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Synthesis and characterization of high density and high aspect ratio Ag_2S nanoparticle nanowires from a paired cell method

LI XiaoNing, YANG XiuChun*, HAN ShanShan, LU Wei, HOU JunWei & LIU Yan

School of Materials Science and Engineering, Tongji University, Shanghai 200092, China

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Ag_2S nanoparticle nanowires were prepared in a porous anodic aluminum oxide template by a simple paired cell method, and were characterized by XRD, FESEM, HRTEM and EDS. The results showed that the as-prepared nanowires were composed of monoclinic Ag_2S nanoparticles. The nanowire diameters ranged from 165 to 270 nm, and Ag_2S nanoparticles were nearly spherical with diameters of 40 to 60 nm. The paired cell method is simple, low cost and easy to control for the fabrication of high density and high aspect ratio Ag_2S nanoparticle nanowires. A formation mechanism for the nanoparticle nanowires was suggested.

α-Ag_2S, nanoparticle nanowires, anodic aluminum oxide (AAO), paired cell method, formation mechanism

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Silver sulfide is known to exist in three different allotropic forms including α-Ag_2S (monoclinic, stable up to 178°C), β-Ag_2S (bcc, 178–600°C), and γ-Ag_2S (fcc, above 600°C). α-Ag_2S is an important II-VI group semiconductor and has a band gap of E_g≈1 eV at room temperature. It has a relatively high absorption coefficient (10^4 cm^{-1}) [1], and has significant applications in optical and electrical devices such as photovoltaic [2] and thermoelectric [3] cells, IR detectors [4], solar-selective coatings [5] and room temperature oxygen sensors [6]. Ag_2S nanowires possess unique optical and electrical characteristics compared with the bulk material, and have been synthesized by sonochemical methods [7], gas-solid reactions [8], microwave irradiation assisted methods [9], surfactant-assisted solvothermal routes [10] and electrochemical methods [11]. Porous anodic aluminum oxide (AAO) has been widely used as a template for synthesizing one-dimensional nanowires and nanotubes of metals, semiconductors and ceramics. Filling the pores of AAO using electrochemical, sol-gel, paired cell, physical or chemical vapor deposition methods allows the control of the growth direction and size of the filled material [12–19]. Among these methods, the paired cell method is very simple, electrodeless, low cost and easy to control, and has been widely used to prepare long and dense AgI nanowires [19], polycrystalline CdS nanowires [20], AgCl nanoparticle nanowires [21] and polypyrrole nanowire arrays [22]. In this paper, we report for the first time the synthesis of Ag_2S nanoparticle nanowires using the paired cell method.

1 Experimental

(i) Materials. Anodic aluminum oxide membranes (Whatman Ltd, Anodisc 25) were immersed in deionized water and sonicated for 3 min to remove air bubbles inside the pore channels. Analytical grade $AgNO_3$ and Na_2S were purchased from Sinopharm Chemical Reagent Co., China, and were used without further purification. Their aqueous solutions were prepared by deionized water.

(ii) Preparation of Ag_2S nanoparticle nanowires. A paired cell was constructed using two plexiglass half-cells, which were separated by an AAO template as shown in

*Corresponding author (email: yangxc@tongji.edu.cn)

Figure 1. Aqueous solutions of 0.01 mol/L Na_2S and 0.02 mol/L $AgNO_3$ were separately poured into one of the half-cells slowly. The reaction was kept at 30°C for 20 h. Then the template was removed from the half cells, rinsed thoroughly with deionized water and dried at 60°C for 1 h.

(iii) Characterization. A D/max2550VB3 X-ray diffractometer (XRD) was used to determine the phase compositions. A Quanta 200 FEG scanning electron microscope (FESEM) with an energy-dispersive X-ray spectroscope (EDS) was used to observe the morphologies and elemental compositions. A JEOL JEM-2010F high-resolution transmission electron microscope (HRTEM) was used to determine the morphologies and microstructures of the synthesized nanowires.

2 Results and discussion

Figure 2 shows the XRD patterns of the AAO template before and after the paired cell filling process.

Figure 2 indicates that the Whatman AAO template was amorphous, and the crystalline phase filled within the pores was monoclinic Ag_2S (JCPDS No.14-0072) with lattice constants of a = 4.229 Å, b = 6.931 Å, c = 7.862 Å and β = 99.61°. According to Debye-Scherrer formula, the calculated Ag_2S crystalline sizes were about 42.6, 52.9 and 45.9 nm, based on the diffraction peaks of the planes ($\bar{1}21$), ($\bar{1}03$) and ($\bar{1}12$), respectively.

Figure 3 shows FESEM images of the Whatman AAO template. Figure 3 indicates that the honeycomb-like template was ordered with circular holes and smooth pore walls. The wall thickness was about 160 nm and the pore diameters ranged from 155 to 260 nm. The pore channels were generally parallel to each other and perpendicular to the membrane surface.

Figure 4 shows FESEM images and an EDS spectrum of the Ag_2S nanoparticle nanowires.

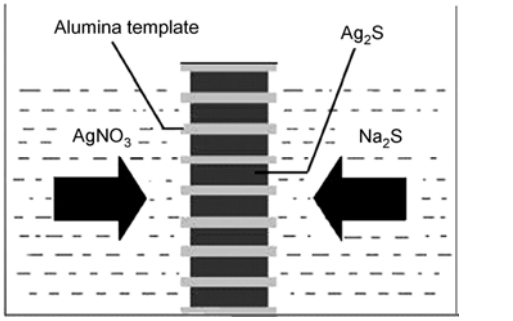

Figure 1 Experimental setup for fabricating Ag_2S nanowires.

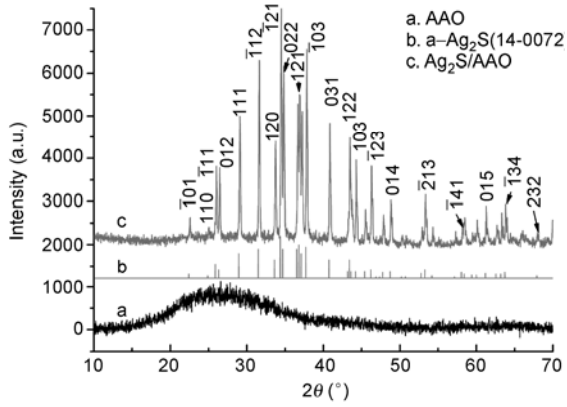

Figure 2 XRD patterns of the AAO templates before and after the paired cell filling process.

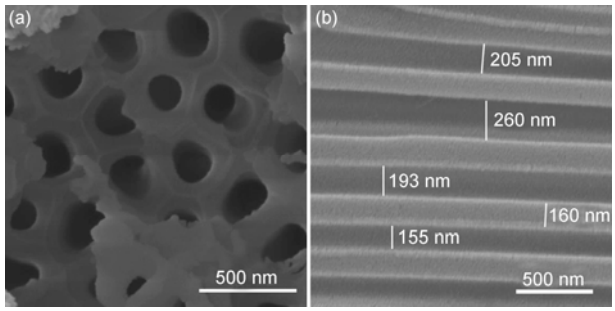

Figure 3 FESEM images of the Whatman AAO template: (a) Top-view; (b) cross-section view.

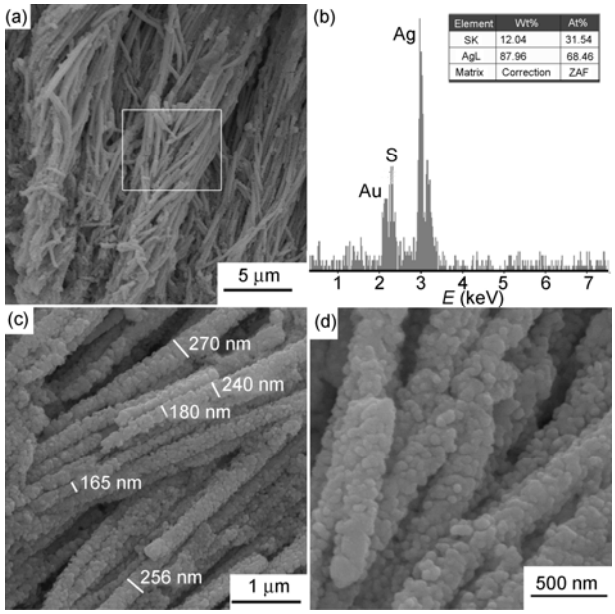

Figure 4 FESEM images and an EDS spectrum of the Ag_2S nanoparticle nanowires. (a) Cross-section view; (b) EDS spectrum; (c) and (d) higher magnification images.

In preparing samples for FESEM observation, alumina on the surface of the Ag_2S /AAO composite was chemically etched for 30 min with 1.0 mol/L NaOH solution at 35°C to release Ag_2S nanowires from the template. High aspect ratio nanowires were generally observed in Figure 4(a), indicating nearly 100% filling of the alumina pores. Ag_2S nanowires

without the support of template often clustered together because of their high surface free energy. The atomic ratio of Ag to S was approximately 2:1 from the EDS spectrum in Figure 4(b), which further indicated that the nanowires were composed of Ag_2S. No Al peaks were detected, indicating that the alumina template was completely dissolved. Au peaks arose from the Au film deposited on the composite for FESEM measurement. Figure 4(c) indicates that the nanowire diameters were between 165 and 270 nm, and were slightly larger than the AAO pore diameters because of the widening of the pore channels during etching. Figure 4(d) indicates that Ag_2S nanowires were composed of a number of spherical particles 40 to 60 nm in diameter, which was consistent with the values calculated from the XRD peaks.

Figure 5 shows TEM and HRTEM images of a typical nanoparticle nanowire. To dissolve the alumina template, a small piece of membrane containing nanowires was immersed in 2.0 mol/L NaOH solution at 60°C for about 5 h. The nanowires were subsequently separated from solution by centrifugation, and then ultrasonically dispersed in 3–5 mL ethanol, a drop of the suspended solution was then placed on a carbon membrane Cu grid for TEM observation.

Figure 5 further indicates that the nanowires were composed of α-Ag_2S nanoparticles. The TEM image indicates that the average nanowire diameter was about 200 nm. The atomic ratio of Ag to S was approximately 2:1 from the EDS spectrum shown inserted in Figure 5(a). The HRTEM image shows clear lattice fringes with spacings of 0.301, 0.243 and 0.280 nm, which could be indexed as the (111) (d_{111}=0.3080 nm), (112) (d_{112}=0.2456 nm) and $\bar{1}12$ ($d_{\bar{1}12}$= 0.2836 nm) planes of monoclinic Ag_2S, respectively. A Moire pattern appeared in HRTEM image with a width of D = 0.662 nm. Moire pattern was described by the following equation [23]:

$$D=\frac{d_1 d_2}{(d_1^{\,2}+d_2^{\,2}-2d_1 d_2\cos\theta)^{\frac{1}{2}}},$$

where D is the width of moire pattern, d_1 and d_2 are the lattice spacings of two interference planes and θ is the angle between the interference planes.

The calculated angle θ between the (112) and $(\bar{1}12)$ planes was 21.2°, which was very close to the measured value of 21.5°. Therefore, the moire pattern originated from interference of the (112) and $(\bar{1}12)$ planes of crystalline Ag_2S.

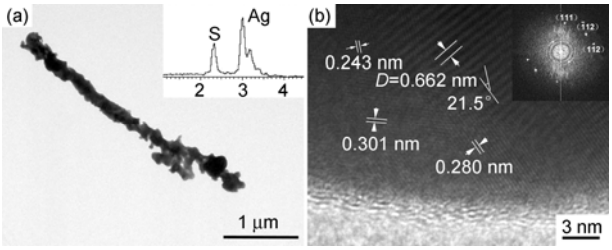

Figure 5 TEM image of a typical Ag_2S nanowire (a) and HRTEM image of the circled region in (a), (b).

Ag_2S molecules formed as soon as Ag^+ and S^{2-} ions met in the pore channels of the AAO template as follows:

$$2Ag^+ + S^{2-} \rightarrow Ag_2S.$$

Crystalline Ag_2S nuclei then formed by heterogeneous nucleation on the pore wall because of a reduction in the Gibbs free energy [24]. Kinetic considerations had an important role in controlling the size of the initial crystallites [25]. As Ag^+ and S^{2-} entered the pores continuously, the Ag_2S nuclei grew and aggregated to form the nanoparticle nanotubes. Upon extending the reaction time, the nanotubes were gradually filled up by newly formed Ag_2S nanaparticles, which induced the formation of Ag_2S nanoparticle nanowires.

3 Conclusions

High density and high aspect ratio α-Ag_2S nanoparticle nanowires were synthesized using AAO templates by the paired cell method. The nanowire diameters ranged from 165 to 270 nm, and the Ag_2S nanoparticles were nearly spherical with diameters of 40 to 60 nm. The Ag_2S nanowire growth mechanism was a simple chemical reaction, nucleation and growth process. The paired cell method is simple, low cost and easy to control for the fabrication of high density and high aspect ratio nanowires.

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