Sensors and Actuators B 193 (2014) 669–678

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Fine-tuning the structure of cubic indium oxide and their ethanol-sensing properties

Fubo Gu, Li Zhang, Zhihua Wang*, Dongmei Han, Guangsheng Guo*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 12 August 2013
Received in revised form 29 October 2013
Accepted 6 December 2013
Available online 17 December 2013

Keywords:
Indium oxide
Sensor
Structure
Sensing mechanism
Ethanol

ABSTRACT

Fine-tuning the structure of cubic indium oxide (In_2O_3) was carried out with different calcination temperatures and atmospheres. The structural properties of the products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, electron paramagnetic resonance spectroscopy (EPR) and X-ray photoelectron spectroscopy (XPS). Ethanol-sensing performance of the products was investigated, and the depletion layer theory was used to explain the sensing mechanism. The experimental results indicated that the ethanol-sensing responses of In_2O_3 increased with the increasing intensity of chemisorbed oxygen, and decreased with the increasing intensity of donor defects. The In_2O_3 annealed at 300 °C or in oxygen had higher responses because of more chemisorbed oxygen. However, the In_2O_3 annealed at 600 °C or in nitrogen had lower responses due to more donor defects (V_o and In_i). In situ diffuse reflectance infrared spectroscopy (DRIFTS) study revealed that surface reduction and reconstruction of In_2O_3 happened at room temperature upon ethanol adsorption, which may lead our results contradicted previous reports.

1. Introduction

Indium oxide (In_2O_3) is an important n-type semiconductor with good gas-sensing properties, which makes it a promising candidate for detecting H_2S, CO, NO_2 and ethanol [1–4]. In recent years, lot of work had been focused on In_2O_3 nanomaterials, which exhibited remarkable gas-sensing performance because of their small size and large surface area. Currently, nanostructured design of In_2O_3 mainly focused on their shape, size, and elemental composition [5–8]. However, few studies concerned about enhancing gas-sensing properties by tuning the microstructure of In_2O_3.

Recently, improving the properties of metal oxides by tuning the microstructures, such as defects and the surface activity has attracted intensive attention [9,10]. Overbury et al. explored the nature of ceria nanocrystals with defined nanoshapes, including rod, cube, and octahedral. The experimental results indicated that although the three ceria nanoshapes were well-structured, they also contained defects on the surface and in the bulk that could have a profound effect during ceria catalysis [11]. Cheung et al. reported an approach to enhance the catalytic activity of ceria nanostructures through engineering high density of oxygen vacancy (V_o) defects [12]. Moreover, Kumar et al. found the intensity of defect could influence the photoluminescence property of In_2O_3 [13].

Herein, the In_2O_3 nanoparticles synthesized by a facile solvothermal method were treated at different calcination temperatures or in different calcination atmospheres to tune their microstructures. Meanwhile, ethanol was used as a probing molecule to study the sensing performance of the In_2O_3 sensors. The sensing mechanism was proposed and the response differences of the In_2O_3 sensors were explained. Finally, the ethanol adsorption behavior and the structure change of In_2O_3 were investigated by in situ diffuse reflectance infrared spectroscopy (DRIFTS).

2. Experimental

2.1. Synthesis of In_2O_3 nanoparticles

All chemicals ($In(NO_3)_3$, ethanol, diethylene glycol (DEG) and $CO(NH_2)_2$) used in experimentations were analytical reagents and used without purification. Distilled water was used throughout the experiments.

The synthesis of In_2O_3 was carried out according to the previously reported procedure [14]. In a typical procedure, 2 mmol $In(NO_3)_3$ and 2 g $CO(NH_2)_2$ were added to the mixture of 35 mL DEG and 2 mL distilled water. The obtained solution was stirred for 3 h. Then the mixture was transferred into a Teflon-lined stainless-steel autoclave and maintained at 200 °C for 24 h. In_2O_3 powder was collected from the autoclave, and centrifuged and washed

* Corresponding author. Tel.: +86 10 64445927.
E-mail addresses: zhwang@mail.buct.edu.cn (Z. Wang), guogs@mail.buct.edu.cn (G. Guo).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.12.026

several times with ethanol and distilled water. Then, the products were dried by using a vacuum oven at 60 °C. The as-formed In_2O_3 nanoparticles were annealed at 300 °C, 400 °C, 500 °C and 600 °C for 3 h in air, and the obtained samples were denoted as IO300, IO400, IO500 and IO600, respectively. In addition, the In_2O_3 nanoparticles were annealed in different atmospheres (O_2, N_2 and Air) with 30-standard-cubic-centimeter-per-minute (SCCM) gas flow, and the obtained samples were denoted as IO-O_2, IO-N_2 and IO-Air, respectively.

2.2. Material characterizations

The In_2O_3 samples were characterized by X-ray diffraction (XRD) with a scanning speed of 10 °/min, on a Rigaku D/Max2500VB2+/PC diffractometer using graphite monochromatized Cu Kα radiation (λ = 1.54056 Å). The morphologies of the products were characterized by transmission electron microscopy (TEM, Hitachi-800). Raman spectroscopy was recorded from 200 nm to 800 nm by a 514 nm excitation (Invia Raman Spectrometer manufactured by U.K. Renishaw Corporation). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Scientific ESCALAB 250 spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded by using a Bruker EMX spectrometer operating at room temperature with a frequency of 9.853 GHz. The center field of the EPR scans was 3510G with a sweep width of 1500G. Specific surface area of the samples was measured by nitrogen adsorption (BET analysis, Micromeritics ASAP 2010).

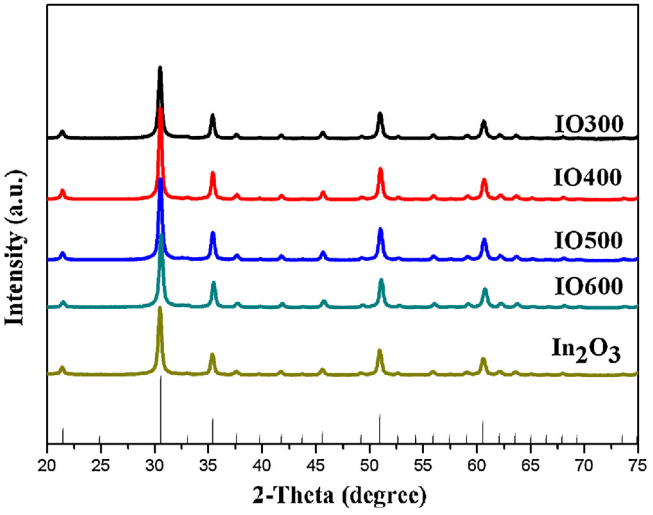

Fig. 1. XRD patterns of the as-formed In_2O_3 and the In_2O_3 annealed at different temperatures.

DRIFTS spectra were collected using a BRUKER VERTEX 70 spectrometer. The In_2O_3 sample (~300 mg) was pretreated in He flow (20 mL/min) at 300 °C for 1 h (heating rate 10 °C/min) and then

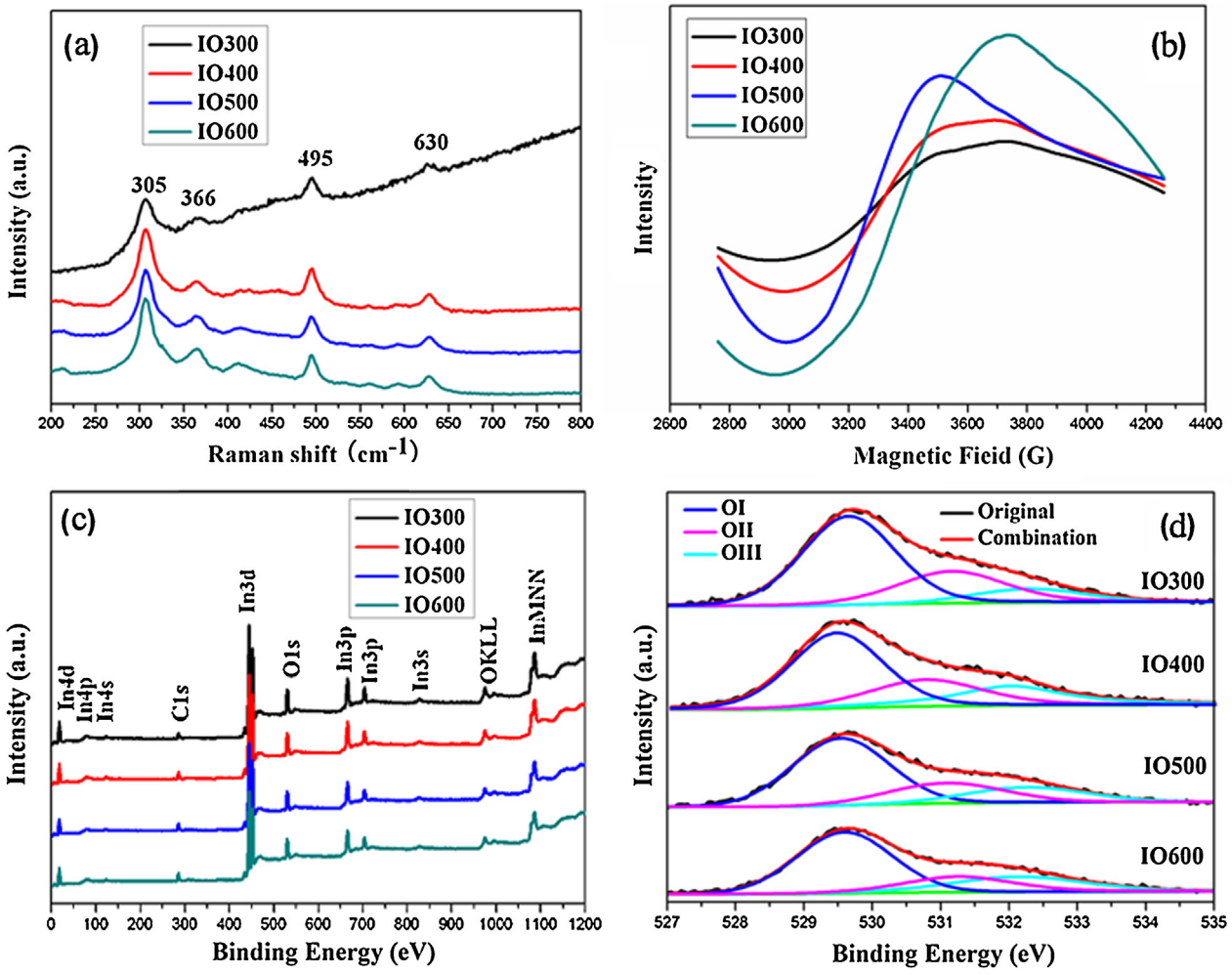

Fig. 2. Raman (a), EPR (b), XPS (c) and high-resolution O1s (d) spectra of In_2O_3 nanoparticles treated at different temperatures.