Sensors and Actuators B 252 (2017) 624–632

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Fabrication of platinum-loaded cobalt oxide/molybdenum disulfide nanocomposite toward methane gas sensing at low temperature

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ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form 7 June 2017
Accepted 10 June 2017
Available online 10 June 2017

Keywords:
Pt-Co_3O_4/MoS_2 nanocomposite
Layer-by-layer self-assembly
Methane gas detection
Operating temperature

ABSTRACT

A novel methane sensor based on platinum (Pt)-loaded cobalt oxide (Co_3O_4)/molybdenum disulfide (MoS_2) nanocomposite was reported in this paper. The sensor was fabricated via layer-by-layer (LbL) self-assembly method for the first time, and was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), elemental mapping, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). The gas sensing properties of the as-prepared Pt-Co_3O_4/MoS_2 composite toward methane gas was investigated under various operating temperature, and the optimal working temperature of 170 °C was determined. The Pt-Co_3O_4/MoS_2 sensor exhibits superior gas sensing performance toward methane as compared to the Co_3O_4, Co_3O_4/MoS_2 counterparts. The underlying gas sensing mechanism of the Pt-Co_3O_4/MoS_2 sensor was systematically discussed, which demonstrates that the enhanced sensing performance of the sensor is attributed to the good synergistic effect of the ternary materials, including high availability of oxygen species, active catalytic effect, and special interactions at MoS_2/Co_3O_4 heterojunction.

1. Introduction

The monitoring and detecting of toxic and flammable gases in various fields, such as coal mine, has attracted considerable attention in the past decade. Methane (CH_4), a kind of colorless but combustible gas, is the most important component of mine gas. As we all known, high concentration (>5%) of CH_4 in coal mine is dangerous and may cause the explosion [1,2]. Therefore, reliable and large range concentration detection of CH_4 is extremely necessary. Currently, metal oxide semiconductors (MOS) such as zinc oxide (ZnO), tin oxide (SnO_2), titanium dioxide (TiO_2), indium oxide (In_2O_3) cobalt oxide (Co_3O_4) and tungsten trioxide (WO_3), have been known as promising gas sensing materials owing to their distinctive performance, including nano-size, easy fabrication, low cost, as well as stable physical-chemical properties [3,4]. Among them, Co_3O_4, as a p-type semiconductor, has generated lots of interest for detecting various kinds of gases, such as NH_3 [5], NO_2 [6], CO [7,8], ethanol [9], toluene [10], acetone [11] and water vapor [12]. However, few literatures have reported that pure Co_3O_4 possess satisfactory performance for detecting CH_4 below 200 °C [13]. With the appeal of reducing low power consumption in sensor development, it is highly worthy of enhancing the sensing performance of MOS-based sensors toward methane gas at lower temperature.

In recent years, single-layer graphene has emerged as a typically two-dimensional (2D) nanomaterial and attracted tremendous interest owing to its unique atomically thin-layered structure and excellent electrical properties [14–16]. However, its application has been limited by its inability to function as a semiconductor, which is critical for the on-off switching operations performed by electronic devices. To overcome this shortcoming, the researchers turned to another emerging 2D nanomaterial, molybdenum disulfide (MoS_2). MoS_2 possesses a layered structure similar to graphene, has been extensively investigated as a promising candidate in various applications due to its exceptional properties [17–20]. Compared with graphene whose band gap is 0, MoS_2 layered structure with bandgap varies from 1.2 eV (bulk MoS_2) for indirect-gap to 1.8 eV (monolayer) for direct-bandgap, leading to stronger effect on electrical properties produced by molecule adsorption, fundamentally improving its sensitivity [21,22]. It is possible to form *p-n* heterojunction with other semiconducting materials as a new type of electronic devices, rendering MoS_2 a capability in detecting various gases at low temperature. For instance, Zhao et al. showed

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http://dx.doi.org/10.1016/j.snb.2017.06.063
0925-4005/

MoS_2-decorated TiO_2 nanotube gas sensor exhibited excellent sensing performance toward ethanol gas at working temperature of 150 °C [23]. Liu et al. reported MoS_2 thin films grown on p-type Si substrates by DC magnetron sputtering technique and exhibited obvious sensing properties to NH_3 at room temperature [24]. In addition, the decorating or doping with noble metals also was recently considered to be alternative effective method to improve the sensing performance of MOS-based gas sensors at low temperature [25,26]. Noble metal nanoparticles (NPs) such as Ag, Au, Pt and Pd, have unique chemical and catalytic properties, which could enhance the adsorption of gas molecules and accelerate the electron exchange between the sensor and the target gas [26,27]. For instance, C. Kuru et al. reported that MoS_2-Pd composite by fabricating field effect transistor (FET) devices exhibited much higher sensor response with shorter response and recovery times than graphene-Pd composite at room temperature [28]. Wang et al. reported Pt-loaded SnO_2 composite-based sensor had a high response to CO at room temperature as well as a good selectivity [29]. Xiang et al. presented a hydrogen sensor based on Pd NPs doped TiO_2 nanotubes, which exhibited short response/recovery time, outstanding selectivity as well as good reproducibility at room temperature [30].

This work reports a methane gas sensor based on Pt-loaded Co_3O_4/MoS_2 nanocomposite fabricated by layer-by-layer (LbL) self-assembly method. The morphologies, microstructures and compositional characteristics of the Pt- Co_3O_4/MoS_2 nanocomposite were sufficiently examined by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscopy (SEM), elemental mapping, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). The methane gas-sensing performance of the as-prepared sensor was investigated and compared with pure Co_3O_4 and Co_3O_4/MoS_2 counterparts. Experimental results reveal that the sensing behavior of the Pt-Co_3O_4/MoS_2 sensor is superior to the other two sensors, in terms of high response, fast response/recovery time as well as outstanding repeatability. Furthermore, the potential sensing mechanism of the sensor toward methane gas was explored in detail.

2. Experiment

2.1. Materials

Sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), thioacetamide (CH_3CSNH_2), oxalic acid ($C_2H_2O_4$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, >98.5%), trisodium phosphate ($Na_3PO_4{\cdot}12H_2O$, >98%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, >99%) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Additionally, poly (dimethyl diallyl ammonium chloride) (PDDA) and poly (sodium 4-sty-renesulfonate) (PSS) were obtained from Sigma-Aldrich Inc. All the chemicals were used as received without further purification.

2.2. Fabrication

The fabrication of Pt-Co_3O_4/MoS_2 nanocomposite is performed by combining hydrothermal synthesis with LbL self-assembly method. Fig. 1(a) and (b) demonstrate the process for synthesizing Co_3O_4 and MoS_2 nanomaterials via hydrothermal method [5,31]. For Co_3O_4 fabrication, an mount of $Co(NO_3)_2{\cdot}6H_2O$, $Na_3PO_4{\cdot}12H_2O$ and $N_2H_4{\cdot}H_2O$ were dissolved into deionized (DI) water with stirring for 1 h and then transferred to a stainless-steel autoclave for heating at 180 °C for 12 h. For MoS_2 fabrication, $Na_2MoO_4{\cdot}2H_2O$, thioacetamide and oxalic acid were dissolved into DI water and stirred over 1 h, and then transferred to a stainless-steel autoclave for heating at 200 °C for 24 h. The Co_3O_4 and MoS_2 solutions were collected for use after washing with DI water several times to remove excess ions. In order to enhance the electrostatic interaction of Co_3O_4 and MoS_2, an equal volume of PDDA and PSS was added into the Co_3O_4 and MoS_2 solutions as cationic and anionic polyelectrolyte, respectively.

Fig. 1(c) shows the LbL self-assembly fabrication of the Pt-Co_3O_4/MoS_2 nanocomposite film. Firstly, two precursor layers of PDDA/PSS were self-assembled on the interdigital electrode (IDE) device with FR4 as substrate for surface modification. Afterwards, the Co_3O_4 and MoS_2 layers were alternately deposited through solution immersion for five cycles via LbL self-assembly technique, in which MoS_2 layer was arranged as top layer. Here, the immersing time of PDDA and PSS were 10 min, Co_3O_4 and MoS_2 were 20 min. Rinsing with DI water and drying with nitrogen gas after each monolayer assembly are required for strengthening the interconnection between layers. Next, the device was immersed into 3 mmol/L $H_2PtCl_6{\cdot}6H_2O$ solution over 1 h to achieve Pt-loading on Co_3O_4/MoS_2 nanocomposite. Finally, the Pt-Co_3O_4/MoS_2 device was heated at 80 °C for 12 h. In order to highlight this work, the comparative devices of pure Co_3O_4 and Co_3O_4/MoS_2 were fabricated. The Co_3O_4 film sensor was fabricated by drop-casting Co_3O_4 solution on the IDE device, and the Co_3O_4/MoS_2 film sensor was fabrication by LbL self-assembly route as the above-mentioned, but without the immersion of $H_2PtCl_6{\cdot}6H_2O$ solution.

2.3. Instrument and analysis

The surface structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD, Rigaku D/Max 2500PC), field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL JEM-2100). The chemical composition analysis was performed by Hitachi S-4800 equipped with an energy dispersive spectrometer (EDS). The elemental mapping was examined by Merlin FE-SEM from Carl Zeiss (Germany) at 2–5 kV range accelerating voltage. X-ray photoelectron spectroscopy (XPS) was performed to examine the elemental composition and chemical state of the as-prepared sample by a Thermo Scientific K-Alpha XPS spectrometer.

The gas-sensing measurement was performed by exposing the prepared sensors to CH_4 gas, and the resistance response was recorded via Agilent 34970A data-logger. The sensing device was placed in a sealed chamber equipped with appropriate inlet and outlet for gas. Air used as background gas and a known volume of CH_4 gas was injected inside the testing chamber to achieve the desired concentration for test. The relative humidity of the atmosphere where the gas sensing tests performed is 45%RH. The working temperature for the sensor is controlled through applying a voltage to a heating resistor by a power source (GPD-4303S). The response value (R) was determined by $R = |R_a\text{-}R_g|/R_a \times 100\%$, where R_a is the resistance of the sensor in air and R_g is the resistance of the sensor in the target gas.

3. Results and discussion

3.1. Materials characterizations

Fig. 2 shows the XRD patterns of Co_3O_4, MoS_2 and Pt-Co_3O_4/MoS_2 samples. The diffraction peaks in the XRD pattern of Co_3O_4 are in good agreement with those on the standard card of cubic spinel Co_3O_4 (JCPDS No. 76-1802). The reflection peaks of MoS_2 are corresponding to the (002), (100), (103) and (110) reflections of MoS_2 (JCPDS 37-1492). The XRD pattern of the Pt-Co_3O_4/MoS_2 sample illustrates all the distinct lattice planes corresponding to the MoS_2, Co_3O_4 and Pt nanoparticles, confirming