Nanostructures

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Synthesis of Trisoctahedral Gold Nanocrystals with Exposed High-Index Facets by a Facile Chemical Method**

Yanyun Ma, Qin Kuang, Zhiyuan Jiang, Zhaoxiong Xie,* Rongbin Huang, and Lansun Zheng*

Anisotropy is one of the basic properties of crystals, and different facets of a single crystal may exhibit different physical and chemical properties. In the past decade, control of the shape of metallic nanostructures has attracted intensive interest, because it may provide an effective route for tuning the electronic, magnetic, optical, or catalytic properties of metals.[1–13] In addition, fundamental studies of single-crystal surfaces of bulk metals have indicated that high-index facets having a high density of atomic steps, ledges, kinks, and dangling bonds usually exhibit much higher chemical-reaction activities, including catalytic activities.[14] However, crystal-growth rates in directions perpendicular to high-index planes are usually much higher than those in directions perpendicular to low-index planes because of the high surface energy of high-index planes. As a consequence, high-index planes rapidly disappear during crystal growth, and crystals are usually enclosed by low-index facets such as {100} and {111} surfaces.

The shape-controlled synthesis of metal nanocrystals (NCs) with exposed high-index facets is, therefore, an interesting and challenging research topic with potential applications. Up to now, although a variety of face-centered cubic (fcc) structured metal NCs with well-defined shapes have been synthesized, almost all of these NCs are enclosed by low-index {100} or {111} surfaces.[1a,4–8,11–13] Very recently, Sun and co-workers prepared tetrahexahedral platinum NCs enclosed by 24 high-index facets (such as {730}, {210}, and {520}) by an electrochemical method for the first time, and found that these high-index surfaces are thermally and chemically stable and exhibit enhanced catalytic activity.[15] The interesting shape and properties of such tetrahexahedral platinum NCs have inspired great efforts to synthesize well-shaped metal NCs with high-index facets by means of some facile methods. In this communication, we report the preparation of trisoctahedral gold NCs enclosed by 24 high-index facets (such as {221}) in high yield by a simple reduction of an aqueous solution of $HAuCl_4$ with ascorbic acid (AA) in the presence of cetyltrimethylammonium chloride (CTAC) at room temperature. To our knowledge, this is the first report of a synthesis of well-shaped metal NCs with high-index surfaces by a wet chemical method, which is facile and high-yield.

Figure 1 a shows a typical large-area scanning electron microscope (SEM) image of the as-prepared product, and Figure 1 b shows a partially enlarged SEM image of the as-prepared product. These images indicate the presence of homogeneous, well-shaped NCs with sizes ranging from 100 to 200 nm. The X-ray powder diffraction (XRD) pattern of the as-prepared NCs (Figure 1 c) matches well with the fcc gold structure (JCPDS 4-0784). As shown in a high-magnification SEM image (Figure 1 d), the as-prepared NCs are well-shaped polyhedra comprising eight trigonal pyramids and are, thus, trisoctahedra. The trisoctahedron, which is a shape rarely observed for NCs, can be generated from an octahe-

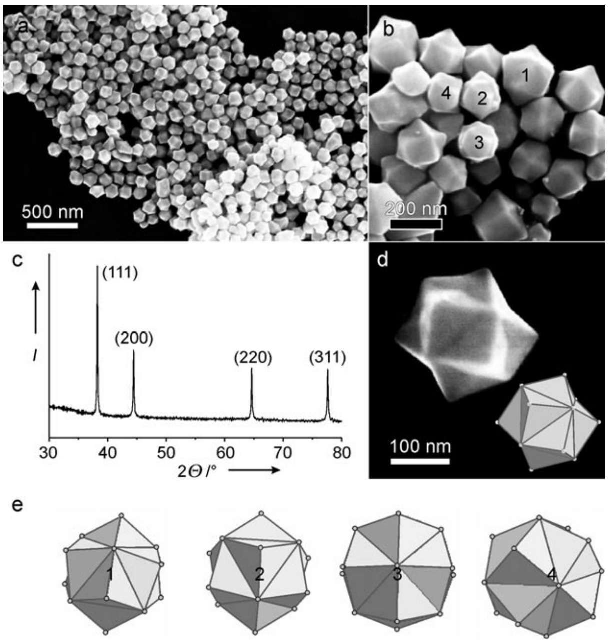

Figure 1. a) Typical large-area SEM image of the as-prepared trisoctahedral gold NCs. b) Partially enlarged SEM image of the NCs. c) XRD pattern of the NCs. d) High-magnification SEM image of a single NC; inset: model of an ideal trisoctahedron enclosed by {221} surfaces, in the same orientation as the NC in the SEM image. e) Models of ideal trisoctahedra in different orientations corresponding to those of the NCs marked with the same number in (b).

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[*] Dr. Q. Kuang, Prof. Z. Xie, Prof. R. Huang, Prof. L. Zheng
State Key Laboratory for Physical Chemistry of Solid Surfaces,
Department of Chemistry
College of Chemistry and Chemical Engineering, Xiamen University
Xiamen, 361005 (China)
Fax: (+86) 592-218-3047
E-mail: zxxie@xmu.edu.cn
qkuang@xmu.edu.cn

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dron by "pulling out" the centers of the eight triangular faces (Figure S1 in the Supporting Information).[16] All the 24 facets of a trisoctahedron belong to crystal planes of the family of the ⟨110⟩ zone axis, the Miller indices of which are *hhl*, and the limiting case is a dodecahedron (*hhl* = 110; Figure S1). In the inset of Figure 1 d, a geometrical model of an ideal trisoctahedron enclosed by {221} surfaces, in the same orientation as the NC in the SEM image, is presented. The proposed model agrees well with the as-prepared NCs. By analyzing the partially enlarged SEM image of the as-prepared NCs in a similar fashion (Figure 1 b), we find that almost all the NCs are trisoctahedra. Although some of the NCs do not seem to be trisoctahedra at first glance, a careful survey of particle shapes demonstrates that most of these NCs are, in fact, differently oriented trisoctahedra. The yield of trisoctahedral NCs is about 85 %. Figure 1 e shows models of ideal trisoctahedra in different orientations, and corresponding NCs are indicated in Figure 1 b. Note that some trisoctahedral NCs do not perfectly match the trisoctahedron enclosed by {221} surfaces, probably because some surfaces deviate from the {221} planes to other trisoctahedral surfaces, such as {332} or {331}.

The intrinsic crystal structure of the trisoctahedral gold NCs was further investigated by transmission electron microscopy (TEM). Figure 2 a shows a TEM image of NCs in different orientations. Figure 2 b shows a TEM image of an individual trisoctahedral NC, and the top-right inset shows the corresponding selected-area electron diffraction (SAED) pattern. The SAED pattern of the NC can be indexed to the [011] zone axis of a single crystal of fcc gold. This result suggests that the NCs are single crystals, rather than multiply twinned crystals. To demonstrate that the exposed surfaces of the NCs correspond to {221} planes, a model of a trisoctahedron enclosed by {221} surfaces, projected from the [011] direction, is shown in the bottom-right inset of Figure 2 b. There is a good agreement between the model and the TEM image of the NC. This result was further confirmed by additional TEM images and corresponding SAED patterns projected from the [001] or [$\bar{2}$33] direction (Figure S2). In fact, the crystal planes of the family of ⟨110⟩ zone axes (the (*hhl*) planes) can be described as combinations of some subfacets of the (111) and (110) planes. For example, the microstructure of a (221) surface can be thought of as the combination of (111) terraces and (110) steps, as shown in Figure 2 c (the (111) terrace consists of three atoms, and the (110) step of one atom; Figure S3). Such a high-index surface was directly captured in a high-resolution TEM (HRTEM) image of a trisoctahedral NC, recorded along the [011] direction (Figure 2 d).

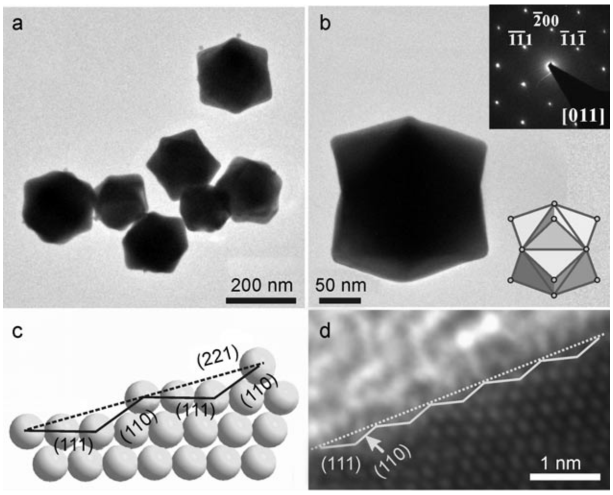

Figure 2. a) Typical low-magnification TEM image of the trisoctahedral gold NCs. b) High-magnification TEM image of a single NC, recorded along the [011] direction; top-right inset: the corresponding SAED pattern; bottom-right inset: model of an ideal trisoctahedron, projected from the [011] direction. c) Atomic model of the (221) surface of a NC, projected from the [011] direction, showing that the (221) surface can be thought of as a combination of (111) terraces and (110) steps. d) HRTEM image of a NC, recorded along the [011] direction, showing the (221) surface, (111) terraces, and (110) steps.

The surface structure of the trisoctahedral gold NCs was also characterized by cyclic voltammetry (CV; Figure 3). The electrochemical behavior of the NCs was different from that of a surface of polycrystalline gold, and also different from that of the (111), (110), and (100) surfaces (the low-index surfaces) of a single crystal of gold.[17] This result suggests that the as-prepared well-faceted gold NCs are not enclosed by low-index surfaces, nor by a polycrystalline surface, consistent with the SEM and TEM findings.

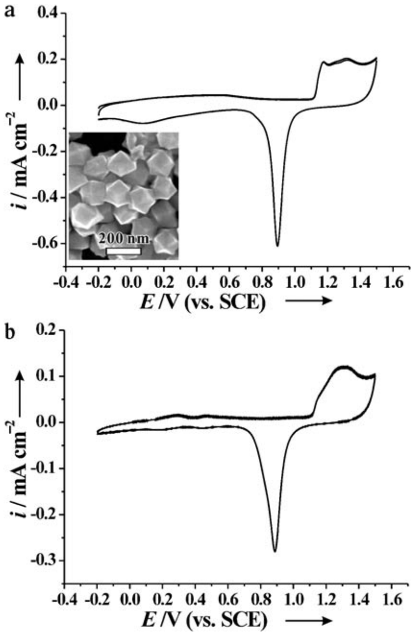

Figure 3. a) CV trace of the trisoctahedral gold NCs loaded onto a glassy carbon electrode; inset: SEM image of the NCs used in the experiment. b) CV trace of a polycrystalline gold wire electrode. See text for details.

To monitor the growth process of the trisoctahedral gold NCs, in situ UV/Vis absorption spectra were recorded during the synthesis of the NCs (Figure 4). When a solution of AA was added to a CTAC-stabilized solution of $HAuCl_4$, the color quickly changed from light yellow to colorless, and the first UV/Vis spectrum was recorded (0 min). UV/Vis spectra were

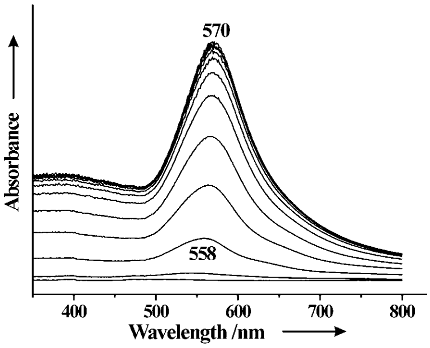

Figure 4. In situ UV/Vis absorption spectra recorded during the synthesis of the trisoctahedral gold NCs at times of 0 (spectrum at the bottom), 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 17, and 23 min (spectrum at the top). See text for details.

then recorded every minute. An obvious absorption band at about 560–570 nm, which is ascribed to the surface plasmon resonance (SPR) of spherical gold particles of about 100 nm in diameter, appeared and increased in intensity during the growth of the NCs. As has been well investigated, the position of such an absorption peak of metal particles is associated with the particle size.[18] The slight red shift of the SPR peak from about 558 to 570 nm over time indicates an increase in the size of the NCs during the growth process. Furthermore, the SPR peaks in the UV/Vis spectra are sharp and smooth, indicating that the NCs are uniform in size during the growth process. After 10 min, the UV/Vis spectra and the intensity of the SPR peak, in particular, did not change, suggesting that the growth process had finished.

Wet chemical methods have been widely applied in the synthesis of metal nanoparticles because of the facility of the synthetic process and the high yield of the products. By using such methods, well-shaped gold NCs have been prepared by seed-mediated growth or by one-step synthesis in the presence of additives such as surfactants,[6–8] biomolecules,[9] buffer solutions,[10] and halide ions.[11] Particles with various shapes, such as cubes, octahedra, decahedra, and prisms, have been prepared. However, the exposed surfaces of the prepared particles were low-index facets, such as {111} and {100}. Furthermore, most of the well-shaped particles are convex polyhedra, which are energetically preferred during crystal growth because of their small surface areas. One exceptional example was reported by Jose-Yacaman and coworkers, who synthesized star polyhedral gold NCs by direct reduction with AA in an aqueous solution of $HAuCl_4$ without any other additives.[12a] Their products contained a small amount of monocrystalline "star particles", which were, in fact, trisoctahedra enclosed by 24 low-index {111} surfaces. The trisoctahedron is not a convex polyhedron, as there are concave edges between the trigonal pyramids. It is, therefore, reasonable to believe that AA or one of its oxidation products may stabilize such high-energy concave edges, assuring the growth of a "star shape".

To clarify the growth mechanism of the trisoctahedral gold NCs with high-index surfaces, studies of the effect of the surfactant CTAC were carried out. Surfactants are often used in the well-controlled synthesis of novel metal nanoparticles, such as gold, silver, platinum, and palladium nanoparticles. Cetyltrimethylammonium bromide (CTAB) is one of the most popular surfactants for the synthesis of multiply twinned gold nanorods.[2b,6,11] When CTAC was substituted by CTAB in the present synthesis and all other experimental conditions were kept the same, rodlike and irregular particles were observed in the product instead of trisoctahedral gold NCs (Figure 5a). This result indicates that the Cl^- ions play a key role in the formation of the NCs. Similarly, we found that the long-chain CTA^+ ion also plays a key role in the formation of the trisoctahedral NCs, as spherical particles of about 100 nm in diameter were obtained when a comparable amount of NaCl (5 mL, 0.01 M) was introduced in the synthesis instead of CTAC (Figure 5b). These preliminary results indicate that the trisoctahedral gold NCs with high-index surfaces result from the interaction of both anion and the cationic surfactant.

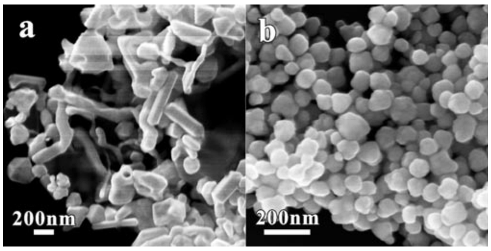

Figure 5. SEM images of gold particles prepared from $HAuCl_4$ (aq, 5 mL, 0.6 mM) and AA (aq, 0.1 mL, 0.1 M) with: a) CTAB (aq, 5 mL, 0.01 M), or b) NaCl (aq, 5 mL, 0.01 M).

In summary, trisoctahedral gold NCs have been successfully synthesized in a large quantity by reducing $HAuCl_4$ with AA in the presence of CTAC at room temperature. The SAED pattern of the NCs suggested that the as-prepared NCs are single crystals enclosed by 24 high-index facets, such as {221} planes. CV studies showed that the as-prepared NCs have an electrochemical behavior different from that of low-index surfaces of a single crystal of gold and from that of a surface of polycrystalline gold. The present study motivates us to further explore wet chemical methods for the preparation of well-defined polyhedral metal NCs enclosed by high-index surfaces, which usually have relatively high chemical-reaction activities.

Experimental Section

Reagents: $HAuCl_4 \cdot 3H_2O$ (99.9%) and CTAC (> 95%) were purchased from Alfa Aesar, and AA, CTAB, NaCl, and H_2SO_4 were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was ultrapure (> 18.0 $M\Omega\,cm^{-1}$). All reagents were used as received.

Synthesis and characterization of the trisoctahedral gold NCs: In a typical experiment, an aqueous solution of CTAC (5 mL, 0.01 M) was added to an aqueous solution of $HAuCl_4$ (5 mL, 0.6 mM) at room temperature. Then, a freshly prepared aqueous solution of AA (0.1 mL, 0.1 M) was quickly added to the solution with gentle shaking. The solution became colorless and transparent in several seconds. With continuous shaking, the solution gradually became light purple in color. Finally, an orange precipitate formed in the light purple solution at room temperature. The as-prepared product was washed several times by alternate centrifugation and ultrasonic cleaning using ultrapure water or ethanol to remove CTAC.

The as-prepared trisoctahedral gold NCs were characterized by SEM (LEO 1500, operated at 20 kV), TEM (FEI Tecnai-F30 FEG, operated at 300 kV), and XRD (PANalytical X-pert). In situ UV/Vis absorption spectra of the reaction mixture were recorded during the synthesis with a spectrophotometer (Beckman DU7400). CV measurements were carried out using an electrochemical workstation (CHI 631b, Shanghai Chenhua Co., China).

Electrochemical measurements: A glassy carbon electrode (diameter of 5 mm) was carefully polished and washed before every experiment. Then, trisoctahedral gold NCs dispersed in ethanol or water were dripped onto the surface of the glassy carbon electrode and dried at room temperature. The last two steps were repeated several times, until the surface of the electrode was fully covered by an obvious and uniform layer of the NCs.

The CV measurements were carried out at room temperature with a conventional two-compartment three-electrode electrochemical cell. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was platinum wire. The electrolyte was an aqueous solution of H_2SO_4 (0.5 M), which was thoroughly purged with N_2 before each experiment. The ramping rate was $50\,mV\,s^{-1}$.

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