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# Effect of the sheet thickness of hierarchical $SnO_2$ on the gas sensing performance

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ABSTRACT

A unique hierarchical $SnO_2$ nanoflower was successfully synthesized via a facile one-step hydrothermal method. The nanoflower was analyzed in detail using X ray diffraction, field-emission electron microscope and transmission electron microscope. It was found that the nanoflowers are all assembled from nanosheets. The nanosheet thickness could be precisely controlled by tuning the dosage of NaOH. Gas sensing tests demonstrated that the thickness of the sheet significantly affects the gas sensing performance. The improved gas sensing properties are attributed to the thinned petals as well as their pores and defects. These results show that the thickness and morphology of hierarchical nanostructures affect the functionality of gas sensors.



## 1. Introduction

Among various metal oxide nanomaterials [1–7], tin oxide is of great importance owing to its physical properties that are relevant for many emerging applications such as gas sensor [8–11], photo catalyst [12–15], supercapacitor [16–19] and electrode materials [20–22].

It is well known that the chemical and physical properties of functional materials are greatly affected by the morphology and surfaces [23]. In recent years, diverse nanostructures and different morphologies [24–26,6,27–33] have been reported in succession, in which the complex three-dimensional (3D) nanoflower has received a huge amount of attention [34,35,9]. The 3D-structure is characterized by robust structure, broad internal space and large surface area, that all contribute to the long service life, sufficient diffusion path and enough reactive sites of the materials [36–38]. The 3-D nanoflowers could be assembled from low-dimensional nanostructures such as nanorods, nanocube, nanoneedle, nanosheets. Among all these different kinds of 3-D structures, nanoflower composed of nanosheets is considered to be the most effective morphology because of its porous structure and large specific surface area. Therefore, one possible way to further upgrade sensing behaviors is via the application of 3-D architectures, especially the sheet assembled flower.

Up to now, most works about $SnO_2$ sensor have been focused on synthesis of different morphological product. Several reports concerning the controlling of dimensionality of $SnO_2$ morphology to enhance its gas-sensing performance can be found in open literature as well [6,39,19,33,40]. However, the fabrication of 3-D hierarchical $SnO_2$ flower assembled from nanosheets with different thickness has been rarely investigated, in spite of its great potential of resulting in unexpected and unprecedented gas-sensing behaviors.

In this paper, we successfully synthesized unique $SnO_2$ hierarchical nanoflowers consisting of numerous smooth nanosheets with precisely tailored thickness. A series of gas sensing measurements were conducted to investigate the effect of nanosheet thickness on the properties of the resultant nanoflowers. Furthermore, a possible growth mechanism of the 3-D hierarchical nanoflower was proposed based on detailed characterization and deep analyses to explain the origin of excellent gas sensing performance.

## 2. Experiment

### 2.1. 2.1Synthesis of 3-D $SnO_2$ nanoflowers

All the chemical reagents were used without further purification. To synthesize $SnO_2$ nanoflower assembled from sheets with

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varied thickness, 0 mmol, 10 mmol and 20 mmol NaOH were dissolved in 40 ml mixture of deionized water and anhydrous ethanol (volume ratio: 1/1), respectively. Then, 2.5 mmol sodium citrate was added into mixed turbid liquid, followed by the ceaseless stirring on electromagnetic stirrer for 5 min. Subsequently, the turbid liquid was transferred into Teflon-lined stainless steel autoclave of 50 ml and heated in oven at 180 °C for 12 h. The precipitate was collected by centrifuging, washing with deionized water and anhydrous ethanol for 3 times, respectively. Dry powders were obtained after the precipitate being dried in 60 °C for 48 h. In order to investigate the impacts of reactant concentration and reaction time on morphology, the concentration of $SnCl_2$ solution and reaction time were modulated to be 7.5 mmol, 10 mmol and 24 h, 36 h, respectively in the four control experiment group.

### 2.2. Characterization of product

X-ray diffraction (XRD) analysis was taken on a Rigaku D/Max-1200X diffractometer with Cu Kα radiation (30 KV, 100 mA) to verify the component of the product. Morphology and nanostructure of the powder was analyzed by a Nova field emission scanning electronic microscopy (FE-SEM) and transmission electron microscopy (TEM) using a JEOL TEM-3010 electron microscope operated at an accelerating voltage of 300 KV.

### 2.3. Fabrication and measurement of the sensor

The $SnO_2$ powder grounded into tiny flour was mingled with terpineol to produce homogeneous paste. Then a layer of the paste was coated onto an alumina tube using a small brush. At each end of the alumina ceramic tube, there was a gold electrodes connected to two platinum wires. A Ni-Cr alloy coil was inserted through the tube as a heater to control the operating temperature from 0 to 500 °C by tuning the heating current. To improve the stability of the sensors, the aging process was done to the sensors for two hours in a gas sensitivity instrument (Elite tech Co., Ltd.). The response of the sensors to the reducing gas for measuring was defined as Ra/Rg, where Rg is the sensor resistance in a target gas and Ra is the sensor resistance in air, respectively.

## 3. Result and discussion

### 3.1. Structural and morphological characteristics

Fig. 1 displays the XRD diffraction patterns of all the samples S1, S2 and S3 prepared using different quantities of NaOH. The diffraction peaks at 2θ of 26.6°, 33.9°, 39.0° and 51.8° corresponding to (1 1 0), (1 0 1), (2 0 0) and (2 1 1) facet were indexed to tetragonal rutile structure of $SnO_2$, which is in good agreement with standard data file (JCPDS file no.41-1445). There is no other impure diffraction peak detected in all the three samples, indicating the high purity of the synthesized product. The greatest intensity of diffraction peak of (1 1 0) implies the probability that (1 1 0) face encloses the nanosheets of $SnO_2$. In addition, the high crystalline of $SnO_2$ is verified by the remarkable and sharp diffraction peaks.

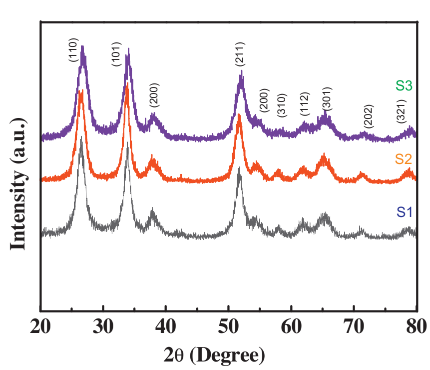


**Fig. 1.** XRD diffraction patterns of the sample S1, S2 and S3.

The morphologies of $SnO_2$ manufactured by hydrothermal process were characterized by FESEM as shown in Fig. 2(a–c). It can be found that the morphologies of the obtained $SnO_2$ are unique hierarchical flower-like architectures, consisting of well dispersed nanoflowers with diameter of 1–3 μm. These three samples were named as S1–S3, separately. By magnifying the image, it can be seen that the unique nanoflowers are assembled from nanosheets. Moreover, significant differences in morphology of the building blocks can be observed from sample to sample. Judging from the presented magnified images, inset of Fig. 2(a–c), the thickness of the nanosheets is obviously varied. The nanosheet thickness of S1, S2 and S3 were further measured to be 62 nm, 44 nm and 25 nm, respectively. Based on the characterization, it can be found that when the thickness of nanosheet gets thinner, they become more crimped. Seen from the Fig. 1(a), the nanosheets of S1 stand straightly on the surface of the nanoflowers. As for S2, the nanosheets tend to bend. When it comes to S3, the nanosheets mingle with each other to form close sections. What is more, the nanosheets have smooth surface and grow in radial orientation. Since the dosage of NaOH is the only intended variable during the synthesis of S1, S2 and S3, it is thus concluded that the dosage of NaOH is the critical parameter governing the morphology of the 3-D nanosheets.

To have a better understanding of the as-prepared $SnO_2$ hierarchical architectures, TEM analysis was performed. The detailed information of the S1, S2 and S3 nanoflowers are demonstrated in Fig. 2(d–f). The nanosheets can be clearly seen with well-arranged shape and uniform size, which further confirms that nanoflowers are assembled with nanosheets of different thickness. In addition, it can be seen that the nanoflowers assembled of nanosheet is porous and S3 has the thinnest sheet structure, indicating that the S3 is of the greatest potential of exhibiting good gas sensing properties.

Additionally, the impacts of the reaction time and precursor's concentration on $SnO_2$ nanostructures were carefully studied. Based on the reaction route of S3, when the $SnCl_2{\cdot}2H_2O$ amount is increased from 5 mmol to 7.5 mmol and 10 mmol, different morphologies were obtained (S3, S4, S5), as shown in Fig. 3(a–c). When $SnCl_2{\cdot}2H_2O$ was 7.5 mmol, no hierarchical nanoflowers but some irregular and bended nanosheets can be formed. The size of nanosheets remains the same. While the $SnCl_2{\cdot}2H_2O$ was further increased to 10 mmol, only trivial sheets were obtained. The result demonstrates that $Sn^{2+}$ concentration affects the produced $SnO_2$ morphology. It may be due to the resistance of high concentration to the movement and rotation of the nanoparticles, which is detrimental to the assembling of the particles and nanosheets.

When the reaction time is prolonged from 12 h to 24 h and 36 h, three different samples were obtained (S3, S6 and S7) and the SEM is shown in Figure 3(e-f). Compared with the morphology of 12 h, the nanoflowers transferred into piled up nanosheets after 24 h reaction. When the time was further prolonged to 36 h, the sheets broke up into small size nanopieces, and the stacking of these pieces was denser. The results indicate that reaction time is an important parameter for the control of morphology. When excessive time is adopted, no sheet-like nanoflower can be manufactured.

### 3.2. Gas-sensing performance

To gain further insight into gas-sensing properties of as-synthesized $SnO_2$ nanoflowers constructed with varied thick nanosheets, a series of gas-sensing tests were conducted. It is well known that the operating temperature is a crucial parameter for the