The influence of hydrothermal temperature on SnO$_2$ nanorod formation

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Received 27 January 2010
Accepted for publication 24 June 2010
Published 3 August 2010
Online at stacks.iop.org/ANSN/1/025010

Abstract
SnO$_2$ nanorods were successfully prepared by a hydrothermal method using tin chloride, liquid ammonia, sodium hydroxide and cetyltrimethyl ammonium bromide (CTAB) as starting materials. Structural properties and surface morphologies of the SnO$_2$ nanorods were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Experimental results showed that the diameter of the nanorods is in the range of 100–300 nm with a length of several micrometers. The hydrothermal treatment temperature was found to play an important role in determining the morphology and diameter of the SnO$_2$ nanorods. Possible growth mechanisms of SnO$_2$ nanorods were proposed.

Keywords: SnO$_2$, nanorods, hydrothermal method

Classification numbers: 4.06, 5.01

1. Introduction
In recent years, there has been a tremendous increase in research activity in the field of nanosized materials. This is because of interesting variations in the properties of materials in nanosized configuration as compared to their bulk counterpart, and hence their novel application potential. The size, shape and crystal structure of nanosized materials are important parameters that control their chemical, optical and electrical properties. Based on metal oxide materials for gas sensor applications, tin oxide (SnO$_2$) has been the most popular sensor material so far investigated and used in practice [1–3], and a great deal of research effort has been exerted to improve the gas-sensing properties of SnO$_2$-based sensors. As the gas sensing 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 [4].

Up to now, SnO$_2$ materials with different morphologies have been fabricated by a few methods. Seong Hyeon Hong of Seoul National University has successfully prepared SnO$_2$ nanoparticles by a magnetron sputtering method [5]. In addition, A Helwig of Corporate Research Centre, Germany, also fabricated SnO$_2$ nanoparticles by a thermal oxidation method [6]. The experimental results show that diameters of SnO$_2$ nanoparticles are around 10 nm to 20 nm and exhibit good sensitivity to LPG gas. The nanorods and nanowires of the SnO$_2$ nanomaterial were synthesized by a vapor–liquid–solid approach [7–10]. Tin oxide nanowires have been grown on Au-coated Si substrates via a conventional thermal evaporation route using Sn powder. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) have been performed to investigate the structure of the products. The as-synthesized nanostructures have been found to have rutile structure. The diameters and the lengths of the SnO$_2$ nanowires are in the ranges of 50–550 nm and 200–500 µm, respectively. SnO$_2$ nanomaterial was obtained by another method, such as chemical vapor deposition (CVD) [11], infiltration technique or pulsed laser deposition method. However, these preparation methods usually require very high temperature and rigorous experimental conditions. In this paper, we report the preparation of tin dioxide nanorods by a hydrothermal soft-chemical process. 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.
In addition, a possible growth mechanism of SnO$_2$ nanorods is discussed.

2. Experimental

Stannic acid gel was precipitated by mixing aqueous solutions of tin chloride SnCl$_4$ (0.2 M) and ammonia:

$$\text{SnCl}_4 + 4 \text{NH}_4\text{OH} \rightarrow \text{SnO}_2 \cdot n\text{H}_2\text{O} + 4 \text{NH}_4\text{Cl} + (2 - n)\text{H}_2\text{O}. \quad (1)$$

The resulting precipitate was thoroughly washed by repeating the procedures of suspending the gel into deionized water and collecting it back by filtration or centrifugation to remove Cl$^-$. The wet gel thus obtained is named the untreated gel. The stannic acid gel (untreated gel) was suspended in water to obtain a suspension, after adjusting the pH of the suspension with ammonia. In this experiment, a pH of 10.5 was selected. This suspension is named the untreated sol. The above untreated sol was treated by a hydrothermal technique to make a more stable sol and better dispersion. The hydrothermal treatment was carried out in an autoclave at 200°C for 3 h. Usually, a transparent sol suspension (hereafter called the treated sol) was obtained after this treatment.

The above treated sol was added to 0.15 M NaOH solution with vigorous stirring to obtain an opaque solution. After that, 2 mmol of cetyltriethyl ammonium bromide (CTAB) was added into the above opaque solution, followed by heating to make the CTAB dissolve completely. Then the mixture was poured into a stainless teflon lined 200 ml autoclave and heated at 140°C for 16 h. After being cooled down to room temperature, the resulting white precipitate was collected by centrifugation, washed with ethanol several times and dried at 600°C in vacuum for 3 h. Thus SnO$_2$ nanorods were obtained. Structural properties and surface morphologies of the as-prepared SnO$_2$ nanorods were characterized by powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). The diagram of preparation of SnO$_2$ nanorods is shown in figure 1.

3. Results and discussions

The XRD pattern of SnO$_2$ nanorods after calcinations at 600°C for 3 h is shown in figure 2. All of the diffraction peaks can be perfectly indexed to the rutile structure of SnO$_2$ with tetragonal lattice parameters $a = 4.7$ Å and $c = 3.2$ Å, which.
The reaction was carried out at a low temperature of 120 °C. If the hydrothermal temperature increases, the reaction was carried out at a low temperature of 120 °C. The results showed that the size of rods increases with the increase in hydrothermal temperature. This can be explained as follows. If the hydrothermal temperature increases, the reaction between Sn(OH)₄ and NaOH will easily take place, the Sn(OH)₂⁻ anions are intercalated in the interspaces between the head groups of CTAB to form CTAB⁺–Sn(OH)₂⁻ ion pairs by electrostatic interaction. The CTAB⁺–Sn(OH)₂⁻ ion pairs form a sandwich-like structure in water [13]. CTAB⁺–Sn(OH)₂⁻ ion pairs are known as seeds of crystals. The nanorods’ growth mechanism can be understood on the basis of oriented aggregation by polar forces. The primary seeds of crystals can transform into SnO₂ nanorods by oriented aggregation. Jiggling seeds of crystals by the driving force may allow adjacent seeds of crystals to construct the low-energy structure, represented by coherent seeds of the crystal interface [12]. The experimental results show that the size of rods increases with the increase in hydrothermal temperature. This can be explained as follows. If the hydrothermal temperature increases, the reaction between Sn(OH)₄ and NaOH will easily take place, the density of crystal seeds becomes larger and the size of the SnO₂ nanorods increases.

**4. Conclusion**

SnO₂ nanorods with diameters of 100–300 nm and lengths of several micrometers have been successfully synthesized by a hydrothermal method. The effects of a hydrothermal temperature on the morphology and diameters of products were also investigated. In particular, when the hydrothermal temperature was increased to 230 °C, the bended foils and plates of SnO₂ were obtained. The success of preparing the bended foils and plates of SnO₂ will promote research and preparation of gas sensors based on SnO₂ materials. In addition, the XRD patterns revealed that the obtained products
exhibit the tetragonal rutile structure of SnO$_2$. Furthermore, a possible growth mechanism of SnO$_2$ nanorods was discussed.

**Acknowledgment**

This work was supported by project code 06/2009/HD-DTDL.

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