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Aligned SnS_2 nanotubes fabricated via a template-assisted solvent-relief process

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ABSTRACT The template-assisted solvent-relief (TASR) process was applied to prepare aligned tin disulfide nanotubes, using $SnCl_4$ and thiourea as the raw materials at 140 °C for 15 h in an alcohol solution. The product was characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The XRD pattern showed that the sample was hexagonal-phase SnS_2 with a preferred orientation. The TEM observations indicate that the as-synthesized SnS_2 nanotubes that were produced were of high quality and uniform size.

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1 Introduction

In the past few years, a great deal of interest in one-dimensional (1-D) nanoscale materials has been stimulated by the discovery of novel properties of carbon nanotubes [1–3]. One-dimensional nanostructures, e.g. nanotubes and nanowires, are of fundamental importance, and hold promise for a wide range of potential applications, in chemistry, physics, electronics, optics, materials science, and the biomedical sciences. Therefore, how to synthesize bulk 1-D nanostructures has become the focus of present research in nanoscience. Many methods have been developed to tailor tubular-structured inorganic materials, such as self-assembly methods [4, 5], chemical processing [6], and the sol-gel hydrothermal method [7, 8].

Apart from the methods mentioned above, template synthesis is one of the most efficient routes for the preparation of well-distributed tubular and fibrillar nanostructures within the pores of an anodic aluminium oxide (AAO) or other nanoporous solid [9, 10]. The important advantage of the template method is that diameter-controlled and well-defined nanostructures can be prepared in this way.

Up to now, our group and other researchers have prepared many kinds of semiconductor tubular crystals, such as Sb_2E_3 (E = S, Se) [11], Ag_2Se [12], and carbon nanotubes [13] by the solvothermal method. However, there were fewer reports on the synthesis of IV–VI semiconductor nanotubes. As an important member of the IV–VI group semiconductors, SnS_2 is a possible candidate in solar cells and opto-electronic devices [14, 15]. In this paper, we put forward a simple template-assisted solvent-relief (TASR) process for synthesizing aligned SnS_2 nanotubes.

2 Experimental

SnS_2 nanotubes were grown in the nanochannels of an AAO membrane via a solvent-relief process. In a typical process, 2 mmol of $SnCl_4$ and 4 mmol of thiourea (Tu) were loaded into a 50 mL Teflon-lined autoclave, which was filled with absolute alcohol up to 80% of capacity. The AAO template, prepared according to the method in [9], was put into the solution. After being sealed, the autoclave was maintained at 140 °C. Alcohol gas was slowly released out of the system by opening the relief value during the reaction time of 15 h. After that time, the system was cooled to room temperature naturally. The yellow-green template with the SnS_2 sample was collected and rinsed with distilled water and absolute alcohol several times. In order to obtain the pure SnS_2 product, the AAO template was removed by putting the sample into a mixture of acid (6% H_3PO_4 and 2% H_2CrO_4) at 60 °C for 1 h. Then the sample was dispersed in absolute alcohol and collected for characterization.

3 Results and discussion

When anodized in an acidic electrolyte, aluminium forms a porous oxide with very uniform and parallel pores. The size of the pore can be controlled by changing the forming conditions. Figure 1a represents a SEM photograph viewed perpendicular to the surface of the membrane. It shows the very high density of pores, with diameters of about 30–70 nm, in the porous AAO template. The SEM photograph in Fig. 1b depicts the cross-section of the AAO template with pores parallel to each other and perpendicular to the surface of the membrane.

The X-ray diffraction (XRD) pattern was recorded on a Japan Rigaku D/max-γ. A X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54178$ Å). A scan rate

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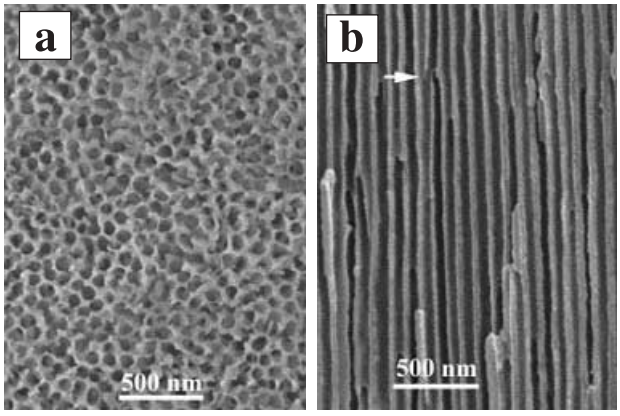

FIGURE 1 SEM images of the AAO template: **a** surface, **b** cross-section

of 0.05°/s was applied to record the pattern in the range 10–70°. A typical XRD pattern of the sample released from the AAO template is shown in Fig. 2. It can be seen that all the peaks could be indexed as the pure hexagonal phase of SnS_2 with cell constants $a = 3.639$ Å, $c = 5.878$ Å, which are in good agreement with the reported values ($a = 3.649$ Å, $c = 5.899$ Å, JCPDS Card 23–677). No impurities were detected in the XRD analysis.

The TEM images (Fig. 3) of the as-prepared product were obtained using a Hitachi H-800 transmission electron microscope. Figure 3a and b show TEM images of aligned SnS_2 tubes grown by the TASR process. These images exhibit that these nanotubes were parallel to each other, uniformly distributed, and high-ordered, and that there were few microscopic defects in the tubes. This is because the nanotubes grew along the nanochannels of the AAO template, which were perpendicular to the surface of template. Figure 3c presents TEM images of some SnS_2 tubes of the same sample dispersed by sonication. It is clear from Fig. 3c that the tubes were of high quality, with uniform diameters ranging from 30 to 70 nm and lengths of up to several micrometers. Interestingly, some "Y"-type tubes were also observed under TEM observation (Fig. 3d). This is also due to the AAO template, which, under SEM observation (as indicated by an arrow in Fig. 1b), exhibits channels with the "Y"-type structure.

The possible reaction mechanism for the formation of nanocrystalline SnS_2 in the solvothermal process has been discussed in previous work [16]. In general, SnS_2 nanocrystallites are laminar particles due to the layered structure of SnS_2. During the TASR process, the $SnCl_4$ and thiourea reagents are allowed to diffuse into the nanochannels of the AAO template and the reagents react within the nanochannels. In addition, due to the space restrictions of the nanochannels, the SnS_2 crystallites grow along the nanochannels in the AAO template. Therefore, the shape of SnS_2 can faithfully replicate the morphologies of the nanopores in the template. On the basis of the above discussion we can conclude that a key point in the process is keeping the nanochannels open during the reaction, which facilitates the diffusion of the ions into the inner parts of the pores and the growth of the products.

To further study the proposed growth mechanism of the tubular SnS_2 crystals, the influence of the solvent-relief process on the morphology of the sample was investigated. It was found that the solvent-relief process is important in the formation of tube-like SnS_2 crystals. In the case of the template-assisted solvent-relief process, the gradual relief of the solvent in gaseous form from the autoclave results in the supersaturation of the solution. The solution can

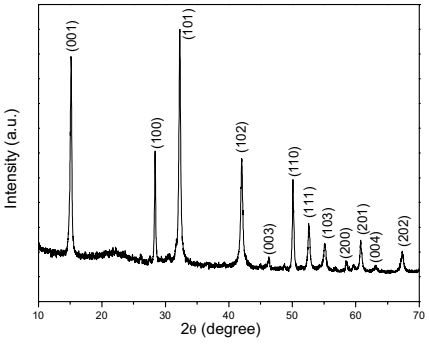

FIGURE 2 X-ray powder diffraction pattern of the SnS_2 sample released from the AAO template

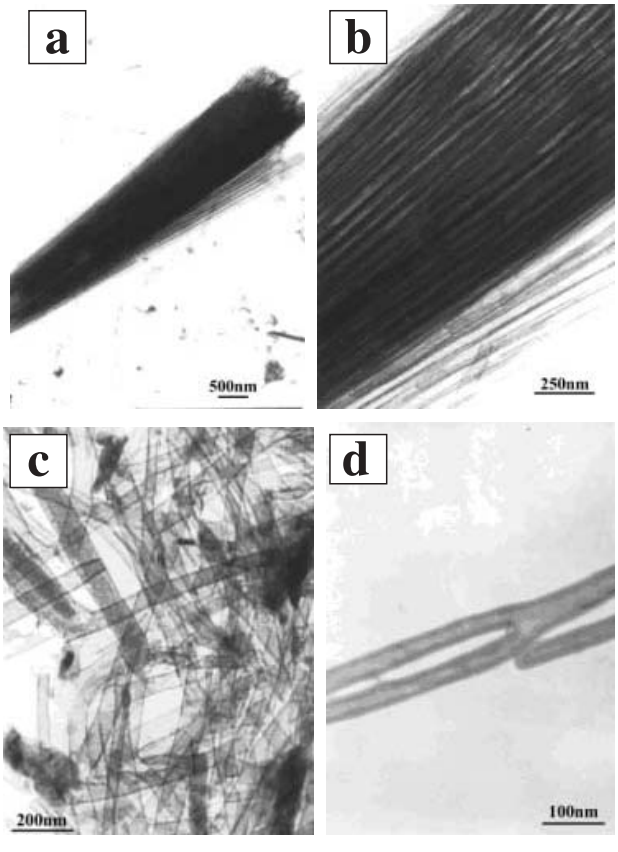

FIGURE 3 TEM images of **a**,**b** the aligned SnS_2 nanotubes sample before, and **c** after dispersal by sonication. **d** Single "Y"-type tube

be maintained in this metastable state during the 15-h reaction time. These metastable conditions are the key factor in the TASR process for the growth of SnS_2 nanotubes. As mentioned above, reagents can diffuse into the nanochannels of the AAO template and form SnS_2 crystallites, namely, crystal seeds. The metastable conditions in the template-assisted solvent-relief process can control the velocity of formation and further growth of these SnS_2 crystal seeds. That is to say, it makes the velocities of nucleation and growth well-matched in the TASR system, and allows crystal seeds to grow into tubular nanostructures along the nanochannels in the AAO template. To confirm the above analysis, the solvothermal process without the relief of pressure was performed. TEM observations showed that the products were nanorods with diameters of about 30 to 70 nm. This result confirms that the relief of pressure in the autoclave is the key factor in the formation of the tubular structure.

4 Conclusions

In summary, a convenient template-assisted solvent-relief process has been successfully developed to synthesize SnS_2 nanotubes using $SnCl_4$ and thiourea as the raw materials in an ethanol solution. TEM observations show that the SnS_2 nanotubes have a uniform size distribution and form highly ordered arrangements. The possible reaction mechanism involved in the process and the influence of the solvent-relief process on the morphology is discussed.

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