Sensors and Actuators B 242 (2017) 15–24

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Room temperature hydrogen gas sensor based on palladium decorated tin oxide/molybdenum disulfide ternary hybrid via hydrothermal route

Dongzhi Zhang*, Yan'e Sun, Chuanxing Jiang, Yong Zhang

College of Information and Control Engineering, China University of Petroleum (East China), Qingdao 266580, PR China

ARTICLE INFO

Article history:
Received 11 August 2016
Received in revised form 29 October 2016
Accepted 2 November 2016
Available online 8 November 2016

Keywords:
Hydrothermal method
Nanocomposites film
Hydrogen gas sensor
Sensing mechanism

ABSTRACT

This paper demonstrates a hydrogen gas sensor based on palladium-tin oxide- molybdenum disulfide (Pd-SnO_2/MoS_2) ternary hybrid via hydrothermal route. The morphologies, microstructures and compositional characteristics of the Pd-SnO_2/MoS_2 nanocomposite were sufficiently examined by X-ray diffraction (XRD), Raman spectroscopy (RS), nitrogen sorption analysis, energy dispersive spectrometer (EDS), scanning electron microscopy (SEM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS). The gas-sensing performances of the Pd-SnO_2/MoS_2 sensor were investigated by exposed to different concentrations of hydrogen gas from 30 ppm to 5000 ppm at room temperature. The experimental results showed that the hydrogen gas sensor has a quite sensitive response, swift response-recovery time, good repeatability and selectivity toward hydrogen gas. Furthermore, the effect of Pd loading in the hybrid on the hydrogen gas sensing was investigated. The sensing mechanism of the Pd-SnO_2/MoS_2 sensor was attributed to the synergistic effect of the ternary nanostructures and the modulation of potential barrier with electron transfer. This work indicates that the as-prepared Pd-SnO_2/MoS_2 composite is a candidate for detecting hydrogen gas in various applications at room temperature.

1. Introduction

Hydrogen gas is expected to be a green and renewable energy source in near future for various applications, such as fuel cells, power generators, automobiles and aerospace [1]. However, hydrogen is an extremely dangerous gas for its explosive and flammable nature, and the existence and leakage in atmosphere may cause potential explosion accidents [2]. Therefore, the detection of hydrogen is extremely important and necessary in many fields [3,4]. Recently, a lot of efforts have been devoted to develop new approaches for fabricating hydrogen sensors, such as optical fiber [5,6], metal oxide including ZnO [7], SnO_2 [8], TiO_2 [9], WO_3 [10] and MOSFET sensor [11]. Among them, the metal oxide demonstrated some advantages such as smaller size, high sensitivity, excellent reliability and simplicity of use for hydrogen sensing [12,13]. As an n-type semiconductor, SnO_2 has excellent physicochemical and electrical properties toward hydrogen detection but requires high operation temperature, which will result in higher power consumption and high risk of explosion. Therefore, developing a reliable and high-performance hydrogen sensor working at room temperature is highly desirable. It is noteworthy that the modification of metal oxide with noble metal such as palladium (Pd) is an alternative route to enhance the hydrogen sensing [14]. Pd-SnO_2 nanostructure based hydrogen gas sensors have been reported due to their inherent catalytic effect [15–18].

Molybdenum disulfide (MoS_2), as a graphene-liked 2D layered semiconductor, is considered to be a promising candidate due to its extremely large surface-to-volume ratio, and exceptional electrical properties. Compared with graphene which band gap is 0, MoS_2 layered structure with band-gap varies from 1.2 eV (bulk MoS_2) for indirect-gap to 1.8 eV (monolayer) for direct-bandgap, playing a critical role in improving its sensing performances [19–22]. Therefore, MoS_2 has attracted tremendous interest in various fields, especially gas sensors to detect NH_3, NO_2, NO and ethanol at room temperature [23–26]. MoS_2 nanosheet-Pd nanoparticle composite for hydrogen gas sensing at room temperature has been reported by Kuru et al. [27]. While, until now, the hydrogen gas sensor based on noble metal modified metal oxide/MoS_2 ternary hybrid has not been reported.

* Correspondence to: No. 66 Changjiang West Road, Economic & Technological Development Zone of Qingdao, PR China.
E-mail address: dzzhang@upc.edu.cn (D. Zhang).

http://dx.doi.org/10.1016/j.snb.2016.11.005
0925-4005/

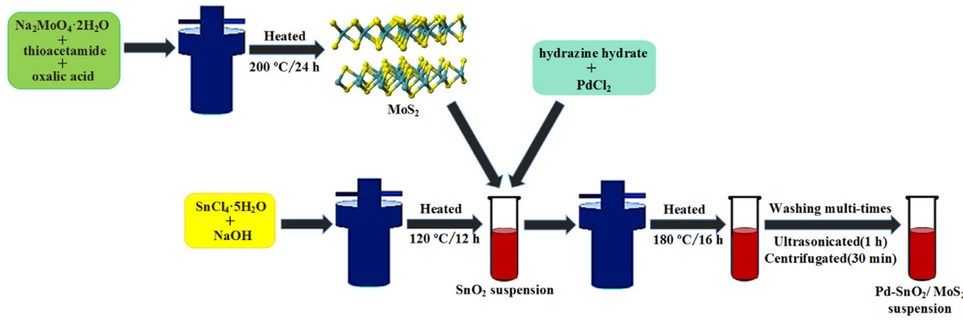

Fig. 1. Hydrothermal route for the fabrication of Pd-SnO_2/MoS_2 suspension.

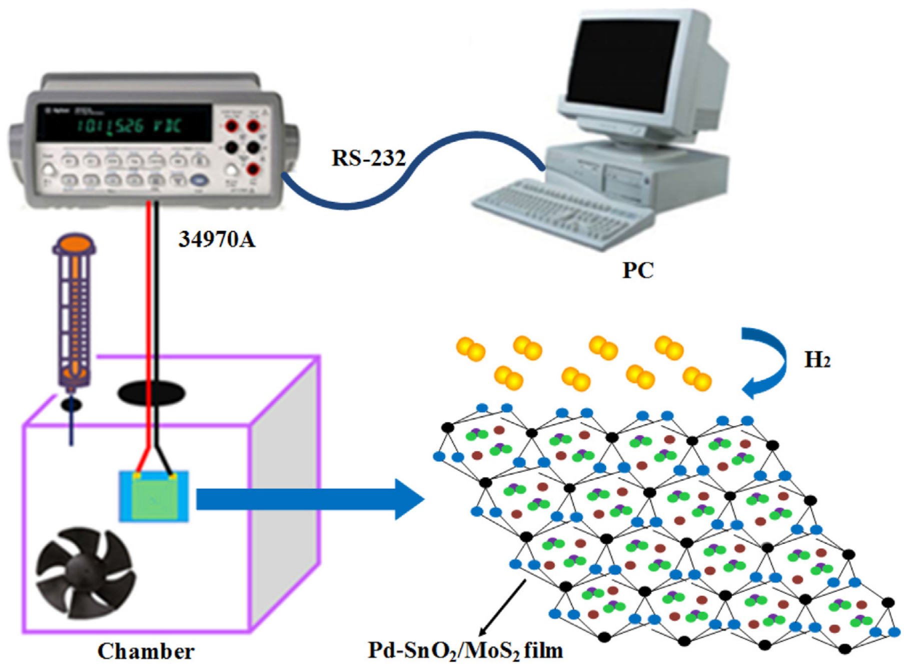

Fig. 2. Experimental setup for hydrogen sensing.

In this paper, we prepared a hydrogen gas sensor based on palladium-tin oxide- molybdenum disulfide (Pd-SnO_2/MoS_2) ternary hybrid via hydrothermal route. The as-prepared hybrid was fully characterized by many means and confirmed its successful preparation, morphology, microstructure and composition. The hydrogen-sensing properties of the sensor were investigated at room temperature, and high response, swift response-recovery time, good repeatability and selectivity toward hydrogen gas were achieved. Moreover, the underlying sensing mechanism of the Pd-SnO_2/MoS_2 ternary hybrid was discussed in detail.

2. Experimental

2.1. Materials

$Na_2MoO_4·2H_2O$, $PdCl_2$ (AR), thioacetamide, oxalic acid and hydrazine hydrate used in this work were purchased from Sinopharm Chemical Reagent Co. Ltd. $SnCl_4·5H_2O$ (99%) was obtained from Shanghai Hansi Chemical Industry Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification.

2.2. Sample fabrication

The MoS_2 was synthesized via a convenient hydrothermal method, as reported in the previous work [26,28]. At first, $Na_2MoO_4·2H_2O$ (1.0 g) and thioacetamide (1.2 g) were dissolved into 80 mL deionized (DI) water, and stirred for 30 min. After that, 0.6 g oxalic acid was added to the above solution, and followed with stirring for 30 min. Next, the obtained solution was transferred to a 100 mL stainless-steel autoclave and heated oven at 200 °C for 24 h. After that, the resulting black product was washed with DI water several times, and further annealed at 700 °C for 2 h under the protection of pure argon to get high-purity MoS_2.

The Pd-SnO_2/MoS_2 sample was prepared according to the following steps. Firstly, $SnCl_4·5H_2O$ and NaOH were added into 80 mL DI water and stirred for 30 min, and then the resulting suspension was thermally treated at 120 °C for 12 h to obtain SnO_2 suspension. Secondly, 4 mL hydrazine hydrate, an amount of $PdCl_2$ and 0.1 g MoS_2 were added into the above solution by ultrasonic treatment for 20 min and stirring for 2 h, followed by hydrothermally heated in a stainless steel autoclave at 180 °C for 16 h. After cooling down to room temperature, the obtained solution was washed several times with DI water to remove the impurity ions. In order to investigate the influence of Pd loading in the Pd-SnO_2/MoS_2 film on the hydrogen sensing, 1 wt%, 2 wt%, 4 wt% and 6 wt% Pd-loaded