Synthesis of silver nanowires by a sonoelectrochemical method

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Abstract

A novel method for the preparation of silver nanowires without any template is presented via a sonoelectrochemical route in an aqueous solution containing silver nitrate and ethylenediaminetetraacetic acid (EDTA) under N2 atmosphere. The electrolysis was carried out with controlled-current and controlled-potential, respectively. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SEAD). Almost uniform silver nanowires were observed in the TEM images. An SEAD revealed the silver nanowires with single crystalline nature.

Keywords: Sonoelectrochemistry; Synthesis; Nanowire; Silver

1. Introduction

In the past decade, one-dimensional (1D) nanostructured materials have been the focus of scientific research due to their unusual properties and potential uses in both mesoscopic research and the development of nanodevices. Synthesis of noble metal nanowires (nanorods) or nanofibers and investigations of their properties arouse considerable interests. Nanosized noble metals have the applications in various fields, due to their conspicuous physicochemical catalytic properties and their potential applications in microelectronics, optical, electronic and magnetic devices [1–4]. Silver nanocrystallites have been extensively studied for their applications in the photographic process [5] and their property of surface-enhanced Raman spectroscopy [6]. In recent years, templates have been utilized to direct the growth of 1D silver nanostructures, including carbon nanotubes [7], mesoporous silica [8], polymer films [9], membrane template [10] and DNA [11]. Preparation of silver nanowires via crystal seeds-mediated growth has also been reported [12,13]. However, preparation of long and continuous silver nanowires without using any templates still remains a great challenge to synthetic chemists and material scientists.

Currently, the sonochemical method has been used extensively to generate novel materials with unusual properties. It offers a very attractive method for the preparation of nanosized materials and has shown very rapid growth in its applications to materials science due to its unique reaction effects. Electrodeposition is a simple and low cost method with many advantages to prepare various materials. However, only recently has the potential benefit of combining sonochemistry with electrochemistry in the preparation of nanosized materials been studied increasingly [14–18].

Recently, we have successfully synthesized silver nanoparticles, nanorods and dendrites by sonochemical method [19–21]. In this paper, we report a novel method for the preparation of the long silver nanowires via a sonoelectrochemical route from an aqueous solution of AgNO3 in the presence of EDTA. It is found to be a mild, convenient and efficient method to prepare silver nanowires without using any templates.
2. Experimental

All the reagents used were of analytical purity. Electrochemical experimental instrument used was CH660 (CHI, USA) electrochemical system. Silver nanowires were prepared via electrochemical reduction with controlled-current and controlled-potential respectively. In the case of a controlled-current electrolysis, a platinum sheet \((5 \times 5 \text{ mm}^2)\) was used as the cathode; another platinum wire was used as a counter electrode in our electrochemical cell. The current was kept at 10 mA and the electrolysis time lasted 30 min. For a typical controlled-potential electrolysis process, a platinum sheet \((5 \times 5 \text{ mm}^2)\) was used as the cathode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The controlled-potential remained at \(-0.3 \text{ V (vs. SCE)}\) during the whole reaction and the electrolysis time was 45 min. The volume of the electrolyte was 50 ml. The electrolytes were prepared by dissolving 0.10 g AgNO\(_3\) and 1.00 g EDTA in 50 ml distilled water. The electrolysis cells were put into an operating ultrasonic bath and the electrolysis was carried out in the presence of an ultrasonic field \((50 \text{ Hz}, 100 \text{ W})\) under N\(_2\) atmosphere. The temperature during the reactions was controlled at ca. 30 °C. At the end of the reaction, the precipitates were centrifuged, repeatedly washed with distilled water and ethanol, and dried in vacuum.

The products were characterized by powder X-ray diffraction (XRD) and transmission electron microscope (TEM) and selected area electron diffraction (SEAD). The TEM and SEAD images were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV and a JEOL JEM-4000EX transmission electron microscope, using an accelerating voltage of 400 kV. The XRD patterns were recorded using a XD-3A CuK\(_\alpha\) X-ray diffractometer \((\lambda = 1.5418 \text{ A, Japan})\).

3. Results and discussions

A typical XRD pattern of the silver nanowires prepared via the controlled-current electrolysis is shown in Fig. 1. The diffraction peaks correspond to the \((111)\), \((200)\), \((220)\) and \((311)\) planes, respectively. All the reflections on the XRD pattern can be indexed to a face centered cubic structure according to the literature pattern (JCPDS, file no. 4-0783). Similar result was also obtained by controlled-potential electrolysis.

Figs. 2(a) and (b) show the TEM images of the products obtained by the controlled-current and controlled-potential electrolysis, respectively. In Fig. 2(a), the as-prepared Ag nanowire appears to be a straight wire with a diameter of ca. 40 nm and a length up to over 6 \(\mu\text{m}\). In the case of the controlled-potential electrolysis, the nanowires become thicker and longer. In Fig. 2(b), a flexural nanowire of ca. 80 nm thick and over 15 \(\mu\text{m}\) long is observed. An individual silver nanowire was characterized by an SEAD, as illustrated in Fig. 2(a). This reveals the nanowire with single crystalline nature. Fig. 3 shows the TEM image selected another area of as-prepared Ag nanowires by the controlled-current process, which reveals multiple nanowires can be obtained. Similar result can also be observed in the TEM picture by the controlled-potential process.
The formation of silver nanowires was based on the reduction of silver (I) ions by electrolysis. Ultrasonic irradiation plays an important role during the formation and growth of the Ag nanowires. If ultrasonic irradiation was not employed, it was observed that Ag was deposited on the electrode. As a result, silver powders cannot be obtained. We think the ultrasonic field also promotes the formation of silver nanowires. During the reactions, the particles can be detached from the electrode surface by the ultrasonic agitation. The ‘cleaning’ effect of ultrasound is extremely efficient to expel silver nanocrystals from the surface of an electrode. However, Ag nanocrystals are not completely detached immediately, so the particles formed can further grow on seed left on the electrode. This growth process can promote the formation of silver nanowires. EDTA also plays a critical role in the formation of the Ag nanowires. In aqueous solution, the strong complexing action between silver (I) ions and EDTA leads to the formation of Ag–EDTA complexes. The formation of the complexes can reduce the concentration of free Ag$^+$ in the solution, and slows the reaction rate, which is favorable for the growth of Ag nanowires. We also found that only when the concentration of EDTA was over 20 g/l can the nanowires be obtained. When the concentration of EDTA was below 15 g/l, only spherical nanoparticles or short nanorods can be obtained. In these cases, the reaction rate is much higher and the newborn particles deposited on electrode surface can be detached very fast, which restrains the further growth of the particles.

4. Conclusion

Silver nanowires have been successfully prepared via a sonoelectrochemical route from an aqueous solution of Ag$\text{NO}_3$ in the presence of EDTA. Long and almost uniform nanowires were obtained by controlled-current and electrolysis respectively. It is found to be a mild, convenient and efficient method to prepare silver nanowires without using any templates or crystal seeds. We can foresee the upscaling of this method to the preparation of other noble metals.

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References