Electronic Supplementary Material (ESI) for Nanoscale.

Agaric-derived N-doped carbon nanorod arrays@nanosheet networks coupled with molybdenum carbide nanoparticles as highly efficient pH-universal hydrogen evolution electrocatalysts

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Figure S1 The comparative digital photographs at different stages of the synthesis process of Mo_2C@N-CANs electrocatalysts from natural agaric.

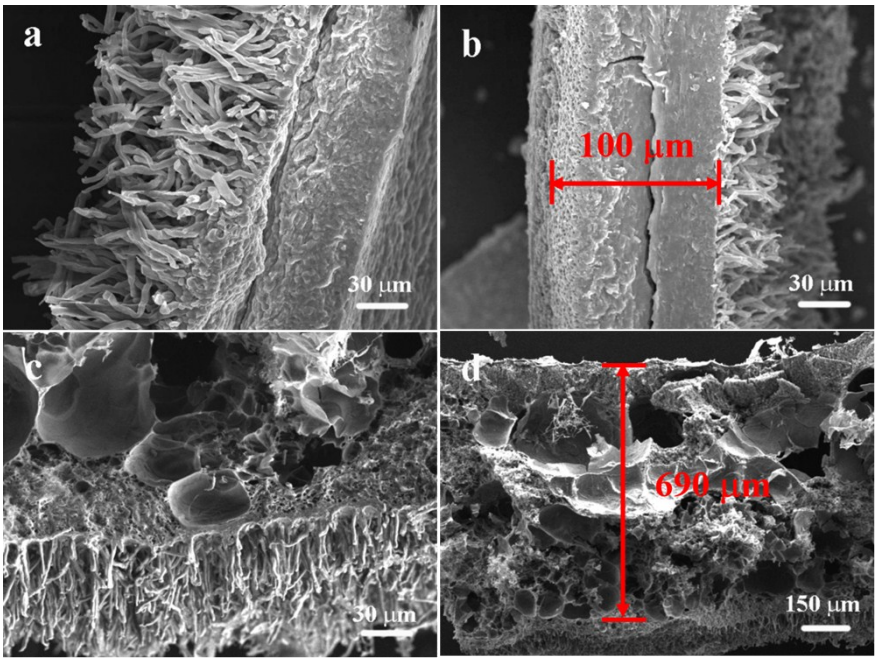

Figure S2 SEM images of Mo_2C@N-CANs prepared with different drying processes (a, b) 60 ℃ drying and (c, d) freeze drying

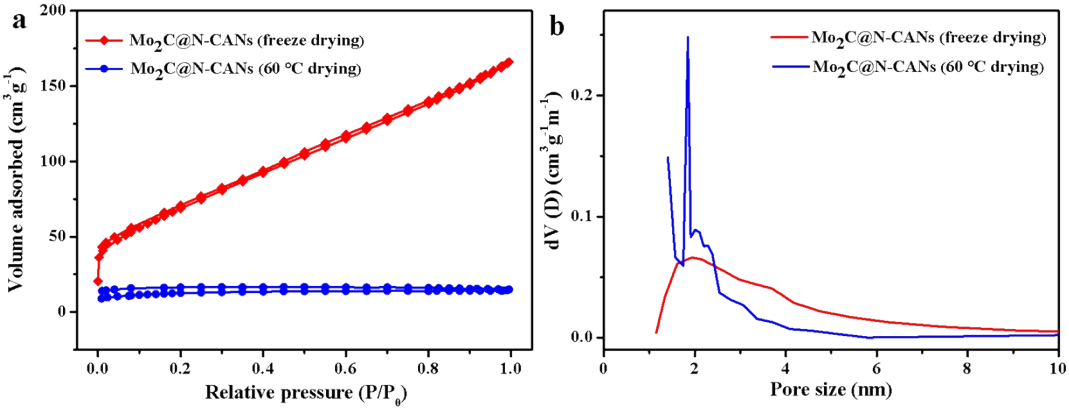

Figure S3 (a) N_2 adsorption-desorption isotherms and (b) pore volume of Mo_2C@N-CANs prepared with freeze drying and 60 ℃ drying

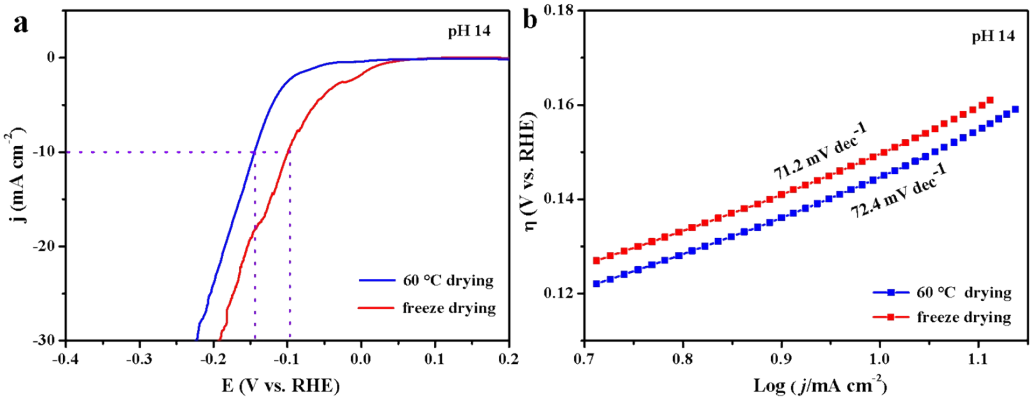

Figure S4 (a) Polarization curves and (b) Tafel curves of Mo_2C@N-CANs prepared with freeze drying and 60 ℃ drying.

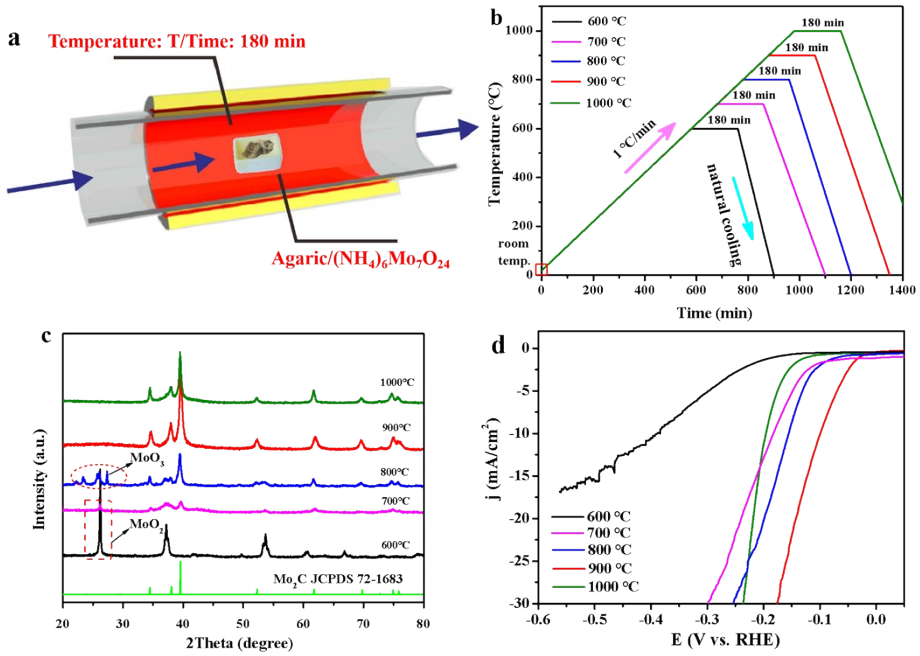

Figure S5 (a) Schematic diagram of the apparatus, (b) Temperature programs for the synthesis of Mo_2C@N-CANselectrocatalysts, (c) XRD patterns of the samples obtained at different pyrolytic temperature and (d) Polarization curves of the samples obtained at different pyrolytic temperature.

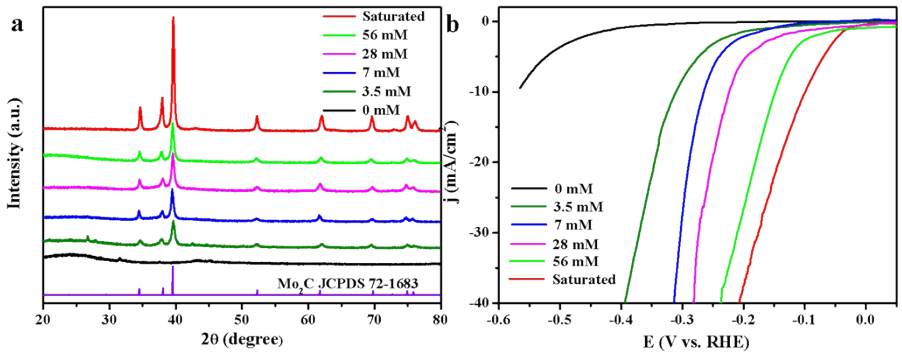

Figure S6 (a) XRD patterns and (b) Polarization curves of the Mo_2C@N-CANs samples obtained with different concentrations of $(NH_4)_6Mo_7O_{24}$ solution.

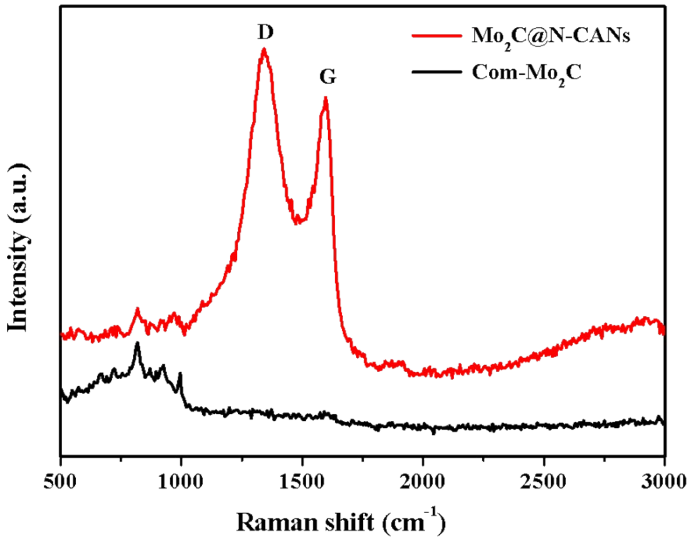

Figure S7 Raman spectra of the Mo_2C@N-CANs sample and commercial Mo_2C powders.

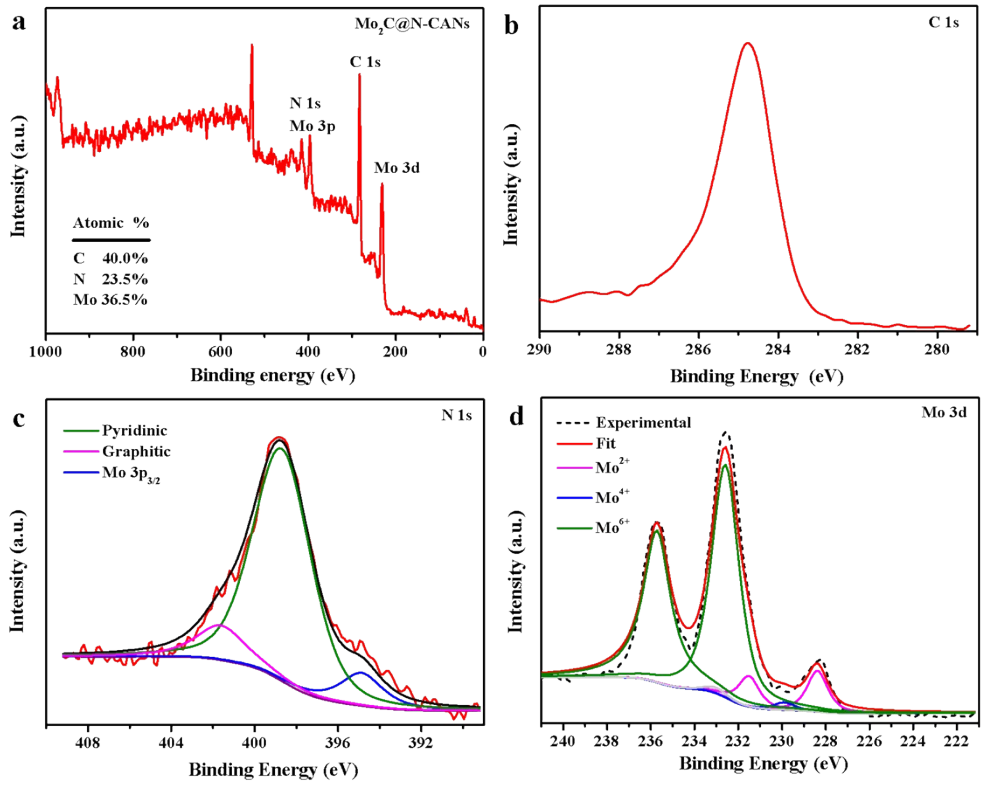

Figure S8 XPS spectra of Mo_2C@N-CANs electrocatalyst: (a) Survey XPS spectrum; and (b~d) High-resolution XPS spectra of (b) N 1s; (c) C 1s and (d) Mo 3d.

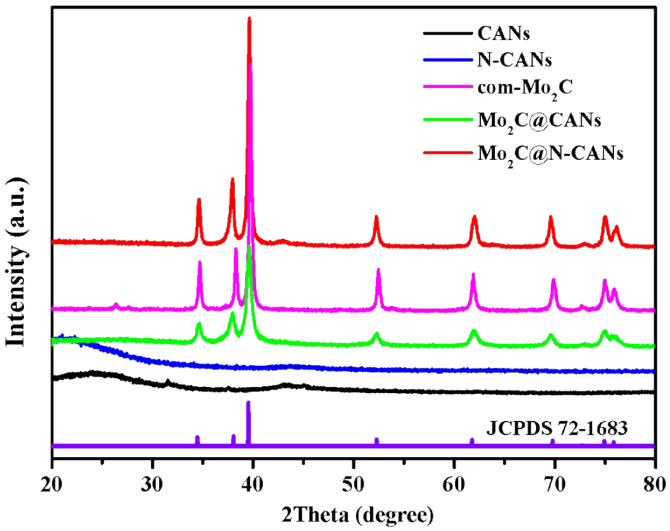

Figure S9 XRD patterns of the different electrocatalysts.

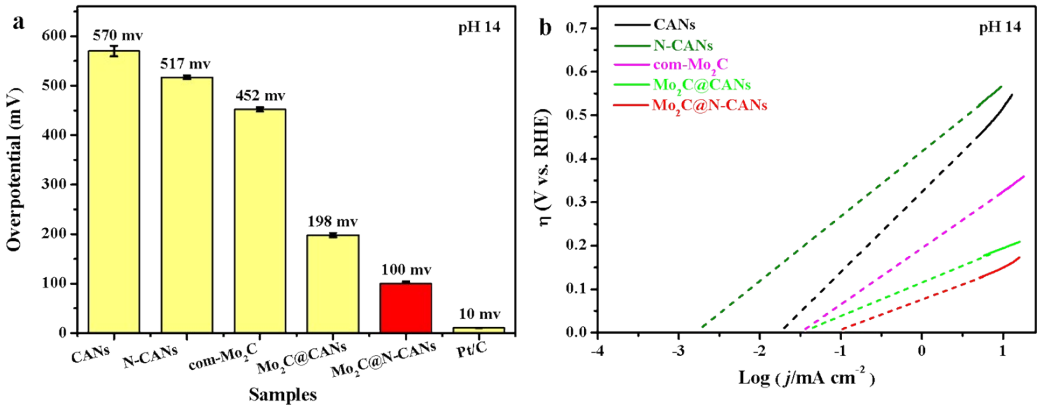

Figure S10 (a) Overpotentials at 10 mA·cm^{-2} and (b) Calculated exchange current density in 1 M KOH of Mo_2C@N-CANs, CANs, N-CANs, Mo_2C@CANs, com-Mo_2C and 20 wt% Pt/C catalysts.

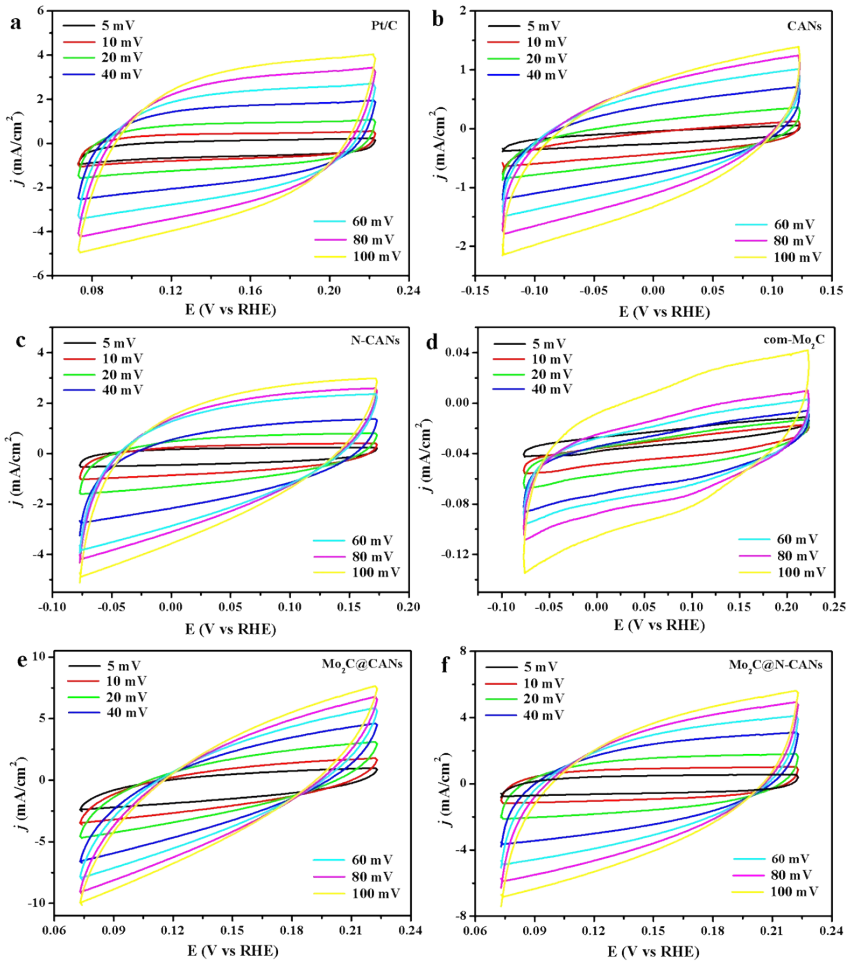

Figure S11 CV curves for (a) Pt/C, (b) CANs, (c) N-CANs, (d) com-Mo_2C, (e) Mo_2C@CANs and (f) Mo_2C@N-CANs electrocatalysts at different scan rates

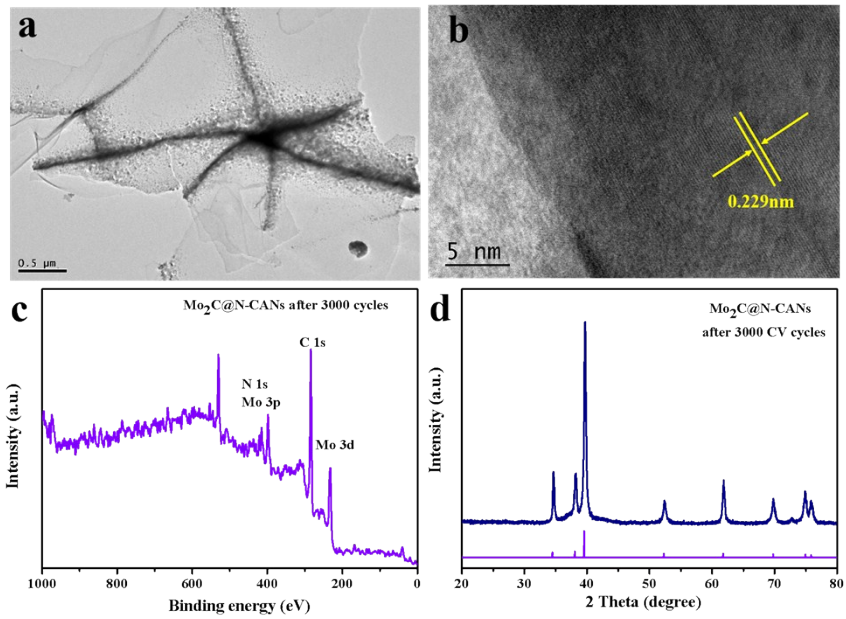

Figure S12 (a) TEM image (b) HRTEM image, (c) XPS spectrum and (d) XRD pattern of Mo_2C@N-CANs electrocatalyst after 3000 CV cycles in 1M KOH solution.

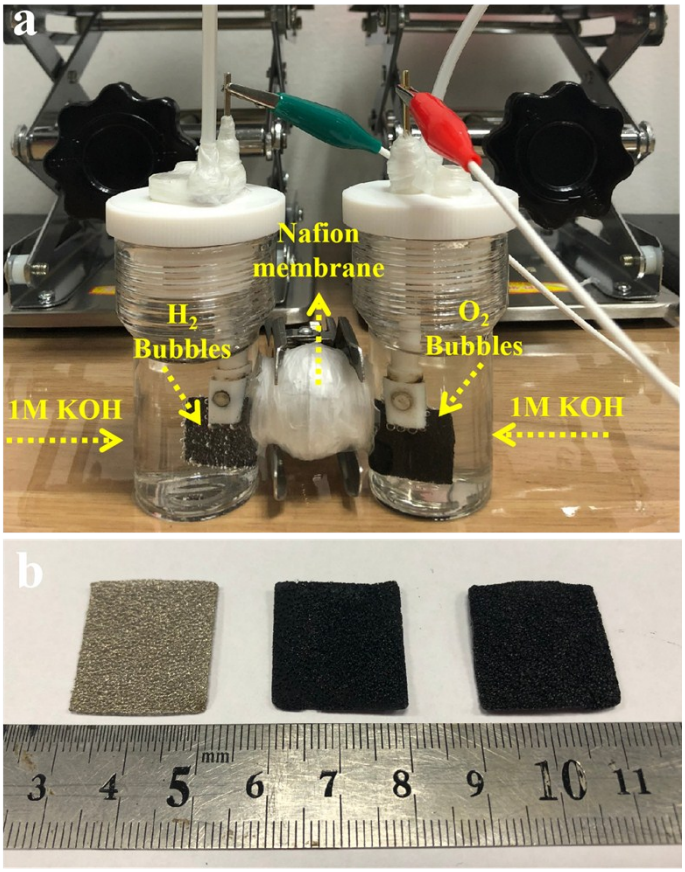

Figure S13 (a) Enlarged digital image of the home-made water-splitting system; (b) Digital image of Ni foam loading nothing (left), Mo_2C@N-CANs (middle), and IrO_2 (right).

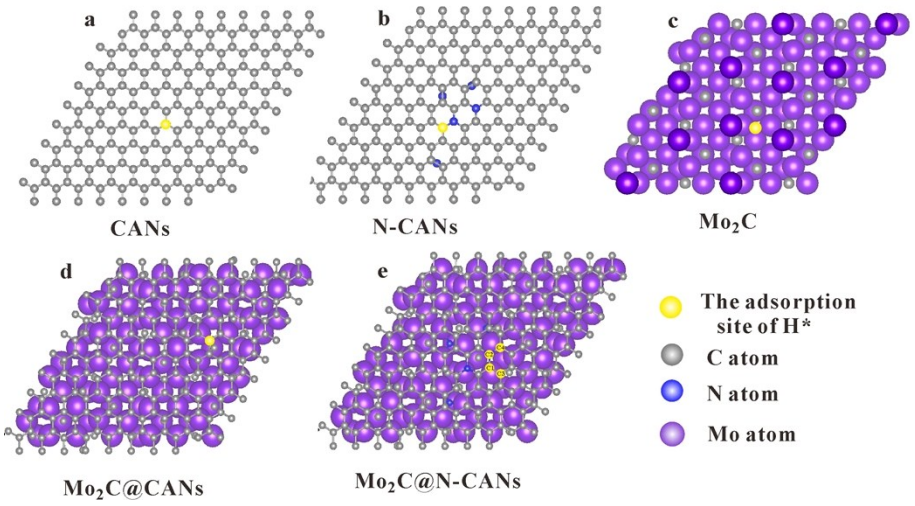

Figure S14 The theoretical models used in DFT calculations and the adopted adsorption sites of H* on the surface of these models: (a) CANs, (b) N-CANs, (c) Mo_2C, (d) Mo_2C@CANs, (e) Mo_2C@N-CANs

Table S1 BET surface area, pore volume and pore size of the different samples

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)
Mo_2C@N-CANs (freeze drying)	239.73	0.2514	3.93
Mo_2C@N-CANs (60 ℃ drying)	43.96	0.0221	2.00

Table S2 ICP result of the Mo_2C@N-CANs samples

Sample	Mo (mg/L)	The load of Mo_2C calculated on the N-CANs
Mo_2C@N-CANs	557	50.8%

The method of ICP test: 0.035g of Mo_2C@N-CANs was dissolved in 3 mL of aqua regia under sonication for 30 min. Then, the solution was diluted to 30 mL and centrifugated under 8000 rmp. The supernatant was used for ICP test. The load of Mo_2C on N-CANs could be calculated by the measured concentration of Mo element by the following formula:

$$\textbf{The load of } Mo_2C \textbf{ on N-CANs} = (C_{Mo} \times 30) / (Mr_{Mo/Mo_2C} / Mr_{Mo_2C}) / 35 \times 100\%$$

where C_{Mo} is the concentration of Mo tested by ICP, 30 is the total volume of the solution, $Mr_{Mo/Mo2c}$ is the relative molecular weight of Mo in Mo_2C, which is 191.88, Mr_{Mo2c} is the relative molecular weight of Mo_2C molecular, which is 203.88 and 35 mg is the total quality of the weighed Mo_2C@N-CANs.

Table S3 EDS analysis of Mo_2C@N-CANs samples obtained at different concentrations of $(NH_4)_6Mo_7O_{24}$ solution.

Samples	C（At%）	N（At%）	Mo（At%）
0 mM	100	—	—
3.5 mM	94.14	1.93	4.93
7 mM	77.74	12.01	10.25
28 mM	81.14	8.07	10.79
56 mM	72.94	13.98	13.08
Staurated	**74.52**	**8.71**	**16.77**

Table S4 EDS analysis of different samples.

Samples	**C（At%）**	**N（At%）**	**Mo（At%）**
CANs	99.65	0.35	—
N-CANs	81.27	18.73	—
Mo_2C@CANs	85.87	0.58	13.55
Mo_2C@N-CANs	74.52	8.71	16.77

Table S5 BET surface area, pore volume and pore size of the different samples

Sample	**S_{BET} ($m^2 \cdot g^{-1}$)**	**Pore volume ($cm^3 \cdot g^{-1}$)**	**Pore size (nm)**
CANs	532.6538	0.337953	2.53788
N-CANs	1145.8126	0.582090	2.03206
Com-Mo_2C	1.9651	0.002419	4.92487
Mo_2C@CANs	145.3180	0.156030	2.95665
Mo_2C@N-CANs	**239.7328**	**0.251360**	**3.93131**

Table S6 Comparison of the electrocatalytic activity of Mo_2C@N-CANs with the Mo_2C based solid-state catalysts reported recently for HER in 1 M KOH electrolyte.

	Loading density ($mg \cdot cm^{-2}$)	Current density (j)	Overpotential at the corresponding j	Reference
Mo_2C@N-CANs	**0.357**	**10 mA/cm^2**	**100 mV**	**This work**
Mo_2C@N-CNFs	0.255	10 mA/cm^2	168 mV	*NPG Asia Mater.* **2016**, *8*, e288.
Mo_2C@NPC	0.14	10 mA/cm^2	260 mV	*Nat. Commun.* **2016**, *7*, 11204.
porous MoC_x nano-octahedrons	0.8	10 mA/cm^2	151 mV	*Nat. Commun.* **2015**, *6*, 6512
β-Mo_2C Nanotubes	0.213	10 mA/cm^2	112 mV (0.1 M KOH)	*Angew. Chem. Int. Ed.* **2015**, *54*, 15395
Mo_2C nanoparticles	0.102	10 mA/cm^2	176 mV	*J. Mater. Chem. A* **2015**, *3*, 8361
Mo_2C nanocrystal embedded N-CNTs	3	10 mA/cm^2	257 mV	*J. Mater. Chem. A* **2015**, *3*, 5783
MoP	0.86	10 mA/cm^2	140 mV	*Energy Environ. Sci.* **2014**, *7*, 2624
$MoC_{0.654}$@CNS nanosheet		10 mA/cm^2	220 mV (0.1 M KOH)	*J. Am. Chem. Soc.* **2015**, *137*, 16, 5480
BCF/Mo_2C	1.41	20 mA/cm^2	115 mV	*ACS Appl. Mater. Interfaces* **.2017**, 9, 22604
Mo_2C/C Nanosheet	0.28	10 mA/cm^2	125 mV	*ACS Appl. Mater. Interfaces*. **2017**, 9, 41314
Mo_2C/C	1.02	10 mA/cm^2	140mV	*Small* **2017**, *13*, 1701246.
Mo_2C/KB	0.213	10 mA/cm^2	210 mV	*ACS Sustain. Chem. Eng.* **2018**, *6*, 983
Mo_2C/C	0.213	10 mA/cm^2	218 mV	*ACS Sustain. Chem. Eng.* **2018**, *6*, 13995
Ni impregnated Mo_2C nano-rod		10 mA/cm^2	130mV	*Appl. Catal. B: Environ.* **2014**, *154-155*, 232.

Table S7 Comparison of the electrocatalytic activity of Mo_2C@N-CANs with the Mo_2C based solid-state catalysts reported recently for HER in 0.5 M H_2SO_4 and in 0.1 M PBS electrolyte.

	Loading density (mg/cm^2)	Current density (j)	Overpotential at the corresponding j	Reference
Mo_2C@N-CANs	**0.357**	**10 mA/cm^2**	**82mV (0.5 M H_2SO_4) 359 mV (0.1M PBS)**	**This work**
N-Doped Mo_2C Nanosheets	0.357	10 mA/cm^2	99 mV 0.5M H_2SO_4	*ACS Nano* .**2017**, 11, 12509
Mo_2C/C Nanosheet	0.28	10 mA/cm^2	180 mV 0.5M H_2SO_4	*ACS Appl. Mater. Interfaces*. **2017**, 9, 41314
Mo_2C/C	1.02	10 mA/cm^2	175mV 0.5M H_2SO_4	*Small* **2017**, *13*, 1701246.
Mo_2C/Carbon Hybrid Nanotubes	0.69	10 mA/cm^2	140 mV 0.5M H_2SO_4	*Langmuir* **2018**, *34*, 10924.
Mo_2C/KB	0.213	10 mA/cm^2	180 mV 0.5M H_2SO_4	*ACS Sustain. Chem. Eng.* **2018**, *6*, 983.
NP-Mo_2C	0.213	10 mA/cm^2	210 mV 0.5M H_2SO_4	*Carbon* **2018**, *139*, 845.
Mo_2C/C	0.213	10 mA/cm^2	233 mV 0.5M H_2SO_4	*ACS Sustain. Chem. Eng.* **2018**, *6*, 13995.
β-Mo_2C Nanotubes	0.213	10 mA/cm^2	172 mV 0.5M H_2SO_4	*Angew. Chem. Int. Ed.* **2015**, *54*,15395
Mo_xC-IOL	2.2	10 mA/cm^2	117mV 0.5M H_2SO_4	*ACS Nano* **2017**, *11*, 7527.
np-Mo_2C	No-reported	10 mA/cm^2	229mV 0.5M H_2SO_4	*Adv. Sci.* **2018**, *5*, 1700601
PDAP-MoCN-CO_2	0.4 (pH=1)	10 mA/cm^2	140 0.5M H_2SO_4	*J. Am. Chem. Soc.* **2015**, *137*, 110
β-$Mo_{0.06}W_{0.94}C$/CB	0.7	10 mA/cm^2	220mV 0.5M H_2SO_4	*Angew. Chem. Int. Ed.* **2014**, *53*, 5131
Mo_2C	1.4	10 mA/cm^2	210mV (1 M H_2SO_4)	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703
porous MoC_x nano-octahedrons	0.8	10 mA/cm^2	142 0.5M H_2SO_4	*Nat. Commun.* **2015**, *6*, 6512
Mo_2C Nanoparticles Decorated Graphitic	0.36	10 mA/cm^2	210 mV 0.5M H_2SO_4	*J. Mater. Chem. A* **2014**, *2*, 18715
Mo_2C@N-CNFs	0.255	10 mA/cm^2	167mV (0.5M H_2SO_4) 431mV (0.1M PBS)	*NPG Asia Mater.* **2016**, *8*, e288.
N-doped Mo_2C carbon nanotubes	3	10 mA/cm^2	645 mV (0.1M PBS)	*J. Mater. Chem. A* **2015**, *3*, 5783.
Mo_2C	1.4	1 mA/cm^2	200 mV (0.1M PBS)	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.

Table S8 The lattice parameters (Å) of the supercells for all the systems

Models	a (Å)	b (Å)	c (Å)
Graphene	22.17619	22.17619	37.74370
N-doped Graphene	22.20219	22.18377	37.74379
Mo_2C(102)	21.61710	21.06020	37.74370
Mo_2C(102)@Graphene	21.61710	21.06020	37.74370
Mo_2C(102)@N-doped Graphene	21.61710	21.06020	37.74370

Table S9 The ΔE (H*), E_{ZPE} (H*), ΔE_{ZPE} and ΔG (H*) values of the H* adsorbed on the given surfaces.

Models	Adsorption Site	ΔE_{H^*} (eV)	E_{ZPE}(H*) (eV)	ΔE_{ZPE} (eV)	ΔG(H*) (eV)
C Graphene		0.9055	0.2985	0.0191	0.6568
N-doped Graphene		0.4310	0.3145	0.0351	0.1978
Mo_2C(102)		-0.7498	0.2492	-0.0301	-1.1233
Mo_2C(102)@ Graphene		0.5856	0.3053	0.0260	0.2739
Mo_2C(102)@ N-doped Graphene	C1	0.3136	0.3163	0.0370	0.0132
	C2	1.2802	0.3431	0.0637	1.0068
	C3	0.4789	0.3043	0.0249	0.1661
	C4	0.3305	0.3124	0.0031	0.0261