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A Simple Hydrothermal Route to Large-Scale Synthesis of Uniform Silver Nanowires

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Abstract: This paper describes the preparation of uniform silver nanowires by reducing freshly prepared silver chloride with glucose at 180 °C for 18 hours in the absence of any surfactants or polymers. Scanning electron microscopy studies indicated that the silver nanowires are about 100 nm in diameter and up to 500 μm in length. High-resolution transmission electron microscopy analyses showed that the silver nanowires grow perpendicularly to the Ag(200) plane. The silver nanowires are believed to grow through a solid–solution–solid process. Some influential factors on the growth of silver nanowires are also discussed.

Keywords: green chemistry • hydrothermal synthesis • nanostructures • nanowires • silver

Introduction

One-dimensional nanostructures of metals have attracted much interest due to their potential applications in fabricating nanoscale electronic, optoelectronic, and magnetic devices, which also provide an ideal model system to experimentally investigate physical phenomena, such as quantized conductance and size effects.[1–6] Among all metals, silver nanowires are particularly interesting to fabricate and study because bulk silver exhibits the highest electrical and thermal conductivity among all metals, and the performance of silver in many applications could be potentially enhanced by processing silver into one-dimensional nanostructures. Much effort has been devoted to the syntheses of silver nanowires, such as electrochemical techniques,[7–9] templates (i.e., mesoporous silica[10,11] and carbon nanotubes[12,13]) directed synthesis, and polymer-directed synthesis.[14–17] Recently, Murphy and co-workers have reported a seedless and surfactantless wet chemical approach to prepare silver nanowires.[18] In their report, silver nanowires are prepared by reducing a low concentration silver nitrate solution with sodium citrate in the presence of NaOH.

Herein, we present a simple hydrothermal route for the synthesis of uniform silver nanowires on a large scale. This method does not need any surfactants or polymers to direct the anisotropic growth of silver nanowires. From the viewpoint of green chemistry, this method is favorable as no organic solvents and hazardous substances are used. In the synthetic process, freshly prepared silver chloride was reduced by glucose to form silver nanowires. Glucose is a type of soft reducer and is widely used for depositing silver films on glass, for example, to produce mirrors and water bottles. The reaction of silver chloride and glucose can be formulated as shown in Equation (1):

$$\begin{aligned}&\mathrm{CH_2OH{-}(CHOH)_4{-}CHO + 2\,AgCl + H_2O \rightarrow}\\&\mathrm{CH_2OH{-}(CHOH)_4{-}COOH + 2\,Ag + 2\,HCl}\end{aligned} \qquad (1)$$

Results and Discussion

Figure 1 shows a typical X-ray diffraction (XRD) pattern of the as-prepared sample. All the reflection peaks can be indexed to face-centered cubic silver. The lattice constant (*a*) calculated from this pattern is 4.087 Å, which is consistent with the standard value of 4.086 Å (JCPDS Card File No. 4–783). No impurities can be detected from this pattern. This indicates that pure silver metal is obtained under the present synthetic conditions. The obtained sample was weighed and the calculated yield of the silver metal product was calculated to be about 95%.

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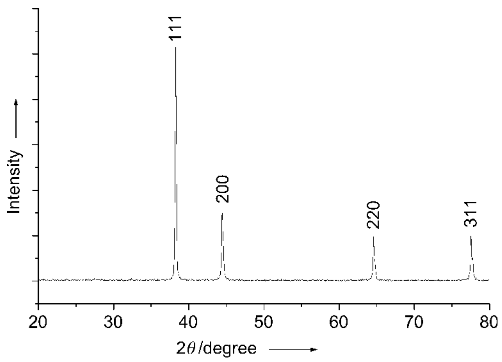

Figure 1. XRD pattern of the as-prepared silver nanowires.

Scanning electron microscopy (SEM) images of the as-prepared sample are shown in Figure 2. The overall morphology of the sample is shown in Figure 2A, which indicates that the sample is composed of a large quantity of uniform nanowires with lengths of up to about 500 μm. Figure 2B shows the morphology of the sample with higher magnification and show that the average diameter of these nanowires is about 100 nm. There is also a small quantity of nanoparticles existing in the products. Figure 3 displays a histogram of about 200 nanowires counted from an SEM image, which shows that the nanowires are uniform in diameter.

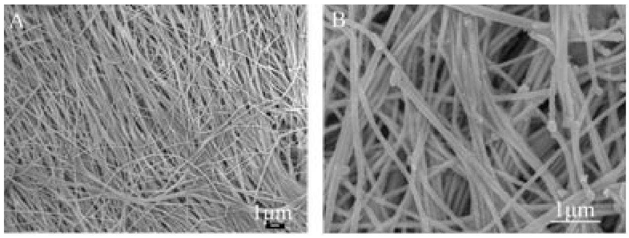

Figure 2. A) SEM image of the as-prepared silver nanowires. B) Image A) with higher magnification.

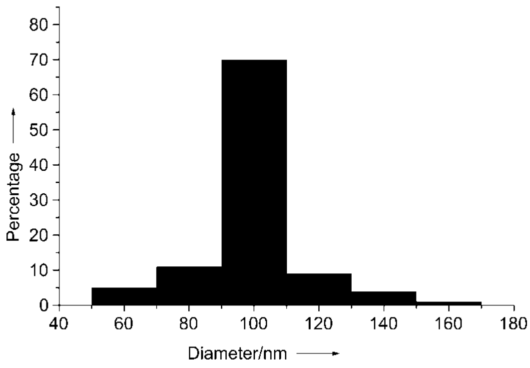

Figure 3. A histogram of about 200 nanowires counted from a SEM image showing the distrubution of nanowire diameters.

The products were further characterized by high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) analyses. Figure 4A shows a HRTEM image taken from the edge of a silver nanowire. Figure 4B is the HRTEM image of the selected area in Figure 4A with higher magnification. The regular spacing of the observed lattice planes is 2.0 Å, which is consistent with the separation of Ag(200) planes. The growth direction of the silver nanowire is perpendicular to this plane. The corresponding SAED pattern indicates the single crystalline nature of silver nanowires (Figure 4C).

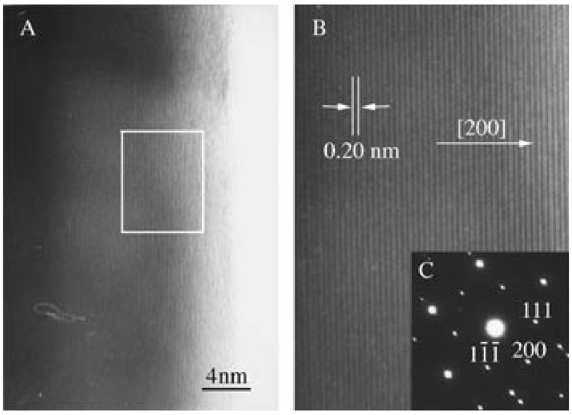

Figure 4. A) HRTEM image of silver nanowires. B) Image A) with higher magnification. C) The corresponding SAED pattern.

Comparative experiments were carried out to investigate the influential factors on the growth of silver nanowires. It was found that the reaction temperature and the concentration of reagents had clear effects on nanowire formation. When the experiment is conducted at 140 °C, silver chloride cannot be reduced by glucose. However, silver nanowires emerge when the reaction is conducted at 160 °C. Here we chose 180 °C as the synthetic temperature because the reaction can be completed quicker. Silver chloride colloidal solution aggregates with heating and forms precipitates. When the dosage of silver chloride is increased, firm silver chloride precipitates of larger size appear. Such precipitates are so firm that the reducing process becomes very slow. In addition, freshly prepared silver chloride instead of commercial silver chloride is used as the starting material because commercial silver chloride mainly consists of firm powders, so the reacting process would be much slower if it were used as the starting material. In our experiment, glucose is slightly in excess to ensure the full reduction of silver chloride. When the concentration of glucose was increased, the content of silver nanoparticles in the final product increased correspondingly. Silver nanoparticles were the dominant product when the dosage of glucose was increased to 1 mmol.

In order to investigate the growth mechanism of silver nanowires, we conducted experiments at 180 °C for different periods of time. The samples obtained at different stages of reaction time were examined by using XRD and SEM techniques. Figure 5A shows the XRD pattern of the sample obtained after the reaction had proceeded for 6 hours. Most of the diffraction peaks can be indexed to silver chloride (JCPDS Card File No. 31-1238). There are only two weak peaks that can be indexed to silver. This pattern indicates that the main component of the sample is still silver chloride and only a little silver metal has been produced. The SEM image of this sample is shown in Figure 6A, which indicates that a few nanowires have emerged among the particles. Figure 5B is the XRD pattern of the sample obtained after the reaction had proceeded for 9 hours. The diffraction peaks of silver chloride have dramatically weakened, while the diffraction peaks of silver have clearly strengthened. This pattern indicates that as the reaction goes on, silver chloride is reduced by glucose to form silver metal. The SEM image of this sample (shown in Figure 6B) indicates that in addition to some particles a large quantity of nanowires exist in the sample. Figure 5C shows the XRD pattern of the sample obtained after the reaction had proceeded for 12 hours. The diffraction peaks of silver are stronger and only several very weak peaks of silver chloride are presented. This pattern indicates that after reacting for 12 hours, most of the silver chloride has been reduced to silver metal. The SEM image shown in Figure 6C indicates that the sample is mainly composed of nanowires. This study demonstrates that silver nanowires are gradually grown from silver chloride during the synthetic process.

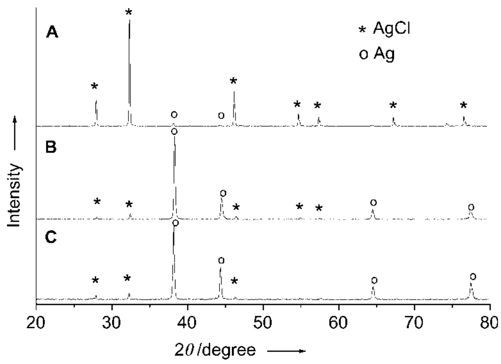

Figure 5. XRD patterns of samples obtained at 180 °C after a reaction time of A) 6 h, B) 9 h, and C) 12 h.

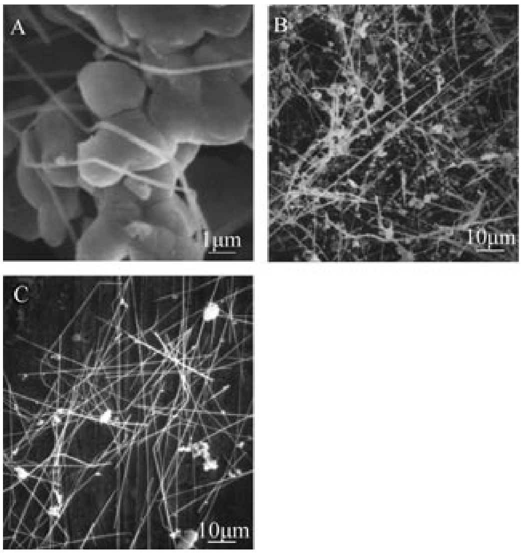

Figure 6. SEM images of samples obtained at 180 °C after a reaction time of A) 6 h, B) 9 h, and C) 12 h.

Based on the experiments mentioned above, we speculate that silver nanowires are grown through a solid–solution–solid process, described as follows. First, silver chloride dissociates in water releasing free Ag^+ ions. Following this, the released Ag^+ ions are reduced by glucose and form silver nuclei. These nuclei grow into silver metal under the current experimental conditions. As the solubility of silver chloride in water is very low, the concentration of free Ag^+ ions in the solution is very low. As a result, the reduction of silver chloride and the formation of silver nuclei are both very slow. Such a slow reaction may be favorable for the anisotropic growth of sliver nanowires.

We have tried other silver sources to confirm such speculation. When silver nitrate was used instead of silver chloride, the reaction was complete in a much shorter time and only near-spherical silver nanoparticles were obtained. As silver nitrate is soluble and easily dissociates in water, the concentration of free Ag^+ ions in silver nitrate solution is much higher than in silver chloride colloidal solution. When silver nitrate is used instead of silver chloride, the reduction of Ag^+ ions to metallic silver is very quick, thus the anisotropic growth of silver metal is almost impossible. As a result, silver nanoparticles instead of silver nanowires are obtained. We have also used other anions such as OH^- and Br^- instead of Cl^- to generate other barely soluble silver compounds, such as silver oxide and silver bromide, to act as the silver source. In these cases, silver nanowires were also obtained. In the case of silver bromide the reaction needed more time to reach completion. As it is known that the solubility product constant (K_{SP}) of silver bromide ($K_{SP} = 5.0 \times 10^{-13}$) is lower than that of silver chloride ($K_{SP} = 1.8 \times 10^{-10}$),[19] the concentration of free Ag^+ ions in the solution containing silver bromide is lower than that containing silver chloride and, as a result, the reduction speed is slower.

Figure 7 shows the UV-visible absorption spectrum taken from the as-prepared silver nanowires suspended in ethanol. The absorption peak at ~350 nm could be attributed to the plasmon response of the long silver nanowires,[15] which is similar to that of the bulk silver. Otherwise, the absorption peak at ~390 nm may be attributed to the transverse plasmon mode of silver nanowires.

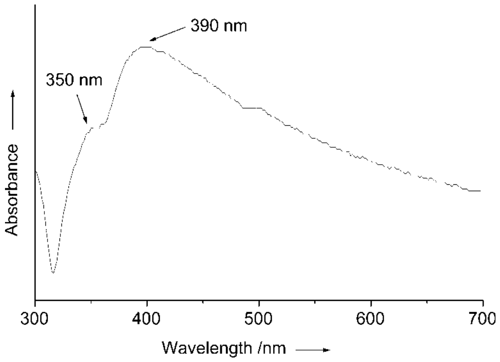

Figure 7. UV-visible absorption spectrum of the silver nanowires.

Conclusion

In summary, uniform silver nanowires with diameters of about 100 nm and lengths up to 500 μm were successfully prepared on a large scale through a simple hydrothermal process without the use of any surfactants or polymers. The influential factors such as reaction temperature, concentration of the reagents, and different silver sources were studied. The synthetic strategy presented here is simple and environmentally friendly, and may provide a promising method for growing nanowires.

Experimental Section

All chemical reagents were of analytical grade and used as received without purification. In a typical procedure, silver nitrate (0.02 M, 5 mL) and sodium chloride (0.02 M, 5 mL) were added to distilled water (30 mL) under stirring to form silver chloride colloidal solution. Then glucose (0.04 g, 0.2 mmol) was dissolved in the above colloidal solution; this was then transferred into a stainless steel autoclave with a Teflon liner of 50 mL capacity, and heated in an oven at 180 °C for 18 h. After the autoclave was air-cooled to room temperature unaided, the resulting silver-gray fluffy precipitate was filtered and washed with distilled water and absolute ethanol, then dried under vacuum at 60 °C for 2 h.

XRD patterns were obtained on a Philips X' Pert PRO SUPER diffractometer equipped with graphite monochromatized $Cu_{K\alpha}$ radiation ($\lambda = 1.541874$ Å). TEM images were recorded on a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. HRTEM images and SAED patterns were taken on a JEOL 2010 high-resolution transmission electron microscope performed at an acceleration voltage of 200 kV. SEM images were taken with an X-650 scanning electron microanalyzer and a JEOL-JSM-6700F field emission scanning electron microscope. The UV-visible absorption spectrum was recorded on a Shimadzu UV-240 spectrophotometer.

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