# A New Approach to Fabricate Sulfur Nanotubes

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Sulfur nanotubes have been synthesized by injecting liquid sulfur into the gaps between the Zn nanowires and the surrounding nanochannels of an anodic alumina membrane (AAM) template under high $CS_2$ vapor pressure.

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In recent years, 1-D nanomaterials including nanowires, nanorods, nanocables, nanofibers, and nanotubes, have attracted great interests owing to their novel physical properties, which differ from those of the bulk materials, and to their potential applications in nanodevices.[1,2] Among various synthetic techniques such as the template,[3] the laser ablation,[4] the electrochemical fabrication,[5] the solution-liquid-solution growth,[6] the solution synthesis,[7] the solvothermal method,[8] and other methods,[9] the anodic alumina membrane (AAM)-based synthesis has been proved to be a versatile, simple method for preparation of 1-D nanomaterials. The AAMs possess an ordered, uniform and parallel pore structure, which makes them an ideal host material for creating highly ordered nanomaterials (metals,[10] semiconductors,[11] carbons,[12] and conductive polymers[13]).

Sulfur is a easily subliming element semiconductor with energy gap of 0.24 eV and melting point at 115 °C. Many of the sulfur compounds are very important semiconductors or photoelectric materials. ZnS and CdS play an important role in nonlinear optical[14] and electroluminescent devices.[15] However, few works and applications of sulfur nanostructures (such as nanopaticles, nanofilms, and nanowires) were reported in literature. As a try, we report herein a new method to prepare sulfur nanotubes by injecting liquid sulfur into the gaps between the Zn nanowires and the surrounding nanochannels of AAM under high $CS_2$ vapor pressure.

The AAM used in this work was prepared via a two-step anodic oxidation process of aluminum foil in a 0.3 M oxalic acid solution, which was similar to that described previously.[16] After anodization, the central part of the aluminum on the back side was removed in 1 M $CuCl_2$ solution, and the surrounding aluminum was retained as a support. Then, the barrier layer was dissolved in 5 wt % $H_3PO_4$ solution at 30 °C for 1 h. Finally, a layer of Au was sputtered onto one side of the through-hole AAM to serve as the working electrode. The electrodeposition was carried out in a common two-electrode electrochemical cell, and a graphite plate was used as the counter electrode. The electrolyte solution consisted of 15 g/L $ZnCl_2$, 120 g/L $NH_4Cl$, and 15 g/L $C_6H_9NO_6$. The pH of the solution was about 6. Before electrodeposition, the AAM was immersed into the electrolyte solution, and evacuated using a pump to get ride of bubbles in the nanopores (This step is very important for electrochemically depositing metals into the pores of the AAM). The Zn nanowires were electrochemically deposited at room temperature for 1 h under a constant current density of 2 mA/cm$^2$, which was strictly controlled by a potentiostat/galvanostat (HDV-7C). After electrodeposition, the color of the sample turned black. After washed with deionized water and dried in air, the AAM template with Zn nanowires was put into an autoclave and covered with 5-g pure sulfur powder and 20-mL $CS_2$ (or other solvent). The autoclave was obturated, put into a furnace preheated at 150 °C, and kept for 1 h. The liquid sulfur was injected into the gaps between the Zn nanowires and the walls of the AAM pores under high $CS_2$ vapor pressure.[17] After sulfur injection, the template was washed with ethanol and deionized water in turn, and dried in air. The color of the as-obtained sample changed to brown. The AAM and the Zn nanowires were removed using 2 M NaOH solution.

The crystal structure of the obtained Zn nanowires and the sulfur nanotubes was analyzed by X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku, D/MAX-$\gamma$A) with Cu K$\alpha$ radiation ($\lambda = 0.15418$ nm). The morphology of the Zn nanowires and the sulfur nanotubes was studied on a transmission electron microscope (TEM, H-800) and a high-resolution transmission electron microscope (HRTEM, JEOL-2010).

Figure 1 presents the XRD patterns for the as-obtained Zn nanowires and the sulfur nanotubes. It can be seen from Figure 1 that all the peaks in curve **a** are indexed to the hexagonal Zn. And, all the peaks displayed in curve **b** are identified to the orthorhombic structure of sulfur (JCPDS, 8-247), which indicates that the phase of the sulfur nanotubes is very pure.

Figure 2 demonstrates a TEM image of the Zn nanowires liberated from the AAM by 2 M NaOH solution. It can be seen that these nanowires have a uniform diameter of about 40 nm, and the surfaces of the nanowires are very smooth.

The TEM images of the sulfur nanotubes are illustrated in Figures 3a–3c. It can be seen that the surfaces of these nanotubes are smooth, the outer diameter is about 50 nm, which corresponds satisfactorily to the pore diameter of the AAM used, and the thickness of the nanotubes is about 5–8 nm. A special TEM image for a single sulfur nanotube is displayed in Figure

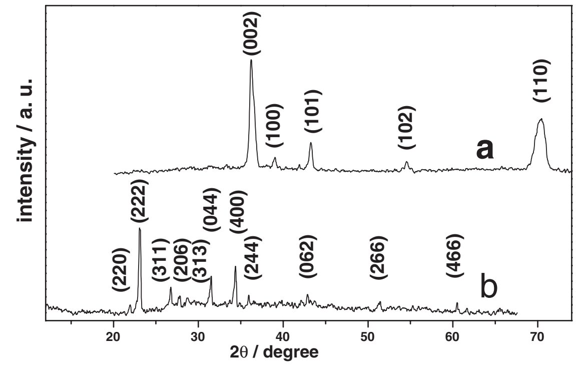

**Figure 1.** XRD patterns for as-obtained products. (a) Zn nanowires; (b) S nanotubes.

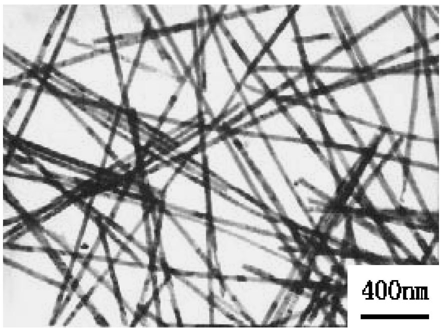

**Figure 2.** A typical TEM image of Zn nanowires.

3c. It can be seen clearly that one part of the nanotube is hollow, and the other is solid, which indicates that the Zn nanowire inside the nanotube has not been removed completely. Figure 3d shows a typical local HRTEM image of a single sulfur nanotube. The lattice-resolution image clearly reveals an interplanar spacing of about 0.474 nm in agreement with the interplanar distance of the (202) ($d = 0.48$ nm) of the bulk orthorhombic sulfur. We could not get the electron diffraction (ED) pattern of the sulfur nanotube, because sulfur was sublimed and melt easily under high-energy electron beams.

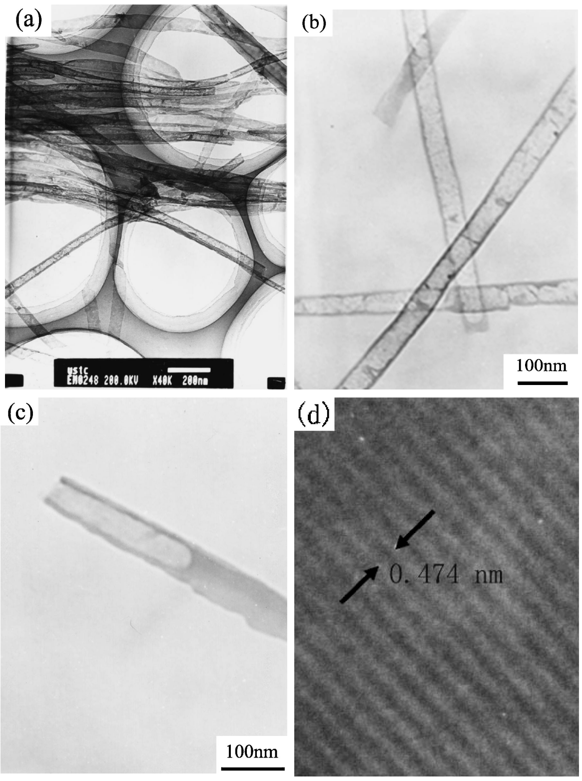

**Figure 3.** TEM and HRTEM images of sulfur nanotubes (a), (b), and (c): TEM images. (d): Local HRTEM image of a single sulfur nanotube.

As we know, the viscosity of the liquid sulfur is the lowest at about 150 °C. That is why we have chosen this temperature to carry out the sulfur injection. Although a few Zn atoms on the surface of the nanowires may react with sulfur to form ZnS during sulfur injection at 150 °C, the formed ZnS can also be removed by 2 M NaOH solution. Therefore, it does not affect the purity of the sulfur nanotubes. It is observed in our experiment that the sulfur nanotubes cannot dissolve in ethanol with large amount, which is quite different from the sulfur powder.

In summary, the sulfur nanotubes have been prepared via sulfur injection under high $CS_2$ vapor pressure. Like carbon nanotubes, many other materials can also be fabricated within the pores of the sulfur nanotubes. And this approach can be used to prepare a variety of nanotubes with a low melting point or subliming easily.

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