A Facile Route to Silver Nanowires

Rui Kong, Qing Yang,* and Kaibin Tang
Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

(Received January 18, 2006; CL-060078; E-mail: qyoung@ustc.edu.cn)

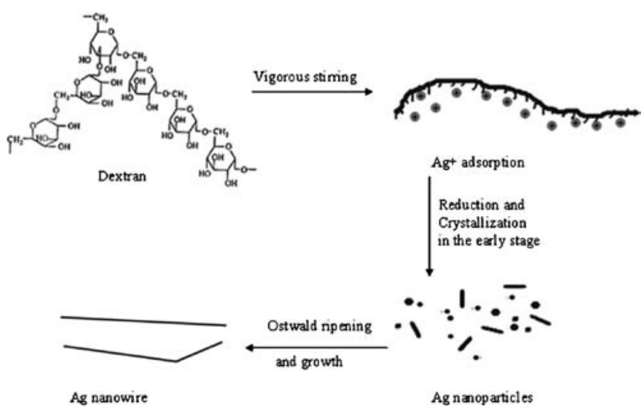
This letter describes a facile self-seeding route to silver nanowires using Dextran which worked as both a sacrificial template and a reducing reagent in aqueous solution. In the entire process, there are not any exotic seeds or stabilizers needed, and the growth mechanism is also briefly discussed.

One-dimensional (1D) nanoscale materials exhibit unique magnetic, optical, electrical, and catalytic properties.[1,2] Of these nanomaterials, silver nanowires have been the focus of many recent research areas because of their potential use as active components in catalysis, photography, electronics, photonics, information storage, optoelectronics, biological labeling, imaging, and sensing.[3] By now, there have been many ways to synthesize silver nanowires, such as the use of electrochemical techniques,[4] polymer-directed synthesis,[5,6] in emulsion or multiphase system.[7] Generally, using 1D nanostructure (i.e., carbon nanotubes,[8] DNA chains,[9] and mesoporous materials[9]) as template is an important one, which may ensure a good control of the morphology of final product, but these templates may also complicate the synthetic procedure and limit the scale of the silver nanowires. Here, a new aqueous self-seeding strategy is reported. A useful polymer of Dextran, previously used for various Ag crystalline nanostructures,[10,11] was chosen as not only a sacrificial template but also a reducing reagent for the synthesis of silver nanowires. By controlling the feedstock, Dextran-capped silver nanowires can also be obtained in the route.

Recently, silver nanowires have been synthesized in the presence of a polymer stabilizer poly(vinylpyrrolidone) (PVP)[6] to direct the anisotropic growth of silver nanowires in organic solution such as ethylene glycol. From the point of green chemistry, aqueous solution is much favorable for the synthesis of 1D silver nanocrystals comparing with organic solutions. The present idea of this letter comes from the well-known silver mirror reaction, in which silver ions were reduced by aldehyde groups within glucose in aqueous solution.[12] The polymer of Dextran also has reductive aldehyde groups, it could also be used as a suitable reducing reagent for silver ions and a stabilizer for the prepared nanocrystals.

Previous investigations have indicated that exotic seeds (e.g., aurum, platinum nanoparticles) were a key factor to direct the growth of wirelike nanocrystals,[6] while at our experiments silver nanoparticles formed in the initial stage[10,11] served as seeds for silver nanowires. In a typical synthetic process, Dextran as structure-directing agent in the system was dissolved in warm distilled water with vigorous magnetic stirring, and then silver nitrate was added with nonstop stirring until Dextran was dissolved completely. After that, the new-generated gel containing minute silver nanoparticles (worked as self-seeds) was transferred into a stainless steel autoclave and heated at 180 °C for 12 h. In the chemical route of using the long chain of Dextran as a templating agent, the aldehyde groups reduce silver ions to form metal silver,[10,11] while the hydroxy groups stabilize the products of silver nanoparticles from their agglomeration. During the growth process, the nanoparticles with larger sizes will grow at the expense of smaller ones because of the effect of Ostwald ripening. Meanwhile, the use of Dextran can also probably promotes the anisotropic growth of silver nanocrystals by controlling the growth rates of various faces via its selective coordination onto the silver facets. Finally, the silver nanoparticles with larger sizes grew into uniform diameter nanowires in the present self-seeding process. It is also noted that these self-generated seeds were much favorable for the preparation of silver nanowires with less impurity, while some particles were produced along with the silver nanowires. The formation of the silver nanocrystals can be described as in Scheme 1.

Figure 1 gives the X-ray diffraction pattern for the as-produced products. The four sharp peaks can be indexed to (111), (200), (220), and (311) diffraction peaks of a face-centered cubic



Scheme 1. Schematic synthesis of silver.

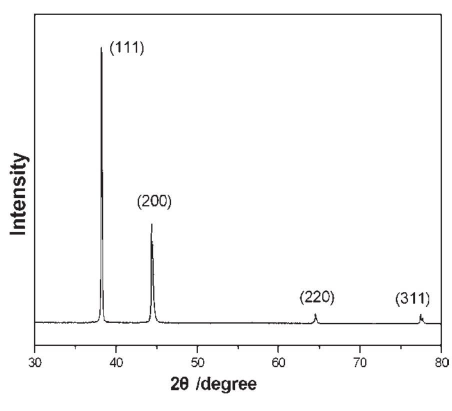


Figure 1. XRD pattern (with Cu Kα radiation) of as-prepared sample.

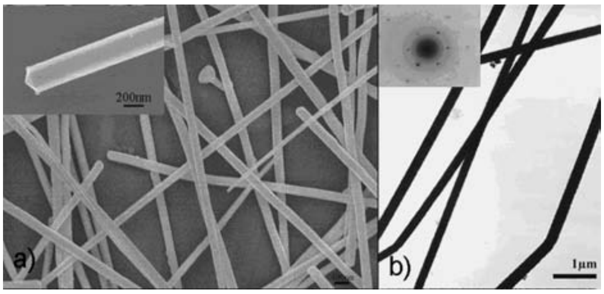


Figure 2. (a) SEM image of silver nanowires, inset: high magnification; (b) TEM image and the corresponding SAED pattern.

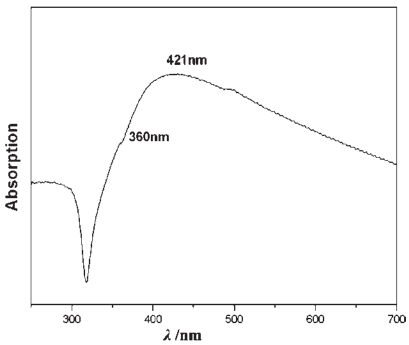


Figure 3. UV–vis adsorption spectrum taken from the as-prepared silver nanowires suspended in ethanol.

silver crystal, respectively, which indicates that the products was silver with good purity.

The typical scanning electron and transmission electron microscopic images of the sample are presented in Figures 2a and 2b, respectively, which illustrate that the sample is mostly composed of uniform nanowires with a range from 20 to 80 μm in length and about 270 nm in diameter. The inserted high-magnification picture in Figure 2a indicates that the microstructures and shapes of the cross section of a single silver nanowire were in fivefold symmetry. The inset in Figure 2b is the electron diffraction pattern for a typical silver nanowire, which indicates that the wires were cubic single crystals.

Figure 3 shows the UV–vis absorption spectrum of the silver nanowires, which was obtained by dispersing the silver nanowires in alcohol under sonication. The spectrum exhibited a broad absorption peak centred at around 421 nm, which could be attributed to the transverse plasmon band of the silver nanowires, as well as a shoulder at around 360 nm, which can be attributed to the surface plasmon excitation of the silver nanowires.[6,13]

The experimental investigations suggested that the optimal conditions for the nanowires are in the feedstock of 0.050 g of Dextran with 0.076 g of silver nitrate (about 0.7:1 by weight) in 45 mL of distilled water at 180 °C for 12 h. The structures and morphologies of the nanowires can be observed in Figures 1 and 2. When reaction temperature was set as 120 and 140 °C for 12 h, the products were silver nonarods and nanowires with a quantity of irregular nanoparticles (see in Supporting Information). In the route, 180 °C was essential for the formation of nanowires, and their diameters were in low distributions (about 270 nm). The distributions of diameters and lengths were affected by various factors, while the former was mainly affected by temperature and the latter affected by the quantity of Dextran used. We note that when more Dextran was used, more particles and fewer wires were produced. An apparent reason for this is that more Dextran resulted in a greater number of Ag nuclei or particles generated from the redox reaction, while the more Dextran made the solution more viscous and so incurred a mass diffusion barrier for succeeding oriented crystal growth during the Ostwald ripening period. Our previous investigation could also give a support for the above explanation.[14] When the quantity of Dextran was increased up to 0.250 g without changing the quantity of silver nitrate (0.076 g), it was also observed that some nanowires were covered with polymer and the sheath was not easily washed out with cold distilled water (see in Supporting Information). The sheath is around a quarter of the width of the nanowires and the surface states of these structures were analyzed by an X-ray photoelectron spectroscope (XPS) (as shown in Supporting Information).

In summary, large scale silver nanowires with uniform diameters and high aspect ratios have been successfully synthesized through a self-seeding process using Dextran as a stabilizer and sacrificial template. It was found that temperature and the molar ratio of Dextran to silver nitrate is a crucial factor to the silver nanostructures. Especially, high-concentration Dextran can yield Dextran-capped silver nanowires. The facile and environmentally friendly synthetic strategy will also provide a worth way to other 1D nanostructures.

Financial support from the National Natural Science Foundation of China (NSFC, Grant Nos. 20571068, 90406024, 20321101, 20371044) and Anhui Provincial NSFC (Grant No. 03044901) is gratefully acknowledged.

References

1 A. J. Cox, J. G. Louderback, L. A. Bloomfield, *Phys. Rev. Lett.* **1993**, *71*, 923.
2 A. P. Alivisatos, *Science* **1996**, *271*, 933.
3 J. Hu, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.
4 Y. Zhou, S. H. Yu, *Chem. Mater.* **1999**, *11*, 545; J. J. Zhu, A. Gedanken, *Langmuir* **2000**, *16*, 6396; Y. Zhou, H. J. Liu, *Mater. Res. Bull.* **1999**, *34*, 1683.
5 Q. Yang, K. Tang, C. Wang, S. Zhang, Y. Qian, *J. Phys. Chem. B* **2002**, *106*, 9227.
6 Y. Sun, Y. Xia, *Nano Lett.* **2002**, *2*, 165; Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176; Y. Sun, Y. Xia, *Adv. Mater.* **2002**, *14*, 11; F. Fivet, M. Figlarz, *MRS Bull.* **1989**, *14*, 29; C. Ducamp-Sanguesa, M. Figlarz, *J. Solid. State Chem.* **1992**, *100*, 272; F.-k. Liu, *J. Cryst. Growth* **2003**, *273*, 439.
7 Y. J. Xiong, Y. Xie, *Adv. Mater.* **2003**, *15*, 405.
8 J. Sloan, D. M. Wright, H. G. Woo, M. L. H. Green, *Chem. Commun.* **1999**, *8*, 699; A. Govindaraj, C. N. R. Rao, *Chem. Mater.* **2000**, *12*, 202.
9 E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, *Nature* **1998**, *391*, 775.
10 D. Walsh, S. Mann, *Nat. Mater.* **2003**, *2*, 386.
11 J. H. Yang, L. M. Qi, *Cryst. Growth Des.* **2004**, *4*, 1371.
12 M. H. Huang, P. D. Yang, *Chem. Commun.* **2000**, *12*, 1063; Y. J. Han, J. M. Kim, G. D. Stucky, *Chem. Mater.* **2000**, *12*, 2068.
13 Z. H. Wang, Y. T. Qian, *Chem. Lett.* **2004**, *33*, 9.
14 Q. Yang, F. Wang, K. B. Tang, C. R. Wang, Z. W. Chen, Y. T. Qian, *Mater. Chem. Phys.* **2003**, *78*, 495.

Published on the web (Advance View) March 18, 2006; DOI 10.1246/cl.2006.402