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A nanosized Y_2O_3-based catalytic chemiluminescent sensor for trimethylamine

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Abstract

The development of a catalytic chemiluminescent trimethylamine (TMA) sensor is demonstrated in the present paper. Intensive chemiluminescence (CL) is detected when TMA is introduced over the surface of nanosized catalysts and subsequently catalytically oxidized by O_2 from the air, and four catalysts are investigated with the strongest CL intensity obtained on nanosized Y_2O_3. This effect is utilized to develop a novel nanosized Y_2O_3-based catalytic CL sensor for TMA which under optimal conditions exhibits a wide linear range of 60–42,000 ppm and a detection limit of 10 ppm. An attractive advantage of this novel CL sensor is its high selectivity to TMA with negligible responses to many other gases such as NH_3 and organic vapors. This CL sensor has a short response time of less than 3 s, and shows good stability when examined by continual introduction of TMA into the sensor for 96 h. The applicability of this sensor to actual fish samples is also demonstrated in the paper.

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Keywords: Intensive chemiluminescence; Nanosized Y_2O_3; TMA

1. Introduction

Trimethylamine (TMA) is one of the volatile gases largely responsible for the pungent and fishy odor generated during the deterioration process of fish after death, which results from the bacterial or enzymatic degradation of trimethylamine oxide (TMAO) in dead fish. The concentration of TMA increases significantly during the deterioration process and hence is an essential objective parameter for fish quality evaluation. The Association of Official Agricultural Chemists (AOAC) recommends a method [1] for the determination of trimethylamine based on extraction of the amine in toluene and subsequent reactions with picric acid. Involving several time-consuming steps, the method is rather complex and hazardous. Accordingly, several other methods based on photometric detection [2], flow injection/gas diffusion coupling with photometric [3] or potentiometric detection [4], gas chromatography coupling with flame ionization detector [5] or surface ionization organic mass spectrometry [6], ion mobility spectrometry [7], as well as liquid chromatography [8] have been developed for TMA detection. These methods are quite suitable for TMA detection in laboratories; however, complex and expensive apparatuses are required in all these methods, making them neither portable nor field applicable.

Modern analysts are continuing to develop sensor systems that are simpler, less expensive and more suitable for personal and domestic applications. During the past decade, much effort has been paid to develop various TMA sensors [9–19], most of which are based on the TMA-induced electrical conductivity changes of semiconductor metal oxides, such as Ru/TiO_2 [9,10], ZnO_2 [11–15], Th/SnO_2 [16] and WO_3 [17]. Most of these sensors are sensitive and stable, but the lack of selectivity limits their applications, as they also respond to other gases such as NH_3 and organic vapors. Egashira et al. [19] have recently developed a chemiluminescence (CL) TMA sensor on the basis of electrochemiluminescence on $Ru(bpy)_3^{2+}$/Nafion coated electrode. However, the stability

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of this kind of Ru(bpy)$_3^{2+}$ sensor is barely satisfactory as the catalytic sites leach or partition into hydrophobic regions over time [20], which deteriorates its performance.

On the basis of catalytic CL phenomenon, a novel sensor is built and studied in the present paper. First observed by Breysse et al. [21] during catalytic oxidation of carbon monoxide on a thoria surface, catalytic CL is found to occur when reductive gases/vapors are introduced over the surface of solid catalysts and subsequently catalytically oxidized by O_2 from the air. Recently, the research on the applications of nanosized materials in catalytic CL has attracted widespread attention due to their high surface areas, good adsorption, high activity and high selectivity. Several CL sensors based on nanosized materials [22–24] have been previously developed in our laboratory; however, most of the catalytic CL sensors thus developed have been limited to the detection of ethanol due to their high selectivity to ethanol.

Here we report a novel catalytic CL TMA sensor based on nanosized catalyst, which to the best of our knowledge is the first report on the catalytic CL of nitrogen-containing organic compounds. The results show that this catalytic CL sensor is not only sensitive but also highly selective to TMA, with a short response time and good stability.

2. Experimental

2.1. Synthesis and characterization of catalysts

All chemicals used in the experiment were of analytical grade and used as received from the supplier (Beijing Chemical Reagents Company, China). The standard sample of 40% TMA in N_2 was purchased from Dalian Guangming Institute of Chemical Engineering. The standard samples with lower concentrations were obtained from the dilution of the standard gas by dried air.

Nanosized Y_2O_3 was synthesized by a wet chemical method described as follows: 2 ml Tween 80 was first added to 10 ml 0.03 M $Y(NO)_3$; then 5 ml ammonia was added with moderate agitation. The obtained precipitate was washed with deionized water for five times and calcined in air at 800 °C for 2 h. The procedure for synthesis of nanosized TiO_2 was as follows: 2 ml $TiCl_4$ was slowly added into 20 ml ethanol solution at room temperature. The light yellow solution thus obtained was gelatinized for 3 days to form a sol-gel, which, after dried, was calcined at 600 °C for 2 h. The resultant TiO_2 powder was then cooled to room temperature in air. Nanosized $SrCO_3$ was prepared as follows: 0.1 M $SrCl_2$ solution and 0.1 M Na_2CO_3 solution were initially cooled to 2 °C separately. Then the Na_2CO_3 solution was rapidly added into the stirred $SrCl_2$ solution at a ratio of 1:1. The precipitate thus formed was immediately filtered and washed with deionized water for five times before calcination at 600 °C for 2 h. Nanosized WO_3 was synthesized as follows: 0.1 M HNO_3 was rapidly added into 0.1 M $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ solution with vigorously stirring to adjust the pH to 3. Yellow precipitate was generated after 10 min and was filtered and washed with deionized water for five times. This precursor was then dried at 100 °C and calcined at 600 °C for 2 h.

The grain size of the nanosized Y_2O_3, which was later identified as the most suitable catalyst, was determined by a transmission electron microscope (H-800, HITACHI). The powder was suspended in ethanol by ultrasonication for 15 min. Then the suspended solution was dipped on a copper grid which was covered with a very thin film of amorphous carbon for specimen preparation. Working at an accelerating voltage of 200 kV, the image obtained is shown in Fig. 1, from which the average grain size of the obtained Y_2O_3 particles was determined to be about 20 nm. The sizes of other three synthesized nanosized particles were determined in the same way, and the average grain sizes thus obtained for TiO_2, WO_3 and $SrCO_3$ were 20 nm, 40 nm and 25 nm, respectively.

For nanosized Y_2O_3, X-ray powder diffraction experiment was carried out in a Rigaku DMAX-2400 diffractometer with nickel-monochromated Cu Kα radiation. The XRD pattern shown in Fig. 2 is assigned to pure and highly crystalline body-centered cubic Y_2O_3.

2.2. Apparatus

Fig. 3 shows a schematic diagram of the sensor system. The nanosized catalyst was sintered as a layer with a thickness of 0.1 mm on a heating tube which was put into a quartz tube with an inner-diameter of 12 mm. The air from the pump was mixed with TMA and flowed through the quartz tube, in which TMA was oxidized on the surface of catalyst by the oxygen in air. The resultant catalytic CL was directly measured with a BPCL Ultra Weak Chemiluminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, China). Changing the optical filters, the wavelengths used for detection could be selected over the range of 400–600 nm.

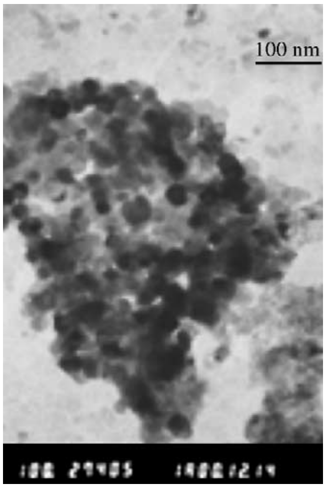

Fig. 1. TEM image of nanosized Y_2O_3.

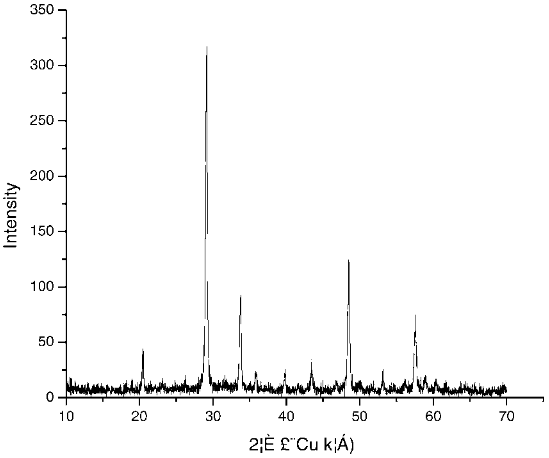

Fig. 2. X-ray powder diffraction pattern of nanosized Y_2O_3.

3. Results and discussion

3.1. *The catalytic CL responses of TMA on the surface of nanosized catalysts*

All the nanosized particles synthesized as described above, which according to our previous research would potentially have good catalytic CL activities (discussed later), were investigated to identify the most suitable one for TMA detection.

As shown in Fig. 4, the highest CL intensity is obtained on nanosized Y_2O_3 at 320 °C. Although intensive catalytic CL is also observed on nanosized TiO_2, the maximum CL intensity is only 42% of that on nanosized Y_2O_3. Moreover, the optimal detection temperature for nanosized TiO_2 is 380 °C, which is 60 °C higher than nanosized Y_2O_3 and hence incurs higher incandescent background noise and an unstable baseline. Consequently, nanosized Y_2O_3 is identified as the best catalyst for our study, with the optimal working temperature determined as 320 °C.

Although nanosized $SrCO_3$, TiO_2 and Y_2O_3 has all been previously regarded as good catalysts for catalytic CL detection of ethanol [22], they behave quite differently when used as catalysts for catalytic CL detection of TMA, which can be attributed to their inherent different catalytic properties. WO_3 has been reported as a good sensing material in TMA electrochemical semiconductor sensors [17], yet no evident catalytic CL is observed on it, demonstrating that the catalytic CL sensing activity and the electric sensing activity of a certain material are unrelated, a conclusion which is also evidenced by the fact that no electrochemical sensor could be designed based on Y_2O_3, which is itself an insulator.

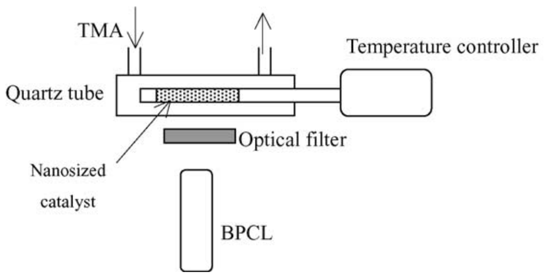

Fig. 3. A schematic diagram of the catalytic CL sensor system.

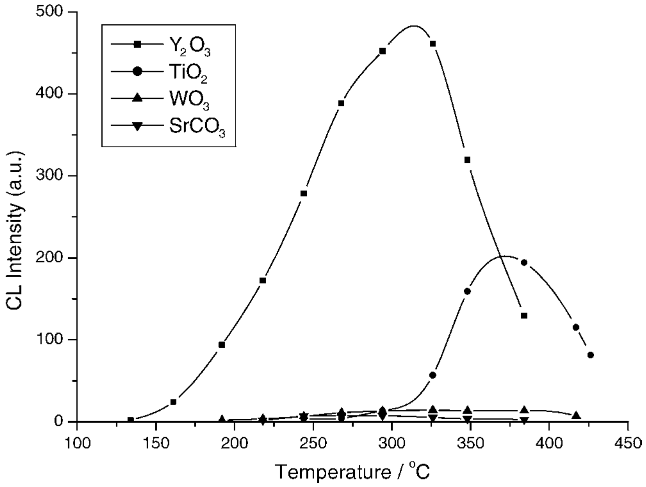

Fig. 4. CL responses to 7200 ppm TMA on the surface of different nanosized materials at different temperatures.

The catalytic CL response profile of TMA on nanosized Y_2O_3 is shown in Fig. 5. The response curves were obtained at 320 °C with a bandpass filter of 555 nm, by injections of TMA vapor into the carrier gas which worked at a flow rate of 120 ml min^{-1}. The results show that the CL sensor has a rapid response to TMA with a short response time of less than 3 s (from baseline to the maximum value) and a short recovery time of about 150 s.

As shown in Fig. 5, the catalytic CL responses also show good repeatability. The relative standard derivation for 10 consecutive injections of 1400 ppm TMA samples is 1.1%. In

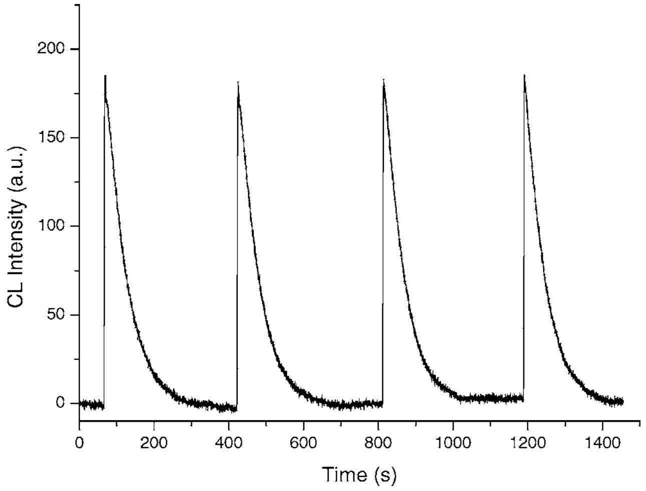

Fig. 5. The catalytic CL response for four consecutive injections of 1400 ppm TMA on the surface of Y_2O_3 nanoparticles at 320 °C with a flow rate of 120 ml min^{-1} through a 555 nm bandpass.

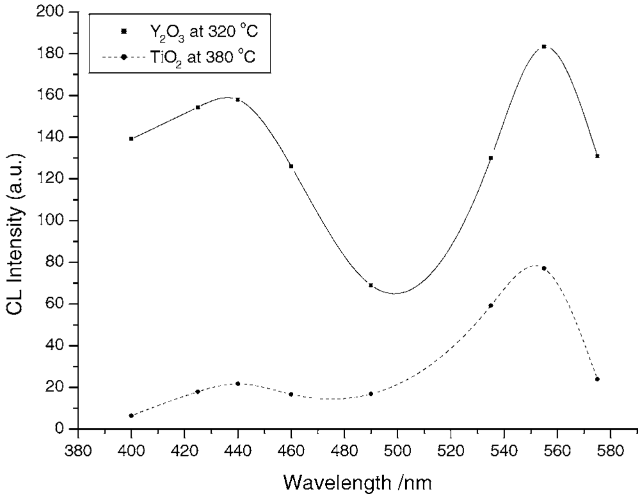

Fig. 6. Catalytic CL spectra of TMA obtained on Y_2O_3 and TiO_2, under the respective optimal conditions of the catalysts, and for the same concentration of TMA.

view of this good repeatability, three measurements are taken for each sample in the subsequent experiments to record the average CL response.

3.2. Catalytic CL spectra of TMA and selection of detection wavelength

The catalytic CL spectra of TMA on nanosized Y_2O_3 and TiO_2 are shown in Fig. 6. With two peaks at 440 and 555 nm, the spectra are essentially different from the reported catalytic CL spectra of ethanol, which have three peaks at 425, 460 and 535 nm [23,24]. This result suggests different CL intermediates for TMA and ethanol, and provides a means to distinguish TMA signal from ethanol signal. According to Fig. 6, the optimal detection wavelength is determined as 555 nm to achieve the best CL intensity.

3.3. Optimization of flow rate

The flow rate dependence of catalytic CL intensity was studied at 320 °C with a bandpass filter of 555 nm. As shown in Fig. 7, the catalytic CL intensity increases gradually with an increase in the flow rate when the flow rate is low, and saturates when the flow rate is above 80 ml min^{-1}. According to Fig. 7, optimal flow rate is selected at 120 ml min^{-1} for TMA detection to achieve the highest CL intensity.

3.4. Analytical characteristics

Under the optimal conditions which have been identified above, the nanosized Y_2O_3-based CL sensor exhibits a wide linear detection range of 60–42,000 ppm with a detection limit (signal/noise = 3) of 10 ppm, as shown in Fig. 8. The linear regression equation for the sensor is $\lg I = 0.579 \times \lg c + 0.438$ ($r = 0.998$, $n = 27$, where 'r' is the correlation coefficient, and 'n' represents the 27 TMA samples tested in the experiment), where I is the CL intensity and c is the concentration of TMA (in ppm).

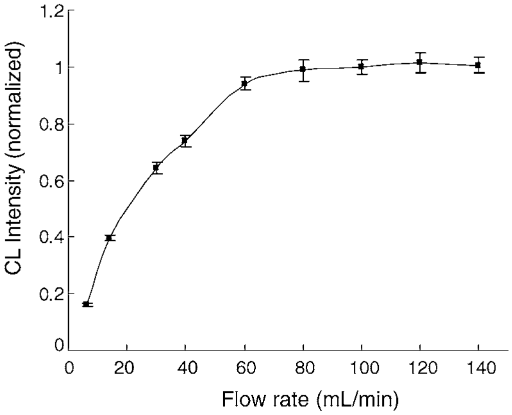

Fig. 7. Effect of flow rate on CL intensity at 320 °C, through a filter of 555 nm.

3.5. Selectivity

A major drawback of the well-studied electrochemical semiconductor TMA sensors lies in the fact that the sensing materials are not only sensitive to TMA, but also to many other gases such as NH_3 and organic vapors [18]. For comparison, the responses to other common gases are investigated for the catalytic CL sensor. No significant CL emission could be detected for either nitrogenous substances such as NH_3, N_2, *N*,*N*-dimethylformamide (DMF), pyridine, or other substances such as CO_2, formaldehyde, formic acid, acetic acid, *n*-propylbenzene, etc. Although CL emission is also detected for ethanol, the compound is easily distinguished from TMA by its entirely different CL spectrum, as discussed previously. The observed high selectivity is attributed to the fact that a gas can be detected only when it can be catalytically oxidized on the catalyst and at the same time produce CL intermediates.

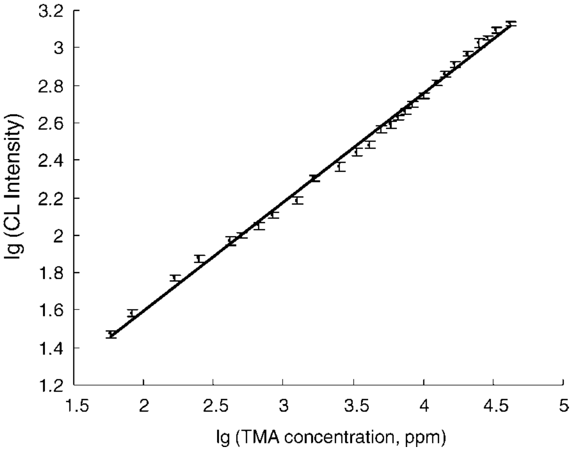

Fig. 8. Calibration curve between catalytic CL intensity and concentration of TMA. The experiment was carried out at 320 °C with a flow rate of 120 ml min^{-1} through a filter of 555 nm.

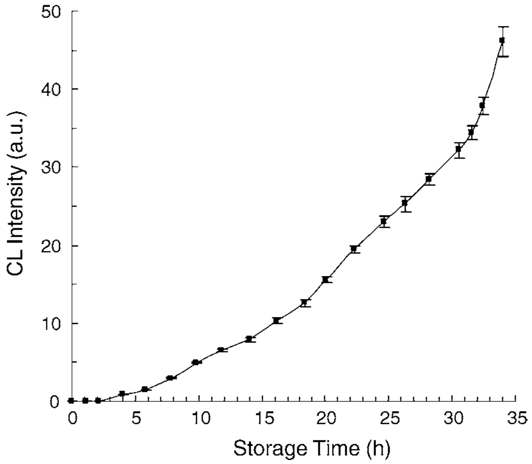

Fig. 9. The catalytic CL responses of the nanosized Y_2O_3-based TMA sensor to the odor of a common perch kept at room temperature, as a function of storage time.

In addition, the CL response of dimethylamine (DMA) and methylamine (MA) was also tested. The result showed that catalytic CL could also be observed with DMA and MA. However, the CL of them was 5–10 times lower than that of TMA. The sensor's response to dimethylamine is 22.7 ± 0.7% of that to trimethylamine, while the response to methylamine is 11.7 ± 0.5% of that to trimethylamine at concentration of 720 ppm for all of the three compounds.

3.6. Stability

The stability of the sensor was examined by continual introduction of 2000 ppm TMA into the sensor for 96 h. The results show that the catalytic CL intensity thus obtained remained stable during the time. Compared with electrochemiluminescent sensors [20,25] based on immobilized reagents, our catalytic CL sensor shows good stability, as solid catalysts eliminate the problems like catalytic site leaching and solution evaporation.

3.7. Applicability to actual fish samples

The applicability of this nanosized Y_2O_3-based TMA sensor to actual fish samples was tested by periodically introducing the odor from a common perch (*Perca fluviatilis*) kept at room temperature into the sensor which worked under the optimal conditions as discussed above. As shown in Fig. 9, the CL intensity in this way obtained experiences a continuous and accelerating increase as the time goes on, corresponding to the deterioration process of the fish after death. This result demonstrates that this sensor would provide a quite promising method for instant determination of fish freshness.

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