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Dodecahedral Gold Nanocrystals: The Missing Platonic Shape

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Supporting Information

ABSTRACT: Platonic noble metal nanocrystals (NCs) have attracted considerate attention due to their symmetry, aesthetic beauty, and potential applications in catalysis, plasmonics, sensing, and spectroscopy. Although Platonic noble metal NCs with tetrahedral, cubic, octahedral, and icosahedral geometries have been chemically synthesized, the growth of Platonic dodecahedral noble metal NCs remains elusive. Here we propose a crystal structure of Platonic dodecahedral noble metal NCs and show that via a tailored seed-mediated synthetic approach, Platonic dodecahedral Au NCs can be grown from icosahedral multiply twinned Au seeds. By systematically tuning the ratio between {111} and {110} facets grown on the icosahedral Au seeds, NCs with icosahedral, icosidodecahedral, and dodecahedral shapes can be obtained. These shapes represent a family of Au NCs with icosahedral (I_h) symmetry.

Platonic solids have played an important role in the development of philosophy and science.[1] In geometry, a Platonic solid is a convex regular polyhedron with identical faces, edges, and angles.[2] Known since ancient Greece, there are only five forms of Platonic solids that can be constructed: tetrahedron, cube, octahedron, dodecahedron, and icosahedron (Figure 1a).

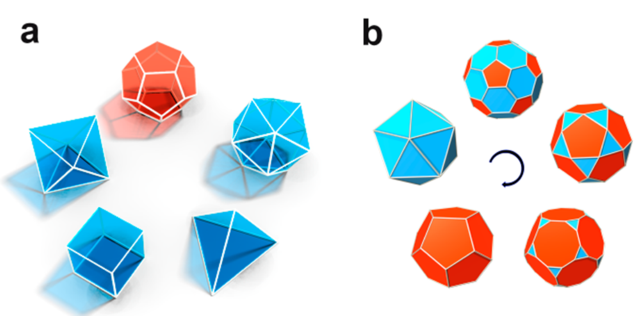

Figure 1. (a) Geometric models of Platonic solids: (clockwise from the top) dodecahedron, icosahedron, tetrahedron, cube, and octahedron. (b) Shape transition from icosahedron to dodecahedron via vertex truncation.

The symmetry and aesthetic beauty of the Platonic solids not only have attracted the interest of geometers for thousands of years, but also have been a fascinating topic in many aspects of chemistry, crystallography, and mineralogy. In the past decade, considerable progress has been made in the field of shape-selective growth of noble metal nanocrystals (NCs).[3−5] Among various shapes, Platonic noble metal NCs with tetrahedral, cubic, octahedral, and icosahedral geometries have been chemically synthesized.[6−13] However, the growth of Platonic dodecahedral noble metal NCs remains as an elusive task. Although Platonic dodecahedra of mixed metals have been observed in quasicrystals with icosahedral (I_h) space-group symmetry,[14] Platonic dodecahedra made of face-centered-cubic (fcc) noble metals have not been achieved.[15] This is presumably due to the fact that the crystal lattice of fcc noble metals does not have intrinsic 5-fold symmetry.

In the past few decades, a number of NCs with 5-fold symmetry, including decahedra, pentagonal nanorods, pentagonal bipyramids, and icosahedra,[16−21] have been synthesized for fcc noble metals. For these NCs, the 5-fold symmetry arises from cyclic pentatwinned structures.[22] For example, a decahedral NC is composed of five juxtaposed tetrahedral subunits; each is joined with two adjacent ones by twin boundaries, and the five subunits share one edge coinciding with the 5-fold axis of the NC.[23,24] Similarly, an icosahedron can be formed by the junction of 20 tetrahedra, which share six 5-fold axes and one common point at the center. The existence of 5-fold symmetry in cyclic pentatwinned structures of fcc noble metals implies that Platonic dodecahedra may be constructed as well.

Indeed, because icosahedron and dodecahedron are dual polyhedra and have the same set of symmetries, the two shapes may be converted to each other by truncation of their vertices; a dodecahedron can be formed by truncating the 12 vertices of an icosahedron.[2] As shown in Figure 1b, the truncation of each vertex of the icosahedron forms a regular pentagon, a high-energy {110} facet perpendicular to the 5-fold axis. As these regular pentagons grow larger and join together, a dodecahedron bounded exclusively by 12 {110} facets will be formed. Although the generation of pentagonal faces by truncation perpendicular to the 5-fold axis has been observed in pentatwinned noble metal NCs,[25−28] the seemingly straightforward conversion from icosahedra into dodecahedra during crystal growth in solution has never been realized for noble metals. Here we show that via a tailored seed-mediated growth approach, Platonic dodecahedral Au NCs can be obtained.

Platonic dodecahedral Au NCs were grown from icosahedral Au seeds that were synthesized through a modified polyol process.[19] Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the icosahedra Au seeds are shown in Figure S1 (Supporting Information). The 5-fold symmetry from the assembly of five triangle faces around one axis can be observed through SEM (Figure S1c,d, Supporting Information). Both selected area electron diffraction (SAED) and high-resolution TEM (HRTEM) studies confirmed their

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multiply twinned structure (Figure S1e,f, Supporting Information). For the growth of Platonic dodecahedra Au NCs, the icosahedral seeds were subsequently introduced into a *N,N*-dimethylformamide (DMF) solution containing polyvinylpyrrolidone (PVP) and $HAuCl_4$. DMF played dual roles as both the solvent and reducing reagent that favors the formation of {110} facets of Au.[26,29]

The morphology of the Platonic dodecahedral Au NCs was first investigated with SEM. As shown in Figure 2a, the

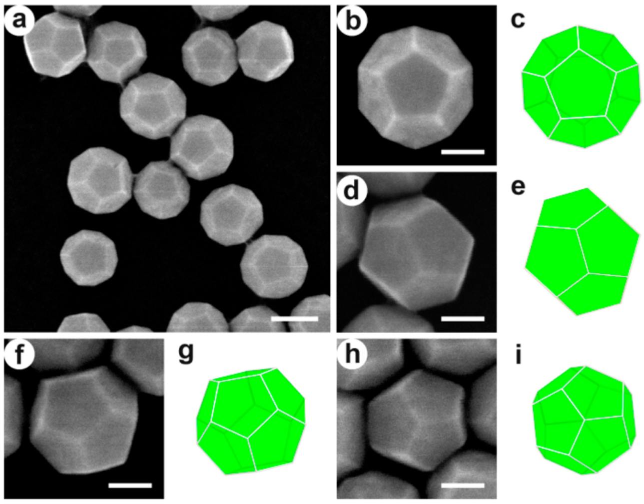

Figure 2. (a,b,d,f,h) SEM images and (c,e,g,i) corresponding geometric models of dodecahedral Au NCs. Dodecahedral Au NCs viewed from their 5-fold, 2-fold, and 3-fold axes were shown in (b,c), (d,e), and (h,i), respectively. Scale bars: (a) 100 nm; (b,d,f,h) 50 nm.

icosahedral seeds were all grown into dodecahedral NCs with regular pentagonal faces. To confirm to structure of the Platonic dodecahedral NCs, SEM images of the NCs with different orientations were obtained as shown in Figure 2b,d,f,h. Similar to an icosahedron, there are three types of axes in a Platonic dodecahedron: (i) six 5-fold axes, each passing through the centers of two opposite pentagonal faces; (ii) 15 2-fold axes, each passing through the midpoints of two opposite edges; and (iii) 10 3-fold axes, each passing through two opposite vertices. The geometric models of dodecahedral NCs viewed along the 5-fold, 2-fold, and 3-fold axes were shown in Figure 2c,e,i, respectively. All the SEM images match well with those schematic illustrations of the three-dimensional (3D) models of a Platonic dodecahedron.

The crystal structures of the dodecahedral NCs were further analyzed with TEM. When viewed along a 5-fold axis, the projection of a dodecahedron can be seen as a regular decagon (Figure 3a−c). The SAED of the dodecahedral NCs along the same 5-fold axis (i.e., along [011] zone axis) shows 10 $(\bar{1}00)$ spots around the center (Figure 3c, inset). This diffraction pattern is the same as that of an icosahedral Au NC viewed from one of its 5-fold axes, as investigated both theoretically and experimentally by Yang and Gomez et al.[30,31] This result suggests that the dodecahedral NCs share identical internal crystal structure with icosahedral NCs. To confirm the facets of the Platonic dodecahedral NCs, a NC oriented with two of its opposite facets perpendicular to the Cu grid is given in Figure 3d,e. This is the optimum orientation to image the lattice planes of the pentagonal faces. As shown in the HRTEM image (Figure 3f), the distance between adjacent lattice fringes is 0.144 nm,

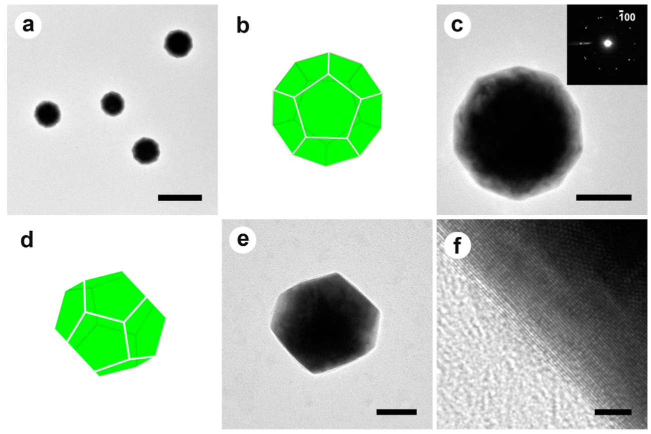

Figure 3. (a,c,e,f) TEM images and (b,d) corresponding geometric models of dodecahedral Au NCs. (b,c) Geometric model and TEM image of a dodecahedral Au NC viewed from [011] zone axis. The inset shows the corresponding SAED pattern. (d,e) Geometric model and TEM image of a dodecahedral Au NC in an orientation with two of its opposite pentagonal facets perpendiclar to the Cu grid. (f) HRTEM for the dodecahedral NC in (e) shows (220) lattice planes along the direction indicated with the arrow. Scale bars: (a) 200 nm, (c,e) 50 nm, (f) 2 nm.

consistent with the *d*-spacing of (220) planes of fcc Au.[29] The above results clearly demonstrate that the dodecahedral Au NCs have the same multiply twinned structures as icosahedral Au seeds but are exclusively enclosed by {110} facets.

To better understand the growth process of the Platonic dodecahedral Au NCs, intermediate nanocrystals produced at different reaction times were monitored by TEM and SEM. After 1 h, the icosahedral seeds grew into nanospheres with rough surfaces (Figure S2a−c, Supporting Information). After 2 h, the NCs started faceting and the overall dodecahedral shape was emerging (Figure S2d−f, Supporting Information). However, these NCs exhibited defects around their edges and vertices. As the reaction proceeded, these defects gradually disappeared, and Platonic dodecahedral NCs with smooth faces and well-defined edges and corners were finally obtained after 4 h.

As discussed above, the icosahedral and dodecahedral NCs share the same pentatwinned crystal structure. It is found that if the growth environment favors the formation of Au {110} facets (i.e., DMF as the solvent at 80 °C in the presence of PVP), Platonic dodecahedral NCs will be the final product. It is worth noting that dodecahedral Au NCs could also be obtained in the absence of PVP, but with relatively low quality (Figure S3, Supporting Information). The use of PVP can improve the dispersity and consequently the morphological uniformity of the NCs. If Au {111} facet is favored during the growth (when DEG is used as the solvent at 245 °C), icosahedral Au NCs will be formed as the final product (Figure S4, Supporting Information). It has been reported that high reaction temperature and water concentration favor the formation of {111} facets.[26] If the reaction was performed at 120 °C with additional 2 mL of water in DMF, icosidodecahedral Au NCs with an intermediate shape between icosahedron and dodecahedron were obtained (Figure 4). These NCs are enclosed by 12 pentagonal {110} facets and 20 triangular {111} facets. An icosidodecahedron can be formed from either an icosahedron via truncation perpendicular to its 5-fold axes or a dodecahedron via truncation perpendicular to its 3-fold axes, respectively. Icosidodecahedron is one of the 13 Archimedean solids and, more particularly, one of the only two

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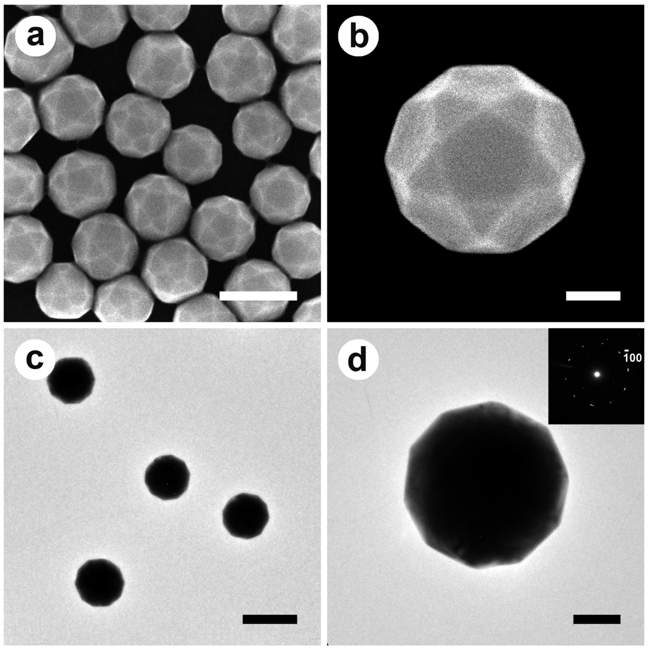

Figure 4. (a,b) SEM and (c,d) TEM images of icosidodecahedral Au NCs. The inset of (d) shows the corresponding SAED pattern. Scale bars: (a,c), 200 nm; (b,d) 50 nm.

quasiregular polyhedra.[2] By changing the reaction temperature to 140 or 110 °C, truncated dodecahedral and truncated icosahedral Au NCs can be obtained, respectively (Figure S5, Supporting Information). These results demonstrate that by tailoring the ratio between {111} and {110} facets, icosahedral, icosidodecahedral, and dodecahedral Au NCs can be synthesized precisely. These shapes represent a family of Au NCs with icosahedral (I_h) symmetry.

In summary, an unprecedented synthesis of Platonic dodecahedral Au NCs is realized. The dodecahedral Au NCs share the same pentatwinned crystal structure with icosahedral Au seeds but are exclusively enclosed by {110} facets. The growth of Platonic dodecahedral Au NCs not only addresses the unanswered question of whether dodecahedra can be built from fcc crystals without intrinsic 5-fold symmetry, but also leads to the discovery of a family of Au NCs with icosahedral (I_h) symmetry. This study demonstrates the diverse shapes of NCs with multiply twinned crystal structures and indicates the possibility of designing more unconventional shapes of noble metal NCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, SEM and TEM images of icosahedral Au seeds, shape evolutions of dodecahedral Au NCs, SEM images of dodecahedral nanocrystals synthesized in the absence of PVP, SEM images of large icosahedral Au NCs, SEM images of truncated dodecahedral and truncated icosahedral Au NCs, UV−vis spectra, and XRD patterns of the Au NCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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