Supplementary Information

Single metal atom supported on N-doped 2D M₂C MXenes: an efficient electrocatalyst for overall water splitting

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1. Calculation details

1.1 Reaction Gibbs free energy of hydrogen adsorption

Under standard conditions, the HER activity of materials can be evaluated by using the reaction Gibbs free energy of hydrogen adsorption (ΔG_{H*}). [1] ΔG_{H*} is defined as eq (S1),

$$\Delta G_{H*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \tag{S1}$$

where ΔE_H, ΔE_{ZPE} and $T\Delta S_H$ are the difference of hydrogen adsorption energy, zero-point energy and the entropy between adsorbed hydrogen and hydrogen in the gas phase, respectively. In addition, ΔE_H, ΔE_{ZPE} and ΔS_H are calculated at 0K temperature, T is set at room temperature (298K). The ΔS_H can be regarded as eq (S2),

$$\Delta S_H \cong -\frac{1}{2}S_{H_2}^0 \tag{S2}$$

where $S_{H_2}^0$ is the entropy of H_2 under the standard conditions. According to the previous studies, [2] it can be found that the vibration entropy of the adsorbed state is very small and can be almost ignored. The values of ΔE_{ZPE} and $T\Delta S$ are referenced from Ref.[3]. Thus, eq (S1) can be rewritten as eq (S3),
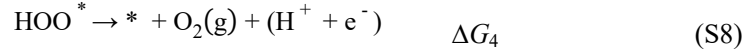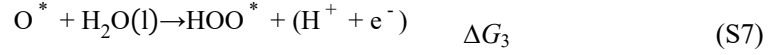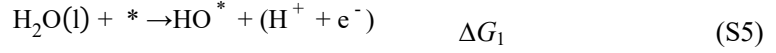
$$\Delta G_{H*} = \Delta E_H + 0.3 \text{ eV} \tag{S3}$$

The overpotential of HER is defined as $\eta_{HER} = -|\Delta G_{H*}|/e \times 10^3$ in unit of mV. The optimal ΔG_{H*} is 0 eV, and therefore the corresponding overpotential is 0 mV.[4] Based on the assumption of Nørskov, the theoretical exchange current (i_0)[5] was calculated to draw the volcano curve of the HER, which is expressed by eq (S4),

$$i_0 = \begin{cases} -ek_0\dfrac{1}{1 + exp\left(-\Delta G_{H^*}/k_B T\right)} & for\ \Delta G_{H^*} \leq 0 \\[3mm] -ek_0\dfrac{1}{1 + exp\left(\Delta G_{H^*}/k_B T\right)} & for\ \Delta G_{H^*} > 0 \end{cases} \tag{S4}$$

where k_0 and k_B represent the Boltzmann constant and rate constant, respectively.

1.2 Standard free energy for oxygen evolution reaction

When the pH = 0, i.e., in a strongly acidic environment, under standard conditions, the oxygen evolution reaction consists of four electron reaction steps, as follows:

$$H_2O(l) + * \rightarrow HO^* + (H^+ + e^-) \qquad \Delta G_1 \tag{S5}$$

$$HO^* \rightarrow O^* + (H^+ + e^-) \qquad \Delta G_2 \tag{S6}$$

$$O^* + H_2O(l) \rightarrow HOO^* + (H^+ + e^-) \qquad \Delta G_3 \tag{S7}$$

$$HOO^* \rightarrow * + O_2(g) + (H^+ + e^-) \qquad \Delta G_4 \tag{S8}$$

where * stands for an active site on the surface of catalyst, and O*, OH*, and OOH* are called the adsorbed intermediates, (l) and (g) represent the liquid and gas states, respectively. ΔG_1, ΔG_2, ΔG_3 and ΔG_4 are the reaction Gibbs free energy of (S5)-(S8). In the OER process, the OER performance is mainly determined by calculating the reaction free energies of the four elementary steps. For each step, the ΔG is obtained via eq (S9):

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \tag{S9}$$

For such electrochemical reactions, the calculations are mainly performed by DFT calculations combined with methods such as the SHE model developed by Nørskov and colleagues. [6] The theoretical overpotential η_{OER}, can be obtained from the following equation.

$$\eta_{OER} = \max\left(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right)/e - 1.23[V] \tag{S10}$$

1.3 d-band center

The d-band center (ε_d) [7] of TM (TM=Fe, Co, and Ni) on the surfaces of the three models is defined as:

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} x d(x)dx}{\int_{-\infty}^{\infty} d(x)dx} \tag{S11}$$

where x represents the energy level, and $d(x)$ is the density of states of the d orbital at the corresponding energy level.
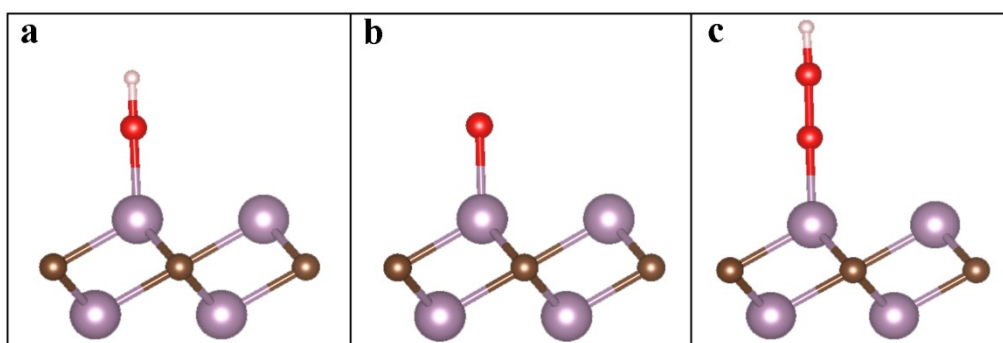
1.4 Binding energy

The binding energy (E_b) [8] of 2D TM/M$_2$C MXenes was evaluated by eq (S12),
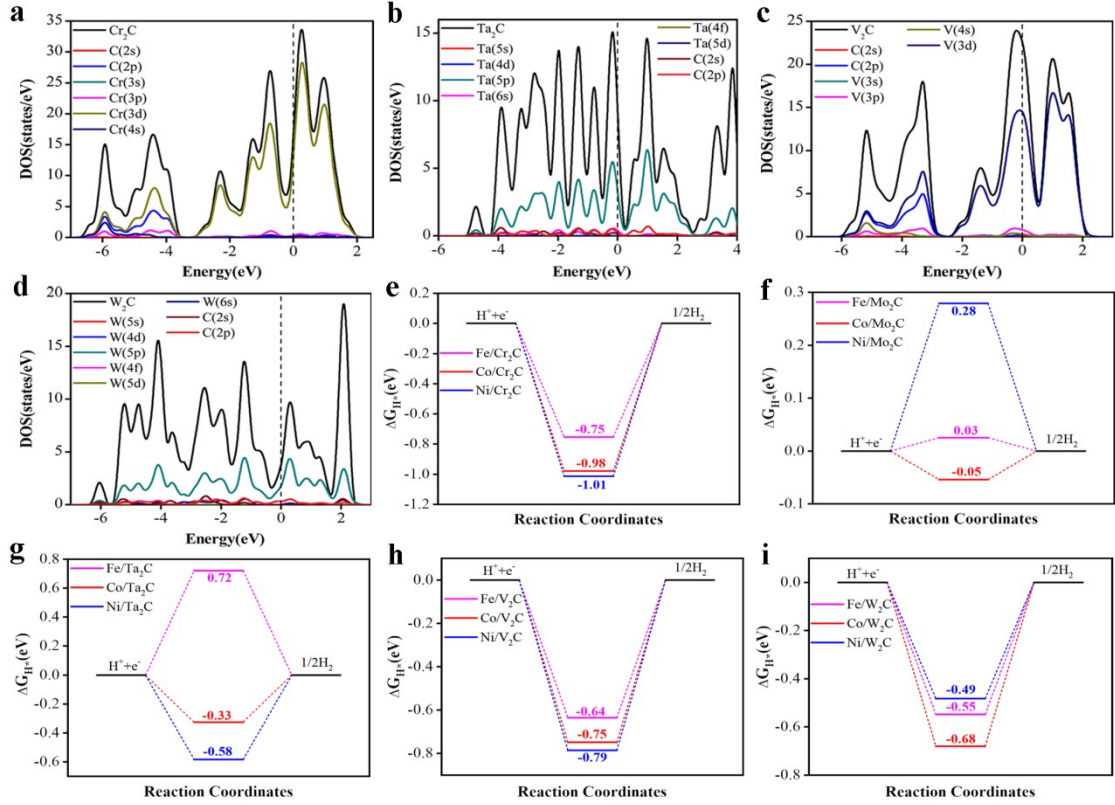
$$Eb = E_{(TM/M_2C)} - E_{(M_2C)} - E_{(TM)}$$

(S12)

where $E_{(TM/M_2C)}$, $E_{(M_2C)}$, and $E_{(TM)}$ represent the total energies of M$_2$C with and without TM loading, and single metal atom, respectively.
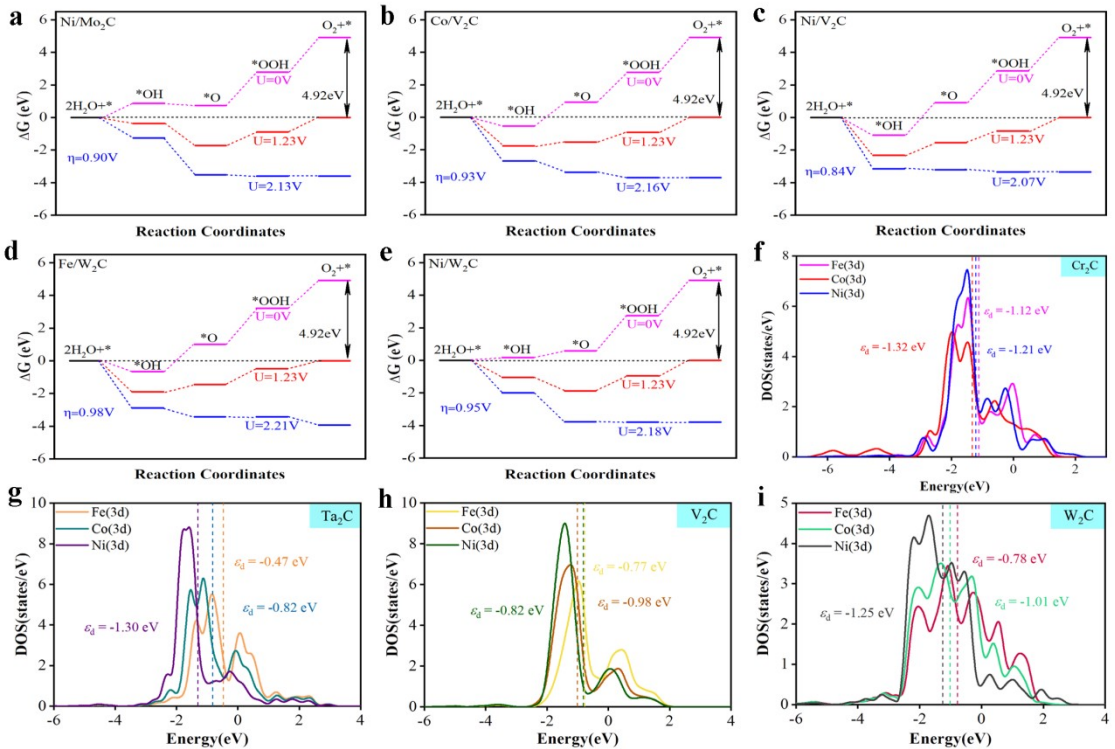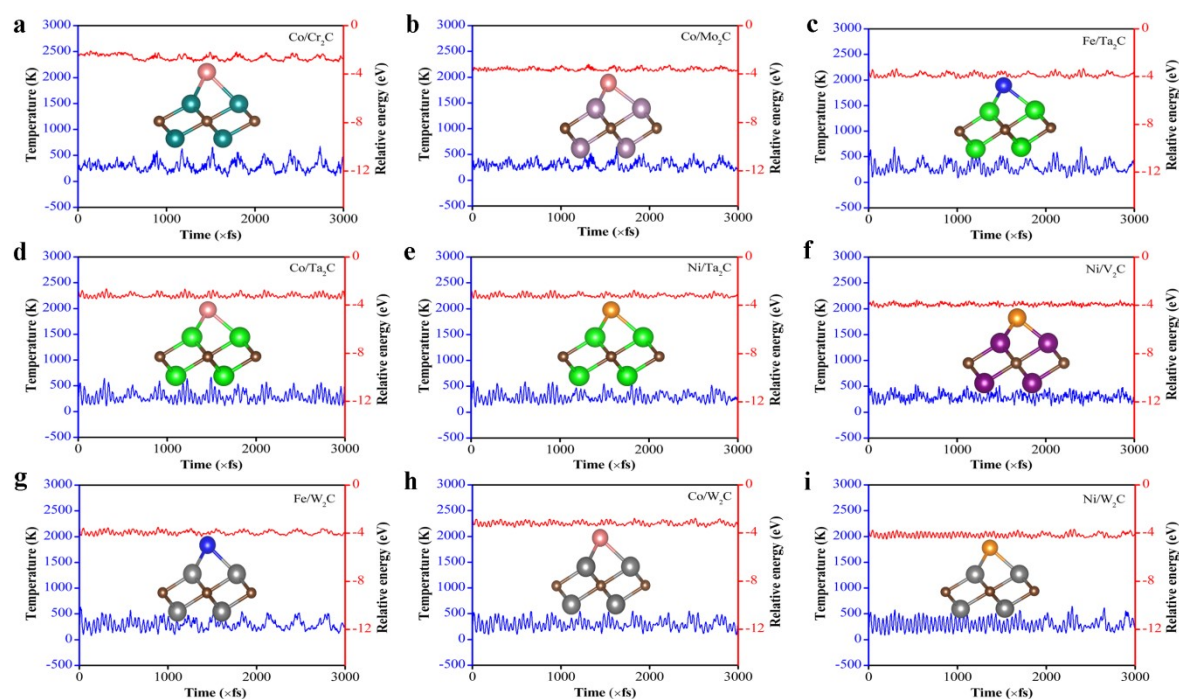
2. Figures

Figure S1. Schematic structure of (a) HO*/Mo$_2$C, (b) O*/Mo$_2$C, and (c) HOO*/Mo$_2$C. The purple, brown, red, and white balls represent the Mo, C, O, and H atoms, respectively.

**Figure S2.** Density of states of (a) Cr$_2$C, (b) Ta$_2$C, (c) V$_2$C, and (d) W$_2$C. Reaction Gibbs free energy diagrams of hydrogen adsorption (ΔG_{H*}) of (e) TM/Cr$_2$C, (f) TM/Mo$_2$C, (g) TM/Ta$_2$C, (h) TM/V$_2$C, and (i) TM/W$_2$C.

Figure S3. Free energy diagrams for OER under different electrode potentials U (0 V, 1.23 V, and downhill potential for all reaction steps) for (a)Ni/Mo$_2$C, (b) Co/V$_2$C, (c) Ni/V$_2$C, (d) Fe/W$_2$C, and (e) Ni/W$_2$C. The ε_d of surface TM atoms in (f) TM/Cr$_2$C, (g) TM/Ta$_2$C, (h) TM/V$_2$C, and (i) TM/W$_2$C, respectively.

Figure S4. The AIMD simulations results of (a) Co/Cr$_2$C, (b) Co/Mo$_2$C, (c) Fe/Ta$_2$C, (d) Co/Ta$_2$C, (e) Ni/Ta$_2$C, (f) Ni/V$_2$C, (g) Fe/W$_2$C, (h) Co/W$_2$C and (i) Ni/W$_2$C.
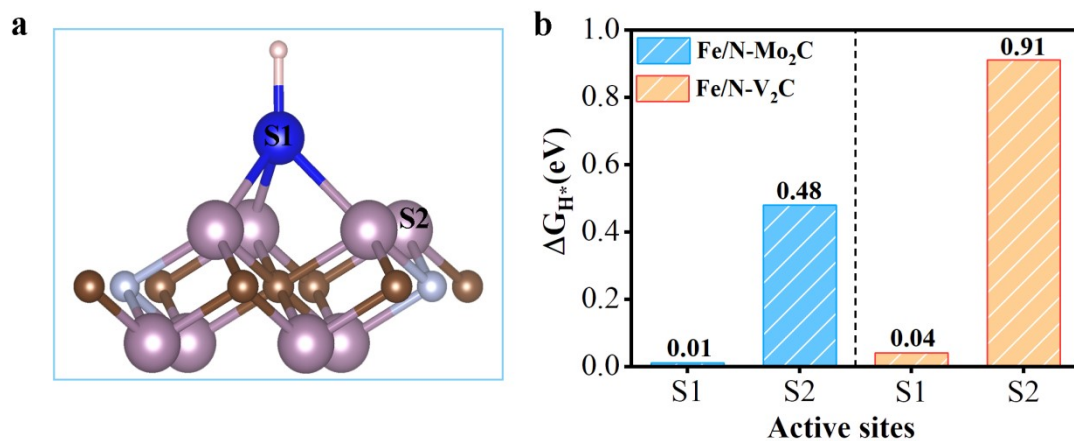
Figure S5. (a) Schematic structure of H* adsorbed on the Fe/N-Mo$_2$C surface, where S1 and S2 represent the active sites for H* adsorption. (b) Reaction Gibbs free energy of hydrogen adsorption (ΔG_{H*}) on Fe/N-Mo$_2$C and Fe/N-V$_2$C at S1 and S2 sites.

	Cr$_2$C	Hf$_2$C	Mo$_2$C	Nb$_2$C	Ta$_2$C	Ti$_2$C	V$_2$C	W$_2$C	Zr$_2$C
θ=1/8	-1.10	-1.24	-0.15	-0.59	-1.28	-0.84	-0.94	-0.60	-0.92
θ=1/4	-0.32	-1.27	-0.86	-1.21	-0.81	-1.17	-0.55	-0.29	-0.66
θ=3/8	-0.29	-1.08	-0.87	-0.85	-0.69	-1.07	-0.84	-0.23	-1.05
θ=1/2	-0.16	-1.14	-1.18	-0.79	-0.46	-0.94	-0.76	-0.08	-1.09
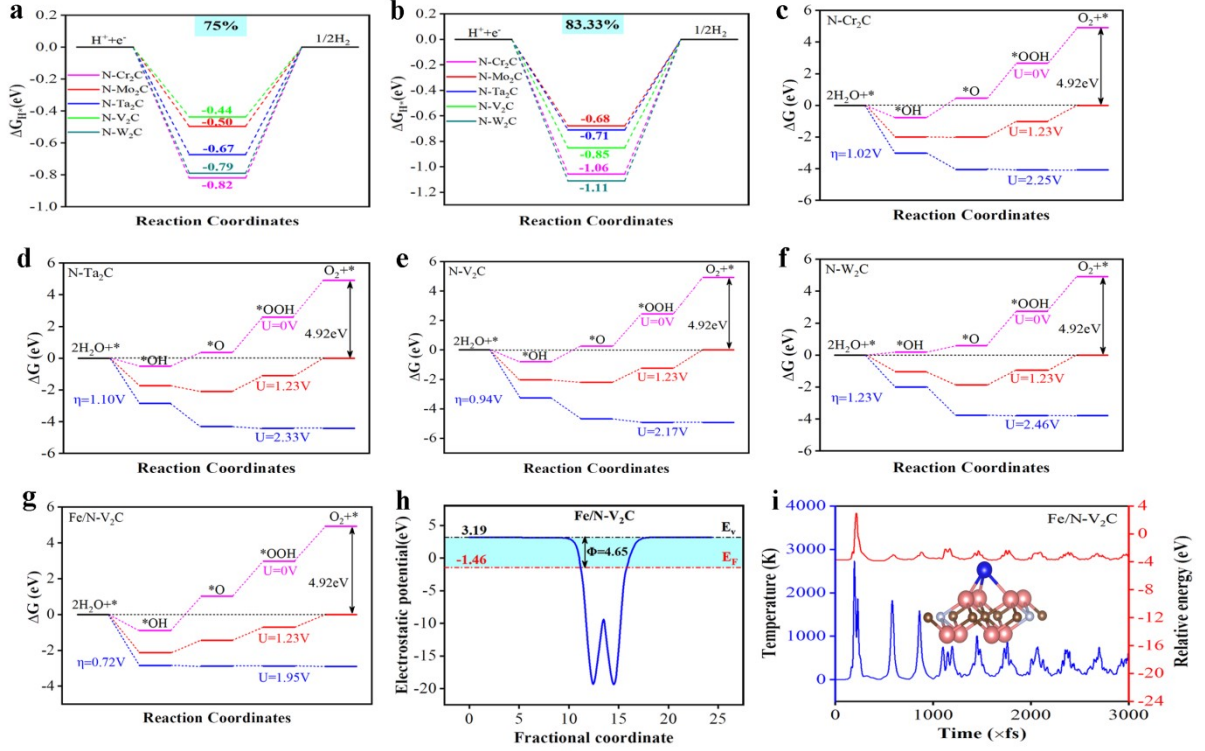
Figure S6. Reaction Gibbs free energy diagrams of hydrogen adsorption (ΔG_{H*}) of (a) N-M$_2$C (N-doping concentration of 75%), and (b) N-M$_2$C (N-doping concentration of 83.33%). Free energy diagrams for OER under different electrode potentials U (0 V, 1.23 V, and downhill potential for all reaction steps) for (c) N-Cr$_2$C, (d) N-Ta$_2$C, (e) N-V$_2$C, (f) N-W$_2$C, and (g) Fe/N-V$_2$C. (h) The work function of Fe/N-V$_2$C, E$_F$ and E$_v$ are the Fermi level and vacuum level, respectively. (i) The AIMD simulations of Fe/N-V$_2$C.

Table S1. Reaction Gibbs free energy of hydrogen adsorption (ΔG_{H*}, in unit of eV) for bare M$_2$C MXenes at different hydrogen coverage (θ=1/8, 1/4, 3/8, and 1/2).

Table S2. The reaction Gibbs free energy of hydrogen adsorption (ΔG_{H*}), the overpotential of HER (η_{HER}), exchange current density (log(i_0/Acm^{-2})), OH* adsorption (ΔG_{OH*}), O* adsorption (ΔG_{O*}), OOH* adsorption (ΔG_{OOH*}), the overpotential of OER (η_{OER}), the d-band center (ε_d) of TM/M$_2$C MXenes.

	ΔG_{H*}/eV	η_{HER}/mV	$\log(i_0/Acm^{-2})$	ΔG_{O*}/eV	ΔG_{OH*}/eV	ΔG_{OOH*}/eV	η_{OER}/V	ε_d
Fe/Cr$_2$C	-0.75	-750	-12.67	0.66	-0.43	2.97	1.07	-1.12
Co/Cr$_2$C	-0.98	-980	-16.46	0.73	-0.59	2.56	1.13	-1.32
Ni/Cr$_2$C	-1.01	-1010	-17.02	1.03	-0.52	2.48	1.21	-1.21
Fe/Mo$_2$C	0.03	-30	-0.56	1.15	-0.67	3.03	0.66	-0.88
Co/Mo$_2$C	-0.05	-50	-0.93	0.99	-0.22	2.79	0.81	-1.09
Ni/Mo$_2$C	0.28	-280	-4.69	0.74	0.82	3.45	0.90	-0.92
Fe/Ta$_2$C	0.72	-720	-12.09	1.07	-0.85	3.16	1.15	-0.47
Co/Ta$_2$C	-0.33	-330	-5.48	1.19	-0.37	3.27	0.74	-0.82
Ni/Ta$_2$C	-0.58	-580	-9.81	0.50	0.13	2.75	1.02	-1.3
Fe/V$_2$C	-0.64	-640	-10.67	0.99	0.62	3.01	0.79	-0.77
Co/V$_2$C	-0.75	-750	-12.58	0.93	-0.54	2.76	0.93	-0.98
Ni/V$_2$C	-0.79	-790	-13.19	0.91	-1.09	2.85	0.84	-0.82
Fe/W$_2$C	-0.55	-550	-9.21	1.01	-0.67	3.21	0.98	-0.78
Co/W$_2$C	-0.68	-680	-11.42	1.15	-0.20	2.65	1.04	-1.01
Ni/W$_2$C	-0.49	-490	-8.15	0.59	0.18	2.74	0.95	-1.25

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