

Supporting information for

Synthesis of Shield-like Singly Twinned High-Index Au Nanoparticles

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Experimental Details

Materials. Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, Alfa Aesar, Au 49.87%), sodium borohydride (NaBH_4 , Fluka, 98%), cetyltrimethylammonium chloride (CTAC, Alfa Aesar, 95+%), cetyltrimethylammonium bromide (CTAB, Sigma Aldrich, $\geq 98\%$) and L-ascorbic acid (Merk, 99%) were all used as received. Ultrapure Millipore water (18.2 M Ω) was used as the universal solvent throughout. All glassware was cleaned with Aqua Regia and rinsed with ethanol and ultrapure water.

Preparation of gold seeds. Au seeds were synthesized by the sodium borohydride reduction of HAuCl_4 in the presence of CTAB capping agent. For a typical synthesis, 87.5 μL of 20 mM HAuCl_4 solution was added to 7 mL of 75 mM CTAB solution. The solution was heated at 30 °C with stirring to dissolve the CTAB. Then 0.42 mL of an ice-cold NaBH_4 solution (10 mM) was injected quickly under vigorous stirring. The solution was stirred gently at 30 °C to decompose excess NaBH_4 and was used within 2-5 hours after preparation.

Synthesis of shield-like gold nanoparticles (NPs). The growth solution was prepared by adding 0.25 mL 20 mM HAuCl_4 solution to 9.8 mL 20 mM CTAC solution in a clean test tube at 28 °C. 0.5 mL 100 mM NaCl was added to the growth solution (4 mM in the combined mixture). 1.93 mL 38.8 mM ascorbic acid solution was added to make a final ascorbic acid concentration of 6 mM. On the other hand the seed solution was diluted 100 folds with ultrapure water and 50 μL of the diluted seed solution was added to the growth solution. The solution was thoroughly mixed after each addition and left undisturbed overnight. The resultant Au NPs solutions were centrifuged at 8000 rpm for 3 min. The precipitate was redispersed in deionized water and centrifuged for two more time (6000 rpm, 3 min) to remove the excess reactants.

Materials characterizations. TEM and HRTEM images were obtained with a JEOL JEM-2010 TEM operating at an accelerating voltage of 200 kV. SEM images were acquired on a JEOL JSM-6700F field emission SEM operating at 25 kV. EM samples were prepared by dispensing a drop of the

washed product on a copper grid followed by drying in air at room temperature. A Shimadzu UV-2450 spectrometer was used to record the UV-vis spectra of the NPs at room temperature.

Electrochemical measurements. A glassy electrode (diameter 5 mm) was carefully polished and washed before each experiment. A washed Au NP suspension was dispensed onto the glassy electrode to a fixed Au mass loading of 40 μg and dried. The deposited NP layer was then coated with a 10 μL Nafion solution prepared from diluting 50 μL commercial 5 wt% Nafion solution with 5 mL ethanol and 5 mL DI water. Electrochemical measurements were carried out in a conventional 3-electrode glass cell under the control of an Autolab PGSTAT12 potentiostat/galvanostat. A Pt gauze and a Ag|AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode respectively. The supporting electrolyte was 0.1 M HClO₄ aqueous solution. The solution was deaerated with argon before each experiment. Electrochemical measurements were based on cyclic voltammetry carried out at a scan rate of 20 mV/s.

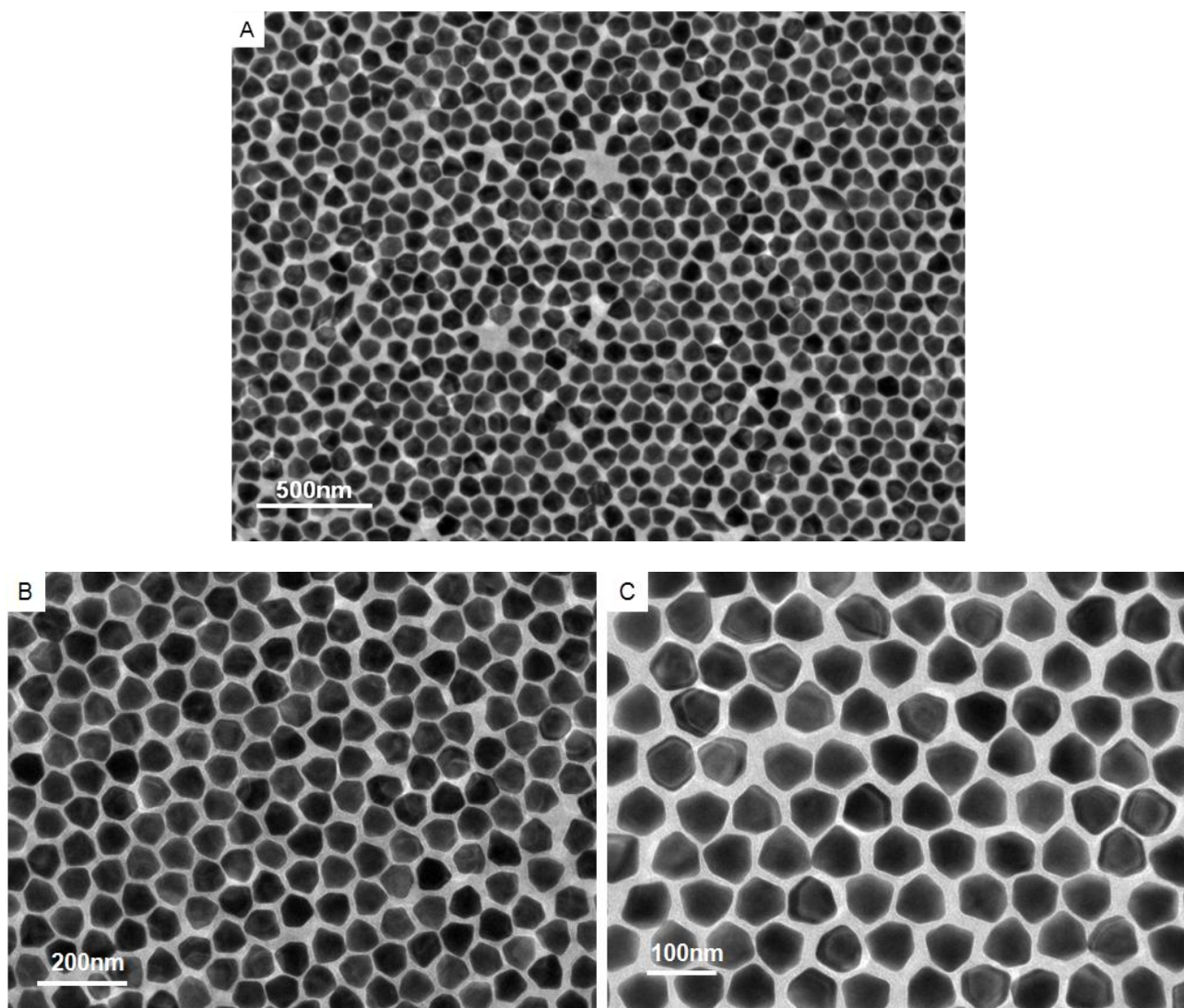


Figure S1. TEM images of shield-like Au NPs at different magnifications.

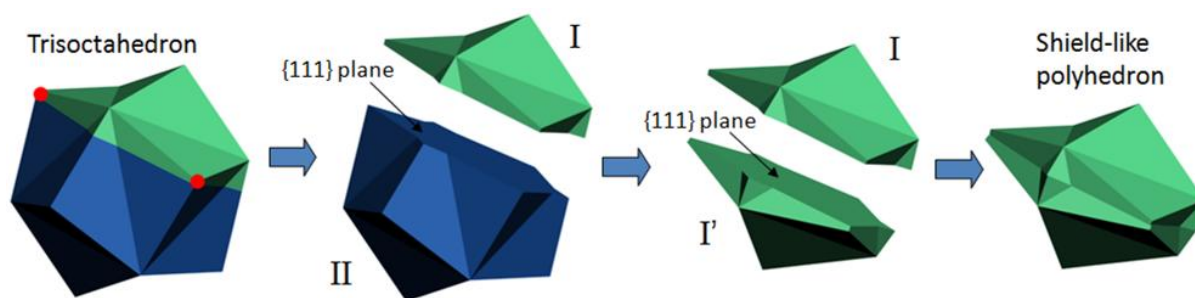


Figure S2. Schematic illustration showing the construction of the shield-like polyhedron viewed from the $\{111\}$ twin plane. The shield-like polyhedron can be understood as a trisoctahedron which is cut along a $\{111\}$ plane that connects the vertices of three corner-sharing triangular pyramids (only two of the three vertices, which are shown as red dots, can be seen in this view) and joining the smaller part of the cut-polyhedron (I) and its mirror image (I') along the $\{111\}$ cutting plane.

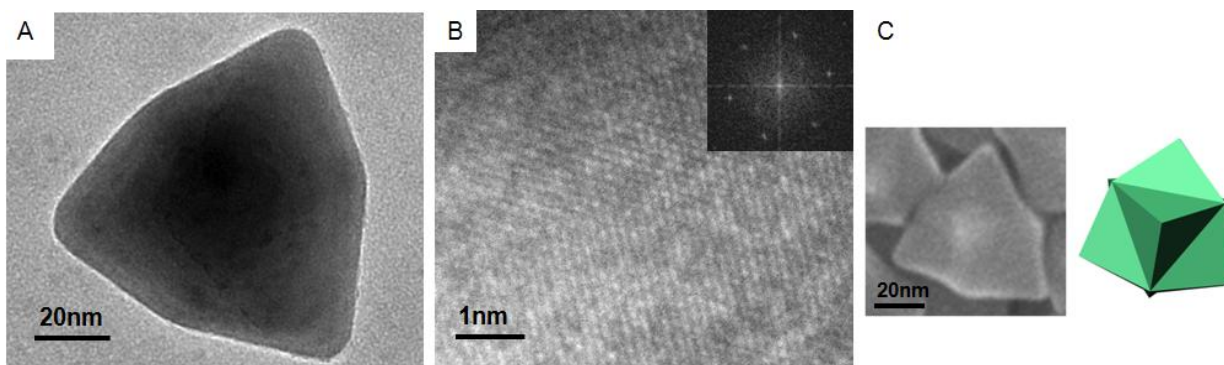


Figure S3. Shield-like Au NP viewed along its $\langle 111 \rangle$ direction. The (A) TEM and (C) SEM images clearly reveal the three-fold quasi-triangular shield-like shape. (B) The hexagonal atomic packing in the HRTEM image and hexagonal pattern in the corresponding FFT pattern (inset) indicate that the NP is oriented with its $\langle 111 \rangle$ direction perpendicular to the substrate. The geometrical model shown in (C) agrees well with the SEM and TEM images. A pot projecting out of the plane can be clearly seen in the SEM image. Projection in the $\langle 111 \rangle$ direction can only result in one particle orientation. The diffraction spots were contributed by the two halves of the NP.

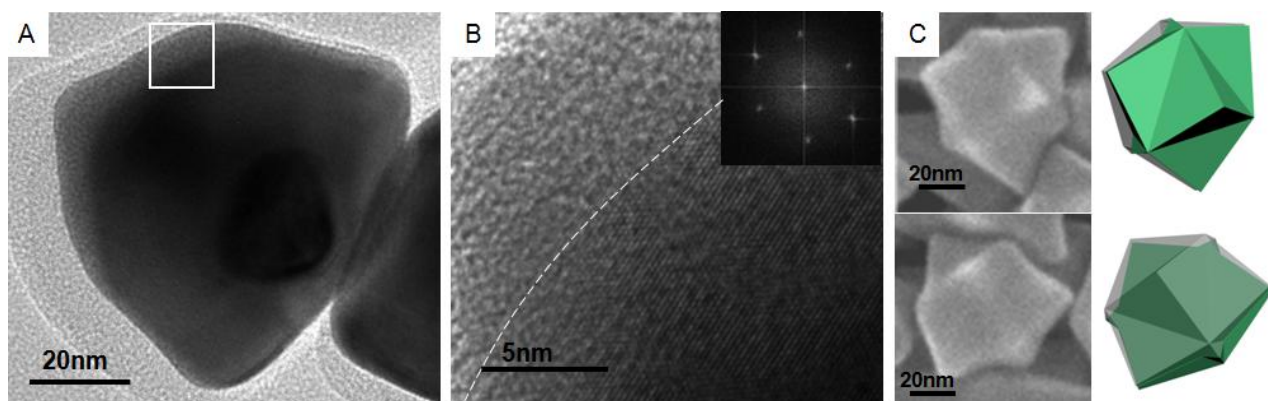


Figure S4. Shield-like Au NP viewed along its $\langle 110 \rangle$ direction. The (A) TEM and (C) SEM images show the shield-like shape. (B) HRTEM image of the square region marked in (A) and the corresponding FFT pattern (inset) indicate that the NP was oriented with its $\langle 110 \rangle$ direction perpendicular to the substrate. The geometrical model given in (C) agrees well with the SEM and TEM images. Different from the $\langle 111 \rangle$ projection, the $\langle 110 \rangle$ projection could display the particle in two orientations, since the NPs were assembled by two halves along a single twin plane, either of the halves which aligned along the $\langle 110 \rangle$ direction would give rise to the $\langle 110 \rangle$ projection. The contributing half is shown in color in the models in (C). The grayed-out part did not contribute to the diffraction. This was further confirmed by HRTEM image. A dash line is scribed in (B), $\{110\}$ lattice was only observed to the right of the dash line (the half that contributed to the diffraction) but not to the left (the half that did not contribute to the diffraction). This is also evidence that the NPs are not single crystals.

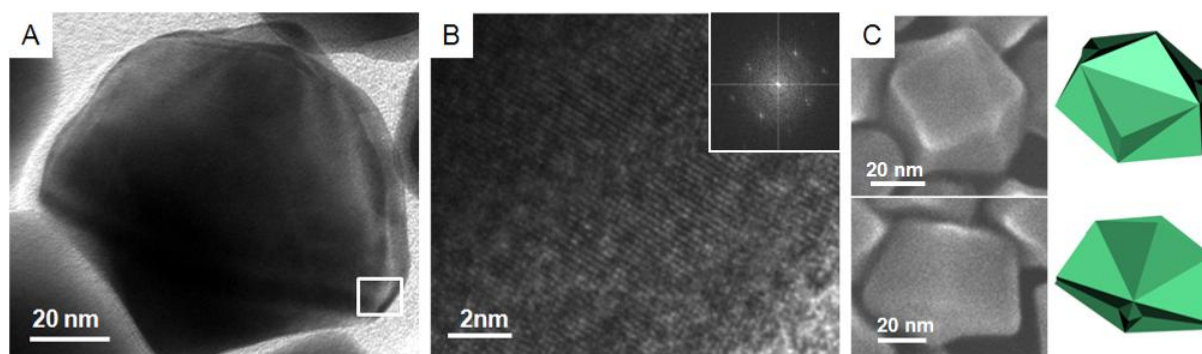


Figure S5. Shield-like Au NP viewed along its $\langle 100 \rangle$ direction. The (A) TEM and (C) SEM images reveal the shield-like shape. (B) The square atomic packing in the HRTEM image and the square diffraction pattern in the corresponding FFT pattern shown as inset indicate that the NP was oriented with its $\langle 100 \rangle$ direction perpendicular to the substrate. The geometrical models given in (C) agree well with the SEM and TEM images. Similar to the $\langle 110 \rangle$ projection, the $\langle 100 \rangle$ projection also displays two kinds of particle orientations.

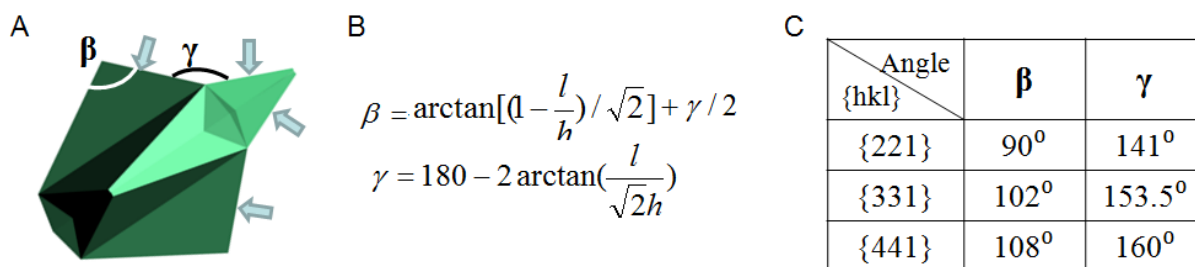


Figure S6. (A) A geometrical model of shield-like NP viewed along the $\langle 110 \rangle$ direction where the $\{111\}$ twin plane and four facets are imaged edge-on. The four edge-on facets are indicated by arrows. (B) The relationships between the two projection angles, β and γ and the Miller indices h and l of the exposed facets. (C) Table of the calculated values for β , and γ when the NP is bounded by different crystallographic facets.

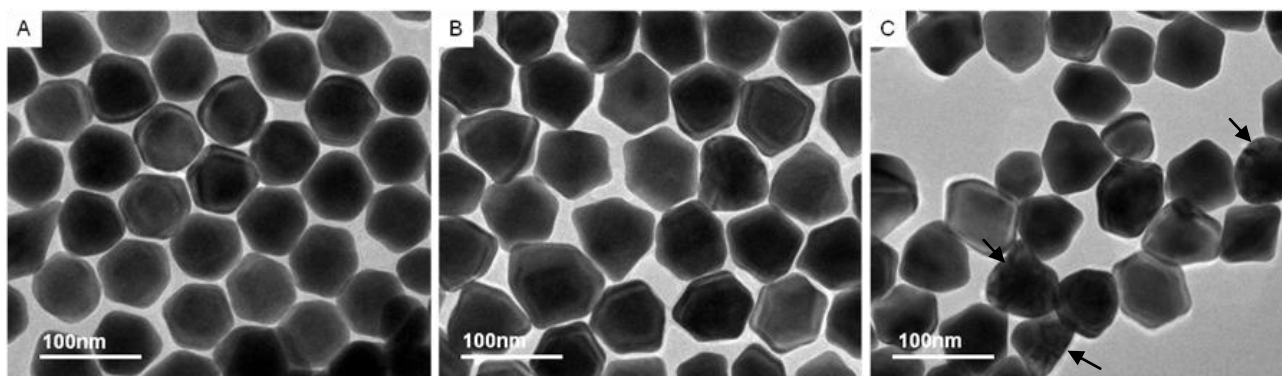


Figure S7. TEM images of NPs synthesized with different NaCl concentrations of (A) 0 mM, (B) 8 mM, and (C) 16 mM. The multiply twinned particles (MTPs) are marked by arrows in (C).

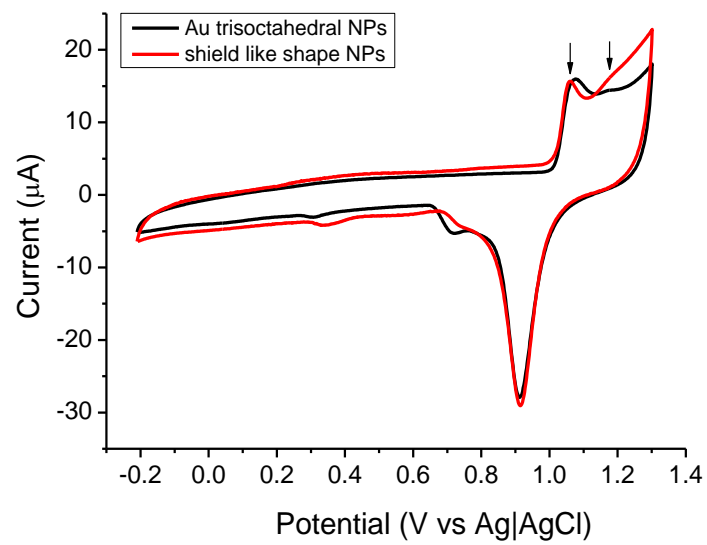


Figure S8. Cyclic voltammograms of shield-like and trisoctahedral Au NPs in 0.1 M HClO_4 measured at 20 mV/s.