



A controllable selective cataluminescence sensor for diethyl ether using mesoporous TiO₂ nanoparticles



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ABSTRACT

Development of selective cataluminescence (CTL) sensors toward volatile organic compounds (VOCs) is of great importance to environmental analysis and daily chemicals safety. Although some reports for the determination of VOCs based on CTL have been reported, part of them suffered relatively low selectivity because of their high sensitivity toward interferences. In this study, mesoporous TiO₂ nanoparticles have been exploited to detect diethyl ether with the usage of a 440 nm bandpass filter. The proposed method showed high selectivity toward diethyl ether over other VOCs, such as acetaldehyde, acetone, butanone and butanol, etc. Such a high selectivity was majorly attributed to the difference of CTL emission profiles of various VOCs reaction intermediates, and only diethyl ether exhibited strong CTL emission at about 440 nm. Under the optimal conditions, diethyl ether could be detected ranging from 2.0 to 50.0 mM. Furthermore, the practical application of this proposed CTL sensor for diethyl ether was validated with artificial samples and commercial perfumes. In general, such a simple method with high selective detection through controlling detection range could be extended to other analytes.

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1. Introduction

Cataluminescence (CTL) is a kind of chemiluminescence emitted during the catalytic oxidation of gas molecules on solid catalyst surfaces in an atmosphere containing oxygen [1]. Over the past few decades, CTL sensors have been greatly improved both in the development of novel catalysts and/or the improvement of instruments [2–5]. They have been widely employed as powerful tools for chemical analysis because of their advantages of simple configuration, fast response and stable intensity [6]. However, low selectivity still seems to be a major limitation for real samples in the developed CTL systems [7]. To overcome this issue, the development of the advanced CTL array of analytical detection devices has attracted growing attention [8,9]. For example, a CTL sensor array with 9 sensing elements for alcohols, amines, and thiols determination has been reported by Na et al. [8]. Later, they developed an extended nanomaterial-based CTL sensor array for recognition and discrimination of flavors in cigarettes with 21 sensing elements [9]. Although the sensor array technology has been successfully applied in volatile organic compounds (VOCs) detection, this method is sometimes limited with the need of complicated and multiple sensing elements. False recognition results would appear once one of these sensing elements breaks [10,11], and each sensor element

needs to be calibrated before the quantitative detection [12,13]. Therefore, it is still appealing to exploit simple CTL methods with high selectivity.

It is well known that CTL spectral profiles depend on reactants and/or solid catalysts, and the maximum emission wavelengths of CTL spectra reply on the reaction intermediates [14–16]. For instance, Hu et al. investigated the intermediates of diethyl ether on borate glass by using CTL spectra and theoretical calculation methods, and demonstrated that the maximum emission wavelength at 440 nm was assigned to CH₃CHO* [14]. However, Zhu et al. proved that the maximum emission wavelengths of ethanol and acetone on TiO₂ nanoparticles were located in 570–620 nm [15]. Taking the CTL intermediate-dependent emission into consideration, it is reasonable to explore CTL probes with high selectivity based on controlling the detection range with a special wavelength bandpass filter.

Nowadays, nanomaterials have brought great opportunities for advance in CTL sensors due to their characteristics of large surface areas and more active sites [17–19]. Among them, TiO₂ nanoparticles as benchmark materials of catalyst have some advantages, such as wide availability, cheapness, high stability and non-toxicity [20–22]. Especially, mesoporous TiO₂ nanoparticles have been widely used as catalysts or catalyst supports in photocatalysis and photoelectric catalysis owing to their unique properties such as larger surface area, uniform pore size distribution and tunable pore structure [23–25]. For example, Hasan et al. found that mesoporous crystalline TiO₂ nanoparticles exhibited higher Li ion insertion

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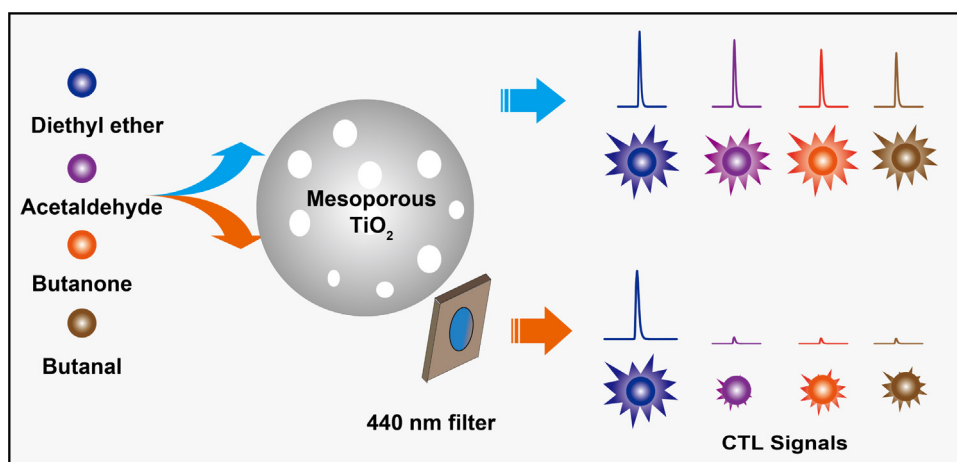


Fig. 1. CTL configuration system for diethyl ether identification on the surface of mesoporous TiO₂ nanoparticles.

capability and better photoactivity than bulk TiO₂ for bleaching methylene blue [23]. Bavykin et al. reported that the catalytic efficiency of selective oxidation of alcohols of Ru(III)/TiO₂ nanotube (turnover frequency [TOF] up to 450 h⁻¹) increased obviously compared with Ru(III)/Al₂O₃ catalyst (TOF = 335 h⁻¹) [24]. Such high catalytic capabilities imply mesoporous TiO₂ nanoparticles may have positive influence on the CTL systems. These results encourage us to design CTL sensors with high selectivity, rapid response and long-term stability based on mesoporous TiO₂ nanoparticles.

Herein, we employed a typical sol-gel method for preparing mesoporous TiO₂ nanoparticles with different pore sizes via simple calcination approach. The as-prepared mesoporous TiO₂ nanoparticles were firstly proved to show high catalytic capability to VOCs CTL systems, including diethyl ether, acetone, acetaldehyde, butanol and so on. Highly selective diethyl ether detection was achieved through controlling the detection range at about 440 nm with special wavelength bandpass filter (Fig. 1). Further studies indicated that CTL intensity of diethyl ether was related to the pore size of the resulting mesoporous TiO₂ nanoparticles, reaction temperature and flow rate. Under the optimal conditions, diethyl ether could be identified in the range of 2.0–50.0 mM with a limit of detection of 1.5 mM (S/N = 3). In addition, the practicability of the proposed diethyl ether detection system was further evaluated by commercial perfume and artificial samples.

2. Experimental

2.1. Chemicals and materials

Analytical grade chemicals were used without further purification. All solutions were freshly prepared with deionized water (18.2 MU cm, Milli Q, Millipore, Barnstead, CA, USA). TiCl₄ was supplied by Aladdin Industry Co., Ltd. (Shanghai, China). Tetrabutyl titanate (Ti(OBu)₄) and P123 were purchased from Alfa Aesar (Ward Hill, MA). Nanosized TiO₂ (P25, 53.0 m² g⁻¹, 30 nm) was supplied by Haitai Nano Co., Ltd. (Nanjing, China). Forty percent acetaldehyde was from Tianjin Fuchen Chemical Reagent Company (Tianjin, China). Diethyl ether, butanol, butanone, acetone, ethanol, ethyl acetate, formaldehyde, glutaraldehyde, methanol, acetic acid, acetonitrile, 1,2-propylene glycol were supplied by Beijing Chemical Reagent Company (Beijing, China). Fifty millimolar stock solution of diethyl ether was freshly prepared by diluting 53.0 μL diethyl ether into 10.0 mL deionized water. Bromothymol blue (BTB) (wt 0.04%, water-soluble) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Saturated Ca(OH)₂ solution was freshly prepared by reaction of CaO with deionized water.

2.2. Apparatus

Wide angle X-ray diffraction (WAXD) patterns were recorded with a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu/Kα radiation (λ = 1.54178 Å). The samples as unoriented powders were step-scanned in steps of 0.02° (2θ) in the range of 20–70°. Small angle X-ray diffraction (SAXS) patterns were recorded on a Rigaku D/max-2500VB2+/PC diffractometer using Cu/Kα radiation with the following operating parameters: 2θ scanning from 0.5° to 5°. An Hitachi (Japan) H-800 transmission electron microscope (TEM) was used for the transmission electron microscopy images. High resolution transmission electron microscope (HRTEM) and fast-Fourier-transform (FFT) analysis were performed by using a Tecnai G220 TEM (FEI, USA) at an accelerating voltage of 200 kV. N₂ adsorption-desorption isotherms were measured through ASAP2020 nitrogen adsorption apparatus (Micromeritics Ins., Corp., USA). Specific surface areas were calculated according to the Brunauer, Emmett and Teller (BET) equation. The pore size distributions were calculated from desorption branch using the Barrett, Joyner and Halenda (BJH) method. A DTA/TGA 1/1100 SF (Mettler, Toledo) was used to carry out the thermogravimetric-differential thermal analysis (TG-DTA) in air at a heating rate of 10 °C min⁻¹. Fourier transform infrared (FT-IR) spectra were collected with a Nicolet 380 FT-IR spectrometer (Thermo, USA) with a resolution of 2.0 cm⁻¹ and 32 scanning numbers. Mesoporous TiO₂ nanoparticles for in situ FT-IR were compressed into self-supporting pellets and then placed in the thermostatic reactor. All FT-IR spectra were measured over the range of 4000–650 cm⁻¹. The gas chromatography-mass spectrometer (GC-MS) experiments were performed using a Thermo Trace 1300-ISQ GC-MS system (Thermo, USA) equipped with a TR-5MS column (30 m, 0.25 mm i.d., 0.25 μm film thickness). The CTL signals were detected by a BPCL chemiluminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). A bandpass filter (Center wavelength: 440 nm, ±5 nm, peak transmission: >56.01%, institute of Biophysics, Chinese Academy of Science, Beijing, China) was used to control the detection range of CTL signals. CTL spectra were obtained using an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at a scanning rate of 3000 nm min⁻¹. And during the CTL spectra recording, excitation lamp was off and the emission slit width was set at 20 nm. Organic gas molecules were delivered by an air pump (Beijing Zhongxing Huili Co., Ltd., Beijing, China). The heater controller (Hongbao Electric., Co., Ltd., Beijing, China) was used to provide heater for the ceramic rod.

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