Sensors and Actuators B 202 (2014) 721–726

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Simultaneous determination of benzene and formaldehyde in air by cross cataluminescence on nano-$3TiO_2$–$2BiVO_4$

Kaowen Zhou*, Yanling Cheng, Hongwei Yang, Chunxiu Gu, Yu Xiao, Minghang Zhao

Biochemical Engineering College, Beijing Union University, Beijing 100023, China

ARTICLE INFO

Article history:
Received 29 March 2014
Received in revised form 26 May 2014
Accepted 28 May 2014
Available online 4 June 2014

Keywords:
Benzene
Formaldehyde
Cross cataluminescence
Gas sensor

ABSTRACT

A novel method based on cross cataluminescence (CTL) generated on the surface of nano-$3TiO_2$–$2BiVO_4$ was proposed for simultaneous determination of benzene and formaldehyde in air. Two analysis wavelengths 470 nm and 600 nm were selected for this method. The surface temperature of sensing materials was 375 °C. The flow rate of air carrier was 135 mL/min. The limits of detection of this method were 0.12 mg/m^3 for benzene and 0.05 mg/m^3 for formaldehyde. The linear ranges of CTL intensity versus analyte concentration were 0.25–57.5 mg/m^3 for benzene and 0.10–51.3 mg/m^3 for formaldehyde. The recoveries of 5 testing standard samples by this method were 96.6–103.1% for benzene and 97.2%–102.8% for formaldehyde. Common coexistence matters, such as toluene, ethyl benzene, acetaldehyde, ethanol, ammonia, sulfur dioxide and carbon dioxide, did not disturb the determination. The relative deviation (RD) of CTL signals from continuous 120 h detection of gaseous mixture containing benzene and formaldehyde was less than 2%, which demonstrated the longevity and steady performance of nano-$3TiO_2$–$2BiVO_4$ to benzene and formaldehyde.

1. Introduction

Benzene and formaldehyde are two of the most ubiquitous hazardous air pollutants in residential and occupational environments [1–3]. They are widely used as base chemical materials to manufacture building materials and numerous household products in many industrial processes including wood fixatives, dry cleaning solutions, cosmetics, pharmaceutical process, paints, inks, rubber, sterilizing agent and so on. Several studies had provided clear evidences of causal association between exposure to benzene and/or formaldehyde and acute nonlymphocytic leukemia [4–7]. Thus, both benzene and formaldehyde are classified as known human carcinogen [8] by IARC (International Agency for Research on Cancer). Prolonged exposure to benzene and/or formaldehyde, even if low concentration, can cause serious health effects [9,10]. In recent years, various methods were applied to determine benzene [11–15] and formaldehyde [16–28]. Fast and simple methods were becoming increasingly important.

Cataluminescence (CTL) is an emission of electromagnetic radiation produced by catalytic oxidation reactions that yield excited intermediates which can emit rays on falling to the ground state on catalyst surface [29]. CTL, a kind of chemiluminescence (CL) based on catalytic reaction, was first observed by Breysse et al. [30] during catalytic oxidation of carbon monoxide on the surface of thoria in 1976, and then was studied by Nakagawa et al. [31–36] during the catalytic oxidation of organic vapors on γ-Al_2O_3 and γ-Al_2O_3 activated by Dy^{3+}. CTL spectra from different reaction are different, so they can be taken as the basis of analysis. Now, CTL has been considered as a promising energy transduction mechanism for fabricating gas sensor because of its outstanding advantages such as long life, easy miniaturization, fast response, no need for luminous reagent, and etc. In recent years, a series of CTL analytical applications have been attempted to develop for a variety of gaseous molecules [37–56].

Past CTL researches in our laboratory [29,39,48,49,57–59] have focused on the screening of selective CTL sensitive materials and the establishing of specific gas molecular response mode. Due to the CTL signals were mainly manifested in the visible region and the spectrum profiles of different molecular are simple and similar, therefore, the thorny cross interference was always difficult to avoid. TiO_2, a widely used photo catalyst, was CTL active for a lot of molecules. In-depth study, we found that the CTL intensities of different molecules on nano-TiO_2 can be changed by adjusting analysis wavelength, but it's hard to make CTL signals from coexistence molecules disappear entirely. That means CTL signals from different molecules will interfere with each other on

* Corresponding author. Tel.: +86 10 52072264; fax: +86 10 52072264.
E-mail address: zhoukaowen@buu.edu.cn (K. Zhou).

http://dx.doi.org/10.1016/j.snb.2014.05.118
0925-4005/

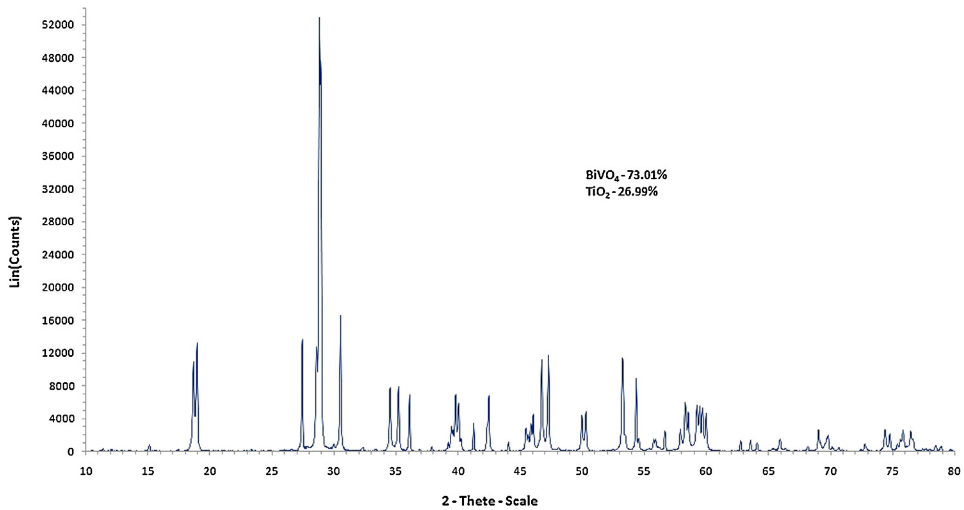

Fig. 1. XRD pattern of nano-$3TiO_2$–$2BiVO_4$.

nano-TiO_2. Further study found that composite oxides of TiO_2 with Bi_2O_3 and V_2O_5 showed good selectivity and activity for benzene and formaldehyde.

In this work, we presented a novel method for simultaneous determination of benzene and formaldehyde at different wavelengths by utilizing their cross cataluminescence that used to be thought of intractable defect. This method is better economy than multiple gas sensors array [37,41,47,50,56,60], and easier to implement than different working temperature [61].

2. Experimental

2.1. Preparation of sensing materials

In order to study the efficiency of different sensing materials in the catalytic oxidation of benzene and formaldehyde, a great deal of nanosized materials and their compound bodies were prepared. The procedure for synthesis of nano-$Ti_3Bi_2V_2O_{14}$ by means of a sol–gel method was as follows: 40 ml $Ti(OC_4H_9)_4$ was dissolved in 200 ml methanol at room temperature, then 20 ml acetic acid and 20 ml distilled water were slowly added into the solution, and Ti sol was formed by continuously stirring the solution more than 10 h. At the same time, 9.2 g NH_4VO_3 and 38 g $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in 200 ml 2 mol/L HNO_3 solution and then 70 ml citric acid was added into the solution. The mix solution was added into Ti sol above, and Ti–Bi–V gel was formed after stirring for 50 min at room temperature. The atom ratio of Ti:Bi:V was 3:2:2. This gel was subjected to aging for 15 h, drying at 105 °C, cooling to room temperature, rubbing, and calcining at 410 °C for 3 h, successively, to finally get nano-$3TiO_2$–$2BiVO_4$ that XRD pattern is showed in Fig. 1. The TEM photograph in Fig. 2 shows that the average granular size was about 18 nm.

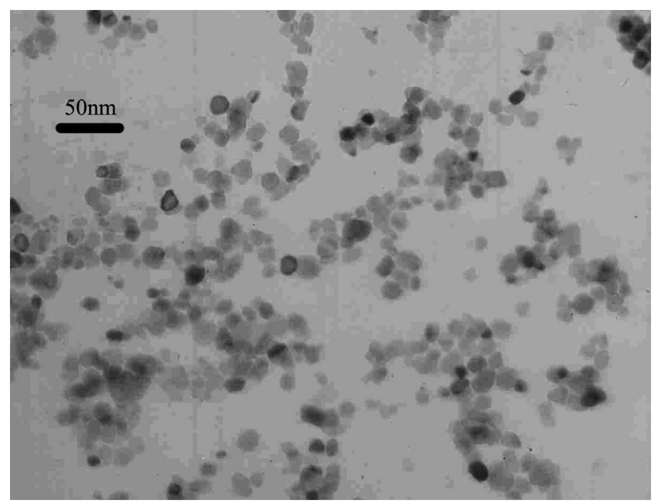

Fig. 2. TEM photo of nano-$3TiO_2$–$2BiVO_4$.

2.2. Apparatus of CTL system

The CTL system used in this work is shown in Fig. 3. The system, an improvement from references [29,57,58], includes four parts. They are (1) CTL chamber (a cylindrical ceramic heater of 5 mm in diameter sintered a thickness of 0.1–0.2 mm sensing materials was placed in the middle of a quartz tube of 10 mm in diameter possessing gas entrance-exit), (2) temperature controller (the surface temperature of ceramic heater can be adjusted from room temperature to 650 °C), (3) optical filter (transitable rays can be selected from 400 nm to 745 nm), and (4) optical detector (CTL singles can be processed by photo multiplier, photons counter and computer).

2.3. Procedures

The gaseous sample is directly introduced to system by sample valve, and carried to CTL chamber by carrier gas. Benzene and formaldehyde in air are oxidized on the surface of chosen sensing material at a certain temperature. The luminescence intensities at

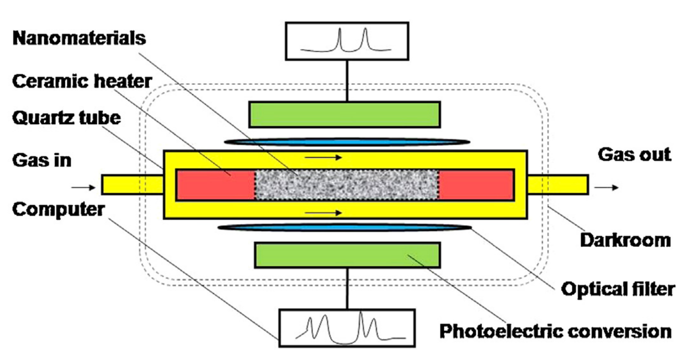

Fig. 3. Schematic diagram of the CTL system.