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# Preparation and gas sensing properties of flower-like $WO_3$ hierarchical architecture

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ABSTRACT

Flower-like $WO_3$ hierarchical architecture has been successfully synthesized through a facile hydrothermal method. The morphology and structure were investigated via X-ray diffraction, field-emission scanning electron microscopy, and transmission electron microscopy. The results indicated that the flower-like $WO_3$ were self-assembled by many ultrathin petal-like nanosheets with thickness of several nanometers. A possible formation mechanism of 3D hierarchical architecture was proposed on basis of time dependent experiments. In addition, the well-defined $WO_3$ hierarchical architectures exhibited high response and good selectivity to ethanol at 300 °C with fast response (5–7 s) and recovery (6–9 s) properties, which might substantially benefit from their layer-by-layer ultrathin petal structure.



## 1. Introduction

Recently, increasing concerns for environmental monitoring and healthcare have led to the growing interest in high-performance gas sensors due to the steady increase in average life expectancy [1,2]. High sensitive and rapid response-recovery characters are imperatively necessary for real-time monitoring of harmful gases to prevent possible disasters [3]. As an important n-type semiconductor, tungsten oxide ($WO_3$) has been proved to be a promising gas-sensing material for sensitive detection of various toxic and dangerous gases [4,5]. Recent research suggests that $WO_3$ with three-dimension (3D) hierarchical architecture often exhibits superior performance for gas sensor because of their high specific surface areas and excellent structural stability, as well as their outstanding surface accessibility [6]. Furthermore, a proven strategy is to tune at least one of the three dimensions of the materials into Debye length ($L_D = \sqrt{\varepsilon_0 \varepsilon_r K_B T / q^2 n_b}$) scale [7,8]. It is believed that when the size of the interacting unit becomes comparable with or smaller than $L_D$, an abruptly increasing proportion of atoms will directly participate in gas sensing reactions, resulting in excellent gas-sensing performance. Yet the simple and cost-effective synthesis techniques remain a significant challenge.

Ethanol, as an important chemical raw material, has been widely used in chemical industry, medicine, paint, cosmetics, etc. But it is volatile and flammable, and the long time exposure to ethanol vapor will result in health problems such as headache, liver damage and central nervous system disorders. Studies show that the maximum recommended exposure level of ethanol is 1000 ppm [9,10]. Moreover, the precise quantitative detection of ethanol vapors is an urgent demand for many other applications, such as the wine quality improvement, breath detector for identifying drunk drivers [11], and product quality monitoring in the beverage, food, and other industries [12], which indicate that the precise detection of ethanol at ppm levels is required. Therefore, the cost effective methods and the high performance of ethanol sensors are highly necessary.

Here, we report a successful synthesis of hierarchical flower-like $WO_3$ (FL-$WO_3$) architectures assembled by ultrathin nanosheets via a facile hydrothermal route with the assistance of the PVP. We also investigate the crystalline structure, morphology, and ethanol-sensing behaviors, based on which a growth mechanism is proposed for the well-defined architectures. The sensing investigations indicate that the FL-$WO_3$ sensors not only show highly sensitive and selective response upon exposure to ethanol, but also exhibit fast response-recovery properties and good repeatability, even to the low-concentration ethanol.

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## 2. Experimental

### 2.1. Synthesis

In a typical synthesis process, 2.0 g $Na_2WO_4 \cdot 2H_2O$ was dissolved in 25 ml deionized water (with ice-water bath) under magnetic stirring to get a transparent solution. Then 6 mol/L hydrochloric acid (HCl) solution was slowly dropped into the upper solution until the light yellow precipitates (just the pH value to 1.0), followed by adding 0.9 g polyvinyl pyrrolidone (PVP) into the solution. The mixture was transferred into a 50 ml Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 18 h. After being cooled to room temperature, yellow-colored powders were collected by centrifugation and washed with deionized water and absolute ethanol several times prior to dry in air at 80 °C for 10 h. Then, the FL-$WO_3$ product was obtained.

### 2.2. Characterization

Microstructures of the product were characterized by X-ray diffraction (XRD, Rigaku Ultima III) with a Cu Kα (λ = 1.5418 Å), field emission scanning electron microscopy (FE-SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, JEOL JEM-2100).

### 2.3. Fabrication and measurement of gas sensors

Fig. 1a is the schematic of the gas, in which a pair of Au electrodes was printed on both sides of the ceramic tube, while a Pt resistance heater inside of the ceramic tube was used to control the temperature of sensor. The final sample was grounded in an agate mortar and mixed with deionized water to form a paste and then the paste was coated on a ceramic tube. After sintered at 500 °C for 2 h to get good stability and welded onto the pedestal, a side-heated gas sensor was formed (inset of Fig. 1a).

A stationary state gas distribution system was used for sensing property measurements (WS-30A, Winsen Electronics Co. Ltd., Zhengzhou, China) as shown in Fig. 1b. Saturated target gas or vapor was injected into the chamber (18 L) through an inlet port and the resistance was measured as a function of time by the analysis system automatically. Then the sensor was exposed to the atmospheric air by opening the chamber and the experiments were repeated. The response ($R$) was defined as $R_a/R_g$, where $R_a$ and $R_g$ were the resistance of the sensor in air and test gas, respectively. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption. According to the reference [13], the volumes of gas or liquid corresponding to different concentrations can be obtained. The humidity in the test chamber was 37% RH.

## 3. Results and discussion

### 3.1. Structure and morphology

Fig. 2a shows the typical XRD pattern of the sample. As can be seen, all diffraction peaks coincide well with those given by the JCPDS card No.43-1035 for monoclinic $WO_3$ with space group P21/n and lattice parameters of $a$ = 7.299 Å, $b$ = 7.539 Å, $c$ = 7.687 Å, beta = 90.91 °C. No diffraction peaks of any other impurities were observed, revealing the high purity of the prepared $WO_3$. The strong and sharp peaks indicate that the products are highly crystallized.

Fig. 2b displays panoramic SEM image of the FL-$WO_3$. The flowers are constructed by many special nanosheets looking like petals and the hierarchical structures disperse uniformly with a mean diameter of about 2–4 μm. Further enlarged image of an individual microflower (Fig. 2c) reveals that the nanosheets are thin and well-arranged with the irregular edges. They show a radial fashion as flowers bloom naturally, forming an open porous structure. The typical TEM image of the microflowers is given in Fig. 2d which clearly presents that the loose-packed nanosheets are assembled into the FL nanostructure. There are a lot of opening spaces between the nanosheets, which is in agreement with the SEM observation. The corresponding HRTEM image (Fig. 2e) indicates more details of the product structure. The thickness of the nanosheet is about 8.7 nm and the mean value distance between the two lattice fringes is 0.384 nm, which is in good agreement with the theoretical spacing for (002) planes of the monoclinic $WO_3$ structure.

### 3.2. Possible grown mechanism of FL-$WO_3$ nanostructure

To better understand the formation mechanism of this novel FL-$WO_3$, their growth process has been further investigated by examining the products collected at different intervals during the hydrothermal process (Fig. 3a–d) and the possible formation process of the novel structure is illustrated in Fig. 3e. As shown in Fig. 3a, numerous nanoparticles with the diameter of about 7–25 nm have been obtained after one hour's hydrothermal reaction. It is well known that high precursor supersaturation levels facilitate nucleation, while low ones benefit crystal growth. At the initial stage, $H_2WO_4$ precipitate firstly formed after HCl was added into $Na_2WO_4$ solution. Then numerous $WO_3$ crystal nuclei were formed through the decomposition of $H_2WO_4$ and the nucleation dominated for the high precursor concentration.

When the time reached 6 h, the reaction entered the crystal orientation growth stage: with the driving force of electrostatic interaction, the nuclei tended to aggregate randomly and shared a mutual crystallographic orientation by means of self-organization of adjacent particles, then grew into nanosheets with the PVP

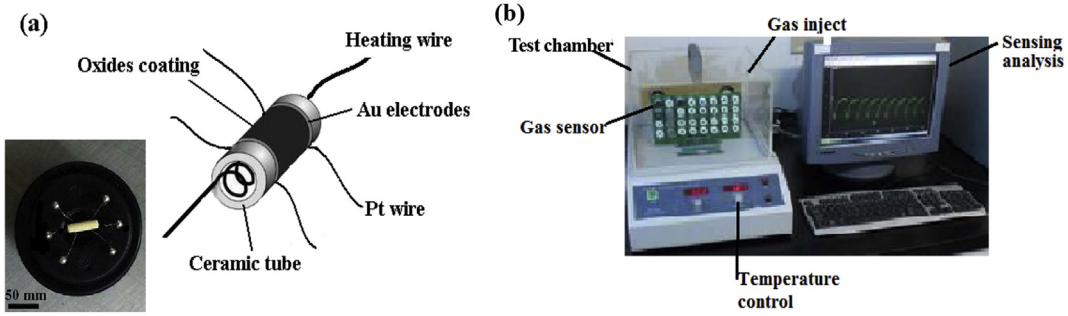


**Fig. 1.** Schematic illustrations of (a) the gas sensor and (b) the experimental setup.