Synthesis of Gold Nanorods from Metallic Gold by a Sonoelectrochemical Method*  

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In this work we report a sonoelectrochemical approach for synthesis of gold nanorods from metallic gold. We examined the effect of temperature and electrochemical duration on formation of the gold nanorods. The UV-vis spectra of the synthesized gold nanorods exhibit two peaks due to the surface plasmon resonance absorption: one at about 520 nm corresponding to the transverse electronic oscillation and the second located in the wavelength interval of 680 - 800 nm corresponding to the longitudinal electronic oscillation. It is observed from the TEM images that the gold nanorods are fairly uniform in shape and size, the aspect ratio of the nanorods is found to be from 3 to 4. The synthesized gold nanorods can be available for application in biomedicine. [DOI: 10.1380/ejssnt.2011.466]

Keywords: Gold nanorods; Sonoelectrochemical method; UV-vis absorption spectra

I. INTRODUCTION

Synthesis of gold nanorods are getting the most attention of scientists [1–3] because they have the ability of application in biomedicine. For precious metals like gold, silver, the physical properties change strongly when the ratio of the surface-to-volume increases [4]. In particular, an electromagnetic field can trigger the phenomenon of surface plasmon resonance, which is the main reason to change the absorption spectrum of the metallic nanoparticles [5]. Solution phase preparation of metallic nanorods and nanowires is a challenging task for two reasons. First, surface energy favors the formation of spherical particles. Second, most metals crystallize in highly symmetric cubic lattices. Therefore, soft and rigid templates had been used to achieve rod-shaped metal nanostructures, so the seeded method [2, 3] and sonoelectrochemical [6, 7] is often used.

In this work we report a sonoelectrochemical approach, which is a method giving a high yield, for synthesis of gold nanorods from metallic gold. We examined the effect of temperature and electrochemical duration on the formation of the gold nanorods.

II. EXPERIMENTAL

The synthesis was conducted within a simple two-electrode-type electrochemical cell, as shown in the schematic diagram of Fig. 1. Anode was a gold metal plate \((1 \times 1 \times 0.05 \text{ cm})\) and cathode was a platinum plate \((1 \times 1 \times 0.05 \text{ cm})\). The spacing between the electrodes was kept at ca. 1 cm. Typically, 25 mL of the electrolytic aqueous solution was used, which contains 0.08 M cationic surfactant, hexadecyltrimethylammonium bromide \((\text{C}_{16}\text{TAB})\), and 83 mg of a much more hydrophobic cationic co-surfactant, tetradodecylammonium bromide \((\text{TC}_{12}\text{AB})\). The \(\text{C}_{16}\text{TAB}\) serves not only as the support for nanoparticles, to prevent their further growth. The glass electrolytic cell containing the mixed solution was then placed into an ultrasonic bath \((\text{ULTRASONIC LC 30H})\). The temperature was maintained roughly at 44°C throughout the preparation process. Right before electrolysis, 2 mL of acetone and 1 mL of cyclohexane are added into the electrolytic solution. The typical current setting was 15 mA/cm², and the preparation time was about 75 min. During the synthesis, the gold ions were dissolved from the bulk gold metal anode to form gold nanoparticles, most likely at the interfacial region of the cathodic surface and within the electrolytic solution, which allows for subsequent growth of the cylindrical shape.

The obtained product was a mixture of the gold nanorods, the gold spherical nanoparticles and the solvents. For separation of the gold nanorods a centrifugation is helpful. First, a centrifugation with the rate of 3000 rpm was required to remove the deposited products with big size, and then the supernatant portion of the just centrifuged solution was separated and centrifuged with the rate of 9000 rpm several times. The deposited precipitate at the bottom of the tube mainly contained the gold nanorods.

The crystal structure of the gold nanorods was analyzed by using an x-ray diffractometer \((\text{SIEMENS D}5005, \text{Bruker, Germany})\) with Cu-\(K_{\alpha1}\) \((\lambda = 0.154056 \text{ nm})\) irradiation. The morphology of the nanorods was characterized by using a transmission electron microscope \((\text{JEOL JEM})\). FIG. 1: The set-up for preparation of gold nanorods by sonoelectrochemical method. 1. Ultrasonic bath, 2. Glass vessel containing electrolyte, 3. Cathode (Pt), 4. Anode (Au), and 5. Power supply.
FIG. 2: (a) Low magnified TEM, (b) Large TEM images of the gold nanorods prepared by the sonoelectrochemical method, and (c) An AR distribution histogram.

FIG. 3: XRD pattern of the gold nanorods prepared by the sonoelectrochemical method.

FIG. 4: UV-vis absorption spectra of the gold nanorods prepared with different sonoelectrochemical times.

1010). The composition of the samples was determined by energy dispersive X-ray (EDX) spectrometer (EDS, OXFORD ISIS 300) attached to the JEOL-JSM 5410 LV scanning electron microscope. UV-vis absorption spectra of the nanorods containing solutions were collected with a Shimadzu UV 2450 PC spectrometer.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show typical TEM images of the gold nanorods synthesized at temperature 44°C with electrolysis current intensity 15 mA/cm² during 75 minutes. It can be noticed from the figure that the nanorods have been prepared with a relatively high yield (Percentage of the created nanorods is about 75-80%) and they are fairly uniform in shape and size. The length-to-width ratio (aspect ratio - AR) distribution histogram presented in figure 2(c) shows that the size of nanorods has a narrow distribution: the nanorods having the AR of 3 make up 55% and those having the AR of 4 make up 24%.

The XRD pattern of the gold nanorods is presented in Fig. 3. The figure shows the position of various diffraction peaks at 2θ values of 38.2°, 44.4°, and 64.6° corresponding to the diffraction planes (111), (200), and (220), respectively. These peaks were perfectly indexed to the face-centered cubic structure of metallic gold. The lattice constant of the cubic structure determined from the XRD pattern is $a = 4.082 \, \text{Å}$ in good agreement with the value of 4.079 Å of the standard diffraction pattern of cubic gold metal (CAS:7440-57-5). The EDX spectra of the nanorods (not shown here) indicated that the synthesized nanorods only consist of the gold element.

Typical UV-vis absorption spectra of the gold nanorods prepared with different sonoelectrochemical times are shown in Fig. 4. All the spectra exhibit two peaks due to the surface plasmon resonance absorption: one at about 520 nm corresponding to the transverse electronic oscillation and the second located in the wavelength interval of 680-800 nm corresponding to the longitudinal electronic oscillation. As seen from this figure, the position of the absorption peak due to the transverse electronic oscillation almost is not changed, while that of the absorption peak due to the longitudinal electronic oscillation strongly depends on the sonoelectrochemical time. When the sonoelectrochemical time is increased from 60 min to 90 min, the absorption peak due to the longitudinal electronic os-
oscillation is shifted toward the short-wavelength side from 796 nm to 696 nm, which indicates the decrease in aspect ratio of the nanorods. The same phenomenon was also observed in previous work [2], but the reason for this is not clear at present.

Figure 5 shows UV-vis absorption spectrum of gold nanorods synthesized at different temperatures. Our results indicated that in the case of sonochemical experiment carried out at temperature 36°C, no reaction occurs, the color of the electrolytic solution did not change; when the experiment was carried out at temperature 44°C, the gold nanorods were prepared with a fairly high yield, but at 56°C, the gold nanorods were formed with a very low yield.

The growth mechanism of the gold nanorods is still not very clear at present. However, according to the authors [7, 8], the C_{16}TAB and TC_{12}AB in solution form cylindrical-shape C_{16}TAB-TC_{12}AB micellar frameworks, which may assist nanorod formation as more and more gold ions are introduced into these micelle structures. At the appropriate temperature, the addition of acetone makes loosening the micellar framework, facilitating the introduction of the gold ions into the micellar frameworks, in this way the gold nanorods are easily developed. When temperature is high enough, the thermal energy is high enough to destroy large cylindrical micelle structures, which prevents the nanorod formation.

IV. CONCLUSION

The gold nanorods were synthesized from metallic gold by sonochemical method. The UV-vis spectra of the synthesized gold nanorods exhibit two peaks due to the surface plasmon resonance absorption: one at 520 nm corresponding to the transverse electronic oscillation and the second located in the wavelength interval of 680-800 nm corresponding to the longitudinal electronic oscillation. The TEM images showed that the gold nanorods are fairly uniform in shape and size, the aspect ratio of the nanorods is found to be from 3 to 4. The effect of temperature and electrochemical duration on the formation of the gold nanorods was studied. The sonochemical temperature and time were 44°C and 75 min, respectively.

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