Self-assembled SnO$_2$ film with low density

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Abstract. A new kind of metallic oxide film consisted of nanodisks with porous structure has been prepared, which is different from that of targetlike multirings previously reported by our group. Herein, the SnO$_2$ film has been prepared by using tin(IV) tert-butoxide as precursor, sodium dodecyl sulfonate (SDS) as template and gelatin as stabilizer. Results show that the SnO$_2$ film is usually composed of series nanodisks with the diameters ranging from 0.1µm to 1µm and each disk displays worm-like porous structure in the transmission electron microscope (TEM) observation. These SnO$_2$ nanodisks are suggested to born inside the solution and gradually rise up to the air-water interface due to low density of the disk or disk cluster. After further treatment, the well ordered SnO$_2$ thin film is considered to have a potential application in gas-sensing materials. Remarkably, this may be a distinctive method to get SnO$_2$ film and may be widely applied to produce other metallic oxide films with low density.

1. Introduction
SnO$_2$ is a typical n-type semiconductor material and has been proved to be sensitive to many reducing gases (e.g. H$_2$, CO, C$_2$H$_5$OH) and oxidizing gases (e.g. NO$_x$) in multiple produced pure [1-4] or doped gas sensors [5-10]. Many past researches paid attention to the good morphologies, mechanisms [11], excellent properties and etc. Remarkably, a new self-assembly technology has been created with many advantages in preparing nano metallic oxide films, which can obtain well ordered structures and excellent properties through simple apparatus, few operations and mild reaction conditions etc. White J W, Elder K J and our group et al. did some important work on TiO$_2$ [12-14], ZrO$_2$ [15, 16], ZnO$_2$ [17, 18], SiO$_2$ [19, 20], which showed good potential applications in optics and electrics etc. Herein, we will put attention into a self-assembly process inside the reaction solution, to obtain air-water interfacial SnO$_2$ film with low density and investigate the gas sensitivity of the samples.
2. Experimental

2.1. Chemicals
Tin(IV) tert-butoxide (Sn(OC_{4}H_{9})_{4}, Sigma Aldrich, 99.99%), sodium dodecyl sulfonate (SDS, Alfa Aesar, 99%), chlorhydric acid (Nanjing chemical reagent Co.Ltd, 36–38%) and gelatin (G, AR, Tianjin Kermel chemical reagent Co.Ltd) were used as purchases.

2.2. Preparations
Preparations for SnO_{2} thin film were as follows. First, 0.65mmol SDS and 0.15g gelatin were mixed with 18.4ml deionized water in a 25ml beaker by stirring magnetically at 40°C for 10mins, beyond which the uniform surfactant solution was kept and cooled at room temperature. Meanwhile, 0.5mmol tin(IV) tert-butoxide was added into 6.5mmol HCl in a 10ml beaker, after which the solution was stirred for 5mins at room temperature until it became clear as the precursor. Then, the precursor was transferred to a Petri dish with a diameter of 90mm and a depth of 10mm and subsequently, the surfactant solution was poured into the Petri dish. Last, the Petri dish was kept standing at room temperature (21°C) for 12h, and then it could be found that the film has floated at the air-water interface.

2.3. Characterizations
SnO_{2} thin film was transferred to a glass substrate and dried for 24h, and then the substrate was directly detected by X-ray diffraction (XRD) with a Bruker D8 diffractometer, using monochromatic Cu Kα radiation operated at 40kV and 30mA. Scanning electron microscope (SEM) of JEOL-6380LV and EDS with EDAX Genesis2000 were applied to detect the dried film. The fresh sample was dropped to a copper grid after ultrasonic dispersion for 10mins, which was observed by a JEOL-2100 transmission electron microscopy (TEM) at 200 kV and a Gatan 794 charge-coupled device (CCD) camera.

2.4. Gas sensitivity
Gas sensitivity measurements of raw SnO_{2} product from direct hydrolysis of Sn(OC_{4}H_{9})_{4} and modified SnO_{2} product from the assembled system were carried out on Hanwei intelligent testing equipment (Hanwei Company, Henan, China). The apparatus contained a closed container with a volume 30L, which was used to store the target gases for testing. The sample was calcined at 500°C for 6h and cooled in the air, following which was ground in an agate motor and deposited to gold electrodes with alumina ceramic tubes as supports. Then the assembled gas sensors were tested by different kinds and concentrations of gases with a constant heat voltage (5V) and circle voltage (5V), such as liquid petroleum gas (LPG) and C_{2}H_{5}OH et al, which was quickly heated, evaporated and filled the container. Sensitivity (R_{air}/R_{gas}) was defined as the ratio of the gas sensor resistance in air (R_{air}) to that in target gas (R_{gas}).

3. Results and discussion

3.1. Morphology and structure
Figure 1 displays the intensity versus angle pattern of SnO_{2} film with 2θ degree in the range 2º-10º. Note that there are no obvious diffractions detected from 10º to 80º. The strongest diffraction peak at 2θ=3.10º with d=2.85nm indicates that a high degree of ordered structure has been retained in the film. Additionally, there are some other peaks in figure 1, which may be caused by the surfactant SDS.

Many SnO_{2} disks with different diameters (the maximum diameter is ~1µm) in the film could be observed by SEM in figure 2. This SEM image is similar to such a TEM result in figure 4(a). EDS analysis of the film is displayed in figure 3. Importantly, the element percents of N (12.44%) and S (1.56%) in the SnO_{2} film suggest that substantial G and SDS have been transmitted into the self-
assembled structure, which provides essential information for following analysis of SnO$_2$ film structure.

![XRD pattern of SnO$_2$ film](image1)

**Figure 1.** XRD pattern of SnO$_2$ film.

![SEM observation of SnO$_2$ film](image2)

**Figure 2.** SEM observation of SnO$_2$ film

![EDS pattern of SnO$_2$ film](image3)

**Figure 3.** EDS pattern of SnO$_2$ film

![TEM observations of SnO$_2$ film with different scale bars](image4)

**Figure 4.** TEM observations of SnO$_2$ film with different scale bars  
(a) with 1µm; (b) with 20nm
TEM observations of SnO\textsubscript{2} film are displayed in figure 4. The disk cluster consisted of many disks and containing many spatial gaps could be observed in figure 4(a). The disk diameters in the cluster range from 0.1\(\mu\)m to 0.8\(\mu\)m. The HRTEM in figure 4(b) shows a worm-porous structure in the scale bar of 20nm, where the diameters of the pores are measured \(~\)3nm, which is consistent with such an ordered structure in the term of the XRD date in figure 1.

3.2. Formation of porous SnO\textsubscript{2} disk
Self-assembly mechanism of ZrO\textsubscript{2} target-like nanodisk from our previous report [16] could be employed to explain the formation of SnO\textsubscript{2} nanodisk. figure 5 shows the probable formation mechanism of self-assembly process of a SnO\textsubscript{2} disk. Due to stable interactions between SDS and G [21, 22], SDS as template [16] and G as stabilizer can be transmitted into self-assembly structure. However, we have observed an obvious porous structur e in figure 4(b), instead of target-like multirings of ZrO\textsubscript{2} nanodisk, which may be attributed to the collapses of SnO\textsubscript{2} lamellar structure with less toughness than ZrO\textsubscript{2} lamellas [16].

![Figure 5. Schematic diagram of the self-assembly process of SnO\textsubscript{2} film](image)

3.3. Structure of SnO\textsubscript{2} film with low density
The suggestion to explain the formation of SnO\textsubscript{2} film with low density is shown in figure 6. There may be two reasons resulting in the generation of this low-density material. First, there were many micropores in each isolated disk. Second, there existed some large gaps inside the disk cluster. The disk cluster and relative gaps have been found in figure 2 and figure 4(a). Hence, the film was suggested to born inside the solution and rise up gradually to the air-water interface.
3.4. Gas sensitivity testing
Sensitivities of two SnO₂ products to different concentrations of gases are displayed in figure 7. The gas sensor of raw SnO₂ product with little sensitivity showed no obvious differences to C₂H₅OH and LPG (L₁). Simultaneously, the gas sensor of modified SnO₂ product from the assembled system was a little more sensitive to LPG, and the sensitivity was 4.8 when the concentration was 600ppm. Note that this low density material performed much more sensitive to C₂H₅OH, which had an average sensitivity above 8 in all the concentrations and achieved 11 at 800ppm. This phenomenon could be attributed to the low density of modified SnO₂ product and well dispersed SnO₂ nanodisks or disk clusters. Accordingly, the more C₂H₅OH adsorbed and the more electrons exchanged, the more sensitivity was attached.

4. Conclusions
It was found that a new kind of SnO₂ film with low density could be prepared successfully by a self-assembly process with SDS as template and gelatin as both dispersant and stabilizer. According to the characterizations of XRD, SEM and TEM, the formation mechanism of nanodisks with porous
structure in the film had been reasonably conjectured. Furthermore, SnO₂ product obtained from the self-assembly process performed more sensitive to C₂H₅OH or LPG than the raw SnO₂ product. Our next work will concern on more gas sensitivity of this SnO₂ product, including its response to hydrogen, carbon monoxide.

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