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Right Bipyramids of Silver: A New Shape Derived from Single Twinned Seeds

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Received January 11, 2006; Revised Manuscript Received February 13, 2006

ABSTRACT

Silver nanoparticles with a single (111) twin were selectively nucleated and grown for the first time to produce right bipyramids 75–150 nm in edge length. Key to the production of single twinned seeds was the addition of NaBr to a polyol synthesis in which AgNO₃ is reduced by ethylene glycol in the presence of poly(vinyl pyrrolidone). Examination of nanoparticles at different stages of the reaction with electron microscopy revealed that the spherical, single twinned seeds grew to become right bipyramids through enlargement of their (100) facets. The UV–vis–NIR spectrum exhibited by right bipyramids is distinct from that of any other silver nanostructure, and their sharp corners make these new nanoparticles especially promising for enhancement of Raman scattering.

Plasmon excitation within a silver nanostructure not only gives it color in far-field imaging, but also greatly magnifies the electric field near its surface.^{1,2} This intense near-field has recently enabled nanoscale waveguiding and localization of light for nanolithography and optical devices, and has long been used to enhance the Raman scattering from adsorbed molecules.^{3–7} Theoretical calculations predict that a 50-nm silver sphere provides a maximum electric field enhancement factor of $\sim 10^2$ in terms of $|E|^2$, but this can be improved 100-fold by a nanostructure with sharp corners, such as a tetrahedron.⁸ Here we report the first synthesis of silver right bipyramids, nanoparticles with sharp corners similar to those of a tetrahedron. This remarkable shape, which is essentially two right tetrahedra symmetrically placed base-to-base, was proposed over 20 years ago by Harris in studying sulfur-induced faceting of platinum nanoparticles in the gas phase,⁹ but there have been no further reports, and it has never before been selectively produced in high yield.

A variety of shape-controlled syntheses have been developed to produce silver triangular nanoprisms, circular nanoplates, nanorods, and nanowires in aqueous solutions containing surfactants.^{10–12} We and other groups have focused on the polyol synthesis, in which ethylene glycol (EG) serves as both the solvent and reducing agent, to produce uniform

silver nanowires, silver nanocubes with controllable corner truncation, as well as a number of different shapes for gold, platinum, palladium, and rhodium.^{13–19} We and others have observed a small proportion of right bipyramids in our nanocube syntheses ($\sim 10\%$ relative to cubes) but did not understand why they formed or how to increase their relative yields.^{20,21} Although addition of NaCl or HCl substantially enhanced the yield of silver nanocubes, variance of synthetic conditions did not improve the yield of right bipyramids with these additives.²² Herein we demonstrate that by simply replacing NaCl with NaBr, we could improve the yield of right bipyramids relative to cubes to over 80%.

To synthesize right bipyramids, 3 mL of two EG solutions, one containing 94 mM AgNO₃, the other containing 144 mM poly(vinyl pyrrolidone) (PVP) and 0.11 mM NaBr, were added dropwise via a two-channel syringe pump into 5 mL of EG heated in an oil bath at 160 °C. A 30 μ L drop of 10 mM NaBr was also added to the preheated EG before the Ag precursor because this was found to prevent formation of small spherical nanoparticles that otherwise contaminated the final product (Figure S1). The only difference between this synthesis and those that produced silver nanocubes or nanowires was the incorporation of Br[–] rather than Cl[–] or Fe³⁺. The reaction solution turned yellow 30 s after addition of AgNO₃ and PVP, indicating the formation of silver nanoparticles. The yellow color faded in intensity after 10 min because of oxidative etching¹⁵ and maintained a light

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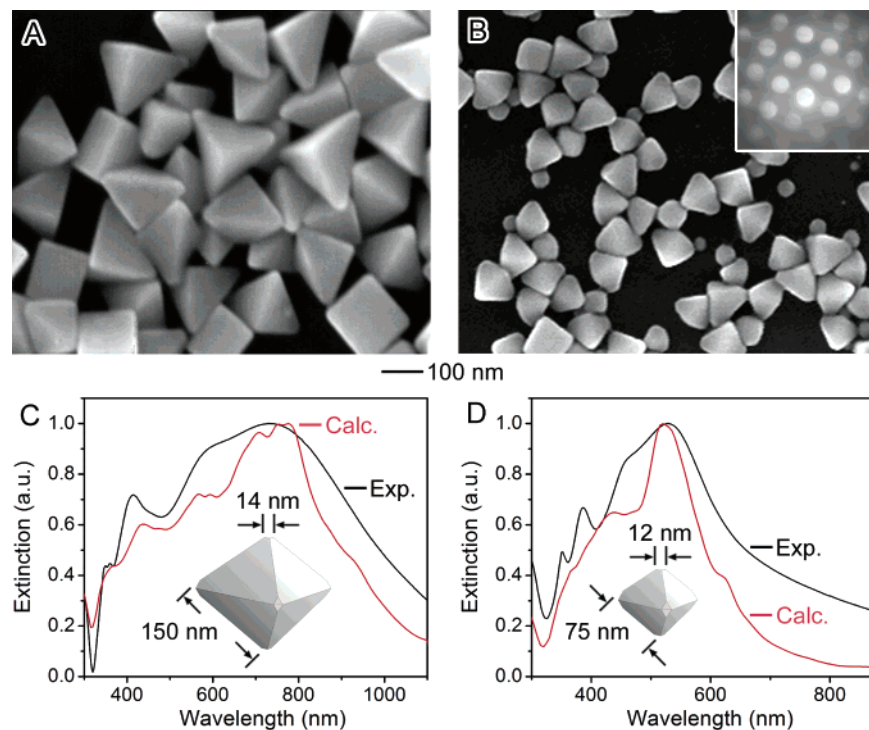


Figure 1. SEM images of bipyramids approximately (A) 150 nm and (B) 75 nm in edge length. The inset in B shows the electron diffraction pattern obtained from a single bipyramid, indicating that it is bounded by (100) facets. (C, D) Comparisons of the UV-vis-NIR spectra taken from the bipyramids in A and B with DDA calculations performed on bipyramids of the same size but with corners truncated by (111) facets 14 and 12 nm in edge length, respectively.

yellow color for approximately 2 h before turning light brown and gray as the nanoparticles increased in size.

Figure 1A shows a scanning electron microscopy (SEM) image of the right bipyramids obtained after 5 h. Their average edge length was 150 nm, and their corners had an average radius of curvature $R = 11$ nm. If the reaction was stopped after 3 h, then right bipyramids 75 nm in edge length were obtained (Figure 1B). Although the corners of the 75-nm right bipyramids appear less sharp, they were actually more so, with $R = 8$ nm. The inset shows a typical electron diffraction pattern obtained from a single right bipyramid, with the beam perpendicular to the substrate. The spot array is characteristic of diffraction from the (100) zone axis and indicates that the bipyramid lies with a (100) facet flush with the substrate. Because every facet on the bipyramid is identical, we can conclude that the bipyramid is bounded by (100) facets, similar to a single-crystal nanocube. The X-ray diffraction (XRD) pattern (Figure S2) obtained from the right bipyramids gives further evidence that they preferentially orient with the (100) plane parallel to the substrate. The (111), (200), and (220) diffraction peaks in Figure 2S are characteristic of face-centered-cubic silver, but the ratio of the (200) to (111) peak is three times that of a powder sample (1.2 versus 0.4, see JCPDS file no. 04-0783). The relatively small contribution to diffraction from the (111) plane may come from the randomly oriented right bipyramids in multilayers (see Figure 1A).

The unique shape of the right bipyramid gives it an ultraviolet-visible-near-infrared (UV-vis-NIR) extinction

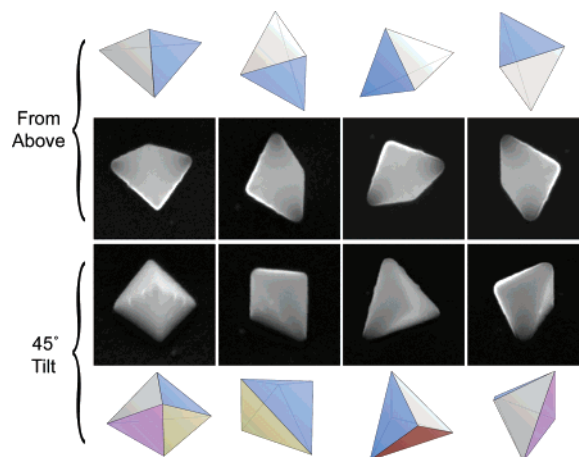


Figure 2. Comparison of SEM images of a single right bipyramid with CAD models. The same bipyramid is viewed under SEM from above and after a 45° tilt away from the viewer at four different clockwise rotations. The right bipyramid sits with one of its six triangular faces flush with the substrate. Each face on the model is given a color so the effect of rotations and tilts can be followed easily.

spectrum distinct from that of any silver nanostructure reported previously. To determine if the experimental spectrum of the bipyramids agrees with the theoretically predicted one, we solved Maxwell's equations with the discrete dipole approximation (DDA) for bipyramids 150 and 75 nm in edge length, with each composed of 2600 dipoles.²³ The calculation used dielectric constant data taken from a handbook.²⁴ To approximate the rounded corners of the

synthesized bipyramids and improve the agreement between calculated and experimental spectra, the corners of the 150- and 75-nm model bipyramids were truncated with (111) facets 14 and 12 nm in edge length, respectively. The fair match between the spectra of calculated and synthesized bipyramids (Figure 1C and 1D) confirms that high yields of right bipyramids were produced by this reaction.

Despite its slight corner truncation, the extinction peak of a 75-nm right bipyramid is red-shifted 50 nm from that of nanocubes of a similar size (Figure S3). This red shift is even more remarkable considering that the longest axis of the nanocube (between opposite corners) is 1.1 times the length of the longest edge of the right bipyramid. The only explanation for this red shift is that the three corners at the junction between the two tetrahedrons of the bipyramid are significantly sharper than the corners of the cube. Such sharp corners cause greater separation of induced charge and thus reduce the restoring force for electron oscillation, causing the resonance peak to red-shift.^{25,26} The separation of induced surface charge into these sharp corners should generate greater localized field enhancement. In addition, because one of these sharp corners will always point up and away from the substrate no matter how the bipyramid lies, it will be free from possible dampening of its localized field through electromagnetic coupling to induced charges in the substrate.²⁷ The top corners of a silver nanocube (those not in contact with a substrate) have already been shown to have a figure of merit ~ 1.8 times that of triangular nanoprisms for single nanoparticle sensing applications;²⁸ the bipyramid may further improve upon these results.

To visualize its shape and orientation more clearly, we obtained SEM images of a single right bipyramid from above and with a 45° tilt at four different rotations. Figure 2 compares this set of images with models (drawn with a CAD program) of a right bipyramid at identical orientations. It is very difficult to imagine the nanostructure as a right bipyramid from the top view alone, but from 45° it becomes clear that one-half of the bipyramid (i.e., one of the two right tetrahedra) points away from and is not in contact with the substrate. The other right tetrahedron that makes up the bipyramid points toward and has one of its sides in contact with the substrate. The reason the bottom tetrahedron cannot be seen from above is that the angles between the faces of the bipyramid are all 90°. Because one facet of the bottom tetrahedron is parallel to the substrate, the other two facets are perpendicular to the substrate and cannot be viewed from above.

The mirror symmetry of the bipyramid, as well as the fact that it is covered by (100) facets, suggests that a (111) twin plane bisects its two tetrahedra halves. In a transmission electron microscopy (TEM) image of a 40-nm bipyramid (Figure 3A) taken from the reaction at 2.5 h, there is an internal difference in contrast between its two halves, suggesting that it is not a single crystal. The bisecting twin plane is apparent after tilting the same bipyramid by 45° (Figure 3B), which aligns the electron beam along the $\langle 110 \rangle$ axis, and parallel with the twin plane. The presence of the twin plane is significant because it differentiates the bipyra-

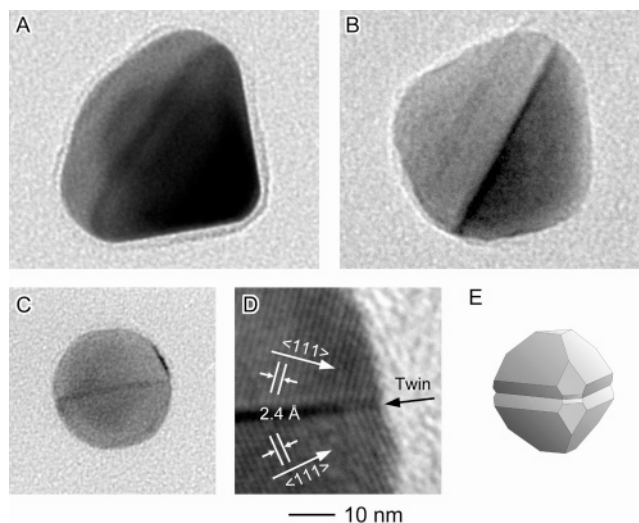


Figure 3. (A) TEM of a right bipyramid ~ 40 nm in edge length taken from the reaction at $t = 2.5$ h. An internal difference in contrast suggests that a twin plane bisects its two halves. (B) The twin plane that bisects the bipyramid is clearly visible after tilting the same particle by 45°. (C) At $t = 1.5$ h, single twinned seeds approximately 25 nm in diameter were observed. (D) HRTEM of a twinned seed shows the lattice fringes reflecting across the (111) twin plane. (E) Model of the seed in C showing (111) truncation of corners, reentrant (111) surfaces at the twin boundary and reentrant (100) surfaces at the twin boundary corners. The 10-nm scale bar applies to all TEM images except D.

mid from the nanocube, which is a single crystal. The difference between the shapes of the bipyramid and cube is a direct result of the presence of this twin plane because it restricts the way in which the nanoparticle can grow.

Just as nanocubes grow from smaller single-crystal seeds, we suspected that the bipyramid grew from a seed with a single twin plane. Indeed, nanoparticle seeds with a single twin could readily be found in TEM images of a sample taken from the reaction at $t = 1.5$ h, although the fact that their twin plane is only visible at certain orientations makes it difficult to determine their yield.²⁹ An example of the twinned seed is shown in Figure 3C. The reflection of the lattice fringes across the twin plane is evident in a high-resolution TEM image of the twinned seed (Figure 3D). The fringe spacing indicates that the seed is aligned along the $\langle 110 \rangle$, confirming that the twin is on the (111) plane. To visualize the shape of the seed, we truncated a CAD model of the bipyramid until its outline matched that of the seed (Figure S4). Figure 3E shows an image of the approximate seed structure rendered in three dimensions. The differences between the seed and the bipyramid are the (111) truncation of its corners, the presence of reentrant (111) surfaces along the twin boundary, and the presence of small reentrant (100) facets at the twin boundary corners. All of these changes lead to a reduction of surface area that gives the seed a more spherelike shape. By comparing the images of the seed with those of larger bipyramids, we can see how the shape evolved as the nanoparticle grew. The selective growth of (100) surfaces on the twinned seed to make a right bipyramid is consistent with our nanocube and nanowire syntheses in

which we hypothesized that selective capping of the (100) facet by PVP led to growth of nanostructures bounded by (100) facets.

High yields of the single twinned seeds necessary for growth of right bipyramids have only been produced in the presence of Br^- , so Br^- must play an important role in their formation. The reason many single twinned seeds selectively formed may be due to the fact that Br^- is less corrosive than Cl^- . We have noted previously that nanoparticles with twin defects are preferentially etched in the presence of Cl^- and air, leading to high yields of single-crystal seeds.¹⁵ Without the addition of Cl^- or Br^- , the Ag precursor is reduced quickly to form multiply twinned particles of 100–300 nm in size in 60 min.¹⁵ Thus, Br^- enables sufficient etching to eliminate the seeds with multiple twin defects but not so much as to eliminate those seeds with only one twin defect.

Placed in the context of pentagonal twinned nanowires and single-crystal nanocubes, the single twinned bipyramid further illuminates the importance of controlling the crystallinity of seeds for selective growth of a silver nanostructure.^{30,31} Additional new shapes could be obtained from pentagonally twinned, single twinned, and single-crystal seeds if the {111} rather than {100} facet was enlarged during the growth stage, and our future work will be directed toward application of capping agents for {111} facet growth. Development of a library of silver nanostructures with distinct surface plasmon resonance peaks could be particularly useful for biological labeling and multiple analyte, localized surface plasmon resonance sensing.^{32,33} Study of the optical properties of single right bipyramids will help elucidate the role of corner sharpness in SERS enhancement.

Acknowledgment. This work was supported in part by the NSF (DMR-0451788) and a fellowship from the David and Lucile Packard Foundation. Y.X. is a Camille Dreyfus Teacher Scholar (2002). B.W. thanks the Center for Nanotechnology at the UW for an IGERT fellowship funded by NSF. Z.-Y.L. was supported by the National Key Basic Research Special Foundation of China (no. 2004CB719804). Y.Y. was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract no. DE-AC02-05CH11231. This work used the Nanotech User Facility (NTUF), a member of the National Nanotechnology Infrastructure Network (NNIN) funded by the NSF. We thank the Molecular Foundry at the Lawrence Berkeley National Laboratory for the HRTEM analysis.

Supporting Information Available: Detailed descriptions of materials and methods as well as supporting figures

referenced in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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NL060069Q