Applied Surface Science 441 (2018) 277–284

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

P-type sub-tungsten-oxide based urchin-like nanostructure for superior room temperature alcohol sensor

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ARTICLE INFO

Article history:
Received 23 October 2017
Revised 26 December 2017
Accepted 1 February 2018
Available online 6 February 2018

Keywords:
Suboxide
WO_{3-x}
Nanowire
Hierarchical
Sensor
Alcohol

ABSTRACT

Nanowires assembled sub-WO_3 urchin-like nanostructures have been fabricated via a solvothermal method. The detailed structure and morphology features were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The results reveal that the individual nanowires are grown along the [001] direction, and assembled together to form an urchin-like nanostructure. Sensing performance of the sub-WO_3 was investigated toward alcohol vapor. At room temperature, the sensor devices based on the WO_{3-x} exhibit significantly higher sensitivity comparing to that of the stoichiometric WO_3. The superior sensing performance of this WO_{3-x} sensor is ascribed to the large specific surface area and abundant oxygen vacancies. The obvious enhancement of the gas sensing property can be very useful for the future design and development of room temperature gas sensors for other volatile organic compounds.

1. Introduction

Tungsten oxide is a material of choice for chemical sensor application due to its robustness, chemical stability, inherent electrical conductivity, and excellent sensitivity towards various toxic gases and volatile organic compounds (VOCs) [1,2]. The gas sensing process involves adsorption, desorption and catalytic reactions between the gas molecules and sensor material surface [3], therefore the sensitivity of sensor device is strongly dependent upon the surface-to-volume ratio of the material used and operating temperature [4]. In fact, like any other metal-oxide-based gas sensors, the WO_3 sensor often needs to operate at high temperature (200–500 °C) to ensure its sensitivity [5,6]. However, such high operating temperature often raises issues in material stability, power consumption and safety concerns [7]. In addition, the high temperature operation may also result in ignition of flammable and explosive materials [6]. Therefore, it is desirable to develop more innovative WO_3-based sensors that perform well at room temperature (RT).

A few novel methods have been proposed to lower the operating temperature of the WO_3-based gas sensors, such as noble metal functionalization [8–11], ultraviolet irradiation [6,12], and nanostructure [7,11,13–17]. Among them, the introduction of a moderate amount of oxygen vacancies forming sub-stoichiometric WO_{3-x} has received a notable attention. Comparing with the stoichiometric WO_3, chemical composition of the sub-oxide can be tuned ($0 < x < 1$) to give optimum performance [18]. It has been reported that the WO_{3-x} improved photo-electro-chemical performance of devices in many applications, probably due to its superior electrical conductivity for improved charge transfer [18–26]. The unusual defective structure and oxygen-vacancy-rich surface are expected to bring about some novel properties.

Herein, we report our success in preparation of nanowires assembled three-dimensional (3D) urchin-like WO_{3-x} nanostructure, and their gas sensor properties towards alcohol vapor detection. Such a structure usually has a high surface area and uniform channels, which is in favor of the gas diffusion and host-guest interactions [3,15]. On the other hand, the oxygen-vacancy-rich surface of sub-stoichiometric WO_{3-x} also provides more active sites than the stoichiometric WO_3 [18]. The oxygen vacancies serve as the shallow donor, leading to faster charge transfer and hence more effective sensor response. As a consequence, the WO_{3-x}

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https://doi.org/10.1016/j.apsusc.2018.02.004
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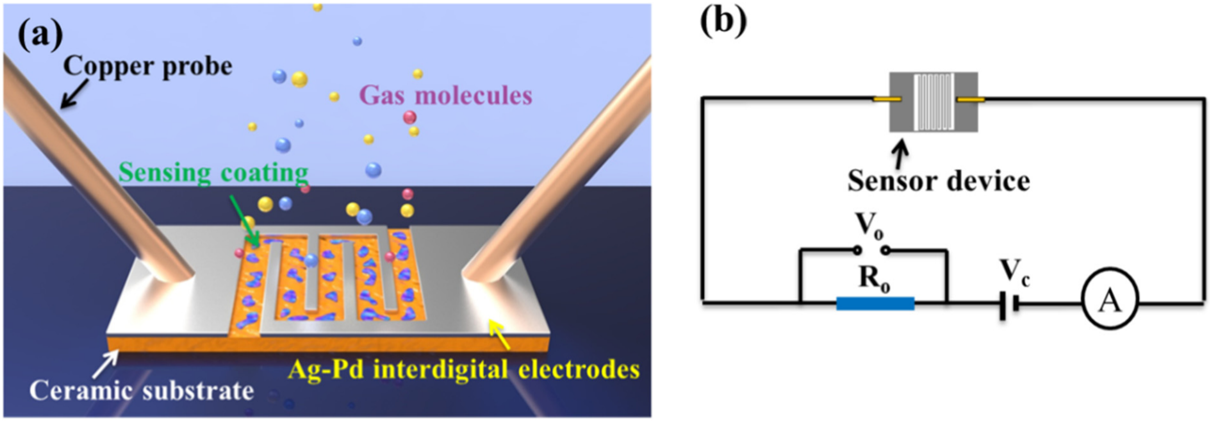

Fig. 1. A schematic of sensor device (a) and measurement configuration (b). The sensing material used for the present work is WO_{3-x} coating.

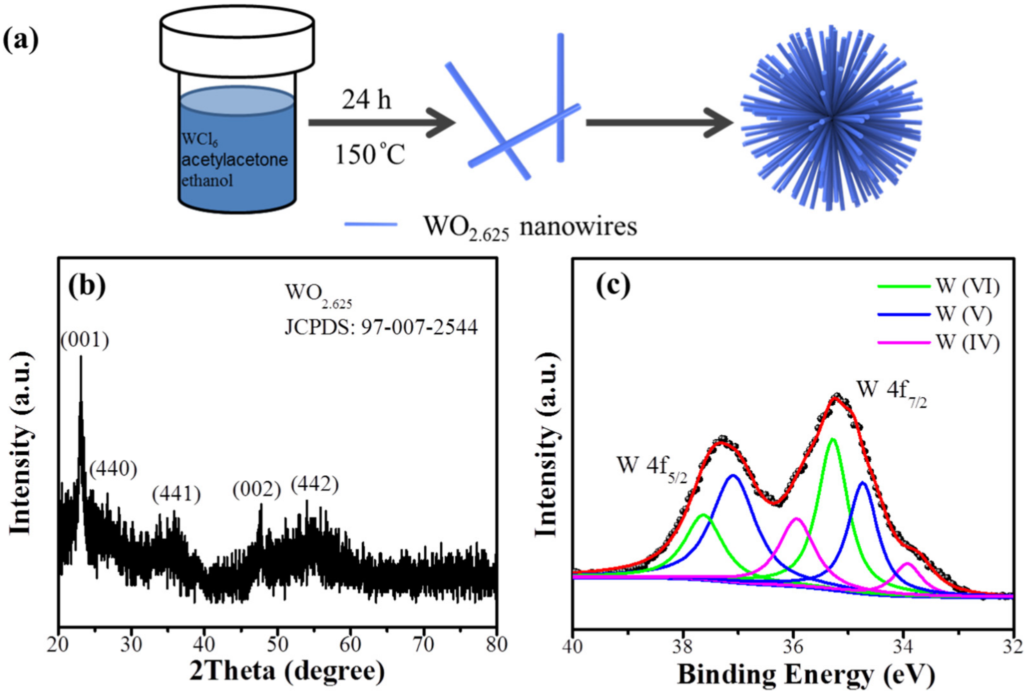

Fig. 2. (a) A schematic illustration of synthesis procedure for the WO_{3-x}; (b) XRD pattern of WO_{3-x} and (c) High-resolution XPS spectra of W 4f.

displayed a superior sensor performance towards alcohol vapor at room temperature without needing any illumination nor thermal treatment [7]. Even though the WO_3 is known to be a *n*-type metal-oxide semiconductor with wide-band-gap of 2.6–3.0 eV [27], however, the sub-WO_{3-x} sensor in this study exhibits a typical *p*-type semiconductor sensing behavior during the sensing measurements at the room temperature. To the best of our knowledge, there is the first report on gas sensors using *p*-type semiconductor WO_{3-x}.

2. Experimental

2.1. Materials

Acetylacetone ($C_5H_8O_2$), ethanol (C_2H_5OH) are from Beijing Chemical Co., Ltd. Tungsten hexachloride (WCl_6) was purchased from Aladdin Industrial Inc. All chemicals were used as received without further purification. All water used was deionized (DI) water purified through a Millipore system.

2.2. Fabrication of WO_{3-x}

0.4 g of WCl_6 was used as the metal precursor dissolved in 50 ml absolute ethanol to form a clear yellow solution. When 0.6 mL of acetylacetone was added into it under active ultrasonication, a dark blue solution was formed immediately. After continuous ultrasonication for about 2 h, the dark blue solution was transferred into a 100 mL Teflon-sealed autoclave, heated in an oven at 150 °C for 24 h. After cooling down to room temperature naturally, the blue solid sample was collected, washed with deionized water and ethanol for three times, and dried at 60 °C for overnight before it was used for device applications.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were performed by a DX-2700 X-ray diffractometer with Cu Kα radiation (k = 0.15418 nm) in 2θ range of 20–80°. The transmission electron microscopy (TEM) images and high-resolution