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# Single-crystalline porous nanosheets assembled hierarchical $Co_3O_4$ microspheres for enhanced gas-sensing properties to trace xylene

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ABSTRACT

Hierarchical porous (HP) nanostructures of p-type metal oxide have attracted great attention in gas-sensing application due to their less agglomerated configurations and the advantages for gas diffusion. However, the contacts between grain boundaries around pores of HP nanostructures are usually too fragile to resist the shear force caused by ultrasonic treatment during sensor fabrication processes and the thermal stress produced from high operating temperature. To solve this problem, uniform $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets were synthesized by an ethylene glycol (EG) mediated solvothermal method with the co-assistant of water and polyvinyl pyrrolidone (PVP). Due to the structural stability of single-crystalline nanosheets, the as-synthesized HP $Co_3O_4$ is well kept during the sensor fabrication processes. Moreover, the $Co_3O_4$ shows a high response ($R_g/R_a$ = 74.5–100 ppm) to xylene at the optimized temperature (150 °C), which is almost 4 times larger than that of commercial $Co_3O_4$ (19.1). It also exhibits excellent long-term stability with small deviations (less than 6%) for two months, which can be ascribed to the structural stability of single-crystalline nanosheets. Combined with their high selectivity and low detection limit, the as-prepared HP $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets are highly promising gas-sensing materials for xylene detection.
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## 1. Introduction

Metal-oxide semiconductor nanomaterials, including n-type and p-type oxides, have been widely used as gas-sensing materials for monitoring air quality due to their low cost, high sensitivity, and excellent stability [1]. At present, most efforts in the field of metal oxide gas sensors have been devoted to n-type oxide semiconductors, while the gas-sensing properties of the p-type oxide semiconductors have received relatively little attention [2]. Compared with n-type oxide, p-type oxide chemiresistors have distinct advantages in selective oxidation of volatile organic compounds (VOCs) and low working temperatures owing to high catalytic effect with regard to oxidation, favorable redox behavior, and abundant oxygen adsorption [3]. Among the p-type oxide semiconductors, $Co_3O_4$, with an indirect band gap in the region of 1.6–2.2 eV, is a good candidate in gas-sensing field [4]. Generally, the gas-sensing properties of $Co_3O_4$ are strongly dependent on their morphologies and structures [5]. In this case, the gas-sensing properties of $Co_3O_4$ can be optimized by structural design.

Among different kinds of structures, hierarchical porous (HP) structures are always desired in the field of gas-sensing application due to the unique advantages, such as numerous pores for gas transport, abundant active sites for surface reactions, etc [6,7]. However, the contacts between grain boundaries around pores of HP nanostructures are usually too fragile to resist shear force caused by ultrasonic treatment during sensor fabrication processes and thermal stress from high operating temperature [8–10]. For example, after ultrasonic treatment and subsequent sensor fabrication process, hierarchical $SnO_2$ microrods assembled by nanoparticles were serious damaged and only a small fraction of microrods was remained [9]. To solve this problem, many strategies have been developed. For example, metal oxides with HP structures were synthesized in situ on the surface of gas sensors to avoid the damage from sensor fabrication processes [11,12]. However, the fragile feature of HP structures is not improved fundamentally, leading to a weak strength in resisting thermal stress from high operating temperature. Therefore, to improve the gas-sensing properties, a HP

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structure with firm contact between grain boundaries around pores is thus urgently needed.

Recently, single-crystalline porous structures have attracted much attention due to their unique properties such as excellent structural stability and high degree of crystallinity [13,14]. For example, benefited from structural stability of single-crystalline structure, single-crystalline porous ZnO nanosheets exhibited high response and significant long-term stability [15]. In a single-crystalline porous structure, there exist no grain boundary around the pores but strong chemical bonds between atoms, leading to a firm and indestructible property. Accordingly, single-crystalline porous structures are regarded as good candidates to resist the damage from the sensor fabrication processes and thermal stress from high operating temperature. In addition, single-crystalline porous building blocks can also serve as electrical pathways for charge-carrier transfer in the process of gas-sensing reaction, which is much beneficial for their gas-sensing performances [16]. In contrast, the grain boundaries act as electron captures, thereby hindering efficient electron transport. Therefore, there is of great significant to design and synthesis hierarchical $Co_3O_4$ assembled by single-crystalline porous building blocks in order to optimize the performances of gas sensors.

In this paper, uniform hierarchical $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets were synthesized by an EG-mediated solvothermal method with the co-assistant of water and PVP as a soft template. The formation mechanism is explored. Benefiting from the structural stability of single-crystalline nanosheets, the HP structure of $Co_3O_4$ can be well kept during the sensor fabrication processes. Moreover, this $Co_3O_4$ with well-kept HP structure shows a high response to 100 ppm xylene ($R_g/R_a$ = 74.5) at the optimized temperature (150 °C). Moreover, it exhibits excellent long-term stability with small deviations (less than 6%) for two months, which can be ascribed to the structural stability of single-crystalline nanosheets. With their high selectivity and low detection limit, the as-prepared hierarchical $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets are highly promising for xylene detection.

## 2. Experimentation

### 2.1. Synthesis of HP $Co_3O_4$

All the chemical reagents used were of analytical grade and used without further purification. The uniform hierarchical $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets were prepared via two steps. First, 1 g of cobalt acetate ($Co(AC)_2{\cdot}4H_2O$) was added to 80 mL of mixed solution of EG and distilled water. Then, 0.05 g polyvinyl pyrrolidone (PVP) was added into the above solution. After vigorous stirring for 30 min, the violet mixture was transferred into a 100 mL Teflon-lined autoclave, sealed and heated at 180 °C for 12 h. The system was then allowed to cool down to room temperature naturally. The precipitate was collected by centrifuging, washed with distilled water and absolute ethanol for seven times, and then dried in vacuum. Second, the obtained precursor was oxidized in air at 350 °C for 2 h and the as-expected $Co_3O_4$ was obtained.

### 2.2. Sensor fabrication and measurements

The sensors were fabricated as follows. First, a certain amount of HP $Co_3O_4$ was uniformly dispersed in ethanol by ultrasonication for 15 min to form a suspension. Second, several drops of the suspension were deposited onto a ceramic flat which had been coated with Au electrodes. After the ethanol evaporated, a $Co_3O_4$ film was left on the electrode. The as-prepared $Co_3O_4$ film was oxidized at 350 °C in air atmosphere. For the convenience of description, the as-obtained element was named as HP-$Co_3O_4$. As a comparison, another gas sensor based on commercial $Co_3O_4$ (50–100 nm) was also fabricated under the same processes, which was named as C-$Co_3O_4$. The gas-sensing properties were characterized in a static testing instrument (Wuhan Hua Chuang Rui Ke Co. Ltd) including a test chamber (about 30L in volume) and a personal computer as shown in Fig. S1. During the gas-sensing tests, the target gases were injected into the test chamber. After a few minutes, the chamber was lifted to introduce ambient air (humidity: 16–22%). Meanwhile, the electrical resistance of the sensors was captured and displayed by the personal computer. The gas-sensing response was calculated by the resistance ratio $R_g/R_a$, where the $R_g$ and $R_a$ stood for the electrical resistance in the tested gas and in dry air, respectively. The response time was evaluated by the time to reach 90% variation of the sensor resistance upon exposure to xylene. Here, due to the low operating temperature, the recovery rate of these sensors may be slow and only a parts of resistance data during the recovery process was recorded. The recovery rate thus was calculated by the ratio between ($R_g$-$R_{air\text{-}recovery}$) and ($R_g$-$R_{fresh}$), Where $R_{fresh}$ and $R_{air\text{-}recovery}$ stood for the resistance before exposure to the detected gas and after subsequent exposure to air for 100 s [17].

### 2.3. Characterization

The crystal structure of HP-$Co_3O_4$ and C-$Co_3O_4$ scraped from sensing film was examined on Philips X'pert X-ray diffractometer with Cu Kα1 radiation from 20° to 80°. ZEISSEVO microscope was selected to test the morphology of HP-$Co_3O_4$ and C-$Co_3O_4$ scraped from sensing film which was operated at an acceleration voltage of 15 kV. The transmission electron microscopy (TEM) images of HP-$Co_3O_4$ were measured by using JEM-2100 microscope working at 200 kV. The nitrogen adsorption-desorption isotherms were acquired by using BELSORP-mini II.

## 3. Results and discussion

### 3.1. Structure and morphology

The typical morphologies of the as-prepared products before and after calcination were firstly investigated by SEM. Fig. 1 shows the general morphology of the as-prepared cobalt-containing precursors before calcination. It indicates that the cobalt-containing precursors are composed of uniform microspheres with diameters of 3–4 μm (Fig. 1a and b). Fig. 1c and d reveal that these microspheres are consisted of many two dimensional (2D) nanosheets. All of these 2D nanosheets intercross with each other, forming a firm microsphere structure. Moreover, it can be observed that these 2D nanosheets possess smooth surface without any pores in Fig. 1d.

The hierarchical $Co_3O_4$ microspheres assembled by single-crystalline porous nanosheets were generated after oxidation of the obtained precipitates from solvothermal treatment. Fig. 2 shows the XRD patterns of the corresponding products. All the diffraction peaks of the samples belong to JCPDS No. 42-1467. The diffraction peaks at 31.4°, 37°, 38.8°, 45°, 55.9°, 59.6° and 65.6° can be respectively indexed to (220), (311), (222), (400), (422) and (511) reflections. Importantly, no diffraction peaks from any other impurities are detected in the HP-$Co_3O_4$, indicating the high purity of the as-synthesized HP-$Co_3O_4$. Moreover, the as-obtained $Co_3O_4$ still maintain microsphere morphology, as proved by Fig. 3a, b. All of these uniform microspheres have the diameter of 3–4 μm which are also composed of many crossed 2D nanosheets as shown in Fig. 3c, d. The unaffected morphology after thermal treatment satisfies the definition of topology, indicating the as-prepared HP microsphere structures were obtained in the manner of topological

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