Novel SiO_2 Nanotubes: Synthesis from ZnS Nanowires Templates and Visible Photoluminescence at 615 nm

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The novel silica nanotubes with flower-like morphology and hexagonal outer surface morphology were fabricated via a simple ZnS nanowires templates-assisted CVD method. The as-synthesized nanotubes exhibited strong visible photoluminescence at 615 nm and indicated that the method was useful to produce silica nanotubes.

Much attention has recently been focused on the synthesis of nanotubes due to their unique properties,[1–3] such as the structural versatility and the anisotropic chemical and physical properties, which make them as promising materials for advanced technologies. Among various nanotubes, the silica nanotubes have the characteristic of light-emission properties in the visible range at room temperature and can be used as the host materials in bioanalysis, bioseparation[4] as well as potential applications in optoelectronic nanodevice design.[5] As to the fabrication of silica nanotubes, many methods have been developed, including the templated-surface sol–gel (SSG) technique,[6,7] templated-assistance method,[8,9,13] surfactant intercalation method[10] and thermal evaporation method.[11–13]

Among them, template-based methods offer various advantages.[14,15] In this letter, we report that it is possible to fabricate silica nanotubes using the ZnS template-based CVD method. The results show that the as-synthesized nanotubes exhibit the flower-like bundles morphology or hexagonal cross section shape which are different from the previous silica nanotubes, and have strong visible photoluminescence at room temperature.

The experiments were conducted in a simple CVD system. The ZnS powder (Aldrich) was placed onto one side of the alumina boat and the silicon wafer was on the other side. Then the alumina boat was placed at the center of the tube. After the furnace had been purged with Ar for 2 h, the temperature of the center was increased gradually to ≈1300 °C and kept at this temperature for 2 h under a constant flow rate of 40 sccm of Ar gas. Finally, the as-synthesized product was deposited on the tube wall in the downstream of the furnace.

The final products were characterized by field emission scanning electron microscopy (FESEM) (JEOL JSM-6700F) equipped with an energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM) (JEM 200CX), and selected area electron diffraction (SAED). Photoluminescence (PL) measurements were carried out on an Edinburgh luminescence spectrometer (FLS920) at room temperature.

Figure 1 is the SEM images of the silica nanostructures. From Figure 1a, it can be found that numerous silica nanostructures exhibit flower-like morphology. Figure 1b depicts high-magnification SEM image of the flower-like nanotubes. EDS result shown in the inset of Figure 1b indicates that the nanotubes are mainly composed of Si, O, and the ratio for them is close to 1:2.

TEM images are presented in Figures 2a–2d. From Figure 2a, the silica nanostructures exhibit the flower-like assembly of nanotubes which are 200–250 nm in diameter, and 60–80 nm in wall thickness. The selected area electron diffraction (SAED) pattern (up right inset of Figure 2a) taken from the area of the encapsulated segment of the tube shows only diffuse rings without diffraction spots, which indicates that the as-synthesized tubes are amorphous in nature. A typical nanotube is shown in Figure 2b, which reveals that the nanotube is sealed at one end. Figure 2c shows that some nanotubes have hexagonal morphologies of the outer wall different from the results reported by Wang et al.[13] The SiO_2 nanotubes with polygonal shapes of the surface have been reported before by Zygmunt et al.[9] who use crystalline fibers of vanadium oxide hydrate as template through chemical approaches. In our experiment, due to the crystalline nature of the template nanowires of ZnS, the cross-section may be hexagonal. The finding of the hexagonal outer surface of the SiO_2 nanotubes suggests that ZnS powder may play an important role in forming these SiO_2 nanotubes. As shown in Figure 2d, residual segment of the ZnS nanowire template remains in the open-ended silica nanotube with decreasing the center temperature to 1200 °C. The hollow segment of the tube has a narrower cavity and a thicker and rougher inner wall. It is possi-

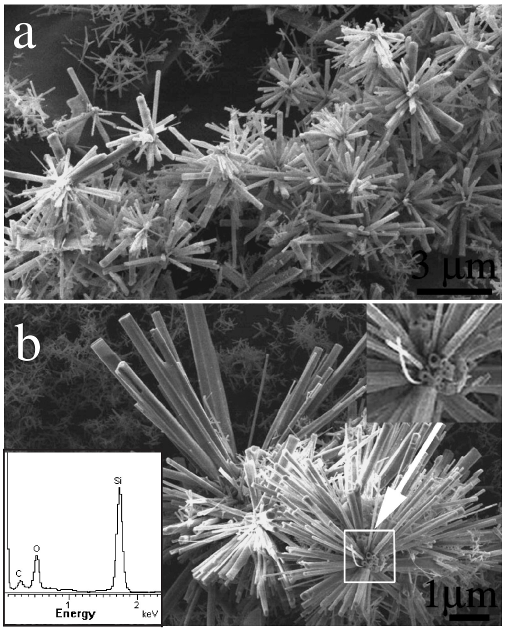

Figure 1. SEM images of the synthesized products: (a) and (b) correspond to low-and high-magnification SEM images (the insets are EDS spectrum and higher-magnification SEM image).

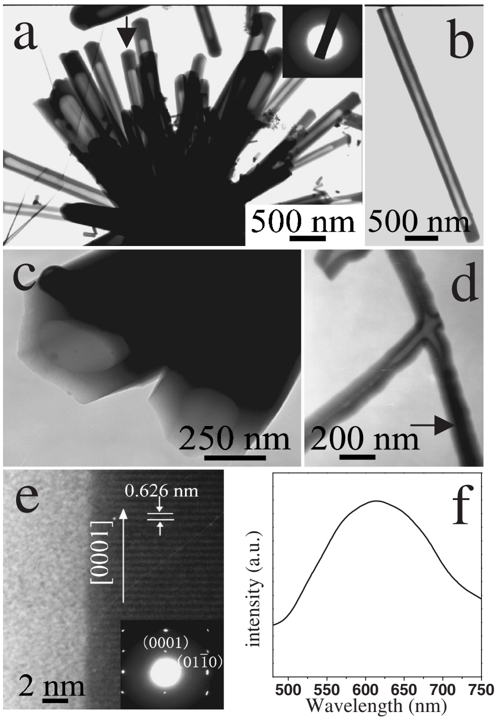

Figure 2. TEM images and HRTEM image of the as-prepared silica nanotubes: (a) TEM image of the flower-like nanotubes (the inset is SAED pattern taken from the region indicated by arrow); (b), (c) A single silica nanotube corresponding to (a) and silica nanotubes with polygonal shapes; (d) Typical partially filled silica nanotube; (e) HRTEM image taken from the the segment-filled silica nanotube indicated by arrow (the inset is corresponding SAED pattern); (f) Photoluminescence spectrum of as-synthesized nanotubes at room temperature.

ble that the formation of the rougher inner wall is related to the amorphous materials, which were transported inside the tube. The SAED pattern (low right inset of Figure 2e) further confirms that the filled phase can be identified as wurtzite ZnS. The corresponding HRTEM (Figure 2e) reveals that the ZnS nanowires inside the nanotubes are single crystalline with an interplanar spacing of 0.626 nm along the growth direction. The ZnS-partly filled silica nanotubes suggest that during the synthesis process ZnS is an essential factor in the growth of these nanostructures of silica.

To explain the growth mechanism, the template-based growth of the silica nanotubes is proposed. The above findings suggest that the two-step processes are responsible for the formation of the silica nanotubes. It is believed that the nanocables of SiO_2-sheathed ZnS were first achieved in the experiments. In this stage, after the ZnS powders were evaporated at the lower temperature, ZnS nanoclusters nucleated from the ZnS vapor and ZnS nanowires grew from the same nucleus that resulted in the appearance of the flower-like morphology. Meanwhile, the surface of the silicon was oxidized to form SiO (the trace remnant of oxygen coming from the reaction system that was not eliminated completely by flushing with Ar and/or the leakage of the furnace) during heating. The SiO vapor surrounding ZnS nanowires was oxidized to form SiO_2 and deposited on the outer surfaces of the ZnS nanowires, resulting in the formation of ZnS/SiO_2 core-shell structures. At the second stage, the ZnS nanowires evaporated away and thus the flower-like nanotubes of silica would be formed. Silica nanotubes were obtained at a temperature range about 1100–1150 °C. The proposed mechanism is supported by the fact that residual segment of the ZnS nanowire template remains in the open-ended silica nanotubes and by the finding of the hexagonal outer surface morphology.

The PL properties of these nanotubes were measured at room temperature. As shown in Figure 2f, the emission spectrum reveals that the as-synthesized nanotubes have a strong visible emission band centered at 615 nm. The origin of this PL band could be attributed to the formation of defects, such as oxygen vacancies suggested by Li et al.[16]

In summary, a new and inexpensive ZnS templated CVD method was used to fabricate silica nanotubes. The results showed that the nanotubes appeared the morphology of flower-like bundles or hexagonal shapes. Additionally, it was found that ZnS was an important factor that affected the formation of these silica nanotubes. The prepared nanotubes exhibited strong visible-light emission peaked at 615 nm. The silica nanotubes, providing some interesting shapes, may open up new and exciting possibilities for further functionalization in many fields.

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