



## Growth of silver nanowires on metal plates by conventional redox displacement

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Received 7 January 2003; in final form 7 May 2003

### Abstract

Silver nanowires (diameter 20–50 nm, length of the order of  $\mu\text{m}$ ) have been synthesized in a high yield from nitric acid-treated iron plates dipped in a silver nitrate solution of an appropriate concentration. The formation of the silver nanowires is discussed in terms of silver nitrate concentration, substrate surface morphology and elemental nature of substrate.

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### 1. Introduction

One-dimensional nanostructural materials such as nanowires, nanotubes and nanorods are of fundamental and technological interest as they find applications in conductance quantization and nanodevices [1–6]. Of particular interest are silver nanowires owing to their exceptionally high conductance, and numerous advances have been made in the fabrication silver nanowires materials in a variety of nanofabrication and crystal growth methods [7–10]. More accessible methods such as electrochemical and chemical reduction syntheses generally employ a template for the exclusive growth of nanowires in the direction normal to the substrate surface [11–14]; however, the removal of the template poses practical problems.

A recent investigation of the preparation of silver nanowires without the use of a template used nanocrystalline AgBr and a developer with AgNO<sub>3</sub> component as precursors [15]; others [16,17] prepared silver nanorods by using wet chemical methods. Silver nanorods have also been prepared by an electrochemical technique [18] and by UV photoreduction in the presence of polymers and other materials [8,19–21]. In an extension of these studies, we present our research on the synthesis of silver nanowires in which we have used a conventional redox displacement reaction that uses neither a porous template nor a soft template.

### 2. Experimental

In a typical redox experiment, a  $1 \times 1 \text{ cm}^2$  Fe or Cu plate was first treated by dilute HNO<sub>3</sub> (0.02 M)

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and then immersed in 800 ml  $\text{AgNO}_3$  solution ( $5 \times 10^{-4}$  M) at room temperature. After 1 h, the material growing on surface was collected, washed with water and ethanol, and dried in vacuum. The material was characterized by powder X-ray diffraction (XRD) on a Rigaku D/Max-rC X-ray diffractometer equipped with  $\text{Cu-K}\alpha$  radiation. The transmission electron microscopy (TEM) images were recorded with a JEM-100CX II microscope at an accelerating voltage of 100 kV, and scanning electron microscopy (SEM) images with a JEM5600LV microscope (JEOL) operating at 15 kV. The UV–Vis absorption spectrum was recorded on a UV-2501 PC (SHIMADZU) instrument.

### 3. Results and discussion

#### 3.1. Characterization of silver nanowires

More than 90% of the product of the redox reaction of the Fe plate that had been immersed in a  $5 \times 10^{-4}$  M  $\text{AgNO}_3$  for 1 h exists as silver nanowires with diameter of 20–50 nm and length of the order of  $\mu\text{m}$  (Fig. 1a). Nanowires longer than 10  $\mu\text{m}$  could be grown by this procedure (Fig. 1b). Of the remaining 10%, some were branched in a tree motif. A minor amount of nanoparticles was also present that were probably the precursor of the nanowires. The nanowires are single-crystalline, as supported by the electron diffraction pattern (inset in Fig. 1a) recorded by directing the electron beam on to a selected position (marked by the arrow). The electron diffraction pattern suggested a face-centred cubic (fcc) Ag crystallite as the electron beam was set perpendicular to the (111) plane of the crystallite. The diffractogram (Fig. 1c) is interpreted in terms of a fcc Ag phase as it matches that the JCPDS standard (JCPDS 4-0783). The diffractogram did not suggest the presence of possible impurities, such as  $\text{Ag}_2\text{O}$ ,  $\text{AgNO}_3$  and Fe.

The nanowires displayed a UV–Vis spectrum similar to those reported [9,17,18,22,23]. The UV–Vis spectrum of a suspension of as-prepared silver nanowires in ethanol showed a broad peak at ca.

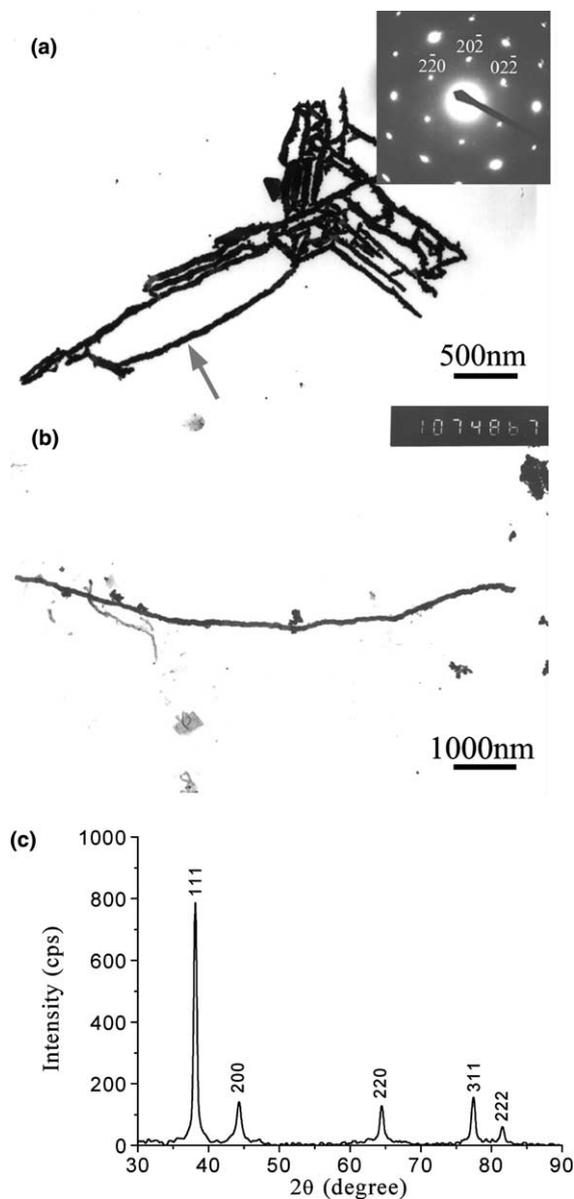


Fig. 1. (a) TEM image of the *as-prepared* silver nanowires from a  $5 \times 10^{-4}$  M  $\text{AgNO}_3$  solution. Inset: electron diffraction pattern recorded by directing the electron beam at a selected point (arrowed) of the nanowire. (b) TEM image of a silver nanowire that is more than 10  $\mu\text{m}$ . (c) XRD pattern of *as-prepared* silver nanowires.

390 nm (Fig. 2) that could arise from surface plasmon excitation of the silver nanostructures [22,23].

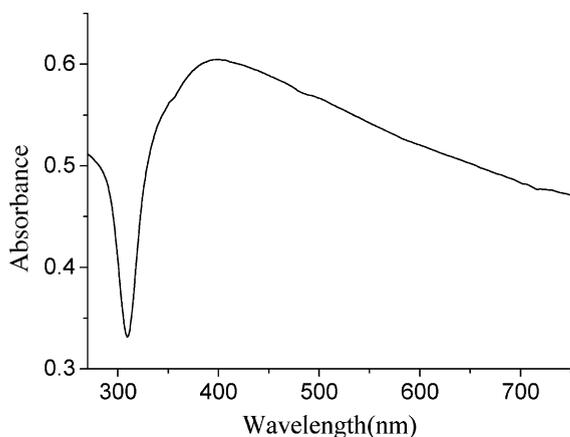


Fig. 2. The UV-Vis absorption spectrum of a suspension of silver nanowires in ethanol.

### 3.2. Parameters influencing the formation of the nanowires

#### 3.2.1. $\text{AgNO}_3$ concentration

The optimum concentration for the preparation of the silver nanowires fell into a narrow range, from  $5 \times 10^{-4}$  to  $1 \times 10^{-3}$  M (for the Fe plates) as the higher concentrations led to the formation of unwanted dendrites and some much larger nanowires. At  $1 \times 10^{-3}$  M, the nanowires exhibited a diameter of 40–100 nm, as characterized by the TEM image (Fig. 3a); however, the use of higher concentration led to a reduction of yield by 20–30%. A comparison of the product from  $5 \times 10^{-4}$  M solution (Fig. 1) with the product from the  $1 \times 10^{-3}$  M solution reveals the presence of nodes on the nanowires at the higher concentration (Fig. 3a). At much higher concentrations (e.g.,  $5 \times 10^{-3}$  M), dendrites were formed (Fig. 3b). On the other hand, lowering the concentration (e.g.,  $1 \times 10^{-4}$  M) led to irregularly shaped nanoparticles (Fig. 3c), their sizes ranging from 3 to 50 nm (average about 20 nm). The uniformity of the nanowires was ensured by the use of a constant concentration of  $\text{AgNO}_3$ , and this was effected by using a large volume (800 ml) of the reagent. Uniform nanowires could be prepared in about an hour.

#### 3.2.2. Surface morphology of the metal substrate

The plates used in the synthesis of nanowires had to be nitric acid-treated plates as such a

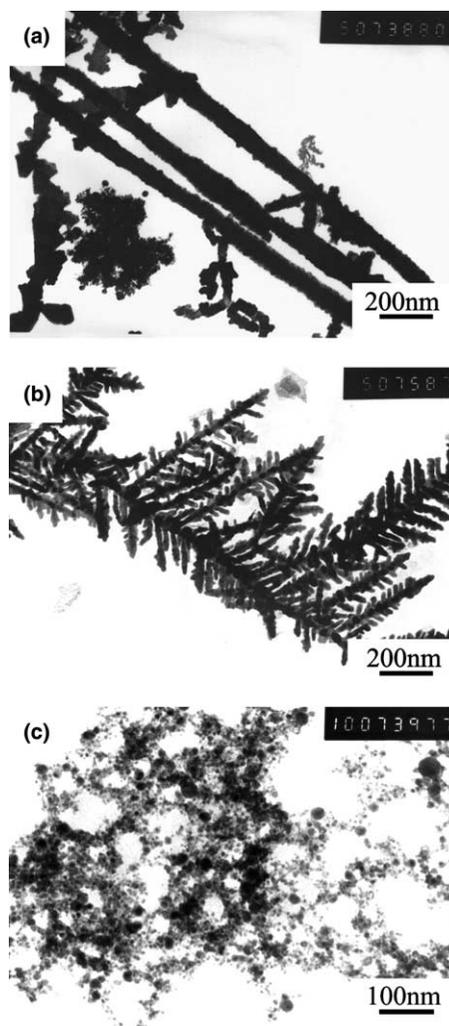


Fig. 3. TEM images of silver nanostructures grown on the surface of an Fe plate that had been immersed in an  $\text{AgNO}_3$  solution. (a)  $1 \times 10^{-3}$  M, (b)  $5 \times 10^{-3}$  M, and (c)  $1 \times 10^{-4}$  M.

treatment affected the yield. For example, an Fe plate that had been only polished mechanically (SEM image shown in Fig. 4a) when reacted with  $5 \times 10^{-4}$  M  $\text{AgNO}_3$  afforded a filmy product with a thickness of a nanometer scale along with nanoparticles. The surface of the plates after the acid treatment (SEM image shown in Fig. 4b) was much rougher; a rougher surface appears to improve the yield of the nanowires.

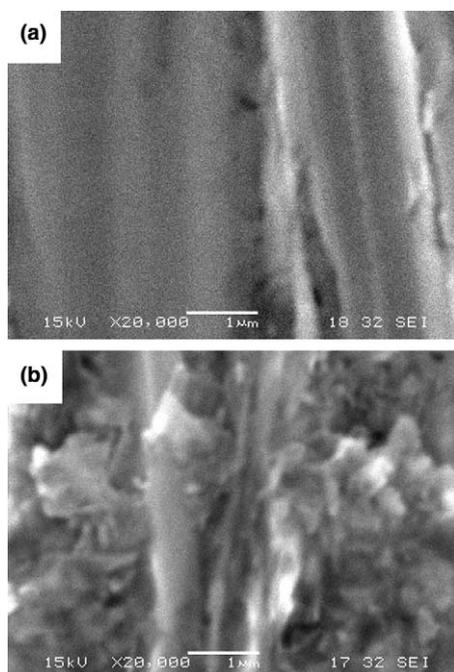


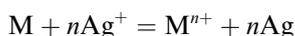
Fig. 4. SEM image of the surface of an Fe plate that had been (a) polished mechanically, and (b) treated with dilute  $\text{HNO}_3$  solution.

### 3.2.3. Elemental nature of the metal plate

The yield of the nanowires was highest with Fe compared with Cu, Al and Mg. For example, only a maximum yield of 10% could be obtained with Cu at all concentrations. In fact, at low concentrations, the product comprised different nanostructures but few silver nanowires whereas at high concentration, large visible crystallites were formed. Mg and Al plates gave only a minor quantity of Ag dendrites.

### 3.3. Mechanism of formation of the nanowires

In the displacement reaction between a metal and Ag, the metal loses electrons and goes into the solution as ions; the  $\text{Ag}^+$  ions in the solution then accept the electrons and Ag metal is deposited on the surface of the metal. The process is represented by the following redox equation:



On the rough surface after the Fe plate had been treated by dilute  $\text{HNO}_3$  solution, larger

number of active sites (such as surface defects) are probably present, which should expedite the reduction of  $\text{Ag}^+$  and also serve as nucleation sites for the reduction of  $\text{Ag}^+$ . Therefore, much more Ag nuclei should be formed on the treated Fe surface. The silver nuclei, Fe plate and the  $\text{AgNO}_3$  solution comprise primary cells: the Ag deposits continuously onto silver islands while Fe simultaneously goes into solution as  $\text{Fe}^{2+}$  (or  $\text{Fe}^{3+}$ ). For the reaction  $\text{Fe} + \text{Ag}^+ \rightarrow \text{Fe}^{2+}$  (or  $\text{Fe}^{3+}) + \text{Ag} \downarrow$ , the difference of the electropotential is large enough to give rise to a non-equilibrium system at a high concentration of  $\text{Ag}^+$ . Non-equilibrium conditions generally leads to fractal growth and the formation of dendrites [24]. This is shown by the dendrites (Fig. 3b) that are formed at a  $5 \times 10^{-3}$  M concentration; however, if the concentration of  $\text{Ag}^+$  ions is drastically lowered, the deposition of the Ag would deplete all the  $\text{Ag}^+$  ions near the surface of the Fe plate. Those  $\text{Ag}^+$  ions that diffuse from the bulk solution will move only to the top of the silver particles to result in the formation of one-dimensional wire; the wires do not grow laterally. In one case, the growth of the dendrites is restricted, but nodes on the nanowires could still be seen (Fig. 3a). The uniformity of the silver nanowires parallels the decrease of the  $\text{Ag}^+$  concentration (Fig. 1). The electron diffraction pattern (Fig. 1a) shows the growth of the Ag nanowire in the [1 1 0] direction. As the nanowires crystallize in the fcc phase, the (1 1 0) face is expectedly a less compact face that must be more chemically active in the growth process. As the reduced Ag atoms preferentially deposit on this face, one-dimensional growth in the [1 1 0] direction takes place. If, on the other hand, the concentration of  $\text{Ag}^+$  ions is too low, the reaction and deposition rate will be correspondingly low, so that the growth is hindered even before the particles can grow into the wires as they can adsorb impurities or react with the oxygen in solution.

On a smooth surface that is more even, the Ag aggregates cover almost the entire surface by the displacement reaction, but this prevents the further reduction of  $\text{Ag}^+$  ions. When the reaction is allowed to proceed for a longer time, a film of silver is formed along with particles of silver. When

mechanically polished Fe plates are used, silver films rather than nanowires are formed.

Ideally, a redox reaction requires two metals whose potentials are different. However, in a practical situation, in addition to this requirement of a potential difference of the standard electrode potentials, the over-potential and concentrations of the different ions also affect the reaction. The relatively high electropositivity of Fe permits the redox reaction in non-equilibrium condition to take place over a wide range of concentrations of  $\text{Ag}^+$  ions, an outcome that can be exploited for the production of nanowires. However, with a less active metal such as copper, the process of building up a non-equilibrium system is difficult to control owing to the smaller electrode potential difference, and the structures and sizes of the product are difficult to predict. Finally, with either magnesium or aluminium, both of which are much more active than iron, the redox displacement takes place at an elevated rate. Although non-equilibrium growth builds up readily for the growth of the dendrites, the metal plates are themselves very active and they react with rapidly water or air, so that the part of the surface is quickly coated with the metal oxide.

This study reports the synthesis of silver nanowires by using a spontaneous redox reaction that merely requires a metal plate to be immersed in an aqueous solution of silver nitrate. This 'green chemistry' procedure permitted the synthesis of silver nanowires of the order of microns. The conditions for this reaction are detailed and a mechanism suggested.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 29890210, 20021002, and 20173046), the Ministry

of Education, and the Natural Science Foundation of Fujian Province.

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