Synthesis of flower-like silica microstructures by a simple thermal evaporation method

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Abstract. Novel flower-like silica microstructures have been synthesized through heating silicon, silicon monoxide and active carbon mixed powders under an H2/Ar (3%) atmosphere at 1050 °C without assistance of any metal catalyst. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectrometer (EDS) analyses reveal that the wires are amorphous and consist only of silicon oxide, generated from the reaction of CO with SiC. A possible growth model based on both of vapor-solid (VS) and the Oxide-assisted growth (OAG) mechanism has been proposed to explain this phenomenon.

1. Introduction
In recent years, the silicon nanostructures materials with special size and morphology have attracted a lot of attention due to the potential applications in various fields, such as nanoscale electronic and optoelectronics devices [1–3], and sensor [4, 5]. Up to now, various nanostructures of silica including nanowires, nanorods, and nanotubes have been prepared by using various approaches, for instance, laser ablation [6], vapor phase transport [7], bio-mimetic strategies [8,9], and sol–gel [10] methods.

The flower-like silica nanostructures is an unusual three dimensions consisting of silicon oxide nanofibers. Liu et al. [11] synthesized flower-like silicon nanostructure through combining the thermal evaporation of silicon monoxide powders in an evacuated quartz tube with the VLS growth mechanism at 1100°C. Zhu et al. [12] synthesized flower-like silica nanofibers through heating SiC, deposited on a silica substrate, in the presence of Co powder. However, these methods suffer from metal catalyst existing in the as-synthesized products.

In this paper, we report the generation of flower-like microstructures by using thermal evaporation of the mixed powders of silicon, silicon monoxide and active carbon, deposited on a quartz substrate, in the absence of metal catalyst. The resulting flower-like microstructures are composed of silica microwires, and appear to have grown via both of VS process and the OAG process. These microstructures may prove to be useful as three dimensional composite materials and as novel catalytic supports.
2. Experimental procedures
Flower-like silica microstructures were prepared in a horizontal electronic resistance tube furnace with a gas supply and a control system. Figure 1 shows a schematic diagram of the experimental setup employed during the course of the present work. Two quartz plate (9×2.5×0.1cm³) plates were used as substrates for the growth of the novel flower-like nanostructures. These plates were ultrasonically washed in acetone for several minutes to clean the surface of plate, and then rinsed with de-ionized water. The raw material was a mixture of silicon (99.00%, Shanghai Chemical Co.), silicon monoxide (99.00%, Beijing Chemical Reagents Co.) and active carbon (Analytically pure, Beijing Chemical Reagents Co.) powders at a weight ratio of 6:3:4. It was placed in a ceramic boat that covered with cleaned quartz plate, and then the boat was transferred into the centre of a ceramic tube mounted in the horizontal tube furnace. The other cleaned quartz plate in another ceramic boat was placed next to the first boat on the downstream side of the flowing high-purity Ar. Prior to heating the tube furnace was purged with a mixture gas of Ar (97%) and H₂ (3%) for 10 min to eliminate air in the furnace. Under the ambient pressure and a constant flow of high-purity Ar (60 sccm), the furnace temperature was heated to 1050°C and held for 1 hour. After furnace was cooled down to room temperature, gray products were observed on the surface of substrates.

The morphology of the as-synthesized products was 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 dropped onto a microgrid covered with a holey carbon thin film.

3. Results and discussion
The morphology of the products was examined using SEM. Figure 2a is a low-magnification SEM image and it shows that the as-prepared flower-like microstructures products grown on the quartz substrate. It clearly shows that the flower-like microstructures is made up of many microwires. All the wires have cone-shaped tips at their ends. In addition, these microwires are rooted in one center and have a length of several micrometers, and the diameter of wires decrease along with the growth of wires increase. Figure 2b is the close view image in Figure 2a, it shows that the surface of microwires is neat and smooth. Figure 2c is a SEM image of as-prepared flower-like nanostructures grown on substrate at downstream position. Figure 2d is the close view image in Figure 2c, it shows that the surface of the wires is severely roughened. We speculate that the different local concentration of the SiOₓ may be responsible for the different surface morphologies of silica microwires. In our system, their concentrations would decrease gradually with the increasing distance from the source. Figures 3a and b are the corresponding energy dispersive X-ray spectroscopy (EDX) data of Figure 2b and Figure 2d, it indicates that they consist of elements Si and O with an atomic ratio about 1:2.

The morphology and structure of flower-like silica microstructures have been characterized in further detail using TEM and selected area electron diffraction (SAED). Some short microrwires with length of about several µm are shown in Figure 4a. They may be broken from a whole flower-like
silica microstructure because of the ultrasonic vibrations. The selected-area electron diffraction (SAED) pattern from white rotundity area marked in one arm (inset in Figure 4a) with only diffusive rings (without diffraction spots), revealing the amorphous nature of the silica wires. Figure 4b is the HRTEM image of the white pane area marked in Figure 4a, revealing that no fringes exist in the silica microwires.

![Figure 2](image)

**Figure 2.** (a) SEM image of as-synthesized flower-like silica microstructures grown on the quartz substrate; (b) closer view showing flower-like silica microstructures in (a); (c) as-prepared flower-like silica microstructures grown on Si substrate at downstream position; (d) closer view showing flower-like silica microstructures in (c).

In order to understand the growth formation of flower-like silica microstructures, many questions about it formation must be clarified. For example, (1) How do silicon powders supply? (2) How do carbon powders supply? (3) How about the reactions of the mixed powers should be occurred in the chamber? In the next sections, detailed analysis and explanation are made to answer above questions.

![Figure 3](image)

**Figure 3.** EDX spectrums of (a) silica microstructures in Figure2 b; (b) silica microstructures in Figure2 d.
Figure 4. (a) TEM image of the as-synthesized silica microstructures (broken from the flower-like microstructures) and the inset is the corresponding SAED pattern; (b) HRTEM image of (a).

In our experiment, at first, when the furnace is heated to high temperature, silicon and silicon monoxide powders could be oxidized in the furnace, the chemical reaction equation can be written as below:

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$  \hspace{1cm} (1)

$$2SiO(s) + O_2(g) \rightarrow 2SiO_2(s)$$  \hspace{1cm} (2)

In our system, the carrier gas (Ar) was filled into the tube furnace, and most of oxygen can be eliminated. However, due to the poor obturation of ceramic tube system, there was still leaked or residual oxygen. The concentration of the residual oxygen met the requirement on $O_2$ partial pressure, thus the above reaction could occur. Well then how do active carbon powders supply in the process of flower-like nanostructures formation?

In previous reports, carbon powders often played an important role during the growth of silica nanostructures [13]. Here, we propose a possible reaction between the carbon powders and as-obtained silicon oxide to explain its role:

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$$  \hspace{1cm} (3)

leading to the formation of solid SiC and in situ liberation of CO. We have found SiC nanowires in our products, which provide a strong support for Equation 2. Details of these results will be reported separately. The CO then immediately reacts with the SiC, at an unspecified temperature [12]:

$$SiC(s) + CO(g) \rightarrow SiO(g) + 2C(g)$$  \hspace{1cm} (4)

The resulting silicon oxide have deposited and aggregated in one centre lead to the formation of flowers. Carbon (in Equation 3) may have been oxidized and vented with Ar gas after reaction. So we speculate that the formation of flower-like silica microstructures involves solid-solid reaction (Equation 3) and gas-solid reaction (Equations 1, 2 and 4) processes.

In order to provide support for the effects of the adding active carbon powder on the formation of the flower-like silica microstructures, we performed the additional experiment by using raw sources without adding carbon powders under the same experiment parameters. However, we have not found any products on the substrates through observing SEM. This result indicated that reaction (3) did not occur. It provides strong evidence for adding active carbon powder play a key role during the growth of flower-like silica microstructures.

On the basis of the results of above analysis, it can be considered that the growth mechanism of those flower-like silica microstructures is via both of VS process and the OAG [14] process. In the
initial stage, a large amount of silicon oxide nanoparticles (in Equation 3) have deposited on the surface of the substrate and some nuclei of silica wires have also formed (see black arrow in Figure 5a), which is described as the VS process. Then, the newly formed silicon oxide SiO will stack on the silicon oxide nuclei, forming shorter silica wires on the substrate (see white arrow Figure 5b), which is described as the OAG process. In the mean time, a lot of silica microwires grow and aggregate in one center. As a result, flower-like microstructures are formed (see Figure 5c). At last, the novel flower-like silica microstructures would be formed by growing continuously silica wires in one centre (see Figure 5d).

Figure 5. SEM images (a) some nucleis of silica wires grown on the quartz substrate; (b) short silica wires on the substrate; (c) forming flower-like microstructures; (d) formed flower-like silica microstructures.

4. Conclusion
The novel flower-like silica microwires have been fabricated by heating the mixed powders of silicon, silicon monoxide and active carbon powders. Investigation results demonstrate that these microflowers are made up of silica microwires. The surface morphology of these wires is affected by different local concentration of the silicon oxide. The formation of flower-like silica microstructures is via both of VS process and the OAG process. These microflowers may prove useful in reinforcing composite materials or in further modifying other nanostructures.

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References
[1] Dai H, Wong E W and Lieber C M, 1996 Science 272 523-526
[2] Ebbesen T W, Lezec H J, Hiura H, Bennett J W, Ghaemi H F and Thio T, 1996 Nature 382 54-56
[3] Cui Y, Zhong Z, Wang D, Wang W U, and Lieber C M, 2003 Nano Lett. 3 149-152
[4] Patolsky F and Lieber C M, 2005 Mater. Today 8 20-28
[5] Cui Y, Wei Q, Park H and Lieber C M, 2001 Science 293 1289-1292
[6] Morales A M and Lieber C M, 1998 Science 279 208-211
[7] Xu C X, Sun X W, Yu M B, Xiong Y Z, Dong Z L and Chen J S, 2004 Appl. Phys. Lett. 85 5364-5367
[8] Davis S A, Burkett S L, Mendelson N H and Mann S, 1997 Nature 385 420-423
[9] Huo Q S, Zhao D Y, Feng J L, Weston K, Buratto S K, Stucky G D, Schacht S and Schuth F, 1997 Adv. Mater. 9 974-978
[10] Zhang M, Bando Y, Wada L and Kurashima K, 1999 J. Mater. Sci. Lett. 18 1911-1914
[11] Liu Z H, Sha J, Yang Q, Su Z X, Zhang H and Yang D, 2007 Physica E 38 27-30
[12] Zhu Y Q, Hsu W K and Terrones M, 1998 J. Mater. Chem. 8 1859-1864
[13] Du X W, Zhao X, Jia S L, Lu Y W, Li J J and Zhao N Q, 2007 Mater. Sci. Eng. B 136 72-77
[14] Pan Z W, Dai Z R, Xu L, Lee S T and Wang Z L, 2001 J. Phys. Chem. B 105 2507-2514