Improved gas sensing performance with Pd-doped $WO_3 \cdot H_2O$ nanomaterials for the detection of xylene

Feng Li[a], Qixuan Qin[a], Nan Zhang[a], Chuan Chen[c], Liang Sun[c], Xin Liu[c], Yu Chen[a,**],
Chuannan Li[a,c,*], Shengping Ruan[a,b,*]

[a] State Key Laboratory on Integrated Optoelectronics and College of Electronic Science & Engineering, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory on Applied Optics, Changchun 130023, PR China
[c] Global Energy Interconnection Research Institute, Beijing 102211, PR China

ABSTRACT

In order to sensitively, selectively, and rapidly detect xylene, the sensing properties of $WO_3 \cdot H_2O$ nanomaterials are regulated by tailoring the doping level of Pd. In this work, Pd- doping $WO_3 \cdot H_2O$ nanomaterials were synthsised by a simple, effective and economical hydrothermal method at a low temperature. The responses of the sensors fabricated by $WO_3 \cdot H_2O$ nanomaterials with different Pd-doped levels were tested and the nanomaterials with an atomic ratio of 0.6% realized low optimum operating temperature, high gas response of 21.0–10 ppm xylene at 230 °C, fast response/recovery speed, low detection limit (100 ppb) and strong selectivity to trace gas. And the crystalline nature, chemical composition, morphology and microstructure of the as-prepared Pd-doped $WO_3 \cdot H_2O$ nanomaterials were studied by X-ray diffraction (XRD), Energy Dispersive X-ray Spectrometer (EDX) and scanning electron microscopy (SEM). Also, the mechanism involved in improving xylene sensing properties of $WO_3 \cdot H_2O$ -based sensor by Pd doping was discussed. The sensitization effect of Pd could be attributed to the tremendous effect caused by promoters which were found to be distributed at an atomic level on the surface and in the bulk of the supporting sensing material.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In pursuit of a better life, rapid development in science and technology is of crucially important. However, the great developments have led to a wide variety of environmental problems [1,2]. And among all kinds of environmental problems, gaseous pollutants which come from industries and automobiles have resulted in atmospheric pollution and caused major concerns such as human health issues, acid rain, ozone depletion and the greenhouse effect [3]. Xylene, a kind of colorless and toxic aromatic hydrocarbon with sweet smelling widely used as a solvent in industry and medical technology, accounts for a great proportion of gaseous pollutants [4]. The National Institute for Occupational Safety and Health recommended that the time limit for exposure to xylene at

200 ppm was just 10 min [5], for its poisonousness will put people at seriously health risks [6]. As a result of this, it should be placed more importance on detecting xylene sensitively. Although gas fluorescence spectroscopy [7] and chromate graphy mass spectroscopy [8,9] provide precise measurement tools to detect xylene, they require expensive instruments, sampling processes and prolonged time periods for analysis. So it's understandable that people take great effect to develop simple, cost-effective, and diminutive gas sensors with good selectivity, high sensitivity, fast response/recovery speed to trace xylene reliably and expediently.

As a kind of n-type oxide semiconductor, the band gap of tungsten trioxide (WO_3) is reported to be about 2.6–2.8 eV [10]. Hence, it will lead to an increase of chemical resistance upon exposure to oxidizing gas and a decrease after the material reacts with reducing gas [11,12]. Up to now, plenty of methods have been reported for synthesis of WO_3 nanomaterials with various morphologies, such as nanorods [13–15], nanowires [16–18], nanoplates [19–21], nanofibers [22,23] and nanoparticles [24,25], etc. From 1967 when WO_3 was used as gas sensor for the first time, numerous scientists have done a lot of work to enhance the sensitivity and selectivity of the WO_3-based sensors [26]. However, as everyone knows, it is difficult to achieve a good balance between high selectivity and

sensitivity of sensors based on pure materials at the same time. And during the past years, numerous articles concerning theoretical and experimental work on sensors have proved that doping and surface-functionalization are two effective methods to achieve superior sensitivity and selectivity of WO_3, such as such $Pt-WO_3$ [27], $Cr-WO_3$ [28], $Si-WO_3$ [29] and so forth. Furthermore, after continuous researches, plenty of high performance gas sensors fabricated by doping have been obtained to detect CH_3CH_2OH [30], CH_3COCH_3 [31], H_2S [27], etc. However, the reactions between ionized oxygen species (O_2^-, O^-, or O^{2-}) and gases which possess physico-chemical properties similar to xylene, always induce similar chemical changes [11,12,32] that will lead to similar resistance changes of oxide semiconductors. So studies in xylene gas sensor are not as ideal as expected and the task remains challenge in selective and sensitive detection of this specific gas until now. Therefore, great efforts are required to focus on the fabrication of xylene gas sensor which is reliable and practical.

In this work, Pd was selected as an ideal dopant to $WO_3 \cdot H_2O$ by a simple, effective and economical hydrothermal method at a temperature as low as 120 °C for 24 h without using any special equipment to provide demanding high temperature or vacuum experimental conditions [33,34]. And these procedures result in reducing the cost in roll-to-roll production tremendously. Moreover, through doping, the performance of xylene gas sensor was enhanced obviously comparing with the undoped one by achieving faster response/recovery speed, higher sensitivity and stronger selectivity in tracing xylene. At last, the possible mechanism involving in the enhancement of xylene sensing properties induced by doping Pd was also discussed in detail.

2. Experimental

2.1. Synthesis of materials

In this experiment, $HOOC(CHOH)_2COOH$ (tartaric acid) was purchased from Beijing Chemicals Works; $Na_2WO_4 \cdot 2H_2O$ (Sodium Tungstate Dihydrate) and $PdCl_2$ (Palladium chloride) were all obtained from the Sinopharm Chemical Reagent Co. Ltd. And all the chemical reagents used in the experiment were of analytical grade and no further purification processes were carried out subsequently.

$WO_3 \cdot H_2O$ nanocubes were prepared by a hydrothermal reaction [24,35] as follows: Firstly, $Na_2WO_4 \cdot 2H_2O$ (0.5 g) was dissolved in 30 mL deionized water, and under vigorous stirring for 20 min at room temperature, a homogeneous solution came into formation. Secondly, 4 mL of 3 M HCl aqueous solution was added and the pre-blended solution was stirred for another 10 min in order to dissolve the reagents completely. Thirdly, Different amounts of 0.01 M $PdCl_2$ solution were added into solutions to give different doping concentration (0.3 at%, 0.6 at%, 0.9 at%, 1.2 at% of W). And after that 0.6 g tartaric acid was introduced into the composite solution. Next, the resulting yellow slurry was transferred into a 50 mL Teflon-lined stainless steel autoclave and treated at 120 °C for 24 h. Then, after cooling, distilled water was used to remove the ions in the resulting product by centrifuging. Finally, the product was dried at 60 °C overnight in air to obtain Pd-doped $WO_3 \cdot H_2O$ nanomaterials powder.

2.2. Characterization of materials

The surface morphology of the as-prepared samples was studied using field-emission scanning electron microscopy (SEM, XL30ESEM FEG) at an accelerating voltage of 15 kV with gold sputtered on samples. And the crystalline phase was analyzed by X-ray diffraction (XRD) using a Scintag XDS-2000 X-ray diffractometer

with Cu Kα radiation (λ = 1.5418 Å). Energy dispersive X-ray spectrogram (EDX) was obtained on a JEM-ARM200F.

2.3. Fabrication and measurement of the gas sensor

Sensor was fabricated by similar method as reported [36–38]. The powder was dispersed in deionized water in a weight ratio of 4:1 and ground in a mortar to form a paste. And after that the paste was coated uniformly on an alumina ceramic tube which was attached with a pair of parallel golden electrodes using a writing brush. Besides, a Ni–Cr alloy heating coil was inserted as a heater through the tube to provide operating temperature of the gas sensor.

Then CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China) was employed to measure the gas sensing characteristics at room condition. The testing procedure is as follows. Firstly, when the resistances of the sensors (R_a) achieved stability, the target gas was injected into the test chamber (20 L in volume) through a rubber plug by a microinjector. Then the injected gas was mixed with air by two fans in the analysis system until the resistance of the sensor reached a constant value (R_g). After the measurement, the buttons for heating and mixing the gas atmosphere were turned off and the test chamber was opened to expose the sensor to atmospheric environment. The response value (S) of the sensor is defined by the value of the ratio of R_a/R_g [39], the
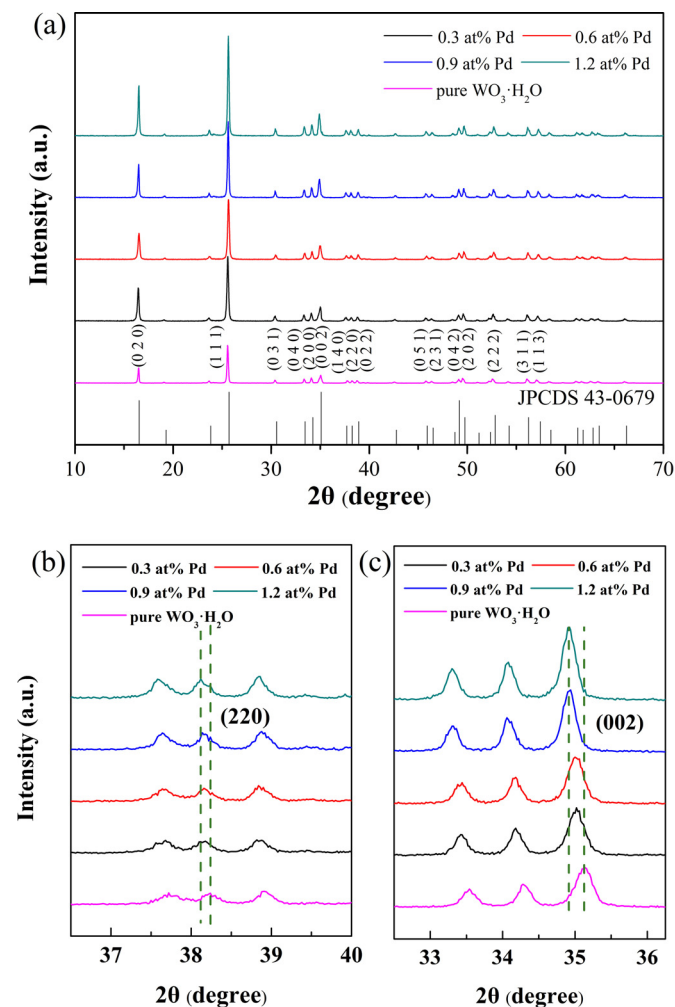

Fig. 1. (a) XRD patterns of bare $WO_3 \cdot H_2O$ samples with 0 at%, 0.3 at%, 0.6 at%, 0.9 at% and 1.2 at% Pd doping; (b) (c) Comparison of (2 2 0) and (0 0 2) peaks from XRD patterns.