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Conventional- vs microwave-hydrothermal synthesis of tin oxide, SnO_2 nanoparticles

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Abstract

Tin oxide nanophases or nanoparticles were synthesized under conventional- and microwave-hydrothermal conditions and characterized by powder X-ray diffraction, BET surface area determination as well as transmission electron microscopy. The use of microwave-hydrothermal (M-H) process led to higher yields in shorter time compared to the conventional-hydrothermal (C-H) process because of increased reaction rates in the former.

Keywords: Nanomaterials; Hydrothermal process; Microwave-hydrothermal process; Tin oxide

1. Introduction

Semiconductor nanoparticles have been extensively studied from both experimental and theoretical viewpoints, because of their potential applications in solar energy conversion, photocatalysis, and in optoelectronics industry [1]. Nanostructured semiconductors have unusual optical, electronic, and chemical properties and wide potential uses as nanoscale devices. The desire for miniaturization is the driving force behind nanoparticle synthesis efforts [2]. Research on the preparation of oxide nanoparticles is an active area that is being pursued all over the world [3]. Tin oxide (SnO_2) is an important n-type semiconductor with a large band-gap and has been used as one of the promising materials for gas sensors, optoelectronic devices and negative electrodes for lithium batteries [4]. Recent research shows that the properties of SnO_2 depend greatly on product's crystallite size and specific surface area [5]. Compared with bulk SnO_2, nanosized SnO_2 has especially good properties and has outstanding advantages of low operating temperature and high sensitivity for gas-sensing applications [6]. For example, the sensitivity begins to increase sharply as the crystallite size of SnO_2 particles decreases below a critical value of 6 nm [7]. Many methods have been developed to synthesize SnO_2 nanoparticles, including evaporation of SnO_2 or SnO powders at elevated temperature [8], solvothermal and hydrothermal routes [9], homogeneous precipitation [10], microwave-assisted aqueous solution using a kitchen oven [11,12] and sol–gel route [13]. The above microwave-assisted method [11,12] did not use precise control of temperature and these results were not compared to conventional-hydrothermal method. A recent paper reports on the microwave-assisted hydrothermal synthesis of nanocrystalline SnO powders under precise control of temperature by Varela's group [14] but not SnO_2. Further improvement of the synthesis method for SnO_2 may save energy while increasing the yield of SnO_2 nanoparticles. We previously developed microwave-hydrothermal (M-H) method [15–18] for the synthesis of many oxides, semiconductors and metal nanoparticles and showed that the M-H method could save energy compared to C-H method through accelerating reactions by one to two orders of magnitude in many cases. Therefore, our objective here is to show whether or not the M-H method is suitable for the rapid synthesis of SnO_2 nanoparticles with high yield compared to the conventional-hydrothermal (C-H) method.

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Table 1
Yield of SnO_2 nanoparticles as a function of experimental conditions including the starting chemicals, reaction time and reaction temperature.

No.	$SnCl_4$–HCl solution	Additive	Heating method	Temperature	Heating time	Yield[a] (%)
1	15 ml	None	C-H	200 °C	4 h	~1
2	15 ml	0.9 g urea	C-H	100 °C	4 h	~5
3	15 ml	0.9 g urea	C-H	120 °C	4 h	~35
4	15 ml	0.9 g urea	C-H	140 °C	4 h	~45
5	15 ml	0.9 g urea	C-H	160 °C	4 h	~45
6	15 ml	0.9 g urea	C-H	200 °C	4 h	~45
7	5 ml	0.9 g urea	C-H	160 °C	1 h	<1
8	5 ml	0.9 g urea	C-H	160 °C	2 h	~80
9	5 ml	0.9 g urea	C-H	160 °C	4 h	>95
10	5 ml	0.9 g urea	C-H	160 °C	24 h	~90

[a] First, theoretical amount of tin oxide was calculated based on the molarity and volume of $SnCl_4$–HCl solution used. The amount of tin oxide crystallized by hydrothermal treatment was weighed. Yield was calculated using the formula: [amount of tin oxide crystallized × 100]/[theoretical amount of tin oxide].

2. Experimental

2.1. Materials

Ammonium hydroxide (ACS reagent, 28–30% as NH_3), urea (98% purity), and anhydrous $SnCl_4$ (99% purity) were purchased from Aldrich Chemical Company. Hydrochloric acid (98% purity) was purchased from J.T. Baker Company.

2.2. Synthesis of SnO_2 nanoparticles

The starting $SnCl_4$–HCl stock solution was prepared as follows: 65.13 g $SnCl_4$ was dissolved in a beaker with 29 ml 1 M HCl solution and the HCl solution with $SnCl_4$ was transferred to a 250-ml volumetric flask with 1 M HCl and homogenized. In a typical procedure for the synthesis of SnO_2 nanoparticles under conventional-hydrothermal (C-H) conditions, 5–10 ml of the above $SnCl_4$–HCl stock solution was put into a Teflon® container of a Parr autoclave. An appropriate amount of urea or NH_4OH was added into the container. After sealing, the autoclave was treated at 100–200 °C for 0.5–8 h.

For the synthesis of SnO_2 nanoparticles under microwave-hydrothermal conditions, 5–10 ml $SnCl_4$–HCl solution and an appropriate amount of base (urea or NH_4OH) were put into a Teflon® vessel of a double-walled digestion vessel. The double-walled digestion vessel has an inner liner and a cover made up of Teflon® PFA and an outer high-strength shell of Ultem polyetherimide. After sealing, the vessels were heated in a microwave digestion system, MARS-5 (CEM Corp.) in the temperature range of 100–200 °C for 0.5–4 h using a 300-W power. Temperature feedback control is achieved with a microwave transparent fiber optic temperature probe. The sensor is placed in a single reference vessel to control the temperature and this same vessel was used for synthesis of SnO_2 nanoparticles. The vessels were brought to temperature in 5 min, kept at temperature for the desired time and then cooled down in 5 min. After the vessel was cooled to room temperature, the powders were collected and washed with distilled water and alcohol several times by centrifugation at 2000 rpm for ~10 min. The powders were then dried at room temperature or in an oven at 60 °C.

2.3. Characterization

Slurries of the synthetic products were deposited on glass slides and dried at room temperature or dried powders were put into cavities of zero background slides for X-ray diffraction (XRD) measurements. XRD patterns were recorded on a Scintag diffractometer operated at 35 kV voltage and 30 mA current with Cu-K_α radiation. Particle shape and size were determined by transmission electron microscopy (TEM) and crystalline phases were determined by selected area electron diffraction (SAED) using a Philips 420 transmission electron microscope operated at 120 kV. Specimens for the TEM measurements were prepared by depositing a drop of the ethanol solution of SnO_2 sample on a 300-mesh copper grid coated with an amorphous carbon film and evaporating the solvent in air at room temperature. BET N_2 surface areas of some of the samples were measured by an Autosorb-1 instrument (Quantachrome Corp.).

3. Results and discussion

3.1. XRD patterns and TEM of the obtained SnO_2

Powders of SnO_2 were obtained under our experimental conditions (Tables 1–3), and the experimental conditions affected the crystallinity and the crystal size to a certain extent. Fig. 1 shows the XRD patterns of the obtained products synthesized under C-H conditions without and with urea as additive and synthesized under M-H conditions with NH_4OH as additive. All the peaks in the figures could be

Table 2
Yield of SnO_2 nanoparticles using ammonium hydroxide as a function of conventional-hydrothermal (C-H) or microwave-hydrothermal (M-H) processing.

Sample no.	$SnCl_4$–HCl Solution	Additive	Temperature	Yield (%)	
				C-H/4 h	M-H/4 h
24	15 ml	2 ml NH_4OH	160 °C	~43	~105
25	5 ml	1 ml NH_4OH	160 °C	~35	~50
26	5 ml	2 ml NH_4OH	160 °C	~100	~100

Table 3
Yield of SnO_2 nanoparticles using urea as a function of conventional-hydrothermal (C-H) or microwave-hydrothermal (M-H) processing.

$SnCl_4$–HCl solution	Additive	Temperature	Heating time	Yield (%)	
				C-H	M-H
10 ml	1.8 g urea	100 °C	0.5 h	0	0
10 ml	1.8 g urea	100 °C	2 h	0	$\sim$59[a]
10 ml	1.8 g urea	100 °C	4 h	$\sim$46[b]	$\sim$99
10 ml	1.8 g urea	100 °C	8 h	$\sim$91	–

[a] Surface area of 158 m^2/g.
[b] Surface area of 183 m^2/g.

indexed as tetragonal SnO_2 (JCPDS Card No. 41-1445). All the half peak widths are very broad, which indicates that the obtained crystallites are small in size, i.e., nanometer size. These results were confirmed by TEM observation. Fig. 2 shows the TEM images of the samples prepared under different conditions. All the TEM images indicate that the obtained SnO_2 grains have particle sizes on nanoscale. The SnO_2 sample (TEM image shown in Fig. 2a) synthesized with 5 ml $SnCl_4$–HCl solution and 0.9 g urea at 160 °C for 4 h under C-H conditions has particles of around 5 nm. Fig. 2b displays the TEM image of the SnO_2 sample synthesized at 160 °C for longer duration of 24 h under the above C-H conditions. With an increase in reaction time, the particle size increased with non-uniform particle size distribution (Fig. 2b). The heating method and the concentration of $SnCl_4$–HCl solution did not change the morphology and the particle size significantly. Fig. 2c and d show the TEM images of the samples synthesized under M-H conditions. The sample synthesized at high $SnCl_4$–HCl solution concentration shows a little bit of agglomeration (Fig. 2c) and its particle size is $\sim$3 nm (sample #24, Table 2). The sample synthesized at lower $SnCl_4$–HCl solution concentration under microwave-assisted conditions (sample #26, Table 2) has an average particle size of $\sim$5 nm (Fig. 2d). The corresponding selected area electron diffraction (SAED) images are shown as inset in the TEM images. The diffraction rings (showed ‘‘d’’ spacings of 3.35, 2.64 and 1.76 Å) clearly confirm that tetragonal structure of SnO_2 has been synthesized successfully.

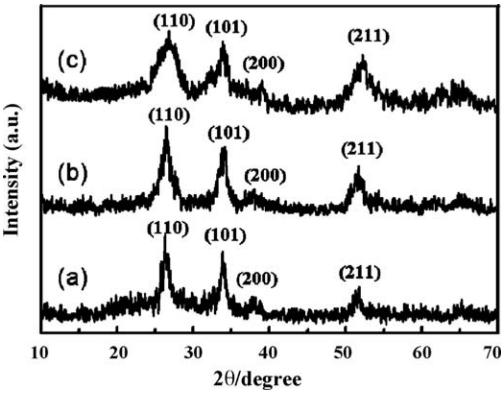

Fig. 1. XRD patterns of the obtained SnO_2 nanoparticles: (a) sample (#1, Table 1) 200 °C, 4 h, without any additive, C-H; (b) sample (#5, Table 1) 160 °C, 4 h, urea, C-H; and (c) sample (#24, Table 2) 160 °C, 1 h, NH_4OH, M-H.

3.2. The yield of SnO_2 nanoparticles

3.2.1. Under conventional-hydrothermal conditions

In our experiments, we used two different kinds of bases, urea and NH_4OH. Urea was confirmed to be a good additive for the synthesis of SnO_2 nanoparticles. The addition of base was found to be very important for the synthesis of SnO_2 nanoparticles. Without the addition of any base, the yield of SnO_2 is very low ($\sim$1%) even after treatment at 200 °C for 4 h (Table 1).

Besides the effects of different base additives, we also investigated the effects of reaction time, reaction temperature and Sn inorganic salt concentration on the yield of SnO_2 nanoparticles (Table 1). In general the higher the reaction temperature, the higher is the yield, as expected. The synthetic reaction could occur at a temperature as low as 100 °C, but the product yield is very low ($\sim$5%). With the increase of the reaction temperature from 100 to 140 °C, the yield increased greatly (Table 1). At temperatures from 140 to 200 °C, the yield did not change much.

When 15 ml of $SnCl_4$–HCl solution was used in the reaction with the assistance of urea, the yield of SnO_2 was not higher than 45% even though the solution was treated at 200 °C for 4 h (Table 1). By decreasing the amount of $SnCl_4$–HCl to 5 ml, the yield of SnO_2 increased to greater than 95% even at a temperature of 160 °C for 4 h (Table 1). This tendency could also be found when we used NH_4OH. The reason for higher yield with lower concentration of $SnCl_4$–HCl solution is that the added base was apparently sufficient to promote hydrolysis and precipitation while the added base was insufficient with higher concentration of $SnCl_4$–HCl solution. However, no pH was measured either before or after the synthesis reactions.

Increased heating time increased the formation of SnO_2, as expected. Under C-H conditions, the heating time of 1 h yielded less than 1%. Heating time of 2 h increased the yield dramatically to $\sim$80%. Heating time of 4 h appears to be optimal for the high yield synthesis of SnO_2 at 160 °C (Table 1).

3.2.2. Under microwave-assisted hydrothermal conditions

Nanoparticles of SnO_2 were also synthesized under M-H conditions (Figs. 1 and 2) using NH_4OH (Table 2) as well as urea (Table 3). Table 2 shows the relationship between the experimental conditions and the yield of the product under both conventional- and microwave-assisted hydrothermal conditions. The yield under M-H conditions was higher compared to the C-H conditions (Tables 2 and 3). Longer times were needed to get 100% yield by C-H process compared to M-H process. Although the rapid reaction under M-H conditions is not clearly understood, one hypothesis is that it may be attributed to the localized superheating [19] where quick nucleation starts followed by rapid growth of nuclei under subsequent volumetric heating [15–18].

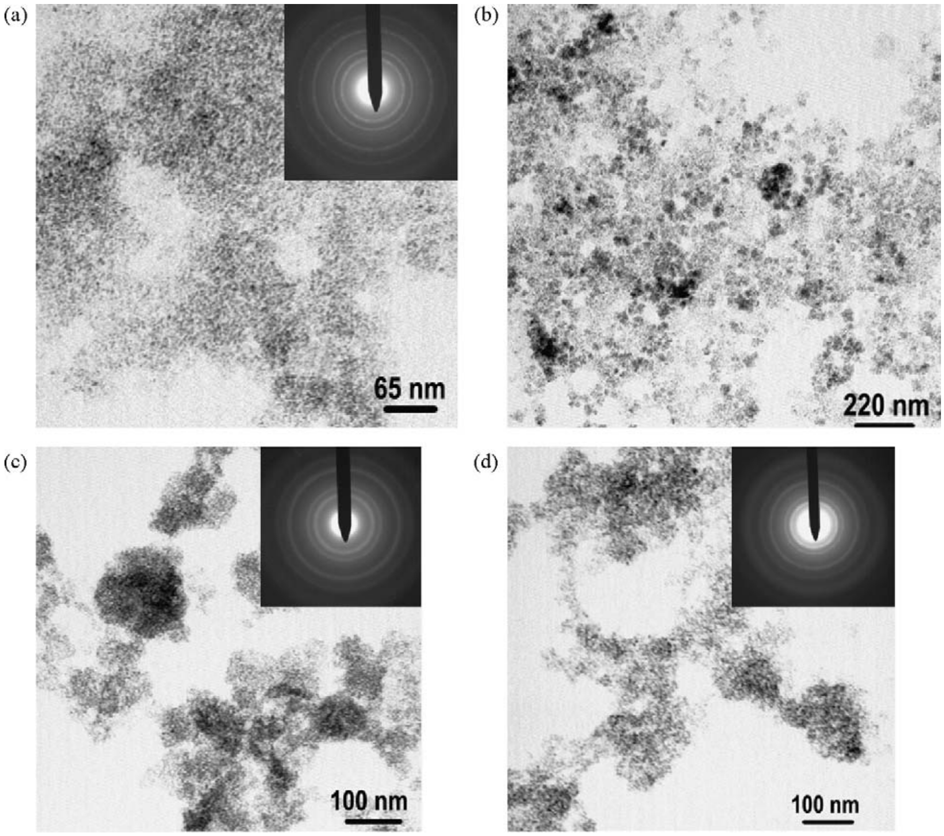

Fig. 2. TEM images of SnO_2 nanoparticles prepared at 160 °C: (a) sample (#9, Table 1), 4 h, low $SnCl_4$–HCl concentration, urea, C-H; (b) sample (#10, Table 1), 24 h, low $SnCl_4$–HCl concentration, urea, C-H; (c) sample (#24, Table 2), 1 h, high $SnCl_4$–HCl concentration, NH_4OH, M-H; and (d) sample (#26, Table 2) 1 h, low $SnCl_4$–HCl concentration, NH_4OH, M-H.

The surface area of SnO_2 sample prepared by M-H process (Table 3) after treatment at 100 °C/2 h showed a surface area of 158 m^2/g while the sample prepared by C-H process after treatment at 100 °C/4 h showed a surface area of 183 m^2/g. Particle sizes calculated based on the above surface areas are 5.4 and 4.7 nm, respectively, while particle sizes based on XRD results by Scherrer's equation (average for 110, 101, 200 and 211 reflections) are 4.2 and 3.9 nm, respectively. These SnO_2 particle sizes based on surface areas and XRD results are in quite good agreement with each other and are further confirmed by the particle size shown by TEM (figure not shown but similar to the TEM pictures shown in Fig. 2).

4. Conclusion

Both the conventional-hydrothermal and microwave-hydrothermal processes yielded nanophase SnO_2 but the M-H process led to higher yield in a shorter time, the latter process could lead to energy savings in processing of SnO_2.

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