Available online at www.sciencedirect.com

ScienceDirect

Electrochemistry Communications 9 (2007) 629–632

electrochemistry communications

www.elsevier.com/locate/elecom

Growth of silver nanowires by an unconventional electrodeposition without template

Xiao-Jun Zheng, Zhi-Yuan Jiang, Zhao-Xiong Xie *, Shu-Hong Zhang, Bing-Wei Mao, Lan-Sun Zheng

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China

Received 6 October 2006; received in revised form 19 October 2006; accepted 19 October 2006
Available online 28 November 2006

Abstract

We describe an unconventional electrochemistry approach to the preparation of silver nanowires. By the electrodeposition in the dilute solution without supporting electrolyte, silver nanowires with diameter 10–50 nm and length up to several μm have been synthesized. It was found that the absence of the supporting electrolyte played a key role in the formation of silver nanowires, and the products from the solution without supporting electrolytes were very different from those with supporting electrolytes. A possible mechanism concerning the transportation of silver ions by electro-migration and the diffusion was proposed.

Keywords: Electrodeposition; Nanowires; Silver; Supporting electrolyte; Unconventional electrochemistry

1. Introduction

In recent years, one of the most exciting areas in material science focuses on nanostructured materials due to their unique properties as well as their potential uses [1,2]. In particular, one-dimensional metal nanomaterials, such as nanotubes [3], nanorods and nanowires [4], are of considerable interest because of their possible potential applications as advanced materials in nano-devices. Therefore, great effort has been devoted to the controlled growth of various kinds of metal 1-D nanostructures. For example, molybdenum nanowires were prepared by a two-step procedure, where molybdenum oxide nanowires were first electrodepositioned selectively at step edges on the electrode [5]. Although a variety of techniques, including hard template, soft-template, template-free methods, have been developed [2–16], there is still a significant challenge in developing facile, cheap and efficient methods for the preparation of 1-D metal nanostructures. In our previous paper, we have found that the silver nanowires can be grown by a simple redox displacement reaction [17]. Such a redox displacement reaction can be thought as a primary cell reaction, which indicates that a similar electrochemical reaction can be applied for the growth of silver nanowires. Based on this idea, we applied the electrochemical methods to the growth of silver nanowires in the dilute solution without the supporting electrolyte. For the electrochemical studies, supporting electrolytes are usually introduced to the dilute solution to reduce the resistance of the solution. The use of solutions without supporting electrolyte is unusual. Electrochemists used to pay less attention to such unusual electrochemical condition both experimentally and theoretically. This study might encourage electrochemists to pay attention to electrochemical reaction in the dilute electrolytes without the supporting electrolyte for both theory and application.

2. Experimental

The growth of silver nanowires was carried out with a CHI electrochemical system. An iron plate or a highly ori-

---

* Corresponding author. Tel.: +86 592 2185667; fax: +86 592 2182432.
E-mail address: zxxie@xmu.edu.cn (Z.-X. Xie).

1388-2481/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2006.10.039

ented pyrolytic graphite (HOPG) sheet was used as the working electrode, and a platinum electrode as the counter electrode. Before the electrodeposition, the iron electrode was mechanically polished and washed with distilled water. For the deposition, a chronoamperometry mode at the current density of 1 mA/cm^2 was applied. Then the black deposits were peeled off and collected from the electrode carefully. The product was characterized by powder X-ray diffraction (XRD) on a Rigaku D/Max-rC X-ray diffractometer equipped with Cu Kα 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 LEO1530 microscope.

3. Results and discussion

Fig. 1a shows a typical TEM image of the deposits collected from the working electrode after electrodeposition for 2 h with the chronoamperometry mode at current density of 1 mA/cm^2. The solution is 1.0 mM $AgNO_3$ aqueous solution. In order to keep constant of the concentration during electrodeposition, a large volume of solution (500 mL) was used. As shown in the image, most of the deposits were nanowires with diameter of 10–50 nm and length up to several μm. The inserted electron diffraction pattern of a selected area on one nanowire showed that the nanowire was single-crystalline. Furthermore, the electron diffraction pattern can be indexed as a face centered cubic (*fcc*) phase of silver. The X-ray diffraction pattern of the deposits also indicated that products were silver, as shown in Fig. 1b. All diffraction peaks corresponded to a *fcc* Ag phase (JCPDS 4-0783). No peak due to possible impurities such as Ag_2O, $AgNO_3$, Fe and its oxides was identified.

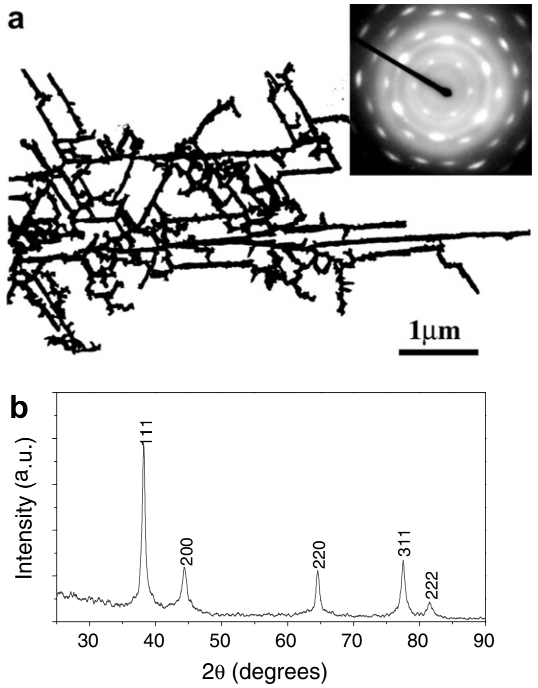

Fig. 1. (a) A typical TEM image of silver nanowires synthesized by the electrodeposition in the aqueous solution containing 1.0 mM $AgNO_3$ for 2 h and at the current density of 1 mA/cm^2, indicating the nanowires have a diameter of about 40 nm and length up to several μm. The selected area electron diffraction (SAED) pattern is inserted in the top-right of the figure, which shows that silver nanowire is single crystalline. (b) The XRD pattern of the silver nanowires synthesized in the same conditions as those of (a).

To clarify the behavior of the silver electrodeposition at different concentration, systematic experiments were carried out at different concentrations of $AgNO_3$. For the concentration of $AgNO_3$ over 0.01 M, dendrites and some larger nanorods formed, as characterized by the TEM image shown in Fig. 2a. Increasing $AgNO_3$ concentration further favored the growth of dendrites, and at last tended to form the silver coating layer. On the other hand, when the concentration is decreased, well-shaped silver nanowires are formed. Fig. 2b shows the SEM image of silver nanowires grown on the HOPG electrode for 10 min in the 0.1 mM $AgNO_3$ (As on the iron plate surfaces, we failed to collect the deposits, the HOPG electrodes were adopted to deposit the silver nanowires; then the HOPG electrode was directly observed with the SEM).

It should be emphasized here that the solutions we used for the growth of silver nanowires were exceptionally dilute and without the supporting electrolyte. For conventional electrochemical studies, usually, supporting electrolytes should be added to reduce the resistance of the solution in a dilute solution. Interestingly, we found that the normal electroplating took place if the supporting electrolyte (e.g., 0.1 M KNO_3) was added, i.e., the uniform silver layer coated the electrode surface. Fig. 2c shows the Ag deposits on HOPG surface from the solution of 0.1 mM $AgNO_3$ + 0.1 M KNO_3. Obviously, no nanowire can be found. Instead, fine silver grains were deposited on the electrode.

How can the silver deposit electrochemically on the electrode surface into 1-D nanowires without confinement of the templates at a dilute solution? Based on the role of the electrolyte concentration in the formation of silver nanowires, we propose a possible interpretation as follow. As it is well known, while a potential is applied to the working electrode in the electrolyte solution, most of the potential drop is in the region of double layer. Considering the case that the concentration of electrolyte is very low, the diffuse part of the double layer becomes very thick, up to hundreds of nanometers or even tens of microns. The potential drop is therefore in a large scale. The electro-migration of the ions then dominates the transportation of ions during the electrodeposition. The ions are then of more probability to diffuse toward the tip of an island, because the electric field gradients near the tip is far larger than that of smooth area. For the electrodeposition at a low concentration (such as 1 mM), deposition of the silver usually exhausts all silver ions near the surface of the electrode. The further deposition of silver is supplied by the transportation of silver ions. The silver ions will then diffuse toward the tip of the silver particles or nanowires,