Synthesis and Isolation of {110}-Faceted Gold Bipyramids and Rhombic Dodecahedra

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Introduction

- Control over architectural parameters of a noble metal nanoparticle allows the surface plasmon resonance (SPR) of that particle to be easily tuned to a desired wavelength

- Among the noble metals, Au nanoparticles are especially appealing due to a combination of properties, including intense SPR

- For Au, which is a face-centered cubic (FCC) metal, the surface energies of the low-index crystallographic facets usually increase in the order $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$

- As {110} facets have the highest surface energy among the low-index facets, they generally provide the most favorable surface for Au atom deposition and this results in the disappearance of {110} facets as a particle grows and makes {110}-faceted nanoparticles difficult to synthesize

In this paper…

- Synthesis and isolation of two high-quality {110}-faceted Au nanoparticle morphologies: rhombic dodecahedra and obtuse triangular bipyramids

Experimental Section

- The rhombic dodecahedra and bipyramids were synthesized using a seed-mediated, Ag-assisted growth procedure

- Au seed particles (7 nm) were prepared by the rapid reduction of $HAuCl_4$ by $NaBH_4$ in the presence of cetyltrimethylammonium chloride (CTAC)

- Growth solution was prepared by sequentially adding 0.5 mL of 10 mM $HAuCl_4$, 0.01 mL of 10 mM $AgNO_3$, 0.2 mL of 1.0 M HCl, and 0.1 mL of 100 mM ascorbic acid to a 10 mL aqueous solution of 0.04 M CTAC and 0.6 mL of 1.0 M NaCl

- The reaction was initiated by the addition of 0.1 μL of the Au seed particles to the growth solution and mixed gently

- The reaction solution was allowed to sit undisturbed overnight

Characterization and discussion

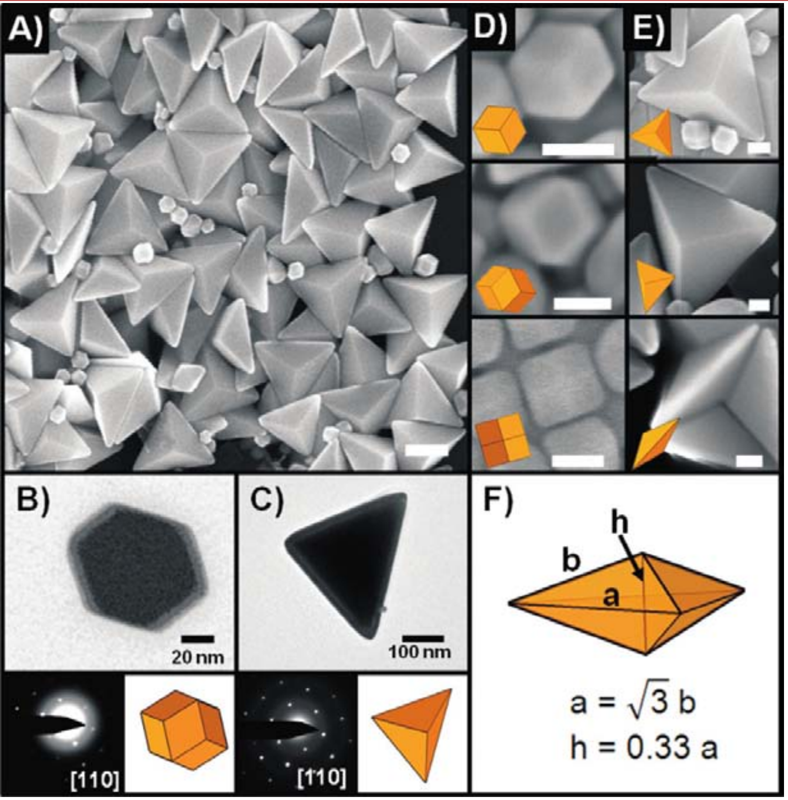

Figure 1. (A) Low-magnification SEM image of the reaction product containing both rhombic dodecahedra and bipyramids (scale bar: 200 nm). TEM image, diffraction pattern, and model of (B) a rhombic dodecahedron and (C) a bipyramid. High-magnification SEM images and models of (D) the rhombic dodecahedra and (E) the bipyramids in various orientations (scale bars: 50 nm). (F) Geometric model of a bipyramid.

- SEM images indicate that the reaction yields two different particle morphologies: smaller rhombic dodecahedra (RD) and larger triangular bipyramids (BP) (Figure 1A). Both particles have well-defined surfaces with sharp edges and corners

- There is a large size discrepancy between the smaller RDs (edge length of 31 ± 5 nm) and the larger BPs (edge length of 270 ± 26 nm), the size dispersity between particles of the same morphology is relatively low

- Typical diffraction patterns obtained from individual RD (Figure 1B) and BPs (Figure 1C) with the electron beam perpendicular to the substrate are characteristic of the [110] zone axis of FCC Au, indicating that both particles lie with a {110} facet flat against the substrate

- High magnification SEM images of the RD show that all of the 12 rhombic faces are identical (Figure 1D), as are the six triangular facets of the BPs (Figure 1E), leading to the conclusion that both particles are bound exclusively by {110} facets

Characterization and discussion

- ❑ The shape of the RD is consistent with single-crystal particles bound by 12 identical {110} facets
- ❑ The shape of the BPs is consistent with two triangular pyramids joined by a (111) twin plane
- ❑ High resolution TEM confirms the presence of a twin defect in the BPs
- ❑ Due to the large size difference between the two products, they can be easily separated by filtration

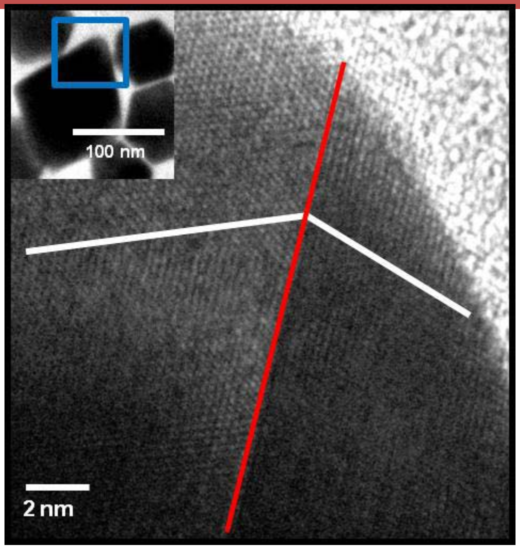

Figure 2. HR-TEM image of a single bipyramid (inset) containing a twin plane (red line)

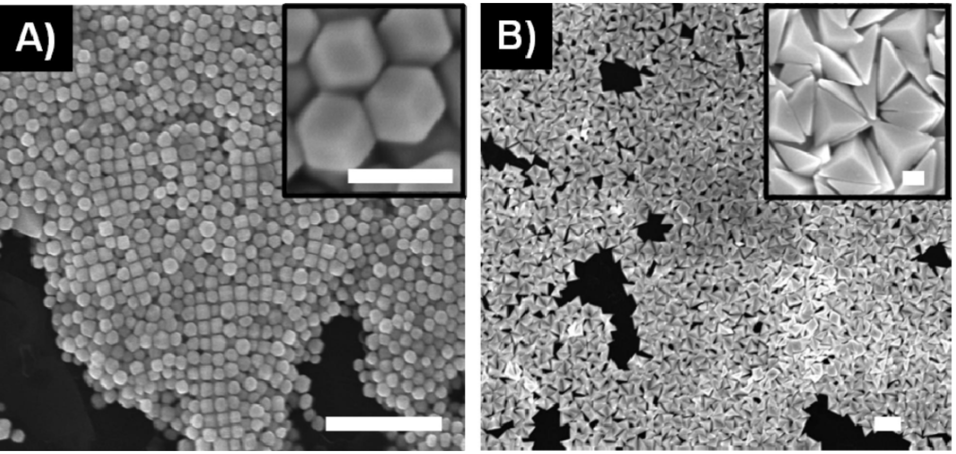

Figure 3. Low-magnification SEM image of separated rhombic dodecahedra (A) and bipyramids (B). Scale bars: 500 nm (low-magnification images), 100 nm (inset).

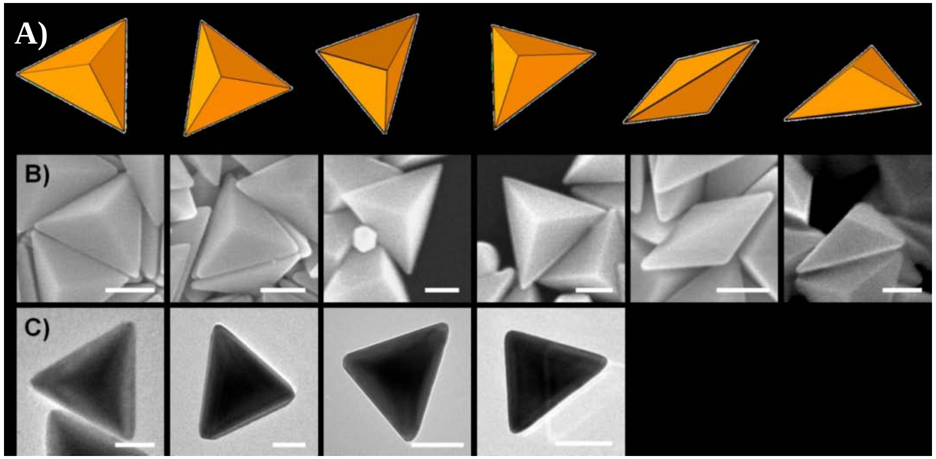

Figure 4. (A) Model, (B) high-magnification SEM, and (C) TEM of individual bipyramids in various orientations. Scale bars: 100 nm.

Characterization and discussion

➢The effectiveness of the separation by filtration was examined by UV-visible spectroscopy

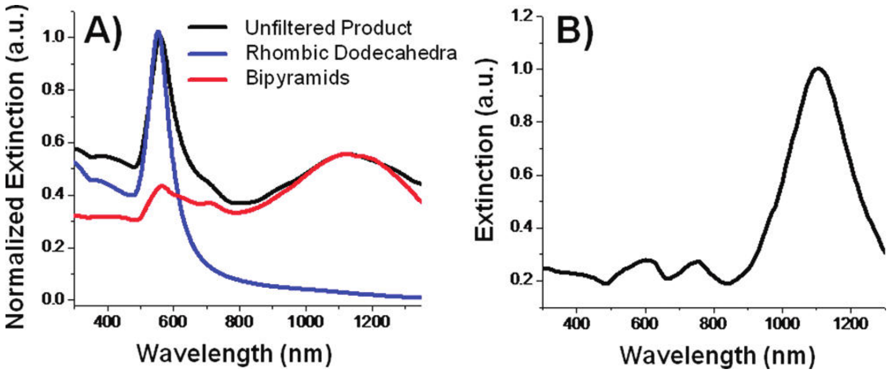

Figure 5. (A) UVvis spectrum of separated RD (blue) and BPs (red)compared to the mixed solution (black). (B) DDA orientationally averaged calculated extinction spectrum for a BP with an edge length of 270 nm.

➢The UVvis spectrum of the product solution before separation(Fig. 5A, black trace) shows two major peaks: one resonance in the visible region (~560 nm) (blue trace) and one in the near-infrared region (NIR) (~1130nm) (red trace)

➢After separation, the solution of pure RD displays only a single resonance in the visible region, while the major extinction peak from the solution of pure BPs is in the NIR

➢Theoretically calculated optical properties of the BPs using the discrete dipole approximation (DDA) method confirm the presence of three major SPRs: a dipole mode at~1110 nm, a higher order quadrupolemode at ~750 nm, and an octopole mode at ~600 nm (Figure 5B).

Characterization and discussion

- RD and BP morphologies arise from the deposition of Au onto single-crystal and planar-twinned seeds, respectively

- CTAC-protected seed particles used to initiate the reaction are, indeed, a mixture of single crystalline and planar twinned structures

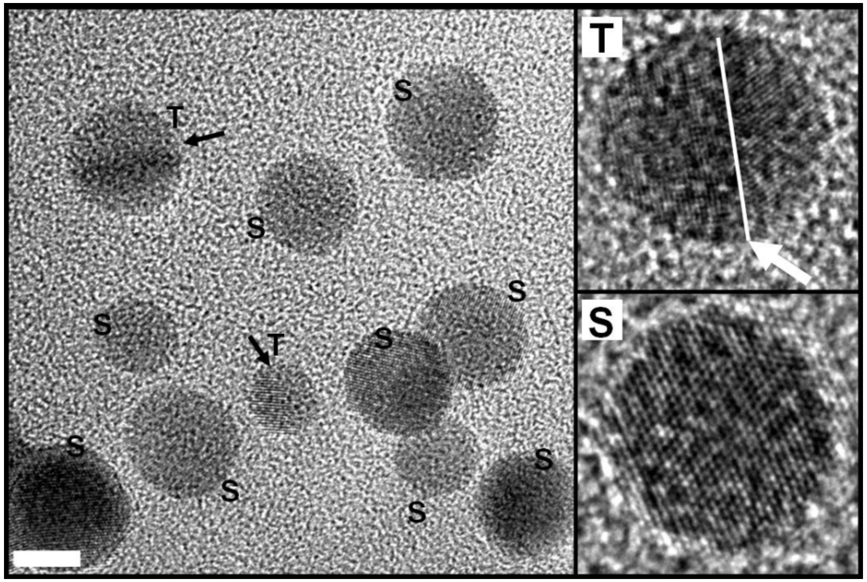

Figure 6. Left: HR-TEM of CTAC-stabilized seed particles. Both twinned and single-crystal seeds are observed, indicated by a T or an S, respectively. Arrows indicate twin boundaries. Scale bar: 5 nm. Right: Examples of twinned (top) and single-crystalline (bottom) seed particles.

- Growth from these seed particles was monitored by UV-vis spectroscopy

Characterization and discussion

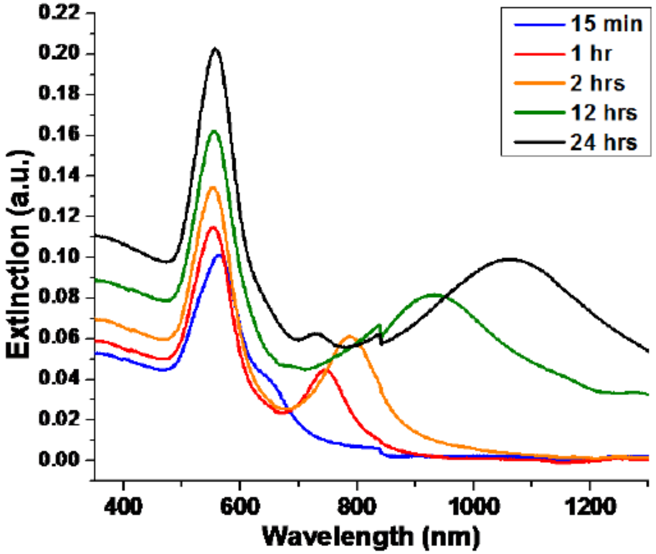

Figure 7. Time-dependent UV-vis spectra monitoring the growth of RD and BPs

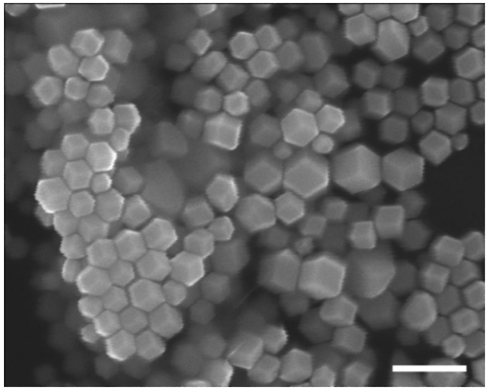

Figure 8. SEM of rhombic dodecahedra synthesized with single-crystal seeds.

Scale bar: 200 nm.

- ❑ As early as 15 min into the reaction, a small absorbance peak and shoulder were detected, which are attributed to the RD and the BPs, respectively

- ❑ As the reaction progresses, the RD peak grows in intensity over time and red-shifts only slightly, while the peak for the BPs has a much more pronounced shift, moving into the NIR

- ❑ The concurrent evolution of both RD and BP from the growth solution suggests that the twin structure of the seed particles dictates the twin structure of the final product.

- ❑ When single-crystal seeds are exclusively used to nucleate the reaction, only RD are observed in the reaction product (Figure 8). This suggests that it is the planar-twinned seeds that are responsible for the generation of BPs

Characterization and discussion

- Size of the product can be controlled by adjusting the amount of seed particles added, with more seed particles providing more nucleation sites and thus leading to smaller nanoparticles

- As the size of the products decreases from the addition of more seeds, the size difference between the BPs and the RD also decreases

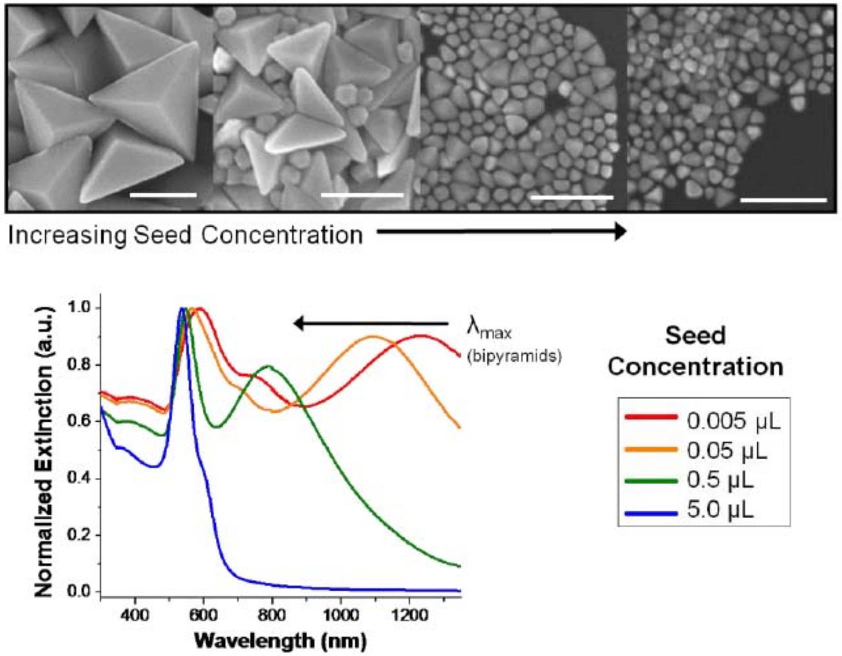

Figure 9. Bipyramids and rhombic dodecahedra grown from the addition of (left to right): 0.005 µL, 0.05 µL, 0.5 µL, and 5.0 µL of seed solution. Scale bars: 200 nm. UV-Vis spectra of RD/BP solutions synthesized from increasing amounts of seed particles. Increasing seed concentration results in smaller product particles

Characterization and discussion

- The use of a Cl-containing surfactant (CTAC) appears to be essential for the generation of {110}-faced RD and BPs.
- When the analogous Br-containing surfactant (CTAB) is used, particles enclosed entirely by {110} facets are not observed, but rather, a variety of nonuniform particles with ill-defined facets are formed

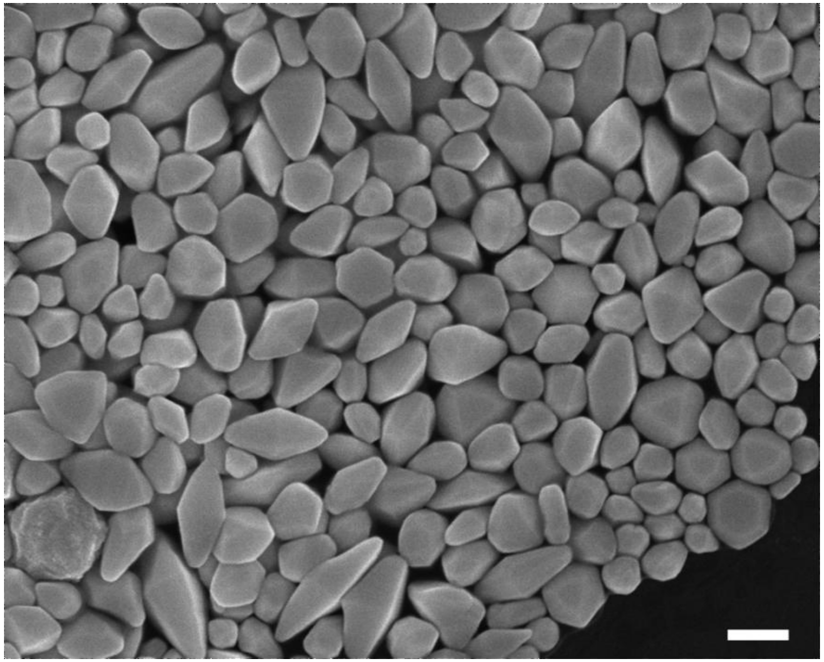

Figure 10. SEM of particles synthesized in CTAB with 10 μM Ag^+. Scale bar: 200 nm.

Conclusion

- High-purity samples of {110}-faceted rhombic dodecahedra and their novel planar-twinned counterpart, {110}-faceted bipyramids, have been prepared by an Ag-assisted seed-mediated synthesis

- The RD have possible utility for catalysis as well as for SERS (already known), and the {110}-faceted bipyramids may be useful for many potential applications due to their NIR resonance

Thank You