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A paper-based plasma-assisted cataluminescence sensor for ethylene detection

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ABSTRACT

The development of paper-based sensing devices has grown exponentially due to the unique properties of paper as a low-cost functional material. For a long period, paper-based cataluminescence (CTL) sensing devices were considered impractical because the operating temperature of CTL reactions is normally higher than 200 °C. Herein, we report, at the first time, a paper-based sensing system based on the CTL emission with the assistance of low-temperature plasma generated by air, which can be operated at room temperature. As demonstrated, enhanced catalytic ability and reactivity of the analytes were achieved, and CTL emission was obtained at room temperature, catalyzed by 0.320 wt% Mn-doped SiO_2 nanomaterials on paper substrates. The CTL emission was affected by the type and relative amount of metal ions or nanomaterials, and different CTL intensities were obtained with different substrates. By optimization of the system, a paper-based CTL sensor was successfully fabricated for ethylene sensing. The sensor exhibited a wide linear response range and a limit of detection (LOD) at the ppm level. Good selectivity as well as the stability of the system was also demonstrated, and the first example of CTL imaging on paper substrates was provided. This approach furnishes a dramatically simplified CTL system, and the paper-based room temperature CTL sensor is expected to expand the applications of CTL.

1. Introduction

In recent years, the development of paper-based sensing devices has grown exponentially based on the unique properties of paper, including its low-cost and easy preparation [1]. Produced by pressing fibers together, paper has a number of other advantages including low-cost, good mechanical properties, a three-dimensional fibrous structure, passive fluid transportation, biodegradability and biocompatibility, as well as ease of modification. Therefore, paper has become an ideal substrate for disposable sensors and integrated sensing platforms for applications in clinical diagnosis, food quality control, and environmental monitoring [2]. Optical signals, including colorimetric, fluorescence, surface-enhanced Raman, transmittance, and chemiluminescence spectra, have been used for sensing. Nevertheless, further investigations are still needed for overcoming issues related to the illumination diversity of fluorescence method, the short service lifetime of colorimetric technique, as well as the high background signal.

Cataluminescence (CTL) is emission generated during the catalytic oxidation of analytes on the surfaces of nanomaterials [3,4]. In contrast with conventional chemiluminescence systems based on irreversible reactions, CTL-based devices have a long lifetime due to the adoption of stable nanomaterials as the catalysts [5]. Thus, many CTL-based optical sensors have been fabricated for the detection of alcohols, amines, thiols, esters, and other gases or vapors [4,6–12]. These sensors are simple and inexpensive, and provide stable responses with non-consumption of the catalysts, and are thus suitable for a wide range of applications [13–19]. However, traditional CTL sensors normally require operating temperatures above 200 °C due to the low CTL reactivity of the analytes. Recently, the use of low-temperature plasma [20,21], which is an active medium for enabling various applications such as ionization, surface treatment, or catalytic reactions, has facilitated the construction of various plasma-assisted cataluminescence (PA-CTL) techniques for sensing [22,23]. Furthermore, the operating temperature has been reduced from a few hundred degrees to a few

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dozen degrees with the use of catalysts on a ceramic chip [24]. However, the main chemical component of the ceramic chip (Al_2O_3) also affects the CTL emission, and further research into CTL sensing based on paper as a much simpler matrix remains a challenge.

Ethylene (C_2H_4) is a quite important gaseous hydrocarbon that is used in many applications, including the preparation of plastics, ethylene oxides, ethylene glycol and polystyrene. In addition, ethylene is an important vegetal hormone involved in several essential processes in plant life, and the ripening of fruit can also be adjusted by controlling the ethylene concentration [25]. As alternatives to the traditional time-consuming and high-costing chromatography-based methods, researchers have attempted to fabricate simple ethylene sensors [26]. However, the limited chemical reactivity of ethylene makes its detection at low concentrations a non-trivial problem, and precise quantification of ethylene at least at the ppm level remains a topical issue. Although electrochemical sensors have been proven to have good repeatability and accuracy, many of these sensors are affected by interfering gases and temperature [27]. The existing optical sensors for ethylene also need to be improved as the non-dispersive infrared instruments lack selectivity and sensitivity, while the cost of laser-based sensors remains prohibitive. Therefore, the fabrication of a low-cost paper-based optical sensor for ethylene sensing is a worthwhile undertaking.

Herein, based on plasma-assisted CTL, a new paper-based sensor was fabricated for the sensing of ethylene. Ethylene could be well detected on the nanomaterial-treated paper based on the CTL signals generated upon exposure of the surface to ethylene. This is the first CTL sensor fabricated using paper, and is expected to expand the application of CTL based on its good potential for ethylene detection.

2. Experimental section

2.1. Chemicals and reagents

All reagents were of analytical-reagent (AR) grade. The nanoparticles were obtained from Nanjing Haitai Co., Ltd. $ZnCl_2$, $Al_2(SO_4)_3{\cdot}18H_2O$, $FeCl_3$, $MgCl_2$, $NiSO_4{\cdot}6H_2O$, and $CuSO_4{\cdot}5H_2O$ were bought from Beijing Chemical Co., Ltd. The ethylene, propylene, ethane, propane, ethyne, and propyne gas were supplied by Beijing Haipu-Gas Co., Ltd. Water was treated by using a water purification system (Millipore, Bedford, MA). The substrates, including the weighing paper, printing paper, filter paper, carbon fiber paper (CFP), and Kraft paper were obtained from Beijing Chemical Co., Ltd.

2.2. Apparatus and software

CTL signals were detected by a BPCL ultraweak chemiluminescence analyzer (Biophysics Institution of the Chinese Academy of Science in China) equipped with a CR-105 photomultiplier tube (PMT) (Hamamatsu, Tokyo, Japan). A continuous air supply was provided by an XWK-III oil-free air pump (Huasheng Analysis Instrument Co., Ltd., Tianjin, PRC), and the flow rate of the air was controlled by a flow meter (Beijing Key Laboratory Instrument Co., Ltd., Beijing, PRC). The data were analyzed and pictorially represented by using Microcal Origin (version 8.0). Scanning electron microscope (SEM) images were obtained with a FESEM HITACHI S-4800 instrument. The imaging system was a UVP EC3 Imaging System.

2.3. Treatment of paper with nanomaterials

The nanomaterials were dispersed in water and then stirred for three hours while adding certain amounts of metal ions. Subsequently, a piece of paper or other substrate (8 mm × 40 mm) was immersed in the nanomaterial solution and shaken for one hour. After reaching equilibrium adsorption, the treated paper or substrate was dried at 80 °C for one hour. Finally, the obtained substrates were stored in a glass desiccator.

2.4. Configuration of PA-CTL system

Based on dielectric barrier discharge (DBD), the plasma-assisted cataluminescence (PA-CTL) system was fabricated according to the method presented in our previous reports [22–24]. As shown in Fig. 1, a copper stick (1.5 mm in diameter) inserted in a T-glass tube (4 mm i.d. × 6 mm o.d.) was used as an electrode, and a piece of copper sheet wrapping the T-tube was used as the other electrode. Air was passed through the T-tube at a flow rate of 300 mL min^{-1}. The air acted as the carrier gas, discharge gas, and the oxidant. The plasma probe was generated by applying an alternating voltage (3.5 kV at 18 W) to the two electrodes. The sample was then injected into the gas flow system for activation by the plasma. The activated sample, carried by the air flow, was then brought into contact with the nanomaterial-treated substrates for the CTL reaction. For detection of the signal, the nanomaterial-treated substrate was placed into a quartz tube with the reaction gas flowing through, and the detection system comprising a CCD or PMT from BPCL was positioned just opposite the transparent quartz tube. Finally, the CTL emission was recorded by using an imaging system or ultraweak chemiluminescence analyzer. All the experiments were performed at ambient temperature and pressure; the actual room temperature was 25 °C.

3. Results and discussion

3.1. Response of paper-based system to ethylene

To study the CTL emission on the nanomaterial-treated paper, ethylene was injected into the air gas flow for the activation process; the surface of the Mn/SiO_2-treated paper was then exposed to the gas for the catalytic reaction. The obtained signals were compared with the responses obtained without plasma assistance, as well as with the responses obtained with the assistance of other kinds of plasma ignited by N_2, He, and Ar. As shown in Fig. 2, activation by the air-ignited plasma led to significant CTL responses of about 4700 a.u., while no signals were recorded without plasma assistance. This observation further confirmed the remarkable enhancement effect of plasma on the CTL reaction, which is in accordance with our previous works [22]. The air flow rate also affected the CTL signals, and the strongest signals were obtained at the flow rate of 300 mL min^{-1} (as shown in the inset of Fig. 2).

No significant response of the paper-based system was recorded when other kinds of plasma ignited by N_2, He, and Ar were employed (Fig. 2). According to a previous report [24], species produced by air discharge, such as long-lived ozone, oxygen radicals, or nitrogen oxides as well as radicals, can act as the oxidant for the CTL reaction [28]. These species could increase the internal energy of the reactants and excite them to chemically active states with a sufficiently long lifetime to initiate the CTL reactions [29]. Therefore, the CTL responses of ethylene could be well recorded on the nanomaterial-treated paper, demonstrating that the functionalized paper could be used to fabricate a simple paper-based CTL sensor.

It should be noted that a detectable signal was still present without the sensing element in place, which could be attributed to energy transfer from the plasma to the sensing gas. Plasma is an active medium with high energy electrons, radicals, and metastable species that activates the CTL reactions via energy transfer from the plasma to the analytes or to oxygen; the plasma also provides sufficient energy for the generation of CTL signals