Formation of One-dimensional Crooked Gold Nanocrystals by Electrochemical Technique with Surfactant Solution

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This study demonstrates the synthesis of one-dimensional (1D) crooked gold (Au) nanocrystals by an electrochemical method with surfactant. For example, the primary surfactant may be cetyltrimethylammonium bromide (CTAB), and the auxiliary surfactant may be tetradodecylammonium bromide (TTAB) with isopropanol (IPA) solvent. The formation of crooked Au nanocrystals was induced by aggregation of many small Au nuclei between the several large Au nanoparticles during growth, causing the small Au nuclei to link to the large Au nanoparticles forming crooked Au nanocrystals.

Extensive and intensive investigation on gold (Au) nanoparticles in biology, nonlinear optical switching, the formation of a modified surface for surface-enhanced Raman scattering (SERS), immunoassay labeling, optical contrast agents and catalysis have demonstrated that the size and shape of nanoparticles strongly depend on physical and chemical properties,[1] thus highlighting the importance of developing a special shape for Au nanoparticles. Hence, adequately controlling the shape and size during nanoparticle synthesis is an emerging research topic. Many investigations have prepared specially shaped two-dimensional (2D) metal nanowires with network structure by using various methods, such as chemical reduction,[2] irradiation of an intense pulsed laser on Au nanoparticles with surfactant solution,[3] nanoparticle deposition within the porous template membrane,[4] laser ablation technique,[5] and electrodeposition.[6] A surfactant micelle serving as the template in an electrochemical system was recently demonstrated.[7] The advantages of this method include fairly simple preparation procedure and easily controllable dimensions of produced particles. This work presents the first example of crooked Au nanocrystals synthesized electrochemically in the presence of isopropanol (IPA) solvent with surfactant solution.

Au nanoparticles were prepared electrochemically using a simple two-electrode cell with anodic oxidation and cathodic reduction. The actual experimental cell was housed in a standard $20 \times 80\,\mathrm{mm}^2$ glass test tube. At dimensions of $30 \times 10 \times 0.5\,\mathrm{mm}^3$, Au plate and Pt plate were cut to form the anode and cathode, respectively. Electrodes in the cell were spaced 10 mm apart and held in place by Teflon spacers. A growth solution of 0.08 M cetyltrimethylammonium bromide (CTAB, Fluka, 98%) and deionized (DI) water in the typical synthesis was prepared. The 3 mL of CTAB, which served as the electrolyte of growth solution, was put in the test tube. A measured amount of powdered auxiliary surfactant with 30 mg (tetradodecylammonium bromide; TTAB, Fluka, 99%) was added to the tube, where it floated on the growth solution. A pipette was employed to add 0.2 mL of IPA solvent into the solution. The tube was then sonicated at 100 kHz for 5 min. The electrolysis was performed under constant ultrasonication at 100 kHz for 25 min. The typical current was set at 5 mA, and the temperature was held constant at 40 °C. The resulting solution was centrifuged at 6500 rpm for 20 min, and the supernatant was collected, which was centrifuged again at 12000 rpm for 20 min. The precipitation was then collected and redispersed with DI water for storage and other uses, such as analysis of transmission electron microscopy (TEM), electron diffraction (ED) (Philips Tecnai G2 F20), and ultraviolet-visible (UV–vis) spectrometer (Hitachi 3310, Japan).

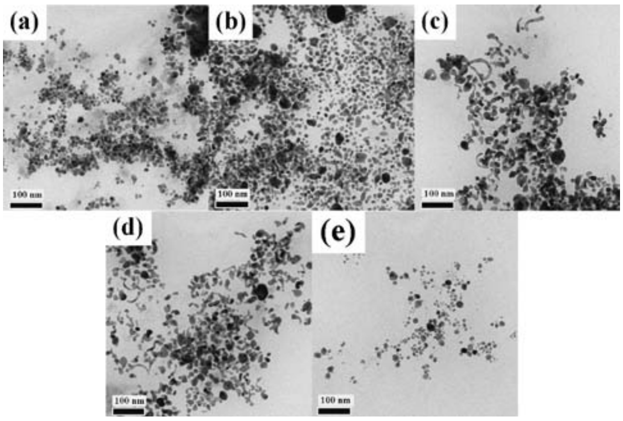

Figure 1. TEM images of Au nanocrystals dispersion electrochemically synthesized with IPA of 0.2 mL at different reaction times of: (a) 10, (b) 15, (c) 20, (d) 25 min, and (e) without IPA at reaction time of 25 min.

Figure 1 shows the TEM images of Au nanoparticles produced electrochemically with IPA of 0.2 mL at different reaction times of (a) 10, (b) 15, (c) 20, and (d) 25 min, and (e) without added IPA at reaction time of 25 min. The experimental results clearly indicate that the shape and size of the Au nanoparticles can be changed by adjusting the reaction time. In Figure 1a obtained at a reaction time of 10 min with IPA, the shape of Au nanoparticles is almost sphere. Additionally, if reaction time is lengthened from 15 to 25 min in IPA, then the Au nanoparticle shape starts to change from 0D sphere to 1D crooked Au nanocrystals, as shown in Figures 1b–1d. However, most of the Au nanoparticles at a reaction time of 25 min were not spherical in shape, but crooked or distorted. The length of crooked Au nanocrystals increased with increasing reaction time. Additionally, the smaller size and good dispersion of Au nanoparticles

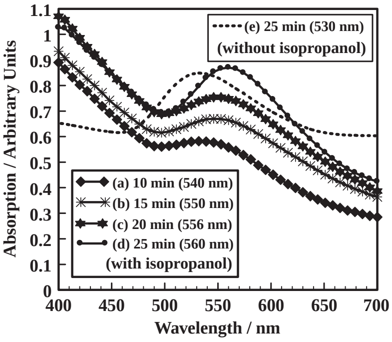

Figure 2. UV–vis absorption spectra of the Au nanoparticles electrochemically synthesized with IPA at different reaction times of: (a) 10, (b) 15, (c) 20, (d) 25 min, and (e) without IPA at reaction time of 25 min.

without IPA at reaction time of 25 min was observed in Figure 1e. Figures 2a–2d show the UV–vis absorption spectra of Au nanoparticles with 0.2 mL of IPA at reaction times of 10, 15, 20, and 25 min, respectively. The absorption band maximum for the Au nanoparticles without isopropanol was obtained at 530 nm, as shown in Figure 2e. The Au nanoparticles should have roughly spherical structures, as indicated by an absorption band at 540 nm when the reaction time was 10 min, as shown in Figure 2a. The particle shape began to change from 0D sphere to 1D crooked Au nanocrystal shape at a reaction time of 15 min, and the absorption band was slightly red-shifted to 550 nm, as shown in Figure 2b. The absorption band shifted more significantly at a reaction time of 25 min with a band maximum at 560 nm, as shown in Figure 2d. However, comparison of absorption spectra with the corresponding TEM morphology reveals that the red shift of the absorption band was mirrored by the appearance of the 1D crooked Au nanocrystal structure.

Figures 3a and 3b shows the bright-field (BF) TEM image of several crooked Au nanocrystals and the corresponding dark-field (DF) TEM image. Figure 3b indicates that this contrast arises from segments of individual grains oriented for strong Bragg scattering. A comparison between the BF image and a corresponding DF TEM image shows that the crooked Au nanocrystals were composed of several large Au grains nanoparticles, which were presented within each of the crooked Au nanocrystals and were not distributed uniformly. The inset of Figure 3a illustrates an ED pattern, in which the concentric rings could be assigned as diffraction from {111}, {200}, {220}, {311}, and {400} planes of face-centered cubic (fcc) Au from the centermost ring, respectively. Furthermore, the structure of the crooked Au nanocrystals was clearly polycrystalline. Figure 3c shows the TEM image of single 1D crooked Au nanocrystals, which clearly shows that the 1D crooked structure consisted of four large Au nanoparticles and many small Au nuclei between the nanoparticles. This finding was further confirmed by high-resolution transmission electron microscopy, as shown in inset of Figure 3c. The small Au nuclei linked the large Au nanoparticles. A lattice plane with an interplanar distance of 0.140 nm was observed, which corresponds well with the lattice spacing between {220} planes of the fcc gold (0.144 nm). Figure 3d schematically shows the formation mechanism of these 1D crooked Au nanocrystals, in which bulk Au is ionized and travels from anode to cathode during electrochemical reactions in the cell. To prevent particle agglomeration and to produce nanoparticles of uniform shape electrochemically, surfactant micelle-templates were adopted for preparation. IPA was added to damage the structure of the surfactant micelle-template.[8] This experiment lead to particle agglomeration forming large Au nanoparticle in the growth solution as previously noted. The small Au ions or Au nuclei from anode to cathode via electrolysis were aggregated onto the surface of the large Au nanoparticle during growth process. It is considered to comprise of mainly two processes: (i) the formation of Au atoms or small Au nuclei at the growth process as the precursors; and (ii) the subsequent anisotropic coalescence of these precursors leading to the 1D crooked Au nanocrystals formation.

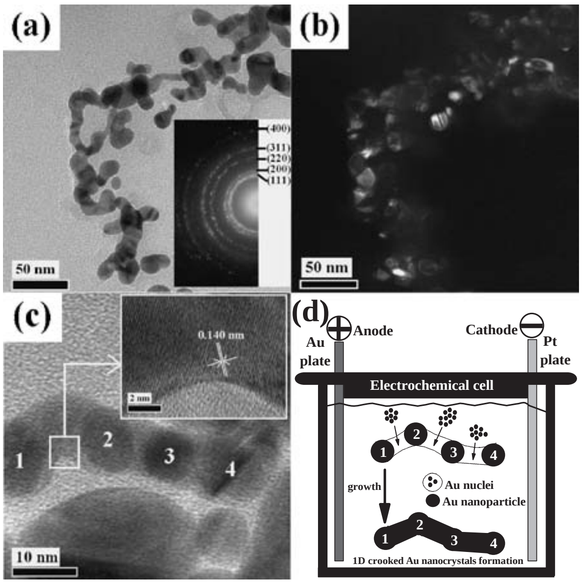

Figure 3. (a) Bright-field TEM image of several 1D crooked Au nanocrystals; insets: (a) electron diffraction pattern, (b) corresponding dark-field TEM image, (c) TEM images of single 1D crooked Au nanocrystals, and (d) schematic illustration of electrochemical formation of 1D crooked Au nanocrystals.

The authors would like to thank the National Science Council (NSC) of the Republic of China, Taiwan for partially supporting this research under Contract No. 93-2215-E-390-005.

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Published on the web (Advance View) December 3, 2005; DOI 10.1246/cl.2006.30