

Supporting Information

"Ethanol-Water Exchange" Nanobubbles Templated Hierarchical Hollow β -Mo₂C/N-doped Carbon Nanospheres as an Efficient Hydrogen Evolution Electrocatalyst

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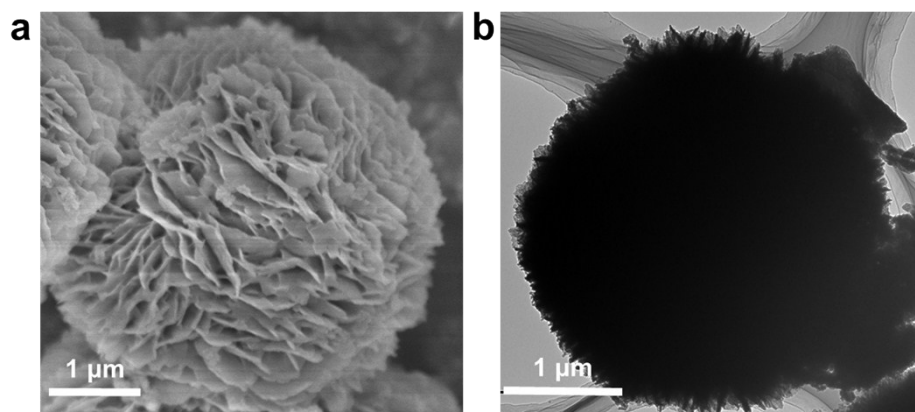


Fig. S1. FESEM (a) and TEM (b) images of the solid spheres produced when ethanol was replaced by an equal volume of water.

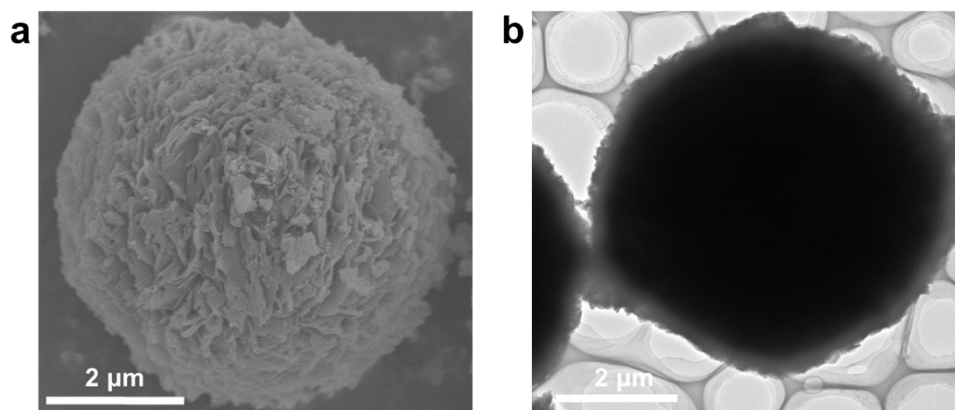


Fig. S2. FESEM (a) and TEM (b) images of the obtained solid spheres consisting of nanosheets produced when ethanol was reduced to 30 mL.

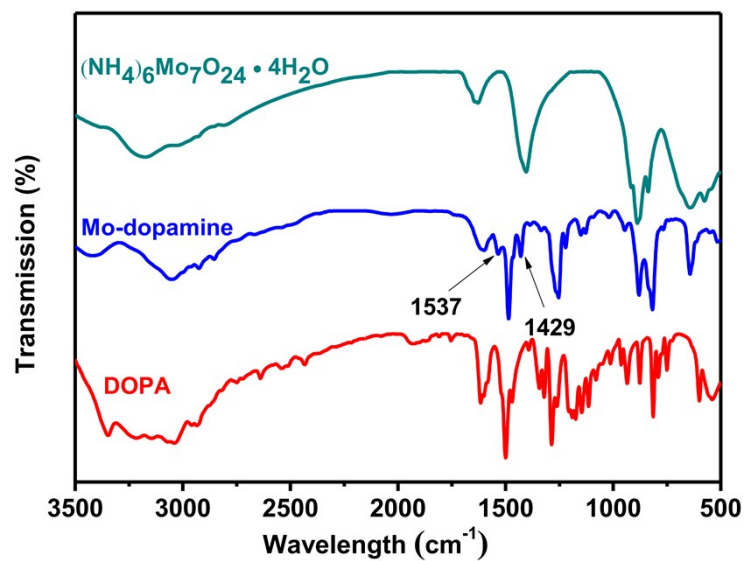


Fig. S3. FTIR spectra of dopamine, Mo-dopamine and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

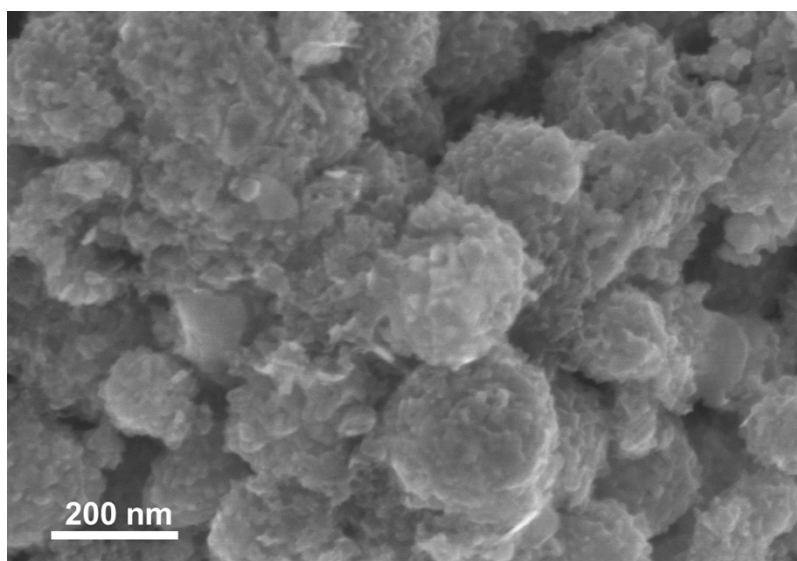


Fig. S4. SEM image of the product extracted from the system at 5 min through high-temperature treatment.

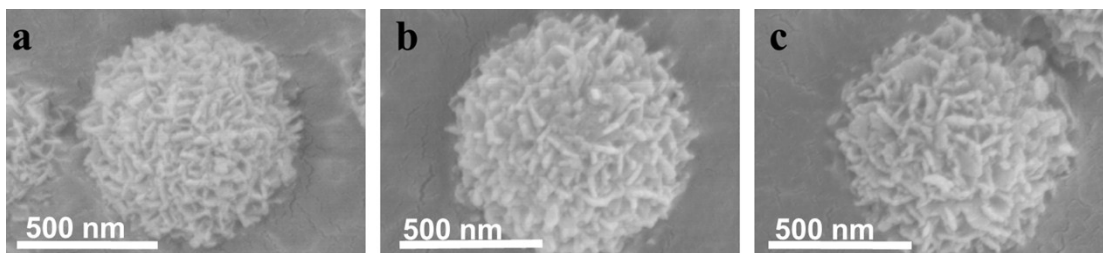


Fig. S5. SEM image of the product extracted from the system at a) 5 min, b) 1 h, and c) 2 h.

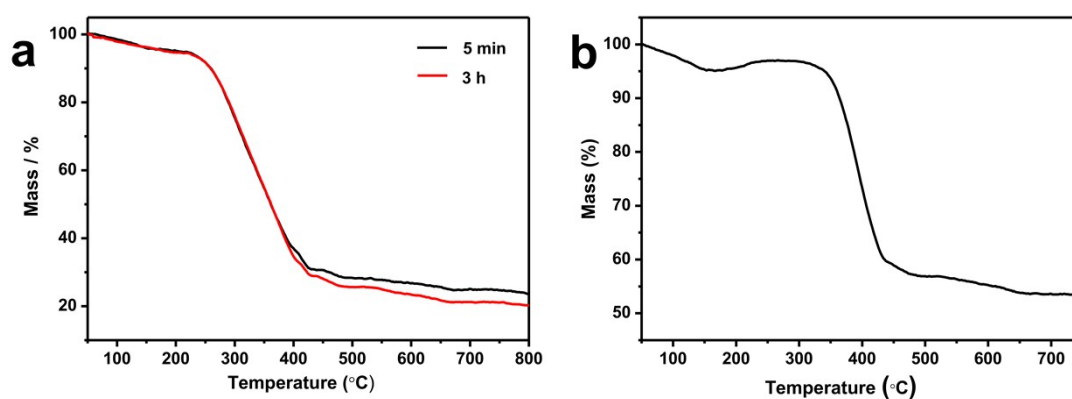


Fig. S6. TGA curve of a) Mo-dopamine complex precursor at different time and b) hollow β -Mo₂C/N-doped carbon composite nanospheres in air with a heating rate of 10 °C·min⁻¹.

$$m_{(\text{Mo}_2\text{C})} = w_{(\text{MoO}_3)} \times M_{(\text{Mo}_2\text{C})} / 2M_{(\text{MoO}_3)} = 53.3\% \times 204 / (2 \times 144) = 37.8\%.$$

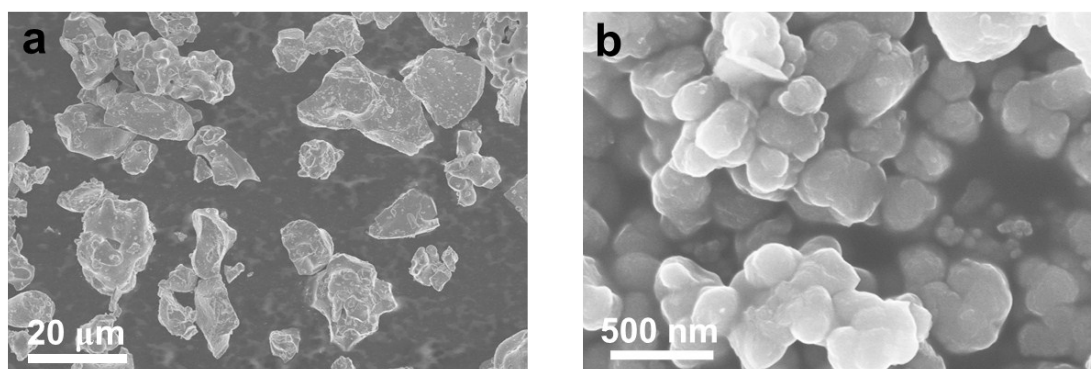


Fig. S7. SEM images of a) commercial β -Mo₂C, and b) N-doped carbon.

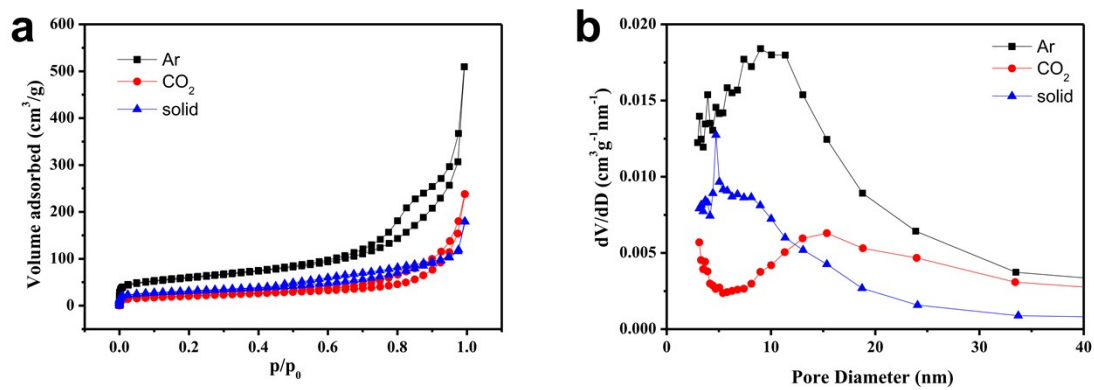


Fig. S8. a) Nitrogen adsorption-desorption isotherm of β -Mo₂C nanoflowers at 77 K, and b) the corresponding pore size distribution derived from the adsorption branches on the basis of the BJH model.

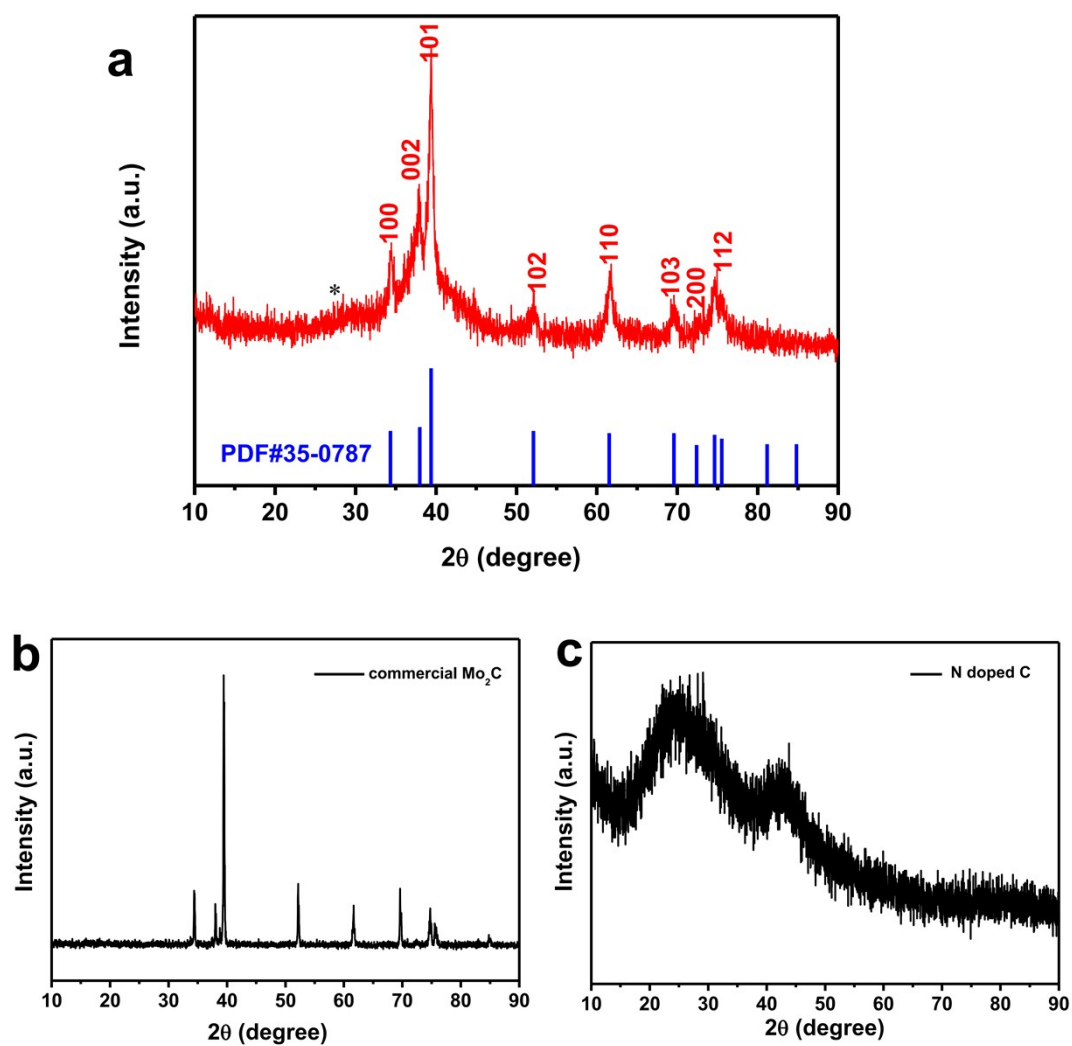


Fig. S9. XRD of the a) hollow β -Mo₂C/N-doped carbon composite nanospheres, b) commercial β -Mo₂C, and c) N-doped carbon.

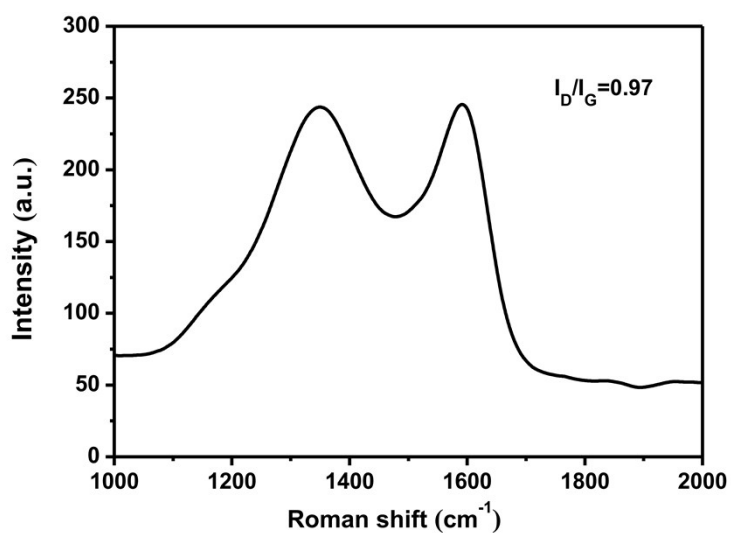


Fig. S10. Raman spectra of the hollow β -Mo₂C/N-doped carbon composite nanospheres.

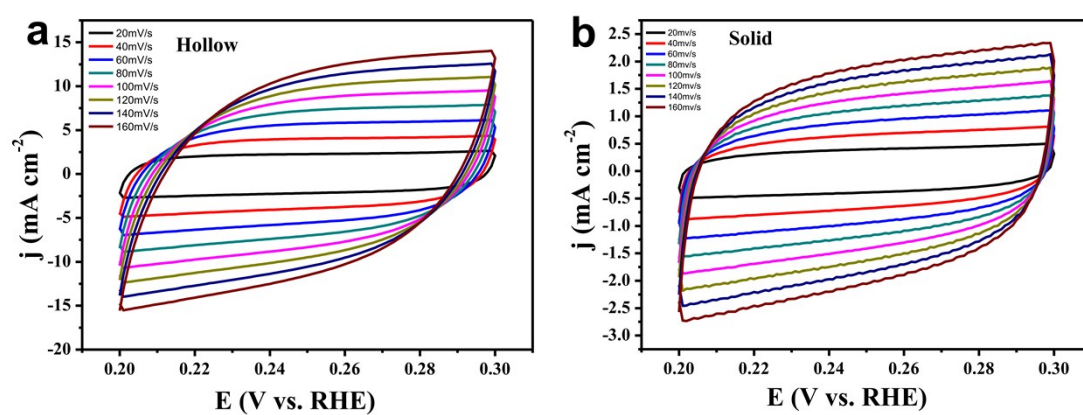


Fig. S11. Cyclic voltammograms in the region of 0.2–0.3 V vs. RHE for a) the hollow β -Mo₂C/N-doped carbon composite nanospheres and b) the solid β -Mo₂C/N-doped carbon composite spheres.

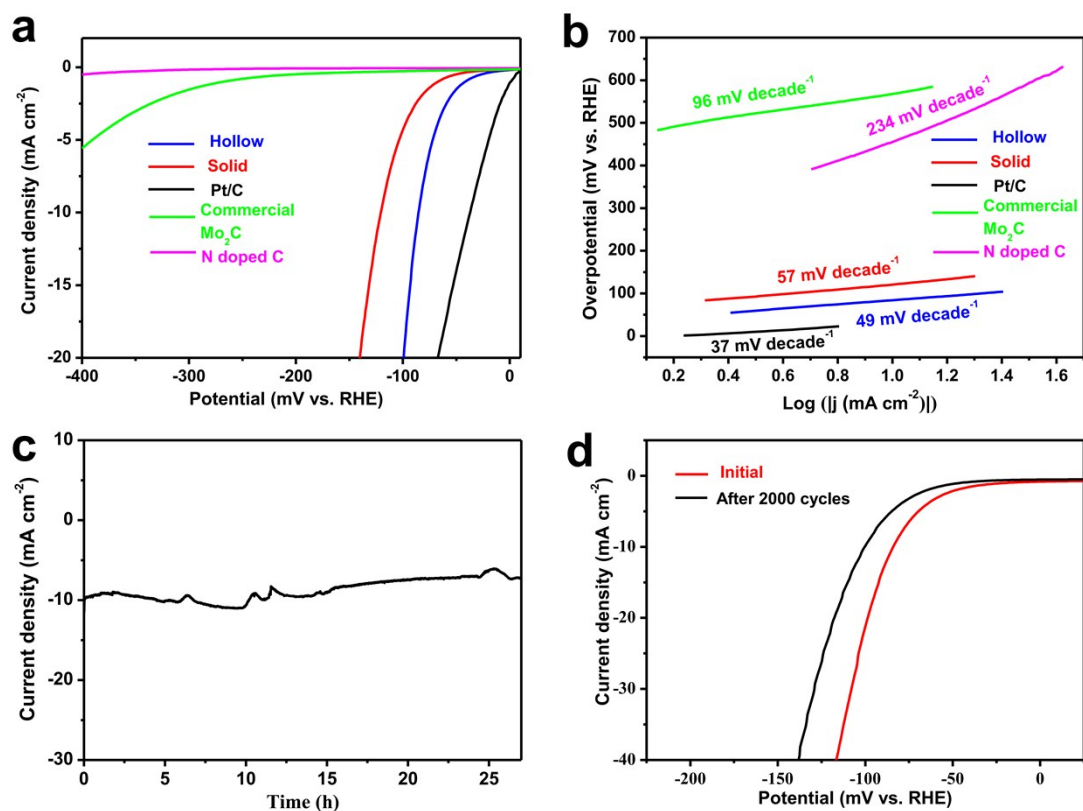


Fig. S12. HER tests in 1 M KOH. a) The HER polarization plots for different catalysts at a scan rate of 5 mV s^{-1} , b) Tafel plots for different catalysts, c) The i - t curve at $\eta=130$ mV, d) Polarization curves of the hollow $\beta\text{-Mo}_2\text{C}/\text{N-doped carbon}$ composite nanospheres before and after 2000 CV scans .

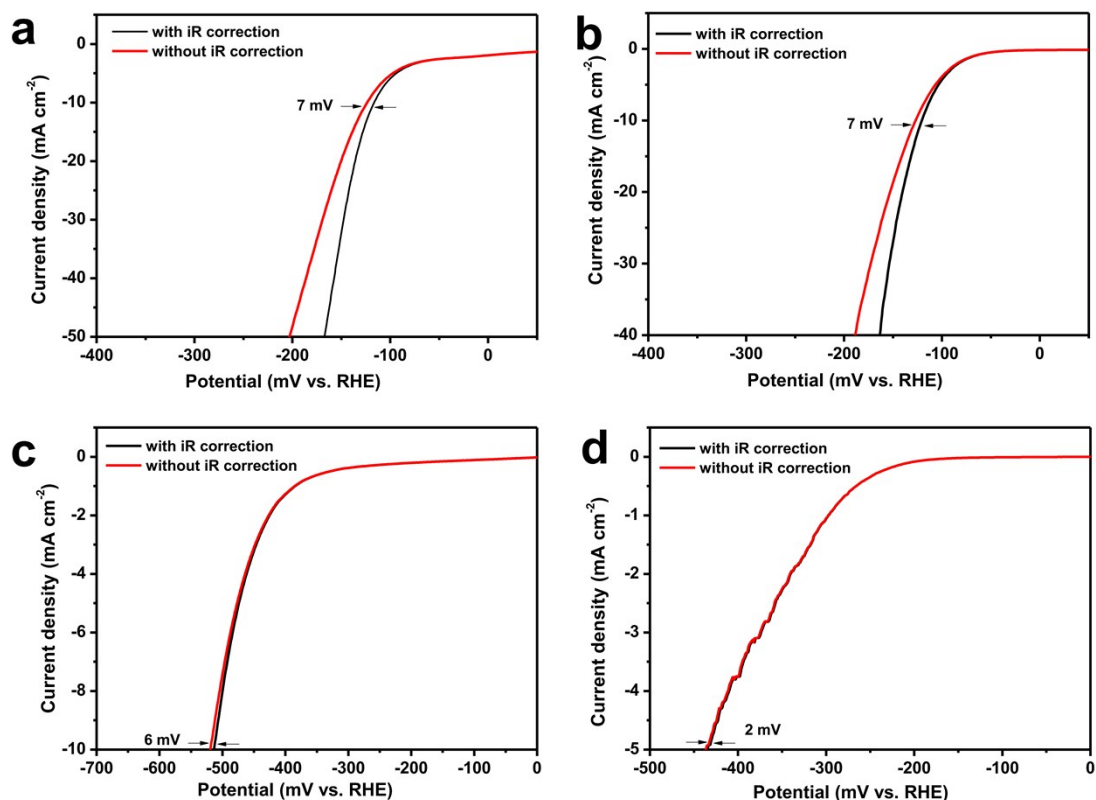


Fig. S13. The LSV curves before and after iR correction in 0.5 M H₂SO₄. a) hollow β -Mo₂C nanoflowers, b) β -Mo₂C nanoflowers, c) N doped carbon, and d) commercial β -Mo₂C nanoflowers.

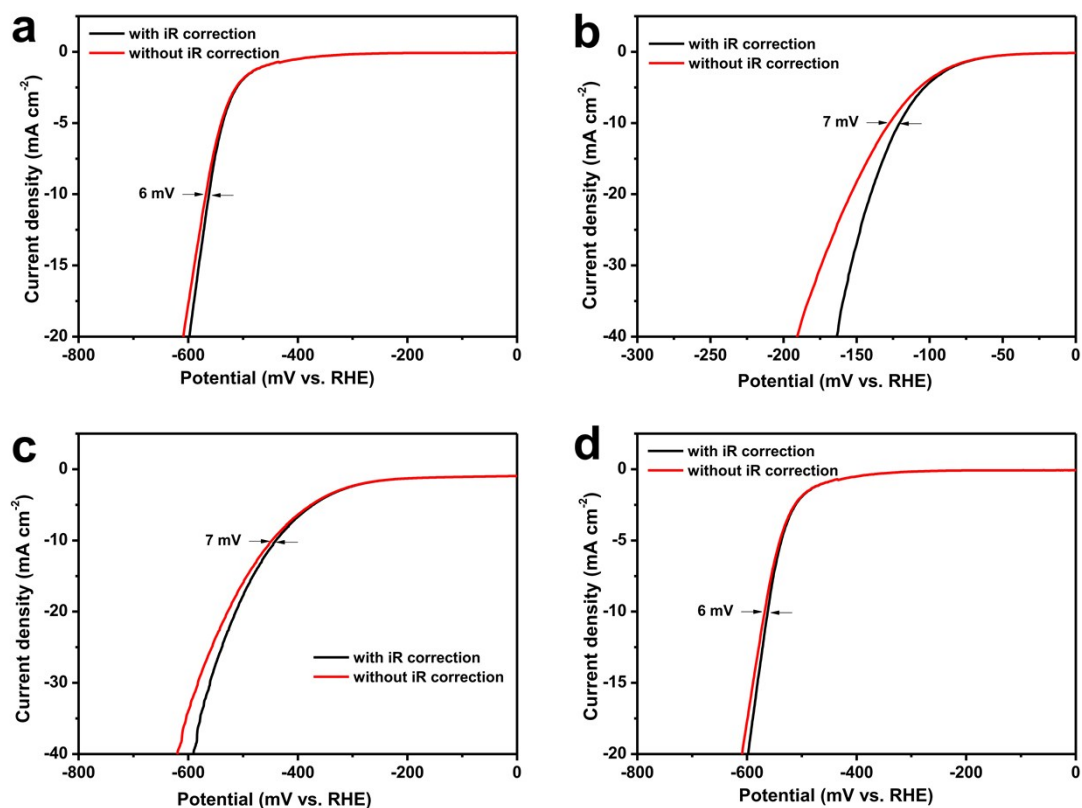


Fig. S14. The LSV curves before and after iR correction in 1 M KOH. a) hollow β -Mo₂C nanoflowers, b) β -Mo₂C nanoflowers, c) N doped carbon, and d) commercial β -Mo₂C nanoflowers.

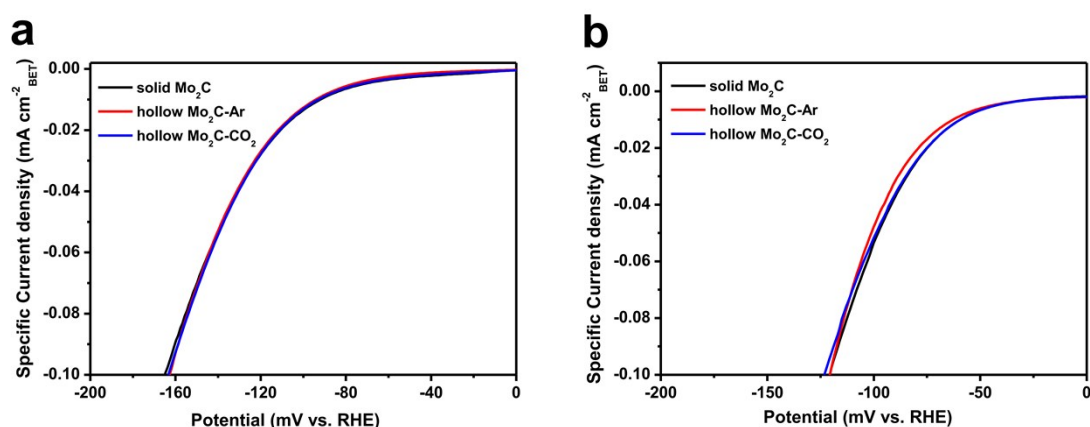


Fig. S15. Polarization curves normalized by the BET a) 0.5 M H₂SO₄, and b) 1 M KOH.

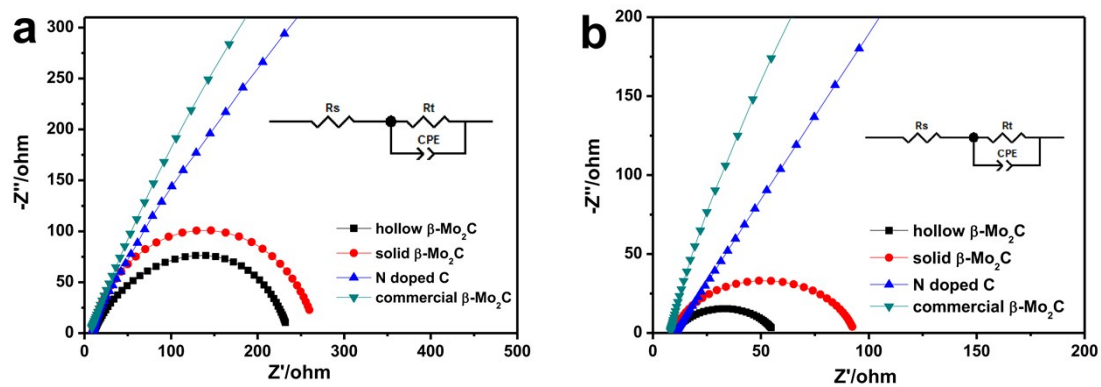


Fig. S16. EIS spectra for hollow and solid β - Mo_2C . a) 0.5 M H_2SO_4 , and b) 1 M KOH.

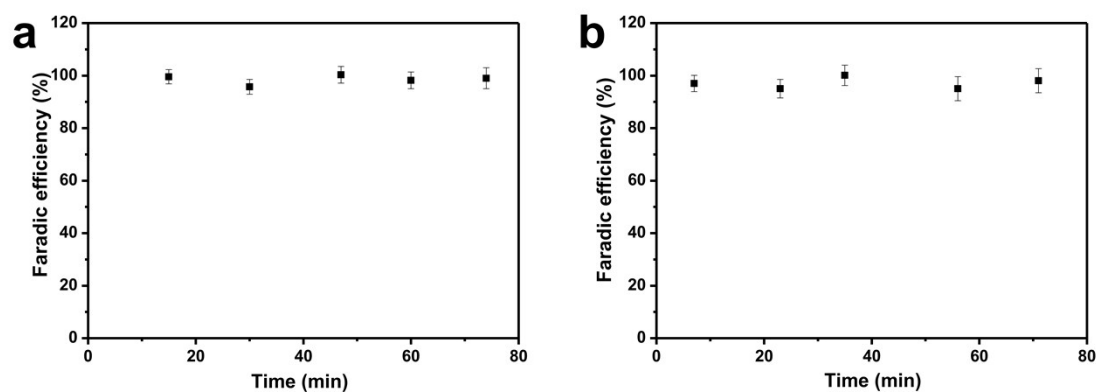


Fig. S17. Faradaic efficiency of the hollow β - Mo_2C /N-doped carbon composite nanospheres from gas chromatography measurement of evolved H_2 to within our available $\pm 5\%$ experimental error. a) 0.5M H_2SO_4 , and b) 1M KOH.

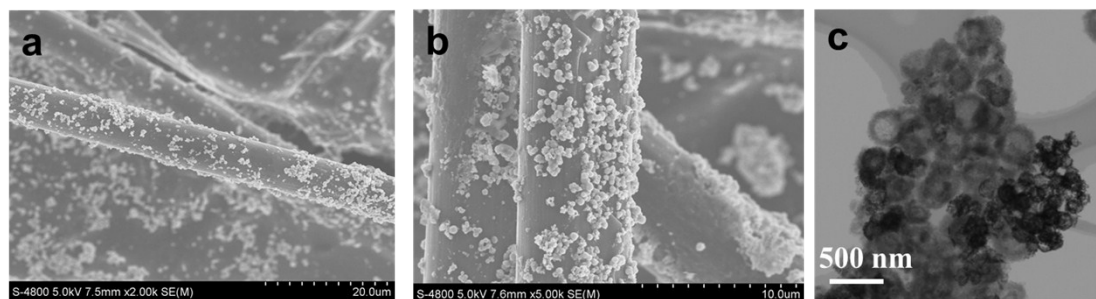


Fig. S18. FESEM (a,b) and TEM (c) images of the hollow β - Mo_2C nanoflowers deposited in carbon fiber paper. (a) before i-t, (b,c) after i-t.

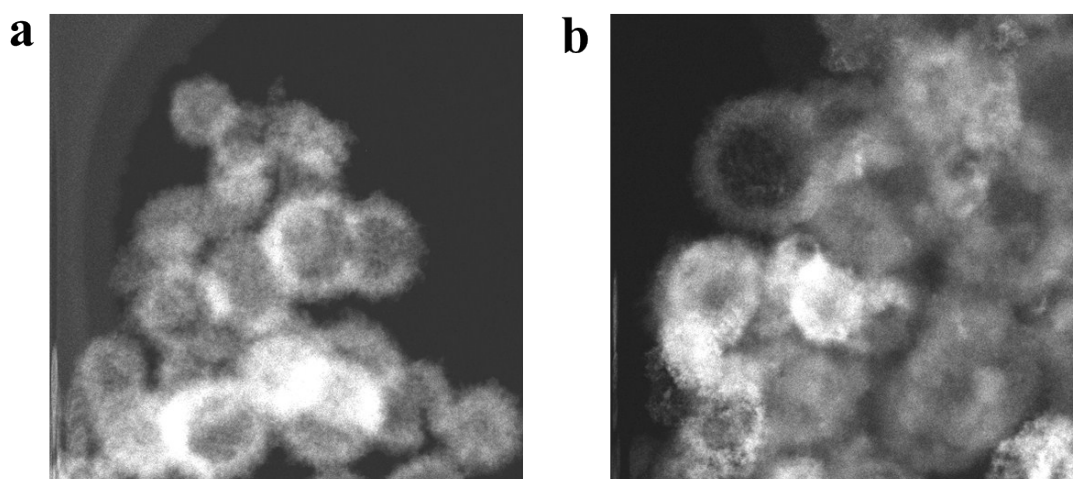


Fig. S19. HAADF-STEM of hollow β -Mo₂C nanoflowers. a) before i-t test and b) after i-t test in 1 M KOH.

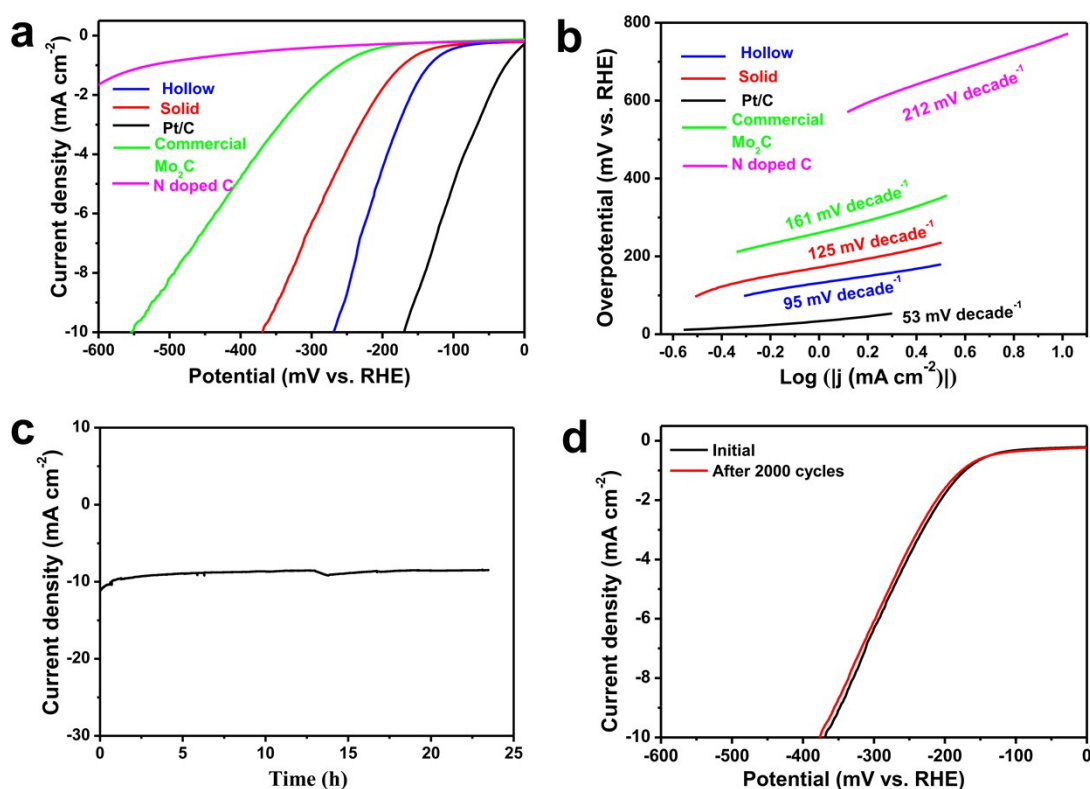


Fig. S20. HER tests in 1 M PBS. a) The HER polarization plots for different catalysts at a scan rate of 5 mV s⁻¹, b) Tafel plots for different catalysts, c) the i-t curve at η =320 mV, and d) polarization curves of the hollow β -Mo₂C nanoflowers before and after 2000 CV scans .

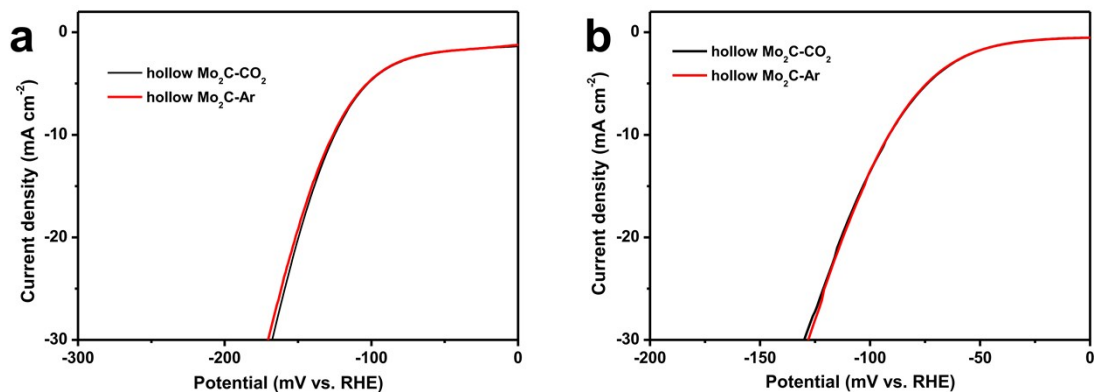


Fig. S21. Polarization curves of the hollow β -Mo₂C-CO₂ and β -Mo₂C-Ar. a) 0.5 M H₂SO₄, and b) 1 M KOH.

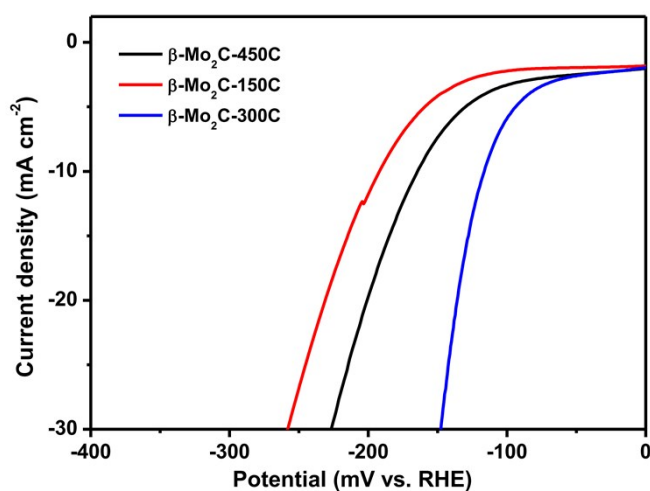


Fig. S22. Polarization curves of the hollow β -Mo₂C-150C, β -Mo₂C-300C and β -Mo₂C-450C in 0.5 M H₂SO₄.

Table S1. Relative atomic ratio of the hollow β -Mo₂C/N-doped carbon composite nanospheres from XPS analysis.

element	C1s	N1s	O1s	Mo3d
Relative atomic ratio (atm.%)	51.85	16	21.09	11.07
Binding energy (eV)	284.80	398.80	530.89	228.84 232.77

Table S2. Surface area and pore diameter of the sample.

sample	Surface area (m ² g ⁻¹)	Pore Diameter (nm)
β -Mo ₂ C-Ar	71.7	9.0
β -Mo ₂ C-CO ₂	73.4	15.3
Solid β -Mo ₂ C	25.4	4.7

Table S3. Comparison of the HER activity in acidic electrolyte of the hollow β -Mo₂C/N-doped carbon composite nanospheres and other Mo₂C based electrocatalysts reported in literature.

Catalyst	Current density (j, mA cm ⁻²)	electrolyte	η at the correspondin g j (mV)	Tafel slope (mV/dec)	Reference
pomegranate-like Mo₂C@C nanospheres	10	0.5M H ₂ SO ₄	141	56	ACS Nano 2016, 10, 8851
Mo₂C QD/NGCL	10	0.5M H ₂ SO ₄	136	68.4	Chem.Comm., 2016, 52, 12753
Mo₂C@NC	10	0.5M H ₂ SO ₄	124	60	Angew. Chem. Int. Ed. 2015, 54, 10752
Mo₂C on carbon cloth	10	0.5M H ₂ SO ₄	140	124	J. Mater. Chem. A, 2015, 3, 16320
β-Mo₂C nanoparticles	10	0.5M H ₂ SO ₄	165	55	Journal of Power Sources 2015, 296, 18-22
Mo₂C-N doped CNT	10	0.5M H ₂ SO ₄	147	71	J. Mater. Chem. A, 2015, 3, 5783
MoCx nano-octahedrons	10	0.5M H ₂ SO ₄	142	53	DOI: 10.1038/ncomms7512
Mo₂C	10	0.5M H ₂ SO ₄	198	56	J. Mater. Chem. A, 2015, 3, 8361
MoC-Mo₂C heteronanowires	10	0.5M H ₂ SO ₄	126	43	Chem. Sci., 2016, 7, 3399
MoSoy	10	0.1 M HClO ₄	177		Energy Environ. Sci., 2013, 6, 1818

Mo₂C-C	10	0.5M H ₂ SO ₄	164	85	Nano Energy 2017, 32, 511–519
Mo₂C/C microflowers	10	0.5M H ₂ SO ₄	146	60	Adv. Energy Mater. 2017, 1602782
P doped Mo₂C@C nw	10	0.5M H ₂ SO ₄	89	42	Energy Environ. Sci., 2017,10, 1262--1271
Hollow β-Mo₂C/N-doped carbon composite nanospheres	10	0.5M H₂SO₄	119	67	This work

Table S4. Comparison of the HER activity in alkaline electrolyte of the hollow β-Mo₂C/N-doped carbon composite nanospheres and other Mo₂C based electrocatalysts reported in literature.

Catalyst	Current density (j, mA cm⁻²)	electrolyte	η at the corresponding j (mV)	Tafel slope (mV/dec)	Reference
pomegranate-like Mo₂C@C nanospheres	10	1M KOH	47	71	ACS Nano 2016, 10, 8851
Mo₂C QD/NGCL	10	1M KOH	111	57.8	Chem.Comm., 2016, 52, 12753
Mo₂C@NC	10	1M KOH	60		Angew. Chem. Int. Ed. 2015, 54, 10752
(Mo₂C)_{0.34}-(WC)_{0.32}/NG	10	1M KOH	93	53	DOI: 10.1039/c7ta02864d
Mo₂C@NPC	10	1M NaOH	141	47.5	J. Mater. Chem. A, 2017, 5, 5178
NiMo₂C@C	10	1M KOH	181	84	J. Mater. Chem. A, 2017, 5, 5000
MoCx nano-octahedrons	10	1M KOH	151	59	DOI: 10.1038/ncomms7512
Mo₂C	10	1M KOH	176	58	J. Mater. Chem. A, 2015, 3, 8361
MoC-Mo₂C heteronanowires	10	1M KOH	120	42	Chem. Sci., 2016, 7, 3399
Mo₂C	10	1M KOH	96	62.2	J. Mater. Chem. A, 2017, 5, 4879

Mo₂C-C	10	1M KOH	149	66	Nano Energy 2017, 32, 511–519
Mo₂C/C microflowers	10	1M KOH	140	58	Adv. Energy Mater. 2017, 1602782
Hollow β-Mo₂C/N-doped carbon composite nanospheres	10	1M KOH	85	49	This work

Table S5. The charge transfer resistance of different samples measured in 0.5 M H₂SO₄.

Simple(H₂SO₄)	Rs(Ω)	Rt(Ω)
Hollow β-Mo₂C	10.23	226
solid β-Mo₂C	9.05	258.6
N doped C	8.05	1761
Commercial β-Mo₂C	5.80	2818

Table S6. The charge transfer resistance of different samples measured in 1 M KOH.

Simple(KOH)	Rs(Ω)	Rt(Ω)
Hollow β-Mo₂C	9.39	61.43
solid β-Mo₂C	9.74	90.68
N doped C	10.47	3178
Commercial β-Mo₂C	7.92	3366

Table S7. The concentrations of Mo measured by ICP-AES after HER in both 0.5 M H₂SO₄ and 1 M KOH.

Electrolyte sample	Concentrations of Mo in electrolyte (ppm)
0.5 M H ₂ SO ₄	0.22
1 M KOH	1

Table S8. Comparison of the HER activity in neutral electrolyte of the hollow β -Mo₂C/N-doped carbon composite nanospheres and other electrocatalysts reported in literature.

Catalyst	Current density (j, mA cm ⁻²)	electrolyte	η at the corresponding j (mV)	Tafel slope (mV/dec)	Reference
CoMoS ₄ NTA/CC	10	1M PBS	179	77	Chemistry-A European Journal, 2017, 23, 12718-12723
CoP NA/CC	10	1M PBS	145	123	ChemElectroChem, 2017, 4, 1840-1845
CoP/CC	2	1M PBS	65	93	J. Am. Chem. Soc. 2014, 136, 7587–7590
FeMoS ₄ NRA/CC	10	1M PBS	204	128	Chem. Commun., 2017, 53, 9000--9003
Co ₂ N/TM	10	1M PBS	290	138	Catal. Sci. Technol., 2017, 7, 2689–2694
Co-NRCNTs/GCE	10	1M PBS	540		Angew. Chem. 2014, 126, 4461 –4465
CoO/CoSe ₂ /Ti	10	0.5M PBS	337	131	Adv.Sci.2016, 3, 1500426
WN NAs/CC	10	1M PBS	302	182	Electrochimica Acta 154 (2015) 345–351
Cu-EA	2	0.1M PBS	270		Chem. Commun., 2015, 51, 12954-12957
cobalt @ cobalt-oxo / hydroxo phosphate	2	0.5M phosphate buffer (KPi, pH = 7)	385		Nat. Mater. 2012, 11, 802

Mo₂C	1	1M PBS	200		Angew. Chem. Int. Ed. 2012, 51, 12703
Hollow β-Mo₂C/N- doped carbon composite nanospheres	10	1M PBS	268	95	This work
