

Supporting Information For
In Situ Confinement of Pt within Three-Dimensional MoO₂@Porous Carbon for
Efficient Hydrogen Evolution

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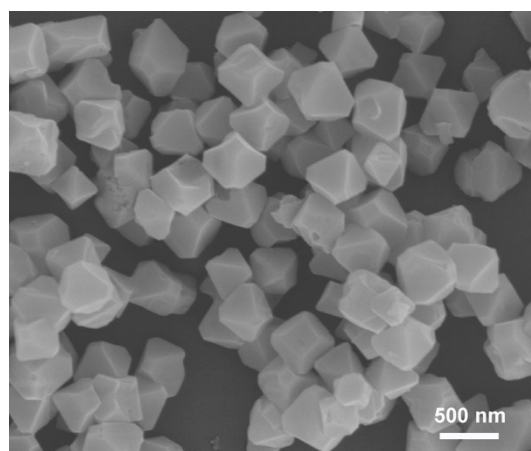


Figure S1 SEM image of as-prepared NENU-5 octahedrons.

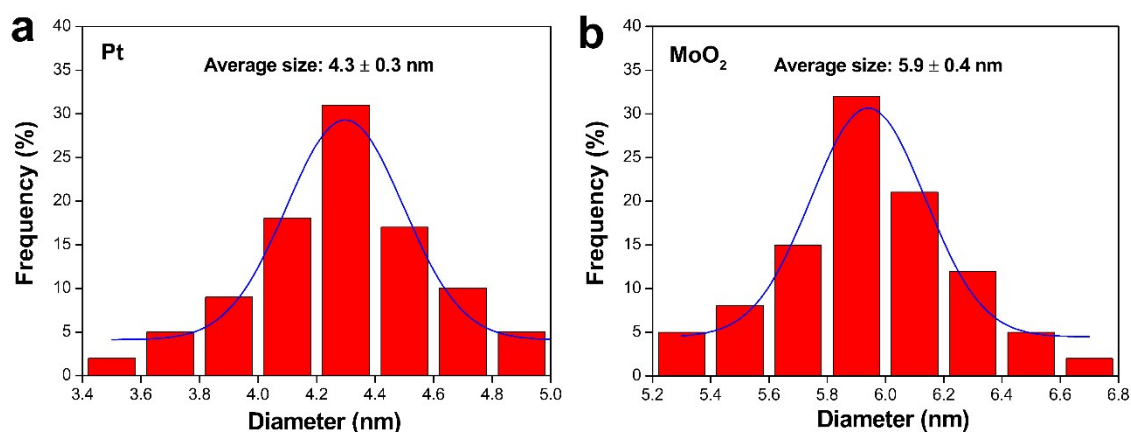


Figure S2 Size distributions of Pt (a) and MoO₂ (b) nanoparticles in the Pt-MoO₂@PC octahedrons.

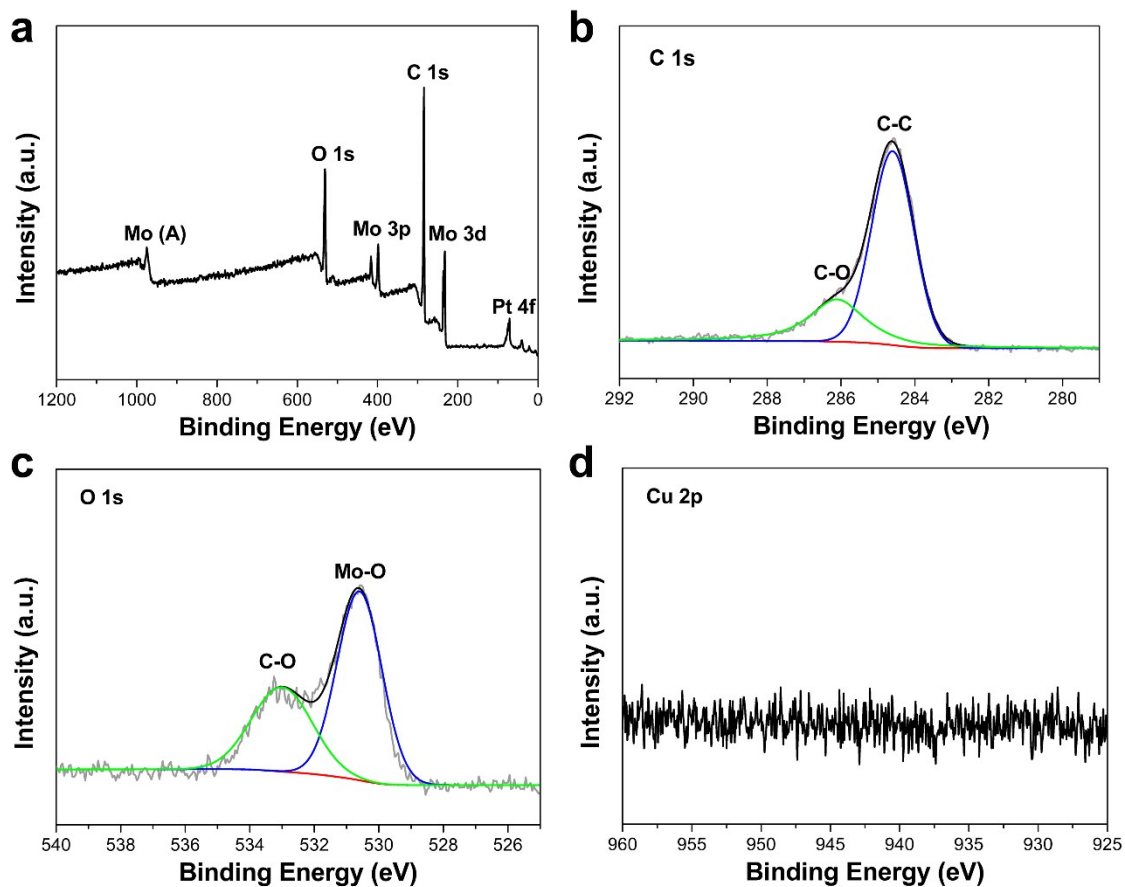


Figure S3 XPS spectra of the Pt-MoO₂@PC octahedrons: (a) survey spectrum; (b) C 1s; (c) O 1s; (d) Cu 2p.

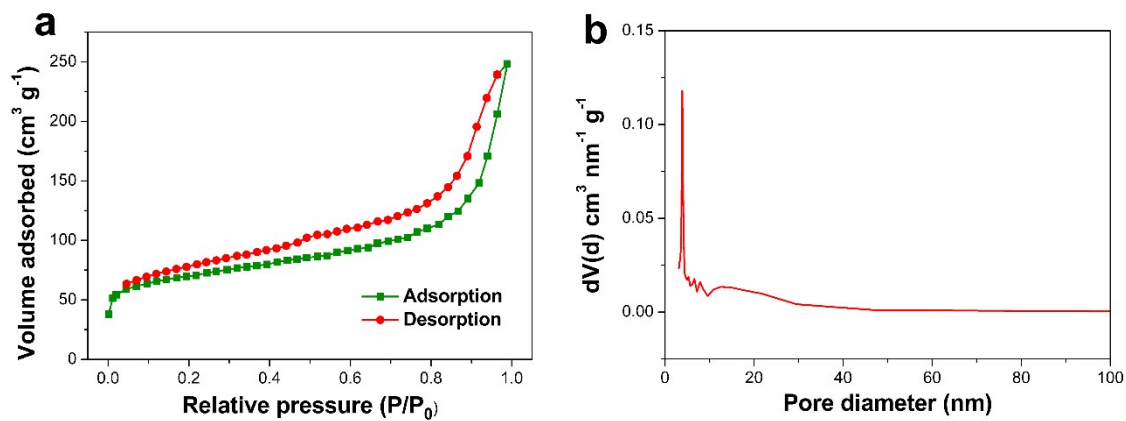


Figure S4 (a) N₂ adsorption/desorption isotherms; (b) the corresponding pore size distribution of the Pt-MoO₂@PC octahedrons.

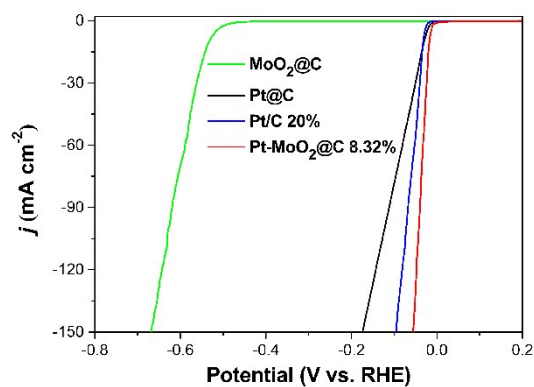


Figure S5 Polarization curves of the MoO₂@PC, Pt@PC, Pt-MoO₂@PC and 20 wt% Pt/C in 0.5 M H₂SO₄ using a GC electrode with a diameter of 5 mm.

Table S1 Comparison of HER activities for the Pt-MoO₂@PC octahedrons and other HER catalysts.

Catalysts	Pt amount ($\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$)	η_{10}	Tafel slope (mV dec^{-1})	Mass activity at – 0.05 V ($\text{mA } \mu\text{g}_{\text{Pt}}^{-1}$)	Reference
Pt@PCM ^a	0.7	105	65.3	0.12	1
Pt-MoS ₂	36.0	60	96	—	2
Mo ₂ C@NC@Pt	21.0	27	28	—	3
Pt/BCF ^b	1.1	55	32	—	4
Pt-MoO ₂ /CNTs	2.4	60	43	—	5
Ru-MoO ₂	45.2 ^c	55	44	—	6
MoP@PC	—	58	59	—	7
MoN-NC	—	62	54	—	8
Pt/MoO ₂	17.9	47	32.6	7.43	9

CDs/Pt-PANI ^d	8.1	30	41.7	3.80	10
Pt@MoS ₂	16.7	70	36	—	11
CuPdPt/C	0.3	48	25	7.15	12
Pd@PdPt	59.6	39	38	—	13
Pt/C	28.0	30	31	1.68	This
Pt-MoO ₂ @PC	11.6	20	22	11.34	This

^a Pt atom in the nitrogen-containing porous carbon matrix

^b bacterial cellulose derived carbon nanofiber

^c the amount of Ru

^d carbon dots/Pt modified polyaniline nanosheets

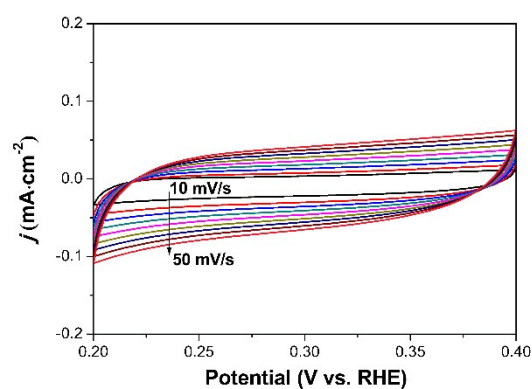


Figure S6 CV curves of 20 wt% Pt/C in the region of 0.2 to 0.4 V with scan rates from 10 to 50 mV s⁻¹.

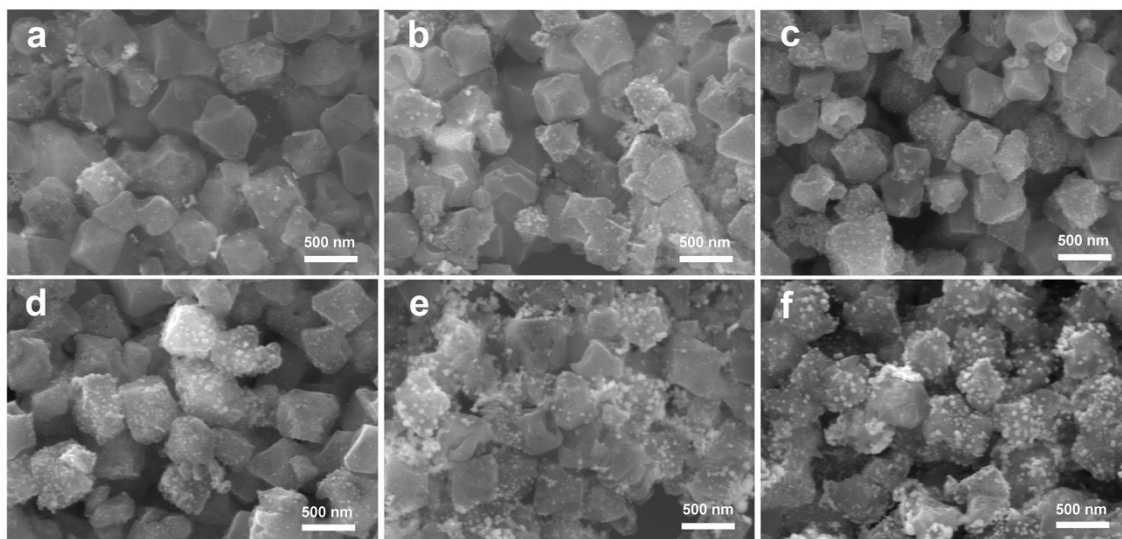


Figure S7 SEM images of the Pt-MoO₂@PC octahedrons with different Pt amounts (wt%): (a) 1.39, (b) 3.88, (c) 6.21, (d) 10.91, (e) 12.76, (f) 13.96.

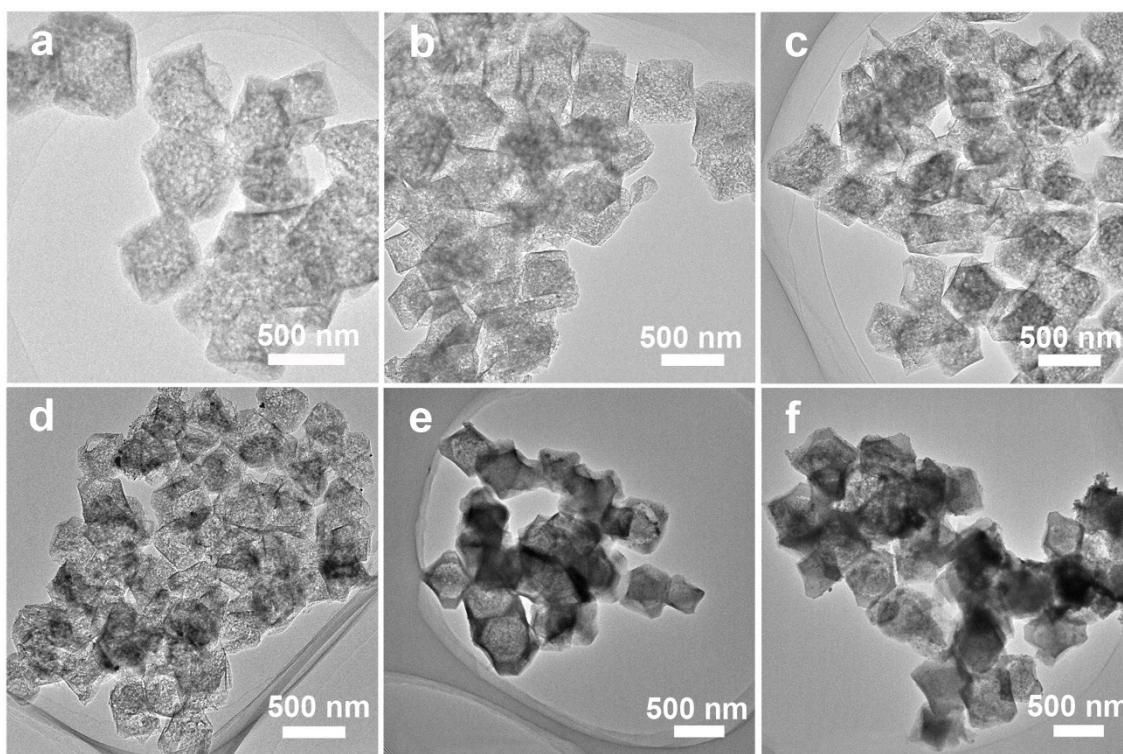


Figure S8 TEM images of the Pt-MoO₂@PC octahedrons with different Pt amounts (wt%): (a) 1.39, (b) 3.88, (c) 6.21, (d) 10.91, (e) 12.76, (f) 13.96.

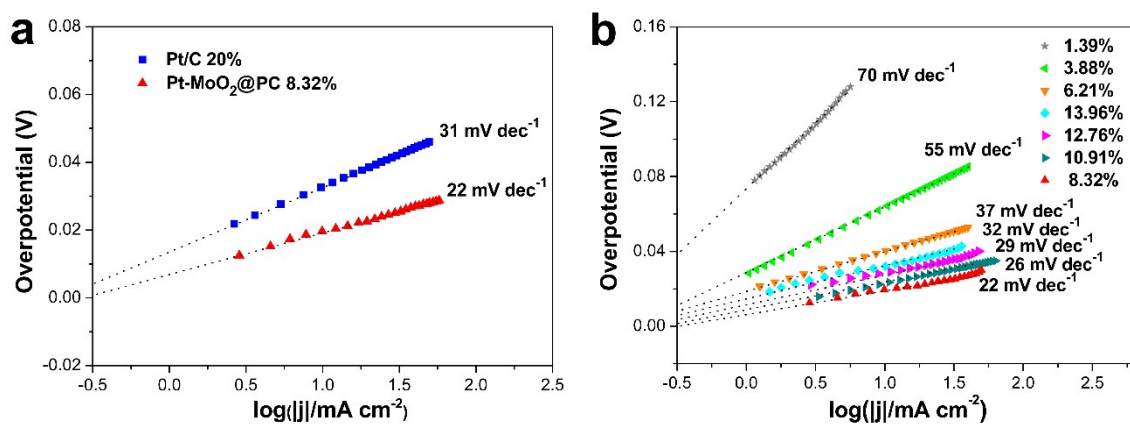


Figure S9 Calculated exchange current densities j_0 of Pt/C (a) and various Pt-MoO₂@PC samples (b) by using the extrapolation method.

Table S2 HER parameters of 20 wt% Pt/C and various Pt-MoO₂@PC samples.

Samples	Tafel slope (mV dec ⁻¹)	j_0 (mA cm ⁻²)
Pt/C	31	0.38
1.39%	70	0.05
3.88%	55	0.22
6.21%	37	0.36
8.32%	22	0.59
10.91%	26	0.45
12.76%	29	0.40
13.96%	32	0.37

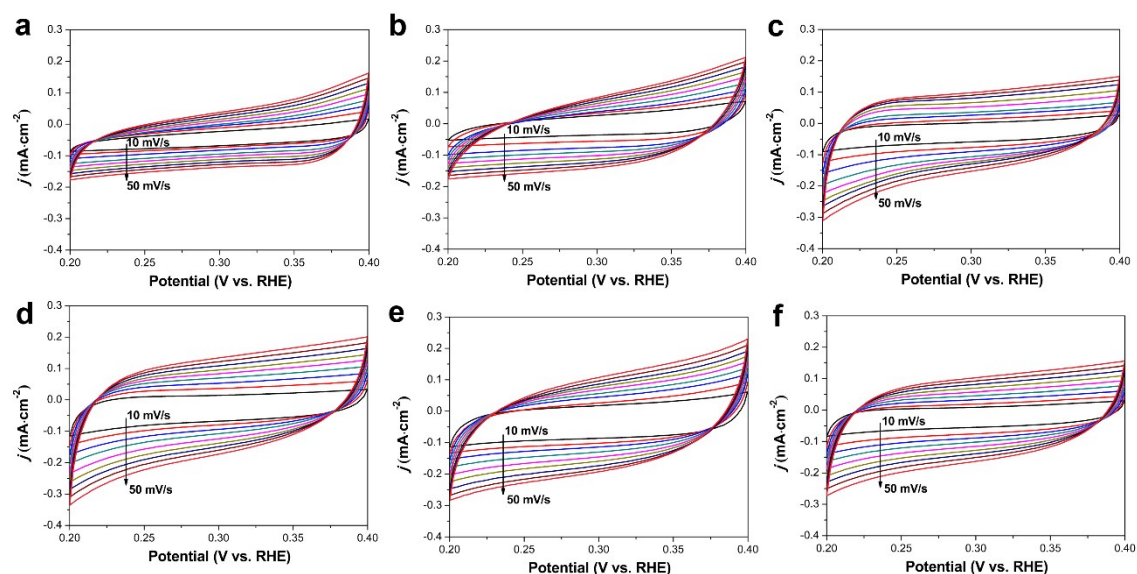


Figure S10 CV curves of the Pt-MoO₂@PC octahedrons with different Pt amounts in the region of 0.2 to 0.4 V with scan rates from 10 to 50 mV s⁻¹: (a) 1.39, (b) 3.88, (c) 6.21, (d) 10.91, (e) 12.76, (f) 13.96.

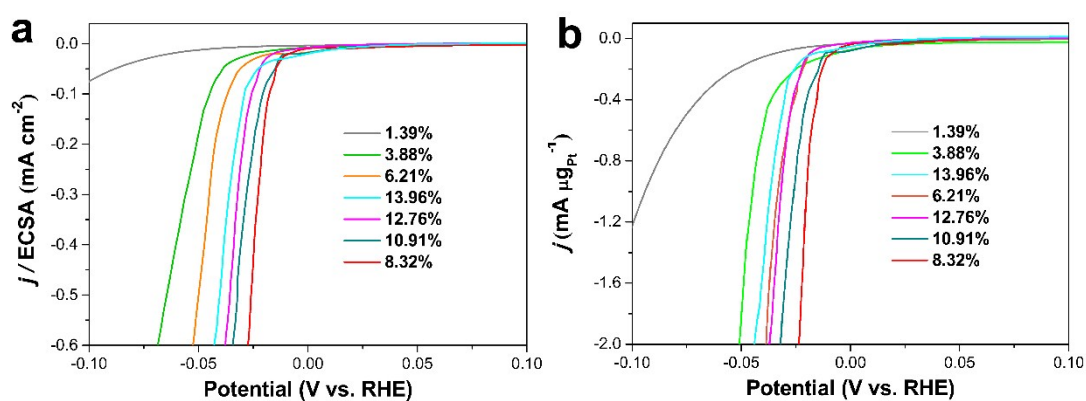


Figure S11 Polarization curves normalized by the ECSA (a) and Pt amount (b) for the Pt-MoO₂@PC samples with different Pt amounts.

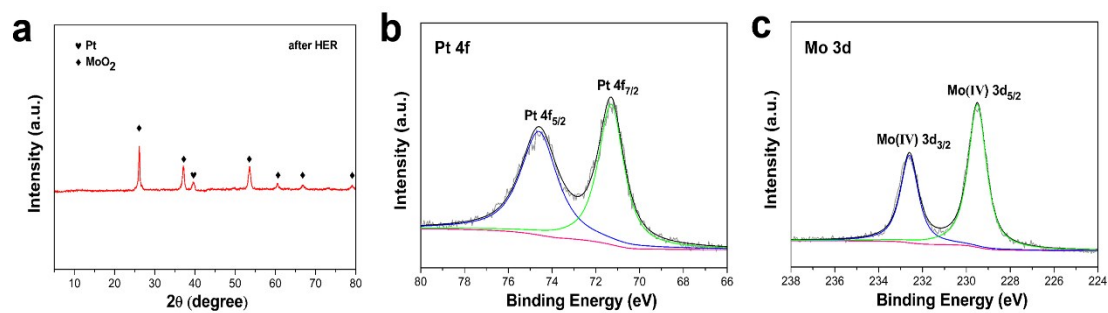


Figure S12 (a) XRD pattern, (b) Pt 4f and (c) Mo 3d spectra of the Pt-MoO₂@PC octahedrons after 1000 potential sweeps in 0.5 M H₂SO₄.

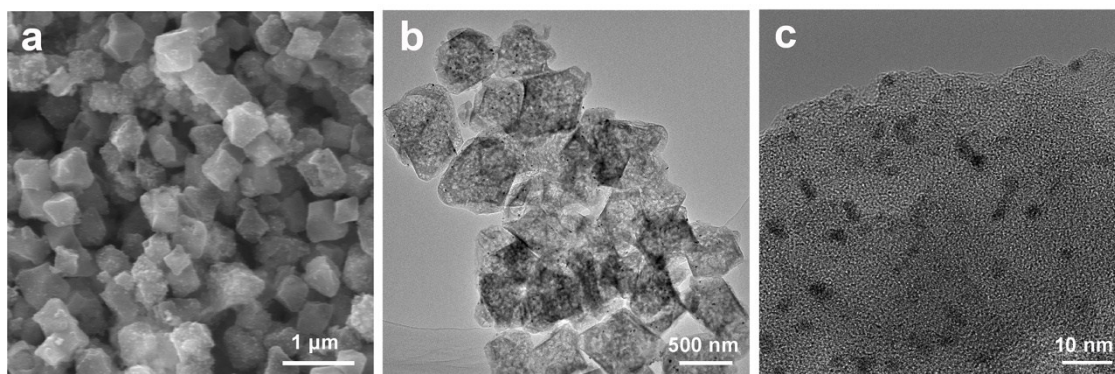


Figure S13 (a) SEM, (b) TEM and (c) HRTEM images of the Pt-MoO₂@PC octahedrons after 1000 potential sweeps in 0.5 M H₂SO₄.

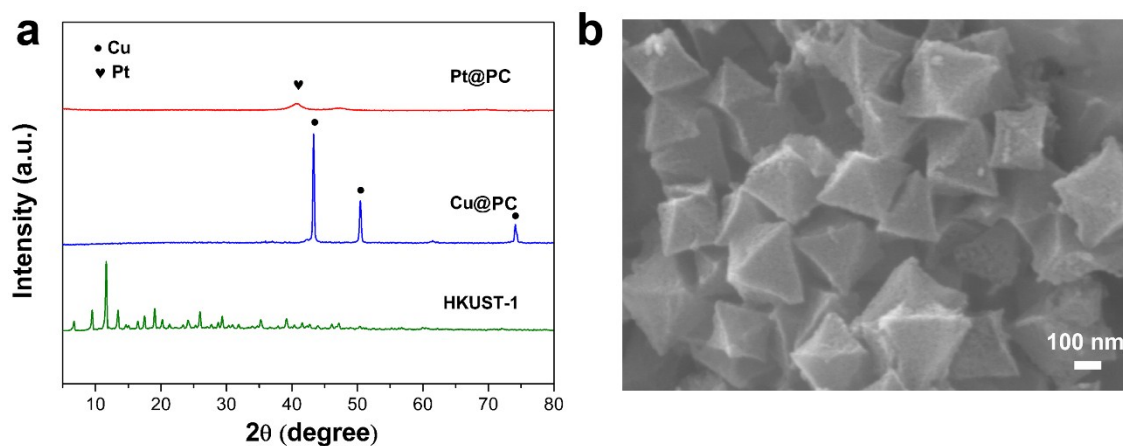


Figure S14 (a) XRD patterns of HKUST-1, Cu@PC and Pt@PC samples; (b) SEM image of the Pt@PC octahedrons.

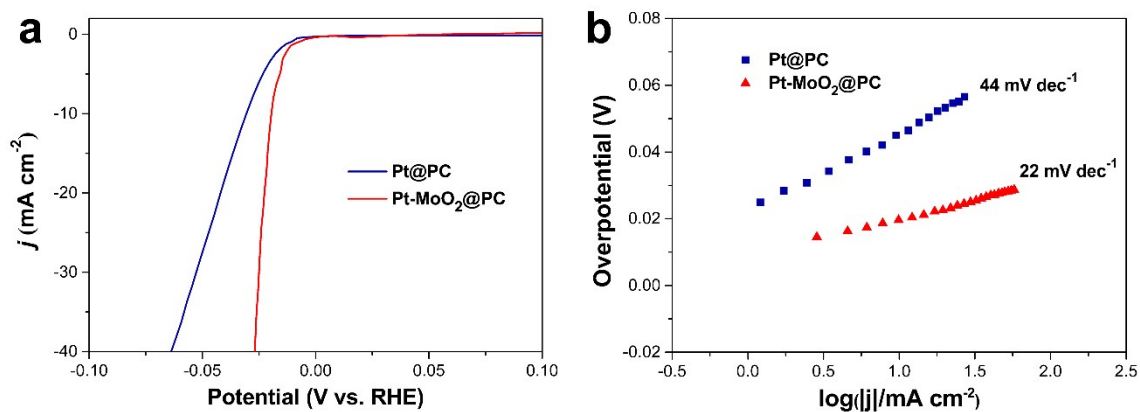


Figure S15 (a) Polarization curves and (b) Tafel plots of the Pt@PC and Pt-MoO₂@PC octahedrons.

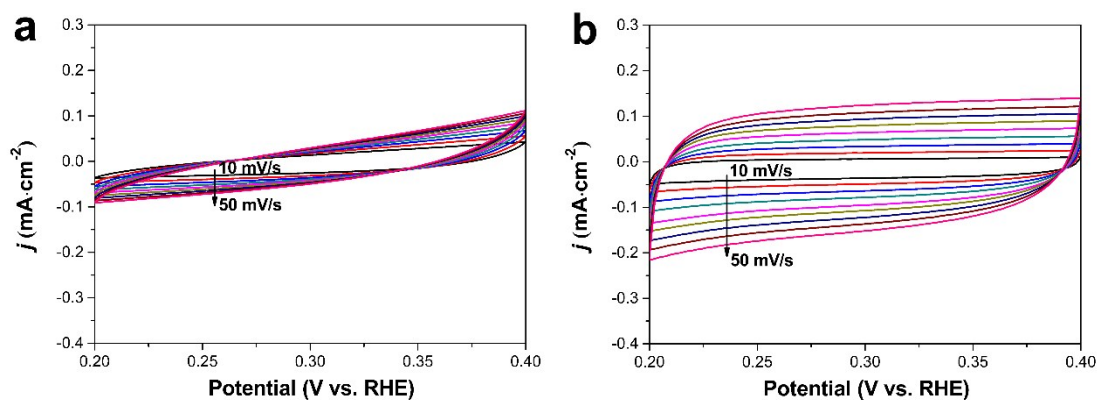


Figure S16 CV curves of the (a) MoO₂@PC and (b) Pt@PC octahedrons in the region of 0.2 to 0.4 V with scan rates from 10 to 50 mV s⁻¹.

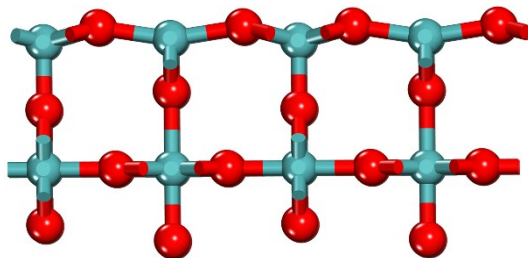


Figure S17 Geometric configurations of MoO₂.

Notes and references

- 1 H. Zhang, P. An, W. Zhou, B. Y. Guan, P. Zhang, J. Dong and X. W. Lou, *Sci. Adv.*, 2018, **4**, eaao6657.
- 2 J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren and X. Bao, *Energy Environ. Sci.*, 2015, **8**, 1594.
- 3 J.-Q. Chi, J.-Y. Xie, W.-W. Zhang, B. Dong, J.-F. Qin, X.-Y. Zhang, J.-H. Lin, Y.-M. Chai and C.-G. Liu, *ACS Appl. Mater. Inter.*, 2019, **11**, 4047.
- 4 Y. Mi, L. Wen, Z. Wang, D. Cao, H. Zhao, Y. Zhou, F. Grote and Y. Lei, *Catal. Today*, 2016, **262**, 141.
- 5 X. Xie, Y.-F. Jiang, C.-Z. Yuan, N. Jiang, S.-J. Zhao, L. Jia and A.-W. Xu, *J. Phys. Chem. C*, 2017, **121**, 24979.
- 6 P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su and Q. Chen, *J. Mater. Chem. A*, 2017, **5**, 5475.
- 7 J.-S. Li, S. Zhang, J.-Q. Sha, H. Wang, M.-Z. Liu, L.-X. Kong and G.-D. Liu, *ACS Appl. Mater. Inter.*, 2018, **10**, 17140.
- 8 Y. Zhu, G. Chen, X. Xu, G. Yang, M. Liu and Z. Shao, *ACS Catal.*, 2017, **7**, 3540.
- 9 X. Li, J. Y. Yu, J. Jia, A. Z. Zhao, L. L. Zhao, T. L. Xiong, H. Liu and W. J. Zhou, *Nano Energy*, 2019, **62**, 127.
- 10 Q. Dang, Y. Y. Sun, X. Wang, W. X. Zhu, Y. Chenm F. Liao, H. Huang and M. W. Shao, *Appl. Catal. B-Environ.*, 2019, **257**, 117905.
- 11 X. Y. Xu, X. F. Dong, Z. J. Bao, R. Wang, J. G. Hu and H. B. Zeng, *J. Mater. Chem. A*, 2017, **5**, 22654.

12 T. Ding, Z. Y. Wang, L. Zhang, C. D. Wang, Y. Sun and Q. Yang, *J. Mater. Chem.*

A, 2016, **4**, 15309.

13 Y. Liu, S. L. Liu, Z. W. Che, S. C. Zhao, X. X. Sheng, M. Han and J. C. Bao, *J.*

Mater. Chem. A, 2016, **4**, 16690.