Electronic Supplementary Information

Controlled Growth of Concave Gold Nanobars with High Surface-Enhanced Raman-Scattering and Excellent Catalytic Activities

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Supplementary Results

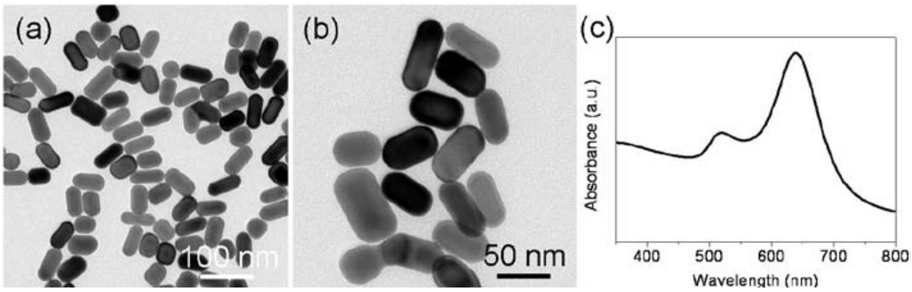


Figure S1. (a, b) TEM images and (c) UV/vis spectra of rod-shaped gold seeds (AR = 2.2).

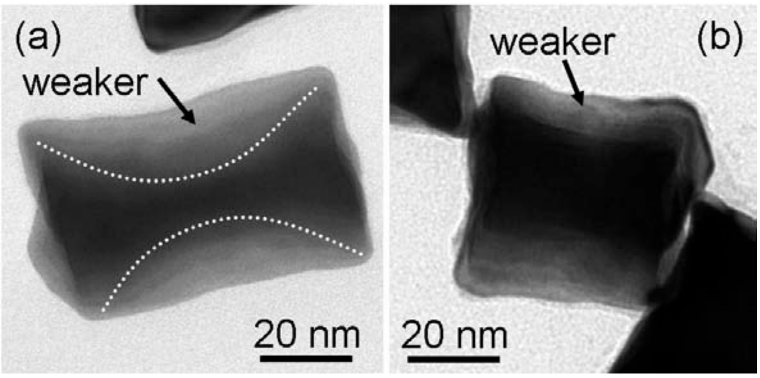


Figure S2. (a, b) High-magnification TEM imges of single concave nanobar.

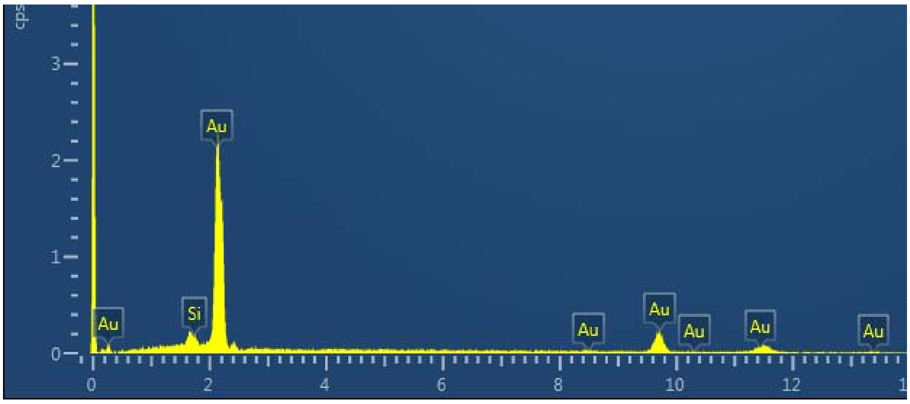
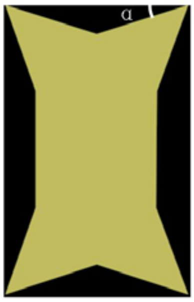


Figure S3. The energy dispersive X-ray spectroscopy (EDS) indicates that the obtained nanocrystals are composed of only gold.

Table S1. Projection angles and geometrical parameters of concave cuboids bounded by different types of high-index facets.

Projection direction	Geometrical model of the polyhedron	Equation for the projection angle	Calculated projection angle	
[001]		$\alpha = \arctan(k/h)$	{h k 0}	α
			{2 1 0}	26.5°
			{4 1 0}	14.0°
			{7 2 0}	15.9°
			{3 1 0}	18.4°
			{8 3 0}	20.6°
			{5 2 0}	21.8°
			{7 3 0}	23.2°

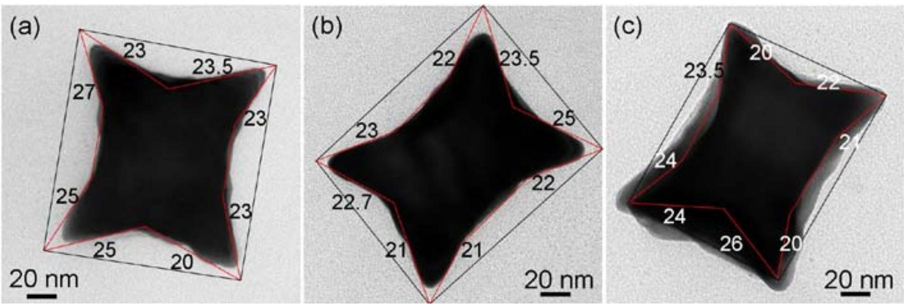


Figure S4. (a, b, c) TEM images of a single concave rectangular gold bar and its interfacial angles.

Table S2. Projection angles between {100} facets from the concave rectangular nanocrystals in Figure S4.

Particle #	θ 1	θ 2	θ 3	θ 4	θ 5	θ 6	θ 7	θ 8
a	23°	23.5 °	23 °	23 °	18 °	25 °	23.5 °	27 °
b	23.5 °	25 °	22 °	21 °	21 °	23.2 °	23 °	22 °
c	20 °	22 °	21 °	20 °	26 °	24 °	24 °	23.5 °
Summary	average: 22.8 °				absolute deviation: 1.65 °			

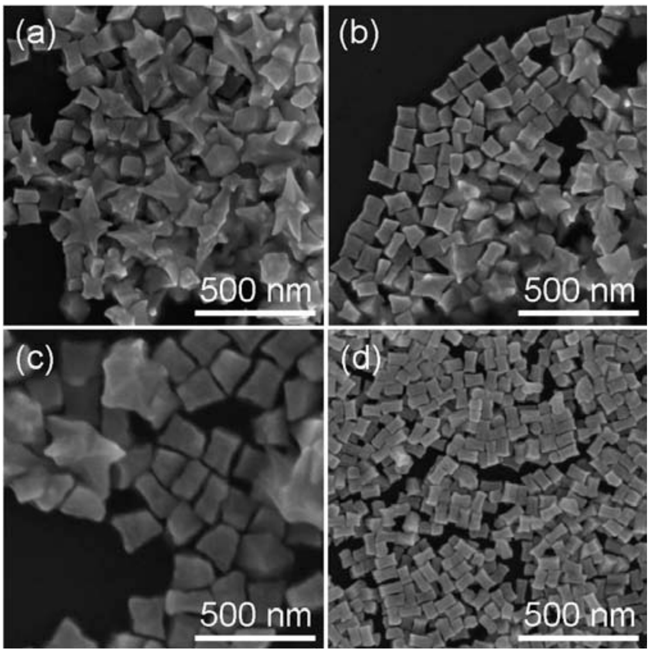


Figure S5. SEM images of aqueous suspensions of gold nanocrystals prepared with different amounts of seed solution: (a) 40, (b) 60, (c) 80, and (d) 100 μL.

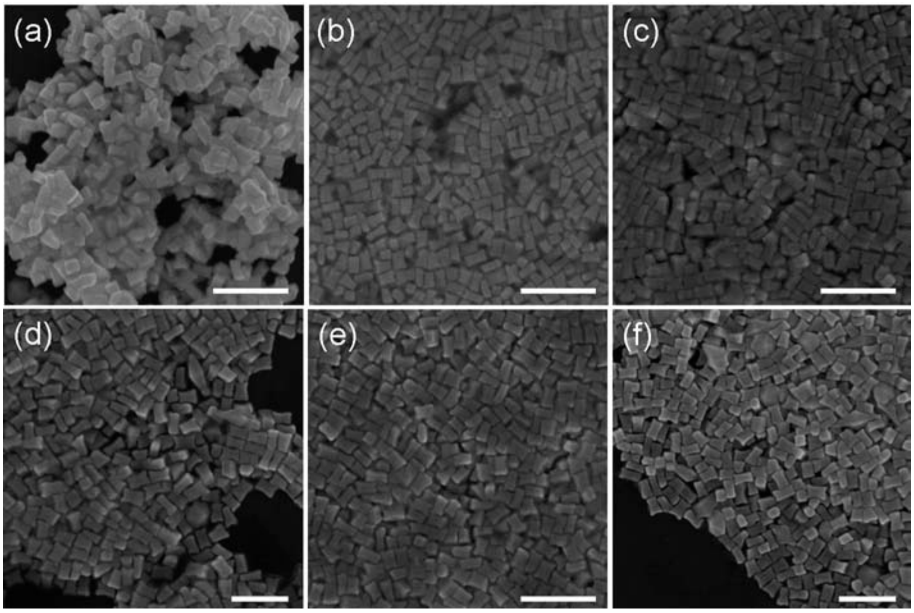


Figure S6. SEM images of aqueous suspensions of gold nanocrystals prepared with different amounts of ascorbic acid: (a) 55, (b) 65, (c) 80, (d) 100, (e) 120, and (f) 150 μL. The scale bar is 500 nm.

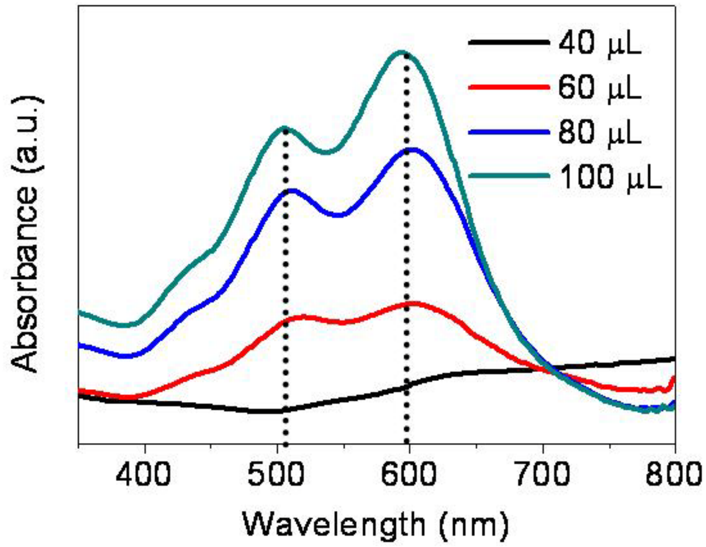


Figure S7. UV/vis spectra of aqueous suspensions of gold nanocrystals prepared with different amounts of seed solution.

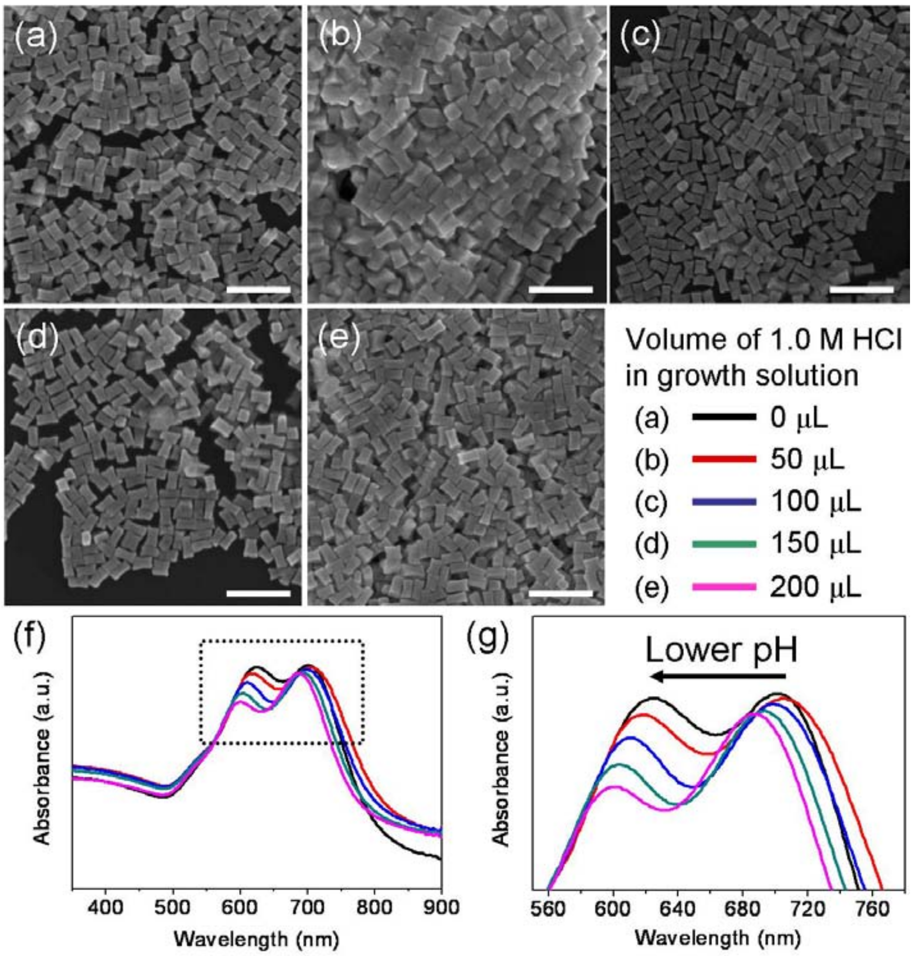


Figure S8. SEM images of concvae gold nanocrystals prepared in growth solutions containing (a) 0, (b) 50, (c) 100, (d) 150, and (e) 200 μL of 1.0 M HCl. The scale bar is 300 nm. (f) UV/vis spectra of the particles in (a-e) display a gradual blue-shift of SPR with the decreasing pH value. (g) Magnified UV/vis spectra of the region marked with a box in (f).

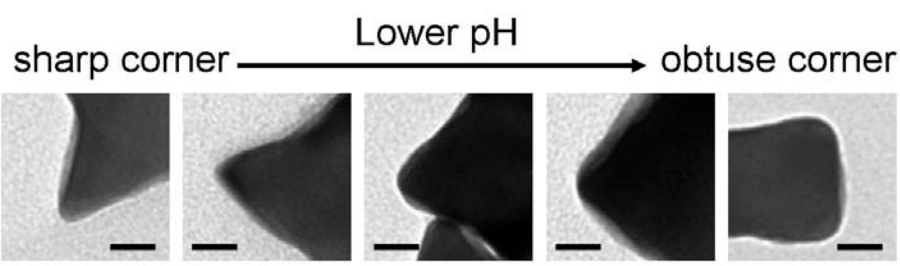


Figure S9. TEM images of concvae gold nanocrystals prepared in growth solutions containing different amount of HCl. The scale bars is 20 nm.

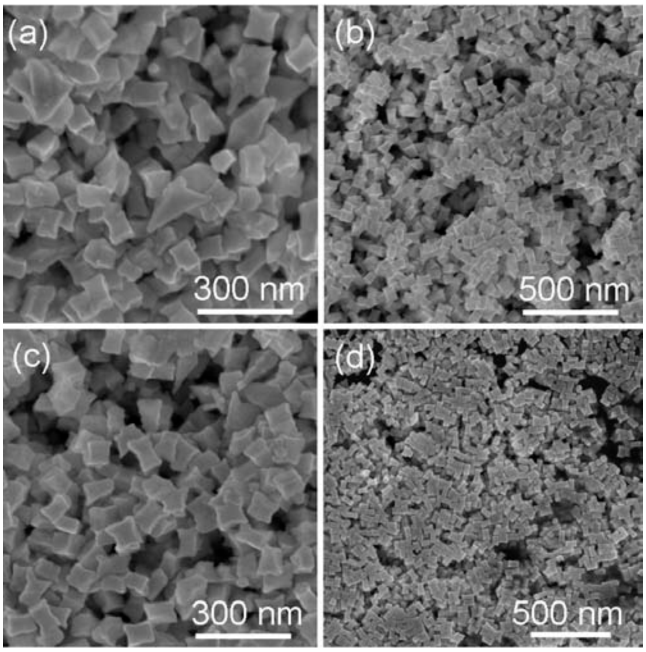


Figure S10. SEM images of concvae gold nanocrystals prepared in growth solutions containing (a) 0.05, (b) 0.2, (c) 0.3 M CTAB. (d) TEM image of concave gold nanocrystals prepared in growth solutions containing 0.05 M NaBr and 0.05 M CTAB.

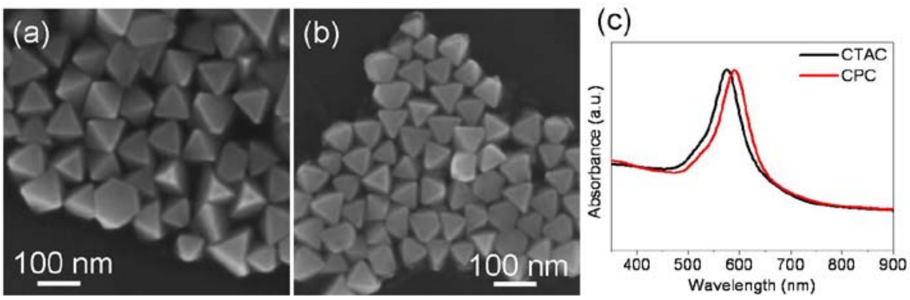


Figure S11. SEM images of gold nanocrystals prepared with (a) cetyltrimethylammonium chloride (CTAC), and (b) cetylpyridinium chloride (CPC). (c) UV/vis spectra of octahedra prepared in the presence of CTAC and CPC, respectively.

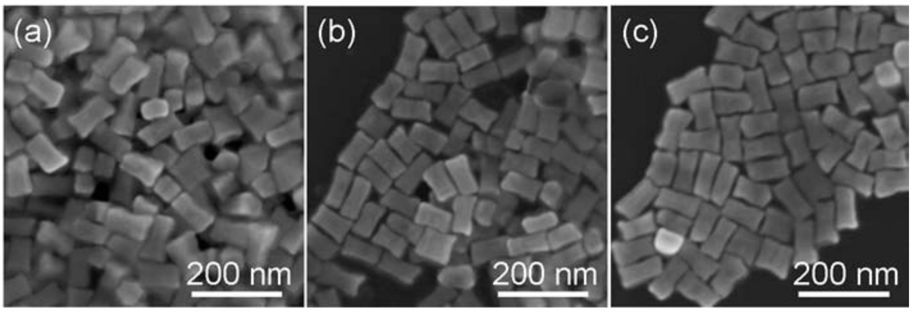


Figure S12. SEM images of gold nanocrystals obtained at different AR seed solution: (a) AR = 2.2, (b) AR = 2.5, (c) AR = 2.8.

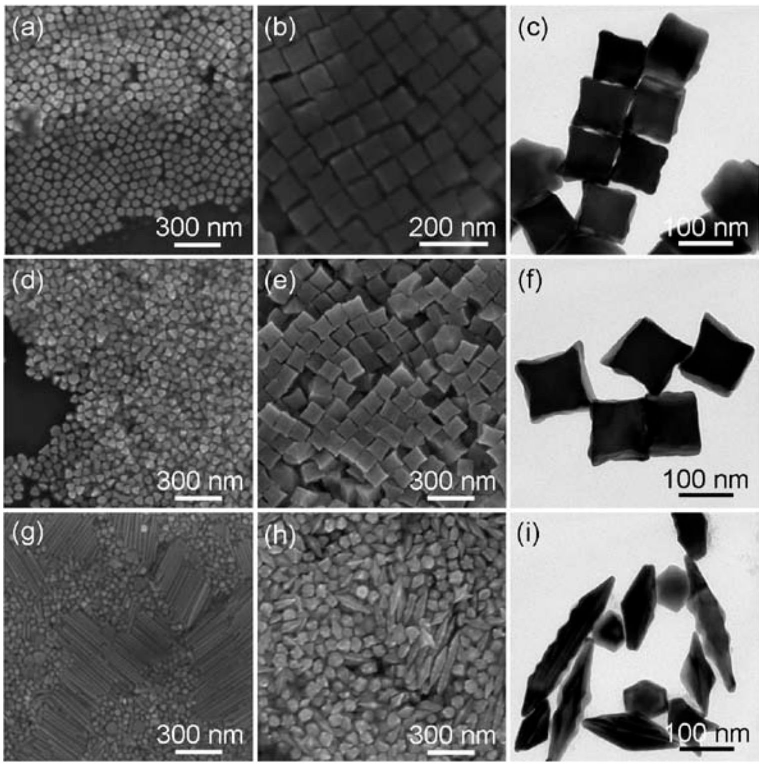


Figure S13. Influence of seed morphology on the final product. SEM images of gold nanocubes (a), octahedra (d), and irregular particles (g) used as the seeds for the growth of gold nanocrystals with concave features. SEM (b, e, h) and TEM (c, f, i) images of the products obtained from the corresponding seeds.

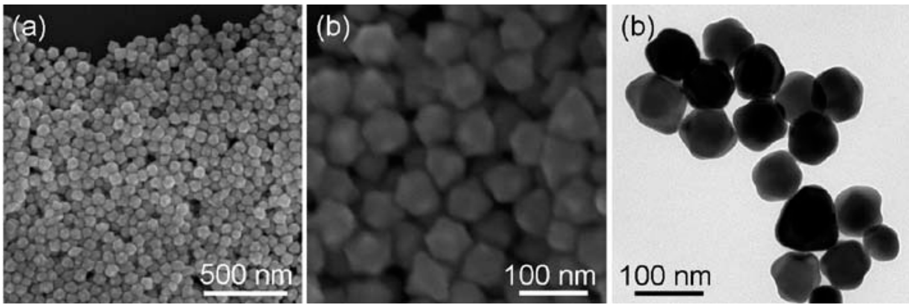


Figure S14. SEM and TEM images of trisoctahedra prepared in the presence of CTAC.

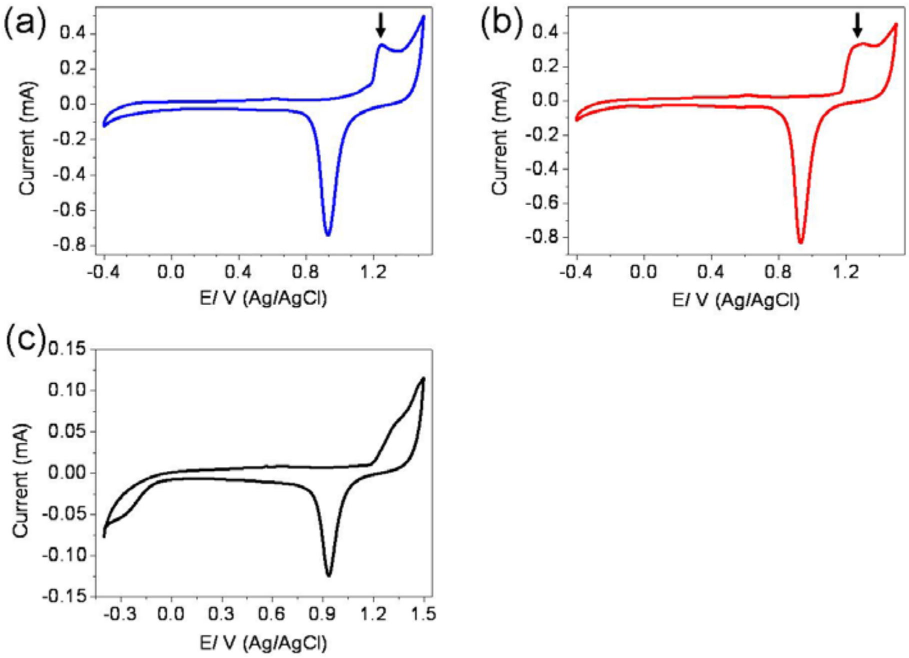


Figure S15. Cyclic voltammograms of concave gold cuboid (a), gold trisoctahedra (b), and gold octahedra (c) at 50 mV·S^{-1} in 0.5 M H_2SO_4.

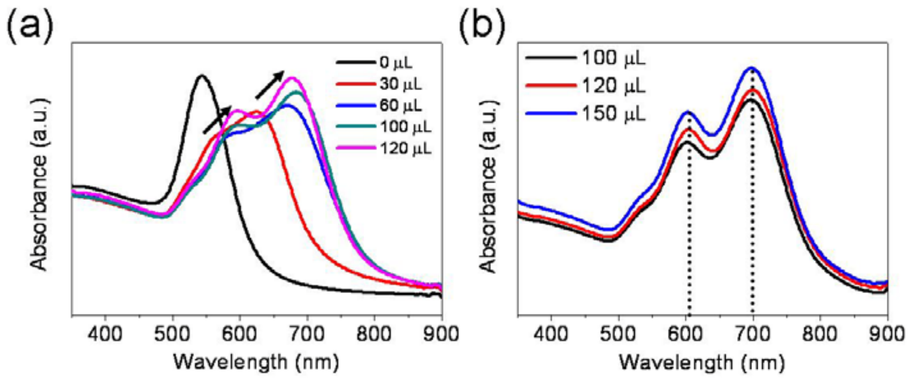


Figure S16. (a, b) UV/vis spectra of concave gold nanobars obtained with different volume of $AgNO_3$.

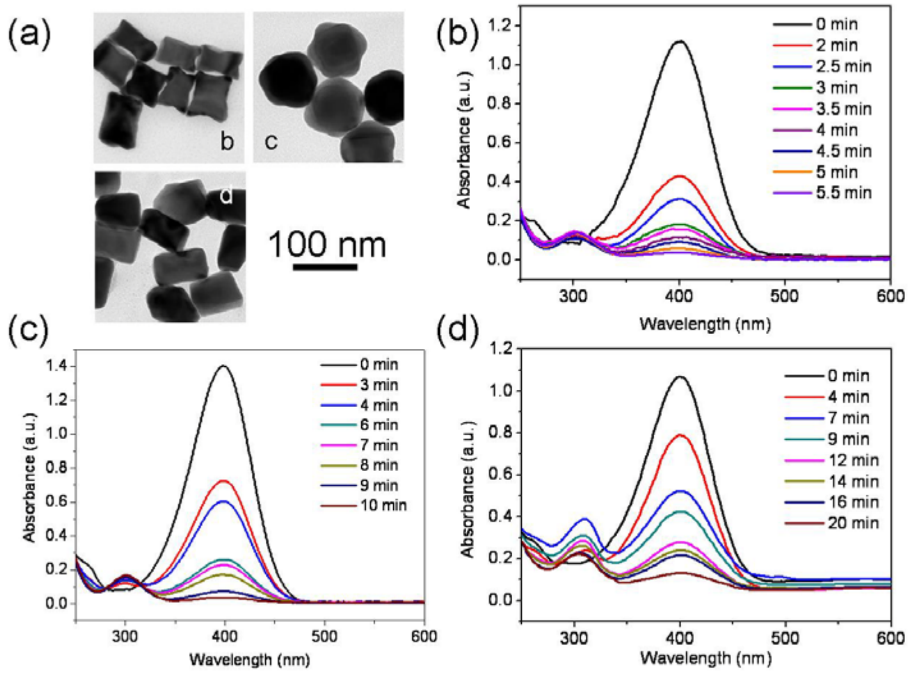


Figure S17. (a) Typical TEM images of gold nanocrystals used in (b-d). (b-d) UV/vis spectra show the gradual reduction of *p*-nitrophenol by concave nanobar (b), concave trisoctahedral (c), and rectangular nanobar (d) gold nanocrystals at room temperature, respectively.

Calculation of the total number of gold atoms contained in a gold nanobar enclosed by {100} or {730} facets, and the total number of gold atoms on the surface.[4, 5]

(a) Conventional nanobars enclosed by {100} facets

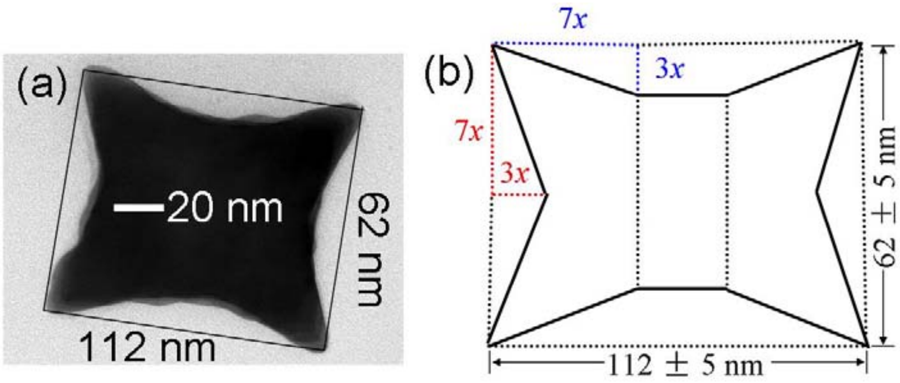


Figure S18. TEM image of (a) a concave rectangular gold nanocrystal and (b) its projection. The nanocrystal is viewed along the [001] axis.

The TEM image shows a rectangular gold concave nanobar with an average width of 62 ±5 nm and length of 112 ± 5 nm (Figure S18a). Since the concave gold nanocrystal is enclosed by {730} facets, the length ratio between the two perpendicular sides of right triangle indicated in red is 7:3. With the assumption that one side is $7x$ and the other side is $3x$, the value of x is calculated from the nanocrystal width to be $x = (62\ \text{nm}) / (7 + 7) = 4.43$ nm. Other related lengths are also calculated and shown in Figure S18b.

(1) Number of gold atoms contained in a nanobars

In a gold nanobar with rectangular side facets and an average aspect ratio of 1.8 (112 ± 5 nm long, 62 ± 5 nm wide, and 62 ± 5 nm high), its volume is (112 nm × 62 nm × 62 nm) = 4.305×10^5 nm^3. Gold has a face-centered-cubic structure with a lattice constant of 0.408 nm.

The volume of a unit cell is (0.408 nm)^3 = 0.068 nm^3. Each unit cell contains 4 gold atoms. As a result, the total number of gold atoms in a single gold nanobar is (4.305 × 10^5 nm^3) / (0.068 nm^3) × 4 = 2.532 × 10^7.

(2) Number of gold atoms on the surface of a nanobar

A gold nanobar is enclosed by six {100} facets. The total surface area is (112 nm × 62 nm) × 4 + (62 nm × 62 nm) × 2 = 3.546 × 10^4 nm^2. Each two-dimensional unit cell on the {100} facets contains 2 gold atoms, and the area of this unit cell is (0.408 nm)^2 = 0.166 nm^2. The total number of gold atoms on the surface of a single nanobar is (3.546 × 10^4 nm^2) / (0.166 nm^2) × 2 = 4.261 × 10^5.

(3) Total number of gold atoms on the surface of nanobars used in the catalytic reaction

The total number of gold atoms in the catalyst is (25 × 10^{-3} mL × 2.8 × 10^{-3} g/mL) / (196.9665 g/mol) × (6.02 × 10^{23} mol^{-1}) = 2.14 × 10^{17}. The number of gold nanobars involved in the catalytic reaction is (2.14 × 10^{17}) / (2.532 × 10^7) = 8.452 × 10^9. The total number of gold atoms on the surface of gold nanobars used in the catalytic reaction is (4.261 × 10^5) × (8.452 × 10^9) = 3.601 × 10^{15}.

(b) Concave nanobars enclosed by {730} facets

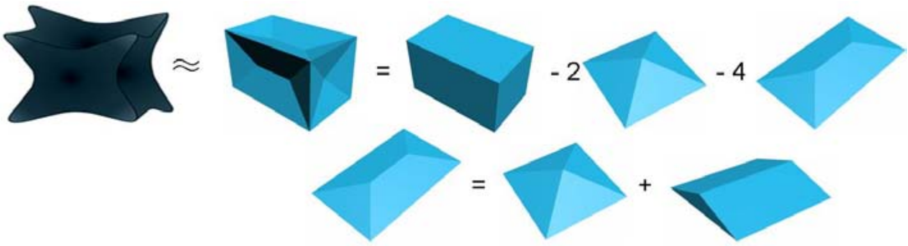


Figure S19. Schematic illustration for the decomposition of a concave rectangular gold nanocrystal into a cuboid, 2 square pyramids, and 4 elongated pyramids, and the decomposition of an elongated pyramid into a square pyramid and a triangular prism.

(1) Volume of a single concave nanobar

The gold concave nanobar with an average aspect ratio of 1.8 (112 ± 5 nm long, 62 ± 5 nm wide, and 62 ± 5 nm high) can be considered as a bar with 2 square pyramid and 4 rectangular pyramids excavated at the center of transverse and longitudinal face. The volume of a bar is (112 nm × 62 nm × 62 nm) = 4.305×10^5 nm^3. The volume of a square pyramid is 1/3 × (62 nm)^2 × (3 × 4.43 nm) = 1.70×10^4 nm^3, and the volume of a triangular prism is 1/3 × (1/2 × 62 nm × 3 × 4.43 nm) × (112 - 62 nm) = 6.8665×10^3 nm^3. As a result, the volume of a concave nanobar is (4.305×10^5 nm^3) - 6 × (1.70×10^4 nm^3) - 4 × (6.8665×10^3 nm^3) = 3.01 × 10^5 nm^3 (see Figure S19).

(2) Number of gold atoms in a concave nanobar

The number of gold atoms contained in a single gold concave nanobar is (3.01×10^5 nm^3) /(0.068 nm^3) × 4 = 1.77×10^7.

(3) Number of gold atoms on the surface of a concave nanobar

The atomic density of {730} facets is 3/7 of that of {100} facets. In a typical bar with 112 nm long, 62 nm wide, and 62 nm high, the total surface area of the bar is (112 nm × 62 nm) × 4 + (62 nm × 62 nm) × 2 = 3.546×10^4 nm^2. The total number of gold atoms on the {730} facets of a single concave nanobar is (3.546×10^4 nm^2) / (0.166 nm^2) × 2 × 3/7 = 1.831×10^5.

(4) Total number of gold atoms on the surface of concave nanobars in the catalytic reaction

The total number of gold atoms in the catalytic reaction is 2.14×10^{17}. The number of gold concave nanobars in the catalytic reaction is (2.14×10^{17}) / (1.77×10^7) = 1.21×10^{10}. As a result, the total number of gold atoms on the surface of concave nanobars in the catalytic reaction is (1.831×10^5) × (1.21×10^{10}) = 2.22×10^{15}.

Table S3. Conversion yields for the reduction of *p*-nitrophenol to *p*-aminophenol with the gold nanobars enclosed by a concave or flat surface as the catalyst.

Gold catalyst	**Reaction time**	**Yield (%)**	**Number of surface atoms**
rectangular bars	5 min	34.7	3.60×10^{15}
concave bars	5 min	94.5	2.22×10^{15}
trisoctahedra	5 min	74.2	No calculation

References

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(3) C. J. Murphy, T. K. San, A. M. Gole, C. J. Orendorff, J. X. Gao, L. Gou, S. E. Hunyadi and T. Li, *J. Phys. Chem. B* 2005, **109**, 13857.

(4) M. S. Jin, H. Zhang, Z. X. Xie and Y. N. Xia, *Angew. Chem. Int. Ed*. 2011, **50**, 7850.

(5) F. Wang, C. H. Li, L. D. Sun, H. S. Wu, T. Ming, J. F. Wang, J. C. Yu and C. H. Yan, *J. Am. Chem. Soc*. 2011, **133**, 1106.