Glucose Reduction Route Synthesis of Uniform Silver Nanowires in Large-scale

Zhenghua Wang, Xiangying Chen, Jianwei Liu, Meng Zhang, and Yitai Qian*
Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

(Received June 1, 2004; CL-040615)

Silver nanowires with average diameters of ≈100 nm and lengths up to 800 μm were hydrothermally prepared in large scale by reducing silver nitrate with glucose in the presence of poly(vinyl alcohol) (PVA) at 160 °C. The reaction temperature, the initial concentrations of the reagents, and the kind of polymer have effects on the formation of silver nanowires. The possible formation mechanism of silver nanowires was proposed.

Recently, the nanoscale one-dimensional (1-D) materials, such as nanorods, nanowires, nanotubes, and nanobelts, have stimulated considerable interest because their unique chemical, mechanical, and physical properties different from the bulk counterparts, and may have potential applications in fabricating nanoscale electronic and optoelectronic devices.[1–4] Among these nanoscale materials, nanowires have attracted much interest as they may play an important role as both interconnects and active components in fabricating nanoscale electronic and photonic devices.[5,6] Various preparation methods have been developed for the syntheses of nanowires such as template directed synthesis,[7,8] laser-assisted catalytic growth,[9] and the CVD (chemical vapor deposition) route.[10]

Metallic silver is an important material due to its highest electrical and thermal conductivity. It has been used in a wide variety of commercial applications, and its properties can be enhanced by processing it into various nanostructures with well-controlled dimensions and aspect ratios. There have been a few reports on the synthesis of silver nanowires.[11–14]

Herein, we have designed a polymer-assisted hydrothermal route for the synthesis of silver nanowires with uniform size. In the synthetic process, silver nitrate was reduced by glucose in the presence of PVA. Glucose is a kind of soft reducer and is widely used in depositing silver films on glass such as producing mirrors and water bottles.

All chemical reagents are of analytical grade and used as received without purification. PVA sol (5 wt %) was prepared by adding 5 g of PVA (average polymerization degrees: 2400–2500) into 95-g distilled water, and then heating this mixture at 90 °C till PVA was fully dissolved. In a typical procedure, 0.1 mmol silver nitrate, 0.2 mmol glucose and 2-mL PVA sol were dissolved in 50-mL distilled water at room temperature, then this solution was transferred into a 60-mL Teflon-lined autoclave. The autoclave was sealed and maintained at 160 °C for 35 h, and then allowed to cool to room temperature naturally. The resulting silver-gray fluffy precipitate was filtered and washed with hot water and absolute ethanol, then dried in vacuum at 60 °C for 2 h.

X-ray powder diffraction (XRD) was carried out on a Philips X' pert PRO SUPER diffractometer with Cu Kα radiation ($\lambda = 0.154187$ nm). The transmission electron microscopy (TEM) images and selected area diffraction (SAED) patterns were performed on a Hitachi Model H-800 transmission electron microscope. Scanning electron microscopy (SEM) images were taken with a JEOL-JSM-6700F field emission scanning electron microscope. The ultraviolet and visible light (UV–vis) absorption spectrum was recorded on a Shimadzu UV 240 spectrophotometer.

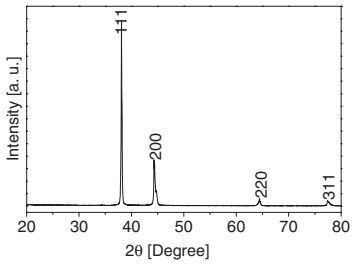

Figure 1. XRD pattern of the silver nanowires.

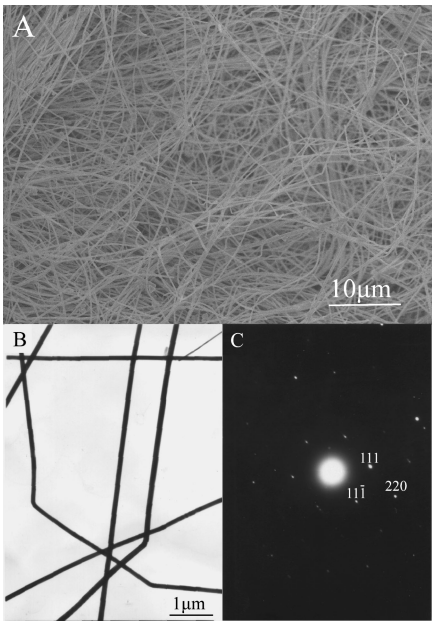

Figure 2. (A) SEM image of the silver nanowires. (B) TEM image of the silver nanowires. (C) SAED pattern of the silver nanowires.

Figure 1 shows a typical XRD pattern of the sample. All the reflection peaks can be readily indexed to face-centered cubic silver. The lattice constant calculated from this pattern is $a =$ 4.089 Å, which is consistent with the standard value of $a =$ 4.086 Å (JCPDS 4-783).

Typical SEM and TEM images of the as-prepared sample are shown in Figure 2. The overall morphology of the sample

shown in Figure 2a indicates that the obtained product is composed of uniform nanowires with average diameters of about 100 nm and lengths up to about 800 μm. There are also a few nanoparticles (<5 wt %) with regular shapes in the product. Figure 2b shows the TEM image of these nanowires. The corresponding SAED pattern is shown in Figure 2c, which indicates the single crystalline nature of these silver nanowires.

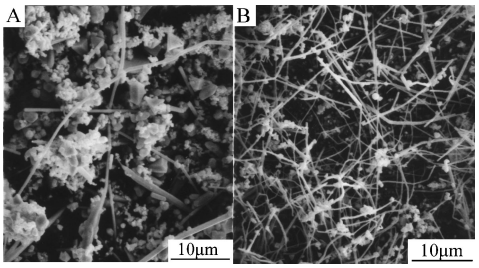

Figure 3. SEM images of the sample prepared at 160 °C for (A) 6 h, and (B) 12 h.

In order to investigate the growth process of the silver nanowires, we have carried out the hydrothermal reaction at 160 °C for different periods of time. Figure 3a shows the SEM image of the samples obtained after heating for 6 h, which indicates that he product is composed of a few short nanowires and a lot of small particles with irregular morphology. Figure 3b shows the samples obtained after heating for 12 h. The nanowires are longer and the amount of these nanowires is more than that shown in Figure 3a. The amount of irregular nanoparticles is dramatically decreased. SEM image (Figure 2a) of the product obtained after heating for 35 h indicates that the product is mainly composed of uniform nanowires, and the irregular nanoparticles are fully disappeared. This study distinctly demonstrates that the silver nanowires are grown from small nanoparticles. This process is similar to the one reported by Sun et al. in preparing silver nanowires by a polyol process.[12] Therefore, the formation of silver nanowires is believed to follow the Ostwald ripening process.[15]

The reaction temperature is important for the formation of silver nanowires. When the reaction is conducted at 120 °C, no nanowires are obtained. Silver nanowires can be obtained in the temperature range of 140–180 °C. At higher temperature, PVA may aggregate and loose its function. The concentration of the reagents also has effect on the formation of silver nanowires. The content of silver nanoparticles in the product will increase with the concentration of reagents and PVA is increased.

Contrastive experiment was carried out in the absence of PVA while the other conditions were kept constant. The product obtained is mainly composed of irregular particles without nanowires. This result indicates that PVA is vital for the formation of silver nanowires. Changing the concentration of PVA in a certain range has no obvious effect on the final products. But PVA may aggregate when its concentration is too high. Other kinds of polymers such as PVP (M_w: 44000–55000) and PEG ($M_w = 20000$) have also been tried in preparing silver nanowires. When PVP was used instead of PVA, silver nanowires with similar diameter and length could be obtained, but the content of silver nanoparticles in the final product was a little higher. When PEG was used, a small quantity of short silver nanowires along with a lot of silver nanoparticles could be obtained. This may be attributed to the different affinity of these polymers for silver.

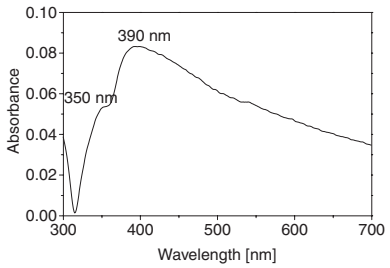

Figure 4. UV–vis absorption spectrum of the sample prepared at 160 °C for 35 h.

Figure 4 shows the UV–vis absorption spectrum taken from the sample obtained at 160 °C for 35 h suspended in ethanol. The absorption peak at ≈350 nm could be attributed to the plasmon response of the long silver nanowires, which is similar to the bulk silver.[12] Otherwise, the absorption peak at ≈390 nm may be attributed to the transverse plasmon mode of silver nanowires. The plasmon peak attributed to silver nanoparticles with small size (20–30 nm) at ≈410 nm is not present here because very few such silver nanoparticles is existed in this sample.[12]

In summary, we have successfully synthesized uniform silver nanowires in large scale by a polymer-assisted hydrothermal process. The synthetic strategy presented here may provide a promising method for directed growth of nanowires and related materials.

Financial supports from the National Natural Science Foundation of China and the 973 Projects of China are gratefully acknowledged.

References

1 S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, *Science*, **280**, 1744 (1998).
2 X. F. Duan and C. M. Liber, *J. Am. Chem. Soc.*, **122**, 188 (2000).
3 Y. Y. Wu, H. Q. Yan, M. Huang, B. Messer, J. H. Song, and P. D. Yang, *Chem.—Eur. J.*, **8**, 1261 (2002).
4 Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science*, **291**, 1947 (2001).
5 X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Liber, *Nature*, **409**, 66 (2001).
6 H. M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science*, **292**, 1897 (2001).
7 D. Xu, Y. Xu, D. Chen, G. Guo, L. Gui, and Y. Tang, *Adv. Mater.*, **12**, 520 (2000).
8 C. R. Martin, *Science*, **226**, 1961 (1994).
9 A. M. Morales and C. M. Lieber, *Science*, **279**, 208 (1998).
10 D. W. Wang and H. J. Dai, *Angew. Chem., Int. Ed.*, **41**, 4783 (2002).
11 Y. J. Xiong, Y. Xie, C. Z. Wu, J. Yang, Z. Q. Li, and F. Xu, *Adv. Mater.*, **15**, 405 (2003).
12 Y. G. Sun, B. Gates, B. Mayers, and Y. N. Xia, *Nano Lett.*, **2**, 165 (2002).
13 K. K. Caswell, C. M. Bender, and C. J. Murphy, *Nano Lett.*, **3**, 667 (2003).
14 Y. G. Sun, B. Mayers, T. Herricks, and Y. N. Xia, *Nano Lett.*, **3**, 955 (2003).
15 A. R. Roosen and W. C. Carter, *Physica A*, **261**, 232 (1998).

Published on the web (Advance View) August 7, 2004; DOI 10.1246/cl.2004.1160