Direct synthesis of straight SiO₂ nanorods

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Abstract. The straight SiO₂ nanorods with a diameter of about 200 nm and smooth surface have been directly synthesized by high temperature vapor deposition method at 1300 ℃. The as-synthesized samples were characterized by means of scanning electron microscopy, energy dispersive x-ray, and transmission electron microscopy. The results show that as-synthesized silica nanorods have a uniform size, well-defined shape, and smooth surface. However, the morphologies and microstructures of silica nanorods are affected by synthesis conditions, such as the concentration of the SiOx and the deposition temperature. On the basis of these experimental results, a possible growth mechanism of silica nanorods in this process is proposed.

1. Introduction

Since silica nanotubes have been first reported by Nakamura in 1995 [1], there has been an increasing interest to the synthesis of various quasi one-dimensional nanometer-sized materials such as nanotubes, nanowires, nanorods etc.. These one-dimensional nanomaterials show some novel physical and chemical properties due to their peculiar structure and size effect, and they are one of the most promising elements for the fabrication of nanoelectronic devices [2, 3] and integrated optical device [4]. Among them, as an important member in the one-dimensional nanomaterials family, silica nanomaterials have been actively studied for a long time. Silica nanomaterials with various microstructures have been synthesized utilizing a variety of methods, such as, laser ablation [5], vapor–liquid–solid (VLS) [6], vapor–solid (VS) [7], and sol–gel [8] methods.

The well straight silica nanorods are important to the future micro-optoelectronic devices [9]. Generally speaking, aligned silica nanostructures can be obtained by using metallic catalysts, such as Ga–In [10], In–Ni [11], Ga [12, 13], Sn [14], and Ni [15]. Whereas, silica nanowires are not very straight if no catalyst is used [16]. However, this communication introduces a simple and effective method to synthesize large quantities of straight silica nanorods without using any catalysts. This method is base on high temperature solid state reactions of the mixed powders of silica and graphite, via the VS mechanism [7]. Further more, the possible growth mode corresponding to these structures was proposed in this paper.
2. Experimental procedures
Silica nanorods were prepared in a horizontal electronic resistance tube furnace with a gas supply and a control system. The procedure is depicted as follows: at first, the mixed powders of silica (99.00%, Shanghai Chemical Co.) and carbon (Analytically pure, Beijing Chemical Reagents Co.) was placed in a ceramic boat, and then the boat was covered with pretreated Si wafer. Subsequently the boat was transferred into the centre of a ceramic tube mounted in the horizontal tube furnace. 3% H₂/Ar gas mixture and N₂ gas were introduced into the tube at the rate of 50 sccm at atmosphere pressure, respectively. 10 min later, the furnace temperature was heated to 1300°C and held for 2 hours. Then the furnace was cooled to about 700°C at 10°C/min with protection gas, and then cooled naturally to room temperature. The white products were observed on the surface of substrates.

The morphology of as-synthesized products were examined by scanning electron microscopy (SEM, JEOL 6500F), structural analysis was carried out using transmission electron microscopy (TEM, JEM-200CX) and selected area electron diffraction (SAD). Compositional analysis was performed by an energy dispersive x-ray spectrometer (EDS) attached to the SEM. The specimens for TEM analysis were prepared by dispersing the samples in ethanol followed by sonication for 10 min. A few drops of the suspension were dripped onto a micro-grid covered with a holey graphite thin film.

3. Results and discussion
Figure 1(a) is a typical SEM micrograph of the as-synthesized products, it is clearly found the substrate is covered with a large amount of silica nano-rods. Figure 1(b) is the closer view image of silica nanorods in Figure 1(a), it shows silica nanorods with a smooth surface and a good uniformity. The diameter of silica nanorods is about 200 nm, and the lengths are up to several micrometers. We can also find these silica nanorods have a straight and cross structure. In order to clarify the composition of deposition, the sample was examined by EDS spectrometer. The inset is a typical EDS spectrum of individual nanorod. It clearly shows that the nanorods consist of oxygen and silicon. The spectrum shows the as-synthesized products consisting of elements Si and O with an atomic ratio about 1:2.

Figure 1. (a) Top–down SEM image of silica nanorods (b) Closer view showing silica nanorods in (a).

Figure 2 indicates SEM images of the silica nanorods at different growth zones. Figure 2(a) shows schematically different growth zones of the silica nanorods on the substrate. From Figure 2(b), it clearly shows some silicon oxide nanoparticles have deposited on the zone I (Figure 2(a) light zone) and some nuclei of silica nanorods have also formed. Figure 2(c) shows a few of silica nanorods are synthesized on the zone II (Figure 2(a) grey zones), and Figure 2(d) shows a large amount of silica nanorods are synthesized on the zone III (Figure 2(a) black zone). Well then what leads to the formation of the phenomenon here?
Although the detailed mechanism for the formation of different morphology of silica nanorods structures is not well understood, we still believe that the different local concentration of the SiO$_x$ may be responsible for the different morphologies of rods structures. A possible explanation is depicted as follows: when the furnace is heated to high temperature, the growth temperature is high enough to produce vapor SiO$_x$ in the ceramic boat. As the process proceeds, a continuous accumulation of the vapor SiO$_x$ in the ceramic boat leads to a continuous increase of vapor pressure and vapor concentration of SiO$_x$. However, their concentrations would increase gradually with the increasing distance from the centre position of growth substrate. These vapors SiO$_x$ will diffuse along in all directions at the growth zone III (black arrows in Figure 2(a)), where is the joint between substrate and boat. So the concentration gradient of SiO$_x$ is formed and distributed along the radial in the ceramic boat. At the deposition area near the Zone III, the concentration of the SiO$_x$ is relatively high, and the silica nanorods would grow fast and long. The presence of a large amount of straight nanorods should be attributed to the strong limiting effect of the high SiO$_x$ concentration to the silica nanostructures surface (see Figure 2(d)). If the SiO$_x$ concentration was reduced a little (zone II), a small quantity of silica nanorods are synthesized on the growth substrate. In the mean time, the second nucleation perhaps could not achieve and finally only leaving the straight silica nanorods(see Figure 2(c)). If the SiO$_x$ concentration reduced more (zone I), few silica nanorods are achieved and only leaving the nuclei of silica nanorods(see Figure 2(b)).

![Figure 2](image)

**Figure 2.** (a) Schematic diagram depicting different growth zones
(b) SEM image of silica nanorods grown on the zone I in (a)
(c) SEM image of silica nanorods grown on the zone II in (a)
(d) SEM image of silica nanorods grown on the zone III in (a)

The morphology and structure of the nanorods have been characterized in further detail using TEM. Figure 3 is a typical TEM image of silica nanorods. An individual straight silica nano-rod (Figure 3(a)) has smooth surfaces with diameter of about 200 nm, in agreement with SEM observations, and highly dispersed selected-area electron diffraction (SAED) pattern taken from one rod (inset) with only diffusive rings (without diffraction spots), revealing the amorphous nature of the silica nano-rod. Furthermore, Figure 3(b) is the HRTEM image of the black rectangular area marked in Figure 3(a), revealing that no fringes exist in the silica nanorods.
On the basis of the experimental results described above and the conventional VS growth mechanism, we have proposed a possible mechanism for the growth of the straight silica nanorods. At first, when the furnace is heated to high temperature, the reaction of the mixed powders of carbon and silica in the boat should be occurred, and forming a large amount of SiO$_x$ molecule have deposited on the surface of the substrate and some nuclei of silica nanorods have also formed. Then, the newly formed SiO$_x$ will stack on the SiO$_x$ nuclei, forming silica nanorods on the substrate. What affects the straight growth direction of rods here?

![Figure 3](image)

Figure 3. TEM images of (a) a straight silica nanorods and the inset is the corresponding SAED pattern. (b) HRTEM image of Figure 3(a).

We supposed that the existence of a lot of SiO$_x$ molecules results in fast growth of silica nanorods, but there is not enough time for SiO$_x$ to stack themselves into tortuous shape. On the other hand, there is no change of the external conditions during the growth of silica nanorods. They are also capable of inducing a subsequent growth in some proper conditions and promoting the growth of straight structures. At last, the straight nanorods would be formed by depositing SiO$_x$ continuously.

According to observations and analysis of SEM and TEM images, the results indicate that silica nanorods lack any catalyst at nanorods tips and the VS model could be accepted. Further experiments are clearly needed in order to explain the exact process for the growth of the straight silica nanorods not being assisted by catalyst, and to research optical properties of these nanorods.

4. Conclusion
Straight silica nanorods have been synthesized through high temperature solid state reactions process without using any catalysts. These silica nanorods have uniform diameters of about 200 nm, neat smooth surface, and lengths of up to several micrometers. The morphologies and microstructures of silica nanorods are affected by synthesis conditions, such as the concentration of the SiO$_x$. On the basis of these experimental results, a possible growth mechanism was proposed for the silica nanorods. The straight silica nanorods offer potential application possibilities in nanodevices design and fabrication.

Acknowledgments
The authors thank Prof. X. M. Meng of Technical Institute of Physics and Chemistry of CAS for the aid in SEM analysis, Prof. X. D. Xu of Beijing University of Technology for the assistance in TEM analysis, and Prof. W. Xu, Mr. Su, Sun, and Miss Sun of Institute of Biophysics of CAS for the assistance in TEM characterization. One of Authors (X.P. Zou) thanks the partial financial support from Founding Program of Science & Technology Activity for Chinese Homecoming Fellow Abroad and Research Program of Beijing Key Lab for Sensor ((No.KM200810772009.).)
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