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SHORT COMMUNICATION

Aspect Ratio Controlled Synthesis of Gold Nanorods

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Abstract−Au nanorods were synthesized by using seed-mediated methods. The aspect ratio of the Au nanorods was controlled by temperature and the amount of surfactant used and the rods were characterized by TEM, HRTEM and UV-VIS spectrophotometer. Au nanorods with high aspect ratio could be prepared by decreasing the temperature used and controlling the surfactant concentration. The UV-VIS absorption spectra of the nanorods also showed variations in the aspect ratio. These results suggest that Au nanorods form, via an anisotropic growth mechanism, and that the surfactant plays a role in this process.

Key words: Gold (Au), Nanorod, Anisotropy, Surfactant, Cetyltrimethyl Ammonium Bromide (CTAB)

INTRODUCTION

Nanoparticles have attracted considerable interest because of their unique optical, electromagnetic and catalytic properties that differ from bulk ones. The origin of these properties is their large surface to volume ratio and from the coherent oscillation of the conduction electrons that can be induced by interactive electromagnetic fields (surface plasmon absorption) [Link et al., 1999]. Since these electromagnetic properties vary with the size and shape of the novel metal particles, the focus of many studies has been on methods for controlling the size and shape of gold nanoparticles [Nicoobakht et al., 2000]. In order to control these parameters, a surface stabilizer or templates are used to overcome thermodynamic instability during their formation.

In the case of Au nanorods, two types of template are used: a hard template and a soft template. Mesoporous alumina [van der Zande et al., 2000], silica [Han et al., 2000] and carbon nanotube [Govindarj et al., 2000] are examples of hard templates that have cylindrical pores and mechanical stability. Au ions or nanoparticles are introduced into the pores or attached to the surface of a hard template. Au nanorods are then formed after removal of the hard templates. It is possible to prepare final products of uniform size by using a hard template, but this procedure is complicated and the length of the nanorods is limited. Surfactants, such as CTAB, are examples of soft templates. They show mechanical instability but are easy to manipulate. Yu et al. conducted studies on Au nanorods using an electrochemical method to prepare them, and investigated their properties [Yu et al., 1999]. In this method, a self-sacrificing Au electrode is electrically ionized, and Au ions are reduced in the surfactant solution. Jana et al. proposed the seed-mediated method, which permits the facile preparation of Au nanorods, and the process is easily scaled up [Jana et al., 2001]. It is noteworthy that high aspect ratios can be attained, which cannot be achieved by the electrochemical method.

In this work, we report that the aspect ratio of Au nanorods can be controlled by using seed-mediated methods. The findings show that not only the reaction temperature but also the amount of surfactant plays an important role in the growth of Au nanorods.

EXPERIMENTAL

The methods used to prepare the nanorods are described elsewhere [Jana et al., 2001], except for the change of the surfactant concentration and reaction temperature. Au seeds were prepared as follows: a solution of 0.6 ml of 0.1 M $NaBH_4$ at 0 °C was injected into a mixture of a 20 ml solution that was 2.5×10^{-4} M in $HAuCl_4$ and tri-sodium citrate with vigorous stirring. The color of the solution instantly turned to reddish brown. In order to prepare Au nanorods, a sufficient amount of cetyltrimetyl ammonium bromide (CTAB) was added into 10 ml of a 2.5×10^{-4} M $HAuCl_4$ solution to give a final CTAB concentration of 0.1 M, 0.05 M, 0.01 M, 0.001 M and 0 M, respectively. These solutions were kept at a constant temperature of 50, 25 and 0 °C. A freshly prepared ascorbic acid solution (0.05 ml, 0.1 M) was added into the solution with vigorous stirring. The solution turned colorless indicating that the Au ions (Au^{3+} or $AuCl^-$) had been reduced to Au^- ions (not Au) by the ascorbic acid. When 0.025 ml of the seed solution was added, the solution changed gradually to pink, indicating that the Au ions were reduced to form Au nanorods. The Au nanorods were separated from by centrifugation at 1,000 rpm for 15 min. After separation, the particles were redispersed into deionized water for further analysis.

Absorption spectra of the separated solutions at each of the conditions used were obtained by Hewlett Packard, HP 8453 spectrophotometer. 4-5 drops of the solutions were placed on carbon-coated copper grids for a transmission electron micrographic examination (Philips CM-20, JEOL JEM-2000EXII) and high resolution TEM (JEOL JEM-3000F).

RESULTS AND DISCUSSION

A high resolution TEM image of a Au nanorod was obtained in order to determine the direction of growth (data are not shown here). From the result, the separation of the longitudinal plane had 0.281

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nm. It is known that the lattice constant of Au has 0. 4078 nm (JCPDS File No. 4-0784) and the separation of {110} planes is d_{110} of 0.2884 nm. This result confirmed the Au crystal grows along the {110} facets [Wang et al., 2000]. Interestingly, {110} facets have not been observed in the surface of spherical particles and have a higher surface energy than other facets. In addition, these facets have a tendency to adsorb surfactants to compensate for instability [Nickoobakht et al., 2001].

Fig. 1 shows the effect of reaction temperature on the formation of Au rods. It can be seen that no Au rods are produced at 50 °C [Fig. 1(a)]. When the reaction temperature was decreased by 25 degrees, various types (sphere, rod and triangular plate) of nanoparticles were formed [Fig. 1(b)]. Various aspect ratios of Au nanorods were observed when prepared at 0 °C [Fig. 1(c)]. These results show that the shapes of Au nanoparticles were competitively formed in the form of spheres, triangles and rods. This suggests that the growth of nanorods can be conctrolled kinetically. Thus, interrelationships of the kinetics involved, such as particle growth rate and surfactant adsorption rate appear to be factors. In order to facilitate the growth of nanorods, the surfatant must be adsorbed to the unstable facet of the intermediate before spherical particles are formed [Wang et al., 2000]. When the solution temperature decreases, the growth rate of Au particles also decreases and, consequently, the intermediates remain in the solution for a relatively long time. Thus, the probability that CTAB will become adsorbed onto unstable facets of the Au intermediate increases at low temperature. While, as the temperature increases, the growth rate of Au increases, the intermediate rapidly disappears. Intermediates not adsorbed by CTAB grow into a relatively stable sphere.

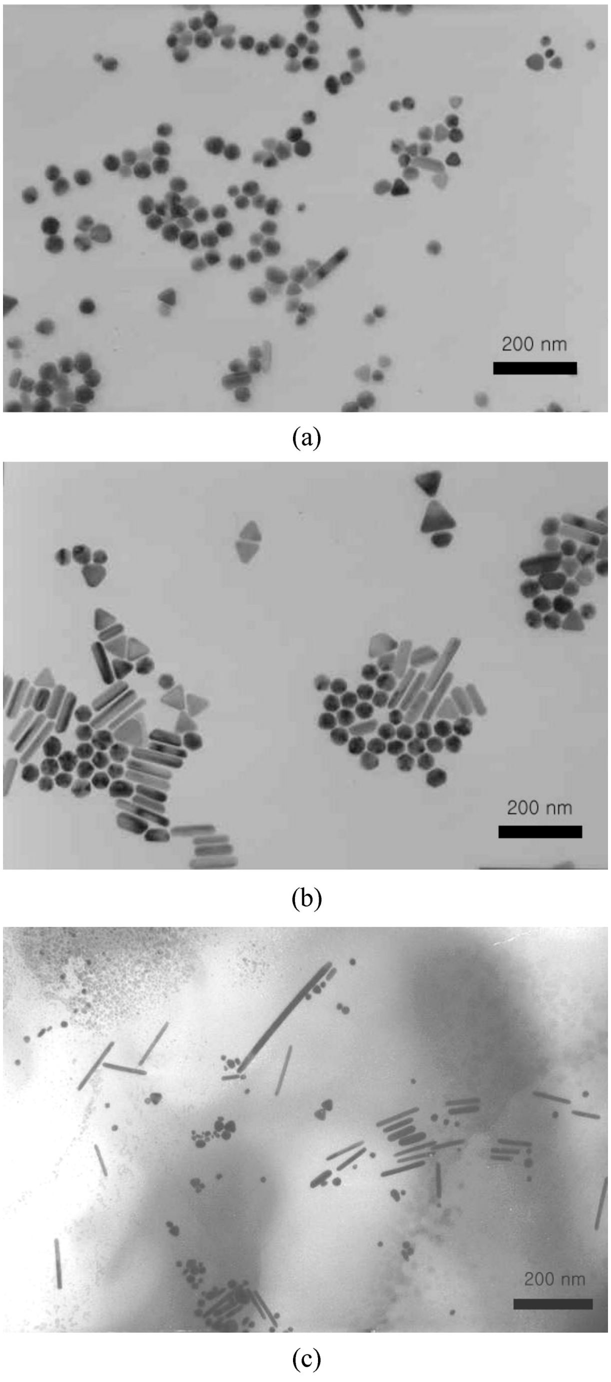

Fig. 1. Change in shape with reaction temperature at a CTAB concentration of 0.05 M.
(a) 50 °C, (b) 25 °C, (c) 0 °C

Variations in aspect ratio were examined by changing the concentration of the CTAB at 0 °C. As shown in Fig. 2, short rods (ca. 3-4 aspect ratio) were formed, where 0.1 M CTAB solution was used [Fig. 2(a)] and rods having several aspect ratios were produced when the CTAB concentration was 0.05 M [Fig. 2(b)]. Importantly, at 0.01 M of CTAB concentration, a very uniform aspect ratio of rods was achieved, as shown in Fig. 2(c). It should be noted that spherical particles were observed in a small amount or the absence of a CTAB [Fig. 2(d), 2(e)]. These results indicate that the aspect ratio of Au nanorods is determined by CTAB concentration. It is likely that the amount of intermediates adsorbed by CTAB determines the aspect ratio, even though the reaction mechanism of nanorod formation is unclear. In addtion, Jana, et al. explained that surfactant micellar templates (elongated rodlike micelle) also contribute to rod formation. However, the condition required for the formation of rodlike micelles of CTAB is known to be above 10 wt% (0.35 M) CTAB [Raman et al., 1996]. From the above findings, we conclude that the adsorption of CTAB molecules is more reasonable.

For Au nanorods, the surface plasmon absorption is split into two parts, as the result of the oscillation of free electrons along and perpendicular to the long axis of the rods [Link et al., 1999]. The plasmon absorption spectrum of Au nanorods prepared in a 0.1 M CTAB solution at 0 °C shows a typical at ca. 520 nm, peak for transverse plasmon absorption and a peak at ca. 730 nm for longitudinal plasmon absorption which corresponds to an aspect ratio of ca. 3.5 for the Au nanorods [Fig. 3(a)]. The spectrum of the Au nanorods prepared in 0.05 M CTAB solution at 0 °C shows a 510 nm for an Au sphere peak and ca. 840 nm peak which corresponds to an aspect ratio of ca. 5 for the Au nanorods [Fig. 3(b)]. This result is in agreement with previously reported results [Yu et al., 1997]; i.e., the longitudinal plasmon absorption peak is red-shifted and the transverse peak is blue-shifted. However, the longitudinal plasmon absorption peak for Au nanorods prepared in a 0.01 M of surfactant solution was not detected because the longitudinal peak is located out of the spectral range [Fig. 3(c)]. It would be predicted that the longitudinal peak corresponding to an aspect ratio of 10-15 should appear at

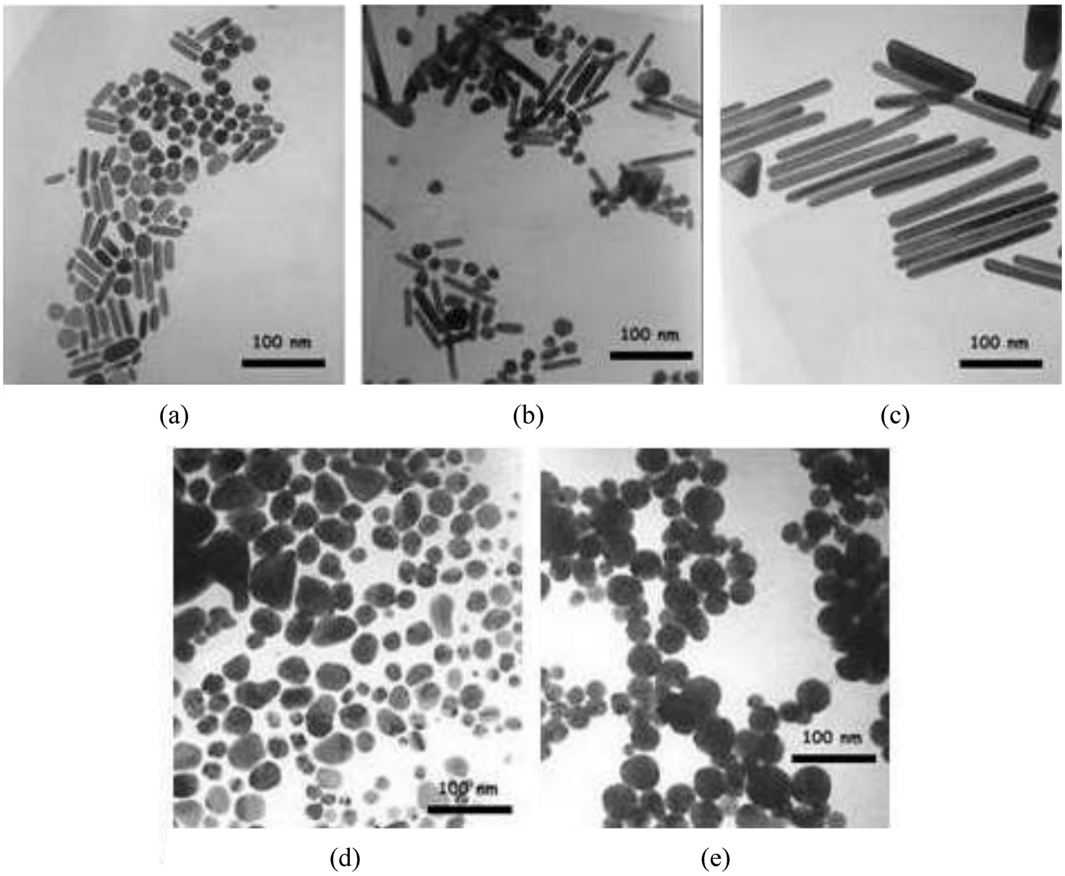

Fig. 2. Variation in aspect ratio with surfactant concentration at 0 °C (scale bar=100 nm).
(a) 0.1 M, (b) 0.05 M, (c) 0.01 M, (d) 0.001 M, (e) 0 M

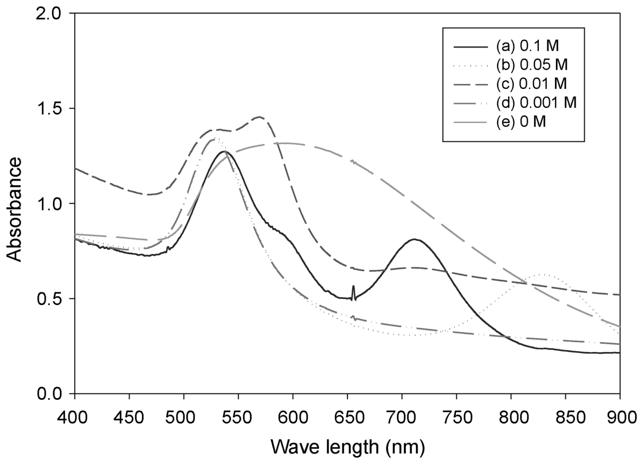

Fig. 3. UV-VIS spectra of nanorods with different aspect ratio.
(a) 0.1 M (3-4 aspect ratio), (b) 0.05 M (3-7 aspect ratio), (c) 0.01 M (above 15 aspect ratio), (d) 0.001 M (spherical particles), (e) 0 M (aggregated spherical particles)

about 1,400 nm [Chang et al., 1997].

CONCLUSIONS

In summary, Au nanorods with a high aspect ratio and uniform diameter can be prepared in a single step by using the seed-mediated method, while a previously reported method requires three steps [Jana et al., 2001]. Based on the results, the growth rates of each facet are influenced by the adsorption of surfactant. It appears that specific faces have a preference for associating with functional groups of the surfactant. These phenomena facilitate the growth of nanorods in one direction because the adsorbed CTAB restricts growth. In addition, surfactant concentration also has an influence on aspect ratio. Therefore, it is possible to control the aspect ratio of Au nanorods by appropriately adjusting the reaction conditions. Spectrophotometric results indicate that the surface plasmon absorption peak of the prepared Au nanorods was red-shifted and the transverse peak was blue-shifted. This indicates that the optical properties of Au nanorods are varied and that they could be used in designing the optical properties of nanodevices. Moreover, their potential uses in catalysis should be exploited because of their anisotropic properties which mean ‘different face, different property’.

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