A Room Temperature Self-sacrificing Template Route to Ag_2Te Fibers

Li Mu, Junxi Wan, Dekun Ma, Rui Zhang, Weichao Yu, and Yitai Qian*
Hefei National Laboratory for Physical Sciences at Microscale and Department of Chemistry, Univeristy of Science and Technology of China, Hefei 230026, P. R. China

(Received October 25, 2004; CL-041254)

Tellurium fibers are first synthesized through the reduction of Na_2TeO_4 by hydrazine hydrate. The as-prepared tellurium fibers are used as templates for further reaction with aqueous $AgNO_3$ solution to get Ag_2Te fibers at room temperature.

Transition metal chalcogenides including sulfides, selenides, and tellurides have attracted considerable attention in recent decades due to their interesting properties and potential applications. Silver chalcogenides have been known as superionic conductors.[1] Among them, silver telluride exhibits some unique properties, for example, the lower temperature phase of monoclinic Ag_2Te is a semiconductor with a narrow band gap in the range of 0.04–0.17 eV.[2] Ag_2Te undergoes a phase transition to the high temperature face centered cubic structure[3] at about 145 °C.[4] In its high temperature phase, Ag^+ ions are mobile within a cubic sublattice formed by Te anions, which leads to the superionic conductivity.[5,6] With these properties, silver telluride could be used as good thermoelectric material and promising material for field sensor.

Bulk Ag_2Te was traditionally prepared through a solid reaction between Ag and Te stoichiometrically at high temperatures.[7] Ag_2Te nanoparticles were also synthesized through soft chemical methods, such as a room temperature approach for the synthesis of Ag_2Te with 5–10% Ag_7Te_4 reported by Parkin et al.[8,9] One-dimensional (1D) Ag_2Te have been reported, including Ag_2Te nanowires prepared by DC electrodeposition in porous anodic alumina templates,[10] Ag_2Te nanorods obtained in mixed solvents.[11]

Herein, we report a useful self-sacrificing template route to synthesize 1D Ag_2Te fibers. Compared with the conventional hard templates method, self-sacrificing templates used in this study do not need to be removed after the reaction. The tellurium fibers used as self-sacrificing templates were first synthesized through the reduction of Na_2TeO_4 by hydrazine hydrate; and the as-prepared tellurium fibers further react with $AgNO_3$ to get Ag_2Te fibers at room temperature.

Synthesis of Te fibers: analytical grade Na_2TeO_4 (0.5 mmol) was first dissolved in 40-mL ethylene glycol to obtain clear solution. Then 0.6-mL hydrochloric acid (35 wt %) was added, and the solution was heated at 80 °C under constant stirring for 5 min. After cooling to room temperature, 0.5-mL hydrazine hydrate (85 wt % content) was dropped into this solution, and the solution changed into dark immediately. The resulting solution was transferred into a 50-mL Teflon-lined stainless steel autoclave, which was then sealed and maintained at 100 °C for 12 h. After the reaction was completed, the resulting solid products were filtered off, washed with distilled water and absolute ethanol for several times each, and finally dried at room temperature for 30 min.

Synthesis of Ag_2Te fibers: the freshly prepared Te fibers (0.5 mmol) were added into a 20-mL aqueous solution containing 0.1 M $AgNO_3$ in a conical flask. The solution was further aged in the dark for 24 h at room temperature. Solid black sample was centrifuged, collected and dried at 50 °C for 6 h under ambient conditions.

X-ray powder diffraction (XRD) patterns were carried out on a Philips X' pert diffractometer with Cu Kα radiation ($\lambda = 0.154187$ nm). The transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were obtained on a Hitachi H-800 transmission electron microscope. Scanning electron microscopy (SEM) image and field emission scanning electron microscopy (FESEM) image were taken on an X-650 scanning electron microanalyzer and a JEOL 6700F field emission scanning electron microscope.

Figure 1 shows the typical XRD patterns of the as-prepared Te fibers and Ag_2Te fibers. All the diffraction peaks in Figure 1a can be indexed to the trigonal tellurium with lattice parameters $a = 4.452$ and $c = 5.921$ Å, which are in good agreement with the reported data of $a = 4.457$ and $c = 5.927$ Å (JCPDS 36-1452). All the reflection peaks in Figure 1b can be indexed to the monoclinic Ag_2Te with lattice parameters $a = 8.166$, $b = 4.470$, and $c = 8.979$ Å, which are consistent with the reported data of $a = 8.164$, $b = 4.468$, and $c = 8.977$ Å (JCPDS 65-1104). No obvious reflection peaks for Te can be detected in Figure 1b.

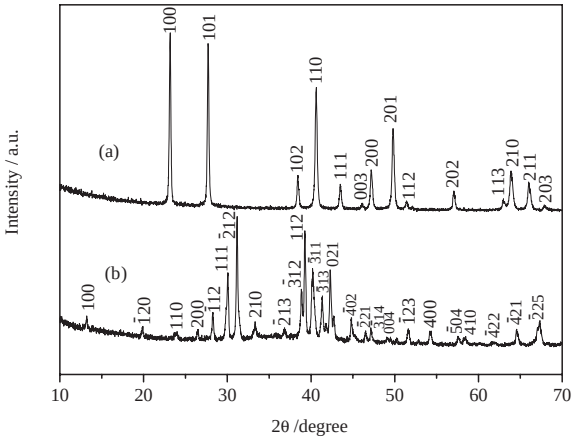

Figure 1. XRD patterns of the as-prepared tellurium fibers (a) and Ag_2Te fibers (b).

The panoramic morphology of the freshly synthesized Te fibers is shown in Figure 2. It can be seen that the sample is composed of 1D fibers with the diameters ranging from 200 to 800 nm and lengths of tens of micrometers.

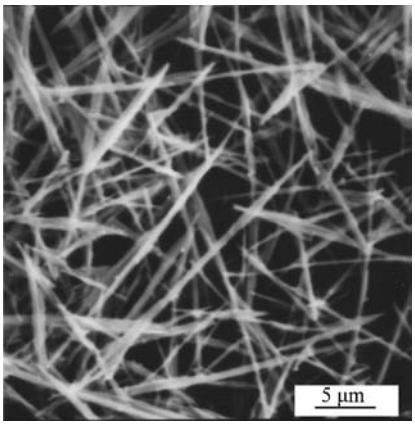

Figure 2. SEM image of the as-prepared tellurium fibers.

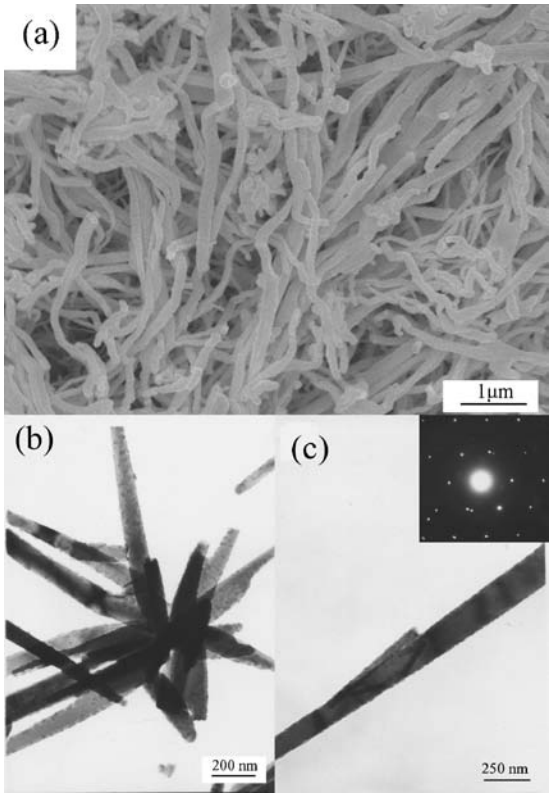

Figure 3. FESEM (a) and TEM (b, c) images of the as-prepared Ag_2Te fibers.

Figure 3a shows the FESEM image of the as-prepared Ag_2Te sample. It can be seen that the products is consisted of a large number of 1D fibers and some fibers assemble together. The TEM image in Figure 3b shows that the average diameters of the Ag_2Te fibers are of 150 nm. TEM image of an individual Ag_2Te fiber and the corresponding SAED pattern are shown in Figure 3c. The SAED pattern confirms that the as-synthesized Ag_2Te fibers consist of crystallines. From the results of SAED pattern and XRD pattern, it can be proved that the Te template transform into Ag_2Te fibers effectively.

As to the possible formation mechanism of the Ag_2Te fibers, it is to some extent similar to that of proposed by Xia et al.[12] In this self-sacrificing template process, the silver ions might catalyze a disproportional process of Te^0 into Te^{2-} and Te^{4+} when silver cations diffused into Te fibers. Then the Te^{2-} species in situ combined with Ag^+ to generate single crystalline fibers of Ag_2Te. As a result, the Te fibers could be converted into Ag_2Te fibers.

In summary, Ag_2Te fibers are successfully synthesized by using Te fibers as self-sacrificing template in an aqueous solution at room temperature. This method might be extendible to other 1D nanostructure materials.

This work is supported by the National Natural Science Foundation of China and the 973 Project of China.

References

1 J. B. Boyce and B. A. Huberman, *Phys. Rep.*, **51**, 189 (1979).
2 W. Gorbachev, "Semicond. Compounds A_2B," Metallurgy Moscow (1980).
3 J. Schneider and H. Schulz, *Z. Kristallogr.*, **203**, 1 (1993).
4 V. Damodara Das and D. Karunakaran, *J. Appl. Phys.*, **66**, 1822 (1989).
5 M. Kobayashi, K. Ishikawa, F. Tachibana, and H. Okazaki, *Phys. Rev. B*, **38**, 3050 (1988).
6 W. S. Howells, A. S. Barnes, and M. Hamilton, *Physica B*, **493**, 276 (2000).
7 R. Coustal, *J. Chem. Phys.*, **38**, 277 (1958).
8 G. Henshaw, I. P. Pakin, and G. Shaw, *J. Chem. Soc., Chem. Commun.*, **1996**, 1095.
9 G. Henshaw, I. P. Pakin, and G. Shaw, *J. Chem. Soc., Dalton Trans.*, **1997**, 231.
10 R. Z. Chen, D. S. Xu, and G. L. Guo, *J. Mater. Chem.*, **12**, 2435 (2002).
11 Y. Jiang, Y. Wu, Z. P. Yang, and Y. T. Qian, *J. Cryst. Growth*, **224**, 1 (2001).
12 B. Gates, B. Mayers, Y. Y. Wu, Y. G. Sun, B. Cattle, P. D. Yang, and Y. N. Xia, *Adv. Funct. Mater.*, **12**, 679 (2002).

Published on the web (Advance View) December 4, 2004; DOI 10.1246/cl.2005.52