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Lanthanum oxide @ antimony-doped tin oxide with high gas sensitivity and selectivity towards ethanol vapor

Mengyun Wang[a,1], Lianfeng Zhu[a,1], Changyue Zhang[a], Guosheng Gai[b], Xuewen Ji[c], Baohua Li[a], Youwei Yao[a,*]

[a] Graduate School at Shenzhen, Tsinghua University, Shenzhen, Guangdong Province, 518055, P. R. China
[b] Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P.R. China
[c] Shenzhen Dovelet Sensors Technology Co., Ltd, 5 Qiongyu Road, Hi-Tech Park, Nanshan District, Shenzhen 518057, Guangdong, P.R. China

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ABSTRACT

An ethanol-sensing powder (La_2O_3@Sb-SnO_2), mixture composed of 1.00 wt.% La_2O_3 and 99.00 wt.% Sb-doped SnO_2 (Sb-SnO_2), was found to possess enhanced sensitivity towards ethanol: typically, for La_2O_3@Sb-SnO_2, the ratio of the response towards 1000 ppm ethanol vapor to that of 1000 ppm CO is 26.1 (60.0/2.3) under operating temperature of 250 °C; while for Sb-SnO_2, the ratio is only 4.5 (9.0/2.0). A suggestive mechanism on enhanced ethanol sensing is discussed.

1. Introduction

Metal oxides have been widely used for detecting reducing gases (toxic or flammable gases) [1]. As one of the most attractive gas-sensing materials, tin dioxide(SnO_2) embodies high chemical stability and sensitivity. Its resistivity would be reversely decreased when exposed to some reducing target-gas, resulting from: (i) decrease of Schottky barrier between contact grains [2,3]; (ii) increase of carrier density in bulk [4]. Unfortunately, surface of SnO_2 is able to simultaneously interact with different reducing target-gas, which results in poor gas-sensing selectivity. In order to solve this problem, catalysts such as noble metal dopants (Pt, Pd) have been adopted [5,6]. However, most results were obtained by the 'trial and error' method and no correlations between the dopants and selectivity were established.

Selective reactions happened on the gas–solid interface have been widely studied in the field of solid catalyst [7]. As classic concepts, acidity and basicity are very often adopted to explain the catalytic properties of metal oxide surfaces and design selective catalysts [8]. For instance, some metal oxides are able to selectively adsorb acid or basic gas molecules depending on their Brønsted or Lewis acidity. La_2O_3, with stable electron configurations containing as many as seven unpaired 4f electrons, may embody strongly basic. It has been reported that La_2O_3 was a selective catalyst for the reduction of acid NO_x to N_2 by CH_4 in excess of O_2 [9]. In study of IR spectroscopy, it was found that La_2O_3 prepared through calcinating $La(NO_3)_3{\cdot}6H_2O$ at 920 K for 2 h did not have proton-donor hydroxy groups (Brønsted acid sites) and hard to adsorb pyridine, a kind of strong base molecule[10]. Meanwhile, significant enhancement on sensitivity towards ethanol by mixing La_2O_3 with SnO_2 was reported [11–13]. For instance, La_2O_3 coated-SnO_2 nano-wire presents response of 57.3 towards 100 ppm of ethanol vapor at 400 °C, while that of un-coated SnO_2 nano-wire was 10.5 [12]. The response was defined as $S = R_a/R_g$, where R_a and R_g represented resistances of the sensors in air and target gas, respectively [12,14]. Another example is that a mixture composed of 5 wt.% La_2O_3 and 95 wt.% SnO_2 nano-rod exhibits high response of 312 towards 100 ppm of ethanol at low working temperature of 200 °C, while that of pure SnO_2 nano-rod is only 45.1[13]. Besides, some other sensitivity enhancements have been reported. Recently, a mixture of 5 wt.% Sm_2O_3 and 95% ZnO nano-flower has been reported, whose response is 60 times larger than that of pure ZnO at 300 °C. Especially this mixture shows no or little response towards methane, toluene and CO [15].

* Corresponding author. Tel.: +86 755 26036796; fax: +86 755 26036796.
E-mail addresses: yw_yao@yahoo.com, yaoyw@sz.tsinghua.edu.cn (Y. Yao).
[1] Mengyun Wang and Lianfeng Zhu contributed equally.

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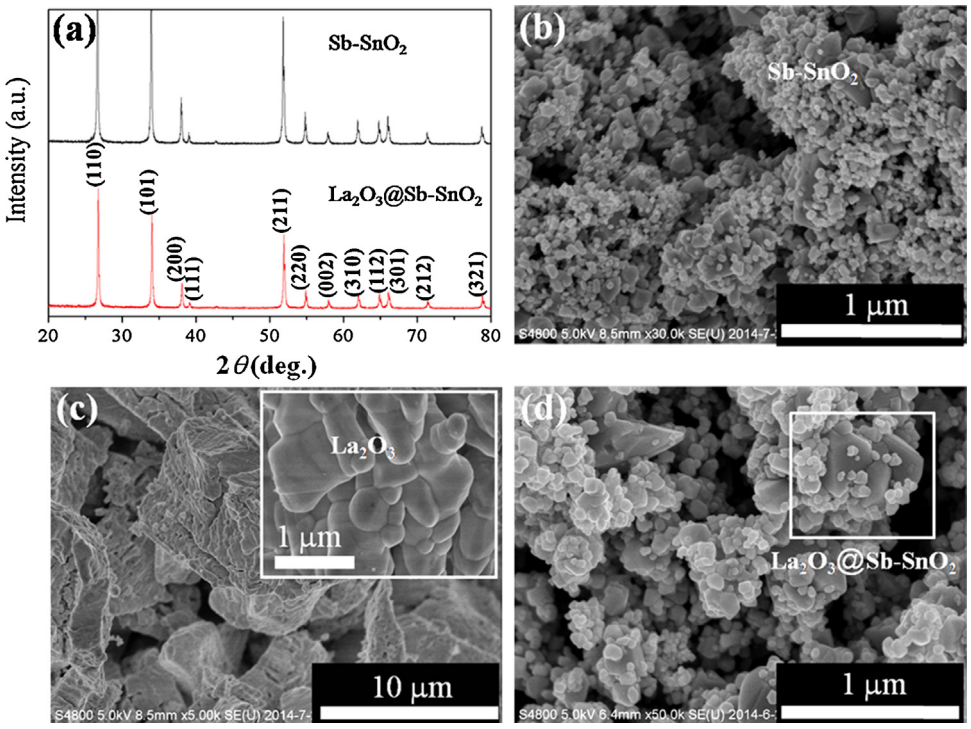

Fig. 1. (a) XRD patterns of Sb-SnO_2 and La_2O_3@Sb-SnO_2; SEM images of (b) Sb-SnO_2; (c) pristine La_2O_3; and (d) La_2O_3@Sb-SnO_2; the white box in (d) indicates a typical structure of La_2O_3@ Sb-SnO_2.

Previously, that mixtures composed of 5 wt.% La_2O_3 (basic) and 95 wt.% SnO_2; 5 wt.% WO_3 (acidic) and 95 wt.% SnO_2 embody significantly different catalytic activities is observed [16]. Namely, the former enhances dehydrogenation of ethanol gas to CH_3CHO and consecutive oxidation of CH_3CHO to CO_2 and the later enhance only the dehydration of ethanol. However, selectivity and sensitivity of mixtures composed of acidic and basic oxides towards different reducing target-gas are rarely reported [17–20], to our best knowledge. In this paper, the sensing enhancement of Sb-doped SnO_2 matrix powders towards ethanol gas by simply mixing with La_2O_3 is repeated, however, no enhancement towards another reducing gas, carbon monoxide, is observed.

2. Materials and methods

2.1. Preparation of SnO_2 matrix

Tin oxides suffer from poor electrical conductivity (10^{-7}–10^{-8} S cm^{-1} at 200 K) [21], which would caused undesired noise and false response during monitoring. To address this vital problem in real-time applications, we doped SnO_2 with Sb^{3+} to decrease the resistivity. The Sb-doped SnO_2 (Sb-SnO_2) nanoparticles were fabricated via co-precipitation in ethanol. The typical process of fabrication is as follows. Firstly, 28.00 g of $SnCl_4{\cdot}5H_2O$ (Sinopharm Chemical Reagent Co. Ltd) was dissolved in 120.0 mL of ethanol (Tianjin Zhi Yuan Reagent Co. Ltd). And 0.0230 g of antimony oxide (Sinopharm Chemical Reagent Co. Ltd) was dissolved in 2.0 ml concentrated hydrochloric acid (Sinopharm Chemical Reagent Co. Ltd). Secondly, the acid antimony solution was added dropwise into the stannic chloride solution under magnetic stirring at 25 °C for 20 min, followed by adding 1.0 ml of acetylacetone ($C_5H_8O_2$) (Sinopharm Chemical Reagent Co. Ltd) as chelating agent, the molar ratio of tin to antimony was 1000:1. Thirdly, excess aqueous ammonia (2 mol/L) (Guangzhou Chemical Reagent Factory) was added dropwise into the mixture of solution under intensive stirring until the value of pH reached 9.0. The resulting product was dried in oven at 80 °C for 24 h. The precursors were annealed in air at 600 °C for 4 h to produce nanocrystalline powders.

2.2. Gas-sensing characterization

Typical fabrication and structure of the sensor device can be found in our early work [22]. The Sb-SnO_2 powder or Sb-SnO_2 powder mixed with 1 wt.% of La_2O_3 (La_2O_3@Sb-SnO_2) was ground with water to form slurry. The La_2O_3 powder was analytical-grade reagent without further purification (Sinopharm Chemical Reagent Co. Ltd). The slurry was then covered onto a pair of gold electrodes fabricated on a piece of alumina substrates. On the backside of substrate, a heater formed by Ru_2O_3 was printed. The sensors were loaded inside a custom-built chamber with mixing fan, in which desired gas concentrations can be provided. Different concentrations of ethanol gas were provided by injecting accurate amount of ethanol (liquid) into the airtight chamber by microsyringe and then vaporised. According to Avogadro's law, vaporizing 1 M of C_2H_5OH in atmosphere generates 22.4 L of ethanol gas. The gas concentrations were determined by volume ratio of gasified ethanol to air in the chamber (volume of the chamber was 16 L). The sensor was mounted in the chamber with conducting wire leading out of the chamber. Bias voltage of 5.0 V was applied to the sensor. A multimeter with data acquisition module (Victor 86B) was used to collect the electrical current.

2.3. Characterization

X-ray diffraction (XRD) patterns were taken with a X-ray diffractometer (D/max 2500/PC, RIGAKU Corp.) using Cu K_a radiation (λ = 1.5406 Å). Radiation operated at 40 kV and 200 mA was applied. The surface morphologies of the powders were observed with a Hitachi Limited S-4800 scanning electron microscope (SEM).