Electronic Supplementary Material (ESI) for CrystEngComm.


Supporting Information

# Shape transformations of Pt nanocrystals enclosed with high-index facets and low-index facets

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## Experimental Procedures

### Chemicals and Reagents

Glassy-carbon electrode (GC, 99.99%, Φ = 6 mm) was purchased from Takai Carbon Co., LTD. (Tokyo, Japan). $H_2PtCl_6$ (99.99%), $Na_2SO_4$ (99.9955%) was purchased from Alfa Aesar. Sulfuric acid (EMSURE® ACS) was purchased from Merck. All chemicals were used as received. The solutions were prepared from super pure water (18 MΩcm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.).

### Prepare different Pt NCs

Electrochemical preparation of Pt nanocrystals was carried out in a standard three-electrode cell at room temperature. The working electrode was a polished glassy carbon electrode. Prior to experiment, the GC electrode was mechanically polished using sequentially alumina powder of size 5, 1, 0.3 μm. Then it was cleaned in an ultrasonic bath. The counter electrode was a Pt foil and reference electrode was a saturated calomel electrode (SCE). All potentials reported in this paper are referred to the SCE scale. Electrode potential was controlled by PAR 263A potentiostat/galvanostat (EG&G) via a home-developed software that can realize arbitrary potential waveform function as required.

The starting Pt NCs were electrodeposited on the GC electrode through a programmed potential steps in Pt plating solution. In detail, the potential was maintained at 1.20 V for 2.0 s to clean the electrode surface, and then stepped to −0.30 V and held for 140 ms to create Pt crystal nuclei. The growth of the Pt crystal nuclei into NCs was mediated by electrochemical SWP with a certain frequency ($f$) for a certain growth time ($t_g$). By changing the potential and frequency of the SWP, and the solutions, the starting Pt NCs with different shapes were obtained.

(i) For preparation of THH Pt NCs, the plating solution was 2 mM $H_2PtCl_6$ + 0.1 M $H_2SO_4$. The $E_L$, $E_U$, $f$, and $t_g$ were 0.04 V, 1.06 V, 100 Hz, and 20 min, respectively.

(ii) For {111}-faceted octahedral Pt NCs, the plating solution was 2 mM $H_2PtCl_6$ + 0.1 M $Na_2SO_4$. The $E_L$, $E_U$, $f$, and $t_g$ were 0.10 V, 1.00 V, 100 Hz, and 7 min, respectively.

(iii) The {100}-faceted cubic Pt NCs with smooth surface were difficult to synthesized by direct SWP electrodeposition, so they were obtained through the shape transformation from THH Pt NCs by SWP ($E_L$ = 0.15 V, $E_U$ = 1.20 V, $f$ = 100 Hz) treatment in 0.1 M $H_2SO_4$ for 20 min.

### Characterization

The morphologies of Pt NCs were acquired by using a scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEM-2100 at 200 kV)

**Supplementary Figures and Tables**

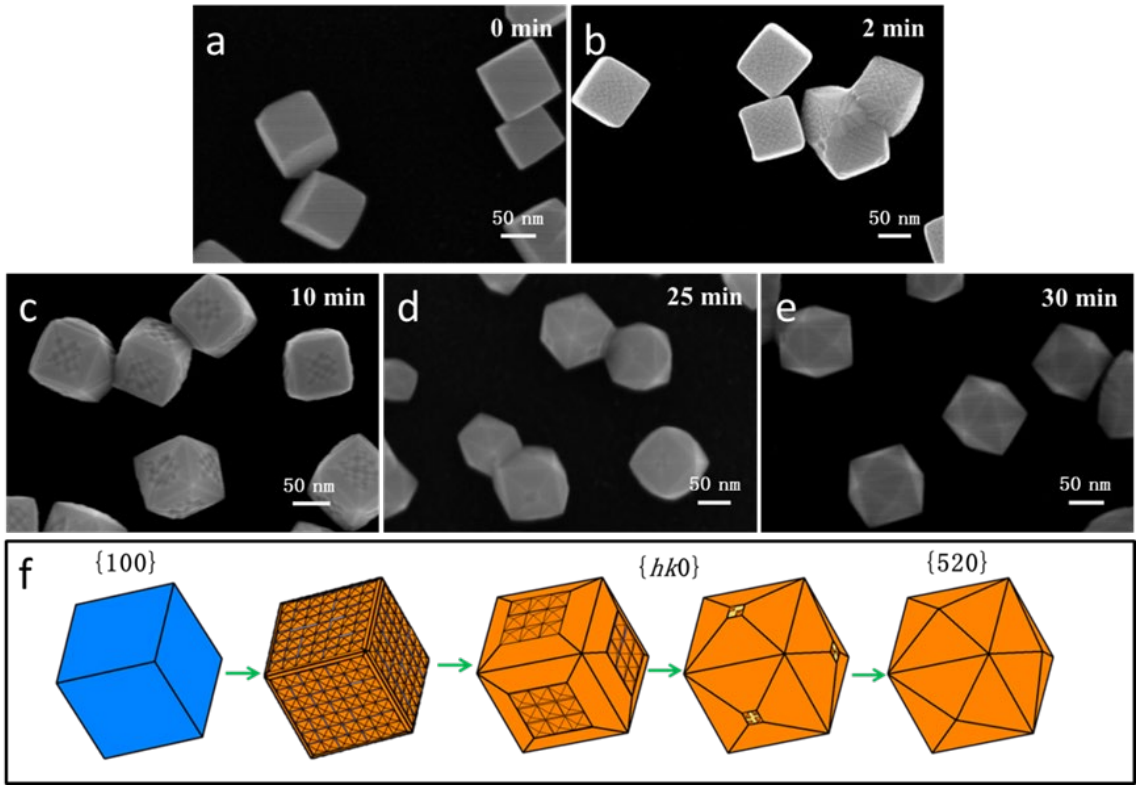



**Figure S1.** Low-magnification SEM images of the transformation from cube to THH at different time of SWP ($E_L$ = 0 V, $E_U$ = 1.15 V) treatment in 0.1 M $H_2SO_4$. (a) 0 min; (b) 2 min; (c) 10 min; (d) 25 min, (e) 30 min. (f) Illustration of shape transformation process from cube to THH.

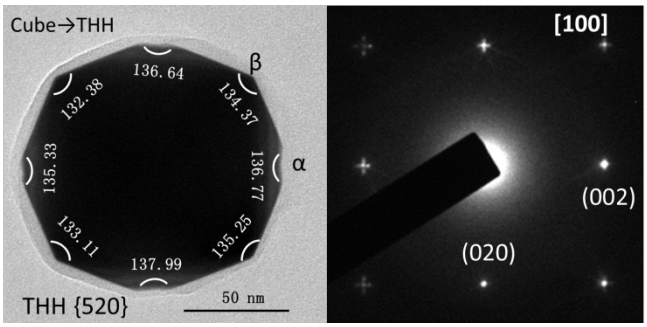



**Figure S2.** TEM and the corresponding SAED pattern of an obtained THH Pt nanocrystal transformed from cube. The surface facets were determined to be {520} by comparing the average value of the interfacial angles $\bar{\alpha}$ = 136.7°, $\bar{\beta}$ = 133.7° with the theoretical values.

**Table S1.** Projections and geometrical parameters of THH and TPH nanocrystals.

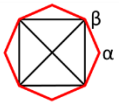
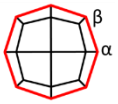
| Polyhedral shape | Miller index | Projection direction | Projection | Character angel / degree |
|---|---|---|---|---|
| THH | {*hk*0} (*h*>*k*>0) | [001] |   | α=2arctan($\frac{h}{k}$) β=270-α |
| TPH | {*hkk*} (*h*>*k*>0) | [001] |   | α=2arctan($\frac{h}{k}$) β=270-α |

**Table S2.** Theoretical values of the interfacial angles of different facets on THH and TPH.

| Angle {*hk*0} | α | β | Angle {*hkk*} | α | β |
|---|---|---|---|---|---|
| {210} | 126.87° | 143.13° | {211} | 126.87° | 143.13° |
| {730} | 133.60° | 136.40° | {733} | 133.60° | 136.40° |
| {520} | 136.40° | 133.60° | {522} | 136.40° | 133.60° |
| {830} | 138.89° | 131.11° | {14 5 5} | 140.69° | 129.31° |
| {310} | 143.13° | 126.87° | {311} | 143.13° | 126.87° |

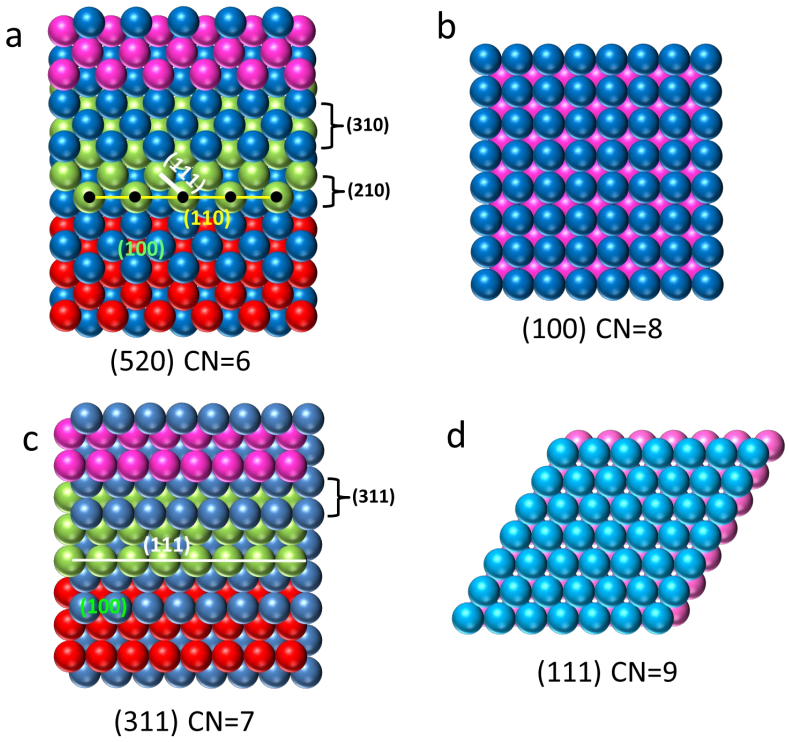



**Figure S3.** Atomic models of different Pt facets. (a) Atomic models of Pt {520} facet. This surface essentially consists of (100) as terrace and (110) as step. Well, the outermost atoms on the surface are all kink atoms (marked by black dot) with a CN of 6. (b) Atomic models of Pt {100} facet with a CN of 8. (c) Atomic models of Pt {311} facet. This surface essentially consists of (100) as terrace and (111) as step. Well, the outermost atoms on the surface are all step atoms (marked by white line) with a CN of 7. (d) Atomic models of Pt {111} facet with a CN of 9.

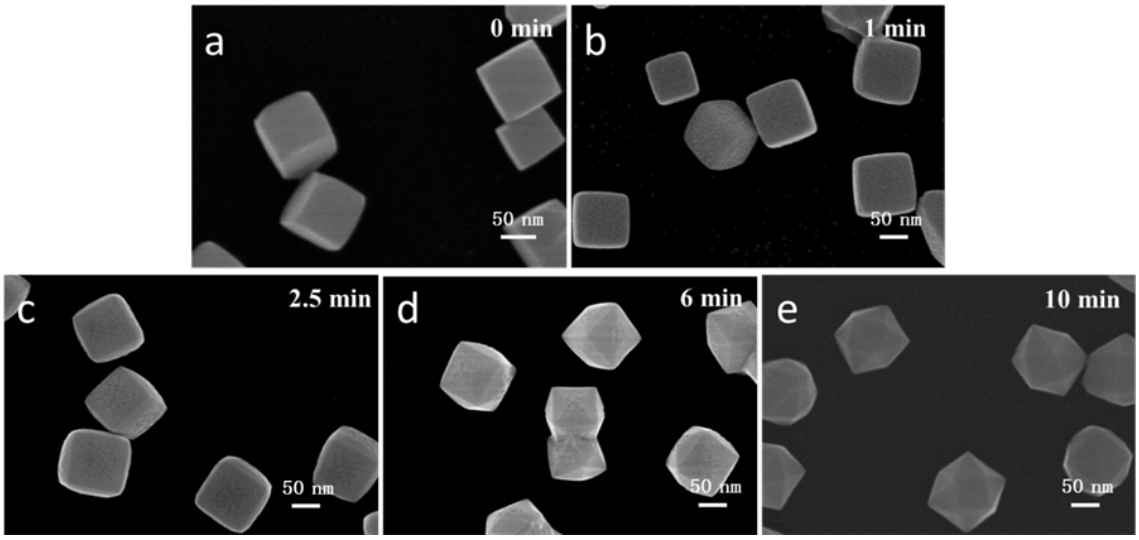



**Figure S4.** Low-magnification SEM images of the transformation from cube to THH at different time of SWP ($E_L$ = 0 V, $E_U$ = 1.15 V) treatment in 2 mM $H_2PtCl_6$ + 0.1 M $H_2SO_4$. (a) 0 min; (b) 1 min; (c) 2.5 min; (d) 6 min, (E) 10 min.

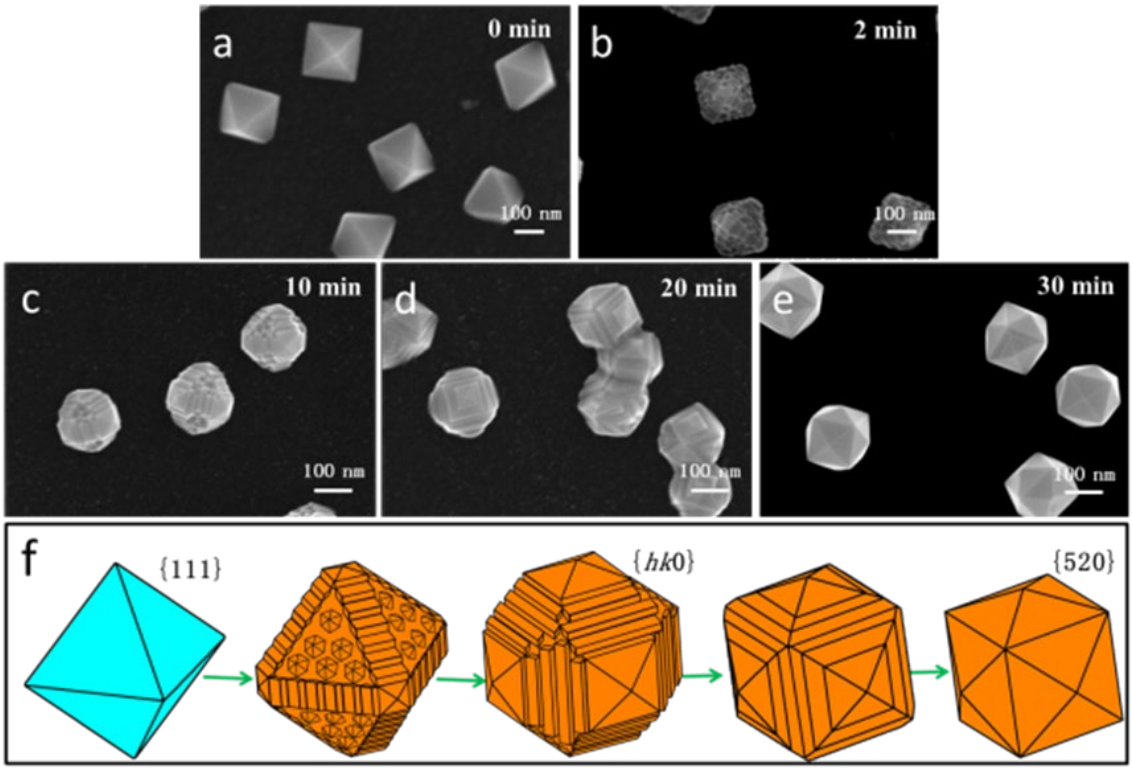



**Figure S5.** Low-magnification SEM images of the transformation from octahedron to THH at different time of SWP ($E_L$ = 0 V, $E_U$ = 1.15 V) treatment in 0.002 mM $H_2PtCl_6$ + 0.1 M $H_2SO_4$. (a) 0 min; (b) 2 min; (c) 10 min; (d) 20 min; (e) 30 min. (f) Illustration of shape transformation process from octahedron to THH.

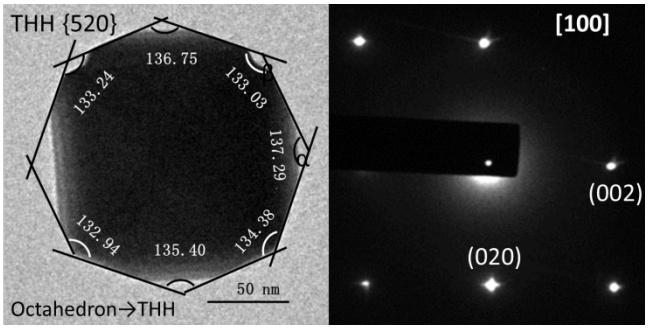



**Figure S6.** TEM and the corresponding SAED pattern of an obtained THH Pt nanocrystal transformed from octahedron. The surface facets were determined to be {520} by comparing the average value of the interfacial angles $\bar{\alpha}$ = 136.8°, $\bar{\beta}$ =133.4° with the theoretical values.

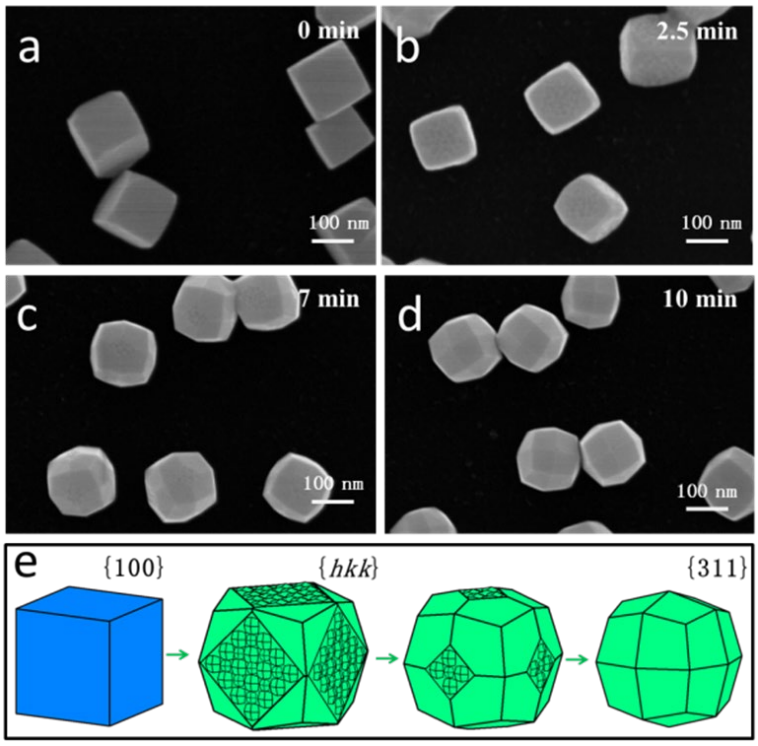



**Figure S7.** Low-magnification SEM images of the transformation from cube to TPH at different time of SWP ($E_L$ = 0.08 V, $E_U$ = 1.18 V) treatment in 2 mM $H_2PtCl_6$ + 0.1 M $H_2SO_4$. (a) 0 min; (b) 2.5 min; (c) 7 min; (d) 10 min. (e) Illustration of shape transformation process from cube to TPH.

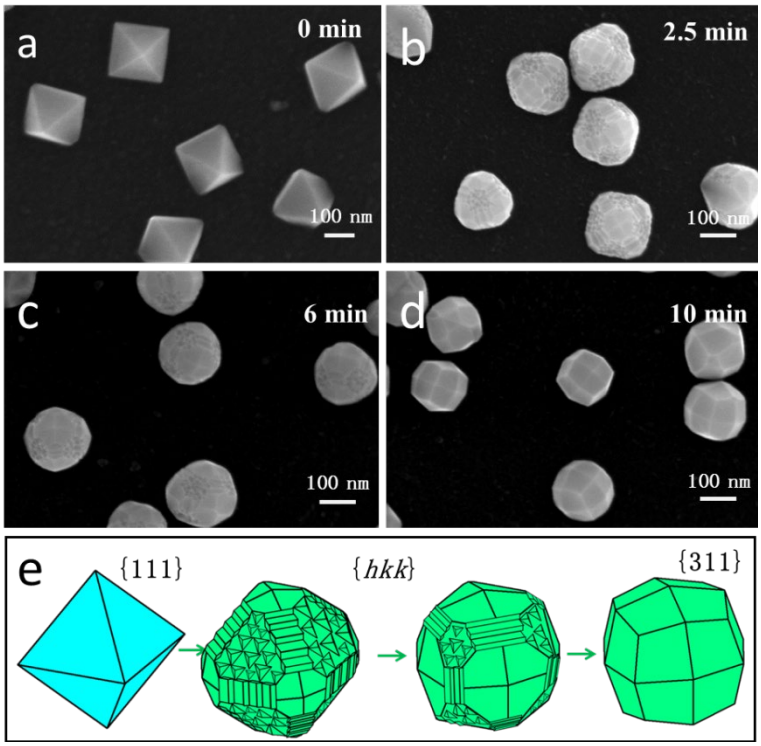



**Figure S8.** Low-magnification SEM images of the transformation from octahedron to TPH at different time of SWP ($E_L$ = 0.08 V, $E_U$ = 1.18 V) treatment in 2 mM $H_2PtCl_6$ + 0.1 M $H_2SO_4$. (a) 0 min; (b) 2.5 min; (c) 6 min; (d) 10 min. (e) Illustration of shape transformation process from octahedron to TPH.

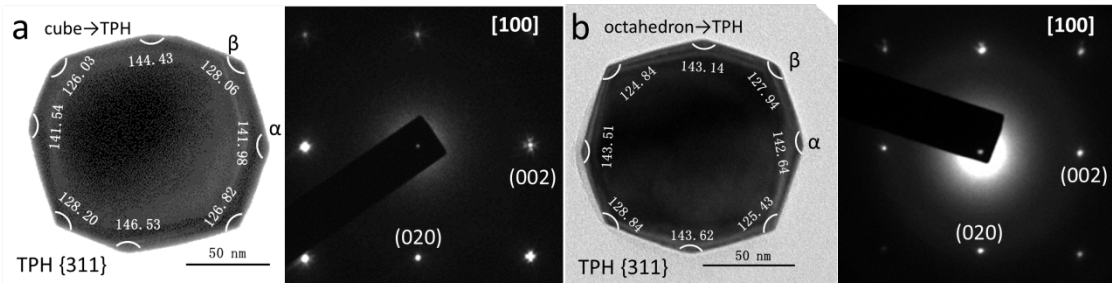



**Figure S9.** TEM and the corresponding SAED pattern of the obtained TPH Pt nanocrystals. The surface facets were determined by comparing the average value of the interfacial angles of α, β with the theoretical ones. (a) {311}-faceted TPH from cube, $\bar{\alpha}$ = 143.6º, $\bar{\beta}$ =127.3º; (b) {311}-faceted TPH from octahedron, $\bar{\alpha}$ = 143.2º, $\bar{\beta}$ =126.7º.

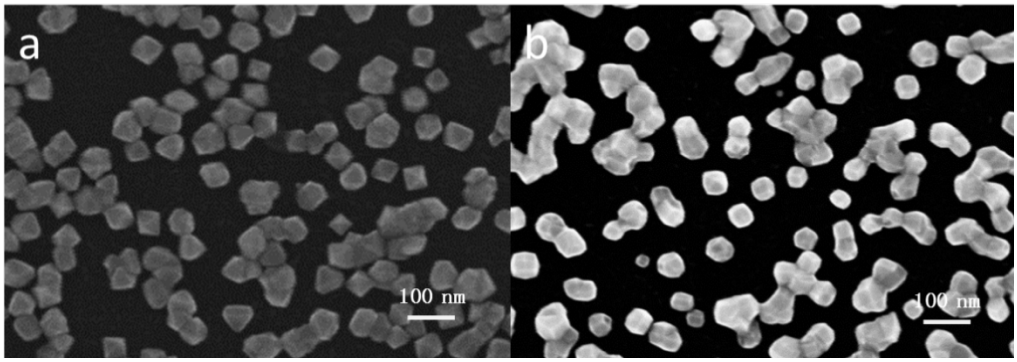



**Figure S10.** (a) SEM image of the Pt octahedron about 50 nm. (b) SEM image of the TPH Pt NCs transformed from octahedron in 50 μM $H_2PtCl_6$ + 0.1 M $H_2SO_4$ solution.

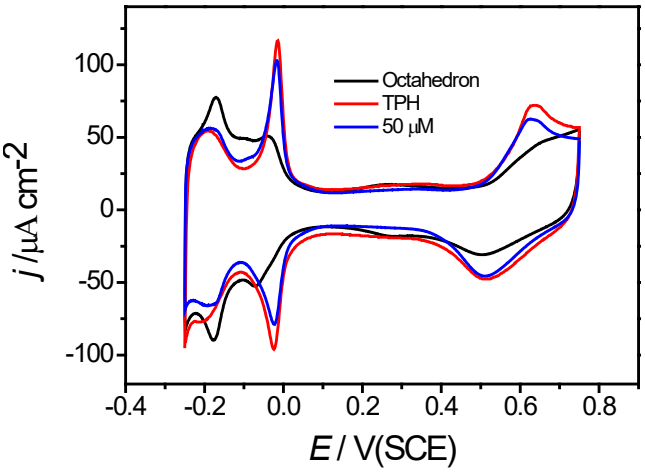



**Figure S11.** Comparison of cyclic voltammograms of Pt octahedron, TPH, Pt TPH NCs transformed in 50 μM $H_2PtCl_6$ + 0.1 M $H_2SO_4$ (marked as 50 μM). Solution: 0.1 M $H_2SO_4$, scan rate: 50 mV $s^{-1}$.

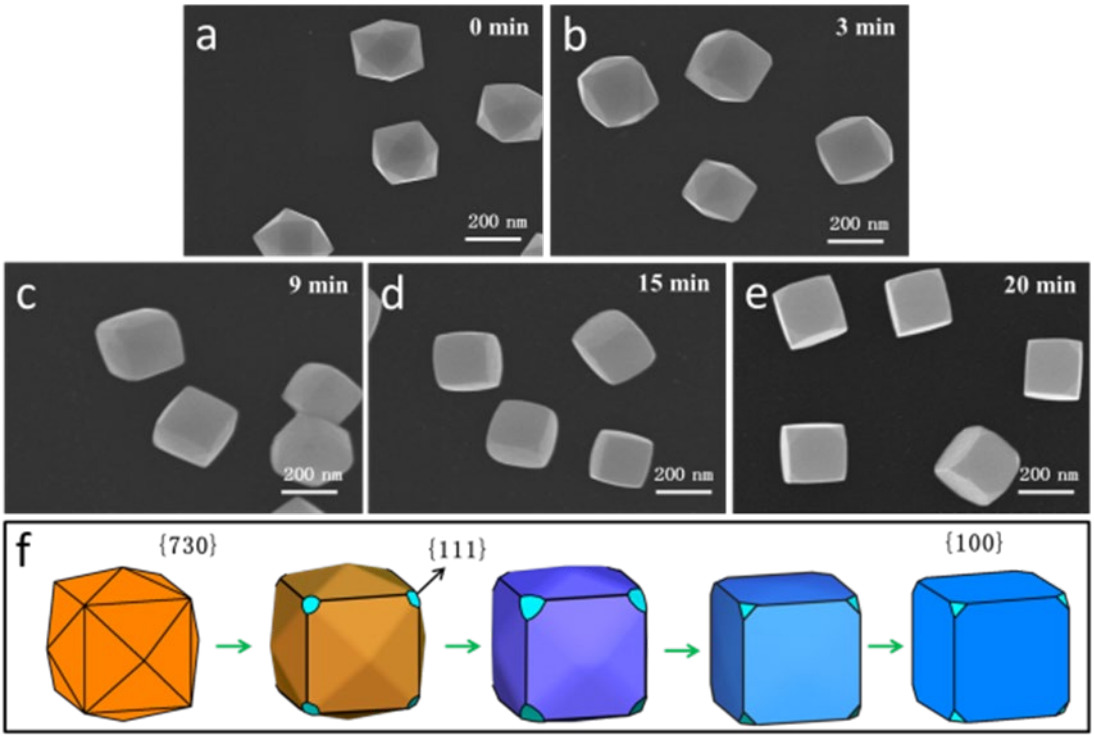



**Figure S12.** Transformation of Pt NCs from THH to cube at different time of SWP ($E_L$ = 0.15 V, $E_U$ = 1.20 V) treatment in 0.1 M $H_2SO_4$. (a) 0 min; (b) 3 min; (c) 9 min; (d) 15 min; (e) 20 min.

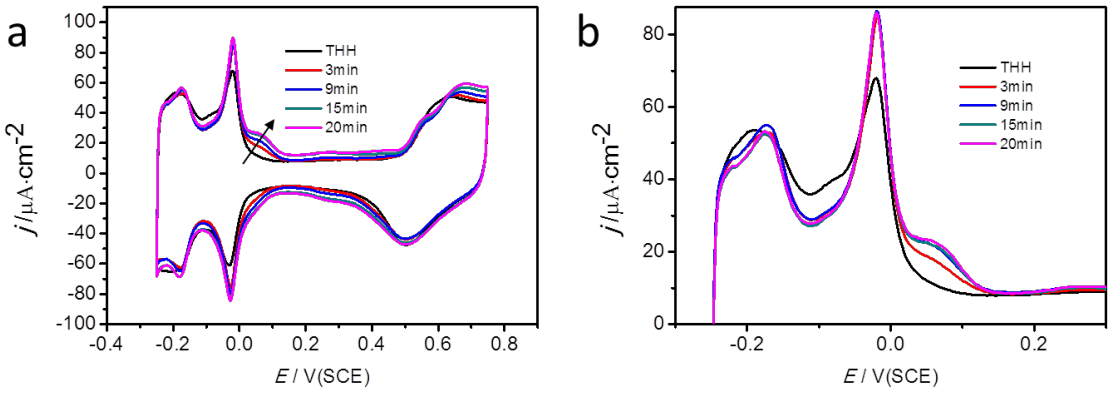



**Figure S13.** (a) CVs of Pt NCs during transformation from THH to cube after different SWP treatment time. (b) Enlarged and baseline-corrected CVs of hydrogen desorption region. Solution: 0.1 M $H_2SO_4$, scan rate: 50 mV $s^{-1}$.

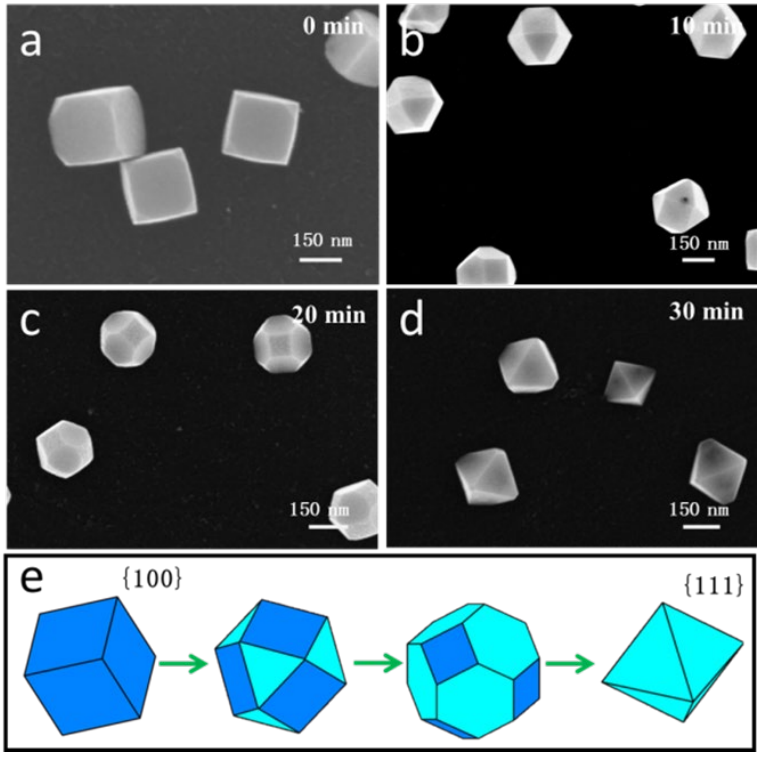



**Figure S14.** Low-magnification SEM images of the transformation from cube to octahedron at different time of SWP ($E_L$ = 0.15 V, $E_U$ = 1.20 V) treatment in 0.1 M $H_2SO_4$. The solution was refreshed after every 10 min to minimize the accumulation of Pt ions in solution through the dissolution of Pt NCs. (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min. (e) Illustration of shape transformation process from cube to octahedron.

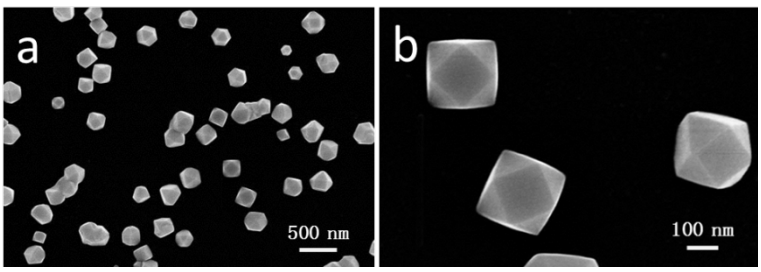



**Figure S15.** Only cubooctahedron can be obtained without renewing the 0.1 M $H_2SO_4$ solution in the shape transformation from cube to octahedron.

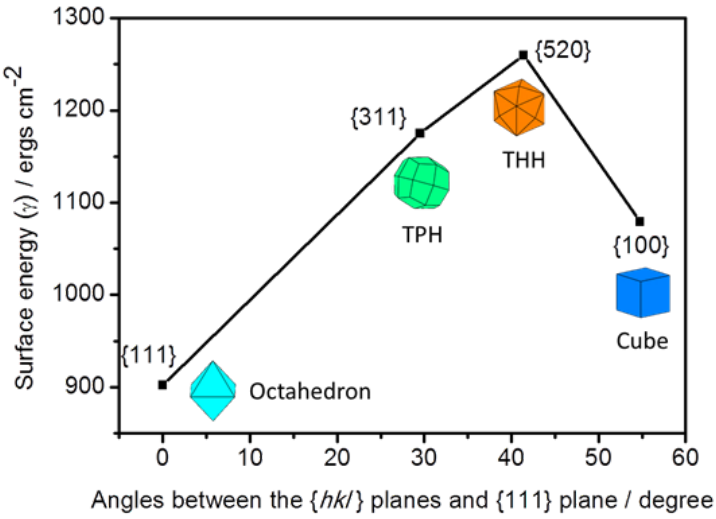



**Figure S16.** Comparison of surface energy of different Pt {*hkl*} facets and the corresponding shape.