Development of a sensitive gas sensor by trapping the analytes on nanomaterials and *in situ* cataluminescence detection

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ABSTRACT

An optical sensor for ethanol has been proposed by trapping the analytes on sensing nanomaterials at room temperature and detecting them *in situ* by recording the cataluminescence (CTL) signals with fast elevated temperature. Sensing nanomaterials of ZrO_2 were directly deposited on heating filament which enables the temperature programming for trapping and detecting the interested analytes. The miniaturized sensing unit has low incandescent radiation so as to provide the high signal-to-noise ratio. Under the optimized conditions, the linear range for the determination of ethanol vapor is 1.0×10^{-3} to $1.0 \, \text{mg L}^{-1}$. A detection limit (S/N = 3) is $2.0 \times 10^{-4} \, \text{mg L}^{-1}$ (0.1 ppm), which is improved about 3000-fold for ethanol compared with previous CTL sensors. The relative standard deviation (RSD) is 1.2% ($n = 7$) for ethanol samples at a concentration of $0.08 \, \text{mg L}^{-1}$. The stability was demonstrated by continuous reaction with ethanol for 120 h. This sensor has been applied to monitor the ethanol concentration in human expired gas after drinking, and the results agreed well with the reference values. This miniature ethanol sensor offers higher sensitivity, faster response and lower power consumption, which make it very promising in developing hand-hold sensing device for field detection.

1. Introduction

The development of sensitive sensors is significantly important due to the great demands in many areas such as environmental monitoring, domestic safety, public security, and food industries [1–4]. Improvement of sensitivity can be achieved by increasing the sensitivity of the sensing element itself, or by preconcentrating the sample before detection [5–7]. Preconcentration techniques such as solvent extraction and solid-phase extraction (SPE) have been widely employed for sensitivity enhancement in the development of analytical methodologies [8]. However, conventional SPE coupling with a specific detector may lead to relative complexity of the equipment, which became an obstacle in the design of portable sensor. *In situ* preconcentration and *in situ* detection by employing dual-functional materials would provide significant benefits for improving the sensitivity of sensors and increasing the practical applicability.

In the field of gas sensors, many types of ethanol sensors have been investigated and developed due to the great demand in biomedical, chemical, and food industries, especially in wine-quality monitoring and breath analysis [9,10]. Semiconductor sensors based on the electrical conductivity changes with the com-

position of gas atmosphere surrounding it are popular and useful for ethanol sensing [11,12]. However, most of the traditional semiconductor sensors suffer from poor selectivity and are still inadequate for sensing multianalyte samples such as expiratory gas. Biosensors using enzyme (alcohol oxidase or alcohol dehydrogenase) catalytic reaction for measurement of ethanol have been developed because of specificity and good selectivity [13–15]. However, short lifetime and low stability limited its application.

Cataluminescence (CTL) refers to the kind of chemiluminescence (CL) that is emitted during the catalytic oxidation of organic vapors. It was first observed by Breysse et al. during the catalytic oxidation of carbon monoxide on a thoria surface [16]. Recently, sensors based on cataluminescence (CTL) have attracted great attention due to the long lifetime because there is no consumption of sensing materials during detection [17,18]. Utsunomiya et al. found that luminescence was generated during a heating course of γ-Al_2O_3 powder with previously adsorbed vapor of organic compound in early 1990s [19]. Nakagawa et al. observed CL emission during the catalytic oxidation of organic vapors on bulk solids such as γ-Al_2O_3 and γ-Al_2O_3 activated by Dy^{3+} [20,21]. We have also observed the CL emission of many analytes during catalytic reaction on nanomaterials, designed a series of sensors and demonstrated a catalytic nanomaterials-based optical chemosensor array for measuring alcohols, amines, thiols and other compounds [18,22–25]. Moreover, Lu et al. and Lv et al. have also been engaged in exploring new sensing materials that exhibit higher selectivity and sensitivity [26–28]. Although CTL gas sensors have shown many promising features such as good selec-

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tivity and long lifetime, they suffer from the fact that few systems have been applied in practical use due to the insufficient sensitivity. Therefore, there is a strong research effort under way to meet the challenge for sensitive detection.

Nanomaterials have been used as adsorbents because of their much larger surface-to-bulk ratio. For example, nanosized TiO_2 and CeO_2 were used as solid sorbents of solid-phase extraction for the preconcentration of trace metal ions [29,30]. Zirconia nanoparticles were used as selective sorbents for organophosphate pesticides [31]. Hiroe et al. chose CeO_2–ZrO_2 mixed oxides as oxygen storage components [32]. Nanosized MgO, CaO, Al_2O_3, CeO_2, and TiO_2 were studied as sorbents for volatile organic compounds [33,34]. In our previous work, nanosized TiO_2 has been used for adsorption of volatile organic vapors and the desorbed species could be detected by a chemiluminescence detector [35]. However, the process had to be carried out apart in two steps which made the equipment relatively complex. Therefore, it is attractive to combine the dual-functions of adsorption and cataluminescence properties of nanomaterials at one site in a sensor to obtain high sensitivity.

In this study, a new CTL sensor based on *in situ* preconcentration and cataluminescence detection has been developed and characterized. Nanosized ZrO_2 as sensing material was directly deposited on heating filament which allowed for improving the sensitivity by trapping the analytes on sensing nanomaterials at room temperature and detecting them *in situ* by CTL at fast elevated temperature. The analytical characteristics of the sensor for ethanol were optimized by the examination of CTL emission of the sensor at various conditions. Compared with the conventional semiconductor-based [11], enzyme-based [9,15], and cataluminescence-based [24,27,36] ethanol gas sensors, the proposed sensor showed high sensitivity with a detection limit (S/N = 3) of 2.0×10^{-4} mg L^{-1} (0.1 ppm). The potential of the present approach was demonstrated by applying this highly sensitive sensor for breath analysis after drinking.

2. Experimental

2.1. Instrumentation

A schematic diagram of the detection system is shown in Fig. 1. ZrO_2 nanoparticles were directly deposited on a home-made heating filament to form a layer with a thickness of 0.1 mm. This heating filament was extracted from commercially available cylindrical ceramic heater and coiled (i.d. = 0.5 mm, length = 10 mm), and then placed in a quartz chamber (i.d. = 20 mm, length = 15 mm). The temperature of the ZrO_2 layer could be controlled by adjusting heating voltage of the heating filament from 6.0 to 18.0 V and monitored by
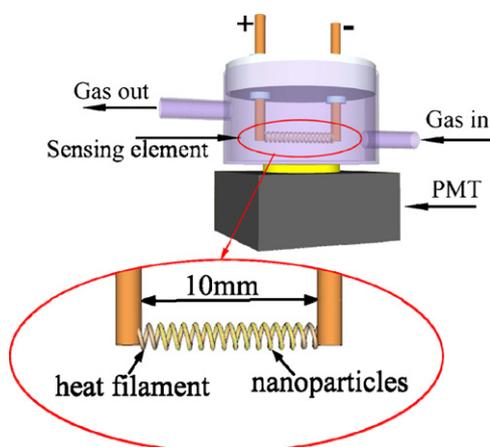

Fig. 1. Schematic diagram of the CTL-based sensor.

a thermocouple. An air pump provided a steady air flow stream as carrier gas at the flow rate from 10 to 300 mL min^{-1}. Sample gas was prepared in a 75 mL flask and could be delivered by the carrier gas and then reached to the surface of nanoparticles. The CTL intensity was measured with a BPCL Ultra Weak Chemiluminescence Analyzer (Biophysics Institute of the Chinese Academy of Science). The data acquisition time for each signal point was set as 0.1 s, and the voltage for the photomultiplier tube was −970 V. The data was recorded with a computer and further processed with OriginPro. The SP-6880 gas chromatography (GC) instrument (Lunan Chemical Engineering & Instrument Company, Shandong, China), equipped with a GDX 201 column (1.5 m × 4 mm) and a flame ionization detector (FID detector), was applied for determination of ethanol concentrations.

2.2. Reagents and materials

ZrO_2 nanoparticles were supplied by Nanjing Haitai. Nano. Co. (Nanjing, China) and used as received. Ethanol (purity ≥99.5%) was purchased from Beijing Chemical Co. Ltd. (Beijing, China). Beer was obtained from Yanjing Beer Co. Ltd. (Beijing, China). Cola and Sprite were purchased from Coca-cola Co. Ltd. (Beijing, China).

2.3. Procedures

The sensor was heated at 270 °C (heating voltage is 18.0 V, with a current of 0.14 A) for 2–5 min in air to avoid the influence of previous absorbates at the beginning of each series of experiments. While conducting enrichment, heating voltage of the heating filament was set at 0 V to keep the sensor at room temperature. After enrichment, the heating voltage was set as 11.0 V (electric current 0.09 A, temperature 130 °C), and a catalytic oxidation reaction occurred on the surface of ZrO_2 nanoparticles accompanying with CTL emission.

In the real sample analysis, GC experiments were carried out to determine the ethanol concentrations in expiratory gases after alcohol consumption as reference method. The conditions for GC experiments were as follows: temperature of sample chamber operated at 120 °C, column temperature operated at 120 °C, and detector temperature operated at 100 °C.

2.4. Sample preparation

The spiked breath gas samples were prepared by injecting a certain volume of ethanol vapor into a 75 mL bottle which was filled with breath gas. After mixing for 1 min, the spiked sample was injected into the sensing cell for detection.

Real sample analysis was conducted by collecting expiratory gases from volunteers after drinking different beverages including beer, tea, Cola and Sprite.

3. Results and discussion

3.1. Design of the sensing cell

The schematic diagram of the CTL-based sensor is shown in Fig. 1. The heating filament was placed in a quartz chamber with two holes for gas in and gas out. ZrO_2 nanoparticles were directly deposited onto the heating filament to form a layer of sensing materials with a thickness of 0.1 mm (inset of Fig. 1). Our preliminary experiment indicated that the temperature of the proposed miniature sensor could be changed fast between room temperatures for enrichment and working temperatures for CTL detection. The CTL signal reached maximum value within 10 s after power on, and decreased to baseline within 3 s after power off. The response speed is about 20 times faster than the CTL sensor based on ceramic heating rod. These features allowed us to conduct enrichment of the