Preparation of silver nanorods by electrochemical methods

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Abstract

Silver nanorods have been prepared by an electrochemical technique from an aqueous solution of AgNO₃ in the presence of polyethylene glycol (PEG). The silver nanorods were characterized by using transmission electron microscopy, X-ray diffraction, and absorption spectroscopy. It was found that the concentration of AgNO₃ and PEG affected the formation of the nanorods. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nanosized particles of noble metals have attracted considerable interest in various fields of chemistry because of their conspicuous physicochemical catalytic properties and their potential applications in microelectronics, optical, electronic, magnetic devices [1–5]. Therefore, it could be critical to develop an effective preparation method of particles with well-controlled shapes and sizes. Recently, one-dimensional (1D) structures with nanometer diameter, such as nanorod and nanotube, have attracted considerable attention due to their special properties [6–11]. Compared with micrometer-diameter whiskers, they are expected to have remarkable mechanical properties, including electrical, optical, and magnetic properties that are in principle tunable by varying the diameter and chirality [12,13]. These new nanoscale materials have potential applications in both mesoscopic research and development of nanodevices. Previous work in this field focused on carbon nanowires and nanotubes, which was the by-product of fullerene research [14]. Conventionally, carbon nanowires or nanotubes can be in arc discharge at a temperature of 3000 K [15], by thermal deposition of hydrocarbon [16]. Comparative litter research has been carried out on other 1D materials and many the previous of preparation nanorods or nanotubes require extreme conditions Therefore, one of the important goals of materials scientists is to prepare nanoscale materials under milder condition.

It is well known that catalytic reactivity depends on the size and shape of the metal nanoparticles and that the synthesis of well-controlled shapes and the size of particles could be critical for their applications [17]. Recently, Some literatures reported the
preparation of metal nanorods [18–24]. However, shape control has been much more difficult to achieve and, hence, the exploration of a novel method for the preparation of differently shaped metal nanoparticles is a challenging research area. Silver nanocrystallites have been largely studied for their application in the photographic process [25] and their ability in having surface-enhanced Raman spectroscopy [26].

In the present paper, we report the use of the electrochemical method for the preparation of silver nanorods. Our experiment was based on the electroreduction of AgNO3 in aqueous solution in the presence of PEG. The as-prepared silver nanorods were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and UV–VIS absorption spectrum.

2. Experimental

AgNO3 was purchased from Shanghai first reagent factory (China), polyethylene glycol (PEG-20000) was purchased from Tianjin third reagent factory (China). Electrochemical experimental instrument used CH660 (CHI, USA) electrochemical system. Silver nanorods were prepared via electrochemical reduction within a simple two-electrode type cell analogous to the system described previously [20,27,28]. A platinum sheet (5 × 5 mm2) was used as the cathode, another platinum wire was used as a counter electrode in our electrochemical cell. The cell was put into ultrasonic clean bar (50 Hz, 100 W). A controlled-current electrolysis was used throughout for a typical current of 10 mA and a typical electrolysis time of 25 min. The volume of the electrolysis cell was 100 ml. The temperature during was controlled at ca. 20°C. The centrifuge was used for separation of the solid product.

1.2 × 10−2 mol/1 AgNO3 and 1% PEG were mixed in an aqueous solution under a N2 atmosphere. The electrolyte volume was 50 ml. The deposition was carried out by using reaction times of 25 min. At the end of the reaction, the precipitate was centrifuged, repeatedly washed with distilled water and ethanol, and dried under vacuum. Transmission electron microscope was performed using a JEM 200CX IU Instrument (Japan). The powder X-ray diffraction patterns were recorded using a XD-3A Cu Kα X-ray diffractometer (λ = 1.5418 Å, Japan); absorption spectrum was carried out on an UV-3100 spectrophotometer (Japan).

3. Results and discussion

The TEM images of the as-prepared silver nanorods are shown in Fig. 1. The TEM image (Fig. 1a) (Ag nanoparticles prepared in 1.2 × 10−2 mol/1 AgNO3 and 1% PEG) shows a nanorod structure with a width of 20–30 nm in diameter and a length up to ca. 840 nm. Fig. 1b (1.2 × 10−2 mol/1 AgNO3 and 0.5% PEG) shows also a nanorod structure, but some convex areas on the surface of the silver nanorods are observed as well, which reveals that the concentration of PEG may affect the formation of Ag nanorods. It is observed that Ag nanorods cannot be obtained in the absence of PEG and if the concentration of PEG is less than 0.5%, white silver appears on electrode and in the solution, it reveals that larger size silver particles are obtained. Increasing the concentration of PEG in the system is found to be favorable for the formation of the silver nanorods as shown in Fig. 1, but when the concentration of PEG is larger than 2%, silver nanorods cannot be obtained easily in electrochemical reaction because the solution became very sticky. In addition, the concentration of AgNO3 can also affect the formation of silver nanorods. If the concentration is larger than 2.4 × 10−2 mol/1 or less than 1.2 × 10−3 mol/1 in 1% PEG solution, the nanorods could not be obtained. This result that the concentration of PEG and AgNO3 influence on the shapes of Ag nanoparticles may be similar to that obtained by Ahmadi et al. [17], who reported that the ratio of the concentration of the capping polymer material to the concentration of the platinum cations can influence the shapes of platinum nanoparticles. In the present work, the protecting agent PEG many also be a kind of capping polymer material, which usually acts as a molecularly dissolved surface modifier or steric stabilizer. Its presence in the system plays an important role in the formation of the Ag nanostructure. The PEG as stabilizer can promote the formation of silver nanorods.
A typical XRD pattern of the as-prepared silver nanorods shows the presence of the diffraction peaks corresponding to the (111), (200), (220), (311) planes. All the peaks in the XRD pattern can be indexed as a fcc structure (JCPDS, File No. 4-0783). The result was similar to that one reported [22]. The size of the Ag nanoparticles estimated from the Debye–Scherrer formula is ca. 18 nm (Fig. 2).

It is very interesting to investigate the optical properties of silver since it absorbs strongly in the visible region due to surface plasmon resonance [29,30]. The UV–VIS absorption spectrum of an aqueous solution containing as-prepared nanorods shows broad absorption peak at ca. 380 nm (Fig. 3). The absorption peak that appeared is attributed to the surface plasmon excitation of silver particles. It is
well known that the size and shape of particles may influence the position and the width of the plasmon resonance. The broad band obtained correlates very well with the theoretical prediction stating that the smaller size has the broader absorption band [31–33].

4. Conclusion

In summary, electrochemical method was successfully developed for the preparation of Ag nanorods in the presence of PEG. It is found that the concentrations of both AgNO$_3$ and PEG play an important part in the formation of nanorods. The shaped Ag nanoparticles may have many important applications especially in catalysis and this present technique may be extended to prepare other metal nanoparticles.

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References