Electronic Supplementary Information (ESI)

Five-fold Twinned Pentagonal Gold Nanocrystal Structure Exclusively Bounded by {110} Facets

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Experiments Details

Chemicals. Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9+%) and N,N-dimethylformamide (DMF, 99.8+%), were purchased from Sigma Aldrich. Silver nitrate ($AgNO_3$, 99.99%) and polyvinylpyrrolidone (PVP Mw=55000) were purchased from Alfa aeser. All of chemicals were used without further purification.

Synthesis of Au-Ag Alloy Seeds (Seed 1). 100μl of 100mM $HAuCl_4$ soltuion, 100μl of 100mM $AgNO_3$ soltuion, 800μl ultrapure water and 15ml of 160mg/ml PVP DMF solution, were added into a 20ml bottle. The bottle was capped and placed into an oil bath for reaction at 120°C with strring. At initial stage, the color of the solution is light-yellow after all the chemicals have been mixed. The solution becomes colorless within ~5min, and subsquently purple color in ~8 min. After continuously reacting for 1hour, the bottle was cooled in an ice bath for 15min.

Synthesis of Ellipsoidal Au Seeds (Seed 2). 100μl of 100mM $HAuCl_4$ soltuion, 500μl of seed 1 soltuion, 900μl ultrapure water and 15ml of 80mg/ml PVP DMF solution, were added into a 20ml bottle. The bottle was capped and placed into an oil bath for reaction at 120°C with strring. The solution turned reddish in color in ~10 min. After reaction for 1hr, the bottle was palced into an ice bath for 15min. The final color of the solution was claret. In this process, Au-Ag alloy seeds were transformed into monometallic Au seeds accompanying with an increase in size due to the galvanic replacement reaction between Au^{3+} ions and Ag atoms.

Sythesis of Different Five-fold Twinned Au Nanocrystals (NCs) Bounded by {110} or {111} Facets. In a typical synthesis of {110}-facet exclusivily bounded pentagon (Pg) Au NC, 100μL of Seed 2 solution was added into the mixture solution of 15 mL DMF, 100μL of 100 mM $HAuCl_4$, 1.2g of PVP. The growth solution was stirred and kept to produce the Pg NCs at 80°C for 5hrs. The synthesis procedure for other five-twinned Au NCs such as {111}-facet-covered decahedron (Dh), {110}-facet-truncated decahedron (TD), {110}-facet-heavily-truncated decahedron (HTD), and {110}-and-{111}-facet-covered pentagonal star (PS) is similar to that for the Pg Au NCs but with a slight modification of reaction conditions, as displayed in Table S1. All of the products were collected by centrifugation and purified by dispersion/ precipitation cycles with water to remove excess PVP.

Table S1. The synthesis condition for different five-fold NCs

	$HAuCl_4$ (100mM, μl)	Seed 2 (μl)	H_20 (μl)	PVP (g)	DMF (ml)	Temp (°C)	Time (h)
{111}-facet-covered decahedron (Dh)	100	100	2000	1.2	15	120	1.5
{110}-facet-truncated decahedron (TD)	100	100	1000	1.2	15	120	1.5
{110}-facet-heavily-truncated decahedron (HTD)	100	100	500	1.2	15	120	1.5
{110}-and-{111}-facet-covered pentagonal star (PS)	100	100	0	1.2	15	120	1.5
{110}-facet-covered pentagon (Pg)	100	100	0	1.2	15	80	5

Characterization. Scanning electron microscopy (SEM) measurements were obtained using a Hitachi S-4800. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), electron diffraction patterns, scanning transmission electron microscopy (STEM) and Z-contrast STEM images were obtained using a Tecnai G2 F20 and its accessory. UV–visible absorption spectra were obtained employing Cary100Bio spectrometer.

Calculated Spectrum. Discrete dipole approximation (DDA) calculations were performed on Dh and Pg Au NCs for average orientation-dependent spectra. The side length of the Dh target was set as 110nm. For the Pg target, its middle side length, top side length and thickness were set as 110nm, 80nm and 80nm, respectively. Orientation averaging was taken over a constant angel via varying the polar and the azimuth angles by $\pi/4$. Water was chosen for ambient medium. The complex refractive index function[1] and the incident light were divided by the refractive index of water to get the relative refractive index. Calculated extinction spectrum of the Dh displayed two shoulder and a broad band located at ~550nm, 650nm and 750nm which were assigned to polar dipolar, quadrupolar and azimuthal dipolar plasmon resonance modes, respectively. The simulation results of the Pg shows two major extinction peaks with dipolor mode at ~670 nm and a quadrupolor mode at ~550nm.

Detailed Structure analysis

TEM images of Dh, TD and PS NCs are provided in top right inserts of Fig. S3 (a), (c), (e) , Typical diffraction patterns obtained from individual Dh, TD, and PS NCs with the electron beam perpendicular to top planes are five set of superimposed diffraction patterns along [110] direction, rotated by ~72° with each other (As shown in bottom right inset of Fig. S3 (a), (c), (e), respectively). This suggests that all of them are five-fold twinned structures.

Dh Au NCs with five-fold twinned structure are completely bounded by {111} facets (see SEM image in Fig. S3(a) and an illustration in Fig. S3(b)). TD NCs are mainly composed of ten low energy {111} facets, each of the two axis points is truncated into a plane, which is a small five-twinned {110} planes. At the same time, each of five lateral vertices is transformed into a couple of new single-twinned {110} planes. That is, the individual TD Au nanocrystal (NC) consists of thirty {110} and ten {111} facets. On the basis of SEM image of the TD Au NCs (see Fig. S3(c)), skeletal structures of the single TD NC are schematically illustrated in Fig. S3(d) with a bird view and a lateral view. The structure of the HTD is similar with TD except difference of extent of {110}-facet-truncation. So we won't analyze the HTD repeatedly. Compared with TD, the SEM image of PS Au NCs shows that all adjacent {110} facets gradually enlarge to encounter with each other. Five new vertexes are formed and twinned boundaries evaluate from vertexes in Dh to middle of lateral facets in PS (see SEM image in Fig. S3(e) and an illustraton in Fig. S3(f)). The individual PS Au NC also consists of thirty {110} and ten {111} facets.

For clarity, we further speculate the evolution process of morphologies and crystal planes of the five-twinned Au NCs, as shown in Fig. S4. In general, a single Dh Au NC can be considered as a junction of five tetrahedrons. We firstly assume an evoluation process from a single tetrahedron exclusively bounded by {111} planes via a {110}-facet-truncated tetrahedron and a {110}-facet-completely-truncated tetrahedron to a rhombic dodecahedron exclusively bounded by {110} planes. Following this, we suggest a hypothetical evoluation process from a five-fold twinned {111}-facet-bounded Au decahedron via a junction of five {110}-facet-truncated tetrahedrons and a junction of {110}-facet-completely-truncated tetrahedrons to a junction of five {110}-facet-bounded rhombic dodecahedrons. When all gaps in the hypothetical Au NC junction of five {110}-facet-bounded Au rhombic dodecahedrons are filled up, a five-fold twinned pentagonal Au NC exclusively bounded by {110} planes can be formed.

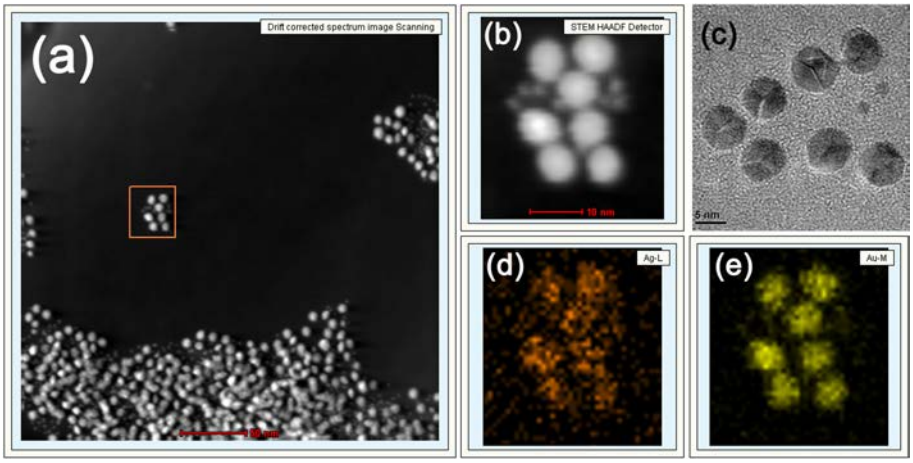

Fig. S1 STEM images of Seed 1 in the scale bar of (a) 50nm and (b) 10nm. (c) A typical TEM image of Seed 1, in which five-fold twinned nanoparticles can be observed. (d) Ag and (e) Au element mapping images of Seed 1. The element mapping images demonstrate that Seed 1 are Au-Ag alloy rather than monometallic.

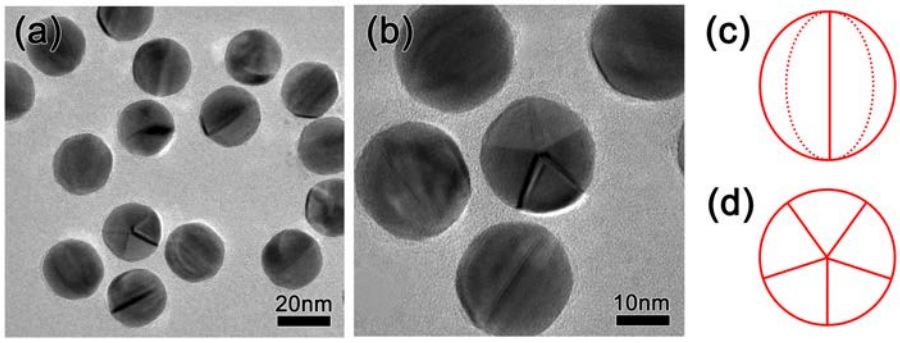

Fig. S2 (a) and (b) TEM images of Seed 2. Because the twined boundaries can't be focused at the same level along the non-axial direction, most of Seed 2 look like single-twined or single-crystalline structure. Illustrations of the twinned boundaries observed in the equatorial and axial direction are given in (c) and (d).

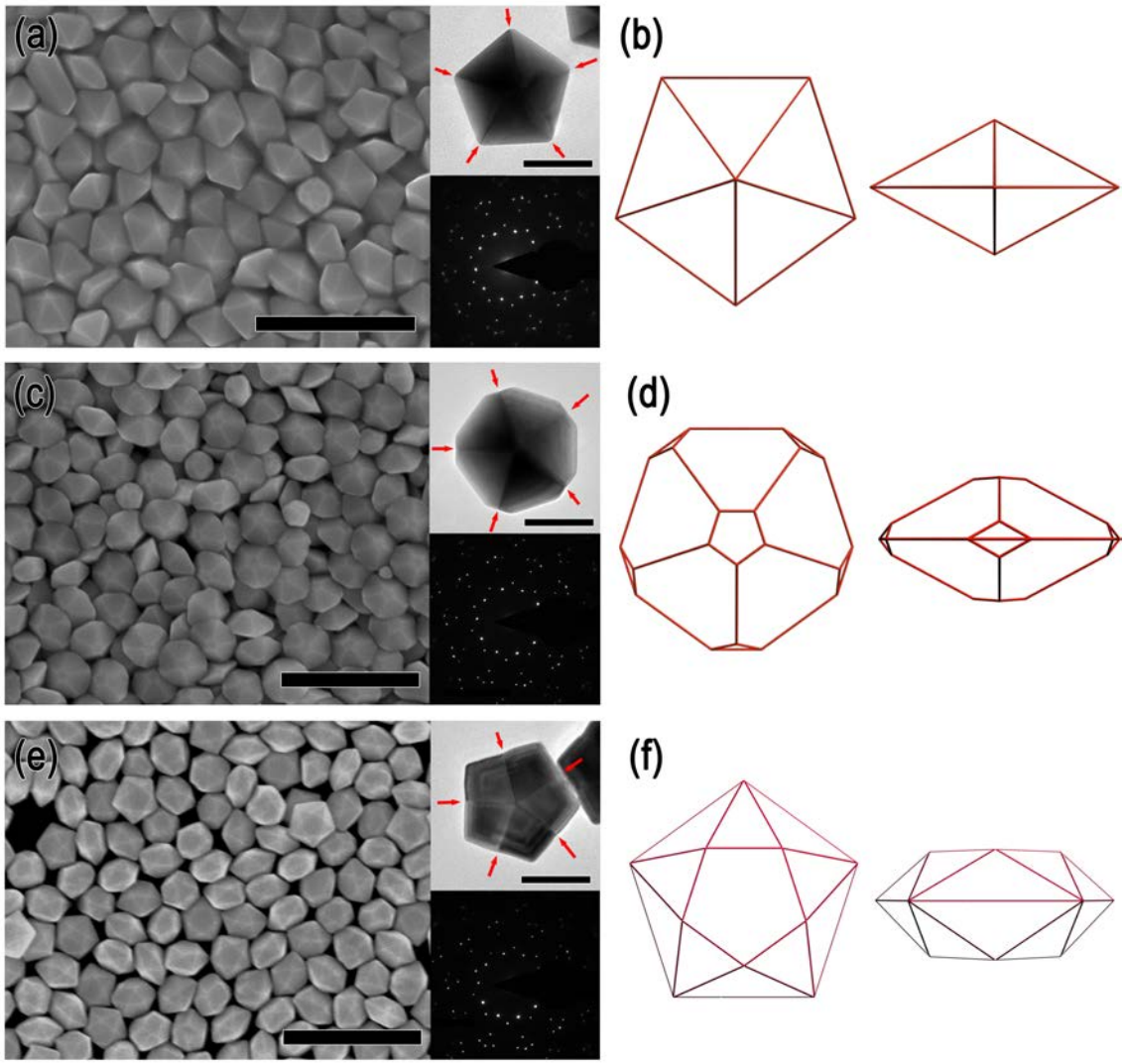

Fig. S3 Typical SEM images (scale bars: 500nm), TEM images (top insets, scale bars: 100nm) and electron diffraction patterns (bottom insets) of the five-fold twinned (a) Dh, (c)TD, and (e) PS Au NCs. The red arrows indicate the twin boundaries. The wireframe of the five-fold twinned (b) Dh, (d) TD and (f) PS in the top view and side view. Twined boundaries aren't delineated in (d) and (f).

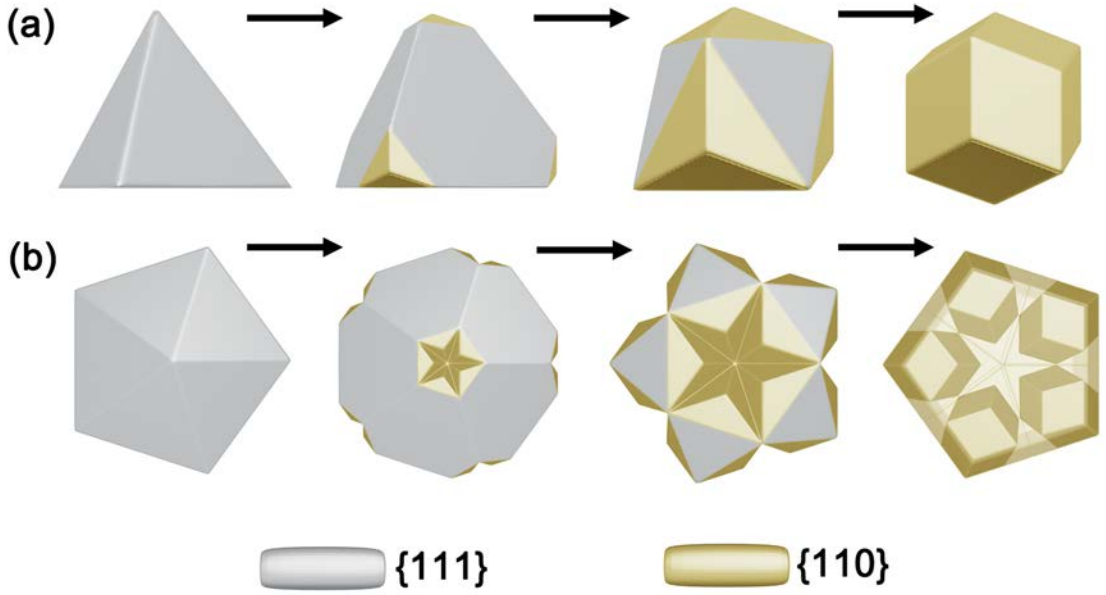

Fig. S4 A hypothetical evolution of morphology and crystal facets of (a) monomer and (b) junction of five monomers, from a tetrahedron exclusively bounded by {111} planes via a {110}-facet-truncated tetrahedron and a {110}-facet-completely-truncated tetrahedron to a rhombic dodecahedron exclusively bounded by {110} planes. A semitransparent Pg is intentionally painted to envelop the junction of five rhombic dodecahedrons, which vividly demonstrate that a Pg Au NC is exclusively bounded by {110} facets.

REFERENCES

(1) P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972**, 6**, 4370.