using the accompanying X-ray energy (EDS) spectrum. The fourier infrared (FT-IR) spectrum of the sample was determined by the NEXUS-670 infrared spectrometer of NICOLET.

2.4 Cataluminescence sensing measurement

The ceramic rods coated with nanomaterials were placed in the quartz tube and the upper cover of the reaction chamber was covered to keep the reaction chamber in an impermeable state. The appropriate flow rate and temperature of reaction can be adjusted by controlling the flow pump and adjustable transformer. After the reaction conditions were stable, a certain amount of VOCs to be detected was injected into the sample inlet by using a microsyringe, and the CTL signal was detected by ultra-weak chemiluminescence analyzer (BPCL-1-TIC).

3 Results and discussions

3.1 Characterization of PEG200/ZnO nanocomposite

The SEM images of PEG200/ZnO nanocomposite are shown in Fig. 1a and Fig. 1b. As can be seen from Fig. 1a and Fig. 1b, the sample shows a wrapped bulk structure. Further, the detection multiple is further enlarged, and the surface of the material is found to be in a loose floc shape, which increases the specific surface area of the material, thereby facilitating the detection of the contact between the gas and the material.

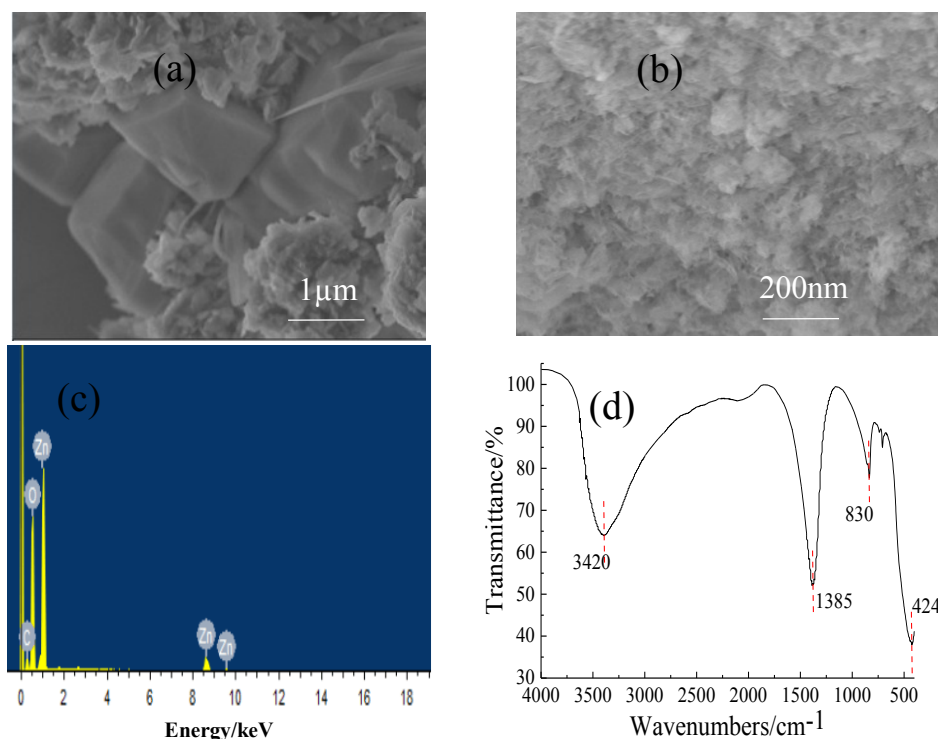


Fig. 1 The SEM images, EDS and FT-IR spectrum of PEG200/ZnO nanocomposite

Combined with Fig. 1c, the sample contains not only Zn and O elements, but also C elements in PEG 200. Fig. 1d shows the FT-IR spectrum of the PEG200/ZnO nanocomposite. Where in 424 cm^{-1} is a characteristic absorption band of ZnO, and 830 cm^{-1} correspond to the O-H feature peaks in the PEG200. While 1385 cm^{-1} and 3420 cm^{-1} corresponds to the absorption band of the ZnO surface O-H [20,21]. So the PEG 200 and ZnO were bonded together to form PEG200/ZnO nanocomposite.

3.2 CTL response of trichloroethylene to nanometer ZnO and PEG200/ZnO nanocomposite

The CTL response of trichloroethylene to nanometer ZnO and PEG200/ZnO nanocomposite was determined under suitable reaction conditions. After injecting the detected material, the signal was monitored by BPCL-1-TIC. The response results are shown in Fig. 2. Fig. 2a shows that trichloroethylene has no obvious CTL response on the surface of nanometer ZnO, but has obvious response effect on the surface of PEG200/ZnO composite nanomaterials. This indicates that the CTL properties of nanometer ZnO have changed after adding PEG200 [16]. The material has a stable response peak in four parallel assays within 400 s, so this method has good reproducibility.

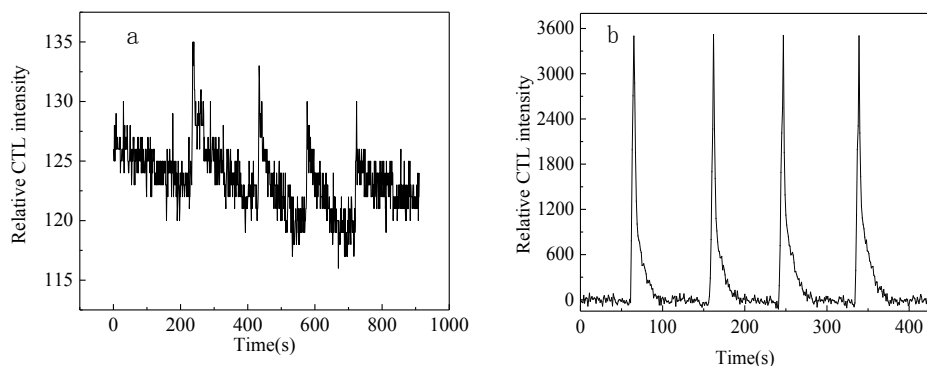


Fig. 2 Response curves of nanometer ZnO (a) and PEG200/ZnO nanocomposite (b) for trichloroethylene based on CTL.

3.3 Effect of working temperature, air flow rate and analyte concentration on CTL intensity

A large number of studies have shown that temperature and air flow rate have a great influence on the intensity of CTL [22-27]. Therefore, under the condition of keeping other conditions unchanged, we investigated the CTL intensity of trichloroethylene on the surface of PEG200/ZnO nanocomposite at different temperatures and air flow rate in order to obtain better response conditions, the specific results are shown in Fig. 3.

As can be seen from Fig. 3a, the CTL signal increases with the increase of temperature. However, under the same time background, the noise is also increasing, and finally the signal-to-noise ratio (S/N) increases first and then decreases. Using this as a reference, the suitable working temperature of the sensor can be determined to be 120 °C, which indicates that the sensor has good CTL activity at lower temperature. Fig. 3b shows that with the increase of air flow rate, CTL signal and signal-to-noise ratio (S/N) increase at first and then decrease. The reason for this result may be that when the air flow rate reaches a certain value, the contact time between the detector and the sensor is not enough, which reduces the sensitivity of the detection system[26,27]. Using this as a reference, the suitable carrier air flow rate of the sensor can be determined to be 180 mL / min.

To investigate the effect of the concentration of the analyte on the intensity of the CTL, a series of concentrations of trichloroethylene were injected into the sensor. The results show that the CTL intensity of trichloroethylene on the surface of nanomaterials increases with the increase of the concentration of trichloroethylene. And there is a good linear relationship between the relative CTL intensity and the concentration of the detected substance ($y = 28.588x - 285.56$, $R=0.9593$). As can be obtained from Fig. 3c, the relative CTL intensity introduced into the trichloroethylene 3 to 5 s reaches the maximum, which indicates that the reactor has the advantage of rapid response. Besides, the limit of detection

defined as 3 N/S (N refers to the noise and S refers to the slope of the calibration curve) is about 8.5 µg/mL.

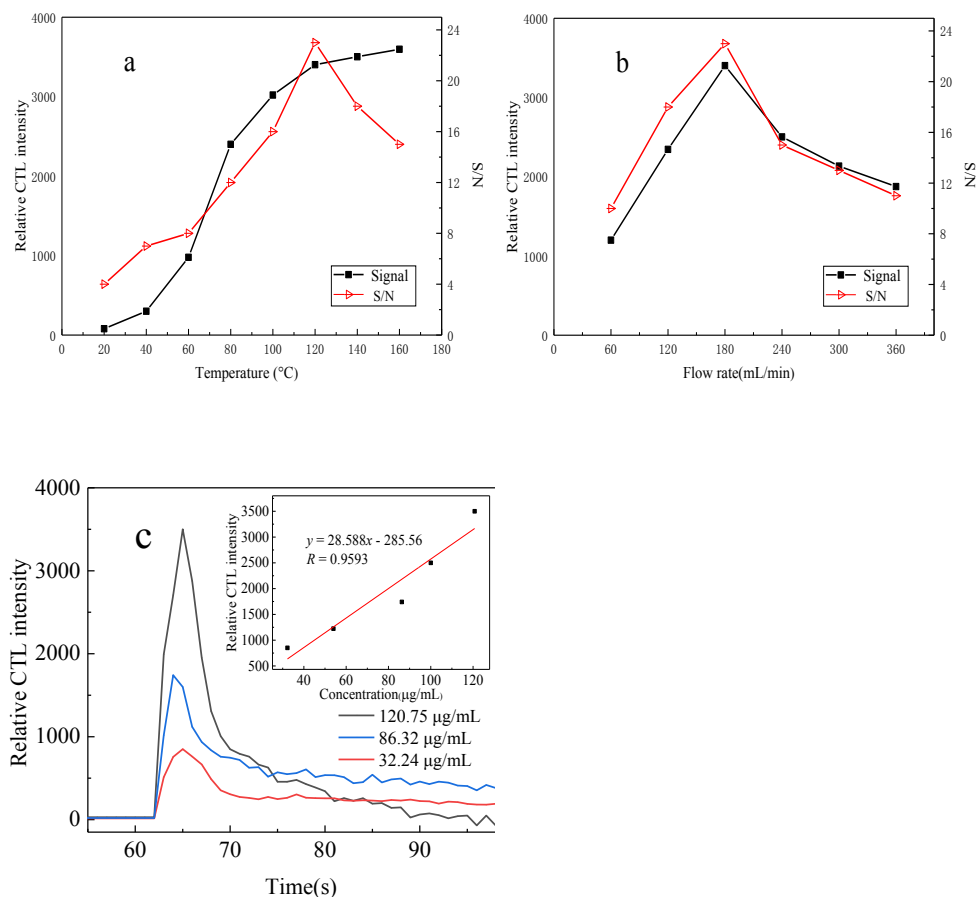


Fig. 3 Effects of operating temperature (a), air flow rate (b) and analyte concentration (c) on the relative CTL intensity. (a) air flow rate: 180 mL/min, trichloroethylene concentration: 120.75 µg/mL; (b) operating temperature: 120 °C, trichloroethylene concentration: 120.75 µg/mL; (c) operating temperature: 120 °C, air flow rate: 180 mL/min.

3.4 CTL selectivity of PEG200/ZnO nanocomposite

During the study, it could be found that the PEG200/ZnO nanocomposite as sensing material showed an excellent selectivity toward trichloroethylene by testing another eight sorts of common possible VOCs, including carbon tetrachloride, n-hexane, chlorobenzene, ammonia, butanone, ethanol, xylene and acetone under the same investigating conditions. At the concentration of 120.75 µg/mL, under the conditions of the air flow rate of 180 mL/min, and the temperature of 120 °C, the object to be examined was injected into the CTL-based sensors of the PEG200/ZnO nanocomposite respectively, and the relative CTL intensity the surface of the material was detected. The results show that trichloroethylene

has a strong rapid CTL reaction on the surface of PEG200/ZnO nanocomposite, while other eight kinds of VOCs on the surface of PEG200/ZnO nanocomposite has no CTL response, which indicates that the material has good CTL selectivity for trichloroethylene (Fig. 4).

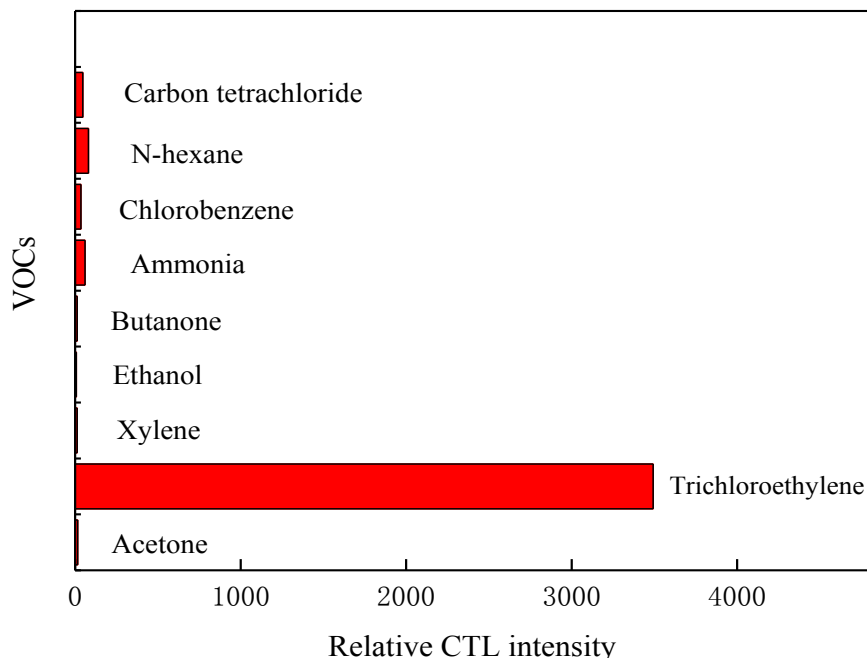


Fig. 4 Gas selectivity of PEG200/ZnO nanocomposite

3.5 Possible mechanisms

According to the widely accepted CTL reaction theory, the CTL response is generated in the process of converting the excited state intermediate into the ground state [28]. Thus, when the trichloroethylene is in contact with the PEG200/ZnO nanocomposite, the reactants are converted from the ground state to the excited state intermediate and a CTL is generated when returning to the ground state again.

The main active species in the CTL reaction are superoxide radical ($\cdot\text{O}_2^-$) and hydroxyl radical (O-H) [28]. Combined with Fig. 3, the composite surface contains O-H and the reason for the CTL signal of trichloroethylene on the surface of PEG200/ZnO nanocomposite is that the surface active agent PEG200 provides the O-H for the CTL reaction. In addition, PEG200 plays the role of adhesive in the composite material, and makes the surface of the material appear loose floc structure, so the adhesion and the contact effect of the PEG200/ZnO nanocomposite to the detection object are better than that of the nanometer ZnO, which caused CTL ability of PEG200/ZnO nanocomposite is naturally stronger than that of nanometer ZnO.

4 Conclusion

The trichloroethylene sensor prepared by using PEG200/ZnO nanocomposite as CTL sensitive material has the advantages of fast response and strong selectivity. Through condition optimization, the suitable reaction temperature and air flow rate of the sensor are determined to be 120 °C and 180 mL/min., respectively. Besides, there is a good linear correlation between the concentration of the detected substance and the relative CTL intensity ($y = 28.588x - 285.56$, $R=0.9593$), and the reactor has good reproducibility for the detection of trichloroethylene.

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