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Supplementary Information

Hierarchical Ni_2P/Cr_2CT_x (MXene) composites with oxidized surface groups as efficient bifunctional electrocatalysts for overall water splitting

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1. Calculation method of HER and OER activity

1.1 Gibbs free energy of hydrogen adsorption

Under standard conditions, the HER catalytic activity of materials can be evaluated by the change of the Gibbs reaction free energy of hydrogen adsorption (ΔG_{H*}). ΔG_{H*} can be evaluated by 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 differences of hydrogen adsorption energy, zero-point energy and the entropy between adsorbed hydrogen and hydrogen in the gas phase, respectively. ΔE_H is defined as

$$\Delta E_{H}=E_{DFT}^{nH*}-E_{DFT}^{(n-1)H*}-\frac{1}{2}E_{DFT}^{H_2(g)} \tag{S2}$$

where E^{nH*}, $E^{(n-1)H*}$, and E_{H_2} represent total energies of the catalyst with n adsorbed hydrogen atoms, n-1 adsorbed hydrogen atoms, and H_2 gas, respectively. The asterisk denotes the catalytic active sites. ΔE_{ZPE} can be calculated by eq (S3)

$$\Delta E_{ZPE}=E_{ZPE}^{nH}-E_{ZPE}^{(n-1)H}-\frac{1}{2}E_{ZPE}^{H_2} \tag{S3}$$

The ΔS_H can be approximated as eq (S4)

$$\Delta S_{H}\cong-\frac{1}{2}S_{H_2}^{0} \tag{S4}$$

due to the fact that the vibrational entropy in the adsorbed state is small according to previous studies,[1]and$S_{H_2}^{0}$is the entropy of H_2 gas under the standard condition.[2] Here, the values of ΔE_{ZPE} and $T\Delta S$ are referenced from Ref 2.Therefore,eq S1can be written as eq S5

$$\Delta G_{H*}=\Delta E_{H}+0.3\ \text{eV} \tag{S5}$$

The optimal ΔG_{H*}value for HER is $\Delta G_{H*} = 0$, which means that the smaller values of $|\Delta G_{H*}|$, the better HER performance of catalysts.

1.2 Volcano curve

To get exchange current, we adopted Nørskov's assumption.[1] When the proton transfer is exothermic ($\Delta G_{H^*}<0$), the expression for the exchange current at pH=0 is:

$$i_0=-ek_0\frac{1}{1+\exp(-\Delta G_{H^*}/k_B T)} \tag{S6}$$

For another case, if the proton transfer is endothermic ($\Delta G_{H^*}>0$), under the same condition as above, the exchange current is

$$i_0=-ek_0\frac{1}{1+\exp(\Delta G_{H^*}/k_B T)} \tag{S7}$$

Where the k_0 is the rate constantand k_B is the Boltzmann constant, andk_0 is the rate constant, which is set as 1 owing to the lack of available experimental data.[3]

For hydrogen evolution reaction, the overpotential is defined as the negative of absolute value of the difference of free energy of hydrogen adsorption. The theoretical calculation overpotential is defined as $\eta_{HER}=-|\Delta G_{H*}|/e\times 10^3$in unit of mV. The optimum free energy for HER is 0 eV, and the corresponding overpotential is 0mV.[4]

1.3Calculation of standard free energy diagram for oxygen evolution reaction

The relation between Gibbs free energy (G) and DFT energy (E_{DFT}) are constructed on the following thermodynamic approximations.[5-7] Hydrogen electrode is assumed to be in equilibrium

$$H^+(aq)+e^-\rightleftharpoons\frac{1}{2}H_2(g) \tag{S8}$$

Thus,

$$\mu^0_{H^+}+\mu^0_{e^-}=\frac{1}{2}\mu^0_{H_2(g)} \tag{S9}$$

The experimental value of 2.46eV of standard Gibbs free energy changed of the reaction:

$$H_2O\rightleftharpoons\frac{1}{2}O_2(g)+H_2(g) \tag{S10}$$

Thereby,

$$\mu^0_{H_2(g)}+\frac{1}{2}\mu^0_{O_2(g)}-\mu^0_{H_2O(l)}=2.46\text{ eV} \tag{S11}$$

$\mu^0_{H^+}$, $\mu^0_{e^-}$, $\mu^0_{H_2(g)}$ and $\mu^0_{H_2O(l)}$ represent the chemical potential of protons, electrons and hydrogen and water at standard conditions, respectively. By definition, G=H-TS, where G is Gibbs free energy which can also be represented by chemical potential μ, H is the enthalpy of the system , which equals to E_{DFT} corrected by the zero-point energy (ZPE). S is the entropy of the system. The ZPE and entropy at 298 K (TS) were retrieved from Ref. 6. As a results,

$$G=E_{DFT}+ZPE-TS \tag{S12}$$

At a standard condition (T=298.15K, P=0.035bars), the approximation chemical potentials of H_2 molecule and H_2O molecule can be defined as:

$$\frac{1}{2}\mu^0_{H_2(g)}=\frac{1}{2}(E^{H_2}_{DFT}+ZPE_{H_2(g)}-TS^0_{H_2(g)}) \tag{S13}$$

$$\mu^0_{H_2O(l)}\approx\mu_{H_2O(g)}=E^{H_2O(g)}_{DFT}+ZPE_{H_2O(g)}-TS^0_{H_2O}(0.035\text{bars} \tag{S14}$$

The proposed mechanism for OER consist of four intermediate steps at standard conditions under electrode potential U are considered, each step on the active sites release of a proton and an electron:

$$H_2O(l)+*\rightarrow HO^*+(H^++e^-)\Delta G_1 \tag{S15}$$

$$HO^*\rightarrow O^*+(H^++e^-)\Delta G_2 \tag{S16}$$

$$O^*+H_2O(l)\rightarrow HOO^*+(H^++e^-)\Delta G_3 \tag{S17}$$

$$HOO^*\rightarrow *+O_2(g)+(H^++e^-)\Delta G_4 \tag{S18}$$

Where O*, OH*, OOH* are the adsorbed intermediates, * represent active sites on the catalysts surface, (l) and (g) refer to liquid and gas phases, respectively. ΔG_1, ΔG_2, ΔG_3 and ΔG_4 are the free energy of reaction (S15)-(S18). The overpotential of OER processes can be determined by calculating the reaction free energies of the four different steps. The thermo-chemistry of these electrochemical reactions was obtained by using DFT calculation combined with SHE model developed by Nørskov and co-work.[8] The thermodynamic approach establishes a minimum set of requirements for the reactions based on the binding of the intermediates and the assumption that there are no extra barriers from adsorption or dissociation of O_2 or proton/electron transfer reactions. In our calculations, the OER were analyzed using intermediate species associated with one electrons transfer at a time. In OER, the rate determining steps can either be the formation of O* from OH*(Eq.(S16)) or formation of O* to OOH*(Eq.(S17)).[6] The adsorption energy of O*, OH* and OOH* are calculated as follows [5]:

$$\Delta E_{HO^*}=E\left(HO^*\right)-E(*)-(E_{H_2O}-{}^1\!/_2\,E_{H_2}) \tag{S19}$$

$$\Delta E_{OOH^*}=E\left(HOO^*\right)-E(*)-(2E_{H_2O}-{}^3\!/_2\,E_{H_2}) \tag{S20}$$

$$\Delta E_{O^*}=E\left(O^*\right)-E(*)-(E_{H_2O}-E_{H_2}) \tag{S21}$$

where $E(*)$, $E(O^*)$, $E(HO^*)$ and $E(HOO^*)$ are the calculated energies of clean catalysts (Ni_2P or Ni_2P/Cr_2CO_2)surface, and surface adsorbed with O*, HO*, and HOO*, respectively. E_{H_2O} and E_{H_2} are the calculated energies of H_2O and H_2 molecules in the gas phase. Considering the ZPE and entropy corrections, the free energies of adsorption, ΔG_{ads}, can obtained by following equation:

$$\Delta G_{ads}=\Delta E+\Delta ZPE-T\Delta S \tag{S22}$$

For each step, the reaction free energy ΔG is defined as the difference between free energies of the initial and final states, and is given by the expression:

$$\Delta G=\Delta E+\Delta ZPE-T\Delta S-eU-k_BTlnH^+ \tag{S23}$$

Where ΔE is the change of energy after adsorbed intermediate species, U is the potential at the electrode. The free energy of reaction (S15)-(S18) can be calculated using Eq.(S23). The values of ΔE_{ZPE} and TΔS of intermediate adsorbates (O*, HO*, HOO*) are referenced from Ref 6. The theoretical onset overpotential η, which is determined by the potential limiting steps (PLS), can be obtained from the following equation.[9]

$$\eta= \max(\Delta G_1,\Delta G_2,\Delta G_3,\Delta G_4) /e-1.23[V] \tag{S24}$$

The value of η is independent of pH. The ideal case for scaling relation requires $\Delta G_3=-\Delta G_2+2.46$ [eV], where ΔG_3 is the free energy change of water dissociation on top of O* and ΔG_2 is the free energy change of proton removal from HO*, the linear scaling relation of our calculation was about fitted to $\Delta G_3=-1.33\Delta G_2+4.14$ [eV] for Ni_2P surface.

2. Calculation method of surface energy and interface binding energy

The surface energy of Ni_2P surface can be obtained as:

$$\gamma=\left[G_{slab}-\sum_i N_i\mu_i\right]/2A \tag{S25}$$

where G_{slab} is the Gibbs free energy of the slab, N_i is the number of each component *i* within the slab, and μ_i is the chemical potential of component *i* per formula unit. A is the surface area of the slab, and the factor 1/2 indicates that there are two surface per slab.[9] The Ni_2P/Cr_2CO_2 interface binding energy can be defined as[10]:

$$E_{ads}=[E_{Ni_2P/Cr_2CO_2}-E_{Ni_2P}-E_{Cr_2CO_2}]/S \tag{S26}$$

where E_{Ni_2P/Cr_2CO_2} is the total energy of Ni_2P/Cr_2CO_2 interface, E_{Ni_2P} and$E_{Cr_2CO_2}$ represents the total energy of the isolated and relaxed Ni_2P, Cr_2CO_2 slabs in the same supercell, respectively. S is the interface area. When calculatedE_{Ni_2P} or $E_{Cr_2CO_2}$, one part of the interface system kept fixed, and the other part was removed.

2. Figures and tables

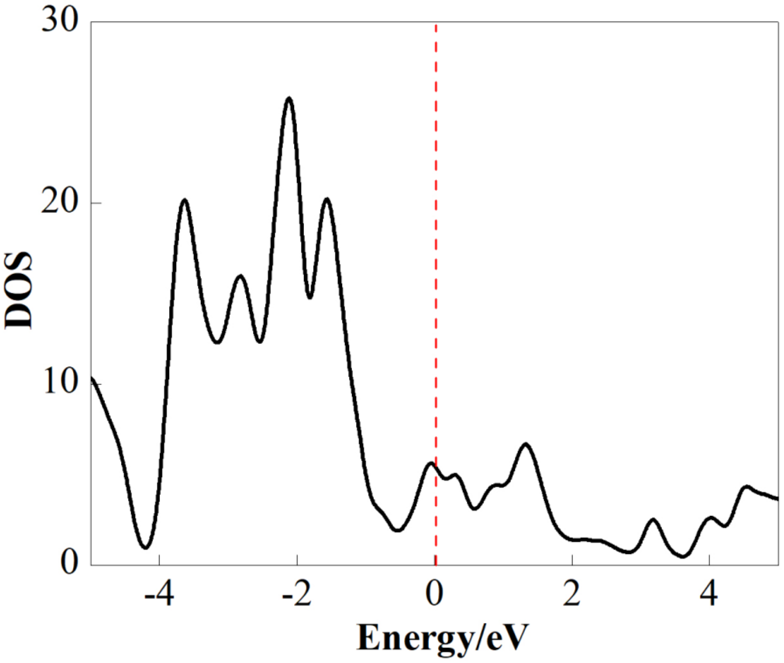


Figure S1. Total density of states of (TDOS) bulk Ni_2P.

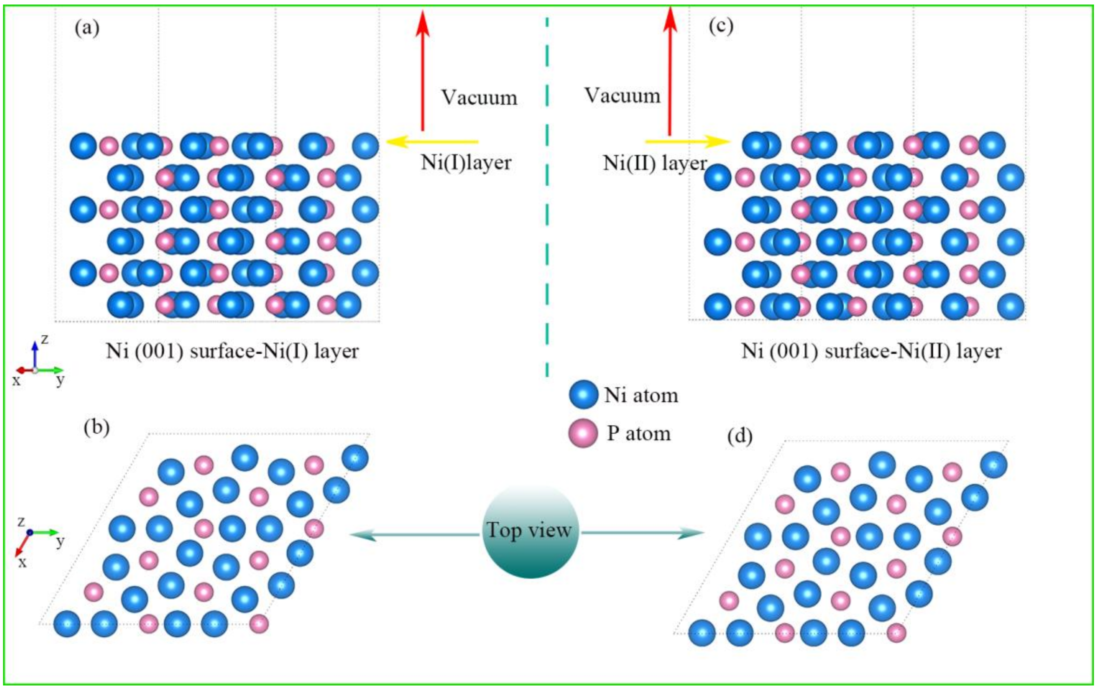


Figure S2. Schematic of Ni_2P (001) surface structure after relaxation, side (a) and top (b) view of Ni (I) termination, side (c) and top (d) view of Ni(II) termination.

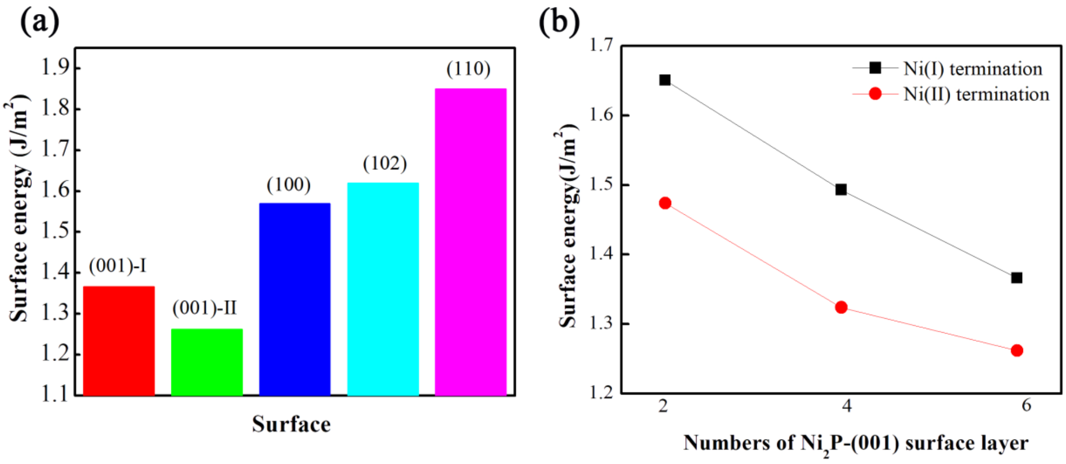


Figure S3. The calculated surface energies of (a) different Ni_2P surface and (b) Ni_2P (001) surface energies as function of number of surfaces layer.

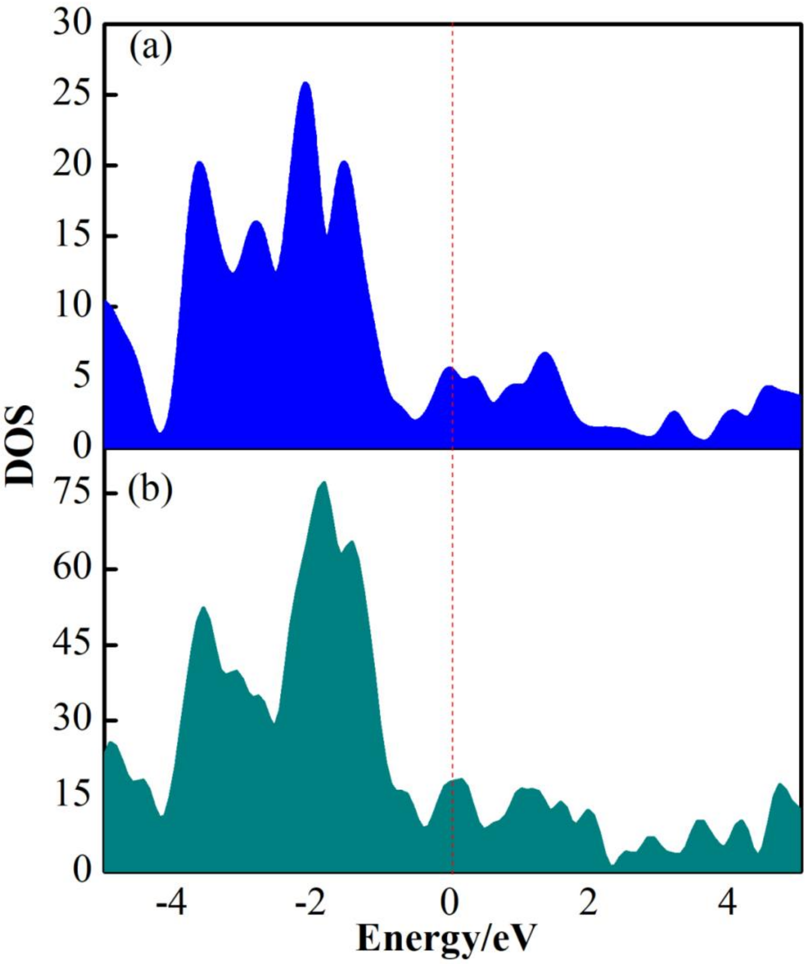


Figure S4. Density of states of (a) Ni_2P bulk and (b) Ni_2P (001) surface.

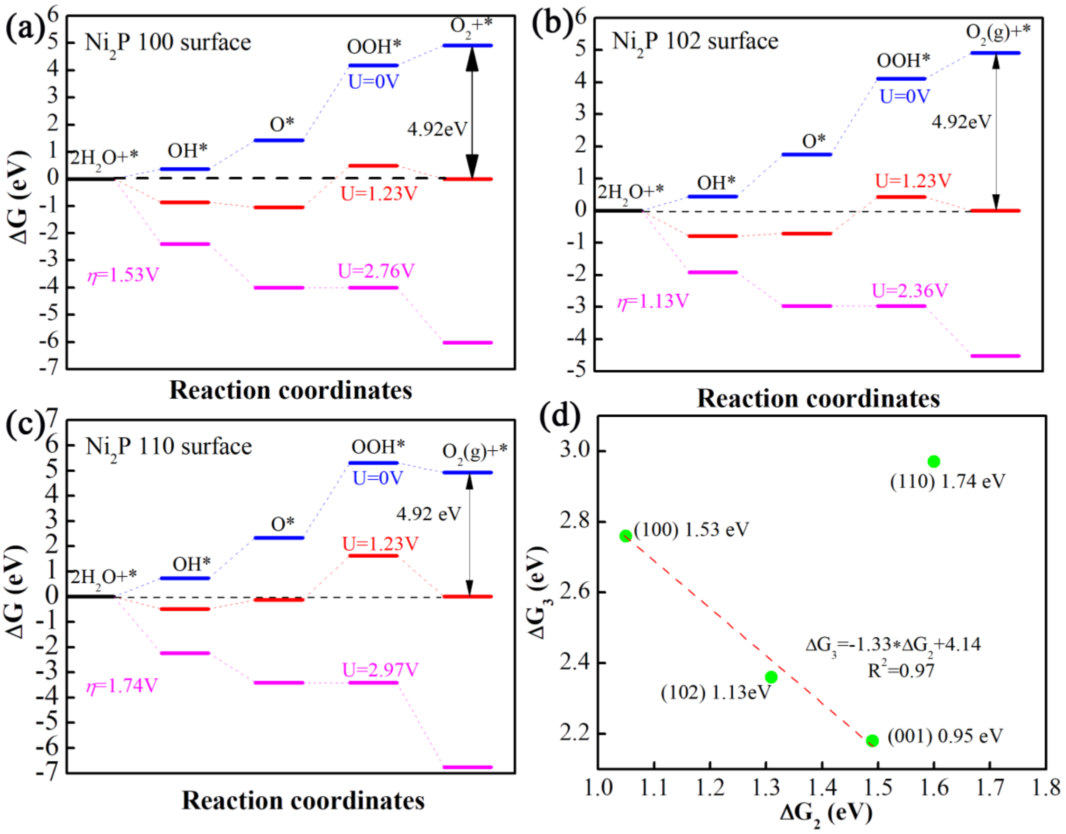


Figure S5. Standard free energy diagrams for OER at different electrode potentials U for different Ni_2P surface,(a) Ni_2P 100 surface, (b) Ni_2P 102 surface, (c) Ni_2P 110 surface. Blue lines for zero potential: 0 V. Red lines at the equilibrium potential of oxygen evolution U = 1.23 V for standard hydrogen electrode (SHE), pink lines for potentials of all downhill reaction steps. (d) The calculated onset overpotentials as function of free energy changes (ΔG_2 and ΔG_3) with the reaction intermediates of different surfaces.

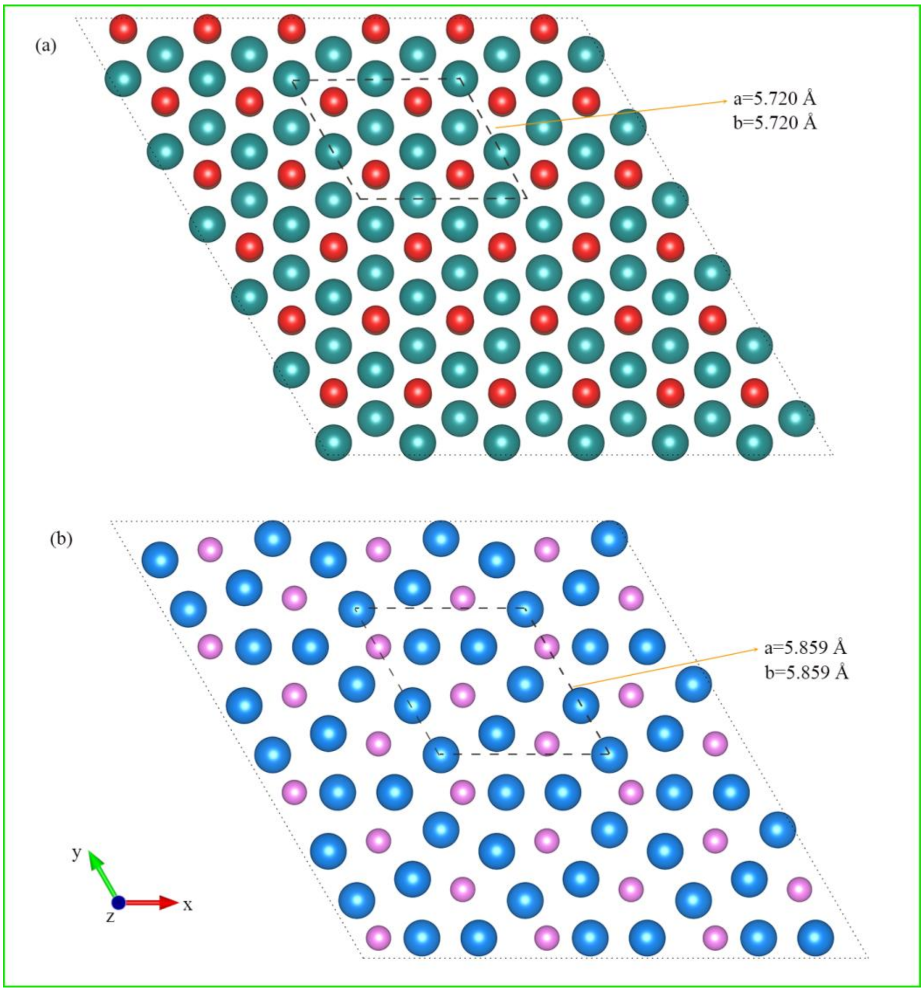


Figure S6. The lattice matching of Cr_2CO_2/Ni_2P interface. (a) Cr_2CO_2 and (b) Ni_2P (001) surface. The unit of lattice parameter is Å.

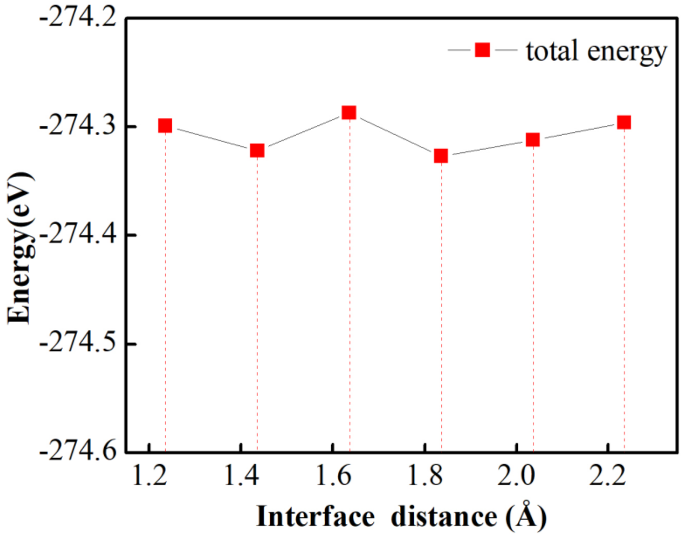


Figure S7. The total energy of Cr_2CO_2/Ni_2P interface (red box) varies with interface distance.

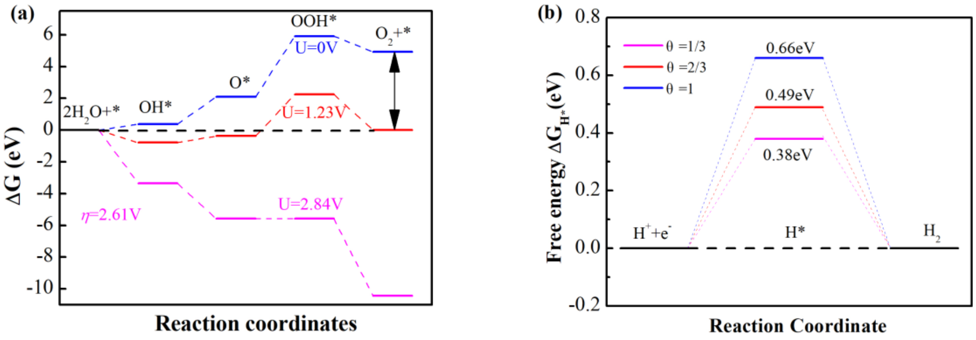
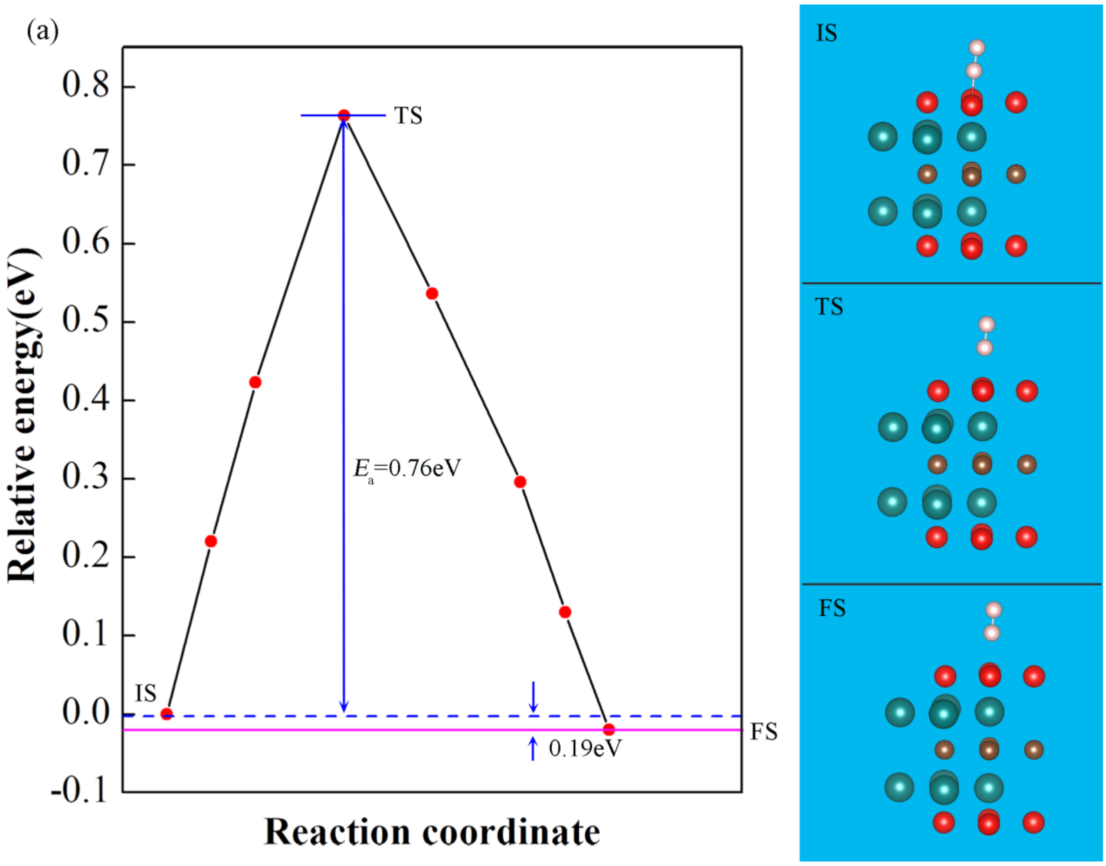


Figure S8. The calculated free energy diagrams of (a) OER on Cr_2CO_2 surface and (b) HER on Ni_2P surface. For Ni_2P 2×2 supercell, there are three Ni atoms, and different H coverage can be set as increment of $^1/_3$.



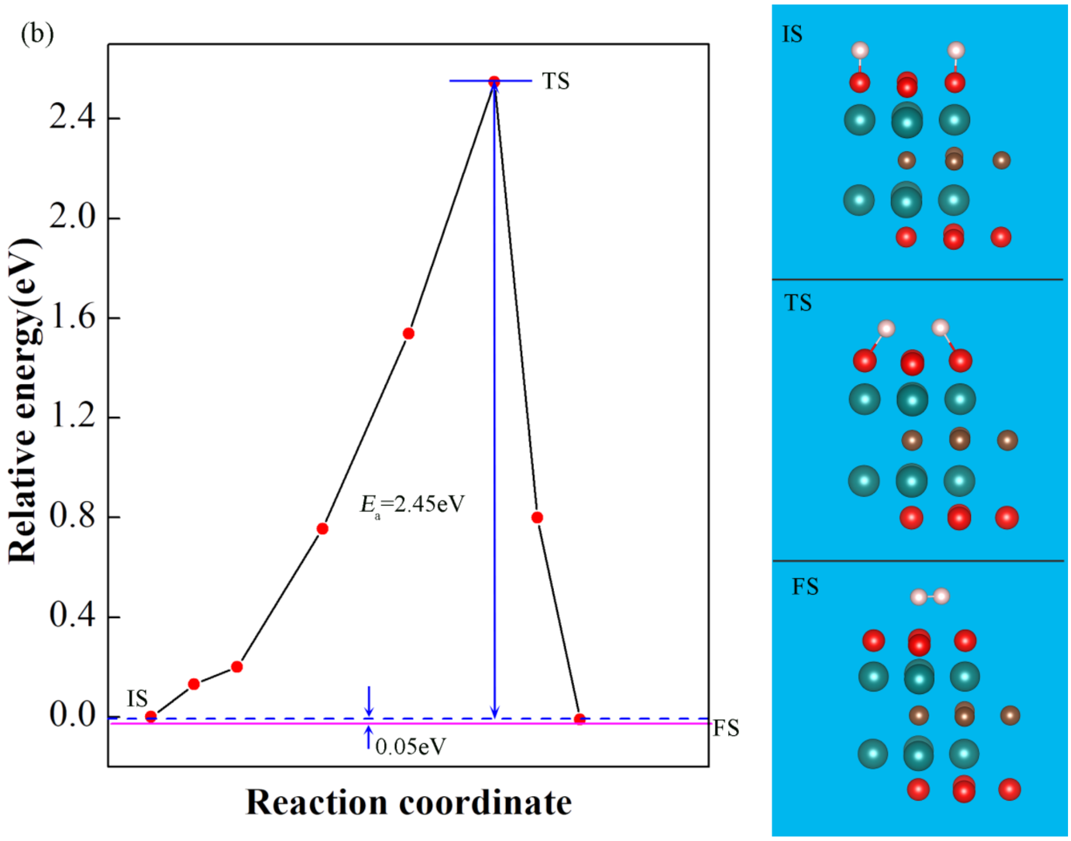


Figure S9. The calculated minimum-energy pathway and the activation energy of Cr_2CO_2. (a)Volmer-Heyrovsky reaction, (b) Volmer-Tafel reaction. In The right panels are show the initial state (IS), transition state (TS) and final state (FS). The green, red, coffee and light pink balls represent the Cr, O, C and H atoms, respectively.

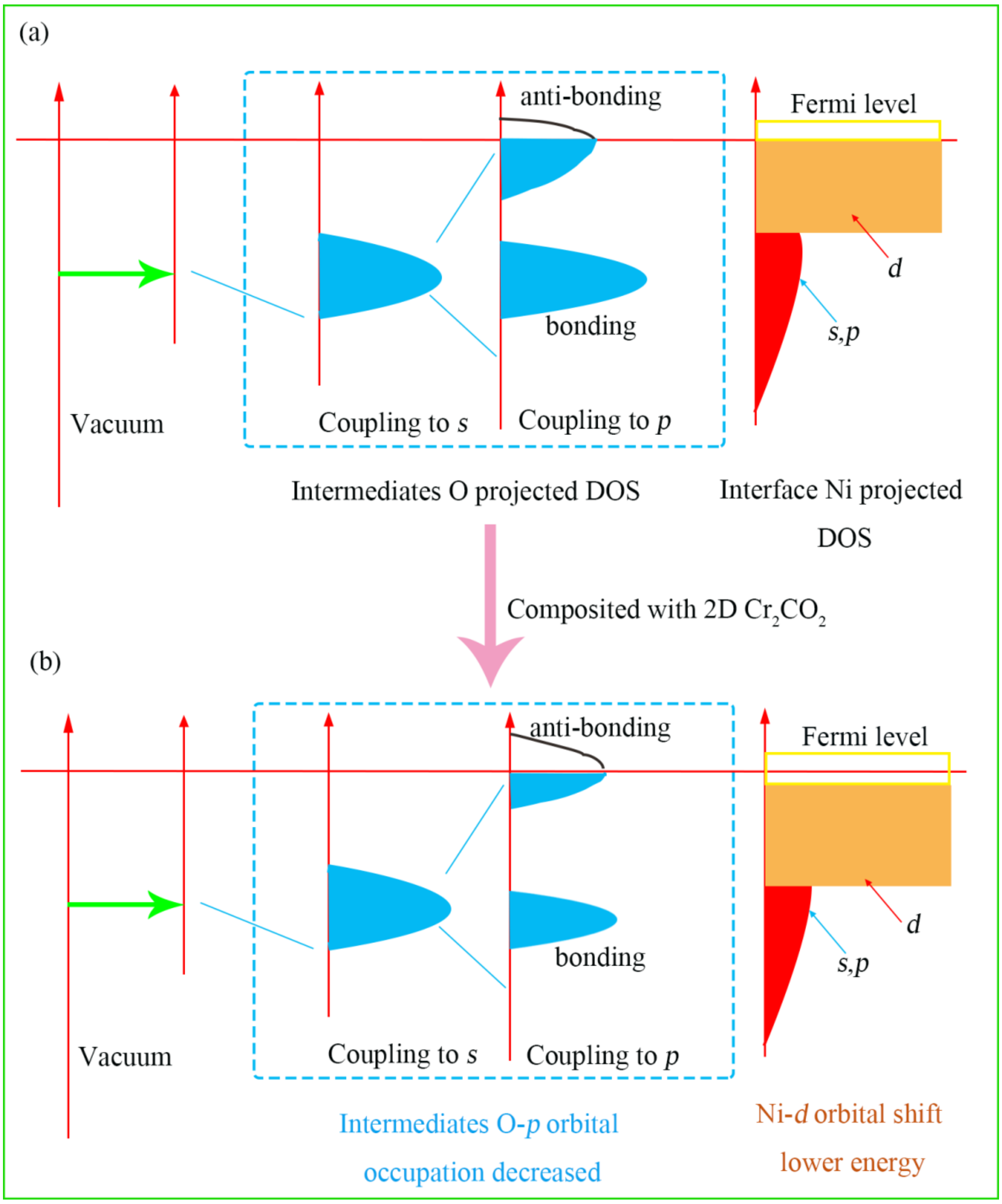


Figure S10. Schematic illustration the changed of the Ni *d*-orbital of Ni_2P, and O *p*-orbital of intermediate after with and without Cr_2CO_2 composite.

Table S1. The free energy changes of $\Delta G_{1\text{-}4}$ of different Ni_2P surface.

Ni_2P surface System	ΔG_1	ΔG_2	ΔG_3	ΔG_4
(001)-I- surface	0.31	1.52	2.25	0.84
(001) -II-surface	1.07	1.49	2.18	0.18
(100) surface	0.37	1.05	2.76	0.74
(102) surface	0.44	1.31	2.36	0.81
(110) surface	0.74	1.60	2.97	-0.39

Table S2. The calculated reaction Gibbs free energies of intermediates via HER and OER on Ni_2P/Cr_2CO_2 interface with and without considerate the Ni magnetic, respectively. The unit of ΔG is eV.

Ni_2P/Cr_2CO_2 interface	ΔG_{*H} $\theta = {}^{1}/_{8}$	ΔG_{*H} $\theta = {}^{2}/_{8}$	ΔG_{*H} $\theta = {}^{2}/_{8}$	ΔG_{*H} $\theta = {}^{4}/_{8}$	ΔG_1	ΔG_2	ΔG_3	ΔG_4
$T_{\text{without Ni magnetic}}$①	-0.31	-0.09	0.36	0.57	0.84	0.97	2.03	1.08
$T_{\text{with Ni magnetic}}$①	-0.35	-0.10	0.34	0.53	0.79	1.12	2.06	0.95

① $T_{\text{with Ni magnetic}}$ and $T_{\text{without Ni magnetic}}$ represent the reaction free energy of Ni_2P/Cr_2CO_2 interface with adsorption intermediates with and without considerate the Ni magnetic, respectively.

From Table S2, one can concluded that the spin polarization effect is quite weak on the Gibbs free energy of hydrogen adsorption (ΔG_{*H}) on Ni_2P/Cr_2CO_2 interface, and it would not alter the trend of ΔG_{*H} varies with hydrogen coverage, that is, the ΔG_{*H} increasing with the increase of hydrogen coverage. The overpotential are 0.10 V and 0.09 V of Ni_2P/Cr_2CO_2 interface for HER with and without considering spin polarization, respectively. The Gibbs free energies of different intermediates ($\Delta G_{1\text{-}4}$) on Ni_2P/Cr_2CO_2 interface show slight change. The overpotential are 0.83 and 0.80 V with and without considerate Ni magnetic, respectively. Therefore, it can be concluded that the effect of Ni magnetic on the OER and HER of Ni_2P/Cr_2CO_2 interface is negligible.

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