Supplementary Information

A Deep Insight to the Exfoliation Properties of MAX to MXenes and Hydrogen Evolution Performances of 2D MXenes

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1. Figures and Tables

Figure S1. The exfoliation energy of Nb$_2$AC to Nb$_2$C ($A$=Al, P, S, Ga, Ge, As, In, and Sn).

Figure S2. The exfoliation energy of M$_2$AlC and M$_2$GaC to M$_2$C, respectively (M=Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta).
Figure S3. The exfoliation energy of Ti_{n+1}AlC_n, V_{n+1}AlC_n, and Nb_{n+1}AlC_n to Ti_{n}C_n, V_{n}C_n, and Nb_{n}C_n, respectively.

Figure S4. Lattice structures of 2D M_{n+1}C_n (a) M_2C, (c) M_3C_2 and (e) M_4C_3, and of M_{n+1}C_nO_2 that
oxygen termination at the fcc site MXenes: (b) $M_2CO_2$, (d) $M_3C_2O_2$, and (f) $M_4C_3O_2$. Red and green bold dashed lines represent fcc site and hcp site, respectively. Light blue, brown, and red balls represent transition metals, carbon and oxygen atoms, respectively.

**Figure S5.** Dependence of hydrogen adsorption free energy ($\Delta G_{H^*}$) of studied $M_2CO_2$ on hydrogen coverages.
Figure S6. Relationship between $\Delta G_{H^1}$ and $E_f$ at 37.5 % (dark yellow squares) and 50% (violet balls) hydrogen coverages.

Figure S7. Relationship between $\Delta G_{H^1}$ and $N_e$ at 37.5 % (magenta squares) and 50% (blue balls) hydrogen coverages.
Figure S8. Relationship between $\Delta G_{H^*}$ and $E_b$ at 37.5% (cyan green squares) and 50% (wine balls) hydrogen coverage.

\[ R^2 = 0.42 \]

\[ R^2 = 0.45 \]

Figure S9. Densities of states of (a) Ti$_2$CO$_2$, (b) V$_2$CO$_2$, (c) Cr$_2$CO$_2$, (d) Y$_2$CO$_2$, (e) Zr$_2$CO$_2$, (f) Nb$_2$CO$_2$.
(g) Mo$_2$CO$_2$, (h) Hf$_2$CO$_2$, (i) Ta$_2$CO$_2$, and (j) W$_2$CO$_2$. The dash line represents the Fermi level energy and the dash arrow line indicates that the shifting of DOS to lower energy with the groups increase (such as Ti→Cr).

**Figure S10.** Schematic of Heyrovsky and Tafel adsorptions on M$_2$CO$_2$ surface.

**Figure S11.** The minimum energy pathway and activation energies of hydrogen desorption from Zr$_2$CO$_2$ surface for (a) Heyrovsky reaction and (b) Tafel reaction. The right panels show the initial state (IS), transition state (TS) and final state (FS) of two pathways for reducing protons to hydrogen.
Figure S12. Densities of states (with considering spin-polarization) of (a) Ti$_2$CO$_2$, (b) V$_2$CO$_2$, (c) Cr$_2$CO$_2$, (d) Y$_2$CO$_2$, (e) Zr$_2$CO$_2$, (f) Nb$_2$CO$_2$, (g) Mo$_2$CO$_2$, (h) Hf$_2$CO$_2$, (i) Ta$_2$CO$_2$, and (j) W$_2$CO$_2$. The dash line represents the Fermi level energy and the arrow line indicates that the shifting of DOS to lower energy with the increase of groups (such as Ti→Cr).

Figure S13. The correlation between adsorption free energy of atomic hydrogen ($\Delta G_{H^*}$) and $\varepsilon_{p-\sigma}$. $\Delta G_{H^*}$ is obtained at hydrogen coverage of 12.5% (solid) and 25% (hollow), respectively.
Figure S14. Electronic structures of four kinds of O-terminal MXenes, (a) $V_2CO_2$, (b) $Nb_2CO_2$, (c) $Mo_2CO_2$, (d) $W_2CO_2$.
**Table S1.** The lattice parameters of bulk Nb$_2$AC and bond lengths of Nb-C and Nb-A bonds (A = Al, P, Ga, Ge, or As).

<table>
<thead>
<tr>
<th>A</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>(d_{\text{Nb-C}}) (Å)</th>
<th>(d_{\text{Nb-A}}) (Å)</th>
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<tbody>
<tr>
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<tr>
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<td>3.524</td>
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<tr>
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**Table S2.** The lattice parameters of bulk V$_2$AC and bond lengths of V-C and V-A bonds (A = Al, P, Ga, Ge, or As).

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**Table S3.** The lattice parameters of bulk Hf$_2$AC and bond lengths of Hf-C and Hf-A bonds (A = Al, In, Sn, Tl, or Pb).

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<th>c/a</th>
<th>(d_{\text{Hf-C}}) (Å)</th>
<th>(d_{\text{Hf-A}}) (Å)</th>
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**Table S4.** The lattice parameters of bulk Zr$_2$AC and bond lengths of Zr-C and Zr-A bonds (A = Al, S, In, Sn, Tl, or Pb).

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<th>c (Å)</th>
<th>c/a</th>
<th>(d_{\text{Zr-C}}) (Å)</th>
<th>(d_{\text{Zr-A}}) (Å)</th>
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<tr>
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Table S5. The lattice parameters of bulk $M_2AC$ and bond lengths of M-C and M-A bonds ($M= \text{Cr, Mo, Sc or Ta, A = Al, Ga, Ge, In, or Ti}$).

<table>
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<th>$M_2AC$</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$c/a$</th>
<th>$d_{M-C}$(Å)</th>
<th>$d_{M-A}$(Å)</th>
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<tr>
<td>Cr$_2$AlC</td>
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<td>Mo$_2$GaC</td>
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<td>Ta$_2$AlC</td>
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Table S6. The lattice parameters of bulk $M_3AC_2$ and $M_4AC_3$ and bond lengths of M-C and M-A bonds ($M= \text{Ti, V, or Nb, A = Al, Si, Ga, Ge, or Sn}$).

<table>
<thead>
<tr>
<th>$M_3AC_2$</th>
<th>$a$(Å)</th>
<th>$c$(Å)</th>
<th>$c/a$</th>
<th>$d_{M-C}$(Å)</th>
<th>$d_{M-A}$(Å)</th>
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</thead>
<tbody>
<tr>
<td>Ti$_3$AlC$_2$</td>
<td>3.423</td>
<td>17.448</td>
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<td>17.487</td>
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<tr>
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<td>18.268</td>
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<td>2.311,2.212</td>
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<td>V$_3$AlC$_2$</td>
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<td>18.556</td>
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Table S7. Calculated exfoliation energy (in unit of eV/Å$^2$) of $M_{n+1}AC_n$ to $M_{n+1}C_n$ phases.

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<th>P</th>
<th>S</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
<th>In</th>
<th>Sn</th>
<th>Ti</th>
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<tr>
<td>Zr₃C₂O₂</td>
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Table S8. Calculated binding energy of A in Mₙ₊₁ACₙ systems (eV).

<table>
<thead>
<tr>
<th>System</th>
<th>Eₘ (eV)</th>
<th>Eᵢ (eV)</th>
<th>Ne (e)</th>
<th>ΔGᵢ* (eV)</th>
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</thead>
<tbody>
<tr>
<td>Ti₃C₂O₂</td>
<td>-5.87</td>
<td>5.43</td>
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<td>V₃C₂O₂</td>
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<td>Cr₃C₂O₂</td>
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<td>0.97</td>
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<td>Y₃C₂O₂</td>
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<td>1.31</td>
<td>0.55</td>
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<td>Ta₃C₂O₂</td>
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<tr>
<td>W₃C₂O₂</td>
<td>-3.39</td>
<td>2.39</td>
<td>1.14</td>
<td>-0.97</td>
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</table>

Table S9. The calculated binding energy (Eₘ), formation energy of oxygen vacancy (Eᵢ), and gained electrons (Ne) of surface O* of M₃C₂O₂, and adsorption free energy of atomic hydrogen (ΔGᵢ*) on the M₃C₂O₂ surface.
Table S10. The calculated binding energy ($E_b$), formation energy of oxygen vacancy ($E_f$), and gained electrons ($N_e$) of surface terminated O* of $M_4C_3O_2$, and adsorption free energy of atomic hydrogen ($\Delta G_{H^*}$) on the $M_4C_3O_2$ surface.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_b$ (eV)</th>
<th>$E_f$ (eV)</th>
<th>$N_e$ (e)</th>
<th>$\Delta G_{H^*}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_4$C$_3$O$_2$</td>
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<td>5.18</td>
<td>1.16</td>
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<td>V$_4$C$_3$O$_2$</td>
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<td>Cr$_4$C$_3$O$_2$</td>
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<td>Y$_4$C$_3$O$_2$</td>
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<td>Zr$_4$C$_3$O$_2$</td>
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<td>5.84</td>
<td>1.30</td>
<td>0.27</td>
</tr>
<tr>
<td>Nb$_4$C$_3$O$_2$</td>
<td>-5.28</td>
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<tr>
<td>Mo$_4$C$_3$O$_2$</td>
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<td>1.31</td>
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<td>1.28</td>
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<tr>
<td>W$_4$C$_3$O$_2$</td>
<td>-3.12</td>
<td>2.11</td>
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<td>-0.93</td>
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</table>

Table S11. Adsorption free energy of atomic hydrogen ($\Delta G_{H^*}$) (eV) on the $M_4CO_2$ surface at different hydrogen coverage.

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<td>Cr$_2$CO$_2$</td>
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<td>-0.24</td>
<td>0.21</td>
<td>0.45</td>
</tr>
<tr>
<td>Y$_2$CO$_2$</td>
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<td>0.13</td>
<td>0.22</td>
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<td>Zr$_2$CO$_2$</td>
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<td>0.98</td>
<td>1.21</td>
<td>1.33</td>
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<td>Nb$_2$CO$_2$</td>
<td>0.41</td>
<td>0.76</td>
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<td>Mo$_2$CO$_2$</td>
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<td>0.05</td>
<td>0.32</td>
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<tr>
<td>Hf$_2$CO$_2$</td>
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<td>0.69</td>
<td>0.84</td>
<td>1.47</td>
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<td>Ta$_2$CO$_2$</td>
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<td>1.01</td>
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<td>0.96</td>
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Table S12. Adsorption energy ($\Delta E$) on the $M_2CO_2$ surface for Heyrovsky and Tafel mechanisms.

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<td>V$_2$CO$_2$</td>
<td>-0.02</td>
<td>1.21</td>
</tr>
<tr>
<td>Cr$_2$CO$_2$</td>
<td>-0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>Y$_2$CO$_2$</td>
<td>-0.22</td>
<td>-1.92</td>
</tr>
<tr>
<td>Zr$_2$CO$_2$</td>
<td>0.01</td>
<td>-0.93</td>
</tr>
<tr>
<td>Nb$_2$CO$_2$</td>
<td>-0.01</td>
<td>-0.53</td>
</tr>
<tr>
<td>Mo$_2$CO$_2$</td>
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<td>Hf$_2$CO$_2$</td>
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</tr>
<tr>
<td>W$_2$CO$_2$</td>
<td>0.01</td>
<td>-0.09</td>
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</table>
2. Supplementary analysis

2.1 DOS of $10\, M_2CO_2$ MXenes with considering the spin-polarized.

The total DOSs of $10\, M_2CO_2$ MXenes with considering the spin-polarization are calculated, results are presented in Figure S12. Like the results of Figure S12, there is a trend that for the same groups, the DOSs of spin-up and spin-down shift to lower energy with the groups increase from Ti to Cr, as illustration of the blue arrow in Figure S12. This trend is demonstrated by the results of $p$-DOS (Figure 5), for example, from Hf to W, the $p$-DOS shifts to lower energy.

2.2 The correlation between $\Delta G_{H^*}$ and $\epsilon_{p\sigma}$

We have calculated fully filled bonding orbital ($\sigma$) center of surface $O^*$, $\epsilon_{p\sigma}$ and correlation between adsorption free energy of atomic hydrogen ($\Delta G_{H^*}$) and $\epsilon_{p\sigma}$ is shown in Figure S13. It can be found that when the $\epsilon_{p\sigma}$ are in the range of $-4.7$~$-3.9$ eV, the absolute free Gibbs free energy($\Delta G_{H^*}$) is less than 0.3 eV (corresponding $\epsilon_p$ values are $-4.1$~$-3.3$ eV), which could deliver a better catalytic performances of MXenes for HER. The two descriptors are indicate that the Ti, V, Cr, Mo, and W based MXenes, which all lie in zone A in Figure 4 (in the revised manuscript) could possess superior HER catalytic performances (see in Figure R4) consistenting with the prediction based on Figure 4

2.3. Electronic structures of $M_2CO_2$ (lie in Zone B)

The electronic structures of $V_2CO_2$, $Nb_2CO_2$, $Mo_2CO_2$, $W_2CO_2$ (lie in Zone A) are further calculated and results are presented in Figure S14. It can be seen that four studied $V_2CO_2$, $Nb_2CO_2$, $Mo_2CO_2$, $W_2CO_2$ MXenes show metallic characteristics. Our previous work indicated that $Cr_2CO_2$ MXenes show metallic characteristics. Therefore, all of five studied $M_2CO_2$ MXenes lie in Zone and displayed metallic characteristics. The MXenes in Zone A with good electrical conductivity of favor it electron transfer during HER and therefore promote HER processes.