Development of cataluminescence sensor system for benzene and toluene determination

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ABSTRACT

A novel and sensitive gas sensor was proposed for the determination of benzene and toluene based on its cataluminescence (CTL) by oxidation in the air on the surface of coral-like TiO_2/SnO_2 nanoparticles. The scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were employed to characterize the as-prepared samples. The luminescence characteristics and the optimal conditions were investigated in detail under the optimized conditions. In gas-sensing measurements, benzene and toluene were employed as target analytes. The results show that the gas sensor based on the TiO_2/SnO_2 nanostructures exhibited outstanding cataluminescence (CTL) properties such as stable intensity, high signal/noise values, short response and remarkably improved sensitivity compared with pure SnO_2 nanostructures. Additionally, a principal component analysis method was used to investigate the recognizable ability of the presented CTL sensor, it is found that benzene and toluene can be distinguished clearly. The fascinating gas-sensing properties including enhanced sensitivity, selectivity, stability and recognizable ability enable the presented TiO_2/SnO_2 nanocomposites to be a promising candidate for fabricating cataluminescence (CTL) gas sensor which can be applied for detecting environmental gas contaminants. The mechanism for the improved performance was also discussed based on the experimental results.

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1. Introduction

Volatile organic compounds (VOCs) are ubiquitous in the air we breath which can cause short- or long-term adverse health effects [1]. Exposure to VOCs may cause serious effects, such as a wide range of sensory irritation and acute or chronic diseases. The detection and identification of VOCs is one of the most serious subjects in the field of chemical sensing, but it remains an enormous challenge. Benzene and toluene are typical volatile organic compounds which are seriously harmful to our health. Besides, desorption of them and their mid-products (such as some small organic species) formed during gas-sensing process is difficult, resulting in great difficulty to develop long-term stable gas sensors of them [2–4]. The increasing demand of benzene and toluene in industry leads to polluting environment via gaseous and aqueous wastes. Therefore, an excellent selective determination method for benzene and toluene vapor is eagerly demanded.

Various methods have been established for the determination of benzene and toluene, such as gas chromatography [5,6], spectrophotometry [7,8], and high performance liquid chromatography [9,10]. Although these techniques are powerful and sensitive for trace benzene and toluene determination, they also have some inherent disadvantages for real-time monitoring in the actual local of the contamination. In addition, the long response time and nonlinear response detection limit of those sensors limited their practical application greatly [11]. In view of this situation, there is an intense demand for simple, portable sensor for the determination of benzene and toluene at very low concentration levels.

Currently, cataluminescence (CTL)-based sensors showed significant advantages such as stability and durable intensity, high signal/noise (S/N) ratio, and rapid response. Furthermore, there is nearly no consumption of analytes during the detection process [12]. The concept of "cataluminescence" was firstly reported by Breysse and his co-worker and they observed that the catalytic oxidation of carbon monoxide on surface of thoria could produce a weak chemiluminescence (CL) emission [13]. Persistent efforts have been made for many years to develop the CTL analytical method for the detection of VOCs such as acetaldehyde [14], benzaldehyde [15], formaldehyde [16], ethanol [17], ether [18] and

acetone [19]. As nanomaterials are one of the most important facts for constructing CTL-based sensor, many efforts have been devoted to synthesize decorated materials with excellent CTL performance. The secondary material deposited on the original material may enhance the total porosity and surface area, which may provide additional sites for the interaction with gas. For example, Xia et al. [20] have explored nano/micro CuO/ZnO which were used as catalyst material for determination of acetic acid. Guo et al. [21] have used cocoon-like Au/La_2O_3 nanomaterials as the sensing material to detect the CTL performance of VOCs.

In the current work, SnO_2 nanostructures with dense TiO_2 nanoparticles were successfully synthesized which would improve the contact opportunity with gas analytes. The cataluminescence phenomenon of benzene and toluene based on these nanomaterials was also investigated. Strong CTL emission could be observed when benzene and toluene vapor passed through the surface of nanosized TiO_2/SnO_2 nanoparticles in the air. Moreover, the performance of the sensor such as sensitivity, selectivity and stability, has been investigated in detail. The study showed that the CTL gas sensor presented here would be a potential candidate for detecting benzene and toluene with excellent performance. The as-prepared coral-like nanoparticles as sensing materials showed an excellent specificity toward benzene and toluene by testing the other ten kinds of common possible VOCs. The mechanism of the enhancement of CTL properties was also discussed based on the experimental results. In addition, a principal component analysis (PCA) method was employed to investigate the recognizable ability of the CTL-based sensor.

2. Experiment

2.1. Chemical reagents and materials

All chemicals (benzene, diethyl ether, butanone, methanol, propanol, formaldehyde, xylene, ammonia, toluene, acetaldehyde) used in the experiment had the high purity ($\geq$99.0%) of analytical grade or even higher grade and were purchased from Shanghai Chemical Reagents Company. Thus they could be used in our experiment without further purification.

2.2. The preparation of TiO_2/SnO_2 nanocomposites

The coral-like SnO_2/carbonaceous precursors were synthesized through a hydrothermal method, as reported previously [22]. Firstly, 10 mmol $SnCl_4 \cdot 5H_2O$ and 20 mmol sucrose were dissolved into deionized water to form a 35 mL solution by constant stirring. Secondly, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed and heated in an oven at 170 °C for 6 h. Thirdly, after the reaction was completed, the brown precipitates were collected by centrifugation and washed for several times with ethanol and de-ionized water alternately. Finally, they were dried in a vacuum oven at 60 °C for 6 h.

The as-prepared SnO_2/carbonaceous precursors were treated by an inductively coupled plasma (ICP) apparatus, which consisted of a three-neck glass bottle and several cycles of copper wire wrapped around the glass bottle. The inside diameter and length of the bottle are 5 and 20 cm, respectively. The radio frequency (RF) power at a frequency of 13.5 MHz was fed to the copper wire. In the plasma treatment, 2 g SnO_2/carbonaceous precursors were put into the flask and evacuated to ca. 10 Pa. The system was flushed with argon gas flow, and then evacuated back to 10 Pa. After three times of flushing and evacuating processes, the SnO_2/carbonaceous precursors were treated by argon/oxygen plasma at a flow ratio of 5:1

under constant stirring for 30 min. After that, the plasma-treated samples were dried in a vacuum oven at 60 °C for further use.

As for the preparation of the TiO_2 nanoparticles-modified SnO_2 nanostructures, an adsorbing process followed by an annealing treatment were carried out. As for the preparation of the TiO_2/SnO_2 nanostructures, firstly, the plasma-treated SnO_2/carbonaceous precursors (0.2 g) were ultrasonically dispersed in 10 mL tetra-n-butyl titanate solution (0.1 M) which was obtained by dissolving a certain amount of $C_{16}H_{36}O_4Ti$ into ethanol. And then, the mixed solution was left for 24 h at room temperature statically. Secondly, after several cycles of washing and centrifugation, the samples were dried in an oven at 60 °C for 6 h. At last, the samples were annealed in a furnace under a program-controlled heating condition (from room temperature to 550 °C at a rate of 10 °C/min, and keeping at 550 °C for 1 h) in air surroundings. The pure SnO_2 were prepared through the same hydrothermal and annealing processes.

2.3. Characterization

The as-obtained samples were characterized by using a Philips X'Pert Pro X-ray diffractometer (XRD) with Cu Kα radiation (1.5418 Å), a FEI Sirion200 field emission scanning electronic microscopy (FESEM), and a JEOL JEM-2010 transmission electron microscopy (TEM) equipped with an Oxford INCA energy dispersive X-ray analysis at an accelerating voltage of 200 kV. The diffraction peaks of crystalline phases were compared with the patterns in the Joint Committee on Powder Diffraction Standards (JCPDS). The elemental mappings and the line scans were performed in the high-angle annular dark-field (HAADF) mode on the same TEM. The chemical composition was determined by an energy dispersive spectrometer (EDS).

2.4. Apparatus

The schematic diagram of the CTL detecting system is shown in Fig. 1. A heating rod smeared by nanomaterials was placed in a quartz tube with an inner diameter of 12 mm. A pump with a gas filter provided a steady air flow stream at a controlled flow rate. The pump could not only control the flow rate but also disperse the tested gas as soon as possible. The gas filter, which is a piece of filterable net, is installed inside the gas input port. The nanomaterials were dispersed in ethanol to form a suspension and laid on the heating rod to form a layer of the nanomaterials with the thickness of 0.5 mm. The work temperature could be adjusted by controlling the voltage of the quartz tube. When the organic vapors flowed through the tube, the catalytic reaction occurred on the surface of the nanomaterials. The CTL intensity was monitored by photomultiplier tube (PMT) of an Ultra-Weak Luminescence Analyzer.

3. Results and discussion

3.1. Morphology, structure and composition of nanostructures

The XRD patterns of the pure sample and the ones modified by TiO_2 are shown in Fig. 2. As shown in Fig. 2(A), all the diffraction peaks can be readily indexed to the rutile structure of SnO_2 with lattice constants of a = 0.4737 nm and c = 0.3186 nm, which are in good agreement with the values in literature (JCPDS no. 41-1445). Seen from Fig. 2(B), the anatase phase of TiO_2 can be observed (JCPDS no. 84-1285).

Fig. 3 shows the FESEM and TEM observations on the plasma-treated SnO_2/carbonaceous precursors, pure SnO_2, and TiO_2/SnO_2 nanostructures. As can be seen from the SnO_2/carbonaceous precursors (Fig. 3(a)), the morphology keeps a coral-like profile without destroying the structure. It should be indicated that the removal of carbonaceous components in the SnO_2/carbonaceous