Journal of Alloys and Compounds 711 (2017) 652–658

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Layer-by-layer self-assembly of tricobalt tetroxide-polymer nanocomposite toward high-performance humidity-sensing

Dongzhi Zhang [a, *, 1], Chuanxing Jiang [a, 1], Yan'e Sun [a], Qu Zhou [b]

[a] College of Information and Control Engineering, China University of Petroleum (East China), Qingdao, 266580, PR China
[b] College of Engineering and Technology, Southwest University, Chongqing, 400715, PR China

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form
20 March 2017
Accepted 22 March 2017
Available online 6 April 2017

Keywords:
Tricobalt tetroxide
Layer-by-layer self-assembly
Humidity sensing
Composite film

ABSTRACT

In this paper, a humidity sensor with tricobalt tetroxide (Co_3O_4)/poly(sodium styrene sulfonate) (PSS) film coated was fabricated using layer-by-layer (LbL) nano self-assembly method. The nanostructural, surface morphology and the specific surface area of the LbL self-assembled Co_3O_4/PSS nanocomposite were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen sorption analysis and transmission electron microscopy (TEM) measurements. The humidity sensing properties of the sensor were investigated by exposing to a wide relative humidity range of 11–97% at room temperature. The experimental results indicate that the presented sensor not only exhibited favorable response of up to 2479.97, but also possessed fast response and recovery time, acceptable repeatability and stability. The sensing performance was greatly better than that of pure Co_3O_4. Moreover, the possible humidity sensing mechanism can ascribed to the synergistic effect of Co_3O_4 and PSS toward water molecules, as well as the layered nanostructure. This work highlights the LbL self-assembled Co_3O_4/PSS film is a candidate material for constructing humidity sensors with high performance for various applications.

1. Introduction

Effective and exact identification of environmental humidity for various fields, including electronic device fabrication, food processing and industrial chemicals synthesis, is considerable important. Therefore, the development of humidity sensor with high sensitivity, short response and recovery time, excellent stability, wide sensing range and low cost is needed [1,2]. Various kind of sensing materials like metal oxide semiconductors, polymers, carbon nanotubes and composites have been employed in humidity sensors [3–6]. They have their own advantages and specific conditions of application. Among these sensing materials, the metal oxide semiconductor is one of the most common materials used for humidity sensors, because they exhibit facile synthesis route, controllable size and morphology, accessible surface modification as well as stable physical and chemical properties. Meanwhile, compared with humidity sensors based on other sensing materials, the remarkable characteristics of metal oxide semiconductor sensors are low cost, simple construction, small size and easy installation [1]. Cobalt oxide, as a kind of metal oxide semiconductor, exists in three different crystalline forms namely CoO, Co_2O_3 and Co_3O_4. Among all stoichiometry, Co_3O_4 have been extensively employed due to its chemical stability and desired electrochemical properties [7], such as solar selective absorber at high temperature, electrochemical capacitors, gas and humidity sensors, heterogeneous catalysts in oxidation process, magnetic materials and lithium-ion battery electrodes [8–14]. However, Co_3O_4 serves as gas sensing materials is usually operated at elevated temperatures above 200 °C to obtain the catalytic properties of surface oxide species [15,16]. Therefore, the application of Co_3O_4 is restricted in commercialization application due to its high resistance and low catalytic activity at room temperature [17,18].

Current research efforts are directed toward developing high-performance humidity or gas sensor working at room temperature with low fabrication costs and low power consumption [19–22]. Remarkably, metal oxide semiconductors modified with conducting polymers have been demonstrated to be an effective method for room temperature detection of gas or humidity. For instance, Lin et al. synthesized WO_3-3, 4-ethylenedioxythiophene:

* Corresponding author. No. 66 Changjiang West Road, Huangdao District, Qingdao, PR China.
E-mail address: dzzhang@upc.edu.cn (D. Zhang).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jallcom.2017.03.365
0925-8388/

4-styrenesulfonicacid nanocomposite on flexible foils, which exhibits a high sensitivity to low concentration NO_2 gas at room temperature [23]. Patil et al. synthesized a nanocomposite of poly (*o*-anisidine)–tin oxide (POA-SnO_2) using an in-situ chemical polymerization route and used it as new humidity-sensing material. The humidity-sensing characteristics of the nanocomposite confirmed a significant enhancement for humidity sensing application in comparison with pure POA [24].

In this work, we demonstrated a facile and cost-effective fabrication route, layer-by-layer (LbL) self-assembly, to prepare Co_3O_4/PSS nanocomposite sensor for humidity sensing. The nanostructural, surface morphology and the specific surface area of the LbL self-assembled Co_3O_4/PSS nanocomposite were examined by SEM, XRD, nitrogen sorption analysis and TEM measurements. The humidity-sensing properties of the presented film sensor were investigated by exposing to various relative humidity (RH) environments. Results indicate that the presented sensor has an admirable response, fast response/recovery time and outstanding repeatability as well as stability. Moreover, the LbL self-assembled Co_3O_4/PSS nanocomposite film sensor exhibits great enhancement for humidity detection compared to the pure Co_3O_4 counterpart, demonstrating the admirable properties of nanocomposite and unique advantages of LbL self-assembly for film sensors fabrication. Finally, the possible humidity-sensing mechanism of the nanocomposite humidity sensor was also discussed.

2. Experiment

2.1. Materials

Reagents used in the experiment including cobalt nitrate hexahydrate, sodium phosphate dodecahydrate and hydrazine hydrate were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Additionally, polycation and polyanion used for enhancing the ionic strength and polyions adsorption in LbL assembly, including 1.5 wt% poly(diallyldimethylammonium chloride) (PDDA) and 0.3 wt% poly(sodium styrene sulfonate) (PSS), which were purchased from Sigma-Aldrich Inc. (USA). All the reagents were used as received without further purification.

A facile hydrothermal route was used to synthesize Co_3O_4 nanorod, as reported in reference [25]. 0.5 mmol cobalt nitrate hexahydrate and 0.0125 mmol sodium phosphate dodecahydrate were dissolved into 70 mL of deionized (DI) water and subsequently stirred for 0.5 h. Then, 2 mL of hydrazine hydrate was added to the mixture dropwise and ultrasonic vibration for 0.5 h. After that, the resulting mixture was hydrothermally treated at 180 °C for 12 h. At last, the obtained sample was further annealed at 500 °C in nitrogen for 5 h to get high-quality Co_3O_4 crystalline.

2.2. Sensor fabrication

Printed circuit board (PCB) was used as mechanical support for the sensor due to its low cost, simple processing and ease-of-integration. The typical MEMS processes for manufacturing the devices are as follows: A Cu/Ni layer with thickness of 20 μm was first deposited on PCB using sputtering system. Subsequently, positive photoresist (PR) was coated on the substrate to make interdigital electrodes (IDEs) pattern using lithography, and then the redundant Cu/Ni layer was etched out to form micro-IDEs via exposure and development. Both width and gap spacing of 200 μm for the IDE fingers was designed. Lastly, the sensing film was self-assembled onto the sensor substrate.

The LbL self-assembly method was adopted to fabricate Co_3O_4/PSS film as sensing materials for the humidity sensor, as shown in Fig. 1. Firstly, the device was immersed into solution of PDDA for 10 min, then rinsed by DI water and dried by nitrogen flow for enhancing the interaction between layers. Then immersing the device into solution of PSS for 10 min and following with rinsing and drying. Repeating once again and completing the production of two bi-layers of PDDA/PSS on the sensor substrate. It namely precursor layers which play an important role for charge enhancement. Secondly, the device was alternately immersed into the solutions of Co_3O_4 and PSS for *n* cycles. The immersion time was 15 min for the Co_3O_4 and PSS, respectively. In this way, the multilayer films $(PDDA/PSS)_2/(Co_3O_4/PSS)_n$ were formed, here the *n* is 1, 3, 5, 7, 9. Finally, the self-assembled sensing device was heated under 70 °C for 3 h, and Co_3O_4/PSS nanocomposite film was obtained. Fig. 1 shows the layer-by-layer fabrication process of Co_3O_4/PSS nanocomposite film and its structure. The layer thickness can be controlled under the layer-by-layer self-assembly route, which is measured about 50 nm. Moreover, for making comparison, the pure Co_3O_4 film sensor was prepared by drop-casting method.

2.3. Instrument and analysis

A schematic diagram of the experimental setup used for humidity sensing measurement is illustrated in Fig. 2. The humidity sensing properties were investigated by exposing the Co_3O_4/PSS film sensor to various RH levels, which were achieved by several saturated aqueous solutions. Saturated aqueous solutions in closed vessel at a stable temperature can provide stable and controllable RH levels in their equilibrium states [26]. The experiment was performed at room temperature of 25 °C. Saturated solutions of

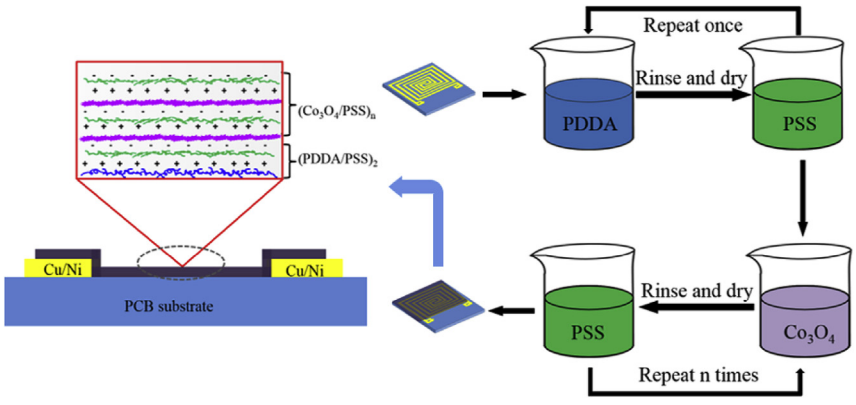

Fig. 1. Layer-by-layer fabrication process of Co_3O_4/PSS nanocomposite film and its structure.