

Electronic Supplementary Information

Morphology Led High Dispersion of Pt Icosahedral Nanocrystals on Carbon Nanotubes for Enhanced Electro-catalytic Activity and Stability

Guifen Du,^a Jiawei Zhang,^a Qiaoli Chen,^{a,b*} Qin Kuang^a and Zhaoxiong Xie^{a*}

^a State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, Fujian, China

^b College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, Zhejiang, China

Experimental section

Chemicals. Single wall carbon nanotubes (CNs) with a purity of 90% and typical lengths of 5-15 μm were purchased from the Shenzhen Nanotech Port Co. Ltd (Shenzhen China); Platinum acetylacetonate ($\text{Pt}(\text{acac})_2$) and Pt/C (20 wt. %, JM) were purchased from Alfa Aesar; N,N-dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co.Ltd (Shanghai, China). Hexadecyltrimethyl ammonium bromide (CTAB) (>99%) and hexadecyltrimethyl ammonium chloride (CTAC) (>99%) were purchased from J&K. The water used in all experiments were ultrapure ($> 18.0 \text{ M}\Omega\cdot\text{cm}$). All reagents were used as received without further purification.

Synthesis of the CPT Pt icosahedra on CNT. In the typical synthesis, $\text{Pt}(\text{acac})_2$ (4 mg), CNT (2 mg) and CTAB (30 mg) were dissolved in 12 mL DMF in a 20 mL Teflon-lined stainless-steel autoclave. The steel was then heated to 180 °C in 45 min and kept for 15 h before it was cooled to room temperature. The black product was collected by centrifugation and washed with ethanol for three times and then with water for twice.

Synthesis of the single crystal Pt cubes on CNT. In the typical synthesis, Pt(acac)₂ (4 mg), CNT (2 mg) and CTAC (25 mg) were dissolved in 12 mL DMF in a 20 mL Teflon-lined stainless-steel autoclave. The steel was then heated to 180 °C in 45 min and kept for 15 h before it was cooled to room temperature. The black product was collected by centrifugation and washed with ethanol for three times and then with water for twice.

Characterization. The morphology and structure of the as-prepared icosahedral Pt NCs and cubic Pt NCs were gained by scanning electron microscopy (SEM, Hitachi S4800) equipped with energy dispersion X-ray spectroscopy, and transmission electron microscopy (TEM, JEOL JEM 2100). All TEM samples were prepared by depositing a few drops of sample suspension dealt with fully ultrasonic dispersion in ethanol solvent on a copper coated with carbon film. The X-ray diffraction (XRD) patterns were obtained from Rigaku Ultima IV diffractometer (Cu K α , $\lambda = 1.54056 \text{ \AA}$). The amount of Pt for the electro-catalytic reactions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The X-Ray photoelectron spectroscopy (XPS) was operated by a PHI Quantum-2000 XPS system with a monochromatic aluminum anode X-ray source of K α radiation (1486.6 eV).

Electrochemical measurements. The glassy carbon electrodes (with 3 mm in diameter) were polished by polished powder (particle size: 300 nm and 50 nm) and then washed by water and alcohol for three times respectively before each electrochemical measurement. The measurements were operated on an electrochemical workstation (CHI 1030b, Shanghai Chenhua Co. China). The saturated calomel electrode (SCE) was used as reference electrode and a Pt sheet was served as the counter electrode. All the electrode potentials are quoted *versus* the SCE. The concentrations of the catalysts (Pt icosahedra, Pt cubes and Pt/C (20 wt. %)) were all 2 mg mL⁻¹. A certain amount of the prepared catalysts were transferred to the glassy carbon electrodes and dried at room temperature. Then working electrode was electrochemically cleaned by continuous cyclic voltammograms measurement at 30 °C between -0.25 V and 0.4 V at the scan rate 50 mV s⁻¹ in 0.5 M H₂SO₄ solution

until a stable CV curve was obtained. Then the electrochemically active surface area (ECSA) of the catalysts was calculated by the equation $ECSA=Q/q_0$, in which q_0 was $210 \mu\text{C cm}^{-2}$ and the Q was decided by the area of the hydrogen desorption peaks in the CV curves. The methanol oxidation was measured in a mixed solution of 0.5 M H_2SO_4 and 0.5 M CH_3OH at a scan rate of 50 mV s^{-1} at $30 \text{ }^\circ\text{C}$. For the CO stripping measurement, 4% CO (96% N_2) was bubbled into the 0.5 M H_2SO_4 for 10 min to ensure the CO adsorb completely onto the catalyst, then N_2 was bubbled into the solution for 15 min to remove the CO dissolved in solution. The CV curves of CO stripping were measured from -0.25 V to 1.1 V at the scan rate of 10 mV s^{-1} .

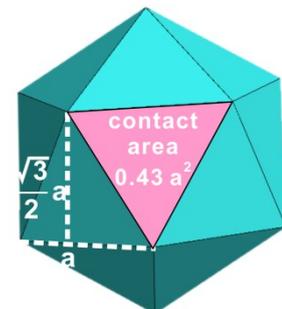
Table S1. The contact areas and specific surface areas of icosahedral and cubes

	Contact area	Specific surface area
Icosahedron	$0.43 a^2$	$3.97 a^{-1}$
Cube	$1.68 a^2$	$4.63 a^{-1}$

It is supposed the volume of Pt icosahedra and cubes have equal volume. When the length of icosahedron is represented by a , the volume of icosahedron is $\frac{15 + 5\sqrt{5}}{12} \times a^3$ ($2.18 a^3$) while the surface area is $5\sqrt{3}a^2$ ($8.66 a^2$). Thus the specific surface area is $3.97 a^{-1}$. The contact area is the area of triangular, which is $\frac{\sqrt{3}}{4}a^2$ ($0.43 a^2$). The cube has the same volume with icosahedra, which is $2.18 a^3$. Thus the surface area could be $6 \times (\sqrt[3]{2.18a^3})^2$ ($10.09 a^2$). Then the specific surface area is $4.63 a^{-1}$. The contact surface area is area of square, which is $(\sqrt[3]{2.18a^3})^2$ ($1.68 a^2$). Detailed calculation is showing below.

1. Icosahedron

$$\text{volume} = \frac{15 + 5\sqrt{5}}{12} \times a^3 = 2.18 a^3$$



$$\text{contact area} = \text{length} \times \text{height} \times \frac{1}{2} = \frac{\sqrt{3}}{2}a \times a \times \frac{1}{2} = \frac{\sqrt{3}}{4}a^2 = 0.43a^2$$

$$\text{specific surface area} = \frac{\text{surface area}}{\text{volume}} = \frac{\text{contact area} \times 20}{\text{volume}} = \frac{0.433 \times a^2 \times 20}{2.18a^3} = 3.97a^{-1}$$

2. Cube

$$\text{volume} = 2.18a^3$$

$$\text{contact area} = \text{length} \times \text{length} = \sqrt[3]{\text{volume}} \times \sqrt[3]{\text{volume}} = \sqrt[3]{2.18}$$

$$\text{specific surface area} = \frac{\text{surface area}}{\text{volume}} = \frac{\text{contact area} \times 6}{\text{volume}} = \frac{1.6}{\text{volume}}$$

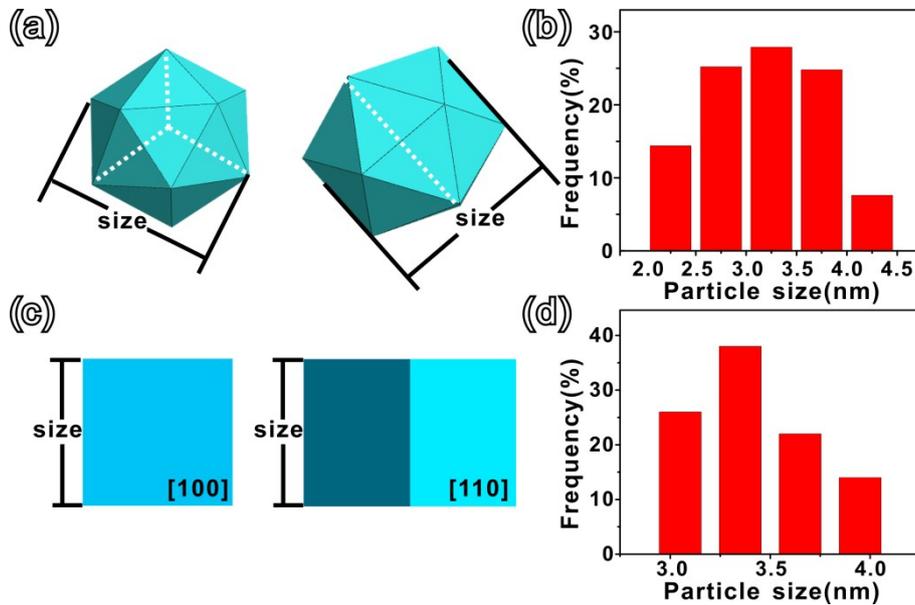
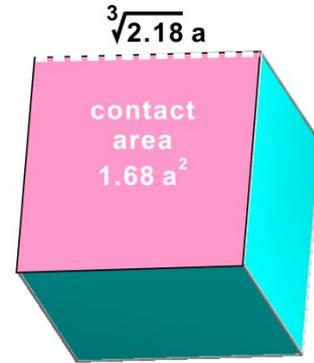


Figure S1. (a) Scheme showing how the sizes of Pt icosahedral NCs are measured; (b) Particle size distributions for Pt icosahedra by counting more than 100 particles in TEM image; (c) Scheme showing how the sizes of Pt cubic NCs are measured; (d) Particle size distributions for Pt cubes by counting more than 100 particles in TEM image.

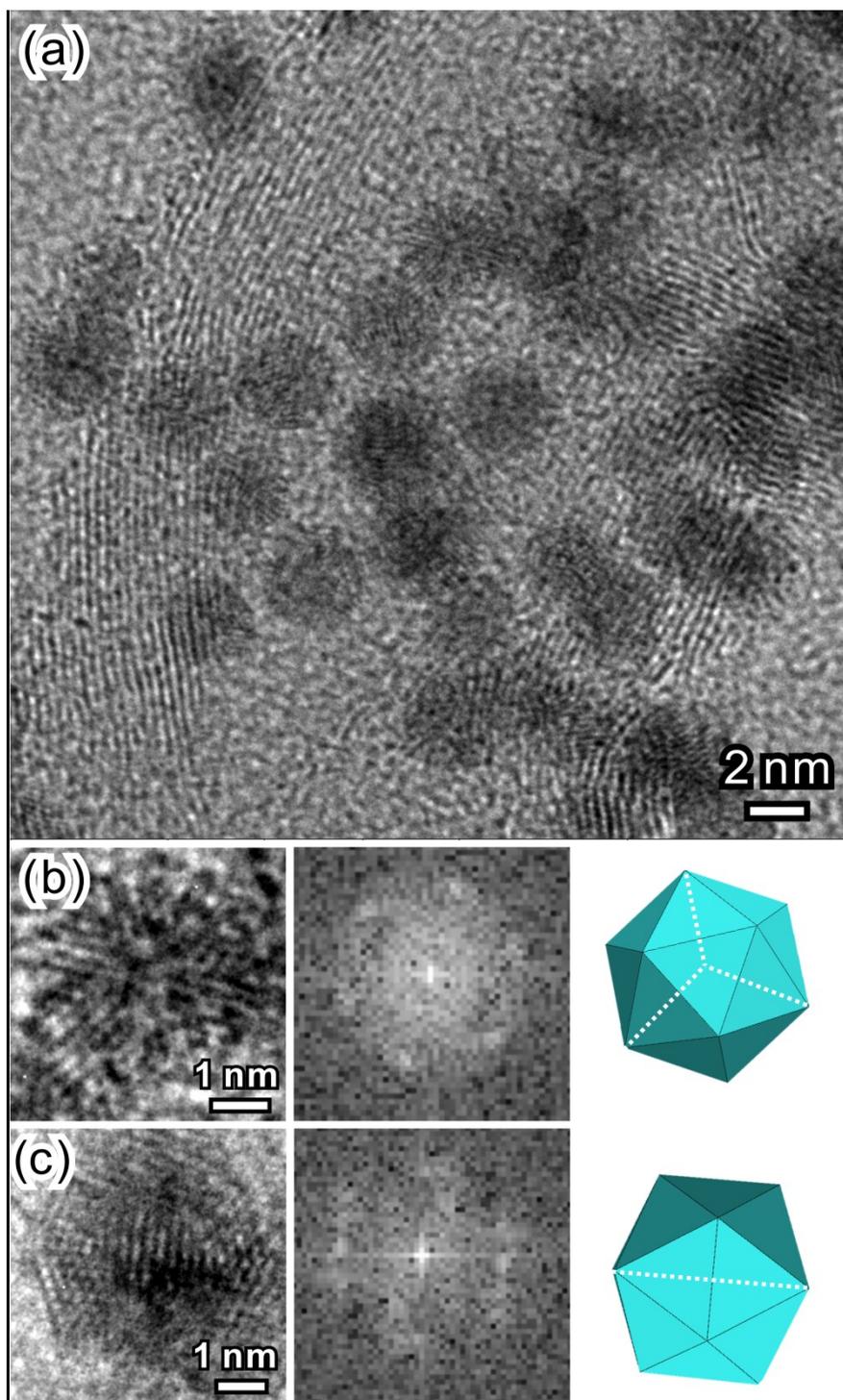


Figure S2. (a) HRTEM image of as-prepared icosahedral Pt NC on a large scale. (b and c) HRTEM images of single icosahedral Pt NC oriented along two typical projections and their corresponding FFT images and geometrical models: (b) 3-fold axis and (c) 2-fold axis.

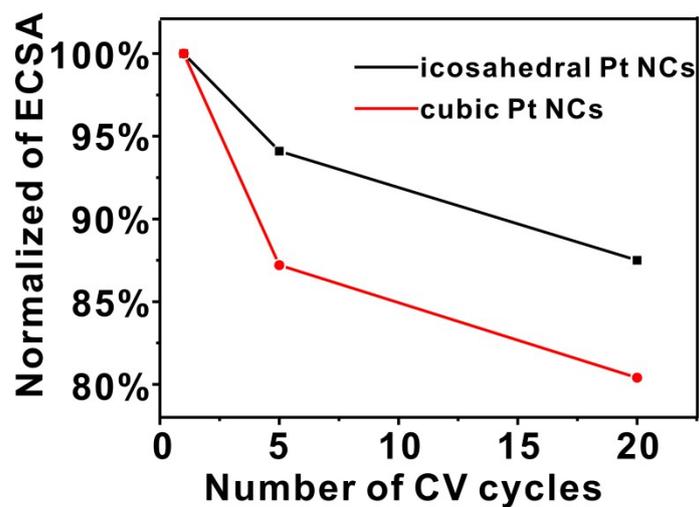


Figure S3. Comparison the changes of electrochemical active areas of icosahedral and cubic Pt NCs after different cycles. The electrochemical active area (ECSA) of the two samples were calculated by the equation $ECSA = Q/q_0$, in which Q is determined by the area of the hydrogen desorption peaks in the cyclic voltammetry measurement performed in 0.5 M H_2SO_4 electrolyte, and q_0 is $210 \mu C cm^{-2}$.

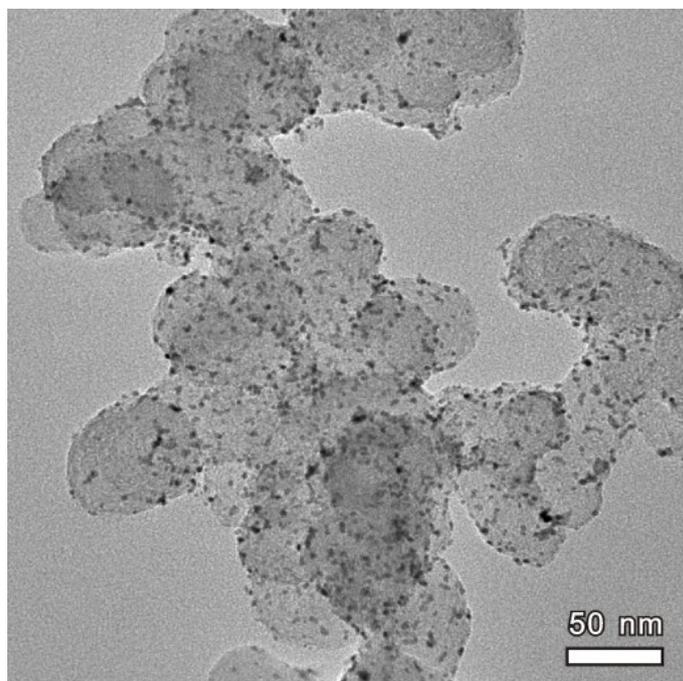


Figure S4. TEM image of commercial Pt/C (20 wt. %).

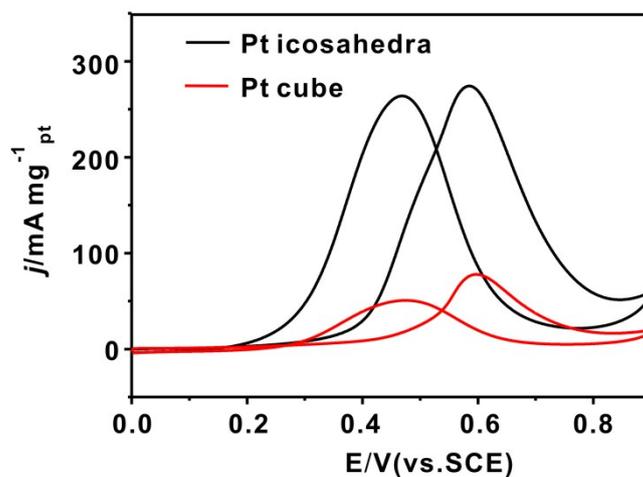


Figure S5. Cyclic voltammograms in N_2 saturated 0.5 M methanol + 0.5 M H_2SO_4 aqueous solution (scan rate: 50 mV s^{-1}). The current density is normalized to the mass of Pt.

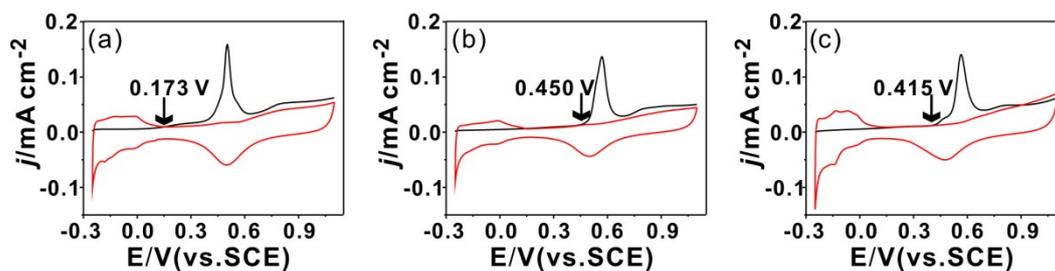


Figure S6. Cyclic voltammograms of CO stripping in N_2 saturated 0.5 M H_2SO_4 (scan rate: 10 mV s^{-1}), (a) Pt-icosahedra (3.2 nm); (b) Pt cubes (3.4 nm); (c) Pt/C (20 wt. %). The onset potentials for CO stripping peaks are derived from the intersection of the segment 1 and segment 3 on CV curves.

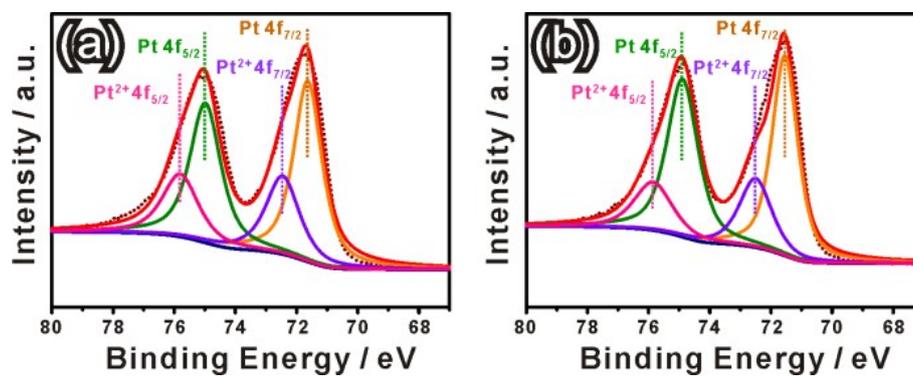


Figure S7. XPS patterns of (a) Pt icosahedral NCs and (b) Pt cubic NCs.

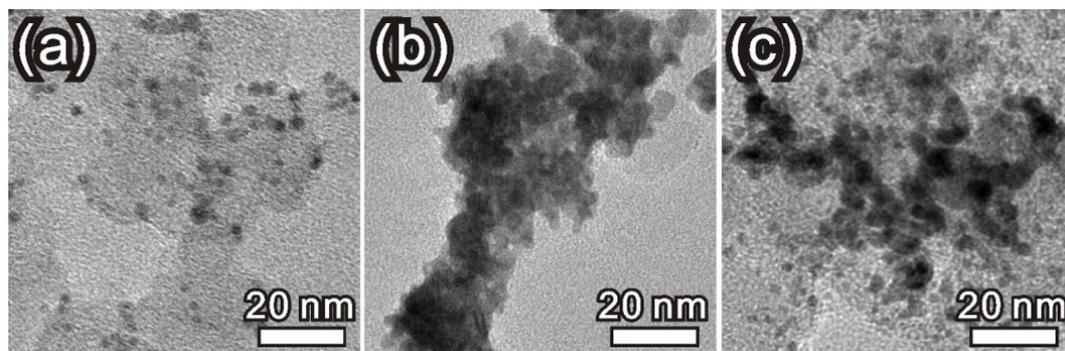


Figure S8. High-magnification TEM images of Pt nanoparticles on CNT after methanol electro-oxidation in 0.5 M H_2SO_4 +0.5 M methanol, (a) Pt icosahedral (3.2 nm); (b) Pt cubes (3.4 nm); (c) Pt/C (20 wt. %).