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A cataluminescence-based vapor-sensitive sensor array for discriminating flammable liquid vapors

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ABSTRACT

This paper describes a cataluminescence-based (CTL-based) vapor-sensitive sensor array containing 10 kinds of catalytic nanoparticles for rapid detection and discrimination of 10 flammable liquid (FL) vapors. The catalytic nanoparticles are directly deposited on heating filaments with the formation of the sensing elements. When the vapor samples are imported to the sensor array with carrier gas, the CTL intensity varies with the nanoparticles. The fingerprints of 10 FL vapors are discriminated according to the distinct CTL response patterns through a linear discriminant analysis (LDA) and hierarchical cluster analysis (HCA) in SPSS (version 16.0). The canonical patterns are clearly clustered into 10 different groups with a classification accuracy of 100%. The sensor array also applies to several real-world samples. Two kinds of simulated actual vapors, originating from the combustion of carpet in the presence and absence of gasoline, can be effectively distinguished. The developed CTL-based vapor-sensitive sensor array offers a new strategy for the rapid detection of FL vapors owing to its stability, reversibility, portability and low costs.

1. Introduction

Flammable liquids (FLs) are liquids that can catch fire and are present in almost every workplace. Analysis of FLs has been performed and developed due to a great demand in environmental monitoring, food industry, biomedical engineering and especially in public security [1–4]. The most common analytical methods, such as gas chromatography/mass spectroscopy (GC/MS) and gas chromatography/flame ionization detection (GC/FID) [4], to discriminate flammable liquids are spectroscopic techniques, often coupled with chromatographic methods. Although these methods ensure high sensitivity, they usually involve sample pretreatment and are time-consuming.

An additional methodology to detect FLs is using accelerant detection canines. In a fire scene, the presence of the FL residues is one of the most important criteria to determine arsons, and therefore detection of FLs is crucial to fire investigations. The fire investigators usually use canines as gas sensors to detect trace evidences in complex circumstances [5]. However, the use of canines in detection is limited because of their vulnerability to chemical damage and high training cost.

Artificial olfactory systems, known as “artificial noses”, can be implemented to detect odors based on a sensing strategy similar to the mammalian olfactory system [6–8]. These kinds of artificial noses employ an array of broadly cross-reactive sensors which consist of a series of nonselective receptors for a wide range of chemical compounds response and diverse mixtures of possible analyte discrimination [9]. To date, numerous artificial noses such as surface acoustic wave resonators [10,11], quartz crystal resonators [12], densely integrated chemiresistor [13], optical-fiber arrays [14,15], surface plasmon resonance-based sensors [16,17], colorimetric sensors [18,19] and so on, have been developed to exploit a wide range of sensing schemes. Despite several successful applications, these artificial noses have some limitations, such as high cost, short lifetime, low stability and irreversible responses. Hence, it is necessary to develop a new strategy for vapor sensing.

Cataluminescence (CTL) is a kind of chemiluminescence emission during catalysts oxidation of flammable gases on the surface of solid catalysts in an atmosphere. CTL was first observed by Breysse et al. through a catalytic oxidation of carbon monoxide on thoria surface [20]. Our group applied a series of catalytic nanoparticles for CTL detection of organic compounds [21–27] due to nanoparticles′ high surface area, good adsorption characteristics, and high catalytic activity. The mechanism of CTL emission is caused by recombinant radiation and radiation from excited species. The analytes on the surface of nanoparticles are oxidized catalytically by oxygen in the air. The released energy of the catalytic reaction is absorbed by some of the reaction products, forming excited intermediates which decay with light emission from excited state to the ground state. Many nanoparticles have

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been used for CTL catalysts [28–32]. In previous studies, both individual and cross-reactive sensors have been applied for detection of volatile organic compounds and explosive gases [24,25,33–35]. Recently, a CTL sensor array based on three nanoparticles was proposed for the first time for the quantitative analysis of xylene isomers [36]. Cao′s group developed a novel CTL sensing method based on simultaneous detection of the luminescent intensities of both the analyte and its products. They also used their method to identify volatile organic compounds at different concentrations [37]. CTL-based sensors hold the promise of achieving both satisfactory sensitivity and good reversibility [21,35]. They are also fast detection approaches with simple and low-cost devices. However, thus far, there is no report of a CTL-based sensor array for the detection and discrimination of FL vapors. Recently, Walt et al. achieved high classification accuracy of vapor samples throughout the field tests using a fluorescence-based cross-reactive sensor [38–40], which encourages us to study whether the sensing array strategy of CTL can be used in “artificial noses” for discrimination of FL vapors.

This paper presents an exploratory study into FL vapors detection by a CTL-based artificial nose system. The distinct CTL responses of 10 kinds of FL samples, including gasoline, which is considered as a common arson accelerant [4], were tested by sensor array and the outcomes were well discriminated by using liner discriminant analysis (LDA) and hierarchical cluster analysis (HCA). We also successfully discriminated the combustion residues of carpet with gasoline and without gasoline. This rapid and efficient strategy might be performed as a safety method to detect hazardous liquids.

2. Experimental section

2.1. Sensor formation and nanoparticles

A schematic diagram of the CTL-based array is shown in Fig. 1, illustrating the main features of the experimental apparatus for the study. The array system was fabricated by 10 home-made heating filaments (i.d. = 0.5 mm, length = 10 mm), the temperature of which was controlled by a transformer adjusting heating voltage (0–250 V, 50 Hz). A portion weighing 2 mg of each kind of nanoparticles was dissolved separately in 1 mL deionized water. The resolution was mixed homogeneously by vortex mixer (QL-901, Kylin-Bell Lab Instruments Co., Ltd.) for 30 s. Then 10 home-made heating filaments were fixed to the circular PTEF platform (diameter = 90 mm) after being soaked in the solution for 3 min to form a layer with a thickness of about 0.1 mm (Fig. S1). The sensing elements were uniformly distributed and the CTL signals from each sensing elements were sequentially recorded by the PMT (CR-105 photomultiplier tube made by Hamatasu). Therefore, the order of sensing elements would not affect the detected results. The filter of PMT is selected to reduce thermal radiation. According to the previous research [35], different nanoparticles have different optimal wavelengths. Since the array system contained 10 kinds of nanoparticles as sensor elements, it is not feasible to install just one type of filter. As an alternative, the heating filament was chosen due to its capability of measuring the highest signal at longer wavelengths without optical filters. As a result, the PMT in our array system was without optical filters and without wavelengths discrimination.

Four nanoparticles MgO, ZrO_2, CaO and γ-Al_2O_3 ($d \sim 20$ nm) were supplied by Nanjing Haitiai. Nano. Co., Ltd. $Ce(NO_3)_{36}H_2O$ (ZSM-8) and $Ni(NO_3)_{26}H_2O$ (ZSM-4) were obtained from Gymnastics Zibo Chemical Technology Development Co. Ltd. Al_2O_3–$Ba(NO_3)_2$–εu, Ag–BaO–Al_2O_3 and $Ba_3(PO_4)_2$ were synthesized by our initial study according to the reports [23,41]. A simple method was used to synthesize the Pt–BaO–Al_2O_3 nanoparticles. Specifically, Pt–Al_2O_3 was synthesized by dipping γ-Al_2O_3 ($d \sim 20$ nm) in chloroplatinic acid solution for 12 h, followed by stirring for 1 h at 80 °C, exsiccation for 12 h, and calcination for 5 h at 500 °C. Pt–Al_2O_3 was dissolved in barium acetate solution for 12 h and stirred for 1 h at 80 °C, then exsiccated for 12 h and calcination for 5 h at 500 °C. The SEM images of three kinds of nanoparticles are supplied in Fig. S2. After heating the filaments with nanoparticles, the surface morphology of nanoparticles was not changed because the heating temperature was lower than the synthesis temperature.

2.2. Vapor delivery system

Vapor samples were injected into a 100 mL bottle and separately presented to sensor array with carrier gas by the delivery system. The proportion of the carrier gas and the vapor samples would affect the responses of CTL. By fixing a flow rate of the

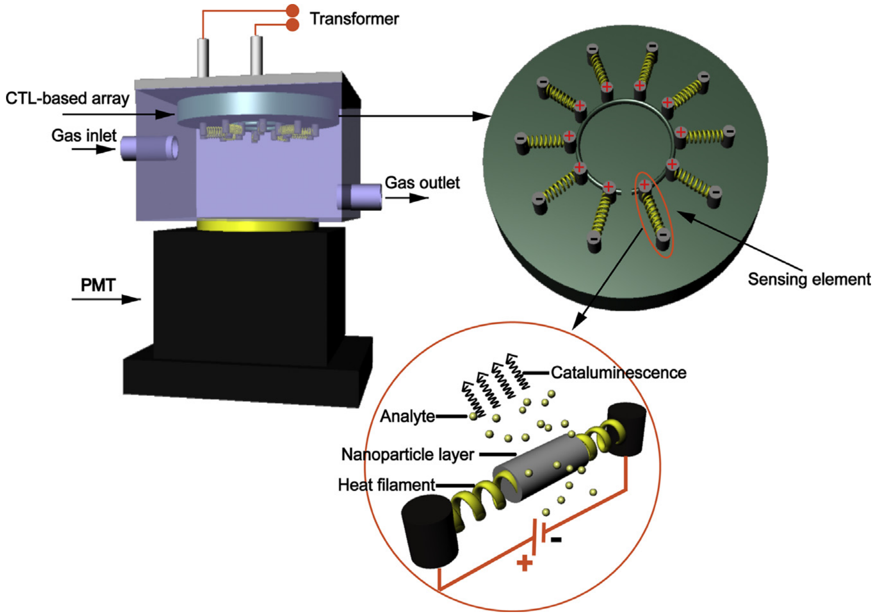

Fig. 1. Schematic diagram of the CTL-based sensor array.