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Supporting Information

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Supporting information:

Shape-controlled Synthesis of Gold Nanoparticles in Deep Eutectic Solvents for Studies of Structure-Functionality Relationships in Electrocatalysis

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1. EDS and UV-vis spectrum

The Energy dispersive X-ray spectroscopy (EDS) indicates that the nanoparticles(NPs) are composed of only gold (see Figure S1 a). The result presented in Figure S1(b) is the absorption spectrum of Au NPs recorded at different time of synthesis. The absorption peaks in these spectrum are red-shifted from 596 nm to 641 nm along with the increase of synthesis time from 1.5 to 5 hours, which is attributed to the growth of Au NPs and the size-effect of the NPs.

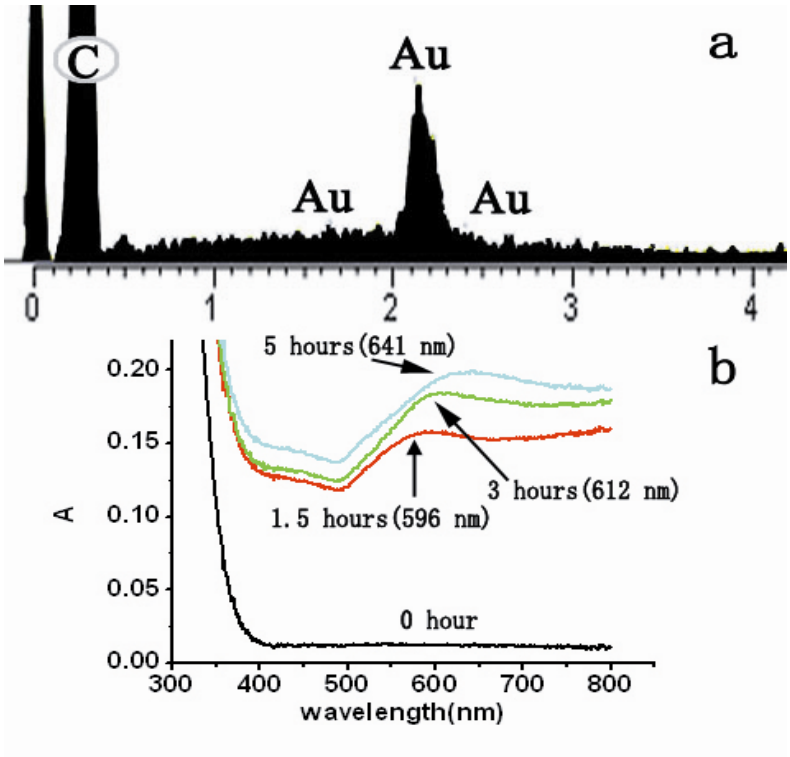

Figure S1 a) Energy dispersive X-ray spectroscopy (EDS). b). UV-vis absorption spectra at different times of reaction (1.5 hours, 3 hours, 5 hours).

2. High-magnified SEM images of star-shaped Au NPs taken at different angles of viewing

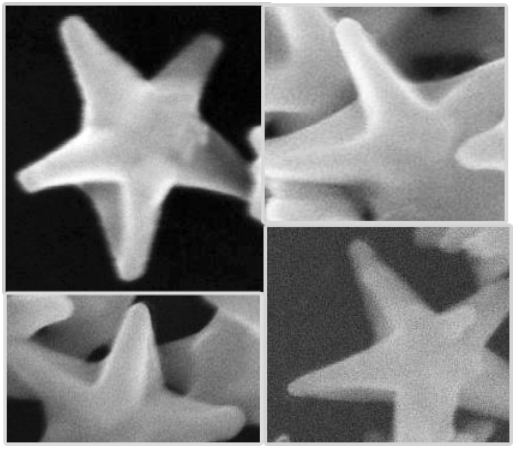

Figure S2. High-magnified pictures obtained from different angles of view.

3. Structure analysis.

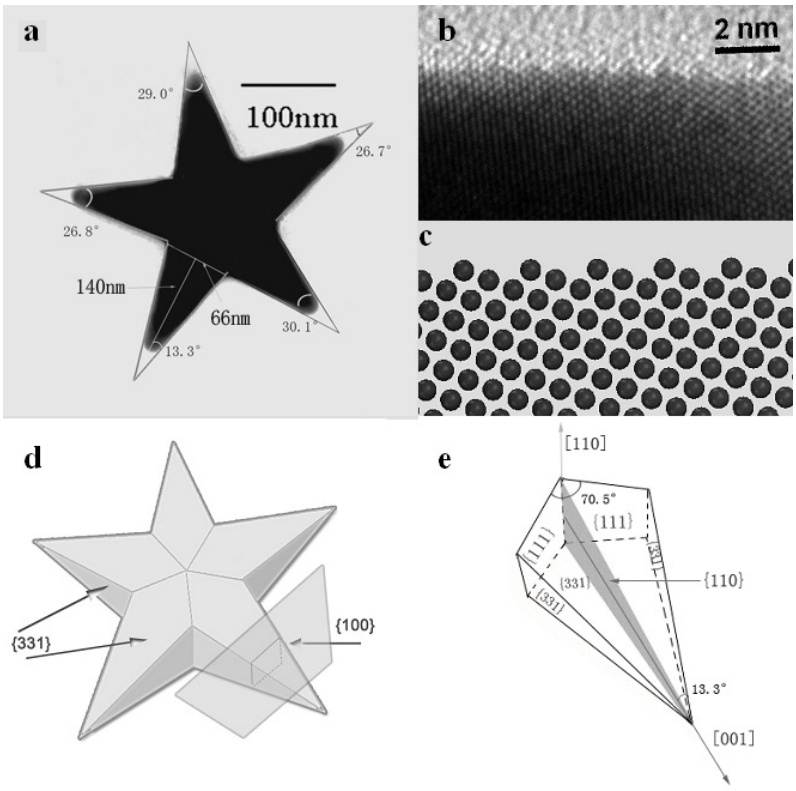

Figure S3. a) TEM image of the star-shaped NPs obtained from [110]-zone axis. b) HRTEM image recorded along [110] to reveal surface atomic steps in the areas made of (331) facets. c) Atomic model of Au {331} plane with a high density of stepped surface atoms. d) The 3D model of the star-shaped NPs. e) Schematic sketch of a single crystal.

Gold is a face-centered cubic (fcc) metal. For a five-fold twinned gold NP, the twinned planes of a single crystal are {111}, bound zone axis is [110]. From the structure analysis we can figure out that, the plane which along the [110] zone axis divides the single crystal into two equal parts is a {110} plane. The cross section of the branch as shown in Figure S3 (d) will be {100}. From Figure S3 (a) we can measure that the height of the branch is about 140 nm, and width of the

button is about 66 nm, then through calculation we know that each tip's interfacial angle is about 26.6°, and half of it is 13.3°. So the side planes of the branch have an interfacial angle of 13.3° with {110} plane. That is in good agreement with theoretical value of 13.3° corresponding to {331}. The atomic arrangement of the Au (331) surface (Figure S3 c) is periodically composed of two (110) terraces and one (111) step. The atom steps have been directly captured in an HRTEM image as shown in Figure S3 (b). The picture is captured in high vacuum, which may cause the relaxation[S1] and reconstruction of the surface atoms, so the atoms do not located as the model shown precisely. Based on the SEM images and combined with the structure analysis we can presume that each branch of the particle is a tetragonal micro-pyramid; the four facets of it are in fact the same, all bare facets are (331) and vicinal high-index facets. Thus we put forward a 3D model of these NPs and a Schematic sketch of a single crystal as shown in Figure S3 (d) and (e).

Table 1 lists the theoretical interfacial angles of pentagonal symmetry NP bounded by different facets. The value of 22.8° is the theoretical value of {772} planes, and 31.6° corresponds to the {552} planes. We measured carefully the angle of tips of pentagonal symmetry NPs for a few particles and the experimental data are presented in table 2. The average value of interfacial angles is 26.9° and the absolute deviation is 1.9°. In comparison the measured angles with the theoretical ones, we may conclude that the pentagonal symmetry NPs is bounded by (331) and vicinal high-index facets. The models of surface atomic arrangement of (331), (552), (772) planes are illustrated in Fig.S4. It can be seen that the (552) surface is made of two (331) and one (221) sub-facets, and the (772) surface is composed of four (331) and one (110) sub-facets, both of them have a high density of stepped surface atoms.

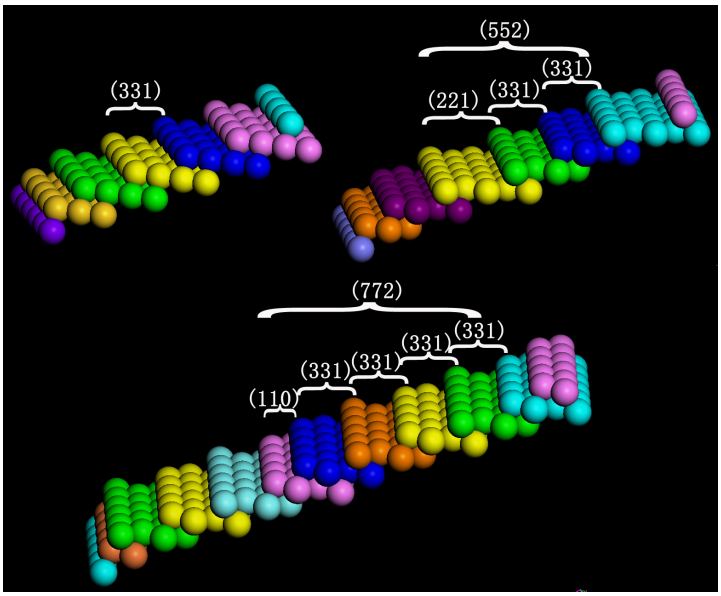

Figure S4. Atomic model of Au(331), (552), (772) planes with a high density of stepped surface atoms. The (552) surface is made of (331) and (221) sub-facets, and the (772) surface is made of (331) and (110) sub-facets.

Table 1. Theoretical interfacial angles of different facets

{hkl}	Angle with (110)	interfacial angles
{552}	15. 8°	31. 6°
{331}	13. 3°	26. 5°
{772}	11. 4°	22. 8°

Table 2. Interfacial angles of tips from more pentagonal symmetry NPs

Particle #	θ1	θ2	θ3	θ4	θ5
1	26.6°	26.7°	26.8°	29.0°	30.1°
2	24.7°	29.1°	29.5°	30.5°	30.9°
3	24.4°	25.7°	26.4°	29.8°	
4	23.9°	25.1°	25.9°	25.9°	29.1°
5	22.8°	23.5°	25.5°	26.1°	26.6°
Summary	average: 26.9°		absolute deviation:1.9°		

And Figure S5 is the high-magnified SEM image of nanothorns. From the morphology of the thorns, we can conclude that the surface facets of the thorns might have both high-index and low-index facets.

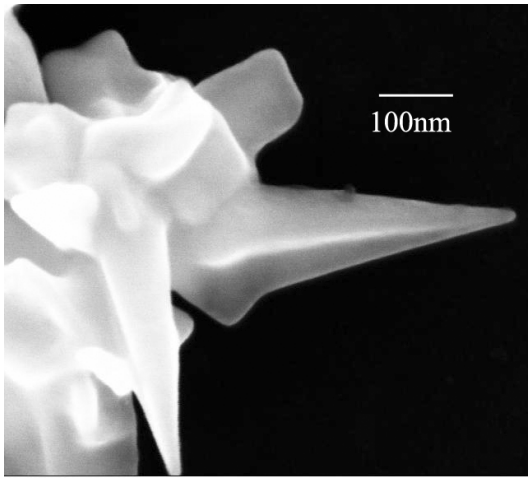

Figure S5. High-magnified SEM images of nanothorns

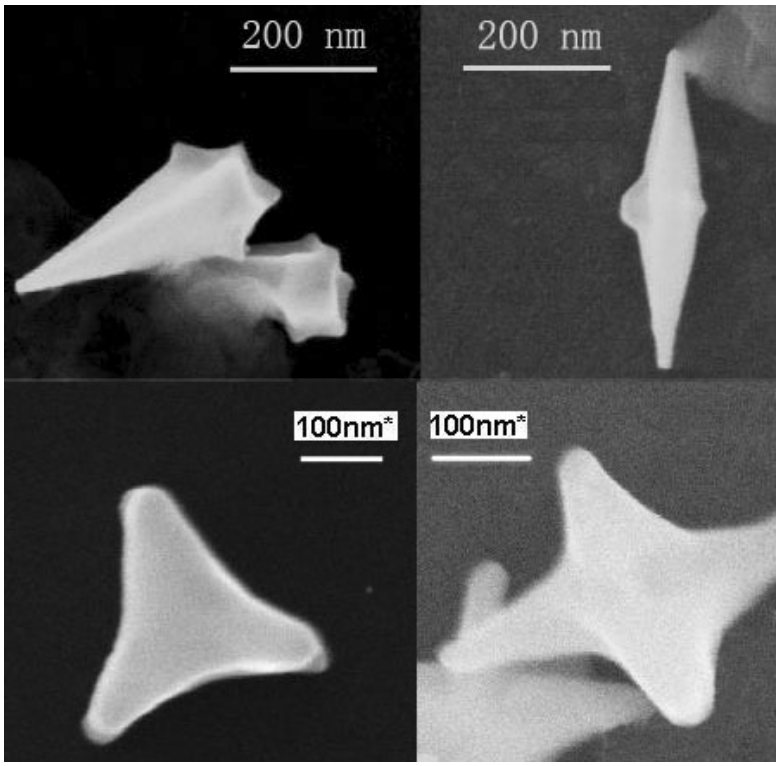

Figure S6. High-magnified SEM images of 1, 2, 3, or 4 branched gold NPs.

4. Experimental details.

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (about 25 ºC). The count electrode was a Pt foil and reference electrode was a saturated calomel electrode (SCE). Glassy carbon electrodes (ϕ 5 mm) were first polished with a 5, 1 and 0.3 μ m alumina slurries successively and then washed ultrasonically in Milli-Q water. The prepared NPs were centrifuged by adding equal volume of water to the DES. Then washed with water and centrifuged again. The prepared gold NPs were dispersed in Milli-Q water to obtain a uniform suspension by sonication. After transferred onto the glassy carbon substrate, the coated electrode was dried in air. Before the electroreduction of H_2O_2 experiment, all prepared electrodes have been cleaned up by potential sweeping 15 cycles in 0.1M H_2SO_4 solution with the upper potential of 1.4 V and the lower potential of -0.20 V. The concentration of phosphate buffered solution(PBS) is 0.1 M, and the pH value is about 7. The electroactive surface area of gold NPs working electrodes was determined from the charge needed to form a gold surface oxide monolayer according to the oxygen adsorption measurement method, and using the reported value of 400 C/cm^2 for a clean Au electrode.[S2]

The DES used in this communication was prepared according to the paper of ref.[S3] In brief, choline chloride (ChCl) (Acros 99%) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Urea (sinopharm chemical reagent) was recrystallized in Milli-Q water. Choline chloride and urea was mixed at the mole ratio of 1:2. The eutectic mixtures were thus formed by stirring the two components at 100 °C until a homogeneous colorless liquid was formed, and then dried in vacuum at 80 °C until it almost have no water to meet our need in the following synthesis.

Supporting references:

[S1] Y. Ding, Y. Gao, Z. L. Wang, N. Tian, Z.Y. Zhou, S.G. Sun, Appl. Phys. Lett. **2007**, *91*, 121901.
[S2] S. Trasatti, O. A. Petrii, *Pure Appl. Chem.* **1991**, *63*, 711-734.
[S3] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and P. Shikotra, Inorg. Chem. **2005**, *44*, 6497-6499.