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# Nanowire (nanorod) arrays-constructed tungsten oxide hierarchical structure and its unique $NO_2$-sensing performances

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ABSTRACT

Novel $WO_3$ hierarchical structure film demonstrates to be a promising material for building highly sensitive and ultrafast responding gas sensors. The individual hierarchical $WO_3$ structure was constructed hydrothermally through double-sided inductive growth of $WO_3$ nanowire (or nanorod) arrays from the central nanosheet. The nanosheet was performed on the substrate via spin-coating and thermal annealing. Composed of well-aligned ultrathin nanowires (nanorods) as building blocks, the as-synthesized hierarchical $WO_3$ shows high active surface area and loose microstructure favorable for gas adsorption and rapid gas diffusion. The $NO_2$-sensing properties of the hierarchical $WO_3$ film-based sensors were evaluated at room temperature over $NO_2$ concentration ranging from 15 ppb to 5 ppm. At room temperature, the $WO_3$ hierarchical structure behaves as an abnormal p-type semiconductor and exhibits unique gas-sensing performances including excellent sensitivity and excellent response characteristics towards $NO_2$ gas. It is found that the sensors based on hierarchical $WO_3$ responses to $NO_2$ gas as low as 15 ppb with an ultrashort response time of short than 5 s at room temperature, highlighting the capability of the material for rapid detection of dilute $NO_2$ at ppb level.



## 1. Introduction

Nitrogen dioxide ($NO_2$) is a highly harmful atmospheric pollutant. It contributes to PM 2.5 and it is also the main source of photochemical smog and acid rain. The fast and reliable detection of toxic $NO_2$ gas is therefore important for both environmental protection and human health. Existing studies have shown that oxide semiconductors are promising materials for facile and reliable detection of various toxic and hazardous gases. In particular, tungsten oxide ($WO_3$), a wide band-gap n-type semiconductor, has exhibited remarkable sensing performance to $NO_2$ gas [1,2].

Semiconductor oxide-based gas sensors rely on the modulation of electrical conductivity due to surface oxidation or reduction caused by gas exposure. The sensing response of a solid-state sensor therefore heavily dependents on the surface structure and morphology of its sensing material used [3,4]. Towards this end, various low-dimensional tungsten oxide nanostructures with high surface-to-volume ratio have been widely examined, including nanoparticles [5], nanowires/nanorods [1,2,6], and nanotubes [7]. They achieve much high sensitivity to $NO_2$ gas and gas sensitivity increases rapidly when the dimensions of the oxide nanostructure become comparable with or smaller than Debye length [8]. However, nano-scale materials easily aggregate to form large and dense secondary aggregates such as much larger particles or relative thicker bundles due to strong and inevitable van der Waals attraction. Such aggregation leads to considerable decrease in active surface area for gas adsorption and difficult diffusion of gas molecules in sensing films. The agglomeration becomes more serious when the sensor operates at high temperature. To date, achieving both high sensitivity and rapid response remains challenging for the gas sensors based on low-dimensional semiconductor oxides. In this aspect, how to keep structure stability of the low-dimensional oxide materials is primarily crucial.

Hierarchical structure is a kind of high dimensional micro-/nano-structure composed of many low-dimensional, nanostructured building blocks (particles, rods, wires, or sheets). Hierarchical structure shows a well-developed porous texture as well as a non- or less-agglomerated feature without scarifying high surface area from the nano-constituents; it is therefore very attractive for efficient gas sensor with high sensing performance [9]. Sensing materials using well-designed hierarchical structures are expected to achieve both high gas response and fast response speed. For instance, $SnO_2$ hierarchical microspheres self-assembled from nanosheets show both the ultra-

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fast response (~1 s) and high sensitivity to 50 ppm $C_2H_5OH$ at operating temperature of 400 °C [10]. The sensor based on hierarchical $ZnSnO_3$ hollow microspheres from ultra-thin nanorods presents very short response and recovery times of 0.9 and 2.2 s respectively, to ethanol vapor at 270 °C [11]. High sensitivity and fast response to ethanol are also observed at room temperature and 250 °C from hierarchical vanadium pentoxide with radially oriented ultrathin nanoneedles and nanoribbons as constituents in our group [12]. The excellent response properties exhibited by above hierarchical structures are all because of the good surface accessibility and the high surface area of ultrathin building blocks. As to tungsten oxide, the synthesis and applications of its hierarchical structure in gas sensor has not been well studied. Up to now, successful assembly of hierarchical $WO_3$ microspheres from nanorods or nanosheets has been realized [13,14], and the nanosheets-constructed $WO_3$ hierarchical spheres are found to show enhanced sensitivity to ppm-level $NO_2$. In this work, a novel $WO_3$ hierarchical structure is hydrothermally constructed through double-sided inductive growth of $WO_3$ nanowire (nanorod) arrays on preformed nanosheet. The constituents of the highly ordered arrays of ultrathin nanowire (nanorod) provide favorable microstructure for gas adsorption and rapid gas diffusion. It is found that the developed hierarchical $WO_3$-based sensors are capable of dilute $NO_2$ detection at ppb level (15 ppb) with superfast response about 1–5 s at room temperature. Meanwhile, good selectivity and stability are also achieved.

## 2. Experiments

### 2.1. Synthesis and characterization of $WO_3$ hierarchical structure

$WO_3$ hierarchical structure films were in-situ prepared on cleaned alumina substrate with a pair of interdigitated Pt electrodes in 100 nm thickness via a hydrothermal method. The electrodes were deposited using RF magnetron sputtering process. For the hydrothermal growth of the hierarchical $WO_3$, a thin $WO_3$ induction layer was firstly preformed on the electrodes-attached substrate by spin coating of precursor solution, followed by thermal annealing. The precursor solution was prepared as follows: 2.5 g sodium tungstate hydrate ($Na_2WO_4 \cdot 2H_2O$) and 1 g potassium chloride (KCl) were dissolved in 15 ml de-ionized water under magnetically stirring. Then 3 ml HCl solution (37 wt%) was added dropwise into the above solution to form a milky suspension. After heating the suspension to 40 °C, 2 ml $H_2O_2$ was then added under vigorously stirring to obtain the yellow precursor solution. To prepare the $WO_3$ induction layer, a cycled spin coating procedure was then performed. More specifically, the above as-prepared precursor solution was spin-coated onto the cleaned electrodes-attached alumina substrate, and subsequently, the wet substrate was baked for 10 min at 80 °C in a drying oven. During spin coating, a physical mask was used to avoid the presence of the solution at the end of the electrodes. The above spin-coating and baking procedures were repeated for four times to ensure a uniform distribution and adequate coverage of the $WO_3$ particles on the substrate. Finally, the obtained substrate was annealed at 550 °C in ambient atmosphere for 1–3 h to transform the precursor into nanosheet-like $WO_3$ particles to induce the subsequent growth of one-dimensional (1D) $WO_3$ arrays and to guarantee adhesion between the induction layer and the substrate.

In the following hydrothermal step, the well-aligned 1D $WO_3$ nanowires (nanorods) were grew from both sides of the tungsten oxide nanosheets simultaneously to form hierarchical structure film on the induction layer-coated substrates. In a typical synthesis procedure, 6 g $Na_2WO_4 \cdot 2H_2O$, 2 g KCl, and 0.4 g P123 surfactant were first co-dissolved in 160 ml deionized water under magnetically stirring. Then the PH value of the mixture solution was adjusted to 2.1–2.5 with a proper volume of HCl (37 wt%). This solution was further aged for about 15 min at room temperature before performing hydrothermal process. After submerging and sealing the induction layer-coated substrates in above resultant solution in a 200 ml Teflon-line autoclave, the hydrothermal reaction was conducted at 180 °C for 9 h in an electric oven. After that, the autoclave was cooled naturally to room temperature. The substrates with products were washed several times with deionized water and ethanol, respectively. Finally, the substrates were dried at 80 °C for 5 h at ambient atmosphere. The resultant samples were directly used as sensors to carry out the sensing performance evaluation.

The morphology and crystalline structures of hierarchical $WO_3$ were characterized using field emission scanning electron microscope (FESEM, Hitachi S-4800), X-ray diffractometer (XRD, RIGAKU D/MAX 2500 V/PC, Cu Kα radiation) and field emission transmission electron microscope (FETEM, TECNAI $G^2$F-20).

### 2.2. Evaluation of gas-sensing properties

The gas-sensing properties of as-prepared $WO_3$ hierarchical structure were evaluated at room temperature in a home-built static gas-sensing characterization system consisting of a glass test chamber (30 L), a flat heating plate, and two sets of data acquisition systems [15], which permits two samples measured simultaneously. This test equipment is equipped in a humidity-controlled testing room. Appropriate volume of pure $NO_2$ gas was injected into the test chamber directly to get the desired concentration. The resistance change of the sensor during the whole measurement was continuously monitored by an UNI-T UT61E professional digital multimeter with the function of automatic measuring range adjustment. The sampling interval was set to 1 s, and the acquired resistance data were stored in a PC for further analysis. After hydrothermal reaction and subsequent washing, the tungsten oxide film was found to grow only on the area precoated with tungsten oxide induction layer. The bare section of Pt electrodes therefore can be used to realize the electrical connection between the sensor and the digital multimeter. To minimize the effect of humidity fluctuation on the gas-sensing properties, the whole measurement was carried continuously. During the measurement, the ambient relative humidity is about 30–35% and the room temperature is about 20 °C.

## 3. Results and discussion

### 3.1. Structure and characterization

In this work, we employ a hydrothermal process to directly synthesize three-dimensional (3D) hierarchical tungsten oxide film on sensor substrate with 1D nanowires or nanorods as building blocks. The typical morphological characteristic of the as-synthesized tungsten oxide hierarchical structure from 1 h-annealed induction layer after hydrothemal reaction of 9 h at 180 °C is illustrated by FESEM observations with different magnifications in Fig. 1. Observe that the well-oriented 1D oxide nanowire arrays grow from both sides of the central nanosheets simultaneously, constructing a kind of 3D hierarchical structure film. Fig. 1(b) and (c) shows the high magnification FESEM images of an individual tungsten oxide hierarchical structure. Clearly, the central nanosheet acts as the architectural core of the whole hierarchical structure, and the constituents of nanowires align perpendicular to its both sides. It can also be observed that each nanowire shows a very small diameter of about 20 nm and the central nanosheet has thickness of about 10 nm. This ultrathin feature of the nanowires and nanosheet is much favorable for achieving high sensitivity when exposure to a detected gas. On the other hand, the ultrathin nanowires trend to assemble together near their tips forming bundles due to much high surface energy [16]. This would affect the alignment of the nanowire arrays in some degree.

The growth process of tungsten oxide hierarchical structure can be effectively illustrated by intercepting intermediate product with much shorter growth time. Fig. 2(a) and (b) gives the low magnification and high magnification FESEM images of the product after hydrothermal reaction of 4 h at 180 °C. The inset in Fig. 2(a) shows the SEM image of the tungsten oxide induction layer formed on the substrate after annealing at 550 °C for 1 h, which is composed of stacked ultrathin nanosheets with thickness in 20–40 nm. The maximum size of these nanosheets is less than 2 μm. After hydrothermal reaction of 4 h, many short and ultrathin nanorods grow vertically from both surfaces of the nanosheets in induction layer to transform into an integrated hierarchical structure. Further TEM characterization in Fig. 2(c) gives us a clearer vision that the double-sided nanorods have an average diameter of about 10 nm and meanwhile exhibit high orientation. Extending the reaction time to 9 h results in the bilateral nanowire arrays with longer length and larger diameter (Fig. 1). When the reaction time is shorter than 2 h, no objective nanorods are observed on the surface of nanosheets.

The above results unambiguously demonstrate the induction of the preformed nanosheets in constructing tungsten oxide hierarchical structures. They serve as the architectural rachises of tungsten oxide hierarchical structures to support the bilateral