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Shape-Controlled Synthesis of Silver Nanoparticles by Pulse Sonoelectrochemical Methods

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Shaped silver nanoparticles with spheres, rods, and dendrites have been prepared by a pulse sonoelectrochemical technique from an aqueous solution of AgNO₃ in the presence of nitrilotriacetate N(CH₂COOH)₃-NTA. The silver nanoparticles were characterized by using transmission electron microscopy, X-ray diffraction, and absorption spectroscopy. The effects of electrosonic time on particle shape have been discussed. It was found that the concentration of AgNO₃ and NTA affects the shape of the nanoparticles.

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.^{1–4} Therefore, it could be critical to develop an effective preparation method of particles with well-controlled shapes and sizes. Recently, some shaped nanoparticles have been synthesized, such as producing one-dimensional (1D) nanostructured materials,^{5–10} particles of noble metal with controlled shapes and dimensions,^{11–13} and self-organized nanostructures of gold particles.^{14–16}

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.¹¹ Moreover, research has shown that the degree of polymerization¹⁷ and concentration of the stabilizing polymer¹² influences the size distribution, stability, and catalytic activity of colloidal particles. El-Sayed and co-workers¹¹ demonstrated a beautiful example of controlling the shape and size of Pt nanoparticles by changing the ratio of the

concentration of the platinum cations used in the reductive synthesis of colloidal particles in solution at room temperature. The produced Pt display tetrahedral, cubic, irregular-prismatic, icosahedral, and cubic-octahedral particle shapes. Zhou and co-workers^{18,19} reported the formation of silver nanorods by the solid–liquid phase arc-discharge method and the ultraviolet irradiation–photoreduction method. Bruaun et al. have also utilized DNA as a template to grow nanometer-scale silver wires.²⁰ Another interesting class of colloids generated by very slow UV-reduction comprises large but thin platelet-like Au nanocrystals with a triangular or truncated hexagonal shape, the size and homogeneity of which also crucially depend on the type of protective polymer.¹³ 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.

Sonochemistry is a very useful synthetic method that has been in use for some time now. It was discovered as early as 1934 that the application of ultrasonic energy could increase the rate of electrolytic water cleavage.²¹ The effects of ultrasonic radiation on chemical reactions are due to the very high temperatures and pressures, which develop in and around the collapsing bubble.²² However, only quite recently has the potential benefit of combining sonochemistry with electrochemistry been studied increasingly. Some of these beneficial effects include acceleration of mass transport, cleaning and degassing of the electrode surface, and an increased reaction rate.²³ Drake found that, during electrodeposition of Cu, 1.2 MHz and 20 kHz ultrasound radiation reduced the diffusion layer from 200 μm to about 20–30 μm and 3.4 μm, respectively.²⁴ In addition, the electrodeposition of metals or alloys (e.g., Zn, Cu/Zn, Ni/Fe)²⁵ and the production of catalytically active powders have been reported as a result of combining electrochemistry and ultrasound radiation.

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Reisse and co-workers^{26–28} have described a novel method for the production of metals, alloys, and semi-conductors using pulse sonoelectrochemical reduction. Their experimental setup exposes only the flat circular area at the end of the sonic tip to the electrodeposition solution. The exposed area acts as both cathode and ultrasound emitter. A pulse of electric current produces a high density of fine metal nuclei. This is immediately followed by a burst of ultrasonic energy, which removes the metal particle from the cathode, cleans the surface, and replenishes the double layer with metal cations by stirring the solution. The metals were obtained as chemically pure, fine crystalline powders of high surface area, with an average particle size of 100 nm.

In the present paper, we report the use of the sonoelectrochemical method for the preparation of silver nanoparticles with different shapes including spherical, rodlike, and dendritic nanoparticles. The sonoelectrochemical device employed is similar to that described by Reisse and co-workers.^{26–28} Our experiment is based on the electroreduction of AgNO₃ in aqueous solution in the presence of NTA. The as-prepared silver nanoparticles are characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and UV–vis absorption spectrum.

Experimental Section

The schematics of the experimental setup assembly for these experiments were reported in ref 29. A titanium horn acted as both the cathode and ultrasound emitter. The electroactive part of the sonoelectrode was the planar circular surface at the bottom of the horn. An isolating plastic jacket covered the immersed cylindrical part. This sonoelectrode produced a sonic pulse that immediately followed a current pulse. One pulse driver (General Valve) was used to control a potentiostat, and a second one (Wavetek function generator 164) to control the ultrasonic processor, which was adapted to work in the pulse mode. A PWR-3 power module/potostat (BAS Inc.) was used to control the constant current regime (without using a reference electrode). A platinum wire spiral (0.5 mm diameter and 15 cm long) was used as a counter electrode. The current pulse was 50 mA/cm², with a duration of ($t_{e(on)}/t_{e(off)}$) 0.5. The ultrasound power density was 60 W/cm². The duration (t_s) of the current pulse was 0.3 s. The diameter of the sonic working electrode was 1.13 cm. The volume of the electrolysis cell was 100 mL. The temperature during the reaction was controlled at 20 °C. The centrifuge used for separation of the solid product was an Eppendorf centrifuge, model 5403.

Quantities of 0.6, 2, 4, and 20 g/L AgNO₃ with nitrilotriacetate N(CH₂COOH)₃, NTA, were mixed in an aqueous solution under a N₂ atmosphere. The electrolyte volume was 50 mL. The deposition was carried out by using different reaction times, typically, 25 min for a 20 g/L sample. The pH of the solution at the starting of the reaction was 4.4. At the end of the reaction, the precipitate was centrifuged, repeatedly washed with distilled water and ethanol, and dried under vacuum. We have looked for degradation products of the NTA at the end of the reaction. For this purpose we have conducted FTIR measurements of the product mixture. We could not identify the formation of IDA {HN(CH₂COOH)₂}. However, it is possible that even if IDA is obtained at small quantities, a complex between IDA and Ag⁺

will still be formed. The instruments used for the characterization in this report for X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV–vis–IR measurements have been described elsewhere.^{30,31}

Results and Discussion

The TEM images of the as-prepared Ag nanoparticles are shown in Figure 1. It is apparent that Ag nanoparticles are formed with different shapes. It is found that the concentration of AgNO₃ plays a significant role in the formation and growth of the silver nanoparticles. Figure 1a presents a typical TEM image of the product obtained by the sonoelectrochemical method with 0.6 g/L AgNO₃ and 1 g/L NTA. It shows that silver nanoparticles are spherical and well-dispersed. The particle size distribution, measured directly from TEM micrographs, is shown as a histogram in Figure 1b. The size of particles is about 20 nm. The TEM image of the products of the 2 g/L AgNO₃ electrolysis shows a nanorod structure with a width of 10–20 nm in diameter. A closer observation of the image shows that many convex areas appeared on the surface of the silver nanorods. These convex areas may further develop into dendrites. Experiment results indicate that the Ag nanorods grow larger and some rods grow dendrites with an increasing concentration of AgNO₃ in the solution. Panels c and d of Figure 1 show TEM images of the product obtained with 4 g/L AgNO₃. The nanorods grow longer. A more careful observation shows that the Ag nanorods already display the starting of a dendritic growth. It may be that the excess of silver in the solution favors the aggregation and grows into the dendritic structure of Ag clusters. Panels e and f of Figure 1 show the TEM images of the products shaped as silver dendritic nanoparticles. These elegant Ag dendrites can be observed when the concentration of AgNO₃ increases to 20 g/L. The model adopted for the explanation of the growth of treelike structure of Ag nanoparticles is known as DLA (diffusion-limited aggregate model).^{32–33} It represents a very wide variety of growths, in which one particle after another is formed and then diffuses, and adheres to the growing structure. Moreover, it was found that the concentration of NTA also effects the formation of Ag nanorods. Without NTA we cannot obtain shaped Ag nanoparticles. If the concentration of NTA is very low (less than 0.1 g/L), only randomly shaped aggregates are obtained. Increasing the concentration of NTA in the system is found to be favorable for the formation of the shaped particles. But after the concentration of NTA reaches a certain value, the quantity of NTA does not influence anymore the shape of Ag nanoparticles. The NTA is known to react favorably with Ag⁺ yielding a complex. The equilibrium constant for the formation of the complex is $\log K = 5.2$. It is suggested that upon the dissociation of the complex it results in Ag⁺ ions which are further reduced. At pH = 4.4, 89% of the NTA is found as N(CH₂COOH)(CH₂COO[–])₂ and 10% as the N(CH₂COOH)₂(CH₂COO[–])³⁴ the former is known to form a complex with Ag⁺ ions. Simultaneously NTA molecules are also released and they act as stabilizers promoting the formation of shaped silver nanoparticles. When electrosonication is performed without NTA, much larger silver particles are obtained.

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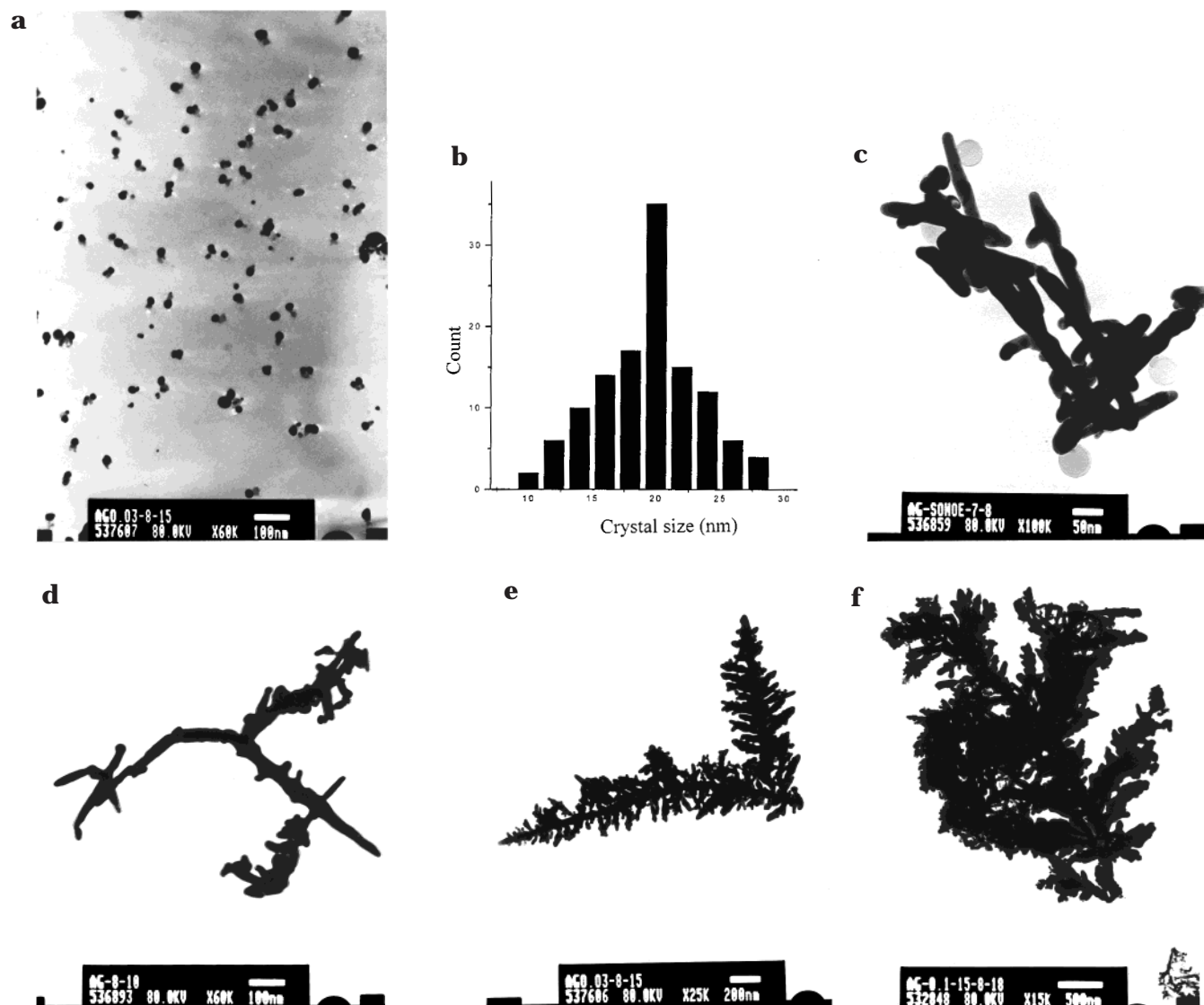


Figure 1. The TEM images for the as-prepared Ag nanoparticles. Experimental conditions: the current pulse, 50 mA/cm²; the duration of ($t_{\text{e(on)}}$ / $t_{\text{e(off)}}$), 0.5; the ultrasound pulse density, 60 w/cm²; the duration (t_s) of the current pulse, 0.3 s; the volume of the electrolysis cell, 100 mL; temperature, 20 °C. (a) Spherical silver nanoparticles (AgNO₃, 0.6 g/L; electrosonication time, 5 min). (b) Size distribution from TEM micrographs. (c), (d) Silver nanorods (AgNO₃, 4 g/L; electrosonication time, 15 min). (e), (f) Silver dendritic nanoparticles (AgNO₃, 20 g/L; electrosonication time, 25 min).

A typical XRD pattern of the as-prepared silver nanorods shows the presence of the diffraction peaks corresponding to the (111), (200), (220), (311), and (222) planes. All the peaks in the XRD pattern can be indexed as an face-centered cubic (fcc) structure (JCPDS, file no. 4-0787).

It is very interesting to investigate the optical properties of Ag since it absorbs strongly in the visible region due to surface plasmon resonance.^{35,36} The UV-vis absorption spectrum of an aqueous solution containing as-prepared nanorods shows a sharp and symmetric absorption peak at ca. 386 nm (Figure 2a). The absorption peak that appeared is attributed to the surface plasmon excitation of silver particles. The absorption spectra of the dendritic (Figure 2b) and spherical (Figure 2c) nanoparticles are similar to that of nanorods. For a solution of 20 g/L AgNO₃, the absorption maximum of Ag solution shifts to ca. 413 nm. It is also found that absorption maximum appears at ca. 383 nm for spherical nanoparticles (0.6 g/L AgNO₃ solution). It is well-known that the size and shape of

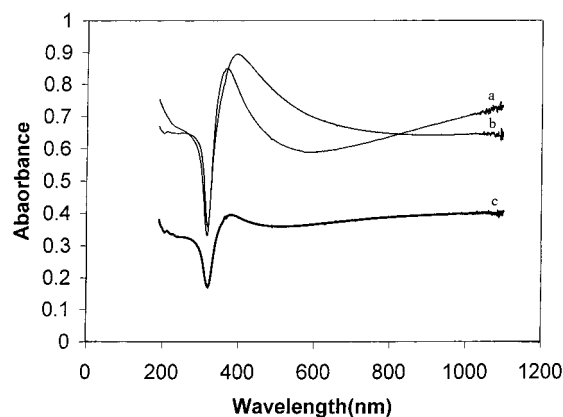


Figure 2. The UV-vis absorption spectra of silver nanoparticles in aqueous solution: (a) silver nanorods; (b) dendritic nanoparticles; (c) spherical nanoparticles.

particles may influence the position and the width of the plasmon resonance. The broad band obtained for the small spherical particles (Figure 2c) correlates very well with

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the theoretical prediction stating that the smaller the size is, the broader the absorption band will be.^{37,38}

There are a few experimental variables involved in the sonoelectrochemical deposition, such as the electrolyte composition and temperature; electrodeposition conditions, including current density, pulse on time, and ratios between pulse on time and off time (duty cycle); and sonic probe conditions (power, pulse parameters). The above factors and their effect on particle size have been discussed in our previous papers.^{29,39} In the current investigation, we have found that the sonic time is also a key factor in controlling the shape of Ag nanoparticles. In the case of dendritic nanoparticles (20 g/L AgNO₃), we have carried out the electrolysis in time frames of 5, 15, 25, and 60 min. It is found that when the reaction is performed in 5 min, only spherical and rodlike particles are observed. For a 15 min period (20 g/L AgNO₃), rod and dendritic shape Ag particles are detected. For a 25 min reaction, only dendritic shape particles are observed. If the reaction is carried out for 60 min (20 g/L AgNO₃), an aggregation is observed without dendritic shaped particles. We explain this phenomenon as follows: during the reaction, the particles are not completely detached from the titanium horn by the ultrasonic waves, so that the particles formed in the next pulse can further grow on seed left on the electrode. This growth can promote the formation of different shaped-silver particles. Longer electrosonications are mechanically breaking the dendrites and promoting aggregation.

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In addition, for the other concentration, the results in this paper represent the optimum conditions for each reaction, for example, 5 min for a 0.6 g/L sample, 12 min for a 2 g/L sample, and 15 min for a 4 g/L sample. For each concentration, longer electrosonications than the optimum time led to the aggregation of the products. The stepwise formation of spheres, nanorods, and dendrites (depending on the electrolysis time) is observed only for the 20 g/L AgNO₃ concentration.

Conclusion

In summary, a novel sonoelectrochemical method was successfully developed for the preparation of spherical Ag nanoparticles, Ag nanorods, and elegant, highly ordered dendritic nanostructured silver. It was found that the concentration of both Ag and NTA plays a key role in the formation growth of different shaped nanoparticles. 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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