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Hydrothermal deposition of tungsten oxide monohydrate films and room temperature gas sensing performance

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ABSTRACT

Tungsten oxide monohydrate ($WO_3 \cdot H_2O$) films on glass substrates were prepared by hydrothermal deposition without using any additives. The resulting crystals were single crystalline and possessed microplate-like shape with preferred growth in the two dimensions perpendicular to [010] direction. Many of the $WO_3 \cdot H_2O$ microplates were found to embed into each other, forming interesting interlocking configuration. The initial distance among the nuclei was considered to play decisive role in the formation of the interlocking structure. Gas sensing tests showed that at room temperature the $WO_3 \cdot H_2O$ films could detect 20 ppm of NO_2 gas. The room temperature-based measurements guaranteed that the collected data really came from the $WO_3 \cdot H_2O$ itself rather than from the dehydrated product that would be easily formed if elevated measurement temperature was applied. Such an additive-free method to prepare $WO_3 \cdot H_2O$ films is promising to provide good candidate materials for applications like gas sensing, solar energy conversion, and so on.

1. Introduction

Tungsten oxide (WO_3) is a class of n-type semiconductor material with band gap of 2.5–2.8 eV [1] and has attracted great interests due to its wide applications in electrochromic devices [2], gas sensors [3], photoelectrochemical devices [4], and dye-sensitized solar cells [5]. Many efforts have been dedicated to various research contents about WO_3, including preparation method [6], nanostructure [7] and morphology control [8], properties [9], and so on [10]. In comparison with the tungsten oxide, tungsten oxide monohydrate ($WO_3 \cdot H_2O$), however, was studied in a much smaller extent. Actually, in most cases $WO_3 \cdot H_2O$ was used as precursor material to prepare WO_3 by heat treatment [11,12], and studies on the properties of $WO_3 \cdot H_2O$ itself were relatively few. Zeng et al. reported the gas sensing performance of $WO_3 \cdot H_2O$ with different morphologies prepared by a hydrothermal synthesis [13]. Ahmadi et al. investigated the current vs. voltage characteristics of $WO_3 \cdot H_2O$ nanoribbons and found the material possessed the behavior of Schottky diode [14]. $WO_3 \cdot H_2O$ was also utilized to degrade some organic molecules like Rhodamine B [15] and methylene blue [16]. The electrochromic and broadband dielectric properties of $WO_3 \cdot H_2O$ were also reported [17,18]. These reports illustrated that the tungsten oxide monohydrate is also one kind of very promising material and thus it is worthy of being studied in a more extensive and intensive manner.

Up to now, tungsten oxide monohydrate was mainly prepared via the solution-based method. In these syntheses, some special additives like tartaric acid [19], Na_2SO_4/K_2SO_4 [20,21], oxalicacid [21], poly(vinyl alcohol) [18], and so on, were often utilized in order to control the crystal morphology and by now tungsten oxide monohydrate in the form of nanoribbons [14], nanosheets [22,23], nanoflowers [24] and nanorods [13,18] have been successfully prepared. Although the use of additives could manage to direct the morphology and structure of the crystals, it simultaneously brings the risk of contaminating the products thereby limiting their potential applications. In addition, the reported syntheses were

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usually carried out at low reaction temperatures. For example, some preparations were conducted at temperatures as low as 40–60 °C [23,25]. In this case, however, very long reaction time even more than several days was needed. Therefore, exploit environmentally benign and at the same time not time-consuming synthetic processes to prepare tungsten oxide monohydrate is still a great task.

Gas sensing ability to some harmful gases like NO_2 [26,27], acetone and formaldehyde [28] is one of the important properties of WO_3-based materials. Such studies, however, were mainly carried out on anhydrous WO_3 and few were reported on tungsten oxide monohydrate. In the reference [13], $WO_3 \cdot H_2O$ was reported to show good response to ethanol, however, the data were collected from the sensors that were firstly undergone heat treatment at 350 °C. Under that conditions, however, $WO_3 \cdot H_2O$ would be easily converted to WO_3 by losing the coordinated water [29]. Therefore, for $WO_3 \cdot H_2O$, it is very important to conduct the gas sensing test at mild temperature to ensure that the measured gas sensing performance is really originated from the $WO_3 \cdot H_2O$ rather than from other crystal phases like $WO_3 \cdot 0.33\ H_2O$ or WO_3. In other hand, low test temperature itself is an advantage for a gas sensor because in principle the work conditions of a device are simpler, its potential of being utilized in real world applications is bigger.

In the present work, $WO_3 \cdot H_2O$ plate-like crystal films on glass substrates were deposited directly by hydrothermal process. The reaction was conducted under mild conditions and without using any morphology- and structure-directing agents. It was found that many of the well-defined $WO_3 \cdot H_2O$ microplates were embedded into each other and formed an interesting inter-locking structure. The probable formation mechanism of the embedding structure was discussed. Room temperature gas sensing tests revealed that the directly deposited $WO_3 \cdot H_2O$ plate-like crystal films possessed good response to NO_2 gas.

2. Material and methods

2.1. Materials

$Na_2WO_4 \cdot 2H_2O$ and concentrated nitric acid were purchased from Damao Chemical Reagent Plant, Tianjin. Glass substrates were purchased from Xintai Medical Equipment Factory, Yancheng. All materials were used without further purification.

2.2. Preparation of $WO_3 \cdot H_2O$ films

$WO_3 \cdot H_2O$ films on glass substrates were fabricated by two times deposition. Firstly, 6 mL of 0.15 mol L^{-1} HNO_3 aqueous solution was added into 6 mL of 30 mmol L^{-1} Na_2WO_4 aqueous solution, keeping stirring for 5 min. The mixed solution was poured into a stainless steel autoclave with a 20 mL of Teflon liner and then put one piece of clean glass substrate (25 mm × 19 mm × 1.1 mm) into it and sealed the autoclave. After heated at 90 °C for 10 h, the autoclave was allowed to cooled down to room temperature naturally. The glass substrate with deposited film was taken out of the autoclave and soaked in deionized water for 2 h and then put into a autoclave with fresh reaction solution to conduct the second deposition under identical conditions with the first deposition. Finally, the as-prepared film on glass substrate was soaked in deionized water for 2 h and then dried at 50 °C for 4 h.

2.3. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded in the range of $2\theta = 10–60°$ on an X-ray diffractometer (Bruker D8 Focus) with Cu Kα1 radiation ($\lambda = 0.15406$ nm) at room temperature while the voltage and electric current were held at 40 kV and 40 mA, respectively. The morphology and microstructure of the films were observed on a scanning electron microscope (SEM, FEI Quanta FEG 250) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). To conduct the SEM observation, a small piece of sample was adhered onto a copper stub using double-sided carbon tape. Thermogravimetry (TG) was performed in air flow with a Perkin–Elmer Diamond TG/DTA Instrument at a heating rate of 10 °C min^{-1}.

2.4. Sensor fabrication and tests

Gas sensors were fabricated by coating two parallel silver lines with a distance of 1 mm onto the $WO_3 \cdot H_2O$ film. The gas sensing tests were performed in a homemade airtight chamber similar to that described in the previous report [30]. After stabilized at 50 °C for 2 h and cooled down to room temperature, the sensors were put into the chamber and connected to the external test circuit through metal tweezers. During the tests, clean dry air flow and static NO_2/dry-air mixed gas were introduced into the chamber alternately. The electric current was recorded by an Agilent B2902A Precision Source/Measurement Unit and was used to evaluate the gas sensing performance of the sensors.

3. Results and discussion

The crystal phase of the hydrothermally deposited films on glass substrates was confirmed by the X ray diffraction (XRD). As shown in Fig. 1, the XRD pattern of the film shows sharp and strong diffraction peaks, indicating the well crystalline nature of the product. All the peaks can be indexed to the orthorhombic tungsten oxide monohydrate ($WO_3 \cdot H_2O$, see the reference bar-chart, PCPDF No. 84-0886, bottom of Fig. 1), and no peaks belong to other than $WO_3 \cdot H_2O$ phase were observed, indicating that the deposited film is composed of orthorhombic $WO_3 \cdot H_2O$. In addition, the XRD pattern shows much enhanced (020) and (040) peaks in comparison with the reference data. Such enhancement generally originates from the preferred orientation of the structure, which sometimes is due to the preferred growth direction of the crystals [31] and sometimes is a result of the oriented arrangement of the polycrystals [32]. The reason in the present study that cause the preferred orientation of the structure will be discussed later together with the morphology analysis.

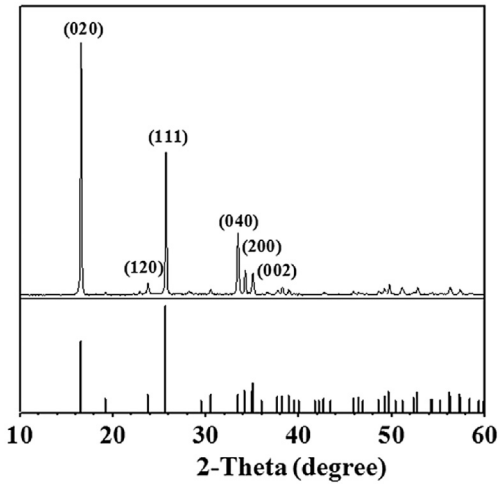

Fig. 1. XRD pattern of the deposited film. The bottom shows the reference bar-chart of orthorhombic $WO_3 \cdot H_2O$, PCPDF No. 84-0886.