Journal of Chemistry, Vol. 47 (5), P. 647 - 652, 2009

INFLUENCES OF THE MOLE RATIO SnO_2/NaOH ON THE GROWTH OF SnO_2 NANORODS

Received 9 June 2009

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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 ($SnCl_4.5H_2O$) and aqueous ammonia (NH_4OH) 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.

$$SnCl_4 + 4\ NH_4OH \rightarrow SnO_2.nH_2O + 4\ NH_4Cl + (2\text{-}n)H_2O$$

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 at140°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.

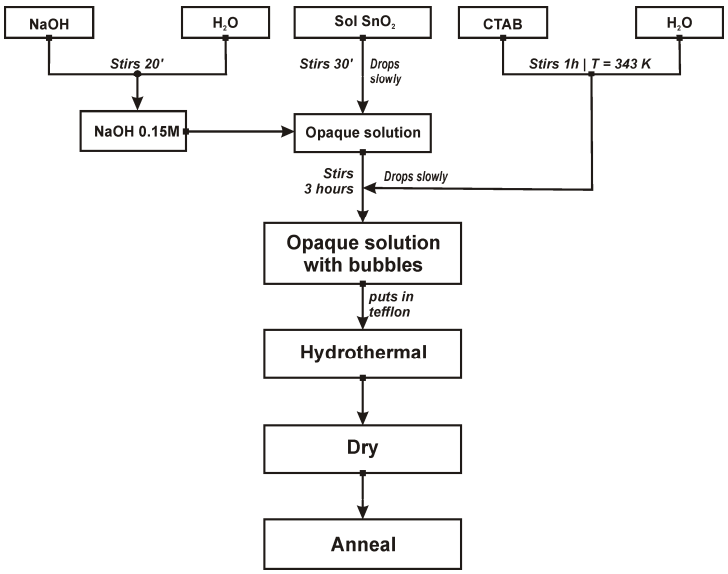

Fig. 1: Diagram of preparation of SnO_2 nanorods

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 600ºC 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 λ is the wavelength of the X-ray radiation ($\lambda_{CuK\alpha} = 0.154$ nm), k is a constant taken as 0.89, β is the line width at half maximum height and θ 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.

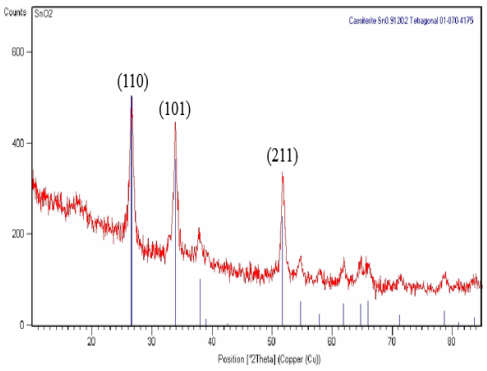

Fig. 2: XRD pattern of SnO_2 nanoparticle after calcination at 600ºC for 30 minutes

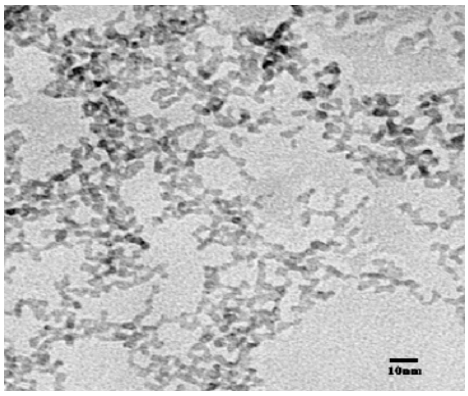

Fig. 3: TEM image of SnO_2 nanoparticles which were derived from 5 wt.% SnO_2 sol

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 140ºC in a teflon- lined autoclave for a desired time. Fig. 4 shows typical SEM images as made of nanorods after annealing at 600ºC 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 140ºC 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.

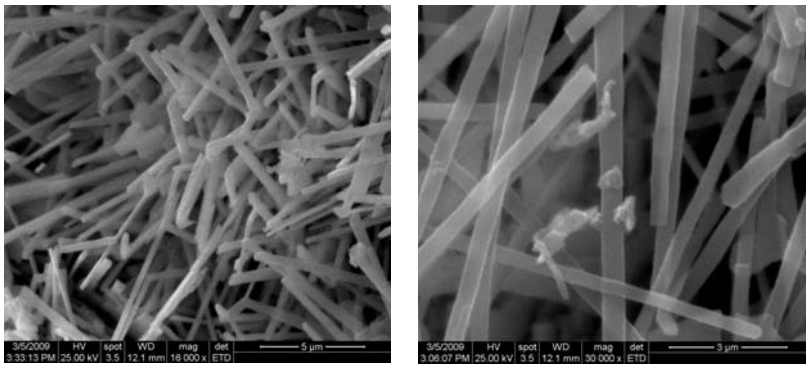

Fig. 4: SEM image of nanorods which were derived from hydrothermally treated SnO_2 at 140°C for 16h

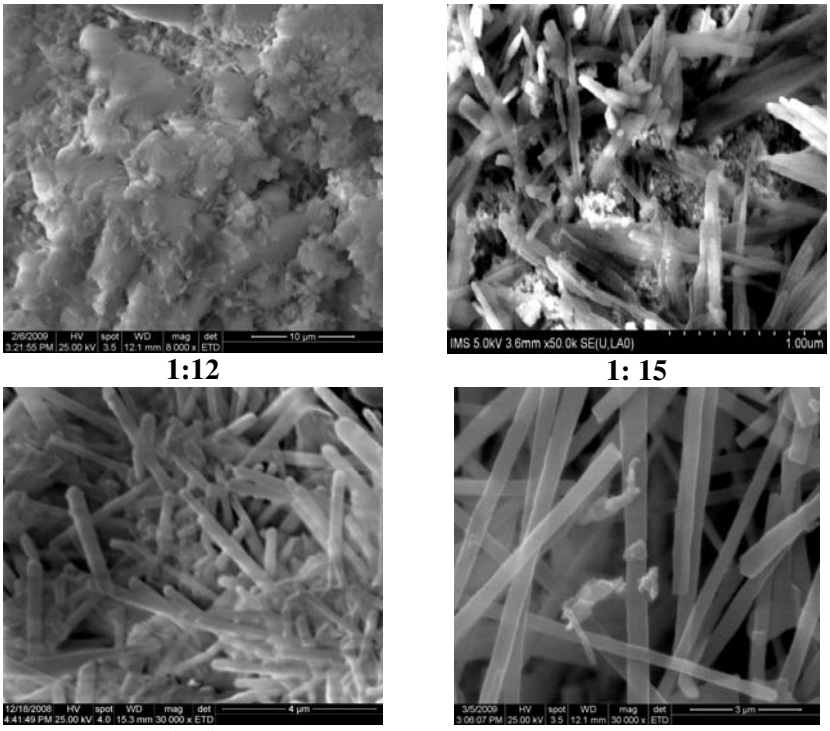

Fig. 5: SEM images of SnO_2 nanorods at different molar ratios of SnO_2 sol/ NaOH solution

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 of an aqueous solution reaction is expected to experience a hydrolysis-condensation process.

Growth of SnO_2 nanorods occurs according to the reaction:

$SnCl_4 + 4\ NH_4OH \rightarrow$

$$Sn(OH)_4 + 4\ NH_4Cl + (2\text{-}n)H_2O$$

$Sn(OH)_4$ is an amphoteric hydroxide which can be dissolved in NaOH solution and form $Sn(OH)_6^{2-}$ anion.

$$Sn(OH)_4 + 2OH^- \rightarrow Sn(OH)_6^{2-}$$

The possible formation process for SnO_2 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 SnO_2 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 $Sn(OH)_6^{2-}$ anions are intercalated in the interspaces between the head groups of CTAB to form $CTAB^+$— $Sn(OH)_6^{2-}$ ion pairs by electrostatic interactions. The $CTAB^+$— $Sn(OH)_6^{2-}$ ion pairs form a sandwich-like structure in water[12]. $CTAB^+$— $Sn(OH)_6^{2-}$ 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 SnO_2 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 $Sn(OH)_6^{2-}$ 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 SnO_2 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.

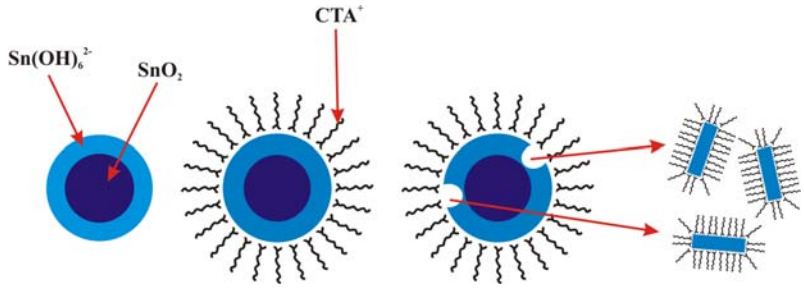

Fig. 6: Schematic illustration of the erosion process.

IV - CONCLUSION

In conclusion, tin dioxide nanorods were successfully prepared from tin chloride as a starting material. SnO_2 nanorods with diameters of 100 - 300 nm and lengths of several micrometers have successfully been synthesized by hydrothermal method. The effect of mole ratio SnO_2/NaOH on the morphology and diameters of products were also investigated. The increase of the mole ratio of SnO_2/NaOH during the synthesis led to a dramatic change in the diameter of these rods. The well SnO_2 nanorods were prepared with the ratio about from 1:20 to 1:25. Besides, possible growth mechanisms of SnO_2 nanorods based on the $CTAB^+$—$Sn(OH)_6^{2-}$ ion pairs are also discussed.

Acknowledgements: *This work is financially supported by the application-oriented basic research program (2009-2012, Code: 06/09/HD-DTDL).*

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ẢNH HƯỞNG CỦA TỶ LỆ MOL SnO_2/ NaOH ĐẾN SỰ HÌNH THÀNH CỦA THANH NANO SnO_2

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