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A new cataluminescence gas sensor based on SiO_2 nanotubes fabricated using carbon nanotube templates

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ABSTRACT

In the present work, two morphologies of SiO_2 nanomaterials (SiO_2 nanotubes and nanoparticles) have been successfully synthesized in supercritical fluids (SCFs). The cataluminescence (CTL) features of the two SiO_2 nanomaterials to some common harmful gases were compared, and the results showed that SiO_2 nanotubes had better CTL sensing characteristic to some common harmful gases. The SiO_2 nanotubes not only had uniform size and shape with a high specific surface area, but also exhibited superior sensitivity and selectivity to ethyl acetate vapor. Using the SiO_2 nanotubes as sensing material, a CTL sensor for ethyl acetate vapor was developed. The proposed sensor showed high sensitivity and specificity to ethyl acetate at optimal temperature of 293 °C, a wavelength of 425 nm and a flow rate of 345 mL/min. With a detection limit of 0.85 ppm, the linear range of CTL intensity versus concentrations of ethyl acetate vapor was 2.0–2000 ppm. None or only very low levels of interference were observed while the foreign substances such as acetone, acetaldehyde, acetic acid, formaldehyde, ammonia, ethanol, benzene and methanol were passing through the sensor. This method allows rapid determination of gaseous ethyl acetate at workshop.

1. Introduction

Cataluminescence (CTL) is chemiluminescence emitted during the catalytic oxidation of organic vapors on the surface of a solid catalyst. The CTL-based sensing of gases or vapors has been reported by many workers. In 1976, Breysse et al. [1] found that chemiluminescence is emitted during catalytic oxidation of carbon monoxide on thoria ThO_2, and named it cataluminescence. This luminescence is ascribed to light emission during catalysis in an atmosphere containing oxygen. Since 1990, Nakagawa and co-workers [2–6] have observed CTL emission during the catalytic oxidation of ethanol or acetone vapor on a heated aluminum oxide powder.

In recent years, nanomaterials have attracted widespread attention of many users and scientists and they were applied to the design of CTL gas sensors, owing to their small size, tremendous specific surface area, and high catalytic activity and good selectivity. Zhang and co-workers established a series of gas sensors [7–13] and sensor arrays [14] for the determination of organic/inorganic compounds. Cao et al. [15,16] reported the vinyl acetate sensor based on MgO nanoparticles [17] and the ether sensor based on $ZnWO_4$ [18] with high sensitivity, selectivity and long lifetime. In addition, a variety of CTL gas sensors based on different catalysts have been reported, such as pinacolyl alcohol on Al_2O_3 nanowires [19], tert-butyl mercaptan on V_2O_5 [20], n-hexane on zeolite [21], ethanol on YVO_4:Eu^{3+} [22].

Although CTL gas sensors have shown many promising features such as long-term stability, fast responses to analytes and relatively simple design, they suffer from the fact that few systems have been applied in practical use due to the insufficient sensitivity. Therefore, there is a strong effort to research high effective catalysts to meet the challenge for sensitive detection.

Recently, some studies have revealed that the nanocatalysts prepared by supercritical fluid drying (SCFD) technology have good catalytic performance owing to their good dispersion, small particle size and high specific surface area [19]. Liu et al. [23] reported a novel route to synthesize metallic oxide nanotubes as highly efficient CTL sensing materials by using carbon nanotubes (CNTs) as templates in supercritical fluids (SCFs). In our previous work [24], we found that the nanomaterials, prepared by SCFD method, had better catalytic activity to some harmful gases than that prepared by common drying method (CD).

The aim of this study is to (1) synthesize SiO_2 nanotubes and SiO_2 nanoparticles by SCFs technology; (2) evaluate their CTL property to some common harmful gases; (3) establish a novel CTL sensor system for determination of gaseous ethyl acetate based on the catalyst mentioned above. Besides, this synthesis method may provide reference to synthesize other sensing materials in future.

It has been found in the present work that by using CNTs as templates in SCFs, the prepared SiO_2 nanotubes, with uniform small

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size and high specific surface area, exhibit higher catalytic activity, better stability and higher sensitivity to some vapors than the SiO_2 nanoparticles prepared in the absence of CNTs. It can be deduced that the SiO_2 nanotubes can be utilized as efficient sensing materials.

In addition, as one of the highly volatile organic compounds (VOCs), ethyl acetate is widely used by a variety of industries, such as adhesives, thinners, degreasers, paints, inks, and dome reagents [25]. This may result in its release to the environment through various waste streams. Its emission is facing increasingly stringent environmental regulations. Ethyl acetate is an irritant of the eyes, nose, throat and the mucous membrane of the respiratory tract. Although it is popularly regarded as relatively low toxic, some researches have indicated that overexposure to it may cause weakness, drowsiness, unconsciousness and chronic severe overexposure even may cause secondary anemia and damage of the liver [26]. Accordingly, it is a very important task to monitor its concentration in many cases.

Our experiments showed that a strong CTL emission could be observed when the ethyl acetate vapor passed through the surface of SiO_2 nanotubes. Based on this phenomenon, a novel gas sensor for ethyl acetate was proposed. The sensor possesses higher sensitivity and wider linear range than the previous ethyl acetate sensor based on SiO_2 nanoparticles [13].

2. Experimental

2.1. Apparatus of the CTL system

The schematic diagram of the detection system was shown in Fig. 1. The sensor was made by depositing SiO_2 nanotubes with a thickness of about 0.5 mm on the ceramic heating tube. The 5 mm in diameter ceramic heating tube was put into a quartz tube with an inner-diameter of 12 mm. The temperature of the catalysts could be adjusted by controlling the voltage of the heating tube. The air from the pump was mixed with detecting vapor and flowed through the quartz tube, a catalytic reaction occurred on the surface of catalysts. The CTL intensity was measured by a BPCL Ultra Weak Chemiluminescence Analyzer (Biophysics Institute of Chinese Academy of Science, PR China). The wavelengths could be selected over the range of 400–575 nm by changing the optical filters.

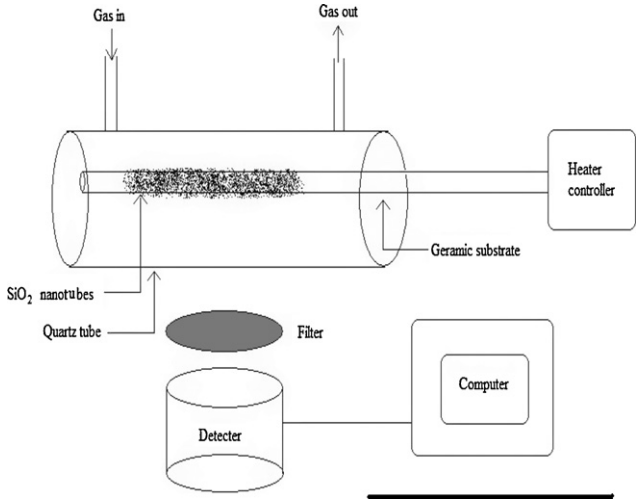

Fig. 1. Schematic diagram of the CTL sensing system.

2.2. Synthesis of SiO_2 nanomaterials

2.2.1. SiO_2 nanotubes prepared by using carbon nanotubes (CNTs) as templates in SCFs

A novel and simple route was used to synthesize SiO_2 nanotubes using CNTs as templates in supercritical (SC) ethanol modified with CO_2. Specifically, (i) $(NH_4)_2SO_4$ (0.2 g) and PEG-4000 (0.5 g) were dissolved in aqueous solution of Na_2SiO_3 (0.1 mol/L, 100 mL) with stirring at 70 °C. (ii) CNTs (0.2 g) was dispersed in absolute ethanol (10 mL) with ultrasonic stirring for 10 min, the solution was added into (i) solution with vigorous stirring for 30 min to form mixture. Then acetic acid solution (0.4 mol/L) was slowly added into the above mixture solution until the pH was 4.44 and kept on stirring for 1 h. The obtained gel was maintained at room temperature for 16 h without stirring. Then it was washed with distilled water until the pH was 7, and with absolute ethanol for five times to replace the water of the gel.

Finally the wet colloid obtained was dried by CO_2/ethanol supercritical fluid drying as follows: (1) the wet colloid was transferred into autoclave (100 mL) and immersed into absolute ethanol (30 mL). Subsequently, the autoclave was purged five times using nitrogen gas in order to weed out air in the autoclave. (2) The autoclave was charged with CO_2 up to 2 MPa. (3) After the temperature of the autoclave was ramped up to 260 °C, while maintaining a pressure of 7 MPa for 0.5 h, the autoclave was brought back to the atmospheric pressure after release the ethanol fluid. (4) Then the autoclave was purged three times using nitrogen gas in order to weed out rudimental ethanol in SiO_2/CNTs aero gel. The dried solid was calcined at 600 °C in an oxygen atmosphere for 6 h to remove the CNT template, and finally SiO_2 nanotubes were obtained.

2.2.2. SiO_2 nanoparticles prepared in the absence of CNTs in SCFs

A simple sol–gel method was used to synthesize the SiO_2 nanoparticles in SCFs. SiO_2 nanoparticles were prepared by using $Na_2SiO_3{\cdot}9H_2O$ as the precursors, $(NH_4)_2SO_4$ (0.5 g) and PEG-4000 (1.3 g) were added into Na_2SiO_3 aqueous solution (0.25 mol/L, 150 mL) at 70 °C. After stirring vigorously, acetic acid solution (1 mol/L) was added into the mixture until pH was 4.44, then stirred for 1 h. The obtained gel was maintained at room temperature for 20 h without stirring. Then it was washed with distilled water until the pH was 7, and with absolute ethanol for five times to replace the water of the gel.

Finally the colloid obtained was transferred into an autoclave and dried under the supercritical fluid condition of ethanol (285 °C, 6.8 MPa, 0.5 h) to produce aero gel. The ethanol supercritical fluid drying processes were carried out as mentioned in Section 2. 2. 1 except that step (2) was omitted. Then the dried aero gel was calcined at 600 °C for 3 h to obtain SiO_2 nanoparticles.

2.3. Characterization of as-prepared nanomaterials

The as-prepared products were characterized using different techniques. An X-ray diffraction (XRD) analysis was used to determine the chemical composition of the nanomaterials by a XD-3 diffractometer (Purkinje General, Beijing) using Cu Kα radiation. Fig. 2 indicates that both of the nano-SiO_2 are disordered amorphous phase.

The morphology and particle size of SiO_2 were investigated by using a JEM-2010HR (JEOL) Transmission Electron Microscopy (TEM). The accelerating voltage of the electron beam was 200 kV, as shown in Fig. 3. Fig. 3a shows the obtained sample consists of bundles of SiO_2 nanotubes and the single nanotube is composed of many SiO_2 nanoparticles with the grain size in the range of about 2–4 nm (Fig. 3b); Fig. 3c shows that the SiO_2 nanoparticles is aggregated and the grain size ranges in 10–20 nm.

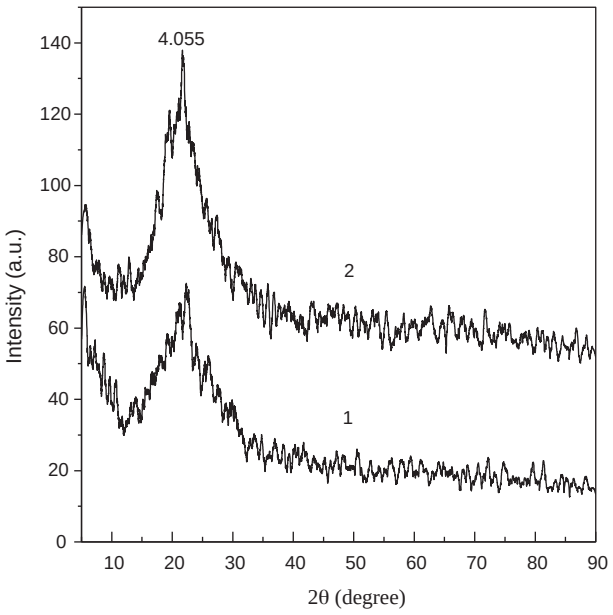

Fig. 2. X-ray diffraction pattern of as-prepared (1) SiO_2 nanotubes and (2) SiO_2 nanoparticals.

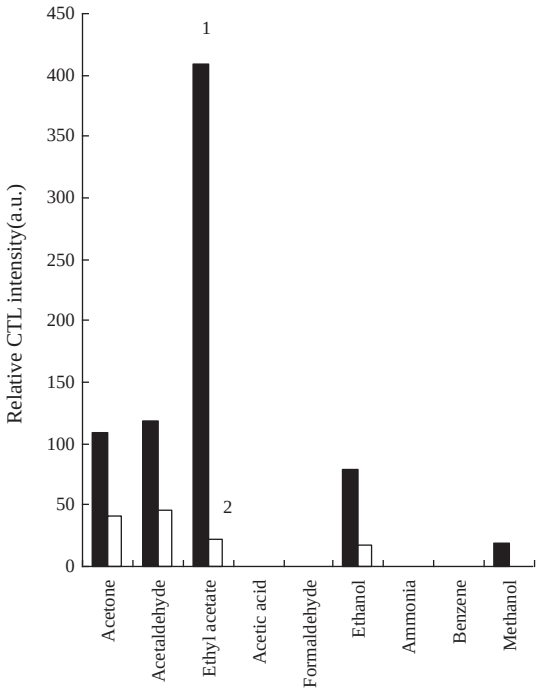

Fig. 4. CTL intensity comparison of different vapors on (1) SiO_2 nanotubes and (2) SiO_2 nanoparticals.

3. Results and discussion

3.1. Evaluation of nanosized SiO_2 materials for CTL

To explore the effect of the SiO_2 morphology on the cataluminescence and select the appropriate sensing materials for ethyl acetate sensor, the prepared SiO_2 nanotubes and SiO_2 nanoparticles were used for constructing the gas sensor, respectively. The CTL responses on the two kinds of SiO_2 surface were detected when all the organic vapors were 400 ppm. The results were shown in Fig. 4. The CTL intensities of all the vapors on the surface of SiO_2 nanotubes were higher in comparison with that of SiO_2 nanoparticles. Moreover, on SiO_2 nanotubes surface, ethyl acetate vapor was produced the strongest CTL intensity, which was about 18 times higher than that on SiO_2 nanoparticles under the same conditions. This means that the SiO_2 nanotubes have a much more catalytic performance to ethyl acetate. The main reason is likely the difference in the morphologies of the two nano-SiO_2. Because the difference in morphological or structural of the catalytic nanomaterials can lead to different CTL responses [14]. The TEM image (Fig. 3a) demonstrates that using CNTs as templates, the obtained sample consists of bundles of SiO_2 nanotubes, and the single SiO_2 nanotube clearly exhibits that the nanotube is composed of many good dispersed nanoparticles with the grain size in the range of about 2–4 nm, as shown in Fig. 3b. Nevertheless, in the absence of CNTs, only aggregated SiO_2 nanoparticles with the grain size ranges in 10–20 nm are obtained, as shown in Fig. 3c, which suggests that CNTs are apparently capable of stabilizing SiO_2 nanoparticles as well as preventing their aggregation [23].

It has been reported that the catalytic performance of nanomaterials would be greatly enhanced with the decreasing nano-particle size and the increasing specific surface area [27]. Compared to the SiO_2 nanoparticles, the as-prepared SiO_2 nanotubes are composed of many smaller particles, so they possess a better dispersion, and a higher specific surface area, which all enhance the fully oxidation of ethyl acetate by air. Therefore, it should have better CTL sensing characteristic to ethyl acetate and was selected as efficient sensor material for the detection of ethyl acetate vapor in the present work.

3.2. CTL response profiles of ethyl acetate on SiO_2 nanotubes

The CTL response profiles of ethyl acetate vapor on the surface of SiO_2 nanotubes were investigated by injecting the vapor into a carrier gas at a flow rate of 345 mL/min. Fig. 5 showed the CTL

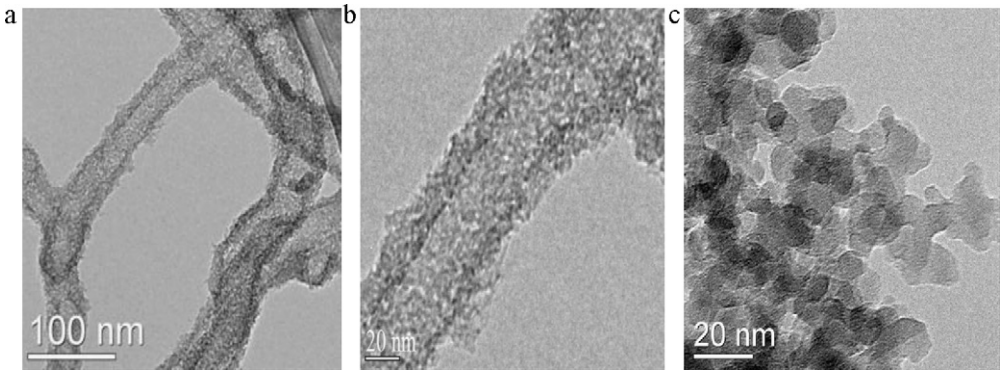

Fig. 3. Transmission electron microscopy images of (a) SiO_2 nanotubes and (b) aggregated SiO_2 nanoparticles.

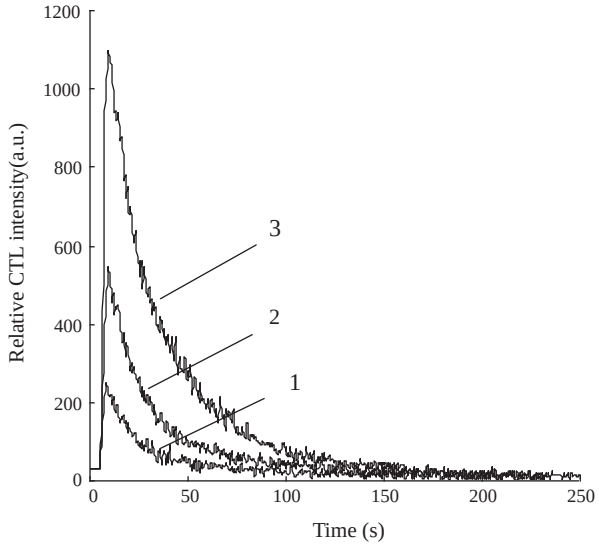

Fig. 5. CTL response profiles of different concentrations of ethyl acetate vapor.

response profiles of different concentrations of ethyl acetate vapor at 293 °C with a bandpass filter of 425 nm. Curves 1, 2 and 3 denote the results for different concentrations of 200, 500 and 1000 ppm respectively. It can be seen that the CTL response profiles are similar to each other. For all three concentrations of ethyl acetate, the maximum signals were achieved at around 10 s after sample injection, indicating a rapid response of this sensing mode to different concentrations of ethyl acetate vapor.

3.3. Optimization of wavelength

In order to investigate the effect of wavelength on the CTL intensity of ethyl acetate vapor. Eight bandpass filters (400, 425, 440, 460, 490, 535, 555 and 575 nm.) were used to select the optimal wavelength. We can see from Fig. 6 that the incandescent radiation noise signals at longer wavelength are higher than those at shorter wavelength, because of the incandescence of the ceramic heater increases with increasing wavelength. Considering this factor, the signal-to-noise ratio (S/N) was used to express the real CTL intensity. The maximum value of S/N was observed at 425 nm. Therefore,

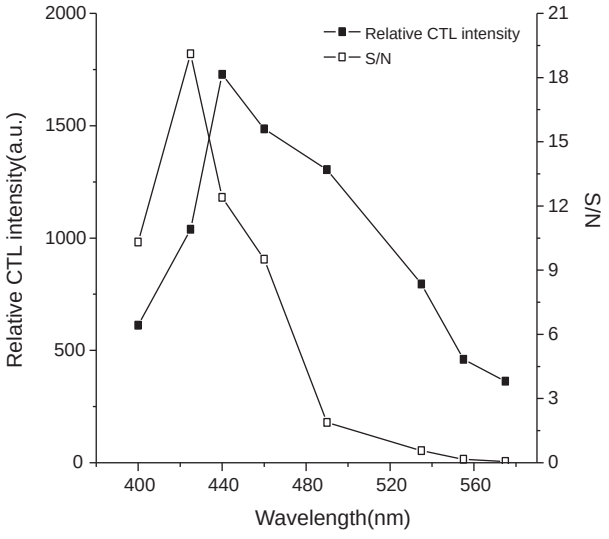

Fig. 6. Wavelength dependence of CTL intensity of ethyl acetate vapor.

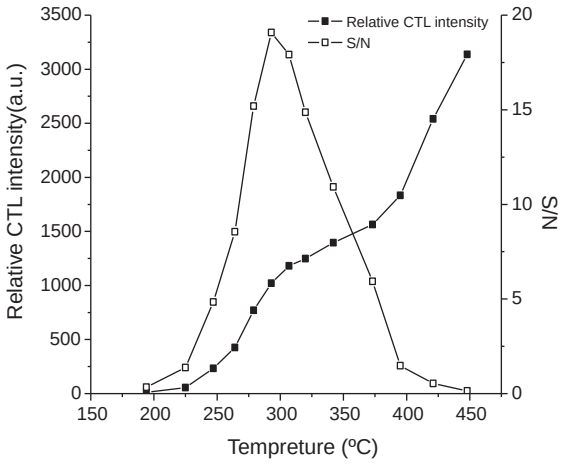

Fig. 7. Temperature dependence of CTL intensity of ethyl acetate vapor.

the 425 nm was the optimal detection wavelength for the current ethyl acetate vapor sensor.

3.4. Optimization of temperature

The effect of working temperature on CTL intensity was shown in Fig. 7. From Fig. 7, it can be seen that the CTL intensity increased with the increase of temperature from 200 °C to 450 °C. But with the increase of temperature, the background signals (which mainly results from the thermal radiation) also increased, the S/N ratio reached a maximum value at 293 °C. Therefore, 293 °C was the optimal detection temperature for the following experiments.

3.5. Optimization of flow rate of carrier gas

As the flow rate of carrier gas has an important influence on the diffusion rate and the residence time of the sample on the SiO_2 nanotubes, and this may affect the reaction rate of the catalytic oxidation reaction, the flow rate of carrier gas dependence on CTL intensity was carefully studied in the range of 75–345 mL/min. Fig. 8 showed that the CTL intensity of 1000 ppm ethyl acetate vapor increased gradually with increasing the flow rate from 75 to 210 mL/min, and kept relatively stable from 210 to 395 mL/min.

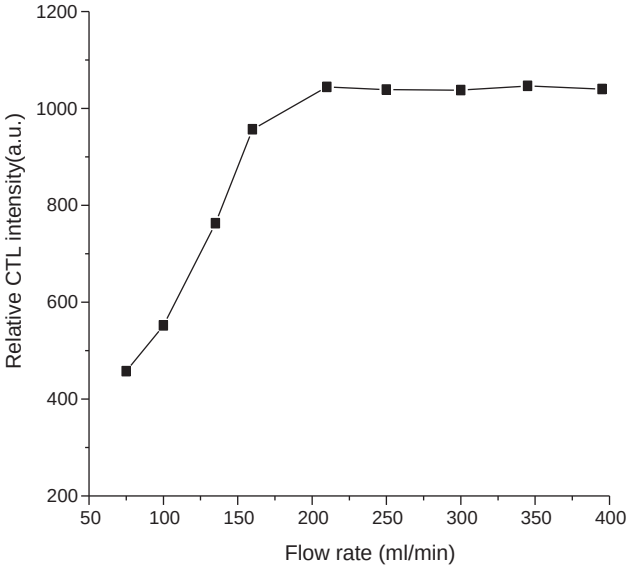

Fig. 8. Effect of flow rate of carrier air on CTL intensity of ethyl acetate vapor.

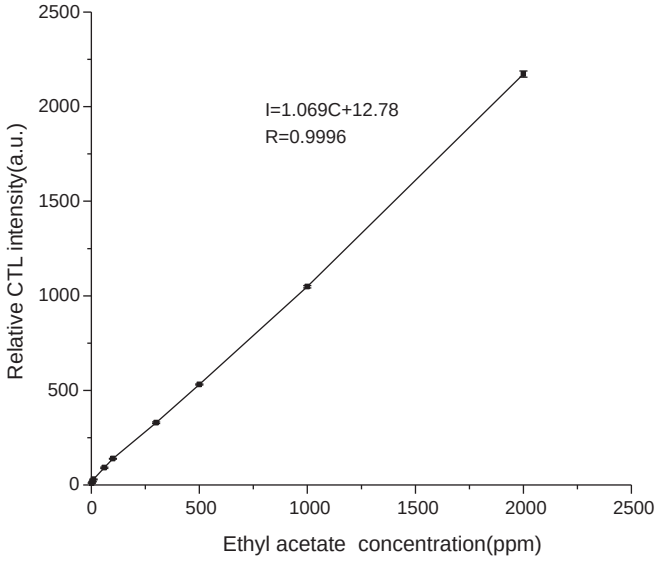

Fig. 9. The calibration curves of ethyl acetate vapor.

These results directly show that the catalytic oxidation process is under a diffusion controlled condition at flow rates below 210 mL/min and is under a reaction controlled condition at flow rates above 210 mL/min [13]. It was considered that a higher flow rate can lead to the CTL signal returning to background quickly, which is very helpful to shorten the cycle of the determination, a flow rate of 345 mL/min was selected as the optimal flow rate.

3.6. Analytical characteristics

Under the optimal conditions described above, the calibration curve of CTL intensity versus ethyl acetate vapor concentration was linear in the range of 2–2000 ppm with a detection limit of 0.85 ppm. The linear regression equations was $I = 1.069C + 12.78$ ($r = 0.9996$), where I was the CTL intensity and C was the concentration of ethyl acetate vapor (Fig. 9). Relative standard deviation (RSD) was 2.0% for five times determination of 1000 ppm ethyl acetate vapor, as shown in Fig. 10.

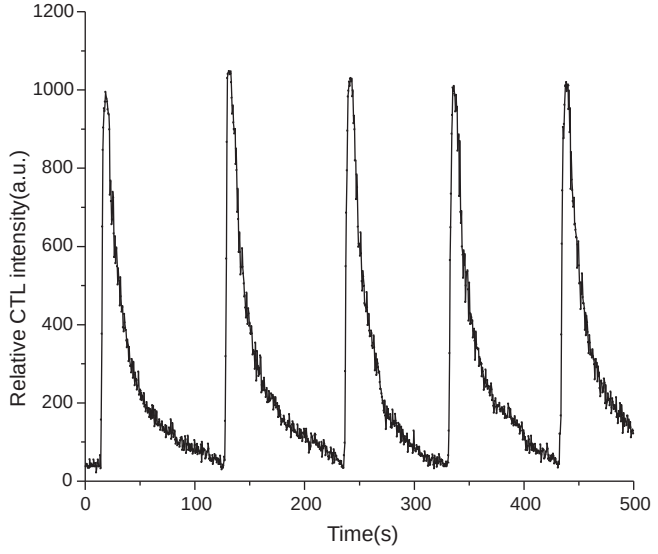

Fig. 10. Typical results obtained from five replicate injections of ethyl acetate vapor.

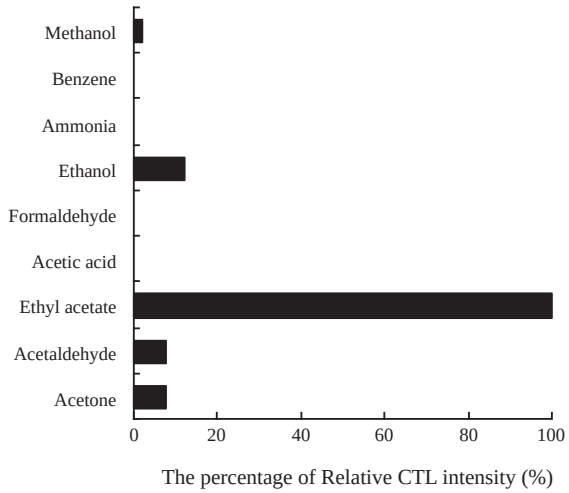

Fig. 11. The percentage of CTL responses of different compounds on the sensor.

3.7. Specificity of SiO_2 nanotubes gas sensor

Specificity plays a key role in a sensor, as poor specificity would result in the ostentation of false positives. Some compounds, which may co-exist with ethyl acetate in contaminated air, e.g., ethanol, benzene, ammonia, acetaldehyde, acetone and formaldehyde, were tested by introducing each compound into the proposed sensor chamber at a concentration of 1000 ppm under the optimized conditions. The result was shown in Fig. 11. No or very weak CTL emissions for most compounds were observed. Although CTL emissions were detected for acetaldehyde, acetone and ethanol, the CTL intensity is much lower than that of ethyl acetate. Therefore, the sensor shows a significantly high specificity to ethyl acetate.

3.8. Lifetime of the sensor

The lifetime of the sensor was examined at the optimal conditions. The CTL intensities were measured once per 10 h by continuously injecting 1000 ppm of ethyl acetate vapor for 100 h in the carrier gas through the sensor. No significant decrease of CTL intensity was observed during the 100 h detection. The relative standard deviations were 2.8% ($n = 11$) in a successive experiment, which indicated good stability and durability of the sensor.

3.9. Sample analysis

In order to test the reliability of the system, three synthetic samples containing known concentrations of ethyl acetate, ethanol, benzene, acetic acid and ammonia were analyzed under the optimized conditions. As shown in Table 1, satisfactory recoveries were obtained.

Table 1
Ethyl acetate vapor analysis in artificial air samples (conditions: wavelength, 425 nm; temperature, 293 °C; flow rate, 345 mL/min).

Sample no.	Composition	Standard values	Measured values	Ethyl acetate
		(ppm)	(ppm, $n = 6$)	Recovery (%)
1	Ethyl acetate	100	97.78 ± 3.62	97.78%
	Ethanol	10		
2	Ethyl acetate	200	198.6 ± 5.23	99.30%
	Benzene	200		
	Acetic acid	200		
3	Ethyl acetate	100	100.3 ± 3.97	100.3%
	Ammonia	100		

4. Conclusion

The results in the present work have demonstrated that the SiO_2 nanotubes, prepared by using CNTs as templates in SCFs, have a much higher catalytic activity in response to organic gases than the SiO_2 nanoparticles. Based on the CTL emission of ethyl acetate on the surface of SiO_2 nanotubes, a novel ethyl acetate sensor was developed. The results showed the sensor has the advantages of high sensitivity, good selectivity, low cost and satisfactory stability. This work may be helpful in developing miniaturized equipment for the determination of ethyl acetate in the industry grounds.

Acknowledgements

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