Electronic Supplementary Material (ESI) for Chemical Communications.

Support Information

Fluorescence Enhancement Mediated by High-index-faceted Pt Nanoparticles: Roles of Crystal Structure

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Materials and methods

1. Reagents, solutions, materials and apparatus

H_2PtCl_6 (99.99%) and Rhodamine B isothiocyanate were purchased from Sigma-Aldrich. Sulfuric acid (98%) were purchased from Alfa Aesar. All chemicals were used as received. The solutions were prepared from super pure water (18 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.).

Electrochemical preparation and characterization were carried out in a standard three-electrode cell working with a 263A potentiostat/galvanostat (EG&G). Counter electrode was a Pt foil and reference electrode was a saturated calomel electrode (SCE). All potentials were quoted versus the SCE scale. The highly ordered pyrolytic graphite (HOPG) was purchased from SPI Supplies, West Chester, PA 19381 U.S.A.

The morphology and structure of the obtained Pt nanocrystals were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, F20).

2. Experimental Section

Electrochemical preparation four shape of Pt nanocrystals and characterization

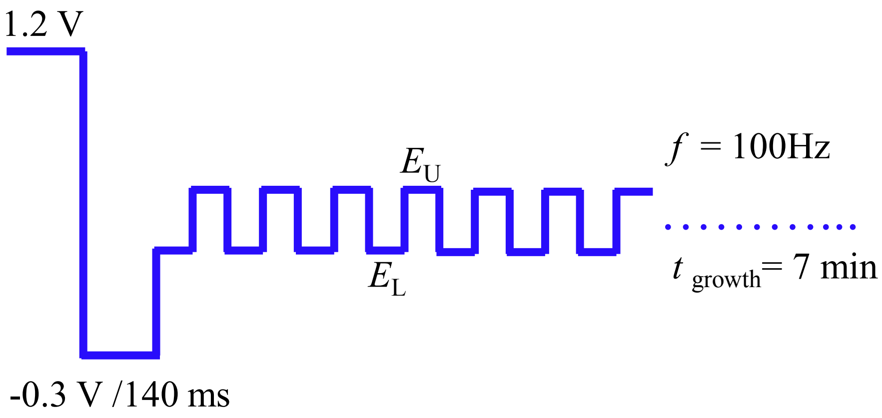


Figure S1. Illustration of the programmed electrodeposition method for preparation of Pt nanocrystals.

Pt nanocrystals were electrodeposited on the HOPG electrode by a programmed potential step as shown in figure S1. The octahedron nanocrystals were electrodeposited in the solution of 2 mM H_2PtCl_6, without adding any supporting electrolyte. The lower limit potential (E_L) of the SWP was 0.09 V (SCE), and the upper limit potential (E_U) was 0.96 V. Other three samples were electrodeposited in the solution of 2 mM H_2PtCl_6 + 0.1 M H_2SO_4 using SWP, the E_L for preparation of sphere, THH, and TPH is 0.2, 0.12, and 0.14 V, respectively; and the corresponding E_U is 0.55, 1.05, and 1.05 V, respectively.

For nanoparticles with smaller size, the nucleation time is longer, the growth time is 7 min. The nucleation time of preparation of ~100 nm and ~150 nm particles is 0.23 s and 0.17 s, respectively.

Quantity of molecules absorbed to the metallic nanoparticles.

To test the quantity of molecules adsorbed to the nanoparticles, we utilized mercaptoethanol to replace the adsorbed dyes and the residual solution was collected on the glass for fluorescence test. The amount of replaced dyes on glass were tested by the fluorescence intensity. The area of nanoparticles was measured through hydrogen area by cyclic voltammetry in 0.1M H_2SO_4 solution.

FDTD simulation of four shape of Pt nanocrystals

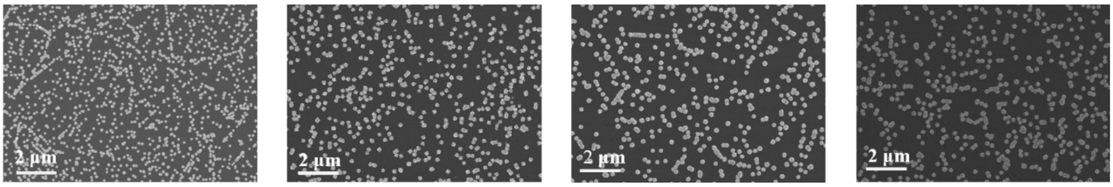
The EM was calculated using three-dimensional finite difference time domain (FDTD) method. In the FDTD calculation, both space and time are divided into discrete segments. Space is segmented into box-shaped “cells” with the electric fields located on the edges of the box and the magnetic fields positioned on the faces. Each E component is surrounded by four H components, and each H component is surrounded by four E components. This orientation of the fields is known as the “Yee cell” in FDTD simulation. Maxwell's equations are discrete in both time and space domain in order to find the E and H fields at different positions and different time steps.

Table S1 Theoretical interfacial angles of α and β of tetrahexahedral nanocrystals bounded by different {*hk*0} high-index facets.

Miller Indices {*hk*0}	{7 3 0}	{8 3 0}	{3 1 0}	{10 3 0}
Angle α /°	133.6	138.9	143.1	146.6
Angle β /°	136.4	131.1	126.9	123.4

Table S2 Theoretical interfacial angles of α and β of trapezohedral nanocrystals bounded by different {*hkk*} high-index facets.

Miller Indices {*hkk*}	{2 1 1}	{7 3 3}	{5 2 2}	{3 1 1}
Angle α /°	126.9	133.6	136.4	143.2
Angle β /°	143.1	136.4	133.6	126.8



Sphere 21.2% Octahedron 19.3% THH 18.5% TPH 18.8%

Figure S2. Low magnification SEM of four difference Pt nanocrystals and corresponding particle distribution density.

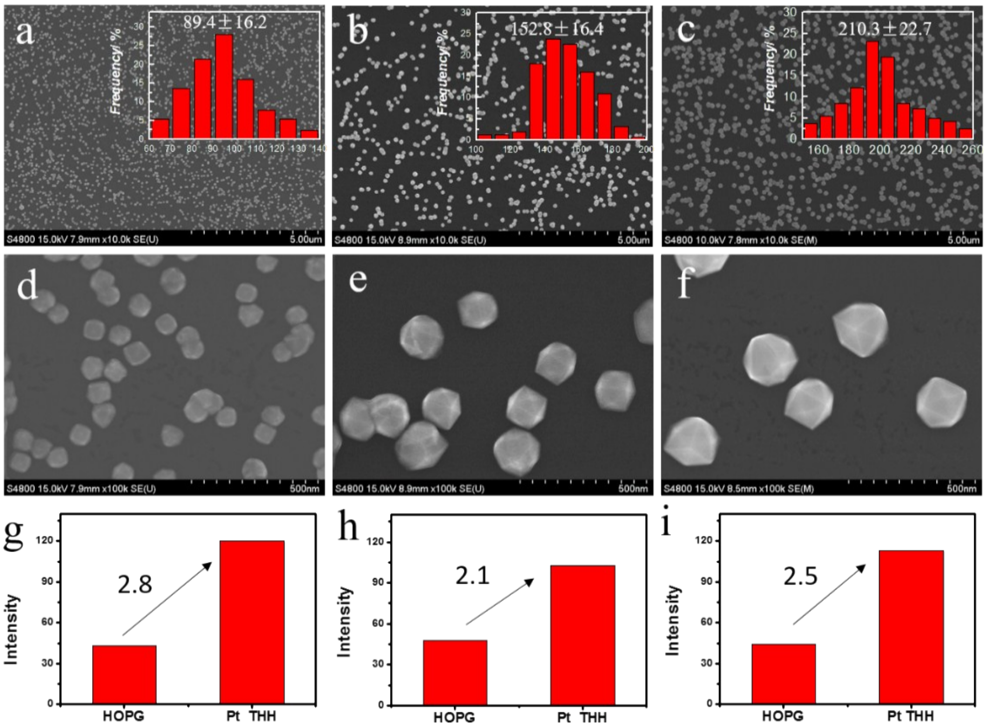


Figure S3. SEM images of Pt THH NCs with different size and the corresponding fluorescence intensity of Rhodamine B isothiocyanate adsorbed on the three Pt samples.

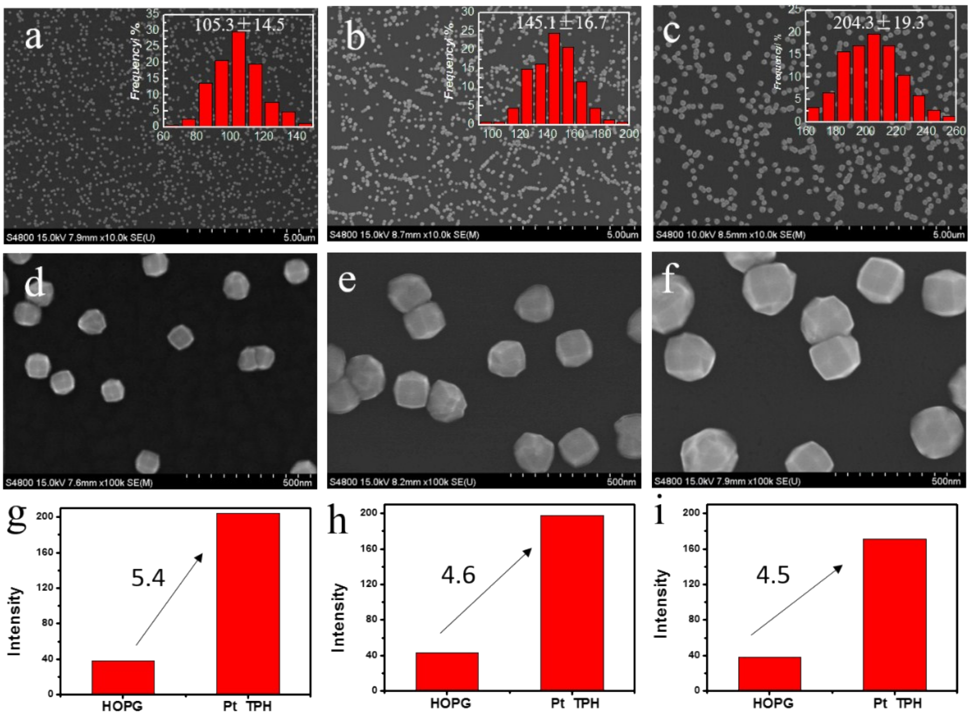


Figure S4. SEM images of Pt TPH NCs with different size and the corresponding fluorescence intensity of Rhodamine B isothiocyanate adsorbed on the three Pt samples.

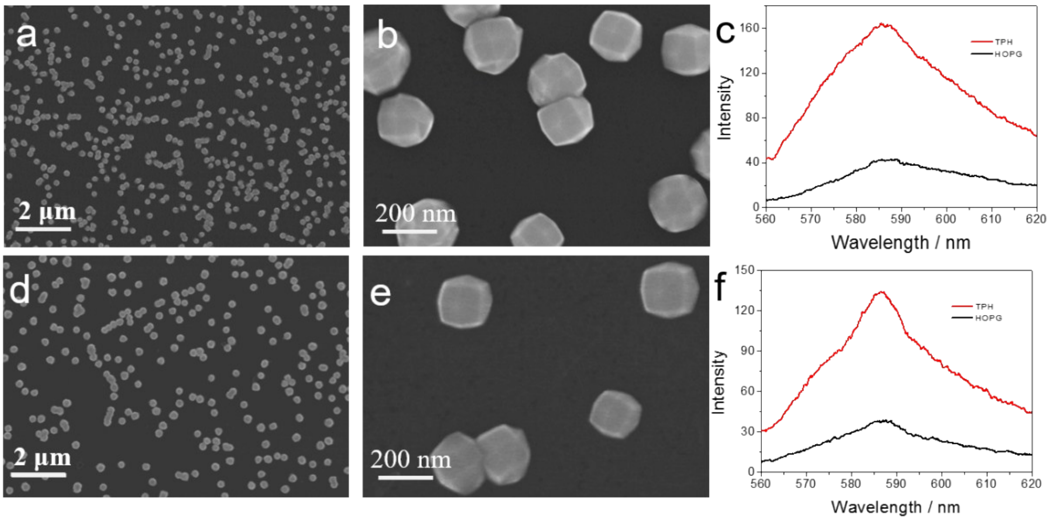


Figure S5. SEM images of Pt TPH with different concentration and the corresponding fluorescence intensity of Rhodamine B isothiocyanate adsorbed on the Pt samples.

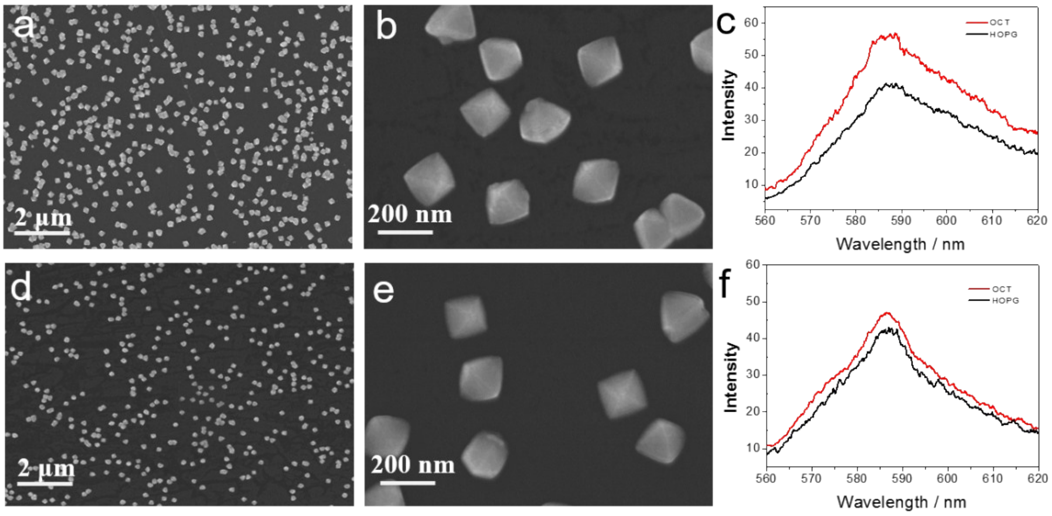


Figure S6. SEM images of Pt octahedra with different density and the corresponding fluorescence intensity of Rhodamine B isothiocyanate adsorbed on the Pt samples.

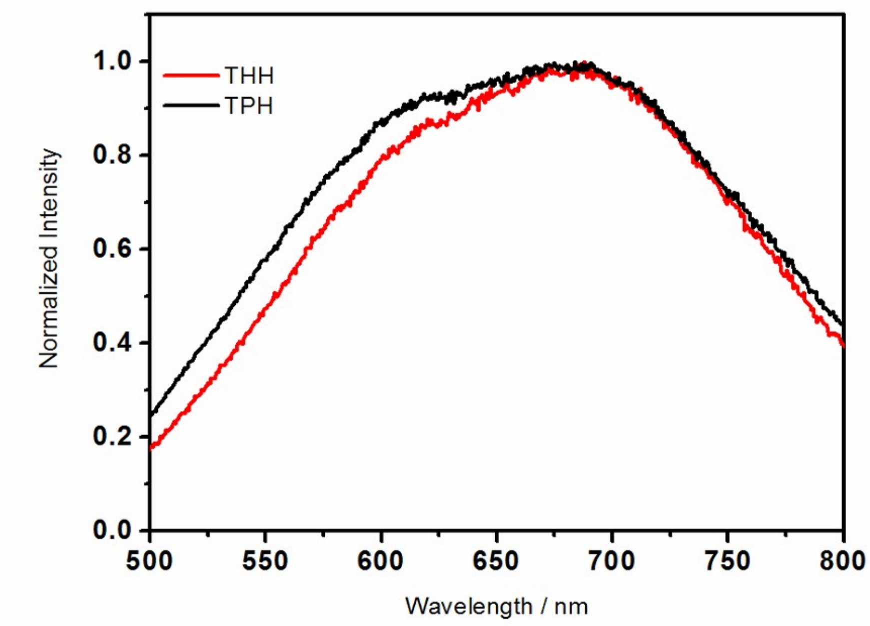


Figure S7. Dark field spectra of Pt THH and TPH nanocrystals.

Dark-field microscopy (Leica DM 2500M, 10×objective, NA=0.25) was used to acquire light-scattering of the fabricated nanoparticles. The large overlap between scattering spectra and fluorescence excitation and emission demonstrate the coupling capacity of nanoparticles

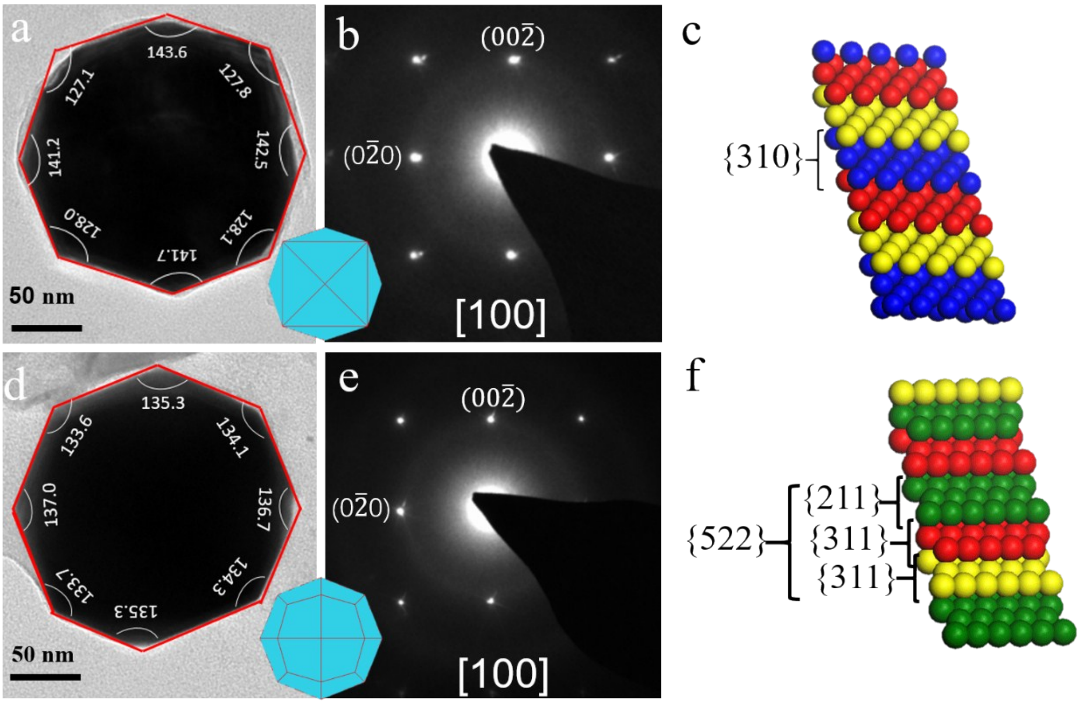
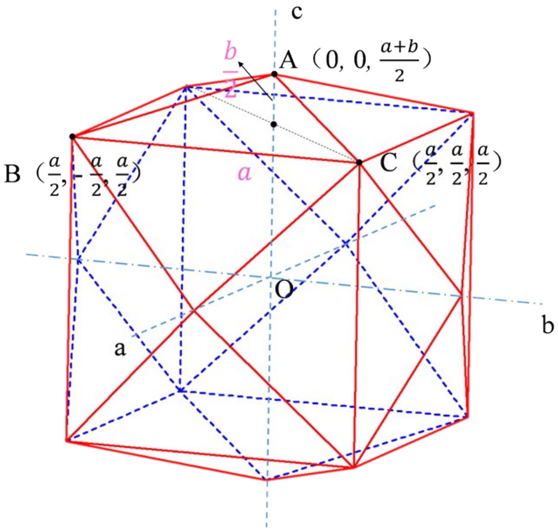


Figure S8. Characterization of THH and TPH: (a, d) TEM image; (b, e) SAED pattern along [001] direction (the insect is the model image); (c, f) atomic arrangement of {310} and {522} facets.



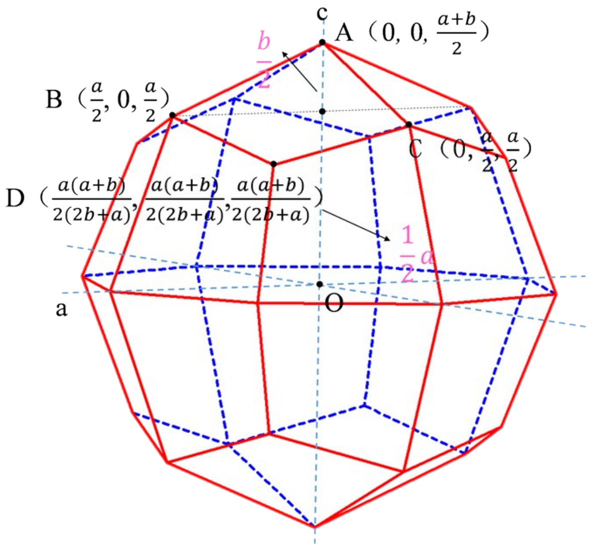
Edge length: $\frac{b}{2}$

Pyramidal height: a

$$m = \frac{b}{a} = \frac{k}{h}$$

$$S=\frac{1}{2}a\frac{\sqrt{a^2+b^2}}{2}\times 24=6a\sqrt{a^2+b^2}=6a^2\sqrt{1+m^2}$$

Figure S9. Volume of THH as a function of edge length and Miller index.



Edge length: $\frac{b}{2}$

Pyramidal height: a

$$m = \frac{b}{a} = \frac{k}{h}$$

$$\begin{aligned}S&=\frac{1}{2}\times BC\times AD\times 24\\&=\frac{1}{2}\times\frac{\sqrt{2}}{2}a\times\frac{\sqrt{2}}{2}\times\frac{a+b}{2b+a}\times\sqrt{a^2+2b^2}\times 24\\&=6a\times\frac{a+b}{2b+a}\times\sqrt{a^2+2b^2}\\&=6a^2\times\frac{1+m}{2m+1}\times\sqrt{1+2m^2}\end{aligned}$$

Figure S10. Volume of TPH as a function of edge length and Miller index.

The size of the particle is about 200 nm

Then aa + b =200 nm

For the TPH {522} particle, a=$\frac{1000}{7}$nm, then S=1.1×10^5 nm^2

For the THH {310} particle, a=150 nm, then S=1.4×10^5 nm^2

The step numbers on one particle is 7.5×10^5 (1.1×10^5nm$^2\times6.8\times10^{14}$cm^{-2}) and 5.9×10^5 (1.4×10^5 nm$^2\times4.2\times10^{14}$ cm^{-2}) for TPH and THH, respectively.