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A novel gaseous ester sensor utilizing chemiluminescence on nano-sized SiO_2

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Abstract

A gaseous sensor for ester vapors has been developed based on their chemiluminescence (CL) on the surface of nano-sized SiO_2 in an airflow. The luminescence characteristics and the optimal conditions for the determination of ethyl acetate by the sensor are investigated. Under the optimized conditions, the linear range of the CL intensity versus the concentration of ethyl acetate vapor is 20–300 ppm with a limit of detection of 3.0 ppm (3σ) and a relative standard deviation (R.S.D.) of 1.80% for eight times determination of 300 ppm ethyl acetate. There is no response or weak response when foreign substances including ethanol, methanol, hexane, cyclohexane, benzene and toluene pass through the sensor. However, acetone shows a little response which interferes slightly in the measurement of ethyl acetate. The sensor exhibits good stability and durability after 100 h reaction with 300 ppm ethyl acetate. The possible mechanism of CL from the oxidation of ethyl acetate on SiO_2 is discussed based on the CL spectra and the GC–MS chromatogram of reaction products.

Keywords: Chemiluminescence; Gas sensor; Nano-sized SiO_2; Ester; Ethyl acetate

1. Introduction

Chemiluminescence (CL) produced on solid surfaces is an interesting phenomenon, which has been observed during various catalytic reactions [1,2]. Recently, the expanding availability of nanomaterials has received much attention in CL of nanoparticles such as quantum dots and colloidal gold [3,4]. We have extensively studied the CL characteristics of many analytes on nano-sized ZrO_2, Al_2O_3, Y_2O_3, TiO_2, Fe_2O_3, etc. and developed a series of sensors for measuring alcohols, amines, thiols, and other compounds [5–10]. The materials are not limited to these traditional catalysts. Even those which are not commonly thought of as catalysts, such as MgO and $SrCO_3$, have intensive CL emission when their size decreases to nanoscale [10]. In addition, the morphological and structural differences of the catalytic nanomaterials can lead to different CL responses [11]. The most appealing advantages of these types of CL sensors are their long stability, high selectivity, fast response to analytes and relatively simple design.

SiO_2 is the most abundant substance on earth and is important in diverse applications such as catalysis, amorphous material, environmental science, bio-compatibility material and electronic device physics. It has been widely used as a carrier for metal oxide catalysts [12]. It is seldom documented, however, that SiO_2 itself is used as a catalyst for oxidation reactions in the scientific literature except for in the partial oxidation of methane [13]. Although a number of papers have studied the CL of alcohols, aldehydes, ketones, hydrocarbons, thiols and amines on various catalytic nanomaterials, CL on nano-sized SiO_2 has not been reported.

Volatile organic compounds (VOCs) are common pollutants produced by a variety of industries and their emissions are facing increasingly stringent environmental regulations. Ethyl acetate is one of the most widely used solvents for chemical intermediates (oils, gums and resins) or additive flavors in cigarettes, wines, beverages, foods and perfumes. Although ethyl acetate is generally regarded to be relatively nontoxic and not irritating, some studies have revealed that it is toxic at higher concentra-

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tions. A research also has reported that chronic overexposure may cause anemia with leukocytosis (transient increase in the white blood cell count) and damage to the liver and kidneys [14]. Several methods have been developed for the determination of ethyl acetate. Most of them are based on UV and GC or GC–MS [15], which are complicated, time consuming and more expensive.

In the present work, CL emission was observed when ester vapors passed through the surface of nano-sized SiO_2. A gaseous sensor for esters was developed based on this phenomenon. Optimal parameters for the determination of ethyl acetate by the sensor were investigated. In addition, the possible mechanism of CL from the catalytic oxidation of ethyl acetate on SiO_2 was studied.

2. Experiments

2.1. Apparatus and reagents

The apparatus for investigating the ester sensor is the same as reported previously [5]. Briefly, the sensor was made by depositing SiO_2 with a thickness of about 0.5 mm on a cylindrical ceramic heater of 3 mm in diameter. It was inserted into a quartz tube with an internal diameter of 12 mm. A voltage of 130 V is applied to the heater to keep the temperature of the sensor at 200 °C. The samples were injected into airflow by a sampling vessel and driven to the sensor by an air pump. The CL intensity at selected wavelengths was monitored by the photomultiplier tube (PMT) of a BPCL Ultra-Weak Luminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, China) through the optical filters. All the CL intensity data was obtained based on the peak height of the CL signals.

To study the possible mechanism of the chemiluminescence, an HP 6890/5973 GC–MS (Agilent Co., Ltd.) was used to identify the products of the catalytic reaction.

The sample vapor was prepared by evaporating liquid ethyl acetate (Beijing Chemical Company) in a sampling bottle at about 100 °C. All the reagents used were of analytical reagent grade.

2.2. Synthesis and characterization of SiO_2 nanoparticles

A simple wet chemical method was used to synthesize the SiO_2 nanoparticles. Briefly, a 0.1 M solution of HCl was slowly added to a 0.1 M solution of Na_2SiO_3 (Beijing Chemical Company) in a 50 °C water bath with continual stirring. The white precipitate was filtered and then washed seven times with deionized water. The precursor was dried at 80 °C and calcined at 300 °C in a muffle furnace for 1 h. The topography and particle size of SiO_2 were measured by using a Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of the electron beam was 200 kV. Fig. 1 shows that the SiO_2 is non-crystalline and the grain size ranges in 60–100 nm.

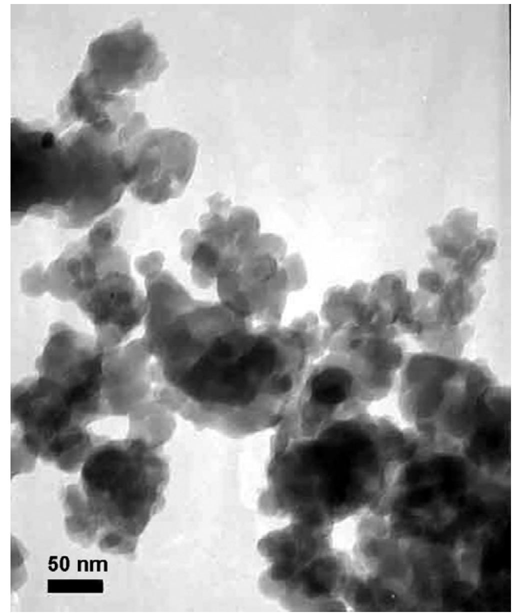

Fig. 1. A TEM photo of nano-sized SiO_2.

3. Results and discussion

In the preliminary experiment, we investigated the CL emission of various vapors on the surface of nano-sized SiO_2. Seventeen compounds including esters, fatty acids and commonly used organic solvents were tested. Table 1 shows the relative CL intensities of various vapors with the same concentration. From Table 1, it can be seen that esters have a stronger CL intensity than other compounds. Therefore, a SiO_2-based gas sensor for esters was developed by using ethyl acetate as a model analyte.

Table 1
The CL intensities of different compounds with the same concentration of 900 ppm (Conditions: wavelength, 460 nm; temperature, 200 °C; flow rate, 200 mL min^{-1})

Compounds	Relative CL intensity ($\times 10^4$)
Esters	
Ethyl acetate	1.71
Ethyl propionate	15.58
Ethyl-*n*-butyrate	5.53
Butyl acetate	0.925
Ethyl-*n*-valerate	1.525
Benzyl benzoate	0
Fatty acids	
Formic acid	0.826
Acetic acid	1.456
Propionic acid	13.24
Butyric acid	3.25
Solvents	
Ethanol	0.05
Methanol	0
Cyclohexane	0
Hexane	0.2
Benzene	0
Toluene	0
Acetone	0.32