Journal of Hazardous Materials 305 (2016) 130–138

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

CO gas sensing properties of $In_4Sn_3O_{12}$ and TeO_2 composite nanoparticle sensors

Ali Mirzaei [a], Sunghoon Park [b], Gun-Joo Sun [b], Hyejoon Kheel [b], Chongmu Lee [b,*]

[a] Department of Materials Science and Engineering, Shiraz University, Shiraz, Iran
[b] Department of Materials Science and Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea

HIGHLIGHTS

- In4Sn3O12–TeO2 composite nanoparticles were synthesized via a facile hydrothermal route.
- The response of the In4Sn3O12–TeO2 composite sensor to CO was stronger than the pristine In4Sn3O12 sensor.
- The response of the In4Sn3O12–TeO2 composite sensor to CO was faster than the pristine In4Sn3O12 sensor.
- The improved sensing performance of the In4Sn3O12–TeO2 nanocomposite sensor is discussed in detail.
- The In4Sn3O12-based nanoparticle sensors showed selectivity to CO over NH3, HCHO and H2.

ARTICLE INFO

Article history:
Received 3 September 2015
Received in revised form 26 October 2015
Accepted 21 November 2015
Available online 30 November 2015

Keywords:
Gas sensor
$In_4Sn_3O_{12}$ nanoparticles
TeO_2 nanoparticles
CO gas

ABSTRACT

A simple hydrothermal route was used to synthesize $In_4Sn_3O_{12}$ nanoparticles and $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles, with $In(C_2H_3O_2)_3$, $SnCl_4$, and $TeCl_4$ as the starting materials. The structure and morphology of the synthesized nanoparticles were examined by X-ray diffraction and scanning electron microscopy (SEM), respectively. The gas-sensing properties of the pure and composite nanoparticles toward CO gas were examined at different concentrations (5–100 ppm) of CO gas at different temperatures (100–300 °C). SEM observation revealed that the composite nanoparticles had a uniform shape and size. The sensor based on the $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles showed stronger response to CO than its pure $In_4Sn_3O_{12}$ counterpart. The response of the $In_4Sn_3O_{12}$–TeO_2 composite-nanoparticle sensor to 100 ppm of CO at 200 °C was 10.21, whereas the maximum response of the $In_4Sn_3O_{12}$ nanoparticle sensor was 2.78 under the same conditions. Furthermore, the response time of the composite sensor was 19.73 s under these conditions, which is less than one-third of that of the $In_4Sn_3O_{12}$ sensor. The improved sensing performance of the $In_4Sn_3O_{12}$–TeO_2 nanocomposite sensor is attributed to the enhanced modulation of the potential barrier height at the $In_4Sn_3O_{12}$–TeO_2 interface, the stronger oxygen adsorption of p-type TeO_2, and the formation of preferential adsorption sites.

1. Introduction

Carbon monoxide (CO) is a colorless, tasteless, and odorless gas that is notorious as an invisible silent killer [1]. It is highly toxic, and it induces acute toxic symptoms such as headache, tachypnea, nausea, dizziness, weakness, irritability, confusion, depression, hallucination, loss of muscular control, and an increase followed by a decrease in the pulse and respiratory rates. Death is likely at high concentrations. Indeed, exposure to 5000 ppm of CO for 10 min is lethal to humans [2,3]. CO is the leading cause of poisoning in the United States, and it may account for more than 50% of fatal poisonings reported in many industrialized countries [4]. The gas is produced mainly by incomplete combustion of organic materials. The risk of exposure to this gas arises from oil or gas burners that are improperly adjusted, e.g. from a burning stove, burning wood, or candles in a closed room [2,3]. This has stimulated considerable interest for scientific research on the development of simple and inexpensive sensors for the detection of low concentrations of CO gas. Today, considerable efforts have been devoted to the synthesis of novel sensing materials with high sensitivity toward CO gas [5–7].

Abbreviations: ITO, indium-tin oxide; SEM, scanning electron microscopy; XRD, X-ray diffraction.

* Corresponding author. Fax: +82 328625546.
E-mail addresses: cmlee@inha.ac.kr, kjmu7164@gmail.com (C. Lee).

http://dx.doi.org/10.1016/j.jhazmat.2015.11.044
0304-3894/

Metal-oxide-based sensors have been widely investigated in the past few decades to detect more than 150 toxic gases [8]. They are selected because of their low cost and power consumption, ease of fabrication and use, high sensitivity, stability in harsh environments, etc. [9]. Some composite oxides such as In_2O_3–ZnO [10], In_2O_3–SnO_2 [11], and Fe_2O_3–In_2O_3 [12] exhibit resistive responses to CO gas. On the other hand, further efforts will be necessary to explore new composite materials with higher CO-gas-sensing ability.

Indium tin oxide (ITO)-based gas sensors with high electrical conductivity and optical transparency have been used for the detection of diverse gases such as H_2, CO, CH_3OH, NH_3, HCHO, and NO_2 [13]. The gas sensing properties of In_2O_3, alone and in combination with Sn, were thoroughly investigated and the best results were obtained for the detection of oxidizing gases [14]. Indium-tin-oxide (ITO) obtained by doping Sn into the In_2O_3 lattice for increasing the conductivity is widely used as a transparent conductor. Owing to the increased technological demand and the escalating cost of indium, the development and optimization of new In_2O_3-based materials for gas sensing applications is a challenge in the gas sensor industry. In this regard, several In_2O_3-based, multi-component oxides have emerged with potential suitability for specialized applications. When the concentration of Sn is increased further than a concentration of 10% SnO_2 segregates. At temperatures above 1600 K it is possible to obtain a new phase $In_4Sn_3O_{12}$ which segregates into ITO and SnO_2 under equilibrium conditions when the temperature decreases [15]. In 2012, Kemmler et al. reported the synthesis of nanocrystalline $In_4Sn_3O_{12}$ which is a high temperature phase of the binary In2O3–SnO2 mixture using flame spray pyrolysis (FSP). $In_4Sn_3O_{12}$, a ternary compound in the In_2O_3–SnO_2 system is a promising material that has a significantly lower indium content than ITO but still exhibits a high performance [16,17]. This phase showed an increased sensitivity to formaldehyde compared to commercially available sensors. For the case of pure $In_4Sn_3O_{12}$ they could double the response of the sensors to 10 ppb HCHO in humid air.

On the other hand, TeO_2 is a p-type semiconductor that has been used as a gas sensor at room temperature [18]. Siciliano et al. used sputtered TeO_2 thin films for room-temperature detection of NO_2 gas and reported that their sensing performances was inadequate (response of ~1.2 for 100 ppm of NO_2 and 1.5 for 500 ppm of NO_2) [19]. Because the formation of heterostructures, in particular, p–n heterostructures is widely accepted as a strategy to enhance the sensing performance of nanostructured gas sensors and both $In_4Sn_3O_{12}$ and TeO_2 nanoparticles show strong responses at low operating temperatures, sensors based on $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles are expected to exhibit high gas-sensing performance in the detection of CO gas. Although the HCHO-sensing properties of $In_4Sn_3O_{12}$ have been reported [20], to the best of the authors' knowledge, no studies on the $In_4Sn_3O_{12}$-based heterostructures for gas-sensing applications have reported up to now. In the present work, a novel gas-sensor structure comprising $In_4Sn_3O_{12}$ and TeO_2 nanoparticles was developed. The nanoparticles were synthesized by a hydrothermal method, and their CO-gas-sensing properties were examined. The $In_4Sn_3O_{12}$–TeO_2 composite-nanoparticle sensor exhibited sensing performance (higher and faster response) that was superior to that of its pure $In_4Sn_3O_{12}$ counterpart. The synthesis, characterization, and CO-gas-sensing properties of pure $In_4Sn_3O_{12}$ nanoparticles and $In_4Sn_3O_{12}$–TeO_2 composite nanoparticle are reported here.

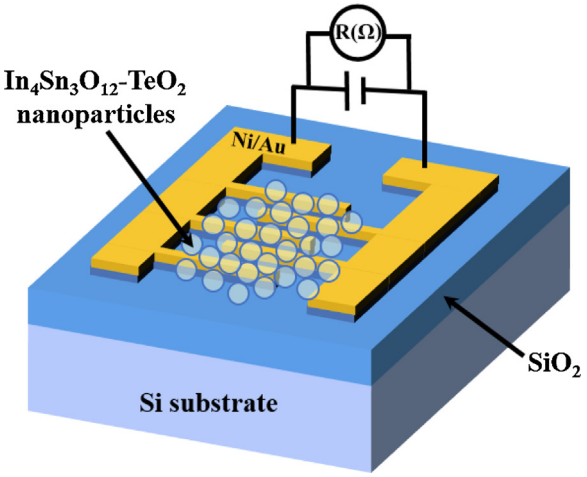

Fig. 1. Schematic of the structure of the multiple-networked nanoparticle sensor.

2. Experimental procedure

2.1. Chemical reagent

Indium acetate ($(In(C_2H_3O_2)_3$, 99%), sodium hydroxide (NaOH, 99%), tin chloride ($SnCl_4$, 99%), and tellurium chloride ($TeCl_4$, 99%) were purchased from Sigma–Aldrich. All chemicals were of analytical reagent grade and used as received.

2.2. Synthesis of $In_4Sn_3O_{12}$ nanoparticles and $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles

To prepare a 30-mM $In(C_2H_3O_2)_3$ solution, the appropriate amounts of indium acetate was dissolved in deionized water and stirred for 2 h at 40 °C (Solution A). In a separate flask the required amounts of $SnCl_4$ were dissolved in isopropanol (IPA) to prepare 25 mL of a 20-mM Sn^{+4} solution (Solution B). Then solution A and B were mixed and this solution was poured into a Chadorok autoclave and maintained at 160 °C for 15 h. The solution was removed using a solution aspirator, leaving behind a white powder. The synthesized powders was washed with a mixture with a component content ratio of deionized water/acetone/IPA = 1:1:1. The synthesized $In_4Sn_3O_{12}$ nanoparticles were dried in an oven at 120 °C for 12 h and heat-treated in a vacuum furnace (1 mTorr) at 500 °C for 1 h.

The TeO_2 nanoparticles were prepared in a similar manner using $TeCl_4$-dissolved deionized water. By dispersing 20 mg of the $In_4Sn_3O_{12}$ nanoparticles and 20 mg of the TeO_2 nanoparticles in 50 mL of IPA and then ultrasonicating the solution for 1 h, a solution of $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles was obtained. The composite solution was then dried in an oven at 120 °C for 12 h and heat-treated in a vacuum furnace (1 mTorr) at 500 °C for 1 h; the final yield was 40 mg of $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles.

2.3. Fabrication of $In_4Sn_3O_{12}$ and $In_4Sn_3O_{12}$–TeO_2 nanocomposites sensors

First, 40 mg of the $In_4Sn_3O_{12}$ nanoparticles and 40 mg of the $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles were dispersed separately in 50 mL of IPA and ultrasonicated for 1 h. A 1 mL drop of the solution containing $In_4Sn_3O_{12}$ nanoparticles and $In_4Sn_3O_{12}$–TeO_2 composite nanoparticles was placed onto an interdigital electrode (IDE) pattern (size: 10 mm × 10 mm) (Fig. 1) and dried at 150 °C in air for 1 h. Before the sensing tests, the sensors were annealed in a vacuum at 1 Torr at 500 °C for 1 h. The nanostructures synthesized via a hydrothermal route contain a high density of OH radicals