

Supplementary Material

Direct synthesis of bifunctional nanorods from Co-Adenine-MoO₃ hybrid for overall water splitting

Anning Jiang,^{#a} Wei Zhang,^{#bc} Zegao Wang,^{de} Naga Pradeep Nidamanuri,^a Qiang Li,^{*a}
Xiao Cheng Zeng^{*c} and Mingdong Dong^{*ad}

^a

^a Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.

E-mail: qiang@sdu.edu.cn

^b Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

^c Department of Chemistry, University of Nebraska-Lincoln, Nebraska 68588, United States.

E-mail: xzengl@unl.edu

^d Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus C, DK-8000, Denmark. *E-mail: dong@inano.au.dk*

^e College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China

[#] These authors contributed equally to this work.

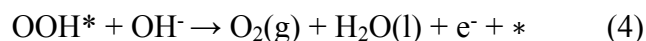
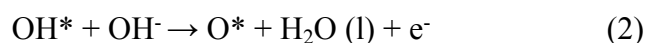
METHODS

Materials

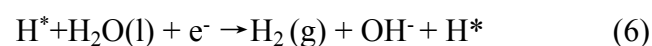
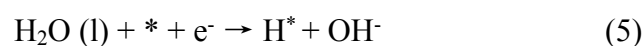
Adenine (C₅H₅N₅) and commercial molybdenum trioxide (MoO₃) powder were purchased from Aladdin (Shanghai, China). Cobalt (II) nitrate hexahydrate (Co(NO₃)₂•6H₂O) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich (Shanghai, China). Commercial RuO₂ (99.9%) was purchased from Macklin (Shanghai, China). All chemicals and materials were used as received.

Computational methods

We computed the theoretical overpotential for the OER and HER by using DFT calculation with the computational hydrogen electrode model.¹ This method has been successful to predict trends in electrochemical activity for model oxide surfaces^{2,3} and for metal embedded nitrogen-doped graphene (M-NG).^{4,5} For OER in an alkaline electrolyte (pH=14), as OH⁻ may act as the electron donor, the overall reaction scheme of the OER can be expressed as:



For HER in an alkaline electrolyte (pH = 14), H₂O can act as the proton donor. Thus, the overall reaction scheme of the HER can be written as:





For each elementary step associated with OER and HER, the Gibbs reaction free energy ΔG is defined as the difference between free energies of the initial and final states, given by the following expression:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (8)$$

where ΔE is the reaction energy of reactant and product molecules adsorbed on catalyst surface, and ΔZPE and ΔS are the change in zero-point energies and entropy in the reaction. The bias effect on the free energy of each initial, intermediate and final state involving electron transfer in the electrode is also taken into account by shifting the energy of the state by $\Delta G_U = -neU$, where U is the applied potential on electrode, e is the transferred charge, and n is the number of proton–electron transferred pairs. The change in free energy due to the effect of pH value of the electrolyte is considered through the correction of H^+ ions concentration ($[\text{H}^+]$) dependence of the entropy, $\Delta G_{pH} = -k_B T \ln [\text{H}^+] = pH \times k_B T \ln 10$, where k_B is the Boltzmann constant and T is the temperature (298 K). Given that the high-spin ground state of the oxygen molecule is poorly described in DFT calculations, the free energy of the O_2 molecule was determined by $G_{\text{O}_2}(\text{g}) = 2G_{\text{H}_2\text{O}}(\text{l}) - 2G_{\text{H}_2}(\text{g}) + 4 \times 1.23(\text{eV})$. The free energy of OH^- was derived as $G_{\text{OH}^-} = G_{\text{H}_2\text{O}}(\text{l}) + e^- - 1/2G_{\text{H}_2}(\text{g})$. The free energy for gas-phased water was calculated at 0.035 bars because this is the equilibrium pressure in contact with liquid water at 298 K. The free energy of gas-phase water at these conditions is equal to the free energy of liquid water.

To evaluate the adsorption strength of OH^* , O^* , OOH^* , and H^* , the adsorption

energies of these molecules and atoms were calculated based on the equation:

$$E_{ads} = E_{total} - E_{catalyst} - E_{adsorbate}, \quad (9)$$

where $E_{catalyst}$ is the energy of the bare catalyst, $E_{adsorbate}$ is the energy of the free O, OH, OOH or H species in the gas phase, and E_{total} is the total energy of the catalyst with adsorbents. Based on the adsorption energies, we can obtain the adsorption free energy of O*, OH*, OOH* and H*. To obtain the exact free energy of O*, OH*, OOH* and H* radicals in the electrolyte solution, the adsorption free energies ΔG_{O^*} , ΔG_{OH^*} , ΔG_{OOH^*} and ΔG_{H^*} are relative to the free energy of appropriate stoichiometric amounts of H₂O (g) and H₂ (g), as defined below:

$$\begin{aligned} \Delta G_{O^*} &= \Delta G(H_2O(g) + * \rightarrow O^* + H_2(g)) \\ &= (E_{O^*} + E_{H_2} - E_{H_2O} - E_*) \\ &\quad + \left(E_{ZPE(O^*)} + E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)} \right) \\ &\quad - T \times (S_{O^*} + S_{H_2} - S_{H_2O} - S_*) \end{aligned} \quad (10)$$

$$\begin{aligned} \Delta G_{OH^*} &= \Delta G(H_2O(g) + * \rightarrow OH^* + 1/2H_2(g)) \\ &= (E_{OH^*} + 1/2E_{H_2} - E_{H_2O} - E_*) \\ &\quad + \left(E_{ZPE(OH^*)} + 1/2E_{ZPE(H_2)} - E_{ZPE(H_2O)} - E_{ZPE(*)} \right) \\ &\quad - T \times (S_{OH^*} + 1/2S_{H_2} - S_{H_2O} - S_*) \end{aligned} \quad (11)$$

$$\begin{aligned} \Delta G_{OOH^*} &= \Delta G(2H_2O(g) + * \rightarrow OOH^* + 3/2H_2(g)) \\ &= (E_{OOH^*} + 3/2E_{H_2} - 2E_{H_2O} - E_*) \\ &\quad + \left(E_{ZPE(OOH^*)} + 3/2E_{ZPE(H_2)} - 2E_{ZPE(H_2O)} - E_{ZPE(*)} \right) \\ &\quad - T \times (S_{OOH^*} + 3/2S_{H_2} - 2S_{H_2O} - S_*) \end{aligned} \quad (12)$$

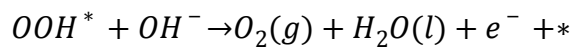
$$\begin{aligned}
\Delta G_{H^*} &= \Delta G(H^+ + e^- + * \leftrightarrow H^*) \\
&= (E_{H^*} - 1/2E_{H_2} - E_*) \\
&+ (E_{ZPE(H^*)} - 1/2E_{ZPE(H_2)} - E_{ZPE(*)}) \\
&- T \times (S_{H^*} - 1/2S_{H_2} - S_*)
\end{aligned} \tag{13}$$

The reaction free energy of (1)-(4) for the OER can be determined from the following equations:

$$\begin{aligned}
OH^- + * &\rightarrow OH^* + e^- \\
\Delta G_1 &= G_{OH^*} + G_{e^-} - G_{OH^-} - G_* \\
&= G_{OH^*} + G_{e^-} - (G_{H_2O(l)} + G_{e^-} - 1/2G_{H_2(g)}) - G_* \\
&= G_{OH^*} + 1/2G_{H_2(g)} - G_{H_2O(l)} - G_* \\
&= \Delta G_{OH^*}
\end{aligned} \tag{14}$$

$$\begin{aligned}
OH^* + OH^- &\rightarrow O^* + H_2O + e^- \\
\Delta G_2 &= G_{O^*} + G_{H_2O} + G_{e^-} - G_{OH^-} - G_{OH^*} \\
&= G_{O^*} + G_{H_2O} + G_{e^-} - (G_{H_2O(l)} + G_{e^-} - 1/2G_{H_2(g)}) - G_{OH^*} \\
&= (G_{O^*} + G_{H_2} - G_{H_2O(l)} - G_*) - (G_{OH^*} + 1/2G_{H_2(g)} - G_{H_2O(l)} - G_*) \\
&= \Delta G_{O^*} - \Delta G_{OH^*}
\end{aligned} \tag{15}$$

$$\begin{aligned}
O^* + OH^- &\rightarrow OOH^* + e^- \\
\Delta G_3 &= G_{OOH^*} + G_{e^-} - G_{O^*} - G_{OH^-} \\
&= G_{OOH^*} + G_{e^-} - G_{O^*} - (G_{H_2O(l)} + G_{e^-} - 1/2G_{H_2(g)}) \\
&= (G_{OOH^*} + 3/2G_{H_2(g)} - 2G_{H_2O(l)} - G_*) - (G_{O^*} + G_{H_2(g)} - G_{H_2O(l)} - G_*) \\
&= \Delta G_{OOH^*} - \Delta G_{O^*}
\end{aligned} \tag{16}$$



$$\begin{aligned}
\Delta G_4 &= G_{O_2}(g) + G_{H_2O}(l) + G_{e^-} + * - G_{OOH^*} - G_{OH^-} \\
&= (2G_{H_2O}(l) - 2G_{H_2}(g) + 4 \times 1.23) + G_{H_2O}(l) + G_{e^-} + * \\
&\quad - G_{OOH^*} - (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) \\
&= 2G_{H_2O}(l) - 1/2G_{H_2}(g) + * - G_{OOH^*} \\
&= 4.92 - \Delta G_{OOH^*}
\end{aligned} \tag{17}$$

With this approach, the theoretical overpotential (U^{OER}) at standard condition is

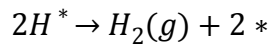
$$\text{defined as:} \quad U^{OER} = (G^{OER} / e) - 1.23 \tag{18}$$

where G^{OER} is the potential determining step defined as the highest free-energy step in the OER, and e is unit charge.

The reaction free energy of (5)-(7) for the HER can be determined from the following equations:

$$\begin{aligned}
&H_2O(l) + e^- + * \rightarrow H^* + OH^- \\
\Delta G_5 &= G_{OH^-} + G_{H^*} - * - G_{e^-} - G_{H_2O}(l) \\
&= (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) + G_{H^*} - * - G_{e^-} - G_{H_2O}(l) \\
&= G_{H^*} - 1/2G_{H_2}(g) - * \\
&= \Delta G_{H^*}
\end{aligned} \tag{19}$$

$$\begin{aligned}
&H^* + H_2O(l) + e^- \rightarrow H_2(g) + OH^- + * \\
\Delta G_6 &= G_{OH^-} + * + G_{H_2}(g) - G_{H^*} - G_{H_2O}(l) - G_{e^-} \\
&= (G_{H_2O}(l) + G_{e^-} - 1/2G_{H_2}(g)) + * + G_{H_2}(g) - G_{H^*} - G_{H_2O}(l) - G_{e^-} \\
&= -(G_{H^*} - 1/2G_{H_2}(g) - *) \\
&= -\Delta G_{H^*}
\end{aligned} \tag{20}$$



$$\begin{aligned}\Delta G_7 &= (G_{H_2}(g) + 2 * - 2G_{H^*}) \\ &= - 2\Delta G_{H^*}\end{aligned}\quad (21)$$

The HER performance was evaluated by computing the reaction free energy (ΔG_{H^*}) for H adsorption, based on the computational hydrogen electrode model⁷ at 0 eV. The equilibrium potential of the HER is given by:

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE(H)} - T\Delta S_H \quad (22)$$

where ΔE_H is the hydrogen adsorption energy. $\Delta E_{ZPE(H)}$ is the zero-point energy difference between the adsorbed state and the gas-phase state of hydrogen, which can be obtained from vibrational frequency calculation. ΔS_H is the entropy difference due to hydrogen adsorption. Here, we approximated the entropy change of hydrogen adsorption as $\Delta S_H \approx 1/2(\Delta S_{H_2})$, where S_{H_2} is the entropy of gas-phase H₂ at standard conditions (25 °C, 1 bar). The theoretical overpotential η for HER was determined by ΔG_{H^*} :

$$\eta = |\Delta G_{H^*}|/e \quad (23)$$

For comparison, we consider several other systems including: graphene (gra), nitrogen doped graphene (gra-N), molybdenum-carbide (Mo₂C), and cobalt doped molybdenum-carbide (Co-Mo₂C) determined from the Co-Mo₂C@NGCS electrocatalyst. For the Co-Mo₂C@NGCS electrocatalyst synthesized in our experiment, the doping concentrations of N atoms and Co atoms were 4% (N/C) and 7% (Co/Mo), respectively. To assure the molar ratio of the number of atoms in the theoretical model to be consistent with the experiment, two N atoms are doped in the gra-N (48 C atoms) and two Co atoms are doped in the Co-Mo₂C (30 Co atoms), as

shown in Figure S7.

FIGURES

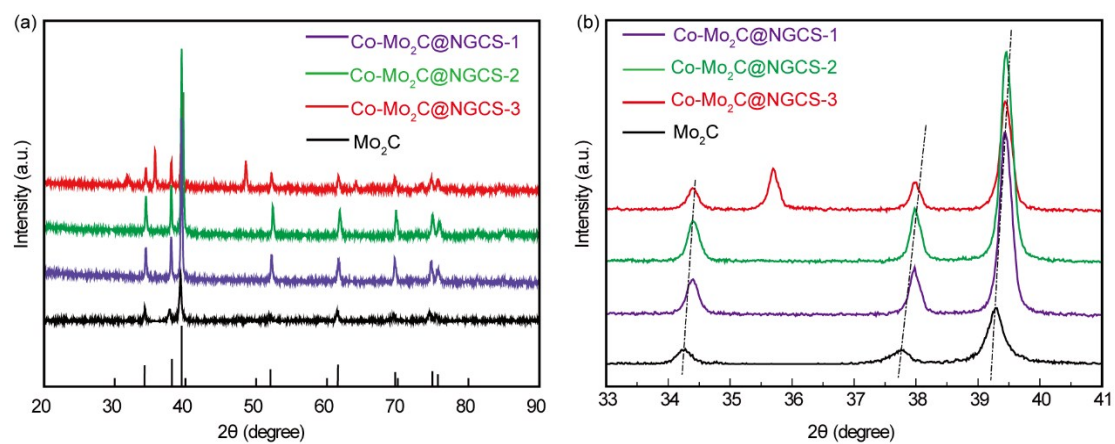


Figure S1. (a) XRD patterns and (b) Zoom-in region of the Co-Mo₂C@NGCS-1, Co-Mo₂C@NGCS-2, Co-Mo₂C@NGCS-3 and Mo₂C catalysts.

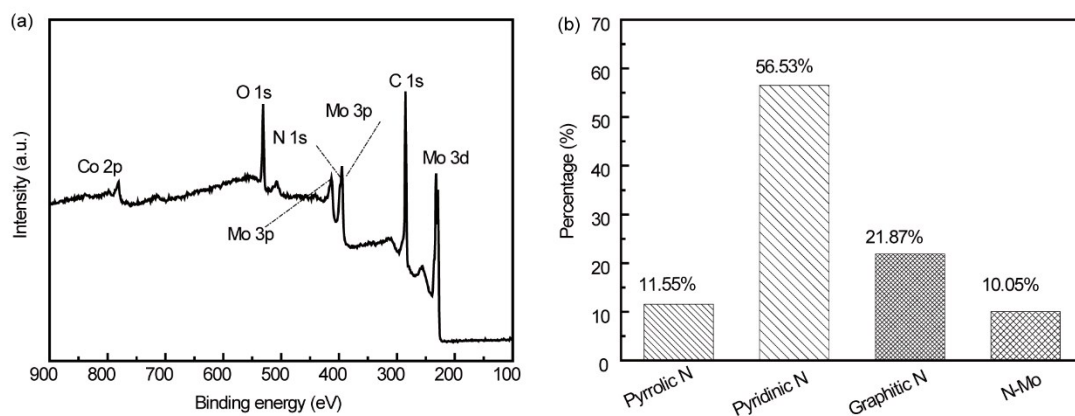


Figure S2. (a) XPS survey spectrum and (b) the calculated content of various nitrogen species of Co-Mo₂C@NGCS-2 sample.

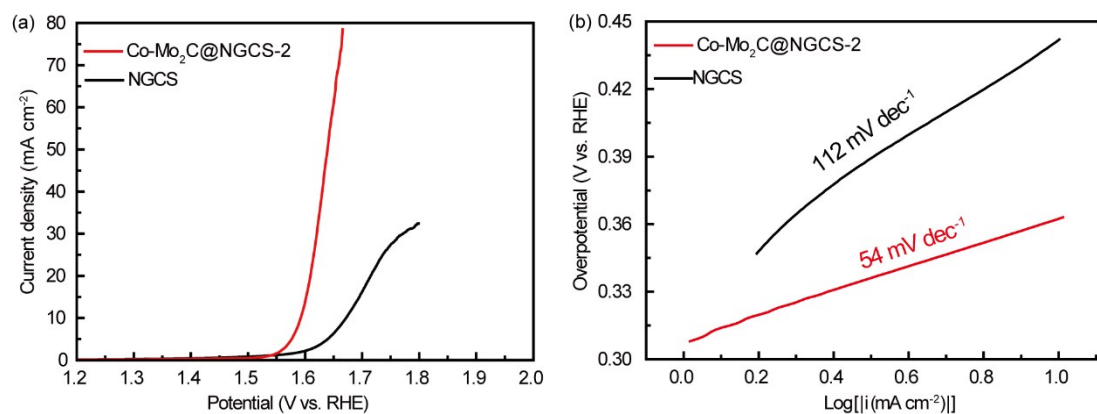


Figure S3 (a) polarization curves and (b) corresponding Tafel plots of Co-Mo₂C@NGCS-2 and collected NGCS for OER measured in 1 M KOH solution.

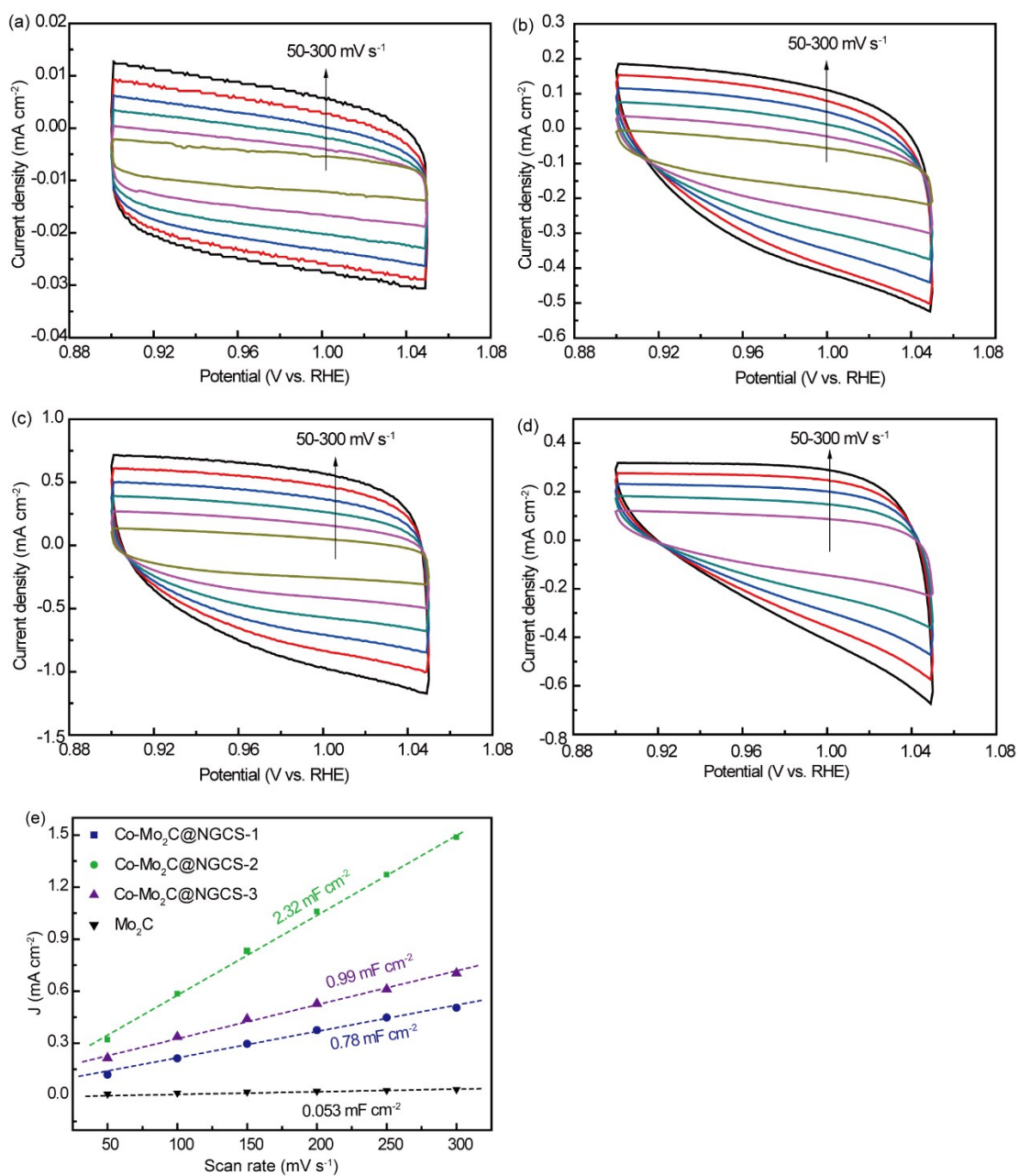


Figure S4. CV curves at different scan rates (50, 100, 150, 200, 250, 300 mV s⁻¹) of (a) Mo₂C, (b) Co-Mo₂C@NGCS-1, (c) Co-Mo₂C@NGCS-2 and (d) Co-Mo₂C@NGCS-3 samples, respectively. (e) Capacitive current as a function of scan rate.

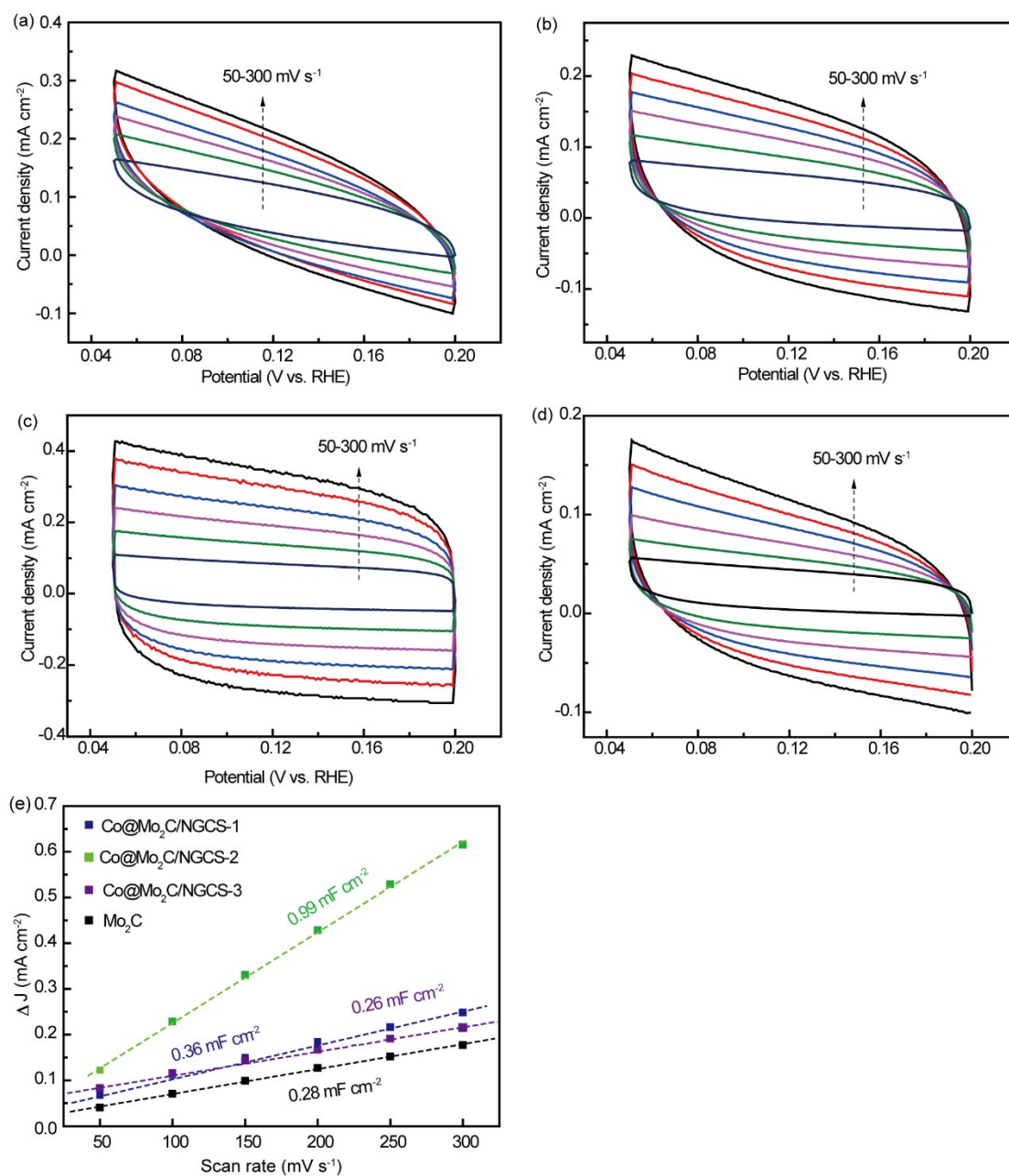


Figure S5. CV curves at different scan rates (50, 100, 150, 200, 250, 300 mV s⁻¹) of (a) Mo₂C, (b) Co-Mo₂C@NGCS-1, (c) Co-Mo₂C@NGCS-2 and (d) Co-Mo₂C@NGCS-3 samples, respectively. (e) Capacitive current as a function of scan rate.

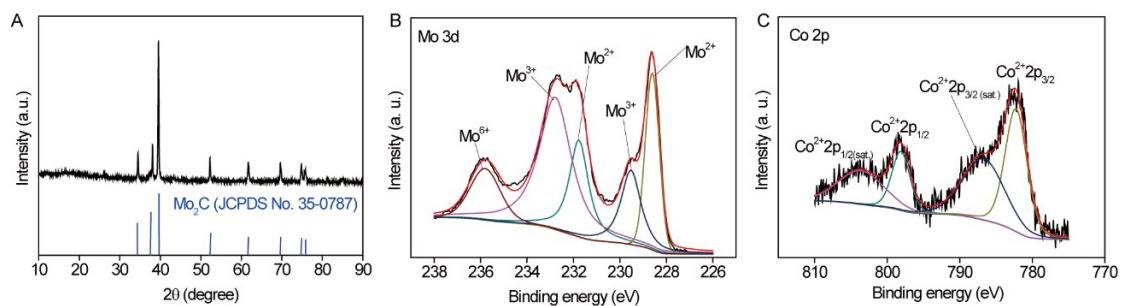


Figure S6. (A) XRD pattern and XPS spectra of (B) Mo 3d region, (C) Co 2p region of Co-Mo₂C@NGCS-2 sample after long-time electrochemical water splitting operation.

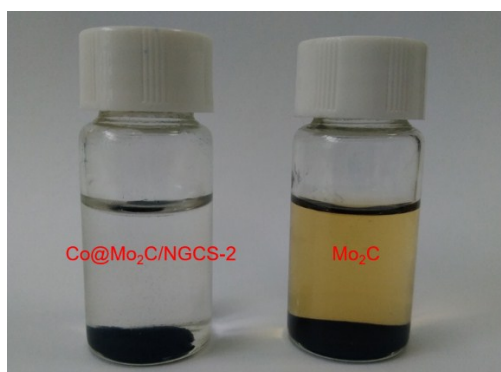


Figure S7. Digital photos of Co-Mo₂C@NGCS-2 and pure Mo₂C samples soaked in 2 M H₂SO₄ solution for one week.

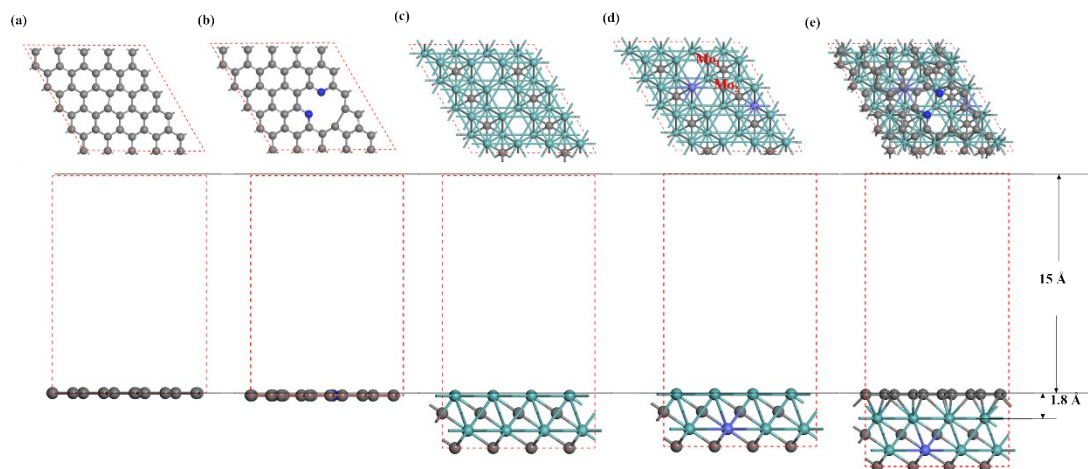


Figure S8. Configuration of graphene (a), N doped graphene (b), Mo₂C (c), Co doped Mo₂C (marked two different Mo atoms) (d), Co doped Mo₂C encapsulated in N doped graphene shell (e). The grey, cyan, and blue color represents C, Mo, and N atom, respectively. Top panels are the top view and bottom panels are the side view.

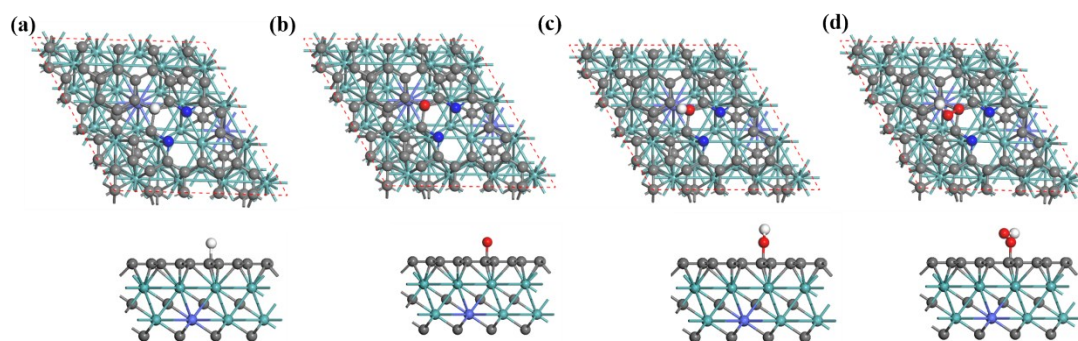


Figure S9. The adsorption configurations of OER/HER intermediates (H^* , O^* , OH^* and OOH^*) on $Co-Mo_2C@NGCS$ catalyst surface. The grey, cyan, blue, red and white color represents C, Mo, N, O and H atom, respectively.

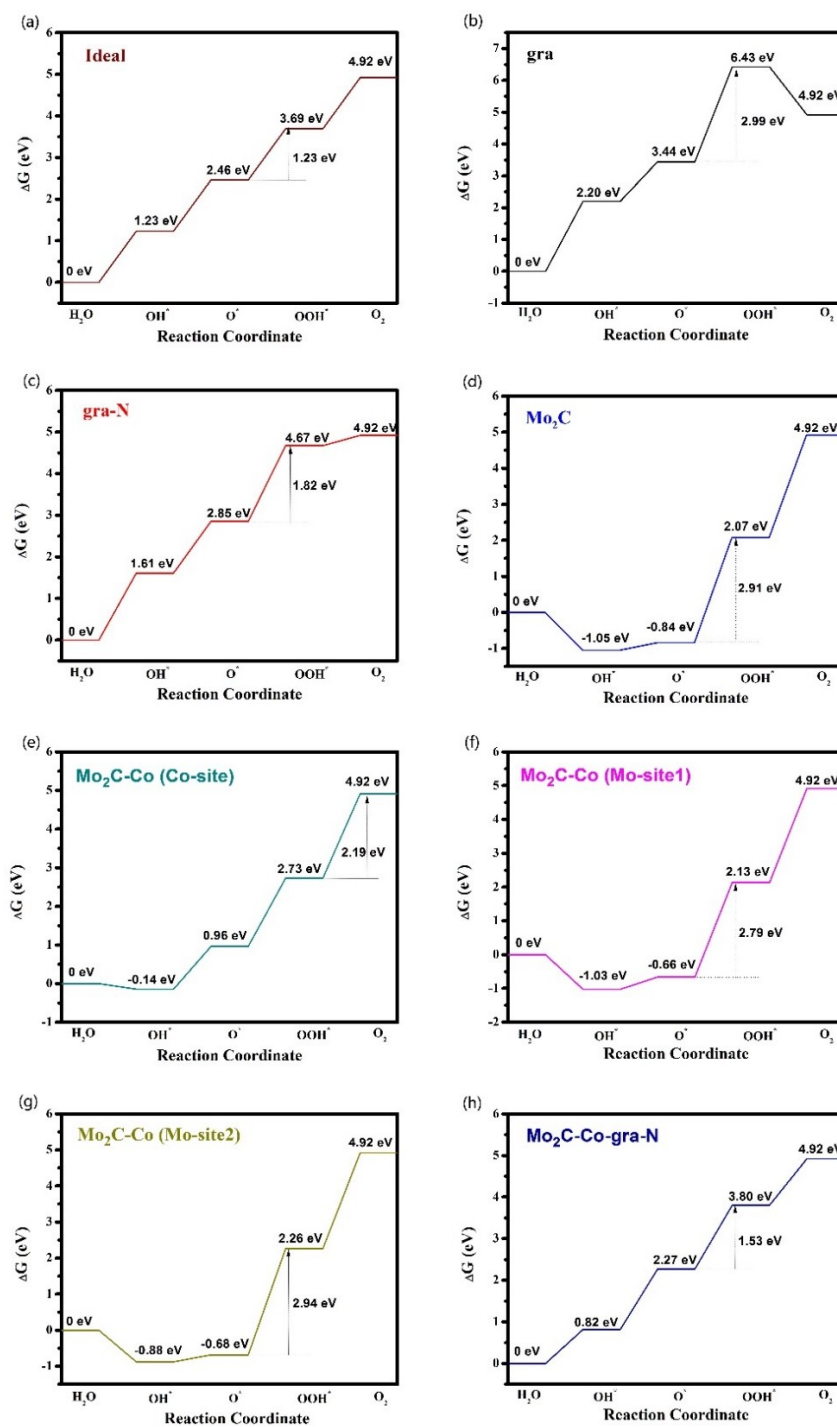


Figure S10. Free-energy diagram for OER on ideal electrocatalyst (a), graphene (gra) (b), N doped graphene (gra-N) (c), Mo_2C (d), Co site in Co doped Mo_2C (Co- Mo_2C (Co-site)) (e), site1 Mo in Co doped Mo_2C (Co- Mo_2C (Mo-site1)) (f), site2 Mo in Co doped Mo_2C (Co- Mo_2C (Mo-site2)) (g), and Co doped Mo_2C encapsulated in N doped graphene shell (Co- Mo_2C @NGCS) (h), at zero electrode potential.

TABLES

Table S1. Molar ratios of cobalt and molybdenum (Co/Mo) added in the hydrothermal reaction and ICP result for Co-Mo₂C@NGCS samples.

Samples	Added: Co/Mo (%)	ICP: Co/Mo (%)
Co-Mo ₂ C@NGCS-1	20	5.6
Co-Mo ₂ C@NGCS-2	33	7.0
Co-Mo ₂ C@NGCS-3	50	19.3

Table S2. Electrochemical activities of molybdenum carbide based electrocatalysts toward water splitting in alkaline solution.

Samples	η_{10} for HER	Tafel slope (HER)	η_{10} for OER	Tafel slope (OER)	References
Mo ₂ C-MoN/Ni@NC	183	107	296	65	6
Co ₄ Mo ₂ @NC	218	74	330	46	7
Ni/Mo ₂ C-PC	179	101	368	NG	8
Co-Mo ₂ C	NG	NG	347	38	9
Co/ β -Mo ₂ C@N-CNTs	170	92	356	67	10
Ni/Mo ₂ C-NCNFs	143	58	288	78	11
Mo ₂ C/CS	178	82	380	98	12
Co-Mo ₂ C@NCNT	186	79	377	NG	13
Co-Mo ₂ C@NGCS	161	60	360	54	Our work

Note:

η_{10} : overpotential at current density of 10 mA cm⁻²;

NG: not given;

Mo₂C-MoN/Ni@NC: Metallic Ni promoted Mo₂C-MoN particles supported on N-doped graphitic carbon;

Co₄Mo₂@NC: nitrogen-doped carbon encapsulating cobalt and molybdenum carbide nanoparticles;

Ni/Mo₂C-PC: Porous carbon-supported Ni/Mo₂C;

Co-Mo₂C: coupling Co to molybdenum carbide;

Co/ β -Mo₂C@N-CNTs: hybrid electrocatalyst of Co and β -Mo₂C nanoparticles encapsulated in N-doped carbon nanotubes;

Ni/Mo₂C-NCNFs: nitrogen-doped carbon nanofibers (NCNFs) integrated with Ni and Mo₂C nanoparticles;

Mo₂C/CS: highly crystalline Mo₂C nanoparticles supported on carbon sheets;

Co-Mo₂C@NCNT: bamboo-structured nitrogen doped carbon nanotube coencapsulated with metallic cobalt and Mo₂C nanoparticles

Table S3. List the zero-point energy (ZPE / eV) corrections to determine the free energy of reactants, products, and intermediate species adsorbed on catalysts.

Species	Gra	Gra-N	Mo ₂ C	Co-Mo ₂ C (Co)	Co-Mo ₂ C (Mo1)	Co-Mo ₂ C (Mo2)	Co-Mo ₂ C /NGCS
O*	0.101	0.098	0.058	0.042	0.064	0.062	0.079
OH*	0.397	0.400	0.325	0.315	0.304	0.312	0.386
OOH*	0.392	0.474	0.382	0.387	0.399	0.396	0.452
H*	0.302	0.306	0.102	0.095	0.177	0.184	0.311
H ₂ (g)				0.306			
H ₂ O(g)				0.610			

Table S4. List the entropy energy (T^*S / eV) corrections to determine the free energy of reactants, products, and intermediate species adsorbed on catalysts.

Species	T^*S / eV (298 K)
O*	0
OH*	0
OOH*	0
H*	0
H ₂ (g)	0.306
H ₂ O(g)	0.610

Table S5. List the adsorption free energies of O, OH, and OOH (eV), the reaction free energy (eV) of elementary step for OER at zero electrode potential, and the theoretical onset potential (U^{OER}) for OER on graphene, N doped graphene, Mo_2C , Co doped Mo_2C and Co- $\text{Mo}_2\text{C}@$ NGCS surfaces.

	GO	GOH	GOOH	ΔG_1	ΔG_2	ΔG_3	ΔG_4	U^{OER}
Gra	3.44	2.50	6.73	2.20	1.24	2.98	-1.51	1.75
Gra-N	2.85	1.91	4.97	1.61	1.24	1.82	0.25	0.59
Mo_2C	-0.83	-1.05	2.07	-1.05	0.21	2.91	2.85	1.68
Co- Mo_2C (Co)	0.96	0.16	3.03	-0.14	1.11	1.76	2.19	0.96
Co- Mo_2C (Mo1)	-0.66	-0.73	2.43	-1.03	0.36	2.79	2.79	1.56
Co- Mo_2C (Mo2)	-0.68	-0.58	2.56	-0.88	0.19	2.95	2.66	1.72
Co- $\text{Mo}_2\text{C}@$ NGCS	2.27	1.12	4.10	0.82	1.46	1.53	1.12	0.30

Table S6. List the Bader charge of the catalytic site C, Mo, and Co atoms in different systems considered.

	C	Mo	Co
Gra	3.874	/	/
Gra-N	4.112	/	/
Mo ₂ C	/	12.334	9.147
Co-Mo ₂ C	/	11.458/11.718	
Co-Mo ₂ C@NGCS	4.200	11.129/11.350	

Table S7. List the adsorption free energies of H (eV), and the theoretical overpotential (η^{HER}) for HER on graphene, N doped graphene, Mo₂C, Co doped Mo₂C and Co-Mo₂C@NGCS surface.

	ΔG_{H}	η
Gra	1.59	1.59
Gra-N	0.72	0.72
Mo ₂ C	0.02	0.02
Co-Mo ₂ C (Co)	-0.04	0.04
Co-Mo ₂ C (Mo1)	-0.03	0.03
Co-Mo ₂ C (Mo2)	-0.02	0.02
Co-Mo ₂ C@NGCS	0.22	0.22

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