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Preparation and characterization of gold nanodumbbells

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Extensive and intensive investigation of gold nanoparticles in biology, nonlinear optical switching, the formation of a modified surfaces for surface-enhanced Raman scattering, immunoassay labeling, optical contrast agents and catalysis have revealed that the size or shape of the particles are strongly dependent on physical, optical and chemical properties. Thus, gold nanoparticles become very reactive in the nanosize range. Most of the previous works regarding gold nanoparticles deals with those that have spherical morphology. However, nonspherical gold nanoparticles should have different, and perhaps more interesting, properties and applications. In recent years, several special shapes and structures have been studied for gold nanoparticles, such as nanorings, nanoplates, dendrimer-like, dog-bones and nano prisms. The development of well-controlled shapes and novel structures for gold nanoparticles therefore has become a very important issue.

Electrochemical techniques are essential for many types of nanoscale materials fabrication and processing such as the porous layers, formation of ultra-thin films and materials with nanoscale compositional and structural variations. Furthermore, the synthesis of noble-metal nanoparticles by the electrochemical method with tetraalkylammonium salts as surfactant molecules has been widely researched for the first time since the early Reetz research work (1994). Recently, gold nanorods with fairly good uniformity using the electrochemical method by introducing a shape-inducing cosurfactant were prepared. For the growth of these nanorods, a template method with a dynamic surfactant micelle system serving as the template is considered to be suitable; the addition of a small amount of organic solvent to the surfactant solution is necessary for enhancing the formation of the rodlike micelle. Therefore, the electrochemical reaction of organic solvent with surfactant solution is critical for obtaining the proper morphology of nanoparticles. In this paper we demonstrate for the first time that electrochemical methods can be used to produce gold nanodumbbells (GNDs) by the addition of acetone solvent in surfactant solution during electrolysis.

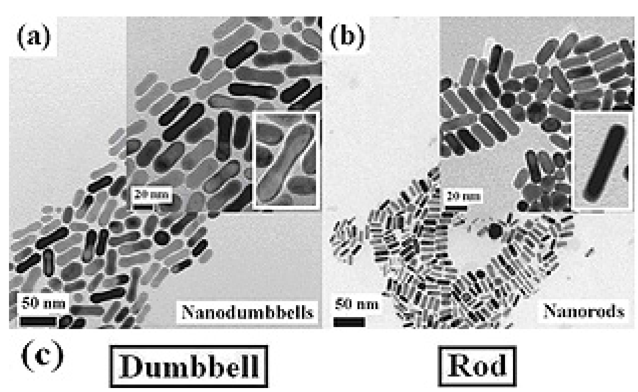

Figure 1(a) shows a TEM image of GNDs using an electrochemical method with the addition of acetone solvent during electrolysis. It can be seen that the structure of a single GND is fatter at the two ends and thinner in the middle section, as shown in the inset of Figure 1(a). Figure 1(b) shows a TEM image using the electrochemical method without the addition of acetone solvent, indicating a large amount and shape of gold

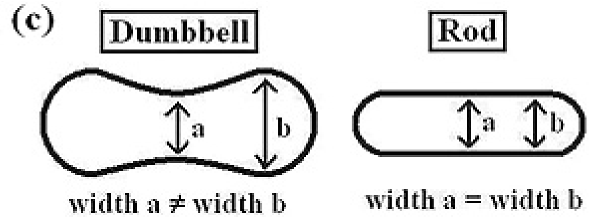

Figure 1. Typical TEM images of gold nanoparticles with different shapes: (a) dumbbell and (b) rod. (c) Drawing of morphology of the dumbbell and rod.

nanorods. Figure 1(c) clearly delineates a schematic illustration of the nanodumbbells and nanorods, and the difference in the shape of the nanodumbbells and nanorods is the diameter (width) section. The nanorod's shape has the same distance in diameter section (i.e. width a = width b). In this study, the nanodumbbells shape is not identical in diameter section (i.e. width a ≠ width b), indicating that the smallest distance in the middle section and the large distances at the two ends are observed.

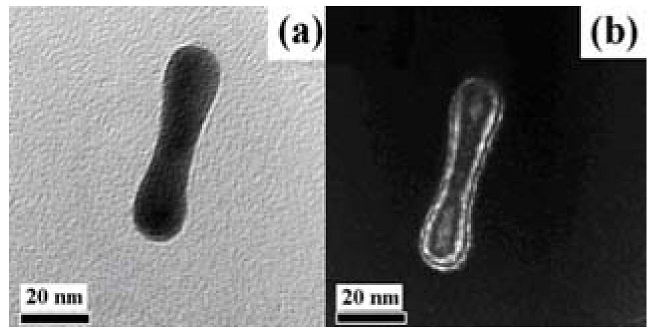

Figure 2. Bright-field TEM image of gold nanodumbbell (a) and corresponding dark-field TEM image (b).

Figures 2(a) and (b) show the bright-field (BF) transmission electron microscopy (TEM) image of single GND and corresponding dark-field (DF) TEM image. Using DF TEM image analysis in Figure 2(b), it was determined that this contrast arises from thickness fringes oriented for strong Bragg scattering. The thickness fringes exhibiting strong diffraction contrast are simultaneously visible as ring pattern, bright regions in the GND surface. From two-beam dynamic diffraction theory, the intensity of the DF TEM image under the Bragg condition follows $\sin^2(\pi d/\xi g)$, where d is the sample thickness and ξg is the so-called extinction distance depending on the crystal structure factor and the electron wavelength. The thickness fringes observed across the GND in the DF TEM image would be symmetric around its axis, as shown in inset of Figure 3(a). When the surface of a single gold dumbbell is oriented nearly perpendicular to the electron beam, the thickness fringes of GNDs in the surface are equally separated at each side of the axis. The configuration of GNDs is presented schematically in the lower part of Figure 3(a). The DF TEM image analysis confirms thickness fringes of GNDs due to varied facets in the nanodumbbell's top surface. Thus, the surface of a GND is not a flat structure. At this stage, the cross-section structure of GNDs is still not fully understood. The images from TEM analysis cannot show the cross-section structure of the gold nanodumbbells directly, but the GNDs should lie on a carbon film with one side of the long axis parallel to the carbon film and perpendicular to the electron beam. In order to study the cross-sectional structure of GNDs, a rotation around the GND axis from 0 ◦ to 23 ◦ by means of a microscope tilting stage reveals three DF TEM image contrast patterns, as shown in Figure 3. When the long axis of GNDs has no rotation in Figure 3(a), the DF TEM image exhibits a symmetric

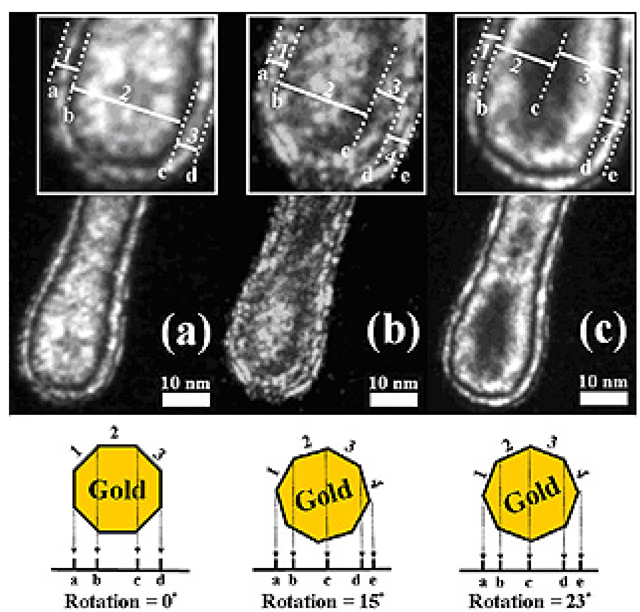

Figure 3. The long axis of gold nanodumbbell with rotation by DF TEM image analysis, and corresponding profiles of gold nanodumbbell in cross-section.

contrast pattern with three lattice plane fringes as planes 1 to 3, which are presented schematically in the lower part of Figure 3(a). Besides, the long axis of the GNDs from the 15 ◦ rotation in Figure 3(b) exhibits a non-symmetric contrast pattern with four lattice plane fringes as planes 1 to 4, which are presented schematically in the lower part of Figure 3(b). The DF TEM image contrast patterns result from different lattice planes in the GND's surface. It was also observed that the DF TEM image from the 23 ◦ long axis rotation in Figure 3(c) exhibits a symmetric contrast pattern with four lattice plane fringes as planes 1 to 4, which are presented schematically in the lower part of Figure 3(c). In this study, the long axis of gold nanodumbbells with rotation by DF TEM image analysis further confirmed that GNDs in cross-section have an octagon structure.

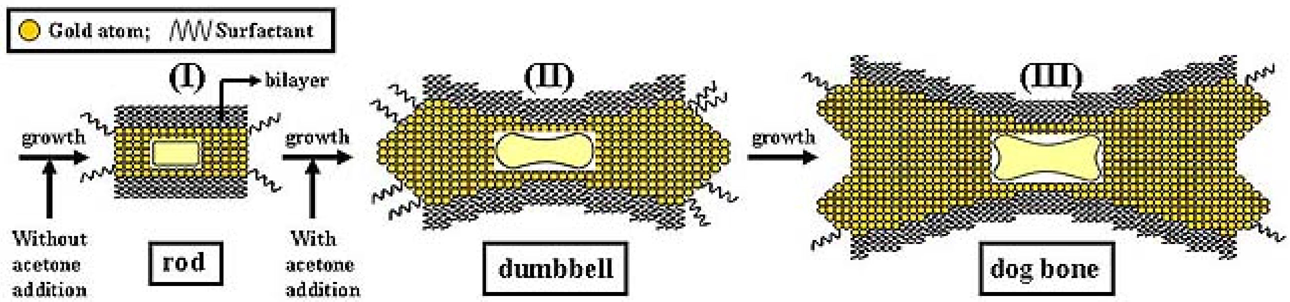

Figure 4. Schematic illustration of the formation process of the gold nanodumbbells by electrochemical method with addition of acetone solvent.

The growth mechanism of these GNDs can be depicted schematically as shown in Figure 4. During electrolysis using the electrochemical method, the bulk metal at the anode is oxidized to metal cations, which then migrate to the cathode where reduction reaction occurs, with the formation of adatoms. These adatoms are trapped by the surfactant to form the nanoparticles. The surfactant as electrolyte and stabilizer in the growth solution is generally considered to be a micelle template for controlling the size and shape of the particle. Hence, the surfactant plays a crucial role here. However, it is considered without the addition of acetone solvent to comprise mainly two processes: (i) the formation of a bilayer of the surfactant on the surfaces of gold nanorods provides enough stabilization as a micelle template during the growth of gold nanorods using the electrochemical method; and (ii) the surfactant micelle template during gold nanorod growth led to the inhibition of growth along the long axis of the rods and enhanced growth at the ends of the nanorods, promoting the formation of longer gold nanorods. The organic solvent could usually dissolve a polar group of surfactant at the hydrocarbon/water interface of the micelle when the organic solvent was added to a surfactant solution. Hence organic solvents decrease the surface charge density of ionic micelles and thereby change the geometric shape of the surfactant micelle template. Therefore, the continuous addition of acetone solvent during electrolysis possibly causes the change in micelle-template shape in this work, leading to gold nanorods with dumbbell structures, as shown in picture (II) of Figure 4.

We have demonstrated the first sample of GNDs prepared using the electrochemical method. It has been shown that the addition of acetone solvent to a surfactant solution plays an important role in the formation of GNDs. The singlecrystalline GNDs were successfully fabricated with an octagon structure in cross-section. The aspect ratio of the GNDs is about 3. This preparation of GNDs is proven to be a simple and effective synthesis method.