

Supporting Information for

Surfactant-free Platinum Nanocubes with Largely Enhanced Activity toward Methanol/Ethanol Electrooxidation

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Synthesis of Platinum nanocubes:

In the typical procedure, a solution of 5 mM platinum(II) 2,4-pentanedionate (Pt(acac)₂) and 50 mM ascorbic acid was prepared in 5 ml of N,N-dimethylformamide (DMF). The light yellow solution was transferred into a 12-mL Teflon-lined stainless-steel autoclave. The sealed autoclave was then heated in an oven at 150 °C for 16 h followed by cooling down to room temperature. The product was separated *via* centrifugation, washed thoroughly with ethanol and finally dispersed into ethanol under ultrasound.

Condition experiments have been conducted on the concentration of ascorbic acid and reaction temperature. Herein, the concentration of Pt(acac)₂ and the reaction time were fixed. The experimental conditions are listed in Table S1.

Table S1 Experimental conditions for the synthesis of Pt nanoparticles

Sample	Reaction temperature / °C	Concentration of ascorbic acid / mM
A1	150	0
A2	150	25
A3	150	50
B1	180	0
B2	180	25
B3	180	50

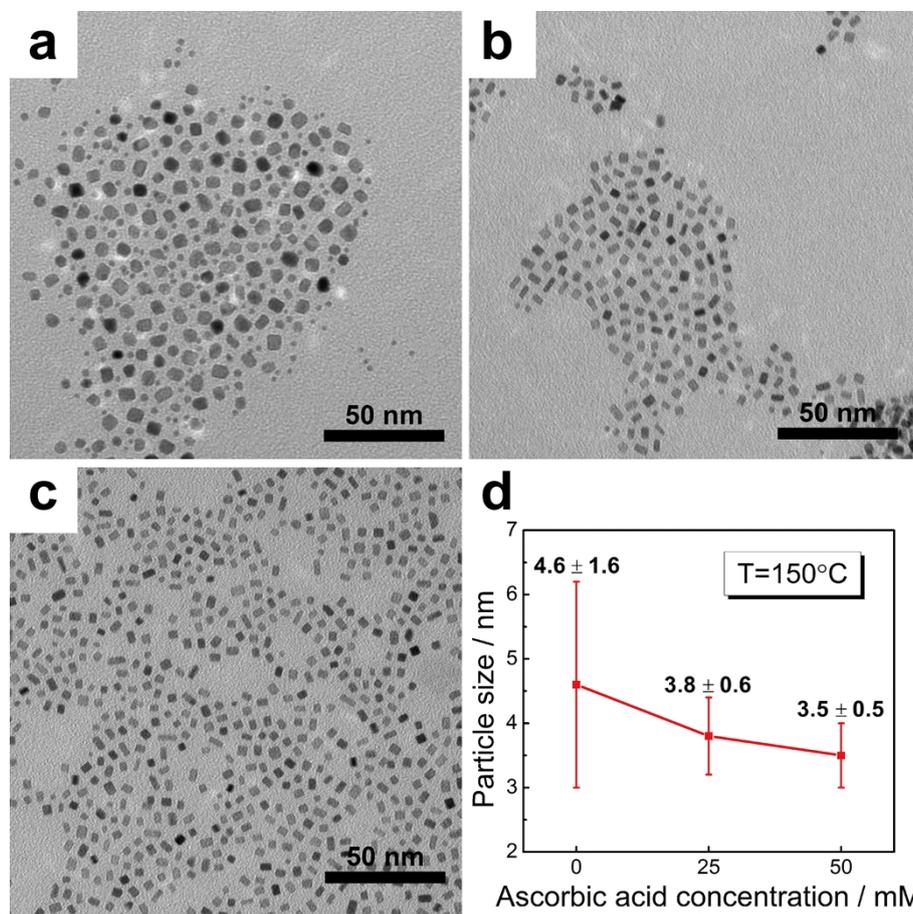


Figure S1 TEM images of sample (a) A1, (b) A2 and (c) A3; (d) the average particle sizes obtained from the TEM images.

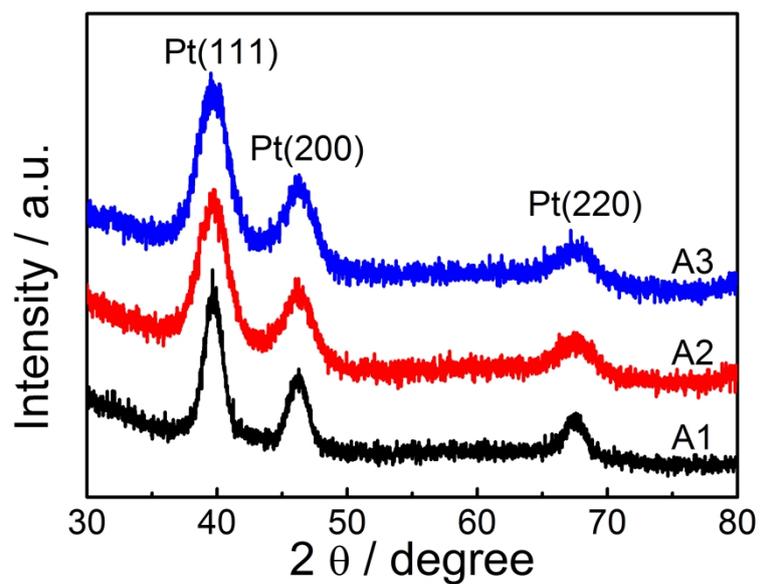


Figure S2 XRD patterns of samples prepared at 150 °C.

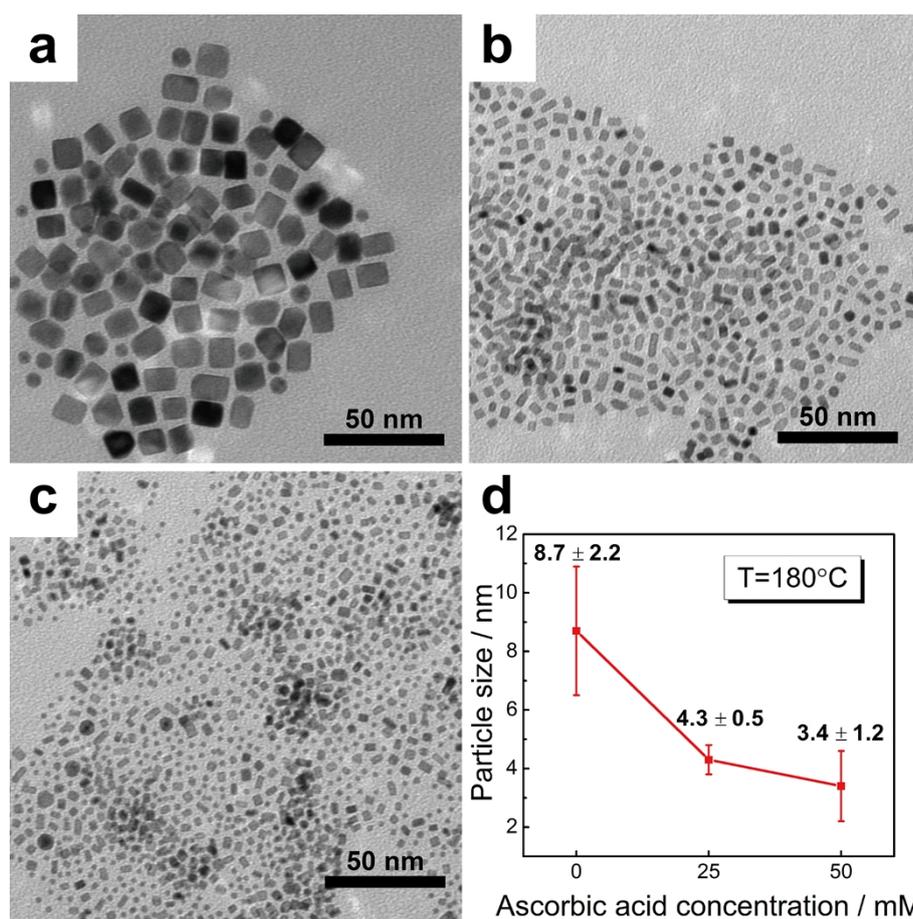


Figure S3 TEM images of sample (a) B1, (b) B2 and (c) B3; (d) the average particle sizes obtained from the TEM images.

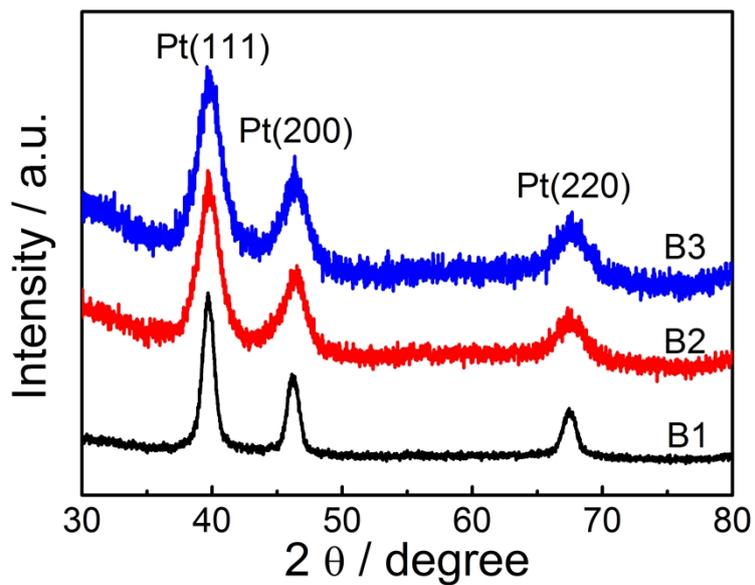


Figure S4 XRD patterns of samples prepared at 180 °C.

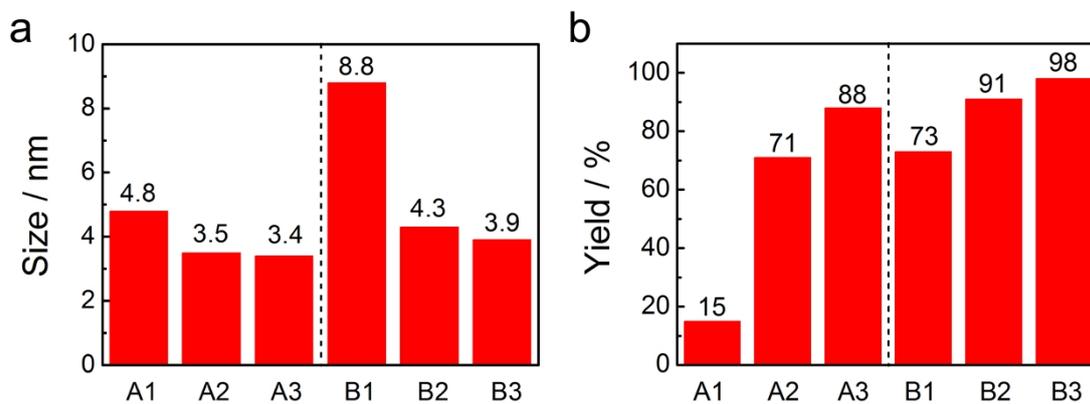


Figure S5 (a) The average particle sizes and (b) product yield of the as-prepared Pt nanoparticles.

Table S2 *d*-spacing of various Pt planes^a

$\{h, k, l\}$	$d_{\{h, k, l\}} / \text{\AA}$
{100} ^b	3.9232
{110} ^c	2.7746
{111}	2.2650
{200}	1.9616
{220}	1.3873
{311}	1.1826
{331}	0.9000
{420}	0.8773
{422}	0.8008

^a JCPDS #04-0802.

^b Calculated based on $d_{\{100\}} = 2 d_{\{200\}}$.

^c Calculated based on $d_{\{110\}} = 2 d_{\{220\}}$.

TEM characterization of the commercial Pt/C catalyst:

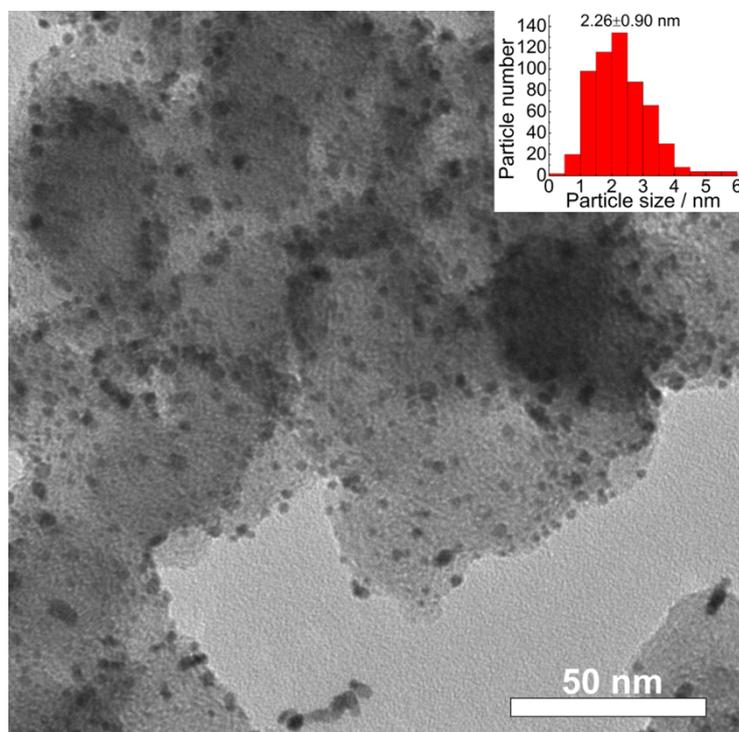


Figure S6 TEM image of the commercial Pt/C sample (inset shows its size distribution).

Activity of the Pt nanocube and commercial Pt/C catalysts based on each Pt atom:

In Table S3, E_p and j_a represent the peak potential (V) and the corresponding charge transfer rate ($e\ s^{-1}$) on each Pt atom in the positive sweep of CV curve (Fig. 3b and 3c), respectively. It can be seen that the Pt nanocube catalyst exhibits both more negative E_p and larger j_a than the commercial Pt/C catalyst, which indicates its superior activity toward methanol/ethanol electrooxidation.

Table S3 Electrochemical parameters for methanol/ethanol electrooxidation on the Pt nanocube and commercial Pt/C catalyst based on each Pt atom

Catalyst	Methanol		Ethanol	
	E_p / V	$j_a / e\ s^{-1}$	E_p / V	$j_a / e\ s^{-1}$
Pt Nanocube	-0.181	4.33	-0.210	1.92
Pt/C	-0.077	3.30	-0.141	1.84

Calculation of the electrochemical surface area of catalyst:

Firstly, the real surface area of Pt catalyst on the electrode is estimated using a conventional procedure based on coulometry of the underpotential deposition of Hydrogen at Pt surface. This procedure assumes that every Pt atom at the surface adsorbs an H during the deposition. The charge associated with $H_{ads/des}$ is calculated *via* the cyclic voltammetry curve as follow:

$$Q_{ads/des} = A_{ads/des} / \beta \quad (1)$$

Where $Q_{ads/des}$ (C) is the charge associated with $H_{ads/des}$; $A_{ads/des}$ (W) is the area of the region associated with $H_{ads/des}$ after subtracting the double layer charge contribution (see Fig. S7); β

(V s⁻¹) is the scan rate of cyclic voltammetry. The charge value (Q) used for calculation always takes the average of Q_{ads} and Q_{des} . Subsequently, the real surface area (RSA (cm²)) of the catalyst is calculated as follow:

$$Q = \frac{Q_{ads} + Q_{des}}{2} \quad (2)$$

$$RSA = \frac{Q}{210 \mu C cm^{-2}} \quad (3)$$

Where 210 $\mu C cm^{-2}$ is the accepted value of charge density over Pt surface. For the as-prepared Pt nanocubes and the commercial Pt/C, the RSAs were determined to be 2.05 cm² and 3.24 cm², respectively.

Finally, the electrochemical surface area (ECSA (m² g⁻¹)) of the catalyst is calculated by the following equation:

$$ECSA = 0.0001 \times \frac{RSA}{m} \quad (4)$$

Where m (g) is the mass of the catalyst on the electrode. In this work, the mass of Pt was fixed at 5 μg . As a result, the ECSAs of the Pt nanocubes and the commercial Pt/C were calculated to be 41.0 and 64.8 m² g⁻¹, respectively.

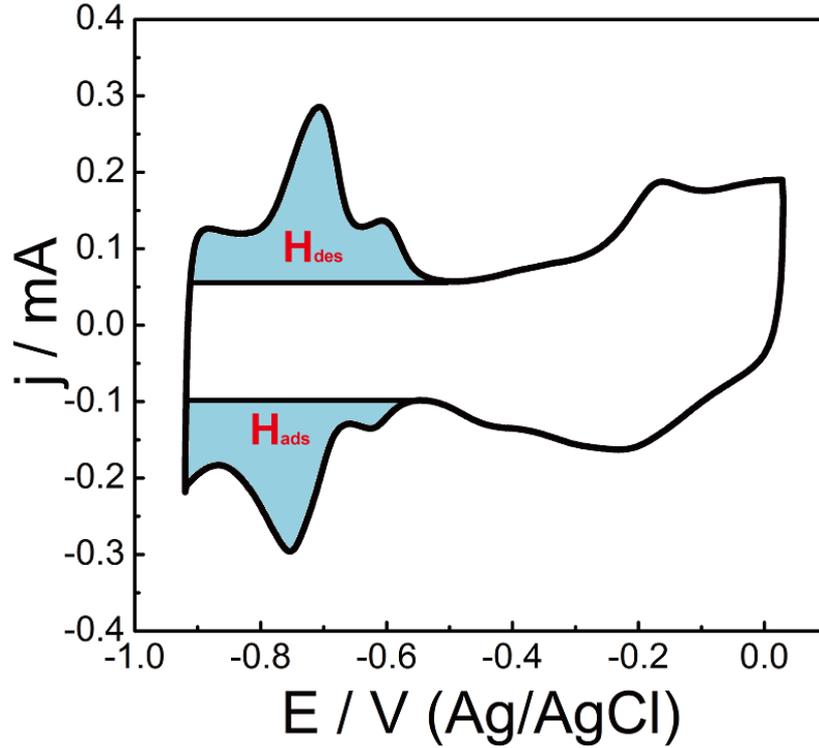


Figure S7. Schematic diagram originated from CV curve of commercial Pt/C shows the blue region associated with $H_{\text{ads/des}}$ after the subtraction of double layer.

Calculation of the real surface area *via* the size distribution:

The specific surface area (SSA ($\text{m}^2 \text{g}^{-1}$)) of smooth particles can be calculated as follow:

$$SSA = \frac{1000 \times \sum_1^N S_i}{\rho \times \sum_1^N V_i} \quad (5)$$

Where S_i and V_i are the surface area (nm^2) and volume (nm^3) of the i th particle with a size of d_i (nm), respectively; N is the total number of particles; ρ (g cm^{-3}) is the mass density of Pt, which is 21.45 g cm^{-3} .

For the Pt nanocubes, d is the edge length:

$$S_i = S_{\text{cube}}(d_i) = 6 \times d_i^2 \quad (6)$$

$$V_i = V_{cube}(d_i) = d_i^3 \quad (7)$$

For the commercial Pt/C, the Pt nanoparticles are treated as spheres where d is the diameter:

$$S_i = S_{sphere}(d_i) = \pi d_i^2 \quad (8)$$

$$V_i = V_{sphere}(d_i) = \frac{\pi d_i^3}{6} \quad (9)$$

According to the particle size obtained from TEM images (See Fig. 1a and Fig. S6), the SSAs of the as-prepared Pt nanocubes and the commercial Pt/C were calculated to be 77.1 and 94.1 m² g⁻¹, respectively.

The results above show that the electrochemical surface area of catalyst is always smaller than the specific surface area. This is due to the existence of some inaccessible surface area at the interface. For example, the existence of micropores, catalyst agglomeration and the contact between the catalyst surface and substrate may decrease the effective surface area.

Reference:

- 1 A. V. Tripković, K. D. Popović, J. D. Lović, V. M. Jovanović and A. Kowal, *J. Electroanal. Chem.*, 2004, **572**, 119.
- 2 A. Balouch, A. A. Umar, S. T. Tan, S. Nafisah, S. K. Md Saad, M. M. Salleh and M. Oyama, *RSC Adv.*, 2013, **3**, 19789.