



A novel acetone sensor utilizing cataluminescence on layered double oxide



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ABSTRACT

This work developed a facile and effective sensor for the determination of acetone, the diabetic biomarker, which was based on cataluminescence (CTL) emission on the surface of layered double oxide (LDO) that is a layered nanomaterial with easy preparation and environmental friendliness. Under the optimized conditions, the linear range of the CTL intensity versus concentration of acetone was 0.1–16 mM with the detection limit of 0.02 mM (S/N = 3). The relative standard deviation (RSD) for 50 repeated measurements of 1.0 mM acetone was 3.6%. Interestingly, there was no or weak response to seven common volatile organic compounds (VOCs), including ethanol, heptanal, ethyl acetate, methanol, formaldehyde, acetic acid and toluene. Furthermore, the proposed CTL sensor was successfully used for sensing acetone in human plasma samples of diabetes patients with a satisfactory recovery. The results demonstrated that the proposed CTL sensor had a promising capability for the sensing of acetone in diabetes diagnosis. The possible CTL mechanism from the oxidation of acetone on the surface of LDO was also discussed.

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1. Introduction

Insulin is a naturally occurring hormone for metabolism and utilization of energy from the ingested nutrients (e.g., sugar and starches). The daily level of insulin is important for the body to function normally [1–3]. Diabetes patients are either unable to generate insulin or the insulin cannot work effectively [4]. Additionally, the medical reports show that a large amount of acetone is generated and acetone concentration is found to elevate by about two degrees of magnitude in the plasma of diabetic patients [5–7]. Hence, acetone is generally regarded as an important biomarker of diabetes or accessorial tool for diabetes diagnosis [8–16]. The commonly analytical techniques for determining acetone for diabetes diagnosis are based on derivatization techniques or mass spectrometry (MS) in conjunction with separation techniques, such as high-performance liquid chromatography (HPLC), gas chromatography (GC) [8–11]. However, the above-mentioned detection methods for acetone often suffer from some disadvantages, such as sophisticated procedures, bulky equipment and low detection sensitivity. In addition, the various types of acetone sensors based on different sensing principles have been fabricated due to their simplicity,

precision and convenience. However, the reported acetone sensors are either poorly selective or inadequately sensitive [12–16].

Cataluminescence (CTL) is a kind of chemiluminescence (CL) during the catalytic oxidation of combustible gases on the surface of solid catalysts in an atmosphere containing oxygen [17,18]. In recent years, the applications of nanomaterial-based CTL to the construction of gas sensors for a variety of volatile organic compounds (VOCs) have attracted considerable attention owing to their advantages of stable intensity, low-cost devices, high sensitivity, and rapid response [19–23]. To the best of our knowledge, there is only one report on CTL determination for acetone in human plasma samples; however, it suffered low selectivity as it was also sensitive to other compounds besides acetone (e.g., methanol, ethanol and formaldehyde) [24]. To improve the selectivity toward acetone, ionic liquids-based headspace solid-phase microextraction technology was used to extract acetone before the CTL detection. Therefore, more efforts should be devoted to the development of a highly sensitive and selective acetone sensor-based CTL.

Layered double hydroxides (LDHs) are an interesting class of inorganic layered solid host matrices with structurally positively charged layers, interlayer balancing anionic species and water molecules [25]. Recently, calcination products of LDHs, known as layered double oxide (LDO), have been paid more attention as catalysts or catalyst precursors owing to their larger surface area, non-toxicity and high chemical stability [26–28]. It has been

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reported that LDO can exhibit stronger catalyzed activity toward aldol condensation of acetone than its LDH counterparts as a result of abundant basic sites [29–32]. Such improvements in catalytic properties are welcome to explore novel applications in sensors.

In the work, calcined Mg/Al-CO₃ LDHs (Mg/Al-LDO) were used as a novel sensing nanomaterial for preparing acetone sensor. Strong CTL emission was generated by the catalytic oxidation of acetone on the surface of LDO. The analytical characteristics were evaluated by the examination of CTL emission from trace acetone on the sensor. The proposed CTL sensor was highly sensitive and selective toward acetone with short response time and good stability. It enabled us to quantify the acetone levels without any sample pretreatments. Validation of the proposed method was checked by determining acetone in human plasma samples of diabetic patients. To the best of our knowledge, this is the first example to employ LDO as CTL sensing nanomaterial for the detection of acetone.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (18.2 MU cm, Milli Q, Millipore, Barnstead, CA, USA). Analytical grade chemicals including Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, acetone, ethanol, ethyl acetate, methanol, formaldehyde, acetic acid, toluene, Na₂CO₃, and NaOH were purchased from Beijing Chemical Reagent Company (Beijing, China). Heptanal and 2,4-dinitrophenyl-hydrazine (DNPH) were purchased from Tokyo Chemical Industry Co., Ltd. HPLC grade acetonitrile was purchased from Merck KGaA (Darmstadt, Germany). CaO was purchased from Fuchen Chemical Reagent Company (Tianjin, China). Mesityl oxide and bromothymol blue (BTB, wt 0.04%, water-soluble) were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). A 200 mM stock solution of acetone was freshly prepared by diluting 75 μL of acetone into 5.0 mL of deionized water. A 0.17 g mL⁻¹ Ca(OH)₂ solution was freshly prepared by reaction of CaO with deionized water.

2.2. Apparatus

The powder X-ray diffraction (XRD) measurements were performed on Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu/Kα radiation (λ = 1.5406 Å). The 2θ angle of the diffractometer was stepped from 5° to 75° at a scan rate of 10°/s. The particle sizes and external morphology of the samples were observed on a transmission electron microscope (TEM, Tecnai G220, FEI Company). The CTL detection was conducted on an IFFM-E flow injection chemiluminescence analyzer (Ruimai, Xian, China). The CTL spectrum of this system was measured with high-energy cutoff filters from 400 to 640 nm between the CTL cell and the photomultiplier tube (PMT). The resultant gases produced by catalytic oxidation of acetone on the surface of LDO nanoparticles were collected in HPLC grade acetonitrile and then introduced into a Thermo Trace 1300-ISQ GC/MS system (Thermo, USA) equipped with a TR-5MS column (30 m, 0.25 mm i.d., and 0.25 μm film thickness) for the analysis of the reaction products. Control experiments were performed using a Waters 1525 HPLC connected to an UV/visible detector (Waters 2489). A Sun-Fire C18 column (4.6 mm × 150 mm, 5.0 μm particle size) was used at room temperature. The LDO was calcined at 450 °C in SX2-5-12 muffle (Boxun, Shanghai, China). Acetone was delivered by the air carrier gas (supplied by a pump, Beijing Zhongxing Huili Co. Ltd., Beijing, China). The heater controller (Hongbao Electric Co. Ltd., Beijing, China) was used to provide heat for the ceramic rod.

2.3. Synthesis of Mg–Al LDO

The Mg–Al–CO₃ LDHs with different Mg/Al molar ratios were prepared by the coprecipitation method. The precipitation process was taken under low supersaturation conditions at constant pH (10.0). Typically, for the synthesis of interlayer carbonate hydroxal-cite sample with a Mg/Al molar ratio of 3, the salt solution including Mg(NO₃)₂·6H₂O (0.045 mol) and Al(NO₃)₃·9H₂O (0.015 mol) was made in 60 mL of deionized water. Then, the mixed solution (60 mL) containing NaOH (0.108 mol) and Na₂CO₃ (0.0075 mol) was prepared. The two solutions were added dropwise to a 250 mL four-necked flask under vigorous stirring at room temperature while the pH value kept 10.0. The resulting white precipitate was continually stirred for 24 h at 60 °C. The products were centrifugated, washed with degassed and deionized water for three times, dried *in vacuo* at 65 °C for 24 h and ground to a fine powder. The resulting solid powder was calcined at 450 °C for 3 h before the CTL analysis.

2.4. CTL measurements

The CTL system was shown in Fig. S1. By diluting 200 mM acetone stock solution with deionized water, a series of acetone working solutions were freshly obtained. A LDO suspension was prepared by diluting LDO powder in deionized water, then it was coated onto the cylindrical ceramic heater (inner diameter = 5 mm, length = 8 cm, Shanghai Anting Factory, Shanghai, China), which was then put into a quartz tube (diameter = 1 cm, length = 10 cm, Institute of Chemistry, Chinese Academy of Science, Beijing, China). A series of acetone solutions (50 μL) were injected into a 2.0 mL gasification chamber, the gas would be conducted into a close reaction cell by air carrier gas. The CTL signals were monitored by a PMT adjacent to the CTL quartz tube. The data integration time of the CTL analyzer was set at 1 s per spectrum, and a work voltage of 900 V was used for the CTL detection. The signal was imported to the computer for data acquisition.

2.5. Sample pretreatment

Whole blood samples from diabetic patients were obtained from China–Japan Friendship Hospital, Beijing, China. The sealed centrifuge tube was used to collect blood samples by a heparin-containing syringe. To minimize the loss of acetone, whole blood samples were stored at –20 °C and thawed at 4 °C just before analysis. After the plasma samples were obtained *via* centrifugation at 5000 rpm for 5 min, it was analyzed immediately by the proposed CTL sensor.

3. Results and discussion

3.1. LDO-triggered acetone CTL

The TEM image and the representative XRD pattern of LDO with the Mg/Al ratio of 4 indicated that the LDH layer collapsed into small pieces with a higher crystallinity after calcination. Additionally, to obtain the CTL response profile of acetone on the surface of LDO, different concentrations of acetone were injected into the air carrier with a flow rate of 400 mL min⁻¹ at 300 °C working temperature. The curves 1, 2 and 3 of Fig. 1 denoted the results for different acetone concentrations of 10 mM, 20 mM and 30 mM, respectively. We could observe that the CTL signals increased with an increase in the concentration of acetone. For the three concentrations of acetone, the signals rapidly increased from the baseline to the maximum value within around 3 s after sample injection, indicating that the proposed sensing mode exhibited a rapid response to different concentrations of acetone.

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