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Highly sensitive and selective Gd_2O_3-doped SnO_2 ethanol sensors synthesized by a high temperature and pressure solvothermal method in a microreactor

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ABSTRACT

Gd_2O_3-doped SnO_2 nanoparticles as highly sensitive and selective ethanol sensor materials with uniform size distributions were synthesized in ethylene glycol at 250 °C and 20 bar in a continuous tubular microreactor. The samples were characterized by DLS, XRD, SEM, EDX, TEM, FTIR, and BET surface area measurement techniques. As 5 wt% Gd_2O_3 is added to SnO_2, the average particle and crystallite sizes of the samples decrease from 22 and 11.9 nm to 10 and 3.8 nm, respectively. The responses of Gd_2O_3-doped SnO_2 sensors containing 0–10.0 wt% Gd_2O_3 calcined at 450 °C were measured in presence of 300 ppm CO, 10–1000 ppm ethanol and 1.0 vol% of methane in air at 150–430 °C. The sensor containing 10 wt% Gd_2O_3 is highly sensitive and selective to ethanol in presence of CO, methane, and three volatile organic compounds, at 150 °C. At the same low temperature, as the Gd_2O_3 content of the sensor increases from 2.5 to 10%, its response to ethanol dramatically enhances by about 263 times and the resistance in air changes by more than 4 orders of magnitude. Relative humidities higher than 50% eliminate the 10% Gd_2O_3–SnO_2 sensor responses to CO and CH_4 and the sensor shows absolute selectivity to ethanol.

1. Introduction

Semiconducting metal-oxides such as SnO_2, ZnO, TiO_2, In_2O_3, WO_3, TeO_2, CuO, CdO, Fe_2O_3, and MoO_3 nanostructures are widely used for gas sensing applications [1]. SnO_2 is an appropriate choice for promising implementation in gas sensing, due to its high sensitivity, suitable chemical stability, and low cost. SnO_2 is an *n*-type semiconductor, which operates at typical working temperatures of about 200–450 °C. The main drawbacks associated with SnO_2 sensor is its unsatisfied selectivity and quite high operating temperature [2–4]. Different ways such as utilizing catalyst and promoters, control of operating temperature, and employing proper physical or chemical filters have been suggested to solve the SnO_2 low selectivity problem [5,6]. Doping SnO_2 with rare earth oxides such as Sm_2O_3 and CeO_2 makes the sensor more selective to a certain gas and reduces the sensor operating temperature with a lower power consumption [7,8].

On the other hand, gas-sensing properties of SnO_2 sensor are extremely dependent on its size, morphology, and texture. Therefore, over the past few years remarkable progress has been made in the synthesis of SnO_2 nanostructures [9–17]. However, most of the batch synthesis methods are complicated, time consuming, and uncontrollable for uniform size distribution of nanostructures and need templates, especial solvents, and/or additives. In recent years, researchers have focused on synthesizing nanostructured materials in microreactors, due to their advantages over controversial batch methods [18–21]. The advantages include precise control on size distribution of nanomaterials, considerable productivity, flexibility in changing the experimental condition or reagent compositions, and shortening the development time from laboratory to commercial production.

Ethanol sensors are widely used for various applications such as breathalyzers, wine making, medical processes, and food industries. In this study, for the first time, 0–10.0 wt% Gd_2O_3-doped SnO_2 was synthesized by a solvothermal method in a continuous flow microreactor. The Gd_2O_3-doped SnO_2 has dramatic sensitivity and

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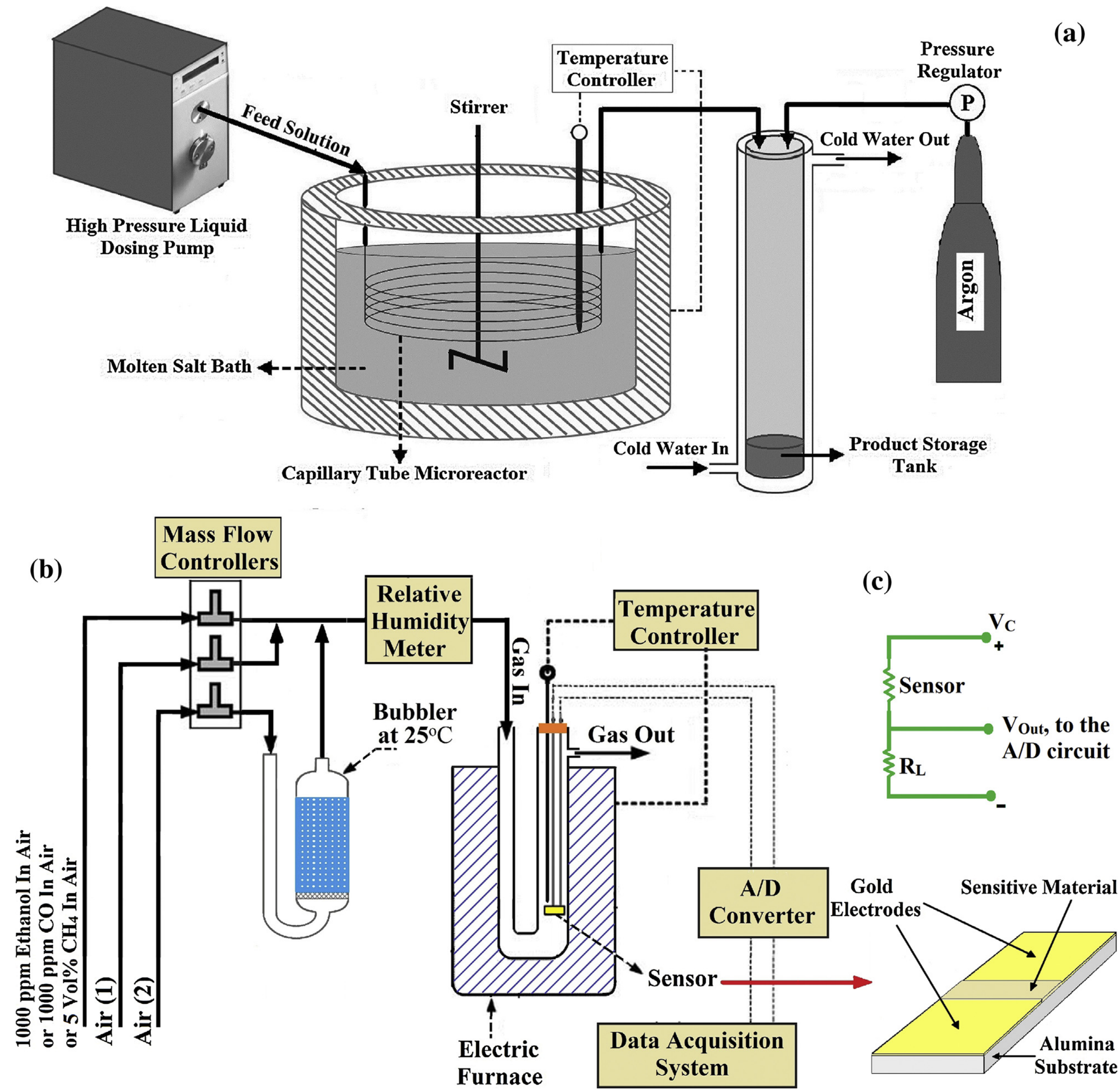

Fig. 1. Schematic illustrations of (a) the experimental setup used for synthesis of the Gd_2O_3-doped SnO_2 nanoparticles in a capillary tube microreactor by the high temperature and pressure solvothermal method, (b) the experimental setup used for measuring response of the sensors and the structure of sensor element, and (c) the electric circuit of sensing system.

selectivity to ethanol, in presence of CO, methane, and three volatile organic compounds (VOCs), at low temperatures.

2. Experimental

2.1. Synthesis of sensing materials

A high temperature solvothermal method was used to prepare pure and Gd_2O_3-doped SnO_2 nanoparticles in a microreactor through the following steps.

2.1.1. Preparation of the microreactor feed solution

Urea, anhydrous tin(IV) chloride ($SnCl_4$), and HCl were purchased from Merck. Gd_2O_3 was purchased from Sigma–Aldrich. Ethylene glycol (EG, Merck) was used as the solvent. 7.85 g urea was dissolved in 110 ml ethylene glycol, to which 13 ml of 1 M $SnCl_4$ in EG solution and 7 ml deionized water were added. For obtaining 2.50, 5.0, and 10.0 wt% Gd_2O_3-doped SnO_2; 0.05, 0.10, and 0.22 g Gd_2O_3 powder, respectively, was dissolved in 7.5 ml HCl-deionized water solution under vigorous stirring for 3 h and the solution was added to the previous solution. The concentration of $SnCl_4$, urea, and deionized water in the microreactor feed solution were 0.1, 1, and 3 M and that of Gd precursor was varied.

2.1.2. Formation of nanoparticles in the microreactor

Fig. 1a shows a schematic diagram of the microreactor experimental setup. The microreactor feed solution was introduced into a stainless steel capillary tube with an internal diameter of 0.8625 mm, immersed in a molten salt bath. An argon cylinder with a pressure regulator was used to adjust the microreactor pressure at 20 bar. A high-pressure liquid dosing pump (Eldex Optos) was employed to introduce the feed solution to the capillary tube