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Electronic Supplementary Information

Facile Synthesis of Concave Decahedra Enclosed by High-Index Facets and Truncated Decahedra with a Large Size

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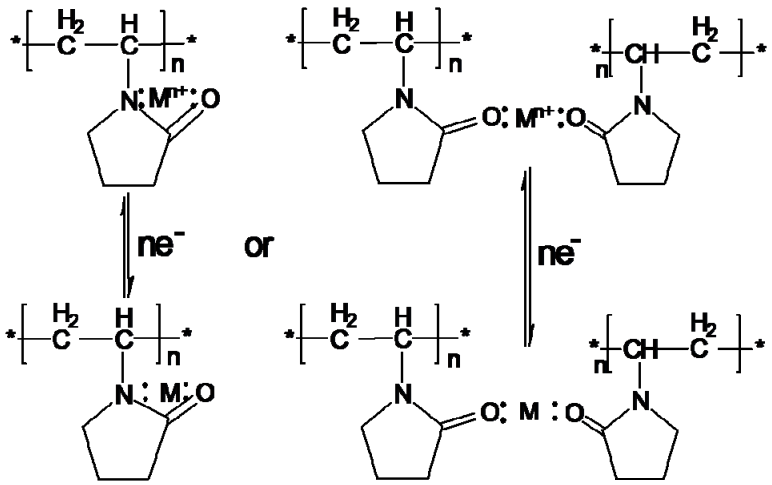

Figure S1 Complexation of metal ions with PVP chains.[S1]

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TABLE S1: Samples and Corresponding Experimental Conditions

sample	Reaction time (h)	Reaction Temperature (℃)	$HAuCl_4$/DMF (μL)	PVP-K30 (g)	DMF (mL)	KI/DMF (μL)	$AgNO_3$/DMF (μL)	Morphology (SEM)
1	4	80	150	2.2	12	0	0	concave nanoparticles
2	8	80	150	2.2	12	0	0	concave decahedra
3	10	80	150	2.2	12	0	0	
4	12	80	150	2.2	12	0	0	
5	24	80	150	2.2	12	0	0	
6	4	100	150	2.2	12	0	0	triangles and regular decahedra
7	6	100	150	2.2	12	0	0	truncated decahedra
8	8	100	150	2.2	12	0	0	dodecagonal plates
9	12	100	150	2.2	12	0	0	Triangles plates
10	10	80	150	4.0	12	0	0	concave decahedra and spheres
11	10	80	120	2.2	12	0	0	rhombic dodecahedron
12	10	60	150	2.2	12	0	0	nanoparticles
13	10	80	150	2.2	12	5	0	ultrathin plates
14	10	80	150	2.2	12	10	0	
15	10	80	150	2.2	12	0	10	Tetrahexah-ed ral

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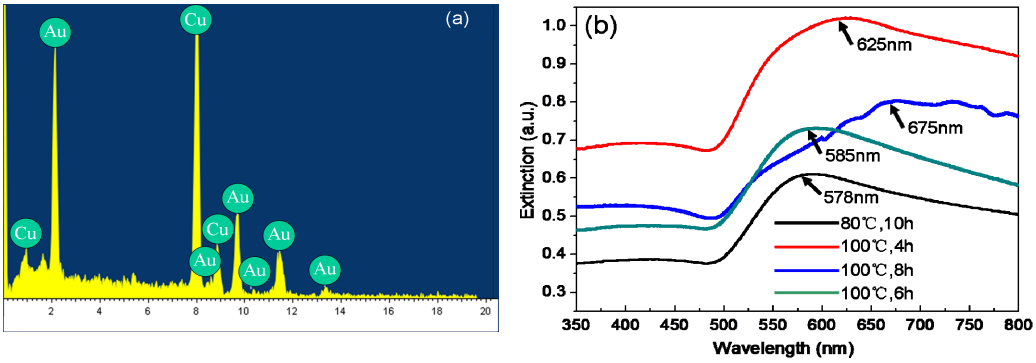
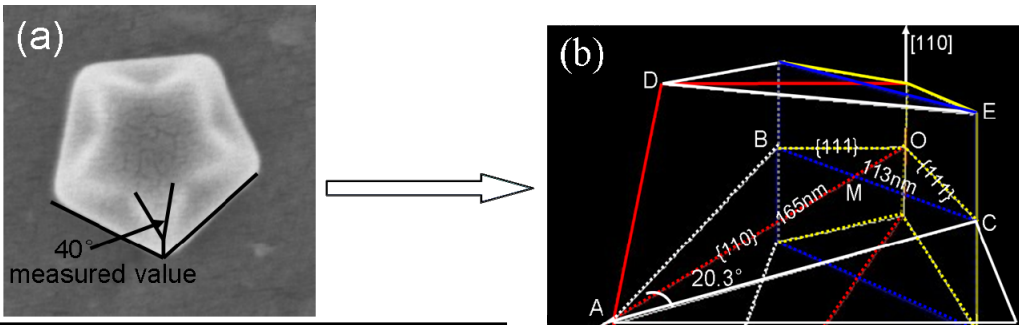


Figure S2 (a) The energy dispersive X-ray spectroscopy (EDS) indicates that the obtained nanoparticles (NPs) are composed of only gold. Cu came from the TEM grid. (b) UV-vis extinction spectra of the obtained samples at the different reaction time and temperature. Black line, at 80 °C for 10 h (concave decahedra); Red line, at 100 °C for 4 h (triangles and regular decahedra); olive line, at 100 °C for 6 h (truncated decahedra); Blue line, at 100 °C for 8 h (dodecagonal plates).



{h h l}	Angle with {110}	theoretical Interfacial angles
{221}	19.5°	38.9°
{552}	15.8°	31.6°
{331}	13.3°	26.5°
{772}	11.4°	22.8°

Figure S3 Gold is a face-centered cubic (fcc) metal. For a five-fold twinned gold NP, the twinned planes of a single crystal are {111}, the zone axis is along [110]. From the structure analysis we can figure out that the plane along the [110] zone axis dividing the single crystal into two equal parts is a {110} plane (red line). The cross section of the branch will be {100} (blue line).[S2] We can measure that the height of the branch (AM) is about 165 nm, and width (BC) of the button is about 113 nm, then through calculation we know that each tip's interfacial angle is about 40.6°, and half of it is 20.3°. So the side planes of the branch have an interfacial angle of 20.3° with {110} plane (b). Form the Table (a, bottom), we know the theoretical value of {221} facets is 19.5°. It is found that the experimental value has a little deviation to the theory value. The interfacial angle of the concave decahedron is measured to be 40° from SEM image (a), and half of it is 20°. Based on analyses mentioned above, the measured value is consistent with the theoretical value of 19.5° corresponding to the angle between {221} and {110}. Therefore, we make sure that the concave planes are {221} high-index facets.

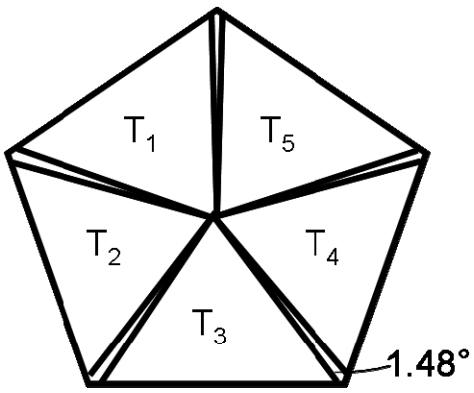


Figure S4 Sketch of a five-fold-twinned decahedral nanoparticle. The twinned

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decahedron particle consists of five tetrahedron units (indicated by T_1 to T_5). All the tetrahedrons share a common axis, which is one of the edges of a tetrahedron unit. As the theoretical geometrical angle is about 70.52° between two {111} planes in a tetrahedron, five such tetrahedrons can cover an angle of 352.6° (5×70.52°) which is 7.4° short of 360°. Therefore, a theoretical angular gap of about 1.48° exists between adjacent tetrahedron units. In real five-fold-twinned nanoparticles, this gap is closed by stretching the interatomic bond distances.[S3]

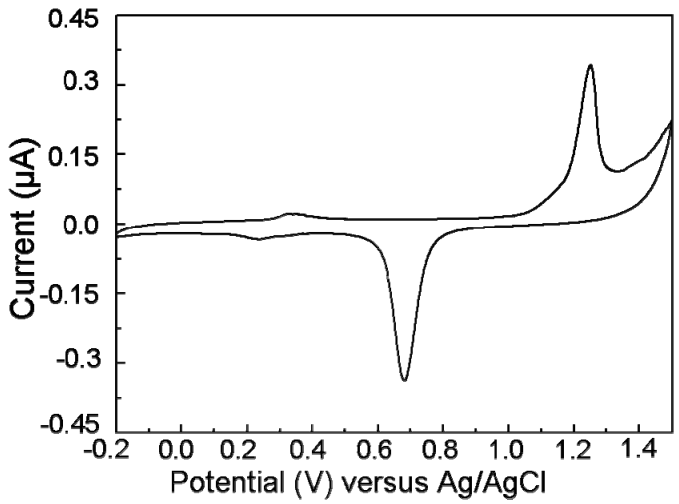

Figure S5 Cyclic voltammograms of concave Au decahedra at 20 $mV \cdot s^{-1}$ in 0.1 M H_2SO_4.

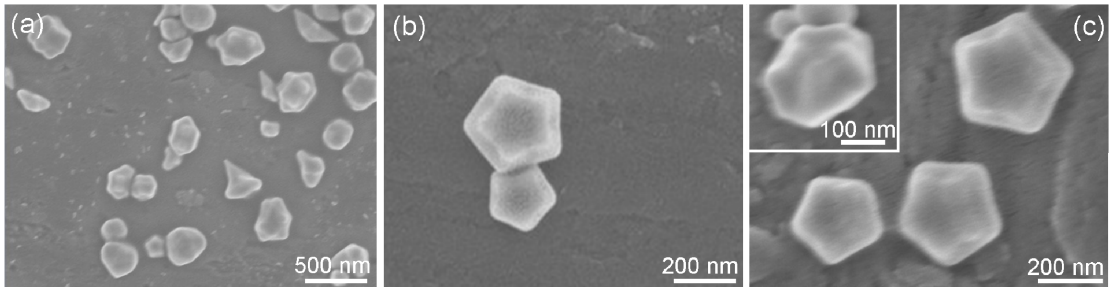

Figure S6 SEM images showing the morphological evolution of the gold nanocrystals synthesized under different reaction time at 80 °C. (a) 4 h, (b) 8 h, (c) 12 h.

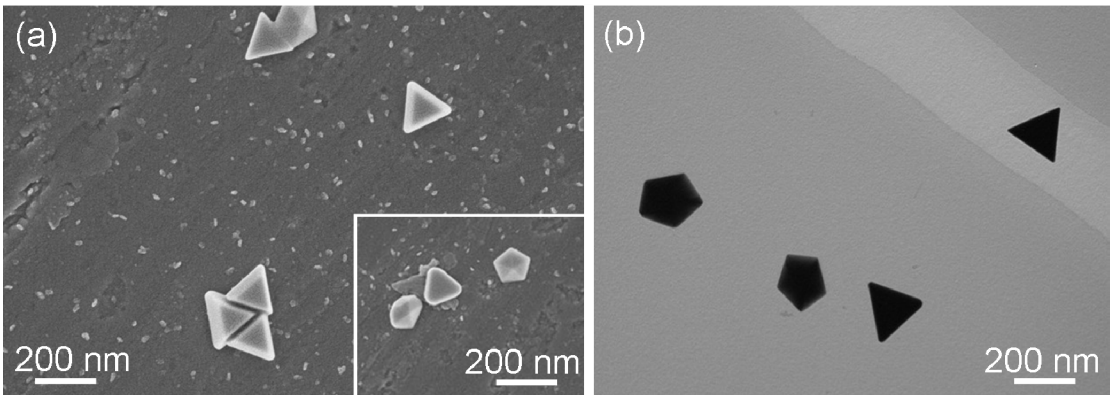

Figure S7. SEM image and TEM image showing the gold nanocrystals synthesized at 100 °C for 4 h.

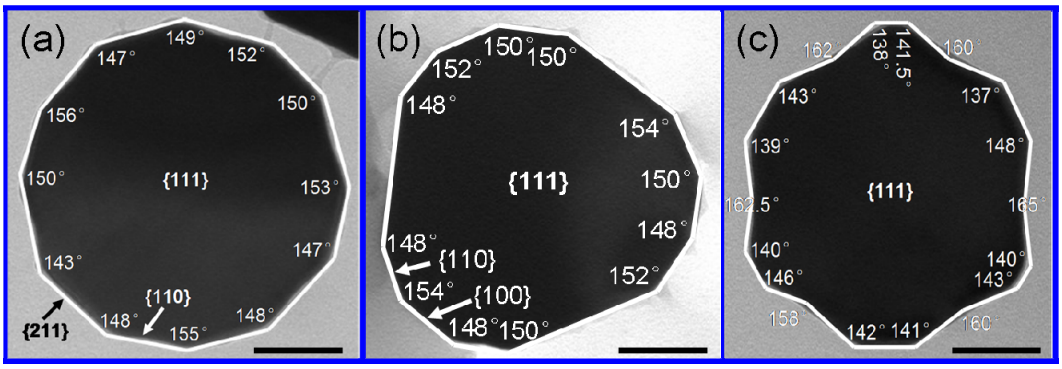

Figure S8. The angels relationship with the planes for various dodecagonal plates, scale bar: 100 nm.

The three types of the dodecagon plates have different facets resulting from different growth rates. Since the side planes of this dodecagon bounded alternatively

by {211} and {110} planes ($E_{\{211\}} = 0.0908$ eV•Å^{-2} < $E_{\{110\}} = 0.0991$ eV•Å^{-2}),[S4] the final shape of the nanoplates is dependent on the competition of growth rates of these two planes. If {211} faces growth is preferentially inhibited, nonequilateral plates are formed (Figure S5b). Similarly, when {110} faces growth is preferentially inhibited, truncated star-like dodecagon plates are formed (Figure S5c). In the case where the growth of the {211} and {110} planes are simultaneously inhibited, the formation of equilateral structures is highly possible (Figure S5a).

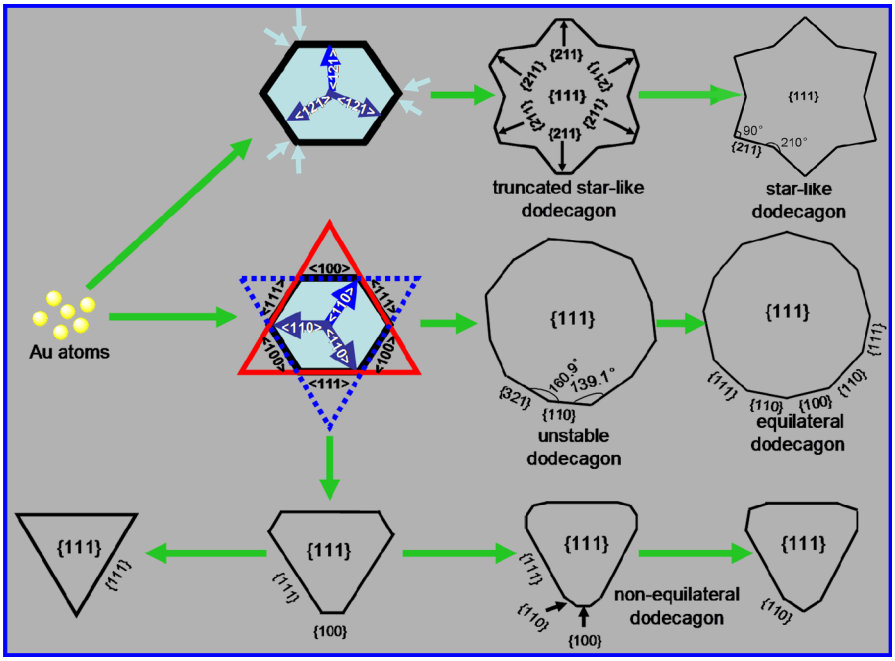

Figure S9. Schematic representation of the kinetically induced transformation of Au nanoplates.

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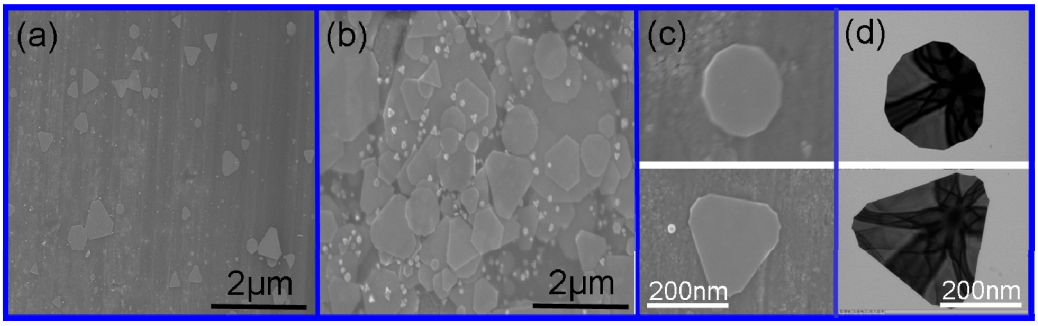

Figure S10. SEM and TEM images of the products obtained after addition of different amount of KI (10 mM) into the reaction solution. (a, c, d) 5 μL, (b) 10 μL.

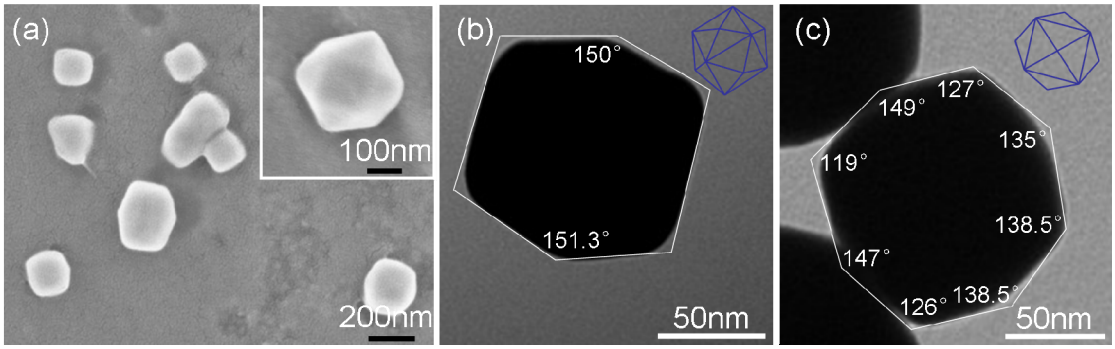

Figure S11. (a) SEM and (b, c) TEM images of the THH Au nanocrystals obtained after addition of $AgNO_3$ (10 μL, 10 mM) into the reaction solution and refluxed for 10 h at 80 °C. The insets are the corresponding structure models

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