High Aspect Ratio Gold Nanorods Grown Normal to High-Energy Surfaces

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Gold nanorods were electrochemically prepared in aqueous micellar solutions consisting of a supporting electrolyte surfactant and a hydrophobic cosurfactant. With the selection of cosurfactant, the nanorods grew to be submicrometers in length with very high aspect ratios. The growth axial direction of the rod was revealed to be [110], the direction normal to high-energy surfaces, by electron diffraction measurements.

Metal nanostructures are attracting a great deal of attention due to their potential use in technological applications.[1] Since the electronic, magnetic, optical and/or catalytic properties of these materials depend highly on their size and shape, morphological controls of nanostructures are indispensable.[2] Although various methods have been developed to synthesize spherical nanoparticles with different sizes, the shape control of these particles still remains a preparative challenge.

Recently, gold nanorods have been prepared in solutions by using a rigid template of mesoporous alumina,[3] or by an electrochemical method in the presence of cationic surfactant systems.[4–6] The electrochemical method has characteristic features in controlling the cylindrical growth of gold by introducing a shape-inducing micellar reagent (cosurfactant) into the electrolysis system in which appropriate surfactants are employed as both the supporting electrolyte and the stabilizer. This method seems to be practical for easy isolation and large-scale synthesis of nanorods.

In the electrochemical synthesis, the aspect ratio (the ratio of length to width) of the prepared nanorods can be substantially controlled by changing the mixing ratio between the surfactant and the cosurfactant. A silver plate is also immersed inside the electrolytic solution because slow silver ion release from the plate is reported to affect the long-axis length of the nanorods.[4] So far, gold nanorods with aspect ratio larger than ~7 have been rarely prepared mainly because the surfactants or cosurfactants used were limited.[5,6] In the present work, we report an electrochemical preparation of gold nanorods with very high aspect ratios in an aqueous solution by controlling the cosurfactant systems without using the silver plate. The rods have grown to be submicrometers in length and possessed one of the highest aspect ratios prepared in the absence of a rigid mesoporous template at present.[7] Furthermore, the growth axial direction of the gold nanorod is directly demonstrated by electron diffraction.

The syntheses were conducted within a simple two-electrode-type electrochemical cell similar to that described by the other groups,[4,5] constituting of a gold electrode ($30\times 10\times 0.5$ mm) as the sacrificial anode and a platinum electrode ($30\times 10\times 0.5$ mm) as the cathode. Both electrodes were fixed in place by using a dielectric spacer with the distance of ~2.5 mm. Typically, the electrolytic solution consisted of a 8.0×10^{-2} M hexadecyltrimethylammonium bromide (abbreviated as HTAB, Wako Pure Chemicals) as the supporting electrolyte surfactant, and a 5.4×10^{-3} M hydrophobic cosurfactant. Tetradodecylammonium bromide ($TC_{12}AB$, Wako Pure Chemicals) or tetrabutylammonium bromide (TC_4AB, Wako Pure Chemicals) was selected as the cosurfactant. The incorporation of the hydrophobic cosurfactant into the HTAB micellar framework is considered to induce a cylindrical micellar shape to support the anisotropic growth of nanometer-sized gold.[5] The electrolysis was carried out for 20 min with a constant applied current of 10 mA at ~40 °C under continuous ultrasonication. During the synthesis, the bulk gold metal was converted from the anode to form mixtures of nanoparticles and nanorods in solution. A centrifugation is helpful to further increase the nanorod yield.

Transmission electron microscopy (TEM) was conducted by a Hitachi-8100 electron microscope operated at 200 kV. The sample was prepared by dropping water-diluted suspension on a carbon-coated copper microgrid and allowing it to dry in air. Selected area electron diffraction pattern was obtained at a camera length of 1 m.

We first examined the effect of cosurfactant $TC_{12}AB$ on the preparation of gold nanorods, however, characteristic nanorods could not be obtained. On the other hand, gold nanorods with high aspect ratios could be synthesized by using TC_4AB instead of $TC_{12}AB$ as the cosurfactant. Figure 1 shows a typical TEM image of the sample. Elongated nanorods, which grew to be submicrometers in length, can be seen in the image together with gold nanospheres. Note that the gold nanospheres were likely to form aggregates. Since both the nanorods and the nanospheres supplied flocculent precipitate at the bottom of the centrifugation tube, separation of nanorods from the sphere/rod mixtures by centrifugation was insufficient. Figure 2 shows the distributions of the aspect ratio and the short-axis length of prepared gold nanorods.[8] The aspect ratio of the gold nanorods ranged between 8 and 30, and the mean aspect ratio was obtained to be 18.1. Two peaks at around 8 and 22 were observed in the aspect ratio distribution, suggesting that optimization of the mixing molar ratio between the surfactant and the cosurfactant would be necessary. The distribution of the short-axis length of the rods was

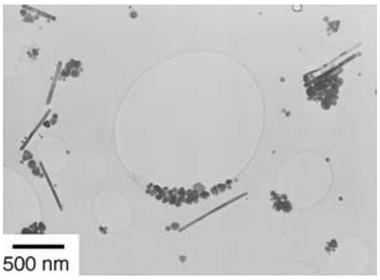

Figure 1. Typical TEM image of gold nanorods prepared electrochemically by using the cosurfactant TC_4AB.

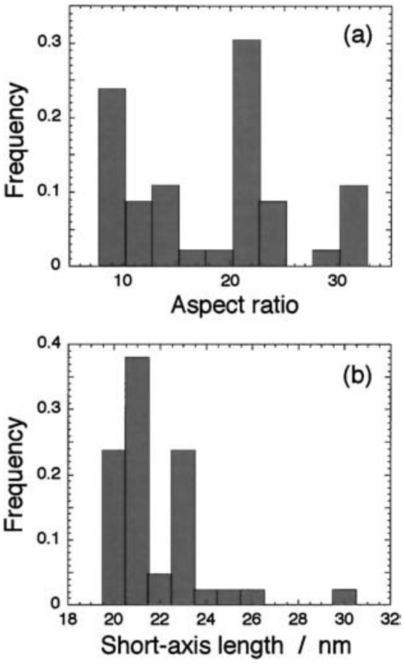

Figure 2. (a): Distribution of gold nanorod aspect ratio. The mean aspect ratio is 18.1. (b): Distribution of short-axia length of gold nanorods. The mean short-axis length is 21.7 nm.

relatively narrow, and the mean value was 21.7 nm.

To examine the crystal structures of the nanorods, electron diffraction measurements were conducted. Figure 3 shows the TEM image of a single 18 aspect ratio gold nanorod and the corresponding electron diffraction pattern. The diffraction pattern shows characteristic spots indicating that the nanorod is not polycrystalline. Moreover, the pattern provides the information on the growth axial direction of the nanorod. Along the long-axis direction of the nanorod (namely, the growth axial direction), two diffraction spots corresponding to the lattice spacing of 1.44 Å were observed. This spacing can be assigned to the {220} reflections of gold in the face-centered cubic (fcc) structure, showing that the growth axial direction is [110]. The results indicate that the nanorod uncommonly grew toward the direction normal to high-energy surfaces {110}.[9] With further analyses, most of the diffraction spots can be indexed as shown in Figure 3b when the electron beam direction is [1 − 10]. However, four spots indicated by the circles in Figure 3b, which correspond to the lattice spacing of 1.44 Å, cannot be explained by the present analysis. The results imply that the rod is not a perfect single crystal containing some stacking faults, dislocations or twins inside the crystals.[10] These volume defects can be seen in the rod image contrasts shown in Figure 3a.

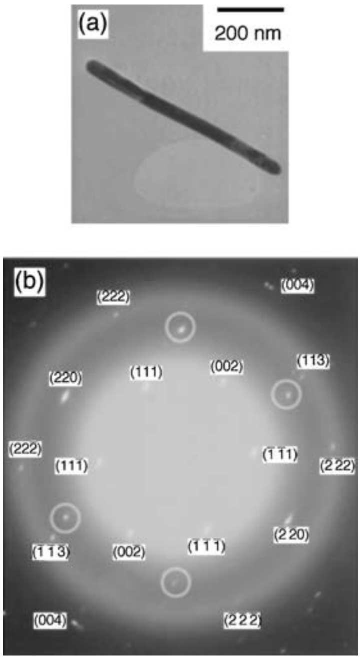

Figure 3. (a): TEM image of a single gold nanorod. (b): Corresponding electron difraction pattern of the single nanorod. The diffraction spots are indexed in the figure when the direction of the electron beam is oriented to [1$\bar{1}$0] axis.

It should be noted that gold nanorods could not be prepared by using cosurfactant $TC_{12}AB$ while TC_4AB led to formation of high aspect ratio nanorods. The results suggest that there exist large differences in the structure of micelles and/or in the cylindrical growth mechanism between these cosurfactant systems. Since $TC_{12}AB$ is a bulky molecule compared to TC_4AB, the size of the cosurfactant would affect the morphologies of micelles or adsorbed molecular structures on gold surfaces. Wang et al. have reported that the growth axial direction of short gold nanorods (aspect ratio: 3–7) prepared electrochemically by using the cosurfactant $TC_{12}AB$ under silver ion release was [001],[9,11] different from our observations. The difference in the growth axial direction of nanorods is probably due to that in the interactions between the cosurfactant and the gold facets. In our case, cylindrical growth along the [110] axis, which is the direction normal to high-energy surfaces of gold,[9] is found to assist the formation of high aspect ratio nanorods.

We believe that controls of the growth axial direction by changing the cosurfactant systems and the consequent cosurfactant/gold surface interactions are of crucial importance for the preparation of high aspect ratio nanorods.

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