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Seed-Mediated Synthesis of Gold Nanocrystals with Systematic Shape Evolution from Cubic to Trisoctahedral and Rhombic Dodecahedral Structures

Hsin-Lun Wu, Chun-Hong Kuo, and Michael H. Huang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

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We report a seed-mediated synthesis method for the preparation of gold nanocrystals with systematic shape evolution from truncated cubic to cubic, trisoctahedral, and rhombic dodecahedral structures in aqueous solution for the first time. Nanocrystals with transitional morphologies were also synthesized. The combination of using cetyltrimethylammonium chloride (CTAC) surfactant and a very small amount of NaBr to control the bromide concentration in the growth solution was found to be critical to the formation of nanocubes. Variation in the volume of ascorbic acid added to the growth solution enabled the fine control of nanocrystal morphology. Nanocubes and rhombic dodecahedra with controlled sizes of 30−75 nm were prepared by adjusting the volume of the seed solution added to the growth solution. They can self-assemble into ordered packing structures on substrates because of their uniform sizes. XRD, TEM, and UV−vis absorption characterization of the different products synthesized have been performed. By increasing the bromide concentration 5-fold that used to make the nanocubes, unusual right bipyramids of gold bounded by six {100} faces were produced. The high product purity and excellent size control of this facile synthetic approach should make these novel gold nanostructures be readily available for a wide range of studies.

Introduction

Morphological control in the synthesis of metal nanostructures is an important and exciting direction in the field of nanomaterials research. This is because optical, catalytic, and other physical and chemical properties of metal nanoparticles are related to their shapes and exposed surfaces.[1−5] Various symmetrical gold nanoparticle geometries such as cubic, octahedral, and icosahedral structures have been synthesized.[6−14] Among these structures, the formation of gold nanocubes is particularly interesting because they are bounded by entirely {100} faces and are more difficult to synthesize. Despite the recent success in the growth of gold nanocubes, further investigations on the various properties and applications of gold nanocubes using these reported procedures are rarely seen.[15−19] This may be related to possible reproducibility problems. Furthermore, the preparation of gold nanocubes with fine size control over the range of 30−80 nm has not been described. The ability to tune gold nanocube sizes over this range is desirable for their optical, surface functionalization, and assembly studies.[16] Besides nanocubes, rhombic dodecahedral and trisoctahedral gold nanocrystals represent two novel gold nanostructures that have been reported recently.[17−23] A rhombic dodecahedron is comprised of 12 rhombic faces, whereas a trisoctahedron is made up of eight trigonal pyramids. Current methods for the synthesis of rhombic dodecahedral gold nanocrystals require either the use of a very complicated procedure,[20] the employment of a solvothermal process at 90−95 °C for ∼15 h,[21] or heating a reaction mixture at 120 °C for 2 h.[22] Particle size control has not been achieved in these studies. Trisoctahedral gold nanocrystals have been synthesized by a simple aqueous solution approach at room temperature with sizes ranging from 100 to 200 nm.[23] The morphological connection among cubic, trisoctahedral, and rhombic dodecahedral gold nanostructures has not been revealed experimentally. Trisoctahedron has been associated with octahedron and rhombic dodecahedron in the unit stereographic triangle of polyhedral nanocrystals becuase they are all bounded by {*hhl*} facets.[24]

*To whom correspondence should be addressed. E-mail: hyhuang@mx.nthu.edu.tw.

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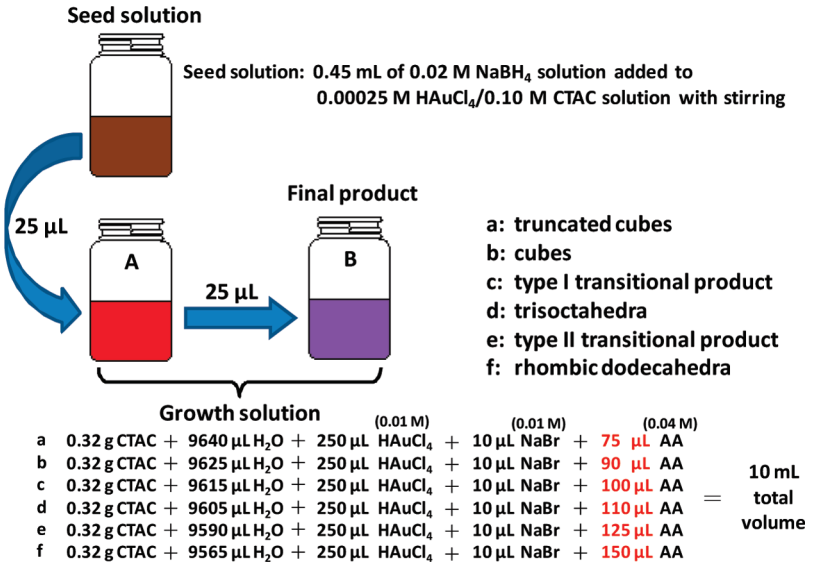
Scheme 1. Schematic Illustration of the Synthetic Procedure Used for the Preparation of Au Nanocrystals with Systematic Shape Evolution



In this study, we have developed a facile seed-mediated synthesis method for the preparation of monodisperse gold nanocrystals with systematic shape evolution from truncated cubic to cubic, trisoctahedral, and rhombic dodecahedral structures for the first time. Transitional products have also been obtained to show how one particle morphology evolves into another. All these unique gold nanostructures can be synthesized by simply varying the amount of ascorbic acid added into the growth solution. Thus, we have demonstrated that trisoctahedral gold nanocrystals are actually intermediate products linking cubes and rhombic dodecahedra. Because of their uniform dimensions, these nanocubes and rhombic dodecahedra can readily form self-assembled structures on substrates. Structural and optical characterization of these nanocrystals was also performed. Furthermore, average particle sizes of the nanocubes and rhombic dodecahedra can be tuned over the range of 30−75 nm by varying the amount of the seed solution added to the growth solution. Finally, we found that this synthetic procedure can also form right bipyramids of gold. With this synthetic simplicity and size tunability, these structurally well-defined gold nanocrystals can readily be used in a wide variety of studies for further investigation of their properties and potential applications.

Experimental Section

Chemicals. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%, Aldrich), cetyltrimethylammonium chloride (CTAC, 95%, TCI), sodium borohydride ($NaBH_4$, 98%, Aldrich), ascorbic acid (AA, 99.7%, Riedel-de-Haën), and sodium bromide (NaBr, UCW) were used without further purification. Ultrapure distilled and deionized water was used for all solution preparations.

Synthesis of Gold Seeds. A volume of 10 mL aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ and 0.10 M CTAC was prepared. Concurrently, 10 mL of 0.02 M ice-cold $NaBH_4$ solution was made. To the $HAuCl_4$ solution was added 0.45 mL of the $NaBH_4$ solution with stirring. The resulting solution turned brown immediately, indicating the formation of gold particles. The seed solution was aged for 1 h at 30 °C to decompose excess borohydride. The seed particles have sizes of 3−5 nm.

Synthesis of Cubic to Rhombic Dodecahedral Gold Nanocrystals. Two vials were labeled A and B. A growth solution was prepared in each of the two vials. First, 0.32 g of CTAC surfactant was added. The concentration of CTAC in the final solution is equal to 0.10 M. Depending on the morphology of gold nanocrystals to be synthesized, slightly different volumes of deionized water (9.640 to 9.565 mL) were added to each vial. The vials were then kept in a water bath set at 30 °C. To both vials were added 250 µL of 0.01 M $HAuCl_4$ solution and 10 µL of 0.01 M NaBr. Finally, 75−150 µL of 0.04 M ascorbic acid was introduced. For example, for the synthesis of gold nanocubes, 90 µL of ascorbic acid was used, whereas 150 µL of ascorbic acid was added for the growth of rhombic dodecahedra. Total solution volume in each vial is 10 mL. The solution color turned colorless after the addition of ascorbic acid, indicating the reduction of Au^{3+} to Au^{+} species. Next, 25 µL of the seed solution was added to the solution in vial A with shaking until the solution color turned light pink (~5 s). Then 25 µL of the solution in vial A was transferred to vial B with thorough mixing for ~10 s. The solution in vial B was left undisturbed for 15 min for particle growth and centrifuged at 3000 rpm for 10 min (Hermle Z323 centrifuge).

Synthesis of Smaller Cubic and Rhombic Dodecahedral Gold Nanocrystals. The gold nanocubes and rhombic dodecahedra synthesized using the procedure described above have average sizes of 72 and 74 nm, respectively. To make smaller gold nanocubes and rhombic dodecahedra, the same preparation procedure was used. Here one just needs to vary the volume of the seed solution used. For the preparation of gold nanocubes with average sizes of 40 and 53 nm (or rhombic dodecahedra with average sizes of 45 and 55 nm), 65 and 45 µL of the seed solution were respectively added to the growth solution in vial A, and the final products were centrifuged at 6500 and 6000 rpm for 10 min, respectively. Nanocubes with an average size of 32 nm (or rhombic dodecahedra with an average size of 37 nm) can also be synthesized by adding 100 µL of the seed solution. The product was centrifuged at 8000 rpm for 10 min.

Instrumentation. Scanning electron microscopy (SEM) images of the samples were obtained using a JEOL JSM-7000F electron microscope. Transmission electron microscopy (TEM) characterization was performed on JEOL JEM-2010 and JEM-2100 electron microscopes with an operating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation. UV−vis absorption spectra were taken using a JASCO V-570 spectrophotometer.

Results and Discussion

A schematic illustration of the synthetic procedure used for the preparation of Au nanocrystals with systematic shape evolution is

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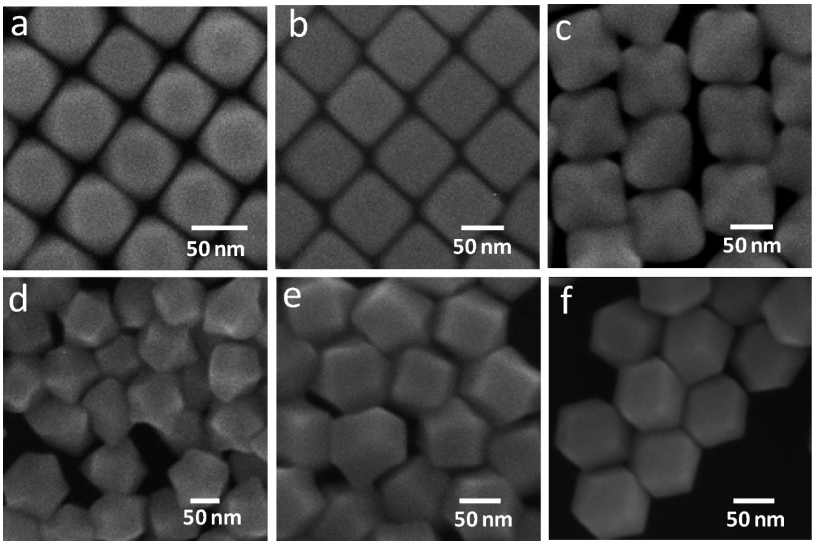

Figure 1. (a−f) SEM images of the gold nanocrystals synthesized with shape evolution from truncated cubic to rhombic dodecahedral structures by increasing the amount of ascorbic acid added. The nanocrystals are (a) truncated cubes, (b) cubes, (c) type I transitional product, (d) trisoctahedra, (e) type II transitional product, and (f) rhombic dodecahedra.

shown in Scheme 1. In this study, CTAC surfactant was used instead of a more typical CTAB surfactant because we found in prior experiments that a sufficiently high surfactant concentration and a very low bromide concentration were necessary to obtain gold nanocubes in high yield. By introducing bromide ions through the addition of NaBr, bromide ion concentration in the growth solution can be precisely controlled without changing the surfactant concentration. This bromide concentration adjustment through the use of CTAC surfactant has been employed to make gold nanostars.[25] Furthermore, by reducing the amount of the seed solution added to the growth solution, only two vials of the growth solution were needed to produce nanocrystals with sufficiently large sizes.[25] Figure 1 shows SEM images of the six gold nanocrystal samples prepared in this study. By simply increasing the volume of 0.04 M ascorbic acid added from 75 to 90, 100, 110,125, and 150 μL, corner-truncated cubes synthesized were found to evolve into cubes, trisoctahedra, and finally rhombic dodecahedra. Two intermediate products were also obtained, and they are called type I and type II transitional particles. These transitional nanocrystals are important because they provide the experimental evidence for identifying the morphological transformation from cubes to rhombic dodecahedra via the formation of trisoctahedra for the first time. Each corner-truncated gold nanocube has six {100} faces and eight {111} faces. A rhombic dodecahedral nanocrystal has 12 {110} rhombic faces. A trisoctahedral gold nanocrystal has been determined to expose mainly high-index {221} surfaces.[23] The nanoparticles in each sample show good size uniformity. These nanocrystals have been found to increase in average size from 57 nm for the truncated cubes to 72, 84, and 83 nm respectively for cubes, type I transitional particles, and trisoctahedra (see Figure S1 in the Supporting Information). Then the average nanocrystal sizes decrease slightly to 80 nm for type II transitional particles and 74 nm for rhombic dodecahedra. Figure 2 gives SEM images of these nanocrystals viewed from two different orientations and the corresponding drawings of the particles to illustrate this morphological evolution process. The transformation from a cube to a trisoctahedron can be conceived by fully pulling out the eight corners of a cube and sharpening the resulting faces. The thin lines between two adjacent trigonal pyramids are the {110} surfaces, and there are 12 such lines on a trisoctahedron. By converting the depressed regions between adjacent trigonal pyramids into flat faces, a rhombic dodecahedron with 12 {110} faces is formed. A ratio R, which is the growth rate along the ⟨100⟩ direction relative to that of the ⟨111⟩ direction, has been used to describe the geometric shape evolution from a cube to an octahedron via a cuboctahedron.[26,27] Here we consider a new series of R values, where $R_{\langle 100\rangle/\langle 110\rangle}$ is the growth rate along the ⟨100⟩ direction relative to that of the ⟨110⟩ direction, is more appropriate to describe the morphological evolution from cubes to rhombic dodecahedra. $R_{\langle 100\rangle/\langle 110\rangle}$ has a value of 0.71 for cubes and 1.41 for rhombic dodecahedra (see Scheme S1 in the Supporting Information). The concentration of ascorbic acid in the final solution is 3.6×10^{-4} M for the synthesis of nanocubes and 6.0×10^{-4} M for the formation of rhombic dodecahedra. Thus, by adjusting the concentration of ascorbic acid in the growth solution to control the rate of gold atom addition on the crystal surface, the relative growth rates along these lattice directions can be tuned leading to the formation of these various nanostructures. The role of bromide ions in this series of particle shape evolution also cannot be ignored; replacing bromide ions with other ions would not produce the same shape evolution.

Because of the uniform dimensions of the truncated cubes, cubes, and rhombic dodecahedra, they can readily self-assemble into ordered multilayer packing structures on substrates (see Figures S2 and S3 in the Supporting Information). The truncated cubes were contacted on all faces with adjacent truncated cubes forming the first layer on a substrate. The second layer of truncated cubes may or may not deposit directly over the truncated cubes beneath; misalignment is typical. The cubes showed more precise positional alignment over multiple layers. Figure 1f shows several rhombic dodecahedra with mostly their rhombic faces contacting the substrate. However, this packing arrangement is not favorable for their long-range multilayer assembly. Instead, the rhombic dodecahedra were found to pack tightly with their 3-fold axes, or the vertices contacting three rhombus faces, perpendicular to the substrate surface. This packing arrangement enables the formation of multiple layer

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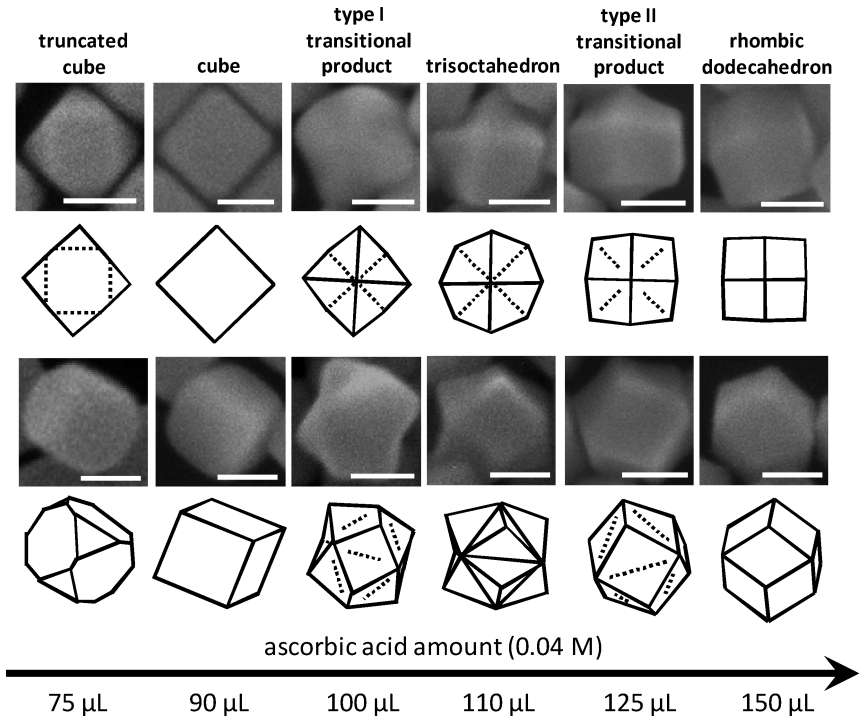

Figure 2. SEM images and the corresponding drawings showing the morphological evolution of the gold nanocrystals synthesized by varying the amount of ascorbic acid added to the reaction solution. Two different particle orientations are shown for each sample. All scale bars represent 50 nm.

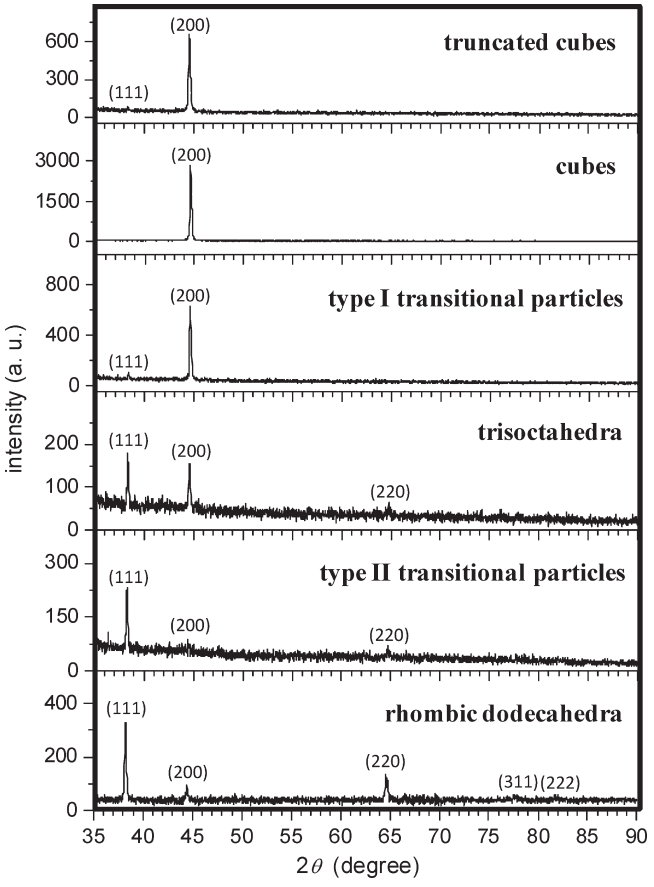

Figure 3. XRD patterns of the various gold nanocrystals synthesized from truncated cubic to rhombic dodecahedral structures.

structures with stability. Trisoctahedra cannot form ordered packing structures.

Figure 3 presents XRD patterns of the various gold nanocrystals synthesized from truncated cubic to rhombic dodecahedral structures. The truncated cubes and cubes showed essentially the (200) reflection peak in their XRD patterns as a result of their preferential orientation of deposition on substrates with their {100} faces. Type I transitional particles were observed to form a monolayer on substrates. They probably deposited with their (200) lattice planes parallel to the substrate surface that these particles exhibited the same XRD pattern as the cubes. Trisoctahedra showed comparable (111) and (200) reflection peak intensities possibly due to their random orientation of deposition on substrates and disordered stacking. Rhombic dodecahedra showed a relatively strong (220) reflection peak as expected. Yet the (111) peak has a particularly strong intensity. This is likely related to the orientation of these rhombic dodecahedra in self-assembled structures with the (111) lattice planes parallel to the substrate surface (The 3-fold axis of a rhombic dodecahedron is perpendicular to the (111) lattice planes.) Type II transitional particles also formed a monolayer on a substrate. Their XRD pattern is dominated by the (111) reflection peak.

TEM images and the corresponding selected-area electron diffraction (SAED) patterns of the six gold nanocrystal morphologies are displayed in Figure 4. The truncated cubes and cubes showed a square diffraction pattern when viewed along the [100] direction. The trisoctahedron, rhombic dodecahedron, and transitional particles were viewed along the [110] direction or along the [0$\bar{2}$2] zone axis. These four nanocrystals gave similar diffraction patterns. When using a more intense electron beam to take the diffraction patterns of rhombic dodecahedra, the diffraction spots can turn into crossed lines (see the Supporting Information, Figure S4). A close examination of the crossed lines shows that each cross is comprised of four spots around the central spot. The crossed lines are at different angles to each other depending on the orientations of the rhombic dodecahedra to the electron beam. The appearance of this unusual diffraction feature is likely caused

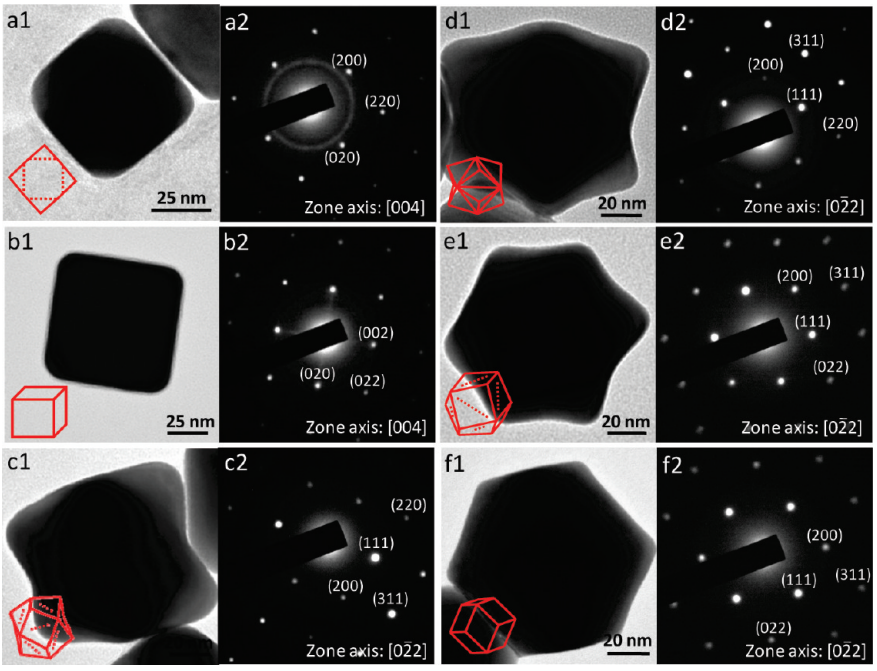

Figure 4. TEM images of (a1) a truncated cube, (b1) a cube, (c1) a type I transitional particle, (d1) a trisoctahedron, (e1) a type II transitional particle, and (f1) a rhombic dodecahedron. Drawings of the nanocrystals are shown. The corresponding SAED patterns and their zone axes are also provided.

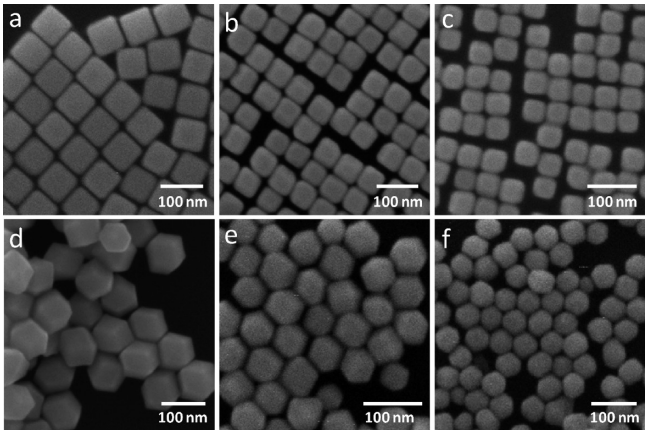

Figure 5. (a−c) SEM images of gold nanocubes synthesized with average sizes of 72, 53, and 40 nm. (d−f) SEM images of rhombic dodecahedral gold nanocrystals with average sizes of 74, 55, and 45 nm.

by double diffraction of the electron beam relating to the special morphology of the rhombic dodecahedra. This special effect can be used to characterize the structure of rhombic dodecahedra with greater certainty.

UV−vis absorption spectra of these nanocrystals were also taken (see the Supporting Information, Figure S5). All the samples showed only a single surface plasmon resonance (SPR) absorption band. The band maxima for the truncated cubes, cubes, type I transitional particles, trisoctahedra, type II transitional particles, and rhombic dodecahedra are at 553, 575, 592, 590, 578, and 567 nm, respectively. The absorption band is more red-shifted for the trisoctahedra due to their larger sizes and special morphology with protruded trigonal pyramids.

Particle size control of gold nanocubes and rhombic dodecahedra can be achieved by simply adjusting the volume of the seed solution introduced into the growth solution. With more seed solution added, smaller particles were produced. Figure 5 shows SEM images of the nanocubes synthesized with average sizes of 72, 53, and 40 nm and rhombic dodecahedra with average sizes of 74, 55, and 45 nm by using respectively 25, 45, and 65 μL of the seed solution for particle growth (see Supporting Information, Figure S6, for their size distribution histograms). The particles are highly uniform in size and shape, demonstrating that this is a simple and effective way to tune the particle dimensions. Even smaller gold nanocubes and rhombic dodecahedra with respective average sizes of 32 and 37 nm can be synthesized by adding 100 μL of the seed solution to the growth solution (see the Supporting Information, Figure S7). They should represent some of the smallest gold nanocubes and rhombic dodecahedra ever prepared. The sharp faces of the particles also become less distinct with decreasing sizes. UV−vis absorption spectra of these nanocrystals are given in Figure 6. The SPR absorption band blueshifts from 575 to 532 nm as nanocube size decreases from 72 to 32 nm. A similar spectral blue shift was observed for rhombic dodecahedra from 567 to 534 nm as particle size reduces from 74 to 37 nm. The SPR absorption bands also become narrower for the smaller nanocrystals, indicating their monodisperse size distribution.

In the process of developing the seed-mediated procedure for the synthesis of gold nanocubes, we discovered that gold right bipyramids can be produced by adjusting the bromide concentration in the growth solution. Right bipyramids of silver and palladium have been made recently by using a polyol synthesis method or heating an aqueous reaction solution in the presence of poly(vinylpyrrolidone).[28−31] A photoinduced synthetic method for the generation of silver right bipyramids has also been reported recently.[32] To the best of our knowledge, right bipyramids of gold

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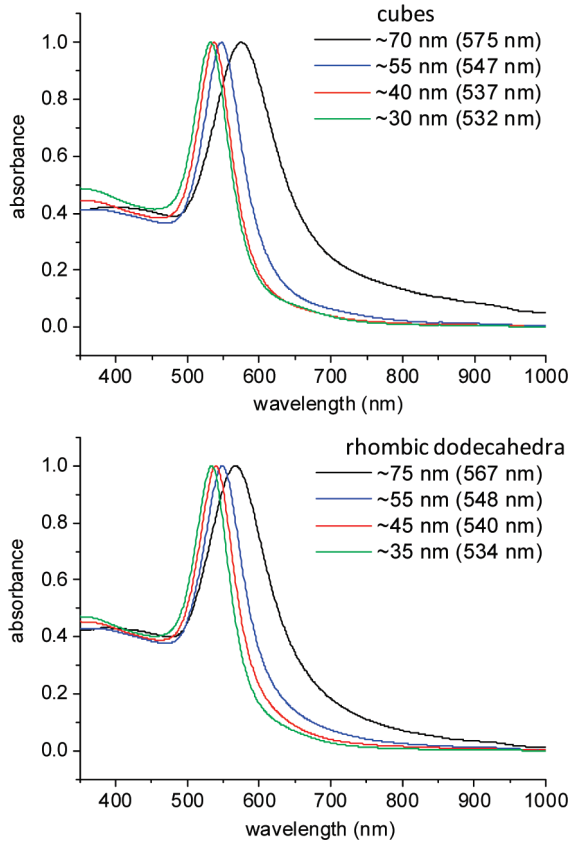

Figure 6. UV-vis absorption spectra of gold nanocubes and rhombic dodecahedra with different sizes. Their absorption band maxima are also given.

have not been reported before. A right bipyramid is formed by making a cut along a (111) lattice plane of a cube and joining two of the resulting trigonal pyramids together. Thus, every triangular face of the particle contains a 90° angle. Right bipyramids have been found to grow from single twinned seeds.[28] Bromide concentration in the growth solution was 1.0×10^{-5} M for the synthesis of gold nanocubes. Many right bipyramids were produced upon increasing bromide concentration to 5.0×10^{-5} M (see Figure 7b). Some nanocubes and short rods were also formed. Further increase of bromide concentration to 2.0×10^{-4} M lowered the yield of right bipyramids. The right bipyramids synthesized have sizes of 70−90 nm. The SAED pattern taken along the [400] zone axis of a right bipyramid (the direction perpendicular to one of its faces) gave a square diffraction pattern, verifying that the faces of a right bipyramid are bounded by the {100} facets (see the Supporting Information, Figure S8). Further tuning of the reaction conditions may improve the yield of right bipyramids of gold.

Although this study demonstrates that rhombic dodecahedral gold nanocrystals are derived from nanocubes, we also consider the possibility of structural evolution from octahedral nanocrystals to rhombic dodecahedra. Edge truncation of an octahedron to expose the {110} facets can gradually transform into a rhombic dodecahedron. A ratio $R_{\langle 111\rangle/\langle 110\rangle}$, defined as the growth rate along the ⟨111⟩ direction to that of the ⟨110⟩ direction, can be used to describe this series of shape transformation (see the Supporting Information, Scheme S2). Cu_2O microcrystals with morphological evolution from octahedra to edge-truncated octahedra and rhombic dodecahedra have been reported recently.[33] If this

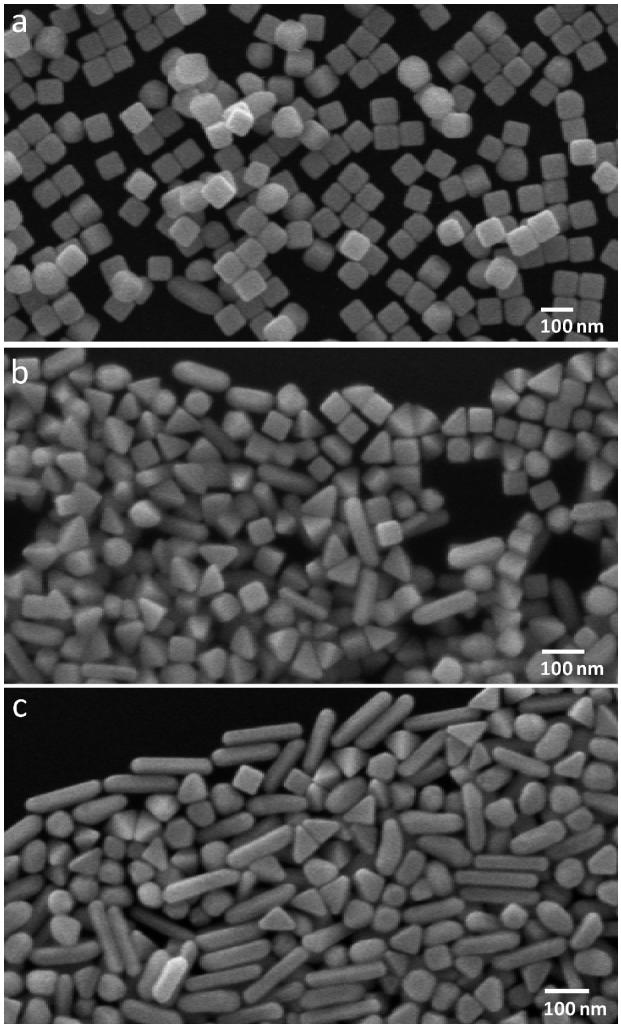

Figure 7. SEM images of the gold nanocrystal products synthesized by varying the concentration of NaBr added to the growth solution: (a) $[Br^-] = 1.0 \times 10^{-5}$ M, (b) $[Br^-] = 5.0 \times 10^{-5}$ M, and (c) $[Br^-] = 2.0 \times 10^{-4}$ M. Panel B shows that a large number of right bipyramids were synthesized.

holds true for metallic nanoparticles, gold and silver nanocrystals with octahedral to rhombic dodecahedral structures may be synthesized. Interestingly, a recent report has shown that this morphological evolution pathway is correct for gold crystals, although the particles produced are micrometer-sized and not so uniform in size and shape.[34] Scheme S3 in the Supporting Information illustrates the morphological relationships among cubes, rhombic dodecahedra, and octahedra via intermediate structures.

Conclusions

We have developed a seed-mediated growth approach for the synthesis of gold nanocrystals with systematic shape evolution from truncated cubic to cubic, trisoctahedral, and rhombic dodecahedral structures for the first time. Transitional products have also been prepared. This study reveals that trisoctahedral gold nanocrystals are the transitional particles between gold nanocubes and rhombic dodecahedra. The combination of using CTAC as the surfactant and a very low bromide concentration in the solution was found to be critical to the formation of nanocubes.

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Adjustment of the amount of ascorbic acid added enabled the morphological evolution. The nanocrystals are monodisperse in size. Nanocubes and rhombic dodecahedra also showed ordered multilayer packing structures on substrates. XRD, TEM, and UV−vis absorption spectroscopy characterization of the nanocrystals have been performed. The sizes of the nanocubes and rhombic dodecahedra can be tuned from 30 to 75 nm by simply varying the amount of the seed solution introduced into the growth solution. Absorption band blue shift was observed as particle size decreases. Interestingly, unusual right bipyramids of gold can be generated just by increasing the bromide concentation in the growth solution for the synthesis of nanocubes. This facile aqueous solution method for the synthesis of gold nanocubes, trisoctahedra, and rhombic dodecahedra with tunable sizes should readily allow their use in various studies for the examination of their catalytic properties, assembled structures, and other physical properties.

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Supporting Information Available: Size distribution histograms, SEM images of the self-assembled structures, TEM images and SAED patterns of rhombic dodecahedra, UV−vis absorption spectra of the gold nanocrystals, drawings of various geometric shapes with morphological evolution, and TEM and SEM images of right bipyramids of gold. This material is available free of charge via the Internet at http://pubs.acs.org.