Full Paper

Studies of the Cataluminescence of Benzene Homologues on Nanosized γ–Al₂O₃/Eu₂O₃ and the Development of a Gas Sensor for Benzene Homologue Vapors

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Abstract: The cataluminescence (CTL) of benzene and the benzene homologues toluene and xylene on nanosized γ–Al_2O_3 doped with Eu_2O_3 (γ–Al_2O_3/Eu_2O_3) was studied and a sensor of determining these gases was designed. The proposed sensor showed high sensitivity and selectivity at an optimal temperature of 432 ºC, a wavelength of 425 nm and a flow rate of 400 mL/min. Quantitative analysis was performed at the optimal conditions. The linear ranges of CTL intensity versus concentration of the benzene homologues were as follows: benzene 2.4~5000 mL/m^3, toluene 4.0~5000 mL/m^3 and xylene 6.8~5000 mL/m^3, with detection limits (3σ) of 1.8 mL/m^3, 3.0 mL/m^3 and 3.4 mL/m^3 for each one, respectively. The response time of this system was less than 3 s. The coexistence of other gases, such as SO_2, CO and NH_3, caused interference at levels around 11.7%, 5.8% and 8.9% respectively. The technique is a convenient and fast way of determining the vapors of benzene homologues in air.

Keywords: Cataluminescence, benzene homologues, gas sensor, nanosized γ–Al_2O_3+Eu_2O_3

1. Introduction

In recent years, environmental contamination has become a very serious problem on a worldwide scale. Among the contaminants, benzene and its homologues such as toluene and xylene are ranked by the U.S. Environmental Protection Agency among the 112 hazardous air pollutants [1]. Benzene is known to have toxicity towards the hematopoietic system (hematotoxicity) and to cause leukemia. Exposure to benzene or benzene homologues occurs worldwide to workers in the oil, shipping, automobile repair, shoe manufacture and other industries and to the general public from cigarette smoke, gasoline and automobile emissions. The measurement of benzene homologues in air is necessary for monitoring air quality and following up on the cause(s) of the contamination.

The common analytical methods used to determine low concentrations of benzene homologues are gas chromatography [2] and gas chromatography-mass spectrometry (GC/MS) [3]. They offer high performance and sensitivity, but they are not easy techniques to use for on-line detection due to the large instruments required or laborious and time-consuming operation. Gas sensors, on the other hand, are particularly useful in the case of *in situ*, on line or remote measurements. Semiconductor metal oxide sensors have been used to monitor gaseous benzene homologues [4-6]. The devices are relatively small and inexpensive, but not adequate as far as selectivity and sensitivity to poisoning and ambient conditions are concerned.

Cataluminescence (CTL)-based sensors have been developed since the 1990s. CTL is a kind of chemiluminescence (CL) emitted during catalytic oxidation of gaseous species and was first observed by Bresse *et al*. [7] during the catalytic oxidation of carbon monoxide on a thoria surface. As the signal from this type of sensors does not come from an immobilized reagent on the sensing membrane, but rather comes from an excited intermediate of the analyte itself during catalytic oxidation on a catalyst surface, the sensors do not suffer from the consumption of reagent(s) or losses from an immobilized membrane, therefore CTL-based gas sensors offer long-term stability, good reproducibility and fast responses to analytes. There have been some reports investigating CTL of organic vapors on the γ-Al_2O_3 catalyst and its application to gas sensors [8-11]. It was reported that high intensity CTL spectra were emitted due to Dy^{3+} during the catalytic oxidation of hydrocarbon gas by depositing Dy on the γ-Al_2O_3 catalyst [12-13].

With the expanding availability of nanoparticles, nanosized ZrO_2, TiO_2, $BaCO_3$, $SrCO_3$ and γ-Al_2O_3 doped with Nd_2O_3-based CTL sensors for determination of gas samples, such as ethanol, acetaldehyde, acetone and ethylene dichloride have been reported [14-19]. Since nanoparticles have higher surface areas, higher adsorption characteristics and higher activity than bulk materials, they can be applied in sensitive, miniaturized gas sensors.

In the present paper, we propose a new CTL-based gas-sensor using nanosized γ–Al_2O_3 doped with Eu_2O_3 catalyst (γ–Al_2O_3/Eu_2O_3) for the detection of benzene homologue vapors. The sensor shows good analytical characteristics and was applied to the detection of vapors of benzene or benzene homologues in synthetic samples. To the best of our knowledge, this is the first report of sensing of benzene homologues with this type of sensor.

2. Experimental Section

2.1. Apparatus

The schematic diagram of the CTL detection system which was presented before [19] is shown again in Figure 1 for convenience. The nanosized γ–Al_2O_3/Eu_2O_3 was sintered on the ceramic heating tube to form a layer with a thickness of 0.1 mm. The 5 mm in diameter ceramic heating tube was placed inside a 12 mm inner-diameter quartz tube. The temperature of the γ–Al_2O_3/Eu_2O_3 layer could be adjusted by controlling the voltage of the heating tube.

When the benzene homologues vapors mixed with carrier air flowed through the quartz tube, a catalytic reaction occurred on the surface of γ–Al_2O_3/Eu_2O_3. The cataluminescence intensity was measured with a BPCL Ultra Weak Chemiluminescence Analyzer (Biophysics Institute of Chinese Academy of Science, P.R. China). The wavelengths could be selected over the range of 400-600 nm by changing the optical filters.

Figure 1. Schematic diagram of the CTL sensing system [19].
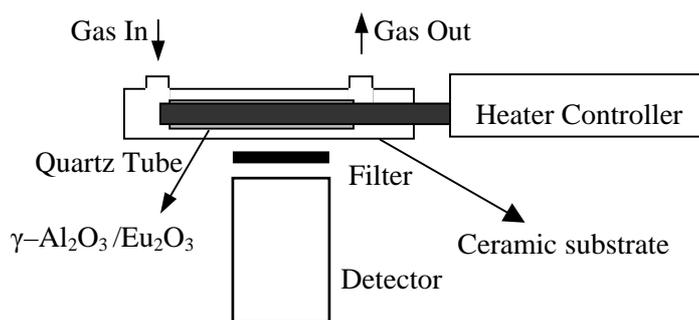
2.2. Preparation of the nanosized materials

A simple chemical precipitation method was developed for the synthesis of nanosized γ-Al_2O_3. First, polyethylene glycol 400 (5g), polyethylene glycol 2000 (5g), polyethylene glycol 10000 (5g) were added into distilled water (250 mL) with continuous stirring until they were completely dissolved. This solution was mixed with an aqueous solution of $Al(NO_3)_3$ (0.2 mol/L, 250 mL), then ammonia was added into the solution while stirring with a magnetic stirrer at 500 rpm until the pH was 8-9. The gel obtained was centrifuged at 6000 rpm and then washed several times with deionized water and dry alcohol. The precipitate was then dried in a muffle furnace at 70 °C for 6 h and at 600 °C for 2 h. The topography and particle size of γ-Al_2O_3 was measured by using a Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of electron beam was 200 kV. Figure 2 shows that the grain size of γ-Al_2O_3 is about 10 nm.

The γ–Al_2O_3/Eu_2O_3 powder was prepared as follows: nanosized γ-Al_2O_3 powder was mixed and ground for 1 h with Eu_2O_3 powder (2 mol %), then calcined at 600 °C in a muffle furnace for 2 h.

A wet chemical method was used to synthesize the ZrO_2 nanoparticles. Ammonia was rapidly added to a $ZrO(NO_3)_2$ solution (0.1 mol/L) with vigorous stirring. A white precipitate was

immediately generated, which was then filtered and washed five times with deionized water. The precursor was dried at 100 °C and calcined at 500 °C in a muffle furnace for 3 h.

Figure 2. TEM photo of γ-Al_2O_3.
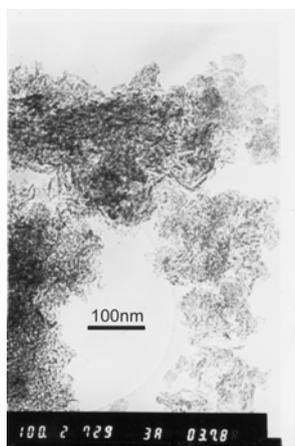
The ZrO_2/Eu_2O_3 powder was prepared as follows: nanosized ZrO_2 powder was mixed and ground for 1 h with Eu_2O_3 powder (2 mol%), then calcined at 500 °C in a muffle furnace for 2 h.

3. Results and Discussion

3.1. Estimation of the nanosized materials

To study the feasibility of the sensing mode, nanosized γ-Al_2O_3, ZrO_2, γ–Al_2O_3/Eu_2O_3 and ZrO_2/Eu_2O_3 were examined. The CTL on the surface of these particles was detected when benzene vapor was passing through at a flow rate of 400 mL/min. The concentration of benzene vapor was 4483 mL/m^3. The results are shown in Table 1. The different temperatures used in the test are aimed at achieving the highest signal/noise ratio for each nanomaterial. The data show that γ–Al_2O_3/Eu_2O_3 (98 mol %/2 mol %) is the best material to obtain highest sensitivity; the corresponding CTL intensity (signal/noise) is 7.50. It was therefore chosen in the present study.

Table 1. The CTL intensities of benzene vapor on the nanosized materials.

Material	CTL intensity (S/N)	Optimum temperature and wavelength
γ–Al_2O_3	4.23	395 °C, 425nm
γ–Al_2O_3/Eu_2O_3 (98 mol %/2 mol %)	7.50	432 °C, 425nm
γ–Al_2O_3/Eu_2O_3 (98.5 mol %/1.5 mol %)	6.59	383 °C, 425nm
ZrO_2	5.45	373 °C, 425nm
ZrO_2/Eu_2O_3 (98 mol %/2 mol %)	4.86	247 °C, 620nm

3.2. The CTL response profile of benzene on the surface of nanosized γ–Al₂O₃/Eu₂O₃

The CTL response profile of benzene on the surface of nanosized γ–Al$_2$O$_3$/Eu$_2$O$_3$ was studied by the injection of benzene vapor at different concentrations into the carrier air with a flow rate of 400 mL/min. Figure 3 shows the CTL response profiles of benzene on the surface of γ–Al$_2$O$_3$/Eu$_2$O$_3$ at 432°C with a bandpass filter of 425 ±10 nm. Curves 1, 2 and 3 denote the results for different concentrations of 1654 mL/m^3, 3308 mL/m^3 and 4962 mL/m^3, respectively. The CTL signal increased with the concentration of benzene and the profiles are similar to each other. The peaks of each curve appear at 3 s after sample injection, which shows that the sensor has a rapid response time of less than 3 s. The half decay time of CTL intensity of each curve is about 30s.

Figure 3. CTL response profiles of different concentrations of benzene vapor (1-1654 mL/m^3, 2-3308 mL/m^3, 3-4962 mL/m^3).
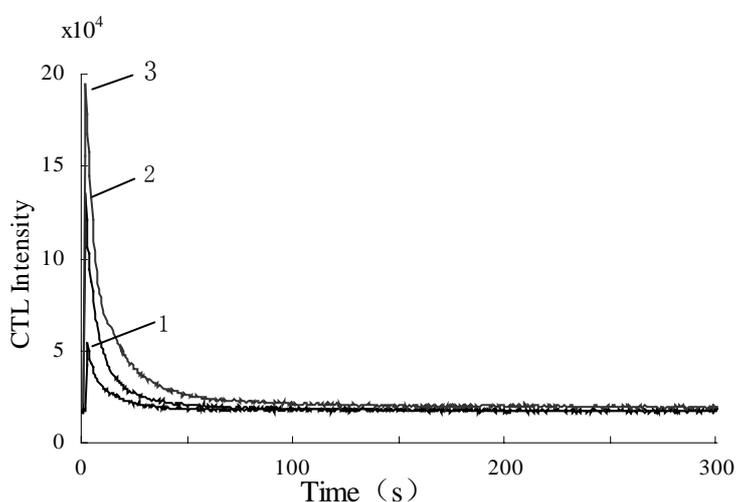
Figure 4. Wavelength dependence of CTL intensity of benzene vapor (432 ℃, 200 mL/min, 4483 mL/m^3).
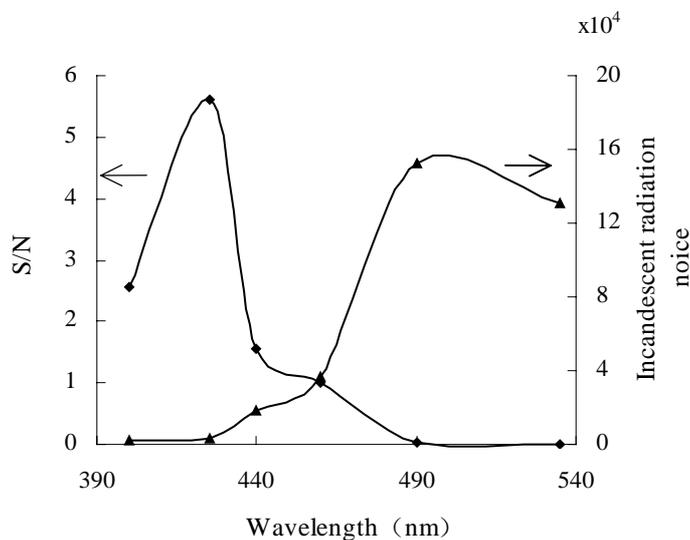
3.3. Optimization of wavelengths

Figure 4 shows the CTL spectra of benzene vapor at a flow rate of 200 mL/min and 432 °C. It shows that the incandescent radiation noise signals at longer wavelength are higher than those at shorter wavelength because of the increasing incandescence of the ceramic heater at higher temperatures. Considering this factor, the signal- to- noise ratio (S/N) was used to express the real CTL intensity. Figure 4 shows that the 425 nm is the optimum wavelength, therefore it is preferred for quantitative detection owing to the lower incandescent radiation noise.

3.4. Optimization of working temperature

The effect of working temperatures of the benzene homologues on the CTL was studied. As shown in Figure 5, the incandescent radiation noise of the substrate increased markedly above 460 °C, therefore 432 °C was selected as the optimum detection temperature owing to the maximum signal-to-noise ratio. The optimum detection temperatures of toluene and xylene were the same as benzene's.

Figure 5. Temperature dependence of CTL intensity of benzene homologue vapors. (425 nm, 400 mL/min, 4483 mL/m^3)
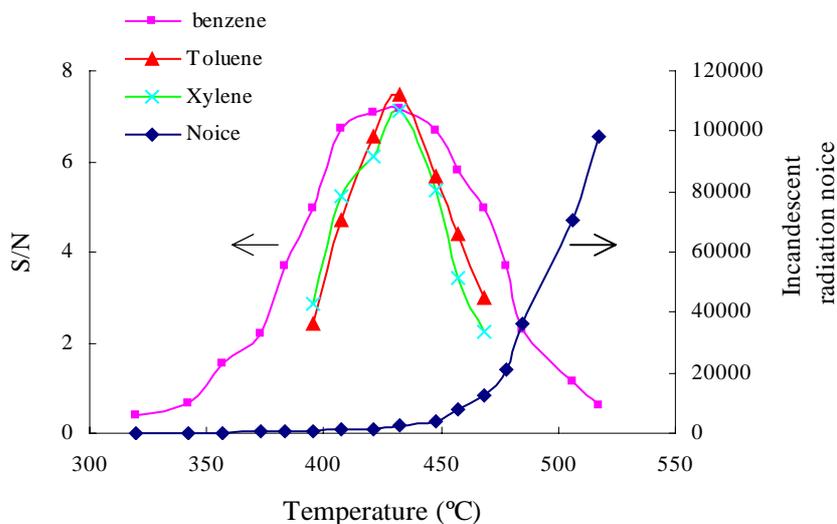
3.5. Optimization of flow rate of carrier gas

The flow rate dependence of the CTL intensity was measured ranged from 80 to 440 mL/min at 432 °C. As illustrated in Figure 6, the CTL intensity of 4483 mL/m^3 benzene vapor increases with an increase in the flow rate, and it saturates above a flow rate of 440 mL/min. Consequently a carrier gas flow rate of 400 mL/min was chosen for the detection.

Figure 6. Effect of flow rate of carrier air on CTL intensity of benzene vapor (432°C, 425 nm, 4483 mL/m^3).
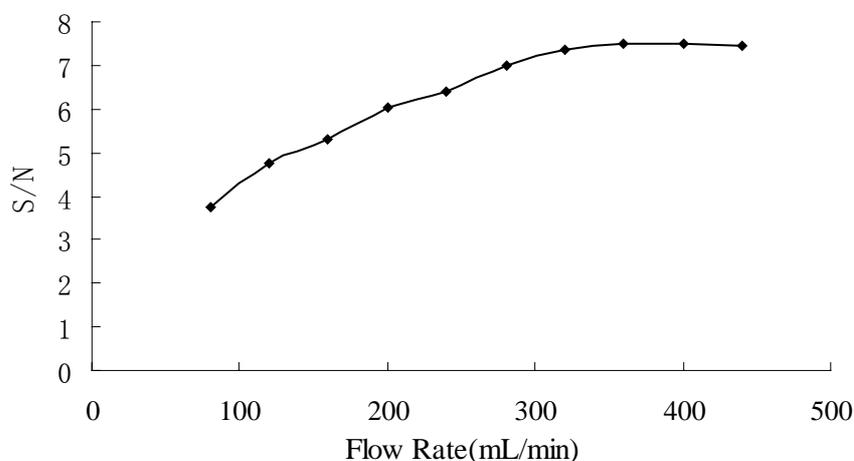
3.6. Analytical Characteristics

Under the selected conditions described above, the regression equation of CTL intensity versus benzene vapor concentration was linear in the range of 2.4 mL/m^3 to 5000 mL/m^3, as shown in Table 2.

The linear regression equation is described by I = 16.31c+119(2.4~100 mL/m^3), I = 2.560c+393(100~5000 mL/m^3), where I is the relative CTL intensity and c is the concentration (mL/m^3). The linear range and regression equation of CTL intensity versus toluene or xylene vapor concentrations were also showed in Table 2. Here the xylene is an isomer mixture. We have found that the xylene isomers showed the same CTL characteristics. The detection limits (3σ) of benzene, toluene and xylene were 1.8 mL/m^3, 3.0 mL/m^3 and 3.4 mL/m^3, respectively. The relative standard deviation was 3.9% (n=7) for 100 mL/m^3 benzene vapor. As the regression equations of the benzene homologues are a little different, we can obtain approximate total amounts of these pollutants if they coexist in a sample (see Sample 3 in Table 3). Nevertheless, it is useful for quality monitoring of environmental air.

According to the hygiene standards for the design of industrial enterprises in China, occupational exposure limits for benzene, toluene and xylene vapor in the workplace are 5.3 mL/m^3, 16 mL/m^3 and 21 mL/m^3 respectively (GBZ2-2002). Due to the fact that the detection limit of the benzene homologue vapors are below the standard permitted concentrations, the proposed sensor can be used for safety control and air quality monitoring of the content of benzene homologues in the workplace.

3.7. Selectivity

Some compounds, which may co-exist with benzene homologues in contaminated air, e.g., sulfur dioxide, carbon monoxide and ammonia were tested to see whether they interfered with the determination of benzene vapors under the optimized conditions described above. The tested concentration of all species was 100 mL/m^3. As shown in Figure 7, no significant CTL signals could

be observed at 95 % confidence level. Sulfur dioxide, carbon monoxide and ammonia caused interference at around 11.7 %, 5.8 % and 8.9 %, respectively.

Table 2. The response of the benzene homologue vapors on the sensor.

Measured Gas	Linear Range (mL/m^3)	Regression Equation	Correlation Coefficient	Limit of Detection (mL/m^3)
Benzene	2.4~100	I=16.31c+119	0.9991	1.8
	100~5000	I=2.560c+393	0.9994	
Toluene	4.0~100	I=30.89c+78.9	0.9997	3.0
	100~5000	I=3.616c+351	0.9921	
Xylene	6.8~100	I=29.79c+18.6	0.9958	3.4
	100~5000	I=3.970c+142	0.9974	

Figure 7. CTL responses of different compound on the sensor.
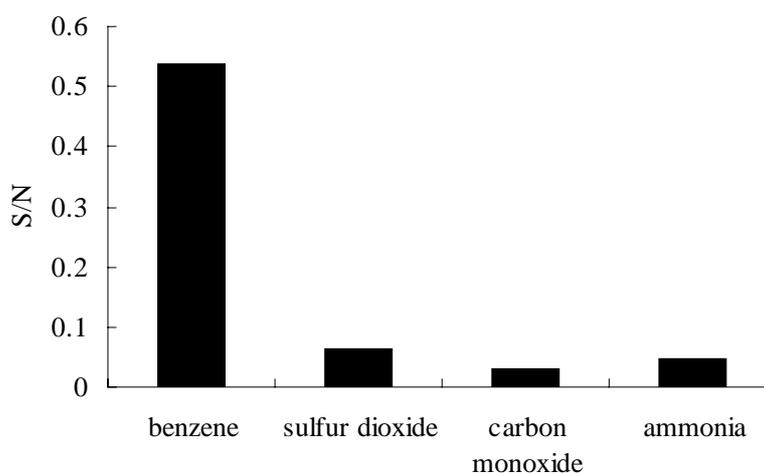
3.8. Lifetime of the gas sensor

An experiment was carried out in order to study the lifetime of the sensor. The CTL intensity was measured 1-time per four hours for 100 hours by continuously introducing 600 mL/m^3 of benzene vapor in carrier gas through the sensor. No significant decrease of CTL intensity was observed during the 100 hours detection. The RSD (n=26) of CTL intensity is 3.97*%*. The results indicated the durability of the nanosized $\gamma–Al_2O_3/Eu_2O_3$-based sensor.

3.9. Determination of benzene or benzene homologues in the synthetic samples

In order to test the reliability of the system, three synthetic samples containing known concentrations of benzene homologues, sulfur dioxide and ammonia were analyzed under the optimized conditions. As shown in Table 3, satisfactory recoveries were obtained.

Table 3. The analysis of benzene or benzene homologue vapors in artificial samples.

Sample No.	Composition	Standard Values (mL/m^3)	Measured Values (mL/m^3, n=6)	Benzene(or Benzene Homologues) Recovery (%)
1	Benzene	807	887±64	110
	Sulfur Dioxide	100		
2	Benzene	807	814±95	101
	Ammonia	100		
	Benzene	897		
3	Toluene	354	1416±64	102
	Xylene	132		

4. Conclusions

The research in this paper has demonstrated the possibility and potential of a nanosized γ-Al$_2$O$_3$/Eu$_2$O$_3$ based sensor to determine low concentrations of benzene homologues. Under optimal conditions, the sensor was sensitive to a wide concentration range of benzene, toluene and xylene. Rapid response, satisfactory stability and high selectivity demonstrate the promise of this sensor for benzene homologue determination in industrial and environmental monitoring. Obviously, this study is also valuable for the future research to develop cataluminescence sensor based on nanosized catalyst activated with rare-earth oxides.

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