INFLUENCES OF THE MOLE RATIO SnO$_2$/NaOH ON THE GROWTH OF SnO$_2$ NANORODS

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ABSTRACT

SnO$_2$ nanorods have been successfully prepared by hydrothermal method at low temperature. The mole ratio of SnO$_2$/NaOH plays important role in the morphology and diameter of SnO$_2$ nanorod. Besides, the possible growth mechanisms of SnO$_2$ nanorods are also discussed. Structural properties and surface morphologies of the SnO$_2$ nanorods were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The experimental results show that diameters of the nanorods are around 100 nm to 300 nm with lengths of several micrometers. With the success of preparing SnO$_2$ nanorods, which will improve in the research and preparation of gas sensor based on SnO$_2$ materials.

Keywords: SnO$_2$, nanorods, hydrothermal method.

I - INTRODUCTION

In the advances of the nanotechnology, scientists have recognized that materials in nanosize will expose preeminent characteristics. Recently, semiconductor nanomaterials have attracted much attention because of their potential scientific significance and technology application. Tin dioxide is an n-type semiconductor material with a wide band gap and high chemical stability [1]. It has been widely applied for various devices, such as gas sensor, dye-base solar cell and transparent conducting electrodes [2-5]. As the gas sensing and other properties of SnO$_2$ materials are strongly dependent on their size and shape, it is obvious that the controlled synthesis of the nano/microstructure of SnO$_2$ materials is very important for special applications [1].

Up to now, SnO$_2$ materials with different morphology have been fabricated by a few methods. For example, SnO$_2$ nanoparticles have successfully been prepared by sol-gel method [5, 6]. SnO$_2$ nanorods were synthesized by a vapor-liquid-solid approach [7]. SnO$_2$ nanowires have been obtained in a chemical vapor deposition (CVD) process [8]. Besides, Toshinari Yamazaki also synthesized SnO$_2$ nanowires with a tetragonal structure on oxidized Si substrates by thermal evaporation of tin grains at 900°C. SnO$_2$ nanowires of a single crystal structure were approximately 30—200 nm in diameter and several tens of micrometers in length [9]. SnO$_2$ nanotubes have been fabricated by an infiltration technique [10]. However, these preparation methods usually require very high temperature and rigorous experimental condition. In this paper, we report the preparation of tin dioxide nanorods by hydrothermal method. By this method, we can easily control a variety of parameters such as temperature, pressure, concentration of chemical species, solution concentration, pH and starting compounds. Beside, possible
growth mechanisms of SnO$_2$ nanorods are discussed.

II - EXPERIMENTAL

We used sol-gel method with hydrothermal treatment technique based on inexpensive precursor such as tin chloride (SnCl$_4$.5H$_2$O) and aqueous ammonia (NH$_3$OH) to fabricate SnO$_2$ sol suspension. Firstly, stannic acid gel was precipitated by mixing aqueous of tin chloride SnCl$_4$ (0.2 M) and ammonia.

\[
\text{SnCl}_4 + 4 \text{NH}_3\text{OH} \rightarrow \text{SnO}_2.\text{nH}_2\text{O} + 4 \text{NH}_4\text{Cl} + (2-\text{n})\text{H}_2\text{O}
\]

The resulting precipitate was thoroughly washed by repeating the procedures of suspending the gel into deionized water and collecting it back by filtration or centrifuge to remove Cl$^-$. The stannic acid gel was suspended in water to obtain SnO$_2$ sol, after adjusting the pH of the suspension with ammonia. In this experiment, pH of 10.5 was selected. The above SnO$_2$ sol was treated by hydrothermal technique to make more stable sol and better dispersion. The hydrothermal treatment was carried out in an autoclave at 200°C for 3 h. This treatment resulted in a transparent sol solution of tin oxide.

The SnO$_2$ transparent sol suspension was added to 0.15M NaOH solution with vigorous stirring to obtain an opaque solution. After that, 2 mol of cetyltriethyl ammonium bromide (CTAB) was added into above opaque solution, followed by heating to make CTAB dissolve completely. Then the mixture was poured into a stainless teflon lined 200ml autoclave and heated at 140°C for 20h. After cooled down to room temperature, the resulting white precipitate was collected by centrifugation, washed with ethanol for several time and dried at 600°C in vacuum for 3h. So SnO$_2$ nanorods were obtained. Structural properties and surface morphologies of the as-prepared SnO$_2$ nanorods and nanoparticles were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The diagram of preparation of SnO$_2$ nanorods is shown in Fig 1.

![Diagram of preparation of SnO$_2$ nanorods](image)

III - RESULTS AND DISCUSSION

1. Preparation of SnO$_2$ sol suspension

The wet gel (tin hydroxide) was synthesized by hydrolyzing tin chloride with ammonia. It was suspended in water to obtain SnO$_2$ sol. The
XRD pattern of SnO$_2$ nanoparticles after calcination at 600°C for 30 minutes is shown in figure 2. All of the diffraction peaks can be perfectly indexed to the tetragonal SnO$_2$ structure with lattice parameters of $a = 4.7$ Å and $c = 3.2$ Å. Furthermore, the crystallite size of SnO$_2$ could be estimated as 6.0 nm according to Scherrer formula:

$$d = k\lambda/(\beta\cos\theta)$$

where $\lambda$ is the wavelength of the X-ray radiation ($\lambda_{\text{CuK}\alpha} = 0.154$ nm), $k$ is a constant taken as 0.89, $\beta$ is the line width at half maximum height and $\theta$ is the diffracting angle. Thus, the XRD result shows that SnO$_2$ nanomaterials have rutile structure and the SnO$_2$ crystallite sizes are very small.

The morphology and size of the initial SnO$_2$ nanoparticles were observed by TEM (Fig. 3). The result showed that the particle size is about 6.0 nm in diameter with a fairly arrow particle size distribution and well dispersion. The particle size obtained from TEM image was almost the same as the crystallite size calculated from XRD pattern.

**Fig. 2:** XRD pattern of SnO$_2$ nanoparticle after calcination at 600°C for 30 minutes

**Fig. 3:** TEM image of SnO$_2$ nanoparticles which were derived from 5 wt.% SnO$_2$ sol

### 2. Preparation of SnO$_2$ nanorods

In a typical SnO$_2$ nanorods preparation, the SnO$_2$ transparent sol was mixed with NaOH 0.15M, stirring for 30 minute to obtain an opaque solution. After that, 2 mmol of CTAB was added into above opaque solution. Then the mixture was hydrothermally treated at 140°C in a teflon- lined autoclave for a desired time. Fig. 4 shows typical SEM images as made of nanorods after annealing at 600°C for 3 h. The results show that the diameters of SnO$_2$ nanorods are around 100 - 300 nm with lengths of several micrometers.

In addition, it is noteworthy that varying the mole ratio of SnO$_2$/NaOH during the synthesis led to a dramatic change in the diameter of these rods. Fig. 5 shows the SEM images of SnO$_2$ nanorods collected from hydrothermal treatment at 140°C for 16 h with different molar ratio of SnO$_2$/NaOH.

We observed the size of rods increased with increasing mole ratio of SnO$_2$/NaOH. The experimental results show that when the ratio = 1:12 (Fig. 5a) SnO$_2$ nanorods started appearing but in small density. There were a lot of nanoparticles in this sample. When the ratio is increased to 1:20, urchin-like nanostructures assembled by short nanorods with lengths of some micrometers was obtained. By raising the ratio up to 1:25, long nanorods and nanowires (Fig. 5d) were fabricated. There was almost no particle in the sample. Besides, the products have good morphology and high density. However, when increasing the ratio to 1:30, only large particles were obtained. Thus, the
optimum mole ratio of SnO$_2$/NaOH for preparation of SnO$_2$ nanorods are in the range of 1:20 to 1:25.

![Fig. 4: SEM image of nanorods which were derived from hydrothermally treated SnO$_2$ at 140°C for 16h](image)

![Fig. 5: SEM images of SnO$_2$ nanorods at different molar ratios of SnO$_2$ sol/ NaOH solution](image)

**3. A proposed growth mechanism**

A proposed growth mechanism of SnO$_2$ nanorods can be explained in term of chemical reactions and crystal growth as follows. From the crystallization point of view, the synthesis of an oxide during an aqueous solution reaction is expected to experience a hydrolysis-condensation process. Growth of SnO$_2$ nanorods occurs according to the reaction:
SnCl₄ + 4 NH₄OH →
Sn(OH)₄ + 4 NH₄Cl + (2-n)H₂O
Sn(OH)₄ is an amphoteric hydroxide which can be dissolved in NaOH solution and form Sn(OH)₆²⁻ anion.

Sn(OH)₄ + 2OH⁻ → Sn(OH)₆²⁻

The possible formation process for SnO₂ nanorods under hydrothermal condition can be represented in figure 6.

The surfactant CTAB is a key in determining the morphology of the products. Because of the existence of surfactant, the surface tension of solution reduced, thus it was easy to carry out reaction between Sn(OH)₄ and NaOH. On the other hand, CTAB could be considered to influence the erosion process tin dioxide and growth process of SnO₂ by the electrostatic and stereochemical effects (Fig. 6). As we have known, CTAB is an ionic compound, which ionizes completely in water. The CTAB⁺ cations condense into aggregates in which the Sn(OH)₆²⁻ anions are intercalated in the interspaces between the head groups of CTAB to form CTAB⁺—Sn(OH)₆²⁻ ion pairs by electrostatic interactions. The CTAB⁺—Sn(OH)₆²⁻ ion pairs form a sandwich-like structure in water[12]. CTAB⁺—Sn(OH)₆²⁻ ion pairs was as know as a seed of crystal. The nanorods’ growth mechanism can be understood on the basis of oriented aggregation by polar forces. The primary seed of crystal can transform in to SnO₂ nanorods by oriented aggregation. Jiggling seed of crystal by the driving force may allow adjacent seed of crystal to construct the low- energy structure, represented by a coherent seed of crystal interface [2]. The experiment results with nanorods formation mechanism show that concentration of NaOH influences directly to the Sn(OH)₆²⁻ shell layer thickness. The higher NaOH concentration, the thicker shell layer and vice versa. As we know, also NaOH and CTAB solution plays an important role as a strong erosive solution. Thus, the formation and erosion processes on the shell layer take place sequentially until reacted completely. This means that we can obtain a lot of pieces of the shell layer or SnO₂ nanorod with bigger length when increasing the NaOH concentration. Furthermore, we realized that by using high concentration of NaOH solution, the nanoparticles seem to disappear entirely, as compared to the sample with lower NaOH concentration.

**Fig. 6**: Schematic illustration of the erosion process.

**IV - CONCLUSION**

In conclusion, tin dioxide nanorods were successfully prepared from tin chloride as a starting material. SnO₂ nanorods with diameters of 100 - 300 nm and lengths of several micrometers have successfully been synthesized by hydrothermal method. The effect of mole ratio SnO₂/NaOH on the morphology and diameters of products were also investigated. The increase of the mole ratio of SnO₂/NaOH during the synthesis led to a dramatic change in the diameter of these rods. The well SnO₂ nanorods were prepared with the ratio about from 1:20 to 1:25. Besides, possible growth mechanisms of SnO₂ nanorods based on the CTAB⁺—Sn(OH)₆²⁻ ion pairs are also discussed.
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REFERENCES


ÁNH HƯƠNG CỦA TÝ LỆ MOL SnO2/NaOH ĐẾN SỰ HÌNH THÀNH CỦA THANH NANO SnO2

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