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Growth of Tetrahexahedral Gold Nanocrystals with High-Index Facets

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Variously shaped nanocrystalline materials have attracted intense attention owing to their shape-dependent properties.[1−4] The shape-controlled synthesis has been very successful with metal nanocrystals (NCs). Examples include various types of polyhedra, plates, and rods.[5−7] Most of them are enclosed by low-index facets, such as {111} and {001}. Metal NCs with high-index facets generally exhibit higher catalytic activities than those with only low-index facets, because high-index facets expose high densities of atomic steps. Atoms at these locations are coordinatively unsaturated. They serve as active sites for breaking and forming chemical bonds. It has remained challenging to synthesize high-index-faceted metal NCs because the growth rate on high-index planes is usually much larger than that on low-index ones. High-index facets can thus be taken over quickly by low-index ones during NC growth. Very recently, the successful growths of trisoctahedral Au NCs enclosed by 24 {122} facets[8] and tetrahexahedral (THH) Pt NCs enclosed by 24 {037} facets[9] have been shown. Here, we report on the high-yield preparation of elongated THH Au NCs enclosed by 24 {037} facets.

A THH has 24 faces (Figure 1a). It can be obtained from a cube by "pulling out" the centers of the 6 square faces. An elongated THH can be generated by "cutting" a THH into two halves and "pulling out" the two halves along any one of the three equivalent directions. During this process, the 8 triangular facets parallel to the elongation direction are changed to trapezoids. So far only trisoctahedral Au and THH Pt NCs have been reported. Our THH Au NCs will be an important addition to the family of metal NCs that are enclosed exclusively by high-index facets. They will useful for fundamental catalytic studies.

Our synthesis is based on a seed-mediated growth in aqueous solutions,[10,11] which has been used widely in the preparation of Au nanostructures. Briefly, the seed solution was prepared by rapidly injecting $NaBH_4$ (0.01 M, 0.6 mL) in a mixture of $HAuCl_4$ (0.01 M, 0.25 mL) and cetyltrimethylammonium bromide (CTAB, 0.1 M, 9.75 mL).[12,13] To grow Au NCs, 10 aliquots of a growth solution were prepared, with each composed of CTAB (0.1 M, 40 mL), $HAuCl_4$ (0.01 M, 2.0 mL), and $AgNO_3$ (0.01 M, 0.4 mL). After the pH of each aliquot was adjusted to 1.9 with HCl (1.0 M, 0.8 mL), ascorbic acid (0.1 M, 0.32 mL) was added. 100, 40, 16, and 8 μL of the seed solution were injected in the first 4 aliquots, respectively. For the remaining 6 aliquots, 250, 200, 100, 50, 25, and 10 μL of the seed solution that was diluted 50 times with CTAB (0.1 M) were applied. They were equivalent to 5, 4, 2, 1, 0.5, and 0.2 μL of the undiluted seed solution, respectively. The growth was left undisturbed overnight. The as-grown nanocrystals were washed twice by centrifugation for further characterizations.

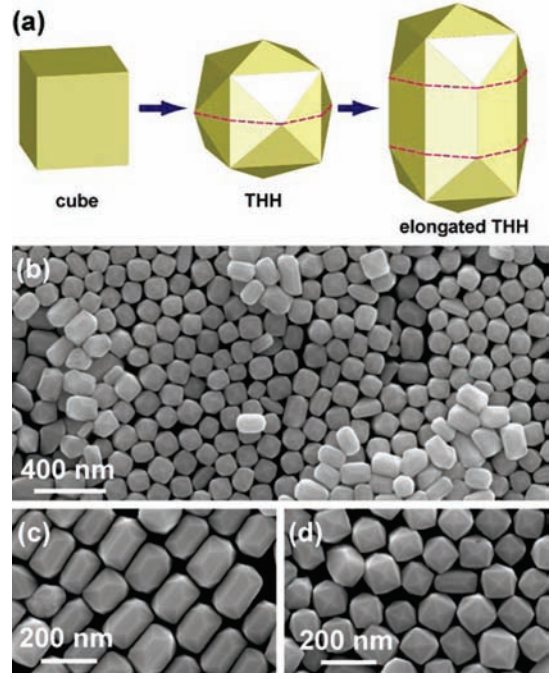

Figure 1. (a) Schematic showing the formation of a THH from a cube. (b) Large-area SEM image of the THH Au NCs deposited on a Si substrate. (c, d) SEM images showing their side and end facets, respectively.

Extinction measurements show that the product obtained with 100 μL of the seed solution has a longitudinal plasmon peak at 852 nm and a transverse one at 512 nm (Figure S1, Supporting Information). As the seed volume is reduced, the longitudinal plasmon peak blue shifts and the transverse one red shifts, suggesting a gradual decrease in the aspect ratio and an increase in the diameter of the products.[12] As the seed volume is further reduced gradually from 5 to 0.2 μL, the longitudinal plasmon peak becomes substantially broader and the transverse one further red shifts. Throughout the variation of the seed volume, the longitudinal plasmon peak decreases steadily in intensity.

The morphological characterization with scanning electron microscopy (SEM, FEI Quanta 400) reveals that the growth with 100 μL of the seed solution gives cylindrical Au nanorods (diameter, 16.3 ± 0.9 nm; length, 71 ± 4 nm; aspect ratio, 4.4 ± 0.4; Figure S2, Supporting Information). These nanorods are similar in size to those obtained in the previous syntheses with 96 μL of the seed solution.[12,13] The Au nanorods grow thicker as the seed volume is reduced. They start to exhibit clear facets when the seed volume reaches 16 μL (Figures S2 and S3, Supporting Information). When the seed volume is below 5 μL, the products evolve into elongated THH NCs. They grow fatter with decreasing seed amounts. Their

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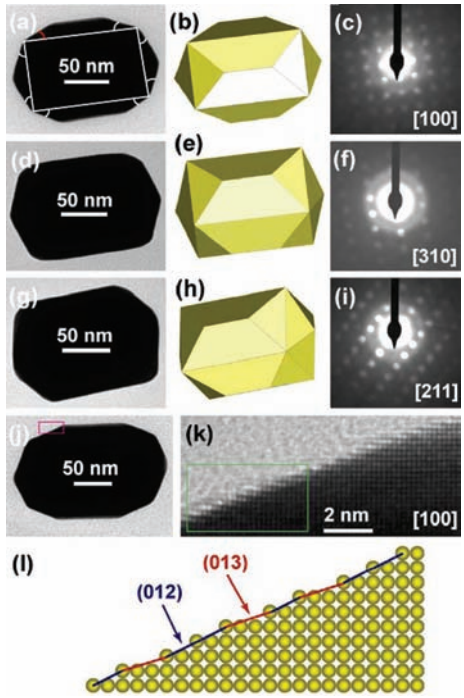

Figure 2. (a−c) TEM image (FEI CM120, 120 kV), schematic model, and electron diffraction pattern of one elongated THH nanocrystal oriented along the [100] direction. (d−f) The same nanocrystal oriented along the [310] direction. (g−i) The same nanocrystal oriented along the [211] direction. (j) A different [100]-oriented THH nanocrystal. (k) HRTEM image (FEI F30, 300 kV) of the region indicated with a box in (j). (l) Atomic model corresponding to the region indicated with a box in (k).

number yields are above 95%. They are stable without observable changes in aqueous solutions for several weeks. Figure 1b−d show the SEM images of the THH NCs (thickness, 118 ± 7 nm; length, 188 ± 5 nm; aspect ratio, 1.6 ± 0.1) grown with 0.2 μL of the seed solution. Their ends are capped with square pyramids. Both large trapezoidal and small triangular facets are visible on the side surfaces.

The solution pH, in addition to the seed amount, is also important for the growth of the THH Au NCs. The reducing power of ascorbic acid and thus the growth rate increase with the solution pH. When the pH is increased to 2−5, more NCs with irregular shapes are produced, so the yield of THH NCs becomes smaller. When the pH is below 1.5, the growth takes weeks, and THH NCs can still be obtained.

We further carried out transmission electron microscopy (TEM) characterizations on the THH Au NCs. Because a THH is derived geometrically from a cube that has 6 equivalent {001} facets, the face indices of the THH Au NC can be determined from the angle between the bevel and base of the square pyramids (Figure 1a). We therefore first tilted an elongated THH Au NC to the [100] direction (Figure 2a) and confirmed its orientation by electron diffraction (Figure 2c). Under this orientation, 8 out of the 24 facets are visible. The projected contour of this NC fits very well the model shown in Figure 2b. We also tilted this NC to its [310] and [211] directions (Figure 2d−i). Both projected contours accord well with the models. These results strongly suggest that the NC has a THH shape. Starting clockwise from the one labeled in red (Figure 2a), the angles between the bevels and bases on the THH Au NC are measured to be 24°, 24°, 26°, 26°, 24°, 23°, 23°, and 24°, respectively. Similar measurements were also made on two other NCs. The angle averaged over a total of 24 values is (24 ± 1)°. This result indicates that the bevels on the elongated THH NCs are high-index {037} planes, which have a calculated angle of 23.2° with the {001} planes.

The atomic arrangements on the {037} facets were further captured under high-resolution (HR) TEM imaging (Figure 2j and k). The (037) facet is multiply stepped and composed of (012) and (013) subfacets (Figure 2l). Taken together, all of the structural characterizations reveal that the Au NCs are single-crystalline THHs enclosed by 24 high-index {037} facets.

There are a number of monosteps on the {037} facets of the elongated THH Au NCs. The atoms at the step edges should be more chemically active than those on the low-index facets. This is confirmed by cyclic-voltammetry (CV) measurements (Figures S4 and S5, Supporting Information). The CV traces of the elongated THH Au NCs exhibit an oxidation peak around 1.18 V. For comparison, CTAB-stabilized octahedral Au NCs (edge length: 17 ± 1 nm) enclosed by 8 {111} facets were grown.[14] Their CV traces show an oxidation peak around 1.35 V.

In conclusion, elongated THH Au NCs have been synthesized in high yields via seed-mediated growth. They are single crystals enclosed by 24 high-index {037} facets. Electrochemical measurements show that they are more chemically active than octahedral Au NCs that are enclosed by low-index {111} facets.

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Supporting Information Available: The extinction spectra, SEM images, and cyclic-voltammetry traces of the Au NCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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