Crystal Growth

Platonic Gold Nanocrystals**

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As was known by the ancient Greeks, there are five platonic solids that can be constructed by selecting a regular convex polygon and having the same number of them meet at each corner: tetrahedron, octahedron, hexahedron (cube), icosahedron, dodecahedron.[1] The beauty in their symmetry and their apparent simplicity continue to inspire generations of mathematicians and scientists. In nature, certain viruses and radiolaria also routinely take the form of these polyhedral shapes.[2] Recently, the concept of shape control has started to revitalize the centuries-old metal colloidal synthesis. Nanoparticles of various shapes[3–5] (rods,[6–9] wires,[10–12] prisms,[13–19] cubes[20,21]), particularly those of silver and platinum, have been prepared by using a variety of different methodologies. The preparation of nanoparticles of highly symmetric platonic shapes with a unified method, however, has yet to be demonstrated, and is by itself a scientific curiosity and great challenge that requires exquisite crystal growth control. Herein, we report a systematic shape evolution of gold nanocrystals with sizes of 100–300 nm in a modified polyol process. By adding surface-regulating polymer and foreign

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ions, we can readily access the distinct shapes of tetrahedron, cube, octahedron, and icosahedron (dubbed platonic nanocrystals) with high yield and good uniformity. These nanocrystals have the perfect symmetry for 2D and 3D packing and therefore could enable the rational tuning of their optical, electrical, and catalytic properties.

Gold nanocrystals were produced by a modified polyol process,[22] with the presence of the surface-regulating polymer poly(vinyl pyrrolidone) (PVP). Briefly, ethylene glycol solutions of hydrogen tetrachloroaurate ($HAuCl_4{\cdot}3H_2O$) and PVP were injected simultaneously into boiling ethylene glycol. Ethylene glycol served as both solvent and reducing agent for the reaction. PVP not only stabilized the particles but also controlled the shape of the particles. The molar ratio between the PVP and the gold precursor was kept between 4.3 and 8.6. Gold particles formed within minutes, and the final diluted colloidal solution was iridescently blue.

A transmission electron microscopy (TEM) image showed that the majority (≈70%) of the particles had a triangular shape (Figure 1a), and sizes of 210 ± 20 nm. Electron diffraction of a single particle (Figure 1b, inset) shows that the particle was single crystalline, with the top and bottom covered with (111) surfaces. This initial inspection of the TEM data suggests the formation of flat nanoprisms as have been reported previously for silver.[14–16] Detailed scanning electron microscopy (SEM) studies, however, revealed otherwise. Interestingly, the sides of the particles were clearly slanted (Figure 1c,d), which indicates that rather than being flat prisms, these particles can be more accurately described as tetrahedra with a truncated corner, or as partially developed tetrahedra (hereafter we will call them tetrahedra for simplicity). The surfaces of these particles are dominated with {111} planes, which make them energetically favorable compared to prisms with other high-energy side surfaces such as $(1\bar{1}0)$ or $(11\bar{2})$. Occasionally, we were able to observe similar-sized particles with nearly fully developed tetrahedral shapes (Figure 1d), which points to the possibility of obtaining gold tetrahedra upon further growth of these triangular particles.

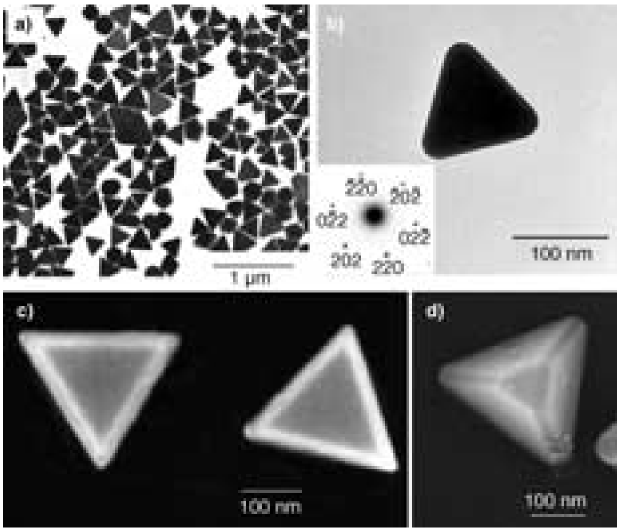

Figure 1. a,b) TEM image of truncated tetrahedral gold nanocrystals. The inset in (b) is the electron diffraction pattern taken along the [111] zone axis from the particle shown in (b). c,d) SEM images of several partially developed gold tetrahedra.

It was found that the nanoparticle shapes were highly sensitive to the concentration of the gold precursor used in the experiments. By slightly reducing this concentration, we were able to produce nanocrystals with icosahedral shapes. In one particular example, the gold precursor concentration was reduced to 80% of that used for the synthesis of tetrahedra, and the final molar ratio between the PVP and the gold precursor was maintained at 8.6. Observation by TEM showed that >90% of the particles had a projected hexagonal shape (Figure 2a) and sizes of 230 ± 20 nm. The size of a particle is defined here as the distance from one edge of the hexagonal projection to the opposite side. Electron diffraction on a single particle showed a complex pattern, indicating that the particle was composed of multiple crystal domains. Further investigation by SEM showed that the particles were mostly icosahedra (Figure 2b and inset). Note that icosahedral particles of face centered cubic (fcc) metals represent one of the most investigated multiply twinned particles (MTP) in gas-phase experiments.[23,24] However, we observed for the first time the preparation in solution of uniform metal particles with such complex yet well defined structures and sizes ranging from several tens to hundreds of

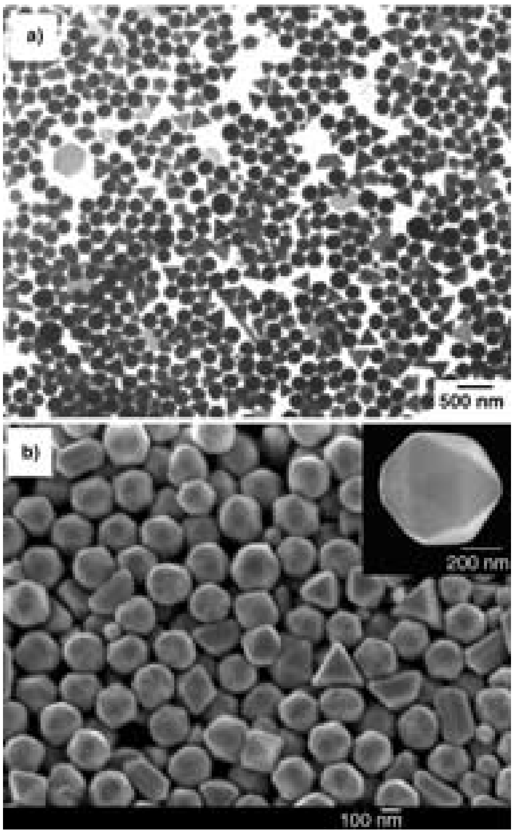

Figure 2. Icosahedral nanocrystals: a) TEM image and b) SEM image of icosahedral gold nanoparticles. Inset in (b) shows clearly all (111) facets of a typical icosahedron.

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nanometers. In addition to the shapes of tetrahedron or icosahedron, which formed the majority of the product, a small portion (≈10%) of decahedra (another type of MTP) and regular octahedra were also commonly observed in the final products (see Supporting Information).

Tetrahedron and icosahedron are two of the platonic solid shapes that are covered with the {111} family of planes. Further shape control can be achieved by introducing foreign ions during the nanocrystal growth process. For example, the addition of a small amount of silver ions prior to the synthetic method normally used to obtain gold tetrahedra yields instead uniform gold nanocubes. Typically, a solution of silver nitrate (0.5 mL, 0.0059 M; 1.1% of the gold precursor) in ethylene glycol solution was injected into the boiling ethylene glycol five minutes before the injection of the gold precursor and the PVP. The final colloidal solution was iridescently bluish-purple. TEM and SEM observation showed that gold nanocubes (>95%) of average size of 150 ± 14 nm were produced (Figure 3). Electron diffraction (Figure 3c inset) on a single particle showed that the cube is a single domain, with (100) surfaces.

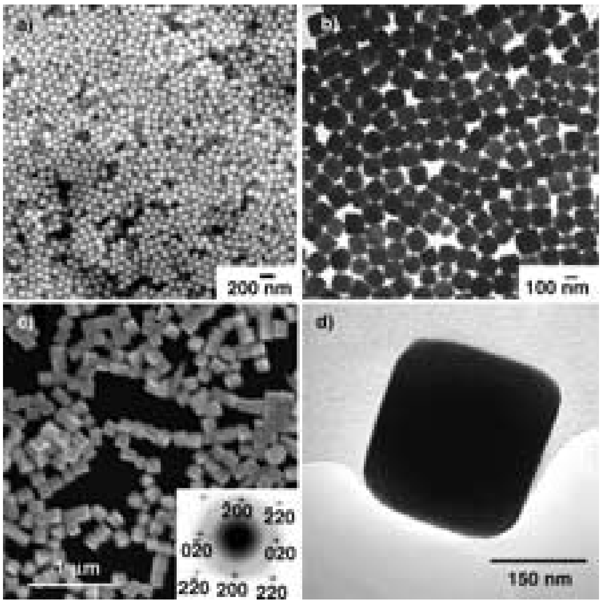

Figure 3. Gold nanocubes. (a–d). TEM and SEM images of gold nanocubes dispersed on a TEM grid and a silicon substrate. Inset in (c) shows the electron diffraction pattern recorded along the [100] axis of a gold nanocube shown in (d).

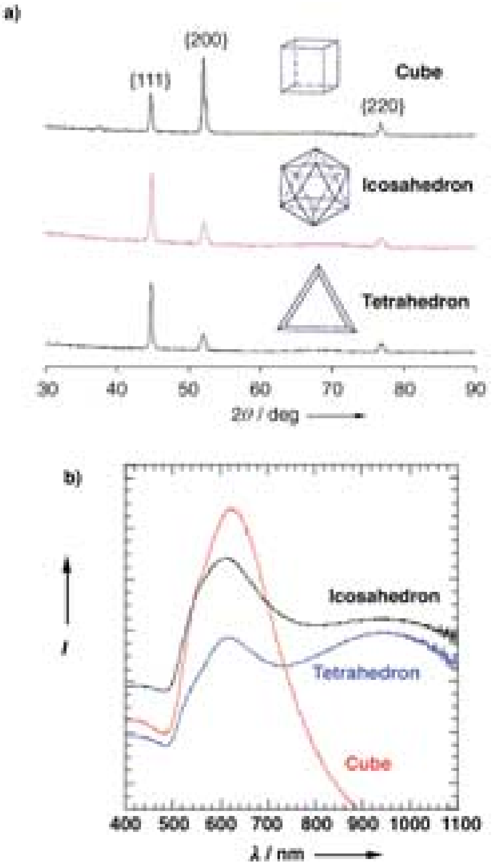

Figure 4. a) X-ray diffraction patterns and b) UV/VIS spectra for the three types of gold nanocrystals: tetrahedron, cube and icosahedron. I is intensity (arbitrary units).

While SEM and TEM often sample only a small portion of the products, X-ray diffraction (XRD) can be used to assess the overall quality and purity of these facetted nanoparticles. Three XRD patterns recorded on three different shapes are compiled in Figure 4a. All peaks of fcc gold. A comparison of the (111) and the (200) diffraction intensities reveals very interesting features that are intrinsically related to the shapes of the particles being examined. For the gold nanocube sample, the intensity ratio between the (200) and the (111) diffractions is 1.93, which is significantly larger than the conventional bulk intensity ratio (≈0.53). This is a clear indication that the faces of these nanocubes, primarily composed of {100} planes, tend to preferentially orient parallel to the supporting substrates, thus giving a significantly high (200) diffraction intensity. On the other hand, the intensity ratios between the (200) and the (111) diffractions are much smaller than the bulk values for the tetrahedron and icosahedron samples, being 0.25 and 0.31, respectively. This again indicates that for tetrahedron and icosahedron samples, the {111} family of planes is dominant. This set of XRD patterns unambiguously demonstrates our capability of synthesizing with a high degree of selectivity, gold nanoparticles of different platonic shapes.

The optical properties of metal nanoparticles are highly dependent on the size and shape of the particles. This has been extensively explored both theoretically and experimentally on several systems including gold nanorods, silver nanorods, prisms, and cubes.[3–21] Several groups have theoretically simulated the optical properties of metal nanoparticles with arbitrary shapes and found distinctive shape-dependent behavior.[25–28] UV/Vis spectra collected on the ethylene glycol (EG) solutions of these three different shapes are compiled in Figure 4b. It was found that gold nanoparticles of different shapes clearly displayed different surface plasmon resonance, 621 nm for the nanocubes, 626, 950 nm for the tetrahedra and 613, 950 nm for icosahedra. The spectral features of the nanocube and tetrahedron are fairly consistent with previous theoretical simulations.[25–28] The UV/

Vis spectrum of the icosahedral nanoparticles resembles that of spherical nanoparticles of similar size. The additional broad near-IR band is most likely to arise from co-existing triangular particles.

It is commonly accepted that the shape of an fcc nanocrystal is mainly determined by the ratio (R) of the growth rate along the [100] versus the [111] direction.[29,30] Tetrahedra and icosahedra bound by the most stable {111} planes will be formed when R is large (≈ 1.73), and perfect cubes bounded by the less stable {100} planes will result if R is reduced (≈ 0.58). The surface-regulating polymer (PVP) and the introduction of foreign ions are believed to play the key roles here. Selective interaction between PVP and the different surface planes of the gold nanocrystals could greatly enhance the growth rate along the [100] direction, reduce the growth rate along [111] direction, and ultimately result in particles with tetrahedral or icosahedral shapes. The mechanism for the selective growth of icosahedral nanoparticles versus that of tetrahedral nanoparticles is yet to be determined. The fact that lower overall gold precursor concentration (under otherwise identical synthetic conditions) results in the selective growth of icosahedra suggests that subtle differences in the gold embryonic seed formation and their subsequent growth might lead to this shape selection.

With another means of shape control, the introduction of foreign ions could greatly influence the relative growth rates along certain directions. We believe that the introduction of silver ions in the current process can significantly reduce the growth rate along the [100] direction and/or enhance the growth rate along the [111] direction, and ultimately cubic particles result. There have been previous studies in which the introduction of silver impurity during gold particle formation resulted in the control of the nanocrystal shape.[3,6,7,9] For example, silver ions were used to control the aspect ratio of the gold nanorods produced by electrochemistry and photochemistry.[3,6,7,9] It is also interesting to note that our shape-control scheme is vastly different from that reported by Xia and Sun for the silver system,[21] in which the interaction of the particles with PVP promotes the nanocube formation. The formation of nanocubes observed in our system may be due to the fact that the gold and silver systems interact differently with the polymer.

The successful preparation of gold platonic nanocrystals exemplifies the exquisite shape control that can be achieved through careful growth rate regulation along different crystallographic directions, and demonstrates a strategy that could be generally applicable to other material systems. These platonic nanocrystals have perfect symmetry for 2D and 3D packing and therefore should lead to interesting research on nanotectonics, the formation of high-order nano- or microstructures, and the rational tuning of optical, electrical, and catalytic properties.

Experimental Section

For a typical synthesis of tetrahedral particles, of ethylene glycol (5 mL) was stirred with a magnetic bar and heated to reflux in a silicone oil bath at 280 °C. Nitrogen was continuously flowed through the entire refluxing system. Solutions of PVP (0.375 M) in EG, and $HAuCl_4 \cdot 3H_2O$ (0.083 M) in EG were prepared. The PVP solution was injected to boiling EG (5 mL) by using a micropipette, then the $HAuCl_4$ solution was injected twice. This process was repeated 15 more times for every 30 seconds. The solution turned red within 8 minutes after the final injection, thus indicating formation of gold nanoparticles. The solution was aged for 45 minutes to ensure that the reaction was complete. The solution was collected, and the large aggregates and unconverted salts were removed by centrifugation. The solution was centrifuged at 1000 rpm for 5 minutes and the precipitate was removed. After repeating this three times, the solution was centrifuged at 3500 rpm for 30 minutes. The precipitate was collected and redispersed in EG (4 mL).

For the synthesis of icosahedral particles, the gold precursor concentration was reduced to 4/5 of that used in the synthesis of tetrahedral particles under otherwise similar conditions.

For the synthesis of nanocubes, a solution of $AgNO_3$ (0.0059 M) in EG (0.5 mL) was first added to the boiling EG 5 minutes before the injection of gold precursor and PVP.

Typically, for the icosahedral- and tetrahedral-particle syntheses, the solution turns from light pink–orange to strong rust red about 7 min after the final injection. When diluted, the solution becomes iridescently blue. For the cube synthesis, the reaction solution shows a similar color change around 4 min after the final injection.

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