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A novel cataluminescence gas sensor based on MgO thin film

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ABSTRACT

Using MgO film as sensing material, a cataluminescence sensor was proposed by the determination of ethylene glycol ethers (2-ethoxyethanol and 2-methoxyethanol). This ethylene glycol ethers sensor showed high sensitivity and specificity. With detection limits of 1.0 ppm and 1.4 ppm, the linear ranges of cataluminescence intensity versus ethylene glycol ethers concentrations were 2.0–2000 ppm for 2-ethoxyethanol and 2.0–1500 ppm for 2-methoxyethanol, respectively. The response time was less than 5 s. Foreign substances passed through the surface of MgO film without response, such as ammonia, benzene, ethyl acetate, acetaldehyde, vinyl acetate, methanol, acetone, ethanol, acetic acid, formaldehyde, and isopropyl ether. The sensor could determine 2-ethoxyethanol and 2-methoxyethanol whether they existed alone or together in air samples.

1. Introduction

Ethylene glycol ethers are frequently used as solvents, detergents, and emulsifiers alone or as components in numerous industrial and domestic products such as paints, varnishes, inks, cosmetics, and cleaning agents industrial. There exist extensive literatures reporting reproductive, testicular, embryotoxic, teratogenic and hematologic toxicity of ethylene glycol ethers in animal experiments [1–3]. In the 1990s ethylene glycol ethers were reported be responsible for a higher risk level of miscarriage amongst women workers in semiconductor factories in USA [4,5].

2-Methoxyethanol (EM, CAS No. 109-86-4) and 2-ethoxyethanol (EE, CAS No. 110-80-5) are two typical members of industrial solvents collectively known as ethylene glycol ethers. They are mainly used as solvents, colorant, and stabilizer in dyes industry. The standard permitted concentrations of EM and EE vapors in ambient air are less than 8.8 ppm and 8.9 ppm ruled by the Occupational Exposure Limit for hazardous agents in the workplace (GBZ 2-2002, China). Short-chained ethylene glycol ethers are phased out due to their health hazards, EE has been forbidden in Germany. However, EM and EE are still widely used in most of other countries [6,7]. The ethylene glycol ethers may readily enter the body by inhalation as well as dermal uptake. A rapid detecting technique of EM or EE is very important in modern industry.

Primary methods determined EM and EE are based on biological monitoring [8], gas chromatograph equipped with flame ionization detector (GC-FID) [9,10], gas chromatography–mass spectrometry (GC/MS) [11], and UV/vis spectrometer [12]. They possessed high performance and sensitivity, however, with difficult operation and no real-time detection. Gas sensors have advantages of on-site and real-time detection of hazard vapors. There is no specific sensor for detection of EM and EE. So, ethylene glycol ethers sensor was developed to detect gaseous quickly in workplace.

In 1976, Breysse et al. observed that a weak catalytic luminescence phenomenon occurred during catalytic oxidation of CO on ThO_2 surface [13]. This chemiluminescence mode was defined as cataluminescence (CTL). In the 1990s, Nakagawa et al. reported CTL sensors using γ-Al_2O_3 as catalyst material for determination of ethanol and acetone [14–18]. Zhang et al. developed the CTL sensors, a porous alumina film with 0.5 mm thick was used for detecting saccharides [19]. Many nano-materials such as TiO_2, ZrO_2, $BaCO_3$, $SrCO_3$, ZnO, γ-Al_2O_3, La_2O_3, γ-$Al_2O_3 + Nd_2O_3$, $V_2Ti_4O_{13}$, and Y_2O_3 were applied to detect organic vapors of ethanol, acetaldehyde, pinacolyl alcohol, propane, butane, acetone, ethylene dichloride, benzaldehyde, ethyl ether, and acetic acid with high sensitivity and specificity [20–33]. Cao reported that the vinyl acetate sensor based on MgO nanoparticles showed good cataluminescence characters [34]. New development of CTL array sensors can distinguish several different gases [35]. CTL gas sensors have advantages of on-site and real-time detection, small size, and no need of lamp-house. Nevertheless, it is still a challenge for scientists to obtain better sensitive and specific CTL sensors to some toxic gases since their low level of concentrations in the air.

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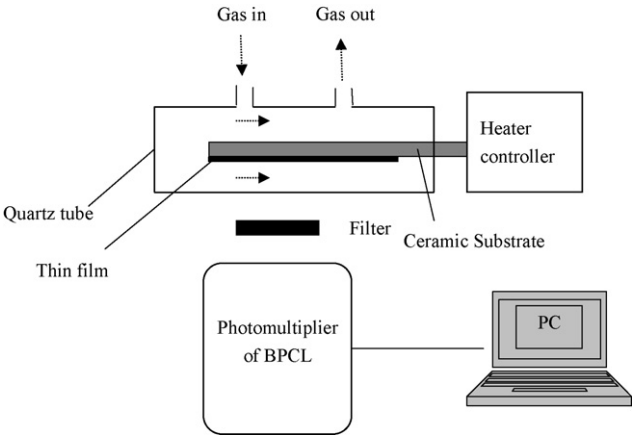

Fig. 1. Schematic diagram of the CTL detection system.

In chemistry sensors, film catalysts were used to improve stability, sensitivity and specificity. ZnO and SnO_2 thin film sensors were reported to enhance the sensitivity of CO and NO_2 [36,37]. MgO is a widely used catalysis, its thin film has also been considered as a suitable material for technological applications. It can be used as sensor elements for humidity sensor [38] and CH_3OH adsorption [39]. However, there are few thin films used in the cataluminescence sensors. Most of nano-materials in cataluminescence sensors are in powder state and might easily come off the substrates. Since thin films could attach firmly and uniformly to the substrate, MgO thin film was synthesized and characterized in the present study. A new CTL-based gas sensor using MgO thin film for the detection of ethylene glycol ethers vapors was developed. MgO thin film exhibited the highest sensitivity of EE and EM and showed good analytical characters. To the best of our knowledge, EE and EM sensors have been reported in the present work firstly.

2. Materials and methods

2.1. Apparatus

The schematic diagram of the detection system was shown in Fig. 1. The catalyst was coated as a layer on the ceramic heating tubes which were coated with nano-size gold. The 5 mm in diameter ceramic heating tube was put into a 12 mm inner-diameter quartz tube. The temperature of the catalysts could be adjusted by controlling the voltage of the heating tube. The air from the pump was mixed with detecting vapor and flowed through the quartz tube, a catalytic reaction occurred on the surface of catalysts. The CTL intensity was measured by a BPCL Ultra Weak Chemiluminescence Analyzer (Biophysics Institute of Chinese Academy of Science, PR China).

2.2. Synthesis and characterization of thin film materials

All regents were of analytical grade. Indium chloride ($InCl_3{\cdot}4H_2O$) was obtained from Reagent No. 1 Factory of Shanghai Chemical Reagent Co., Ltd. Magnesium chloride ($MgCl_2{\cdot}6H_2O$), sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$), polyethylene glycol (PEG-6000), zirconium nitrate ($Zr(NO_3)_4{\cdot}3H_2O$), and oxalic acid were purchased from Tianjin Damao Chemical regent Factory.

In_2O_3, MgO and ZrO_2 were prepared by sol–gel method. (1) In_2O_3 precursor was synthesized as follows: 0.65 g $InCl_3{\cdot}4H_2O$ and 1.0 g PEG-2000 were dissolved in 30 mL distilled water with vigorous stirring for 30 min. Then 10% ammonia solution was added until a white precipitate of $In(OH)_3$ was formed, further addition of ammonia solution resulted in dissolving of the precipitate until pH value reached 5. Then stirred for another 1 h. (2) MgO precursor was synthesized as follows: 2.5 g $MgCl_2{\cdot}6H_2O$ and 2.5 g PEG-6000 were dissolved in 50 mL distilled water with vigorous stirring for 20 min, NaOH solution was added into the mixture until pH value reached 12. Keep on stirring for 1 h. (3) ZrO_2 precursor was synthesized as the above method, the molar ratio of zirconium nitrate to oxalic acid was 4.5:1.

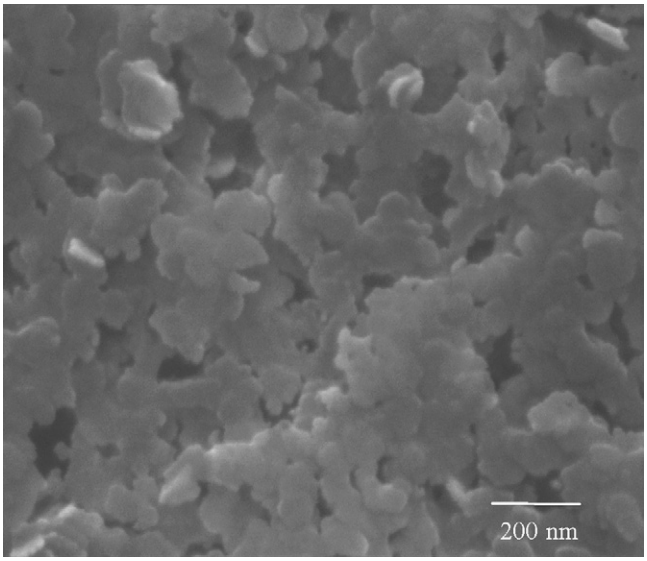

Fig. 2. TFE-SEM photo of MgO thin film.

Fabrication of the thin films: Ceramic heating tubes which were coated with gold were used as the solid substrate for film growth. The substrates were washed with hydrochloric acid, ethanol, and distilled water in sequence and dried in oven at last. Thin film systems were prepared by using the dip coating method from each colloidal and sol–gel solution. MgO thin films were synthesized in the following way: The ceramic substrates were immersed into the MgO precursor solution for five times, dried at 80 °C for 1 h and decomposed to MgO when calcined at 450 °C for 1 h. Other films such as In_2O_3 and ZrO_2 were synthesized following the same method.

MgO film produced in the present work was characterized for its surface morphology and chemical composition. The microstructure of the film was investigated by Quanta 400 thermal field emission environment scanning electron microscope (TFE-SEM). Specimens were observed at accelerating voltages <20 kV. Fig. 2 showed the surface morphology of the film. The thickness of the film was measured by dektak 150 surface profiler (Veeco Instruments Inc.). Subsequently, chemical compositions of the annealed films were determined using the X-ray photoelectron spectroscopy (XPS, model: ESCALAB 250; manufacturer: Thermo Fisher Scientific). XPS analysis was using a Mono Al Kα (1486.6 eV), X-ray source operating at 150 W. The vacuum of the analysis chamber was better than 2×10^{-9} mbar. All spectra were acquired at a fixed analyzer energy mode. Pass energy of 150 eV was applied to wide scans,

Table 1
Chemical composition of the MgO thin film surface.

Name	Peak BE (eV)	FWHM (eV)	Atomic percent (%)
C 1s	284.75	1.83	31.53
O 1s	532.52	2.75	44.84
Mg 1s	1305.89	2.92	18.36
Cl 2p	199.71	2.59	1.61
F 1s	685.95	2.12	0.99
Na 1s	1073.97	3.98	2.66