Talanta 79 (2009) 1223–1227

Contents lists available at ScienceDirect

Talanta

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A vinyl acetate sensor based on cataluminescence on MgO nanoparticles

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ARTICLE INFO

Article history:
Received 8 December 2008
Received in revised form 13 April 2009
Accepted 16 April 2009
Available online 3 May 2009

Keywords:
Cataluminescence
Chemiluminescence
MgO
Nanomaterials
Vinyl acetate
Sensor

ABSTRACT

A novel cataluminescence (CTL) sensor using nanosized MgO as the sensing material for determination of the trace of vinyl acetate in air was proposed in the present study. Eight catalysts were examined and the results showed that the CTL intensity on MgO nanoparticles was the strongest. Under the optimized conditions, the linear range of the CTL intensity versus the concentration of vinyl acetate vapor was 2–2000 ppm with a detection limit of 1.0 ppm (3σ) and a relative standard deviation (R.S.D.) of 1.18% for five times determination of 1000 ppm vinyl acetate. There were no CTL emissions when foreign substances, including ammonia, benzene, acetic acid, formaldehyde and ethyl acetate, passed through the sensor. CTL emissions were detected for methanol, ethanol and acetaldehyde at levels around 5.5%, 10.1% and 13.4% compared with the responsed vinyl acetate. The sensor had a long lifetime more than 100 h.

1. Introduction

Vinyl acetate is used to manufacture important industrial and commercial chemicals that have a wide series of applications. For example, vinyl acetate is primarily used as a monomer in the production of polyvinyl acetate and polyvinyl alcohol. It is also used as a raw material in the production of chemicals, adhesives, water-based paints, non-woven textile fibers, textile sizing and finishes, paper coatings, films, hair spray, inks, films, impregnation materials and lacquers [1,2]. However, vinyl acetate is considered as a “flammable” liquid [3] that has been related to reproductive abnormalities. It is not only an irritant to human skin and upper respiratory but also a central nervous system depressant. Exposure to vinyl acetate can cause gradual deterioration of heart muscles [4]. The U.S. Environmental Protection Agency also ranks vinyl acetate as the hazardous air pollutant [5] and extremely hazardous substance [6].

Subchronic toxicity studies in animals have confirmed that vinyl acetate could be the carcinogen in animals [7]. The hazardous properties of vinyl acetate make monitoring it in air necessary.

The primary analytical methods for vinyl acetate in air are gas chromatography (GC) [8] and gas chromatography–mass spectrometry (GC–MS) [6]. They offer high performance and sensitivity, but they are not easy techniques for on-line detection due to their large size and time-consuming operation. Gas sensors, on the other hand, are relatively small and inexpensive. They can be used for in situ, on-line or remote measurements. Up to date, few gaseous vinyl acetate sensors have been reported. The sensor based on electrochemical principle is relatively small and inexpensive, but not so adequate to name selectivity [9].

Cataluminescence (CTL) based sensors have been developed since 1990s. CTL refers to a kind of chemiluminescence (CL) that is emitted during the catalytic oxidation of organic vapors on the surface of a solid catalyst.

Breysse et al. first observed the phenomenon during the catalytic oxidation of carbon monoxide on a ThO_2 surface in 1976 [10]. In 1990s, Nakagawa et al. developed a sensor using γ-Al_2O_3 as the sensing material for determination of the trace of ethanol and acetone [11–14].

In the CTL-based field of gas sensors, ethanol vapor is one of the most well known exhaustively studied gases and people have devoted ethanol vapor sensors based on nanomaterials, such as $SrCO_3$, TiO_2 and ZnO [15–17].

Many other nanomaterials such as Al_2O_3–Eu_2O_3, $BaCO_3$, Fe_2O_3, $V_2Ti_4O_{13}$, and $LaCoO_3$ were applied to detect volatile organic compounds (VOCs), including benzene homologues, acetaldehyde, hydrogen sulfide, formaldehyde, ammonia [18–22], and so forth.

Some fixed materials like amino acids, saccharides and steroid pharmaceuticals could produce CTL emission on the surface of nanomaterials [23,24].

Recently, an optical sensor array based on chemiluminescent images from spots of nanomaterials has been employed to recognize odorous samples. The distinctive images obtained from the array permit to identify a wide range of analytes and even homologous compounds [25].

The aim of this paper is to develop a CTL-based gas sensor for tracing vinyl acetate in air, especially at workplace. The results

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doi:10.1016/j.talanta.2009.04.038

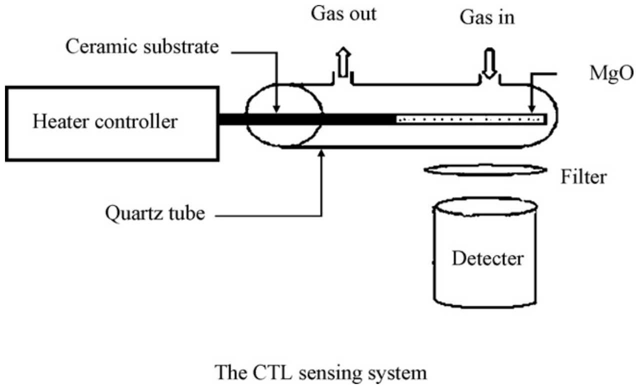

Fig. 1. Schematic diagram of the CTL sensing system.

showed that the gas sensor using nanosized MgO as catalyst had a high specificity to vinyl acetate. To the best of our knowledge, this is the first report of the CTL-based sensor for sensing vinyl acetate.

2. Experimental

2.1. Apparatus

Fig. 1 shows the schematic diagram of the CTL detection system. The MgO nanoparticles were sintered on the ceramic heating tube to form a sensing layer. Details about the sintering process were as follows: some water was added into 0.2 g of MgO nanoparticles under stirring. After about 30 s, a white slurry appeared. Then the white slurry was painted on a ceramic tube of 5 mm in diameter. The ceramic tube was dried naturally and placed into a quartz tube of 15 mm in diameter. The temperature of the MgO layer could be adjusted by controlling the voltage of the heating tube. A catalytic reaction occurred on the surface of MgO when the vinyl acetate vapors mixed with carrier air flowed through the quartz tube. The CTL intensity was measured with a BPCL Ultra Weak Chemiluminescence Analyzer (Biophysics Institute of Chinese Academy of Science, P.R. China). By changing the optical filters, the wavelengths used for detection could be selected over a range of 400–640 nm.

2.2. Synthesis of catalysts

MgO was synthesized as follows: 1.5 g $(CH_3COO)_2Mg$ and 0.15 g CTAB were dissolved in 150 mL distilled water. Then, added ammonia to adjust the pH to 10. The resulting product was put in an ultrasonator for 90 min, aged for 1 h without stirring and washed with distilled water for three times. The precursor was dried at 80 °C for 5 h and calcined at 550 °C in the muffle oven for 2 h. Al_2O_3 and $MgAl_2O_4$ were prepared by the same methods.

Nd_2O_3 was synthesized as follows: 1.05 g $Nd(NO_3)_3$ was dissolved in 16 mL distilled water, and the solution was heated at 100 °C under violent magnetic stirring, then 10 mL of 25% NH_4OH solution was quickly added. The precipitation generated after 3 days and washed with distilled water for three times. The precursor was dried at 80 °C for 12 h and calcined at 450 °C in muffle oven for 5 h. Er_2O_3 was also prepared by the same methods.

The In_2O_3 was synthesized as follows: 0.8 g $In(NO_3)_3$ and 0.6 g H_2NCONH_2 were dissolved in 50 mL distilled water, violent stirring was required for another 2 h to form a suspension. The precipitation was washed with distilled water for three times. The precursor was dried at 80 °C for 12 h and calcined at 400 °C in muffle oven for 1 h. SnO was prepared by the same methods.

The Pr_6O_{11} was synthesized as follows: 0.8 g Pr_2O_3 was dissolved in 16 mL 10% HNO_3 to form a transparent solution. KOH solution was added dropwise into the as-prepared $Pr(NO_3)_3$ solution under violent stirring. Then the suspension was heated by microwave irradiation using a modified domestic microwave oven (650 W, 2.45 GHz) with a refluxing apparatus for 1 h and at 80% of the instrument's maximum power. Then, the precipitation was washed with distilled water for several times. The precursor was dried for 12 h under vacuum at 80 °C and calcined at 500 °C for 6 h.

2.3. GC experiments

To investigate the catalytic reaction processes that involve CTL emission, GC experiments were carried out to identify the intermediates from the catalytic oxidation of vinyl acetate on MgO. The GC instrument (GC7700, Techcomp Limited, P.R. China) with a flame ionization detector (FID detector) was directly coupled to the CTL detection system mentioned earlier for the rapid determination of intermediates from the vinyl acetate oxidation. Products were identified by comparison of their retention time. The conditions for GC experiments were as follows: temperature of spray chamber operated at 120 °C, column temperature operated at 120 °C, pressure of carrier gas of N_2 kept at 30 mL/min.

3. Results and discussion

3.1. Evaluation of the materials for CTL

To study the feasibility of the sensing mode, SnO, In_2O_3, Nd_2O_3, Er_2O_3, MgO, $MgAl_2O_4$, Pr_6O_{11} and Al_2O_3 were estimated. The CTL on the surface of these particles was detected when vinyl acetate or other vapors, which may coexist with vinyl acetate in contaminated air, was passing through at a flow rate of 400 mL/min and wavelength of 425 nm. The concentration of each vapor was 1000 ppm. The different temperatures used in the test are aimed at obtaining the highest CTL intensities for each material. The results were shown in Table 1. The data showed that MgO was the best material to obtain the highest sensitivity with adequate specificity. Therefore, it was selected for the subsequent studies in the present study.

3.2. Characterization of the MgO

To identify the characterization of the MgO catalyst for the subsequent studies, the powder of MgO was examined by trans-

Table 1
CTL intensities on the surface of different particles.

Materials	Relative CTL intensity				Selected conditions
	Vinyl acetate	Acetaldehyde	Methanol	Ethanol	
MgO	1677	211.4	91.1	157.3	331 °C, 425 nm
Al_2O_3	717.9	983.7	91.0	233.5	293 °C, 425 nm
$MgAl_2O_4$	222.9	280.9	20.55	67.36	293 °C, 425 nm
Er_2O_3	54.58	13.55	0.70	0.45	293 °C, 425 nm
Nd_2O_3	38.87	32.65	17.11	24.81	293 °C, 425 nm
SnO	27.52	9.74	27.52	12.52	293 °C, 425 nm
Pr_6O_{11}	17.26	1.25	1.01	0.71	293 °C, 425 nm
In_2O_3	16.65	11.16	0.41	0.81	293 °C, 425 nm

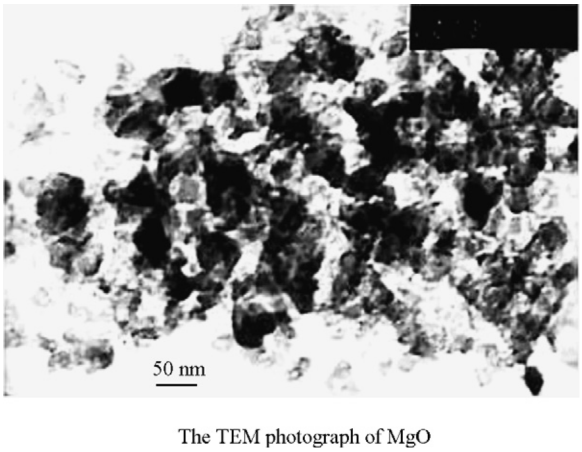

Fig. 2. TEM image of the synthesized MgO nanoparticles.

mission electron microscope and diffractometer. The details about the examining process were as follows: the morphology of the synthesized MgO was examined with a Rigaku DMAX-1200 transmission electron microscope (TEM). The TEM photograph in Fig. 2 shows that the synthesized MgO was nanoparticles with the average length of around 40 nm.

X-ray power diffraction (XRD) experiment was carried out in a Rigaku DMAX-2500 diffractometer using Cu Kα radiation working at 36 kV and 20 mA. The sharp diffraction patterns were clearly observed. It perfectly matches with crystal structure for MgO (JCPDS 04-0829).

3.3. Temporal CTL profiles of vinyl acetate vapor on MgO

Temporal CTL profiles of vinyl acetate vapor on the surface of MgO were investigated by injecting the vinyl acetate vapor of different concentrations into carrier gas with a flow rate of 400 mL/min. The working temperature was controlled at 331 °C with the wavelength of 425 nm. The results were shown in Fig. 3. Curves 1, 2 and 3 represent the different concentrations of 500, 1000, and 2000 ppm, respectively. It could be seen that the temporal profiles of cataluminescence emission were similar to each other, and the relative CTL intensity rapidly increased from the baseline to the maximum value within about 3 s and recovered to the baseline within 70 s. It showed that the proposed sensor had an advantage of quick response.

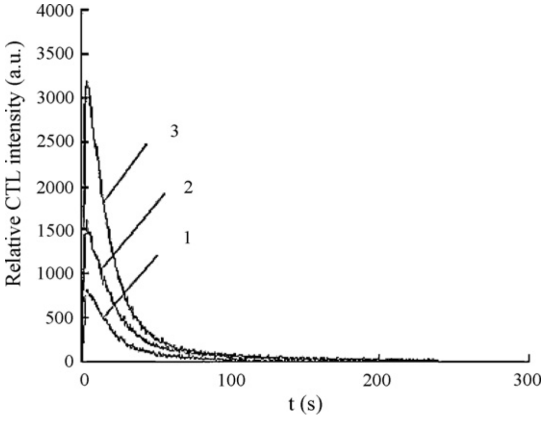

Fig. 3. Typical temporal profiles of CTL emission. Vinyl acetate vapor concentration: (1) 500 ppm, (2) 1000 ppm and (3) 3000 ppm.

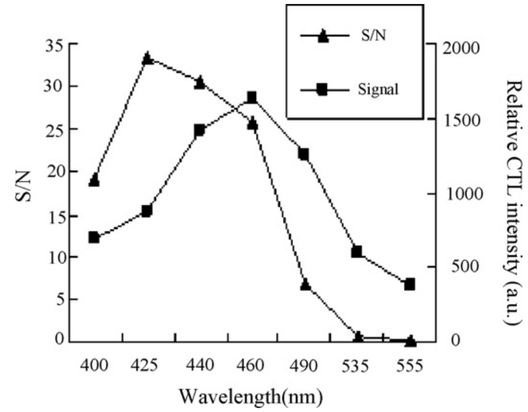

Fig. 4. Wavelength dependence of relative CTL intensity of vinyl acetate vapor. Conditions: flow rate, 400 mL/min; temperature, 331 °C, wavelength, 425 nm.

3.4. Optimization of wavelengths

The preliminary experiment showed that the optimum wavelength of cataluminescence emission on the surface of nanosized MgO particles was 460 nm (see Fig. 4). However, the background signal, which mainly arose from the heat radiation of the ceramic tube, would increase along with increased wavelength, and the maximum signal to noise ratio (S/N) was obtained at 425 nm. Therefore, 425 nm was selected for the quantitative detection of vinyl acetate vapor in the subsequent experiments.

3.5. Optimization of working temperature

Temperature plays an important role in the reaction rate of the catalytic oxidation reaction. To investigate the effect of temperature on the CTL intensity, a 1000 ppm vinyl acetate vapor sample was determined at varied temperatures. Fig. 5 presents the relationships between the relative CTL intensity versus the catalysis temperature at a carrier gas flow rate of 400 mL/min. The results showed that the CTL intensity increased when the temperature increased from 230 to 470 °C. However, the experiment indicated that when temperature increased, the background signal was also increased and even faster than the real CTL intensity increased. Furthermore, the S/N (signal to noise ratio) reached a maximum on the MgO particles surface was at 331 °C. Below or above this temperature, the S/N decreased. Therefore, 331 °C was chosen for the following experiments.

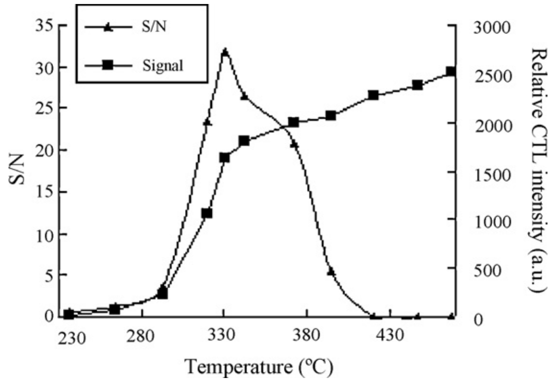

Fig. 5. Temperature dependence of the CTL intensity of vinyl acetate vapor. Conditions: flow rate, 400 mL/min; wavelength, 425 nm, vinyl acetate vapor concentration, 1000 ppm.

Table 2
Vinyl acetate vapor analysis in artificial air samples.

Sample no.	Composition	Standard values (ppm)	Measured values (ppm, $n = 6$)	Vinyl acetate recovery (%)
1	Vinyl acetate	10	9.52 ± 0.29	95.18%
	Acetic acid	10		
2	Vinyl acetate	50	49.78 ± 0.40	99.56%
	Benzene	50		
	Ammonia	50		
3	Vinyl acetate	50	9.52 ± 0.29	99.36%
	Formaldehyde	10		

3.6. Optimization of flow rate of carrier gas

The impact of airflow rate on the CTL intensity was examined in the range of 55–610 mL/min at 331 °C. The concentration of vinyl acetate vapor was 1000 ppm. The CTL intensity increased gradually with the increase of flow rate from 55 to 400 mL/min. It saturated above a flow rate of 400 mL/min. As expected, a proper flow rate could bring a longer contact time between the sample vapor and the selected catalyst, resulting a sufficient reaction. However, when the flow rate was too high, the reaction time between the vapor and the catalyst would be insufficient. Therefore, the CTL intensity decreased slightly. Consequently, 400 mL/min was chosen as optimal flow rate for the subsequent studies.

3.7. Specificity of the MgO sensor

Specificity plays an important role to a sensor, as poor specificity would result in the ostentation of false positives. Some compounds, including methanol, ethanol, ammonia, benzene, acetic acid, formaldehyde, acetaldehyde and ethyl acetate, which could sometimes interfere with vinyl acetate determination, were investigated by introducing each compound into the proposed sensor at a concentration of 200 ppm. None or very weak CTL emissions were observed for most compounds. Although CTL emissions were detected for methanol, ethanol and acetaldehyde at levels around 5.5%, 10.1% and 13.4% compared with the responsed vinyl acetate. Therefore, the sensor exhibited a high specificity to vinyl acetate.

3.8. Analytical characteristics

The calibration curve of relative CTL intensity versus vinyl acetate vapor concentration was linear in the range of 2–2000 ppm with a detection limit of 1.0 ppm (3.5 mg/m^3) under the optimized conditions. The line regression equation was described as $I = 1.657C - 2.101$, correlation coefficient $R^2 = 0.9994$ ('I' is the CTL intensity, 'C' is the concentration of vinyl acetate vapor, and each point was gathered from the average result of two replicated tests). Relative standard deviation (R.S.D.) was 1.18% for five times determination of 1000 ppm vinyl acetate vapor. And the R.S.D. was 1.07% for six times determination of 2.0 ppm vinyl acetate vapor.

According to the occupational exposure limit for hazardous agents in the workplace (GBZ 2.1-2007, China), the permitted concentration time weighted average (PC-TWA [8 h]) [26] for vinyl acetate vapor in the workplace is 2.8 ppm (10 mg/m^3). Because the detection limit of vinyl acetate vapor is below the standard permitted concentrations, the proposed sensor could be used for safety control and air quality monitoring of the content of vinyl acetate in the workplace.

Moreover, the proposed sensor could be used for quality monitoring of a manufacturing process of the vinyl acetate and the process with the vinyl acetate as the produced materials according to the balance of the vapor and liquid.

3.9. Long-term stability of the sensor

To test the lifetime of the MgO sensor, experiments were carried out by continually introducing 10 and 1000 ppm vinyl acetate under the optimized conditions. The CTL intensity obtained from the catalytic oxidation reaction was almost unchanged for 100 h.

3.10. Determination of vinyl acetate in the samples

In order to test the reliability of the system, three artificial air samples were analyzed to evaluate the analytical application, results were shown in Table 2. Sample 1 was a mixture of vinyl acetate and acetic acid, sample 2 was a mixture of vinyl acetate, ammonia and benzene. The results showed in sample 1 and 2 that illustrating the possible co-existing molecules did not interfere with the determination of vinyl acetate under the same concentration. Sample 3 was a mixture of vinyl acetate and formaldehyde. The results indicated that the co-existing molecules of formaldehyde showed evident negative interference with vinyl acetate under the same concentration. However, no interference was generated when the concentration of formaldehyde vapor came to one-fifth of vinyl acetate, as shown in sample 3.

To further demonstrate the practical usefulness of the system, the environmental air samples were analyzed with the CTL method and compared with GC method. The air samples were taken from chemical laboratory where vinyl acetate was used. The analysis results were shown in Table 3. It could be shown that the measured values of vinyl acetate with both methods are in good agreement. Thus, the present CTL-based sensor could be used as an early warning device for vinyl acetate concentrations in the workplace.

3.11. Mechanism

Until now, the CTL mechanism about the phenomenon from the catalytic oxidation of vinyl acetate on the solid catalysts has not been studied. For the sake of studying CTL mechanism of the vinyl acetate sensor, GC experiments were carried out to detect the intermediates of the catalytic oxidation of vinyl acetate, which attributed to the oxidation processes.

The results were shown in Fig. 6. It can be seen that there are two main peaks corresponding to $CH_3COOCH_2CH_3$ and CH_3CHO, which can be identified by comparison of their retention time of the standard gases in GC experiments.

Therefore, possible mechanism of the CTL of vinyl acetate is as the following:

$$MgO + CH_3COOCH_2CH_3 + O_2 \rightarrow CH_3CHO*$$

Table 3
Experimental results of different methods obtained in environmental air samples.

Environmental air samples	1	2	3	4
GC (ppm)	1.63	2.37	1.89	2.12
CTL sensor (ppm)	1.81	2.19	1.73	2.32
Relative deviation (%)	9.94	−8.22	−9.24	8.62

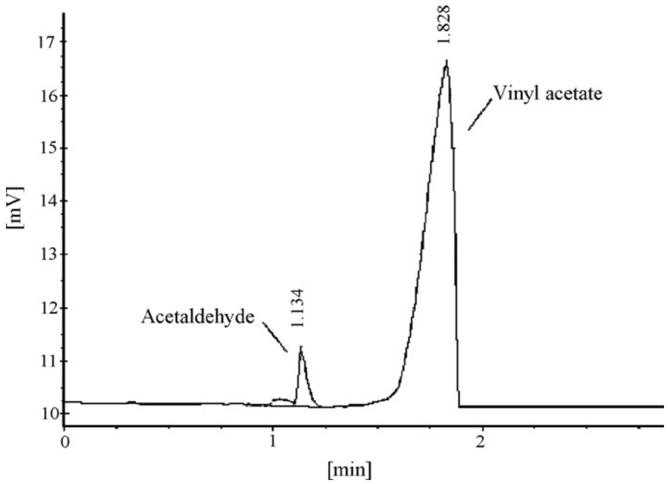

Fig. 6. Analysis of the oxidant products with the GC.

$CH_3CHO* \rightarrow CH_3CHO + h\nu$

When vinyl acetate vapor passed through the surface of the MgO, it was catalytically oxidized by O_2 in the air. The electronically excited acetaldehyde molecules (CH_3CHO^*) could be produced during the reaction and generated photoemission when they returned to their ground state.

4. Conclusion

The results of the present work have demonstrated the feasibility to design a sensor based on MgO nanoparticles for determination of the trace of vinyl acetate in air. The influences of working temperature, wavelength and flow rate of the sensor on the CTL intensity and the specificity of the sensor had been investigated. The results showed that the sensor possessed high selectivity, sensitivity and good repeatability. This work may be useful to develop miniaturized equipment for the determination of gaseous vinyl acetate in the industry workplace.

Acknowledgements

The authors gratefully acknowledge the financial supports by the National Natural Science Foundation of China (20677013), Natural Science Foundation of Guangdong Province, China (8151009101000130), and Science and Technology Project Foundation of Guangdong Province, China (2006B12401012).

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