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Toluene sensing properties of porous Pd-loaded flower-like SnO_2 microspheres

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ABSTRACT

Pd-loaded flower-like SnO_2 microspheres were synthesized by a solvothermal method. Various concentrations of Pd dopant (0 mol%, 0.5 mol%, 1.2 mol%, 2 mol% and 2.3 mol%) were added into precursors. The structure of SnO_2 was characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). The actual atomic ratios of Pd-to-Sn (as deduced from XPS data) are the same as the ratios of raw materials. And the O 1s binding energy of 1.2 mol% Pd–SnO_2 is the lowest in all tested samples. The SEM images show a flower-like microspheres composed of tiny nanoparticles structure of the materials. The sensors made of the Pd-loaded SnO_2 were tested at different operating temperatures to various gases. The sensors fabricated using 1.2 mol% Pd-loaded SnO_2 exhibited good toluene sensing properties at operating temperature 250 °C, and the minimum-detection-limit was down to 0.08 ppm. The sensor also exhibited better sensing characteristics for toluene as compared to other possible interference gases such as benzene, acetone, formaldehyde, ammonia. The sensing mechanisms of Pd-loaded SnO_2 to toluene were discussed.

1. Introduction

As one of the most dangerous indoor pollutants among volatile organic compounds (VOCs), toluene ($C_6H_5CH_3$) is harmful to human skin, mucous membrane and nervous system [1]. It is a kind of aromatous compound which possesses low olfactory threshold concentration, and the threshold limit value of toluene vapor indoor concentration is 0.05 ppm according to the indoor air quality standard (GB/T18883-2002, China) [2]. Toluene is widely used as diluents for varnishes, lacquers and enamels, also in adhesive & ink manufacturing and thinner formulations. Since it is closely to our daily lives, detection towards toluene has great significance for environmental safety and human health.

There are many methods for detecting indoor VOCs gases, semiconductor gas sensor is a popular and common method which is widely used since it is cheap and easy to use. Semiconductor sensing materials, such as SnO_2, ZnO, TiO_2, Cr_2O_3 and V_2O_5 [2–8] have been explored for toluene detection. Among the semiconductor oxides, SnO_2 is a typical n-type semiconductor with a wide band-gap of 3.6 eV at 300 K. It has been demonstrated as a good candidate for gas sensing material and widely studied for detecting many kinds of gases [2,9–27]. Doping some impurities into matrix materials is a useful and common method to improve the sensing performance. When other metals or metal oxides were doped into SnO_2, the sensitivity and selectivity of the doped SnO_2 materials got obvious enhancing for testing target gases [14,15,17,19–25]. Among various impurity materials, Pd (PdO) is one of the most used dopants. For instance, Mizsei and Yamazoe et al. [19,20] found that Pd-doped SnO_2 had response to H_2. Duh et al. [21] reported that Pd doped into SnO_2 ceramic could enhance the CO gas sensitivity and the response rate. Lee et al. [22] reported ethanol response of Pd-doped SnO_2 nanorods, and Vaishampayan et al. [23] found that Pd doping enhanced response of the sensors fabricated by SnO_2 nanospheres towards LPG. Formaldehyde of 0.03 ppm concentration detected by the 1 mol% Pd-doped SnO_2 micro-gas sensor was reported by Wang et al. [24]. Choi et al. [25] found that in the NO_2-sensing performance, the bimetallic Pd/Pt functionalized SnO_2 nanowires revealed faster response and recovery times.

Many experiment results indicated that the surface morphology and structure of the sensing materials were very important for gas sensitivities. Recent years, diverse morphologies of SnO_2 have been synthesized, such as nanocubes [2], nanorods [10], mesoporous

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and microporous structures [14,15], hollow nanospheres and hierarchical nanostructures [11,12]. The synthesis methods include hydrothermal synthesis [9,12,13,16], solvothermal method [11], CVD [10,22], electrospinning [15], sol–gel [24], spray pyrolysis technique [26], template-assisted method [27], and others.

In this work, we reported a simple and economically attractive route for the synthesis of porous flower-like SnO_2 hierarchical structures microspheres via a facile solvothermal method. In order to improve the toluene sensing performance, a certain amount of $PdCl_2$ was added into the reaction precursors. The toluene sensing properties of the Pd-loaded SnO_2 sensors were tested.

2. Experimental

2.1. Preparation Pd-loaded SnO_2

Porous flower-like Pd-loaded SnO_2 microspheres were synthesized by a solvothermal route. In a typical process, 1 mmol $SnCl_2{\cdot}2H_2O$ and different amount of $PdCl_2$ (the molar ratios were 0 mol%, 0.5 mol%, 1.2 mol%, 2 mol% and 2.3 mol%, respectively) were dissolved in 30 mL ethylene glycol under vigorous stirring, respectively. Subsequently, 3 mmol thiourea was added into each of above solutions with stirring for 1 h. Then the homogeneous solutions were transferred into 50 mL Teflon-lined stainless-steel autoclaves and the reaction system was maintained at 200 °C for 12 h. Then black precipitates were collected after the autoclaves naturally cooled to room temperature. The black powders were washed with absolute ethanol several times and then dried in air at 80 °C. Finally, Pd-loaded SnO_2 samples were obtained through calcining the precursors at 620 °C in air for 3 h. The color of the Pd-loaded SnO_2 samples changed from white to brown with the increase of loading concentration.

2.2. Material characterization

X-ray diffraction (XRD) analysis was characterized using Rigaku D/MAX-2400 (Japan) in 2θ region of 20–80° with Cu $K\alpha 1$ radiation. Field-emission scanning electron microscopy (FE-SEM) images were performed by FEI QUANTA 450 (America) with an accelerating voltage of 3 kV. The energy dispersive X-ray spectrometry (EDS) result was measured by the FE-SEM attachment. X-ray photoelectron spectroscopy (XPS) was carried out on a VG ESCALAB MK2 (UK), at a pressure lower than 2×10^{-8} Pa with a standard Al $K\alpha$ excitation source (1486.6 eV).

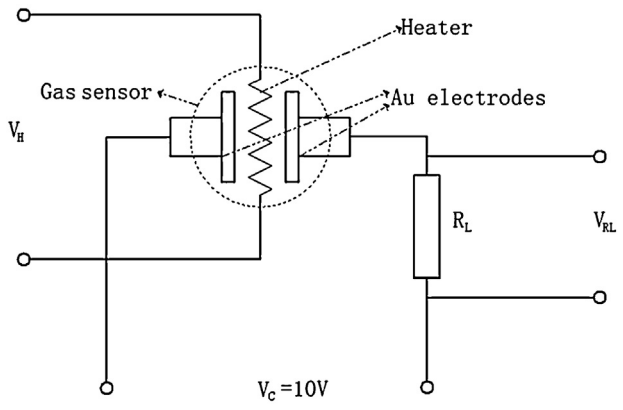

Fig. 1. The schematic circuit diagram of the test system.

2.3. Fabrication of gas sensors and measurements of sensing properties

The as-obtained materials were mixed with deionized water to form pastes. The pastes were coated on alumina ceramic tubes with a pair of Au electrodes previously printed. After the ceramic tubes were sintered at 500 °C for 1.5 h, a Ni–Cr alloy wire was placed through each tube as a heater of the gas sensor. In order to improve their stability and repeatability, the gas sensors were aged at an operating temperature 300 °C for 7 days in air. The sensing properties of the as-fabricated sensors were measured using a static test system. The schematic circuit diagram of the test system is shown in Fig. 1. The operating temperature of the sensor was controlled by a close loop circuit containing the heater. In the gas response measurement, a given amount of target gas was injected into the test chamber by a syringe through a rubber plug. The sensor response value (S) was defined as a ratio of the electrical resistance of the sensor in air (R_a) to that in target gas (R_g):

$$S = \frac{R_a}{R_g} = \frac{(V_C - V_{RL})/(V_{RL}/R_L)}{(V_C - V'_{RL})/(V'_{RL}/R_L)} = \frac{V'_{RL}(V_C - V_{RL})}{V_{RL}(V_C - V'_{RL})} \quad (1)$$

where R_L is the series resistance of the gas sensor, V_{RL} and V'_{RL} are the output voltages of R_L in air and in target gas, and V_C is the working voltage of loop containing the sensor and R_L.

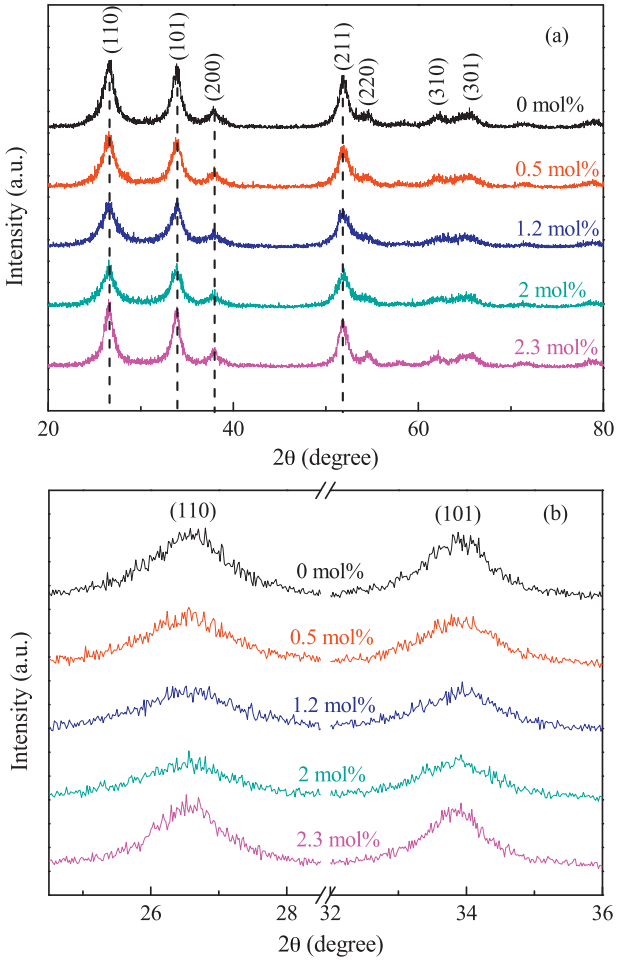

Fig. 2. XRD patterns of Pd-loaded SnO_2 with different loading concentration: (a) 2θ in the range of 20–80°, (b) the enlargement of (1 1 0) and (1 0 1) peaks.