Materials Science-Poland, *Vol. 27*, *No. 1*, *2009*

Silicon oxide nanowires and spheres grown by hydrothermal deposition

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Silicon oxide nanowires and spheres were prepared via a simple hydrothermal deposition using silicon powder as the starting material. Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive spectra (EDS) and high-resolution transmission electron microscopy (HRTEM) were used to observe the structure and morphologies of the products. The results show that the average diameter of silicon oxide nanowires with an amorphous structure is about 500 nm, and that smooth silicon oxide spheres have a definite diameter distribution ranging from several hundred nanometers to several micrometers. The growth process of the silicon oxide nanowires and spheres is discussed.

Key words: *hydrothermal deposition; nanoscale materials; silicon oxide nanowires and spheres*

1. Introduction

Preparation of one-dimensional nanowires has attracted a wide attention since the discovery of carbon nanotubes (CNTs) in 1991 [1]. Silicon oxide, one of the best candidates for photoluminescence materials, has been actively studied for a long time. Great efforts have been devoted to the preparation of silicon oxide nanowires because of their potential application in high-resolution optical heads of scanning near-field optical microscopy, nanointerconnection and microphotonic devices due to their intensive light emission ability [2, 3]. Silicon oxide nanowires have been prepared via different routes such as laser ablation, chemical vapour deposition (CVD) and template method according to the vapour–liquid–solid (VLS) growth mechanism, oxide-assisted growth mechanism and template confinement mechanism [2, 4–9]. Hydrothermal synthesis of CNTs and other one-dimensional nanomaterials [10–15] demonstrates their potential for preparing one-dimensional nanomaterials. As previously reported [16, 17], self-assembled silicon nanotubes and silicon carbide nanotubes have been prepared by a simple hydrothermal method using silicon monoxide, silica and

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silicon carbide as the starting materials, respectively. Recently, we attempted to deposit one-dimensional nanostructures on silicon substrates in order to study the effect of silicon powder as starting material on the formation of one-dimensional silicon-based nanomaterials under hydrothermal conditions. It is very important to prepare large one-dimensional silicon-based nanomaterials for understanding their nucleation and growth mechanisms under hydrothermal conditions and future applications. In the paper, we report that silicon oxide nanowires with an average diameter of about 500 nm were prepared by hydrothermal deposition on silicon substrates using silicon powder as a starting material. At the same time, silicon oxide spheres with the diameter distributions ranging from several hundred nanometers to several micrometers were also deposited on silicon substrates.

2. Experimental

The experiments were performed in a conventional autoclave. The main features of this autoclave are the following: maximum pressure 22 MPa, maximum temperature 500 °C, volume 1000 cm^3, power 1.5 kW and stirring velocity 0–1000 rpm. 1.25 g of Si powder (purity: $\geqslant$ 99%, average particle size: ca.42 μm) was mixed with 48 cm^3 of distilled water. The mixture was placed in the autoclave. The silicon substrate, of dimensions of 4×2 cm^2, was cleaned in distilled water for 10 min using a supersonic wave apparatus. Then, the latter was fixed in the stainless steel bracket situated in the centre of the autoclave. The autoclave heated to 470 °C, was set to a pressure of 6.8 –8.2 MPa, and the rotational speed of the stirrer was 200 rpm. The temperature and pressure were maintained for 24 h. Subsequently, the autoclave was cooled to room temperature in air. Finally, the silicon substrate with bulk light grey deposit was obtained after the experiment.

SEM observation was performed using JEOL JSM-5600LV FESEM with 1 nm point-to-point resolution operating under a a 15 kV accelerating voltage. TEM and HRTEM samples were prepared by administering several drops of solution with samples onto a standard copper grid with a porous carbon film after the samples were dispersed into distilled water and treated for about 10 min using a supersonic wave apparatus. TEM and HRTEM observations were performed using a JEOL JEM 3010 transmission electron microscope with a 1.7 Å point-to-point resolution operating with a 300 kV accelerating voltage with a GATAN digital photography system.

3. Results and discussion

Bulk light grey deposit can be observed on the silicon substrate. SEM observations reveal an abundant number of nanowires and spheres. Figure 1a is the general SEM image of silicon oxide nanowires and spheres. The diameter of spheres ranges

from several hundred nanometers to several micrometers, and can even be greater than ten micrometers The length of the silicon oxide nanowires deposited on the spheres is about several micrometers, and can even be greater than ten micrometers. The SEM image of silicon oxide nanowires under higher magnification (Fig. 1b) shows that the silicon oxide nanowires have a relatively narrow diameter distribution, and that the average diameter is around 500 nm. The surface of silicon oxide nanowires is very smooth. It is obvious that the growth tips of the silicon oxide nanowires are closed semi-circular structures. So the growth tips are similar to those of silicon nanowires prepared by oxide-assisted growth [18–21].

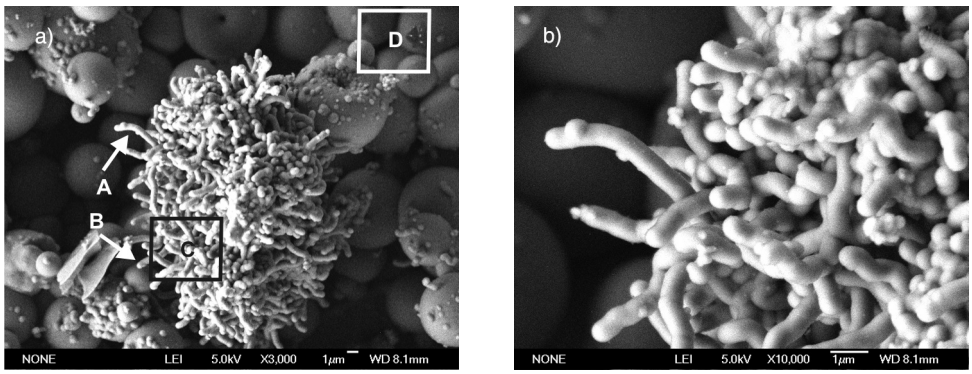

Fig. 1. SEM images of: a) the obtained sample, b) silicon oxide nanowires under higher magnification

The results demonstrate that no metallic catalyst particles exist in the silicon oxide nanowires. The production ratio of silicon oxide nanowires to spheres estimated by further SEM observations is about 1:9. EDS spectra of the nanowires and spheres are measured in order to determine the end product composition. The point, line and plane EDS spectra of the nanowires (Figs. 2a–c) show that the nanowires are composed of only silicon and oxygen. The corresponding quantitative analyses of the chemical composition of these samples using SEM-EDS experiments were performed by the software applied in the Link ISIS300 EDS. The atomic ratio of Si:O of silicon oxide nanowires is about 1:1.9 (point scanning and line scanning) and 1:1.8 (plane scanning), respectively, showing that the silicon oxide nanowires are SiO_x (x between 1.8 and 1.9) nanowires. Such a result also reveals that the element distribution of Si and O in the silicon oxide nanowires is uniform. The plane scanning EDS spectrum performed on spheres (Fig. 2d) reveals that the spheres are also composed of silicon and oxygen. The corresponding atomic ratio of Si:O is about 1:1.6 showing that the O content of the spheres is less than that of the silicon oxide nanowires.

Figure 3a is a general TEM image of silicon oxide nanowires. Different from the SEM results, some silicon oxide nanowires with a smaller diameter of about 200 nm are observed showing that silicon oxide nanowires with smaller diameters can be formed under present hydrothermal deposition conditions. In addition, similar to the

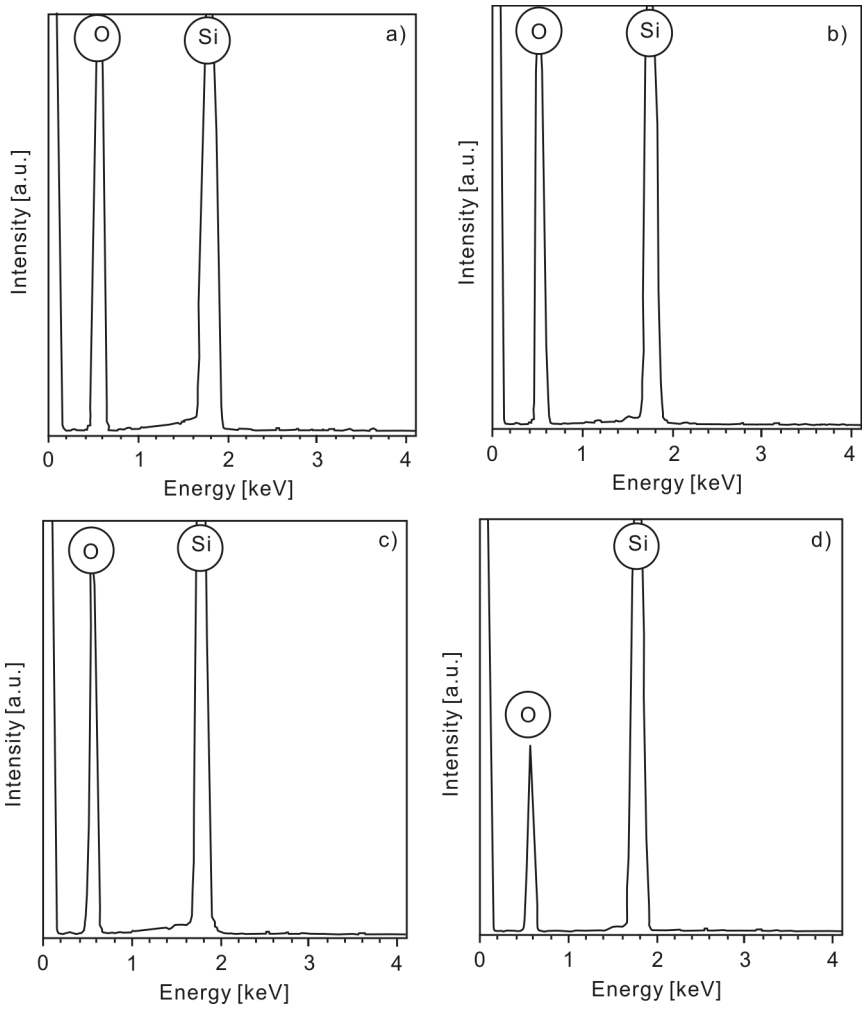

Fig. 2. Results of the EDS analysis of the sample shown in Fig. 1a: a) the point scanning EDS spectrum of the nanowire tip pointed by A, b) the line scanning EDS spectrum of the nanowire pointed by B, c) the plane scanning EDS spectrum of the nanowires pointed by C, d) the plane scanning EDS spectrum of the silicon oxide spheres pointed by D

SEM observation, the growth tips are mainly composed of semi-circular closed caps. The highly diffusive ring obtained from the electron diffraction analysis shown in the inset of Fig. 3a, reveals that these silicon oxide nanowires are amorphous, similarly to those synthesized by other methods [2, 4–9]. The surface of a nanowire is smooth, according to the TEM image of a single silicon oxide nanowire (Fig. 3b). The HRTEM image (the top-right of Fig. 3b) reveals an amorphous structure which is in agreement with the selected area electron diffraction (SAED) result. Spherical structures are also observed from the TEM image (Fig. 4a). The corresponding SAED pattern shown in the inset of Fig. 4a is a kind of highly diffusive ring. The result demon-

strates that the silicon oxide spheres are also amorphous. The HRTEM image of silicon oxide spheres (Fig. 4b) further substantiates the SAED result.

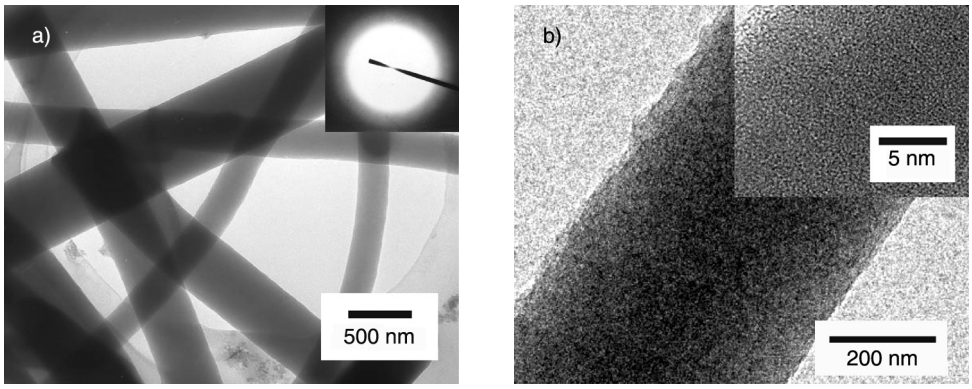

Fig. 3. TEM image of the silicon oxide nanowires (a), the inset is the corresponding SAED pattern and TEM image of a single silicon oxide nanowires (b), the inset is the corresponding HRTEM image

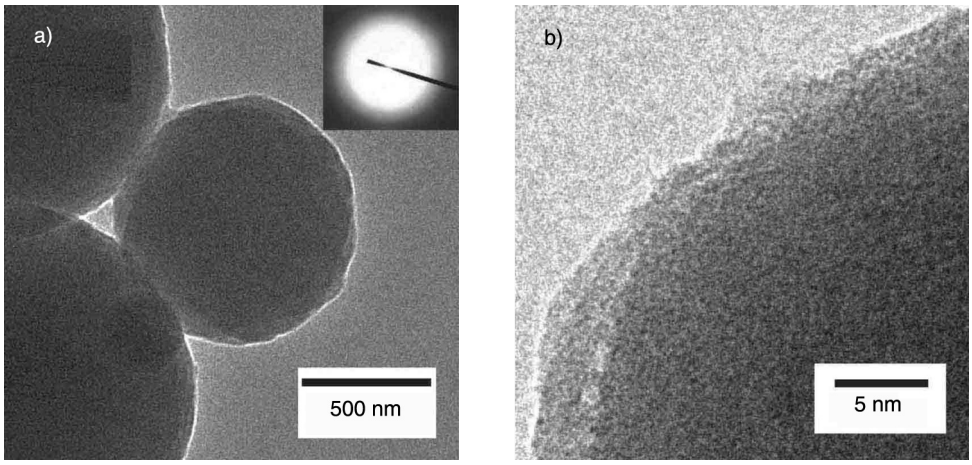

Fig. 4. TEM image of silicon oxide spheres (a), the inset is the corresponding SAED pattern and a HRTEM image of the silicon oxide sphere (b)

The obtained silicon oxide nanowires and spheres are composed of silicon and oxygen. The amount of O is greater than that of Si. Therefore, much oxygen exists in the sample. The amount of O in the starting material is measured in order to determine the origin of the oxygen. Thus, the EDS analysis was performed with the energy spectrometer (Fig. 5). A small amount of oxygen is observed in the plane scanning EDS spectrum. The quantitative analysis with the software applied in the Link ISIS300 EDS shows that the content of O in Si powder is 2.37wt. % which is far less than that of the end-products. The result demonstrates that only a part of the oxygen in the sample comes from the starting material of silicon. Silicon oxide exists mainly in the form

of silicon monoxide because the content of oxygen is far lower than that of Si in the sample. Thus it is reasonable to conclude that only a small amount of oxygen originates from the Si powder. Si is a stable monoatomic element under the standard atmospheric conditions and at room temperature. Thus, silicon oxide cannot be formed from Si under atmospheric pressure and the present experimental temperature. Si is also difficult to gasify. But the deposition process takes place under the pressure of 6.8–8.2 MPa and at the temperature of 470 °C being higher than the critical temperature of water (374 °C [22]).

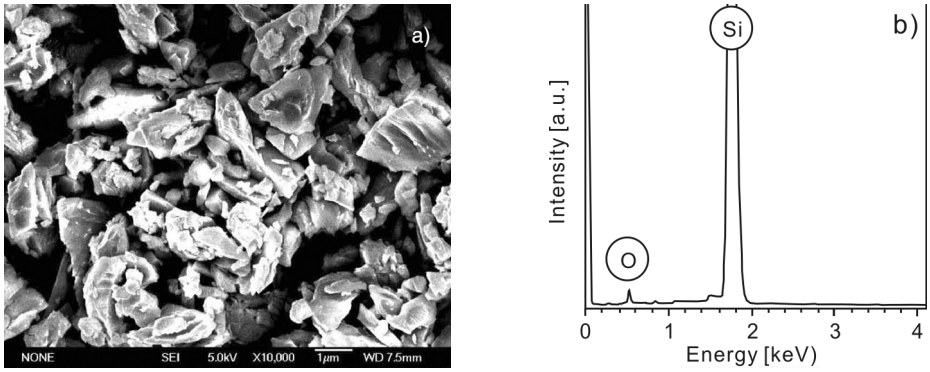

Fig. 5. SEM image of Si powder (a) and plane scanning EDS spectrum (b) corresponding to Fig. 5a

Therefore, the experiments are considered as having been conducted under supercritical conditions. Supercritical water enjoys a different status under high pressure such as sufficient density to dissolve materials, a higher diffusivity than in liquid state, a low viscosity facilitating mass transport, and high compressibility allowing easy changes in density and dissolving power [22]. Thus the supercritical hydrothermal conditions may play an essential role in the gasification of Si. Considering all these, the possibility of the reaction between Si gas and water gas is investigated by calculating the temperature dependence of the Gibbs energy under atmospheric pressure. Si gas possibly reacts with H_2O to form H_2, such as according to the following reaction:

$$\mathrm{Si(gas)+2H_2O(gas) \rightarrow SiO_2(solid) + 2H_2(gas)} \tag{1}$$

The Gibbs energy of these materials can be described by [23]:

$$G_i(T) = -R_G T\left(\frac{C_{i,1}}{T^2} + \frac{C_{i,2}}{T} + C_{i,3} + C_{i,4}T + C_{i,5}T^2 + C_{i,6}\ln T\right) \tag{2}$$

where G_i is the Gibbs energy of the system which consists of two materials, i.e., Si and H_2O and $R_G = 8.314$ J·mol^{-1}·K^{-1} is the gas constant. $C_{i,1}$–$C_{i,6}$ are the coefficients for the two materials. The $G_i(T)$ values of various materials are given in the literature [24]. The ΔG value is lower than -5.5×10^5 J·mol^{-1} at 400 °C according to the calculation. The result demonstrates that the reaction can occur in accordance with the thermodynamics. The hydrothermal pressure can also enhance the reaction rate according to the

chemical reaction theory. Therefore, Si and H_2O gases can react with each other to form SiO_2 and H_2 according to Eq. (1) under the aforementioned supercritical hydrothermal conditions under the pressure of 6.8–8.2 MPa. Thus a large amount of oxygen in the sample originates from the reaction of gaseous Si and H_2O. In addition, the existence of gas in the autoclave when its temperature decreased to room temperature also confirms that an abundant quantity of hydrogen can indeed be generated under high temperate, high pressure conditions.

Silicon oxide is known to play a large role in the nucleation and the growth of silicon oxide nanowires. Therefore, the formation of silicon oxide nanowires is based on the oxide-assisted growth mechanism [18, 21]. The melting point of the starting material, silicon, is 1414 °C [25]. Therefore, the starting material cannot be gasified under the specified experimental temperature and atmospheric environment. The temperature of the formation of silicon oxide nanowires is lower than that in other methods [2, 26–28] which may contribute to the supercritical hydrothermal conditions under the pressure of 6.8–8.2 MPa. Some of the silicon is gasified, forming silicon gas, with the increase of temperature and pressure in the autoclave. Water vaporization reacts with the gasified silicon, forming silica nanoscale clusters. The nanoclusters are suspended in the supercritical hydrothermal environment and are stirred continuously. The melting temperature of these nanoclusters may be reduced, due to their nanoscale size and the effect of a supercritical hydrothermal environment [16, 17, 19, 22]. The nanoclusters might be liquid-like, which can be called semi-molten or in a molten state under the specified hydrothermal conditions. These semi-molten or molten nanoclusters deposit into silicon substrates continuously with the overflow of the atmosphere in the autoclave. The molten or semi-molten silicon oxide at the tip of the initial silicon oxide liquid droplets absorbs a large amount of silicon oxide, resulting in a continuous growth of silicon oxide nanowires. The formation process of silicon oxide spheres is different from that of silicon oxide nanowires. The amorphous structure of the silicon oxide spheres is also different from the crystalline structure of silica nanospheres synthesized by the Stöber–Fink–Bohn method [29]. It is believed that more nanoclusters collide with each other, forming the clusters with larger size and depositing in silicon substrates. A small amount of silicon oxide nanospheres with amorphous structure are formed with diameters measuring several hundred nanometers: these diameters are smaller than those of micro-spheres observed from the SEM experiment. Silicon oxide spheres with different diameter distribution form, owing to the surface tension effect of the liquid-like clusters. The formation process is similar to that of the silicon oxide nanospheres prepared by hydrothermal deposition using silicon and silica as the starting materials [30]. Therefore, fewer silicon oxide nanowires were synthesized out of spheres.

4. Conclusions

In summary, a simple and easily controllable hydrothermal deposition method has been used to prepare silicon oxide nanowires and spheres. The amorphous silicon ox-

ide nanowires have a smooth surface, an average diameter of about 500 nm and the length of a few micrometers, and can even exceed ten micrometers in length. The as-synthesized spheres with the amorphous structure also have smooth surfaces and the diameter distribution ranging from several hundred nanometers to several micrometers. The supercritical hydrothermal conditions are believed to play an important role in the formation and growth of silicon oxide nanowires and spheres. A possible growth process of silicon oxide nanowires is proposed based on the oxide-assisted growth mechanism.

Acknowledgement

This work was supported by the Natural Science Foundation of Anhui Provincial Education Department of China under Grant No. KJ2007B077.

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Received 21 November 2007
Revised 2 February 2009