Sensors and Actuators B 183 (2013) 372–380

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Diameter controlled synthesis of tungsten oxide nanorod bundles for highly sensitive NO_2 gas sensors

Pham Van Tong[a,b,1], Nguyen Duc Hoa[a,*], Vu Van Quang[a,1], Nguyen Van Duy[a,1], Nguyen Van Hieu[a,*]

[a] International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology (HUST), No. 1, Dai Co Viet St., Hanoi, Viet Nam
[b] Department of Physics, Faculty of Mechanical Engineering, National University of Civil Engineering (NUCE), No. 55, Giai Phong Str., Hanoi, Viet Nam

ARTICLE INFO

Article history:
Received 15 August 2012
Received in revised form
27 December 2012
Accepted 21 March 2013
Available online 10 April 2013

Keywords:
Tungsten oxide
Nanorods
Nanoporous
Gas sensors

ABSTRACT

Attempts to improve the performances and cost effectiveness of gas sensors for practical applications have led to the development of advanced nanostructured materials, which enabled the fabrication of highly sensitive and selective sensing devices. This study introduced the diameter controlled synthesis of scalable and large-quantity nanoporous tungsten oxide nanorod bundles for highly sensitive NO_2 gas sensor applications. The diameter controlled nanoporous tungsten oxide nanorod bundles were synthesized by a facile hydrothermal method. The morphologies of the nanorod bundles were controlled by varying the amount of pluronic P123 surfactant. Gram quantities of the nanoporous tungsten oxide nanorod bundles were easily obtained and found effective in the fabrication of scalable gas sensors using a spray technique. Investigation on the gas sensing properties demonstrated that the nanoporous tungsten oxide nanorod bundles based gas sensor exhibited a relatively high response due to their small size (∼20 nm) and nanoporous structure, which provided large adsorption sites and accelerated the accession of the analytic gas molecules. The developed sensor enabled the monitoring of highly toxic NO_2 gas at low concentrations among other contaminants. The response to 5 ppm NO_2 was 126-folds higher than that to 200 ppm NH_3. The sensor also exhibited outstanding stability when operated at 250 °C. No distortion in sensor response was observed after five measurement cycles.

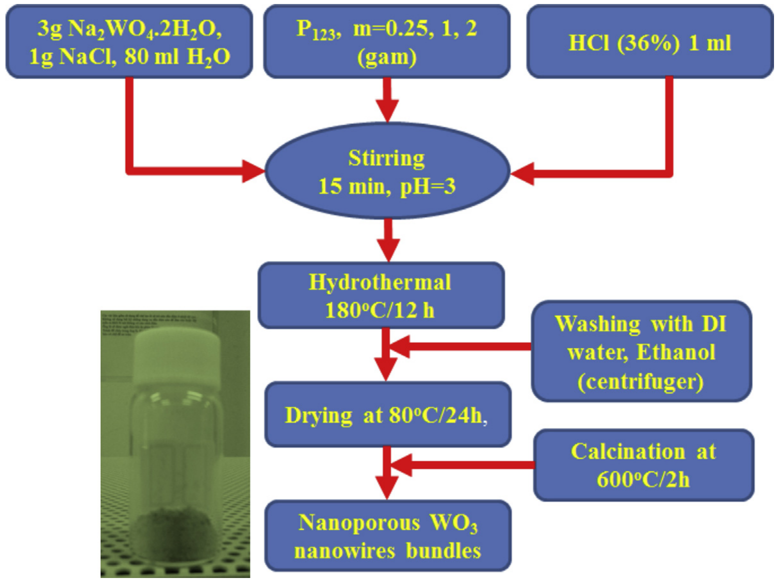
1. Introduction

The effective detection of highly reactive oxidants and the corrosive environmental pollutant nitrogen dioxide (NO_2) gas is extremely important due to environmental protection and health safety issues. Thus, the controlled fabrication of proper geometrical structures and/or materials for gas sensors that can perform this detection is highly desired [1]. According to the US Environmental Protection Agency, NO_2 gas is highly toxic. Exposure to NO_2 gas even at low levels (ppm) may cause increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease, and increased risk of respiratory infections. The permissible exposure to NO_2 gas is 5 ppm for general industries and 1 ppm for short-term exposure. Therefore, extensive efforts have been exerted to develop NO_2 gas sensors with fast response as well as high sensitivity, selectivity, stability, and feasibility [2–4].

Studies on gas sensor technology are focusing on lowering the production expense and improving the sensor performance [5–7]. Gas sensors based on nanostructured metal oxides, such as NiO [8], CuO [9], SnO_2 [10], ZnO [11], and WO_3 [12], are known for their economic advantages and effectiveness in the online monitoring of low-level polluted gases. These sensors have relatively high sensing ability, small size, low cost, and compatibility with silicon technology [13,14]. Among these metal oxide-based gas sensors, tungsten oxide has been received considerable attention. Tungsten oxide is an n-type semiconductor with a wide bandgap of 2.8–3.5 eV and it was first used for the detection of NO and NO_2 by Yamazoe et al. [15]. It can also detect various gases, such as volatile organic compounds (VOCs), H_2S, H_2, O_3, NH_3, NO, and NO_2 [15–19]. The sensitivity of tungsten oxide to highly toxic NO_2 gas has been observed for thin films [20], mesoporous thin films [21], nanoparticles, [22] nanowires array [23], three-dimensional nanowire networks [24], and nanorods [25]. It was reported that the particles of a spherical shape would have advantages for the formation of depletion layer and high sensitivity. However, they also have low stability due to the grain growth [26]. The nanorod or nanowire type has been reported to exhibit significantly high sensitivity and stability with fast response-recovery time [23]. In addition, the use of one-dimensional structure for gas sensor applications enhances sensor performance through the improvement of

* Corresponding authors. Tel.: +84 04 385680787.
E-mail addresses: ndhoa@itims.edu.vn (N.D. Hoa), hieu@itims.edu.vn (N. Van Hieu).
[1] Tel.: +84 04 385680787.

0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2013.03.086



Scheme 1. Diagram of the hydrothermal processes for the synthesis of nanoporous tungsten oxide nanorod bundles.

the active sensing sites [22–25]. The process also utilizes the size effects, i.e., large active sensing sites and dimensions comparable to Debye length are believed to increase the sensitivity of sensors dramatically [26,27]. Tungsten oxide nanowires and/or nanorods can be fabricated by various methods that involve physical and chemical routes. For example, tungsten oxide nanowires can be grown by thermal evaporation using tungsten trioxide powder as the precursor [28], or a tungsten tip can be heated at high temperatures in the presence of Ar flow [29]. Tungsten oxide nanorods have also been prepared using AAO templates through electrodeposition [30]. Choi et al. [31] reported the synthesis of tungsten oxide nanorods, nanowires, and nanosheets by the solvothermal method using tungsten hexachloride as tungsten source. Zhu et al. [32] reported the fabrication of hexagonal single-crystal tungsten trioxide nanorods by the hydrothermal method. The wet chemical routes appear to be suitable for the scalable synthesis of tungsten oxide nanowires and nanorods. However, challenges exist on the synthesis of reproducible and scalable large-quantity nanoporous tungsten oxide nanorod bundles with controllable diameters for the effective fabrication of NO_2 gas sensors by a spray technique.

This paper describes the diameter controlled synthesis of scalable nanoporous tungsten oxide nanorod bundles and their applicability in highly sensitive NO_2 gas sensor applications. Nanoporous tungsten oxide nanorod bundles were fabricated by a scalable hydrothermal method. The diameters and nanopores of the nanorod bundles were controlled using a triblock copolymer P123 surfactant. The gas sensors were fabricated by a facile and scalable spray method on arrays of Pt-interdigitated electrodes, which were pre-deposited on silicon substrate. The gas sensing properties of the synthesized materials were investigated for the detection of highly toxic NO_2 ranging from 1 to 5 ppm. The selectivity of nanoporous tungsten oxide nanorod bundles sensors was also investigated for other gases such as CO, NH_3, and H_2. The results revealed that the developed sensors could effectively monitor the highly toxic NO_2 gas at low concentrations with sufficient stability.

2. Experimental

2.1. Material synthesis

All materials were analytical grade and used as purchased without further purification. Extra-pure sodium tungstate hydrate was purchased from Kanto Chemical Company (Japan). Sodium chloride and triblock copolymer P123 were purchased from Sigma–Aldrich Company, Ltd. (USA). Nanoporous tungsten oxide nanorod bundles were fabricated by a scalable hydrothermal method. Scheme 1 shows the hydrothermal processes for the fabrication of nanoporous tungsten oxide nanorod bundles.

In a typical synthesis, sodium tungstate hydrate (3 g), sodium chloride (1 g), and a given amount of P123 surfactant (0.25, 1, and 2 g) were dissolved in 80 ml of distilled water using a magnetic stirrer. Herein, different amounts of P123 were used to control the morphology of the nanorods. Then, 1 ml of HCl (37%) was added dropwise to the mixture to control the pH to ∼3, resulting in a milky solution. This solution was further aged for about 15 min at room temperature before placing in a Teflon-line autoclave for the hydrothermal process. The sealed Teflon-line autoclaves were loaded in an electric oven maintained at 180 °C for 12 h. After cooling to room temperature, the precipitated products were collected and washed several times using distilled water and ethanol solution by centrifugation at 4000 rpm. Finally, the collected products were air dried at 60 °C prior to being used in sensor fabrication and characterizations. By weighing the final products, up to ∼2 g (∼95%) of tungsten oxide nanorods was obtained. The quantity of tungsten oxide nanorods was easily scaled up using five hydrothermal vessels. Therefore, about 10 g of nanorods was obtained from one set of experiment. This amount was sufficient for the subsequent fabrication of scalable gas sensor by a spray technique. The thermal evaporation method cannot be used to synthesize large quantities of nanorods easily [28,29]. The collected materials were calcinated at 600 °C for 2 h to stabilize the tungsten oxide structure. The morphologies of the synthesized materials were investigated by field-emission scanning electron microscopy (FESEM) (FE-SEM, JEOL model 6500), and high-resolution (HR) transmission electron microscopy (TEM) (JEOL, JEM model 2100F). Elemental analyses were performed by energy-dispersive X-ray spectroscopy (EDS). The crystal structures of the materials were studied by powder X-ray diffraction (XRD) using CuK$_\alpha$ X-radiation with a wavelength of 1.54178 Å (XRD, Bruker HI-Star). The Raman and photoluminescence spectra of the fabricated nanorods were also investigated at room temperature. The specific surface area (a_{BET}) and pore size distribution of the porous nanorod bundles were characterized by nitrogen adsorption/desorption isotherm.