Supporting Information

Significantly Enhancing the Performance of Hydrogen Evolution Reaction through Shape-Controlled Synthesis of Hierarchical Dendrite-Like Platinum

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Fig. S1 SEM images of Pt-12. (a, b) after 10,000 cycles ADTs 0.5 M H₂SO₄.



Fig. S2. SEM images of Pt-12. (a, b) after 1,000 cycles ADTs in 1 M KOH. (c, d) after 5,000 cycles ADTs 1 M KOH.



Fig. S3. TEM images of Pt/C. (a) before, (b) after 1,000 cycles ADTs in 0.5 M H_2SO_4 , (c) after 1,000 cycles ADTs 1 M KOH.



Fig. S4 XRD patterns of Pt-12 (a) after electrolysis in 0.5 M H_2SO_4 , (b) after electrolysis in 1 M KOH.



Fig. S5. Cyclic voltammetry curves of (a) Pt-12, (b) Pt/C recorded in $0.5M H_2SO_4$ at scan rates of 10, 20, 40, 60, 80 and 100 mV/s. (c) capacitive current at 0.16 V vs. RHE with scan rate for Pt-12 and Pt/C.



Fig. S6. Cyclic voltammetry curves of (a) Pt-12, (b) Pt/C recorded in 1 M KOH at scan rates of 10, 20, 40, 60, 80 and 100 mV/s. (c) capacitive current at 0.155 V vs. RHE with scan rate for Pt-12 and Pt/C.

Fig. S7. Electrochemical impedance spectroscopy (EIS) of Pt-12 and Pt/C.

Fig. S8 Chromatogram of standard hydrogen and gaseous product of Pt-12 after electrolysis in $0.5 \text{ M H}_2\text{SO}_4$.

Fig. S9 XPS spectra of the Pt 4f state of (a) Pt-12, (b) Pt-12 after electrolysis in 0.5 M H₂SO₄,(c) Pt-12 after electrolysis in 1 M KOH.

Fig. S10 TEM image (a) and HRTEM image (b) of Pt/C.

Fig. S11 The LSV curves of hydrogen electrode reactions on Pt wire.

The thermodynamically reversible potential gap between reference electrode and reversible hydrogen electrode (RHE) was calculated by Nernst equation.

In order to get the accurate RHE value, the calibration test was conducted in hydrogen saturated 0.5 M H_2SO_4 (or 1 M KOH) with a Pt wire as working electrode, a SCE(or mercury oxide electrodes) as reference electrode and a graphite electrode as auxiliary electrode. The scan rate of LSV experiment was 0.1 mV s⁻¹. As shown in Figure S8, the current of hydrogen electrode reactions reaches zero at -0.256 V (or -0.926 V)

with respect to SCE (or mercury oxide electrodes). Both of the measured and calculated potential gaps between SCE (or mercury oxide electrodes) and RHE is nearly 0.256 V (or -0.926 V). So, we have calibrated the potential with respect to RHE in the revised manuscript according to the following equation.

E (RHE) = E (SCE) + 0.256 V

E (RHE) = E (HgO/Hg) + 0.926 V

Catalyst	Catalysis condition	Current density (j)	Overpotential at corresponding j	reference
Pt-12	0.5 M H ₂ SO ₄	10	15	This work
	0.1 M KOH	10	30	
Pt nano-array	0.5 M H ₂ SO ₄	~15	50	Ref 1
ALDPt/NGNs	0.5 M H ₂ SO ₄	16	50	Ref 2
hcp Pt–Ni excavated nano- multipods	0.1 M KOH	10	65	Ref 3
Pt@CIAC-121	0.5 M H ₂ SO ₄	10	48	Ref 4
Pt-Ni/C	0.1 M KOH	7.68	50	Ref 5
Pt NWs/SL-Ni(OH) ₂	1 M KOH	2.48	70	Ref 6
PtCoFe@CN	0.5 M H ₂ SO ₄	10	45	Ref 7
Pt ₁₃ Cu ₇₃ Ni ₁₄ /CNF@C F	1 M H ₂ SO ₄	5	70	Ref 8
Ni(OH) ₂ /Pt(111)	0.1 M KOH	5	35	Ref 9

Table S1. Comparison of HER activity of Pt-based catalysts in different electrolytes

Dendritic-like Pt at different conditions	The ratio of (220) peak to (111) peak
1h	0.202
2h	0.325
3h	0.343
6h	0.34
12h	0.357
18h	0.33
Pt(JCPDS No.04-0802)	0.31
Pt/C	0.293

 Table S2. The ratio of (220) peak to (111) peak for Pt at different conditions

Table S3 The values of $\Delta E(H^*)$ of the H* at the different adsorption sites on the (220) and (111) surfaces of Pt.

Surface	Adsorption site	$\Delta E(\mathrm{H^*})/\mathrm{eV}$	
(220)	a	-0.8520	
	b	-0.8523	
	с	-0.9473	
	а	-0.7424	
(111)	b	-0.6811	
	c	-0.7454	

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