# Supporting Information

# Rational Design of Janus MXene Monolayers as Promising Frameworks for High-performance Sodium Metal Anodes

Shengbo Wang[a#], Ziang Ren[a#], Jinsen Zhang[a], Shihui Zou[a], Huadong Yuan[a], Jianmin Luo[a], Yujing Liu[a], Jianwei Nai[a], Yao Wang*[ab], Xinyong Tao[a]

[a] College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, 310014, China

[b] Moganshan Research Institute at Deqing County Zhejiang University of Technology, Huzhou, 313000, China

[#] These authors contributed equally to this work.

*Corresponding author: wangyao@zjut.edu.cn .

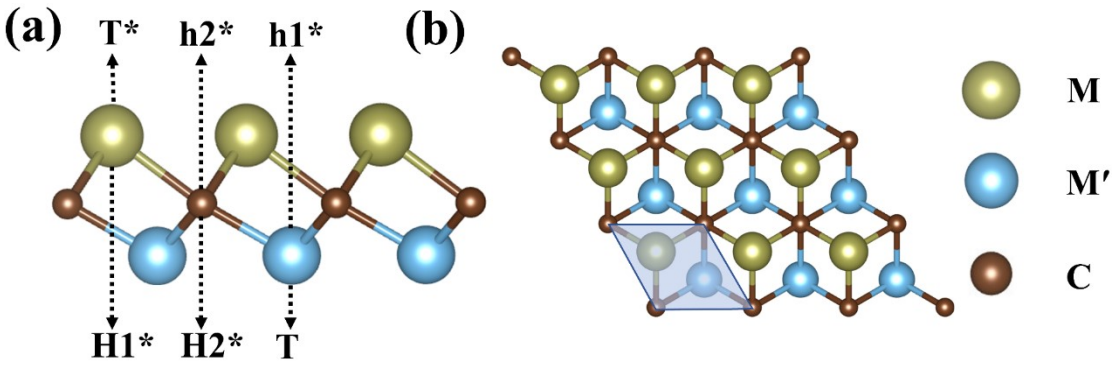


**Fig. S1.** (a) Side view and (b) top view of the MM′C Janus MXene structures. The dark yellow, light blue, and brown spheres represent M, M', and C atoms, respectively.

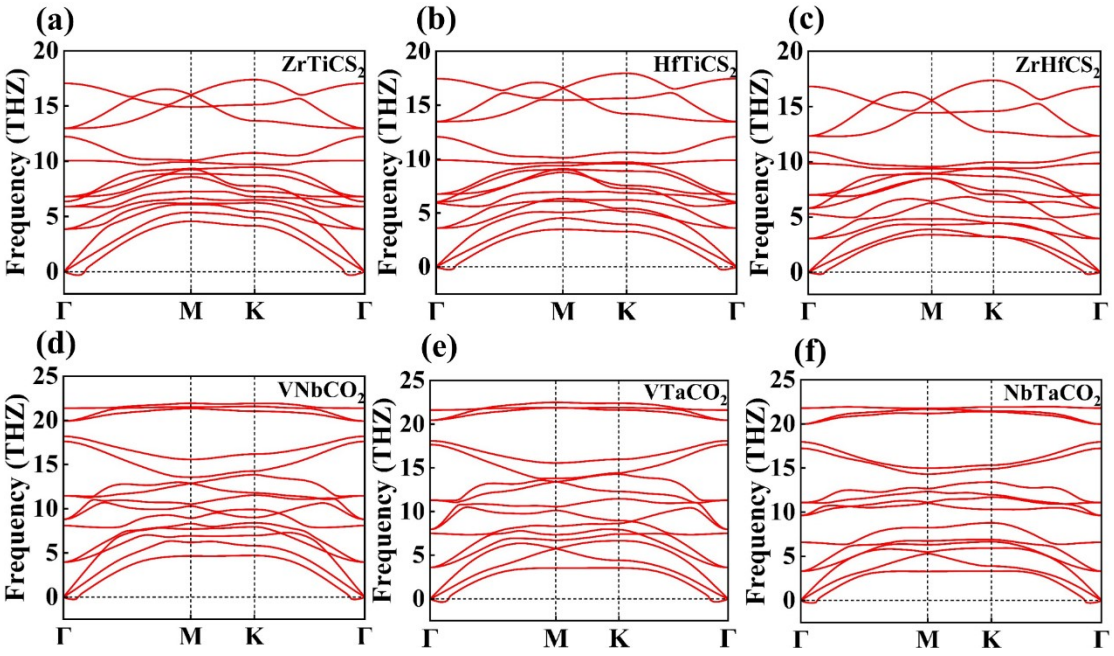


**Fig. S2.** Phonon spectra of (a) $ZrTiCS_2$, (b) $HfTiCS_2$, (c) $ZrHfCS_2$, (d) $VNbCO_2$, (e) $VTaCO_2$, and (f) $NbTaCO_2$.

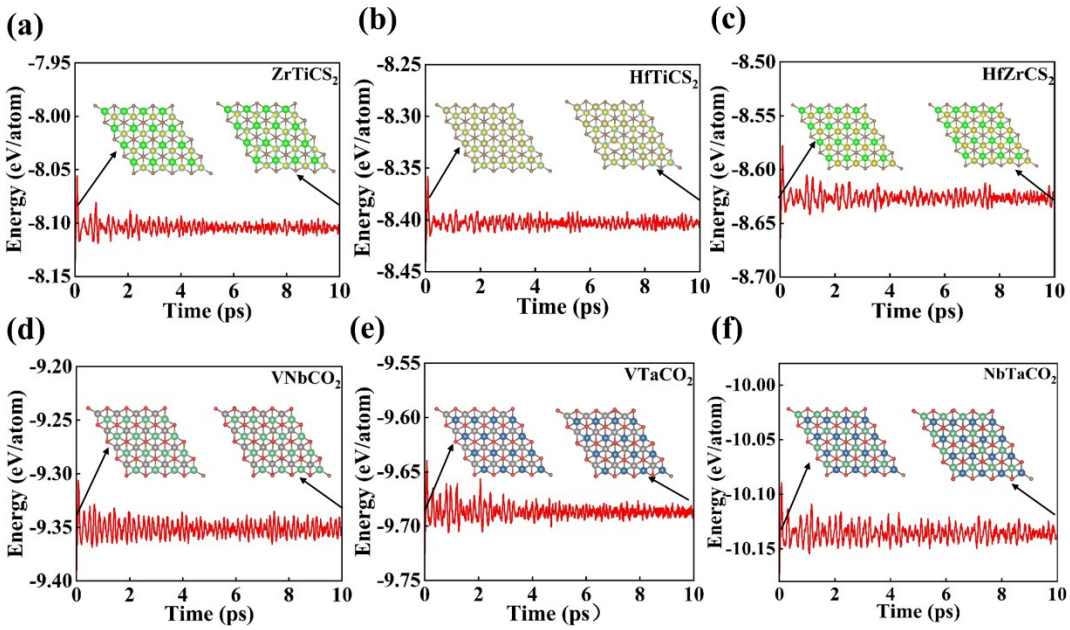


**Fig. S3.** Variation in energy over 10 ps during the AIMD simulation at 300 K of (a) $ZrTiCS_2$, (b) $HfTiCS_2$, (c) $ZrHfCS_2$, (d) $VNbCO_2$, (e) $VTaCO_2$, and (f) $NbTaCO_2$ structure.

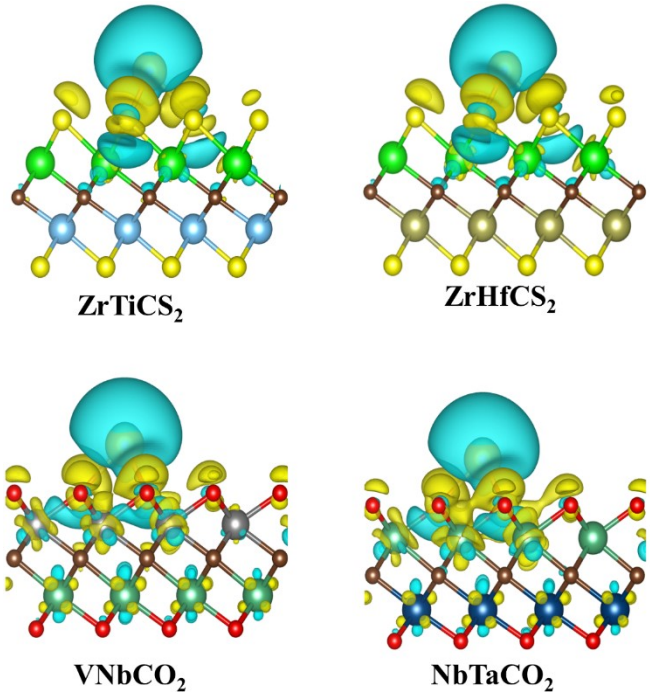


**Fig. S4.** Charge density difference ($e^-$ $Å^{-3}$) of the Na atom on $ZrTiCS_2$, $ZrHfCS_2$, $VNbCO_2$, and $NbTaCO_2$. The isosurface level is set to be 0.0006 $e^-$ $Å^{-3}$. The cyan and yellow regions indicate electron depletion and accumulation, respectively.

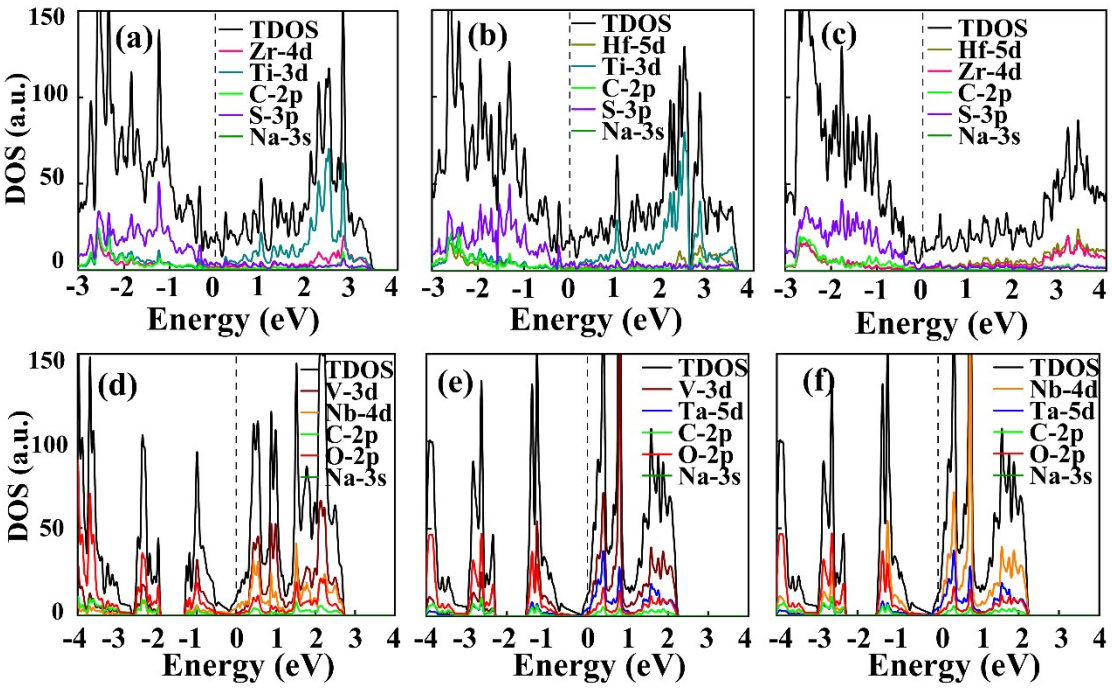


**Fig. S5.** Single-Na adsorption DOS of (a) $ZrTiCS_2$ (b) $HfTiCS_2$, (c) $HfZrCS_2$, (d) $VNbCO_2$, (e) $VTaCO_2$, and (f) $NbTaCO_2$. The Fermi level is set to zero.

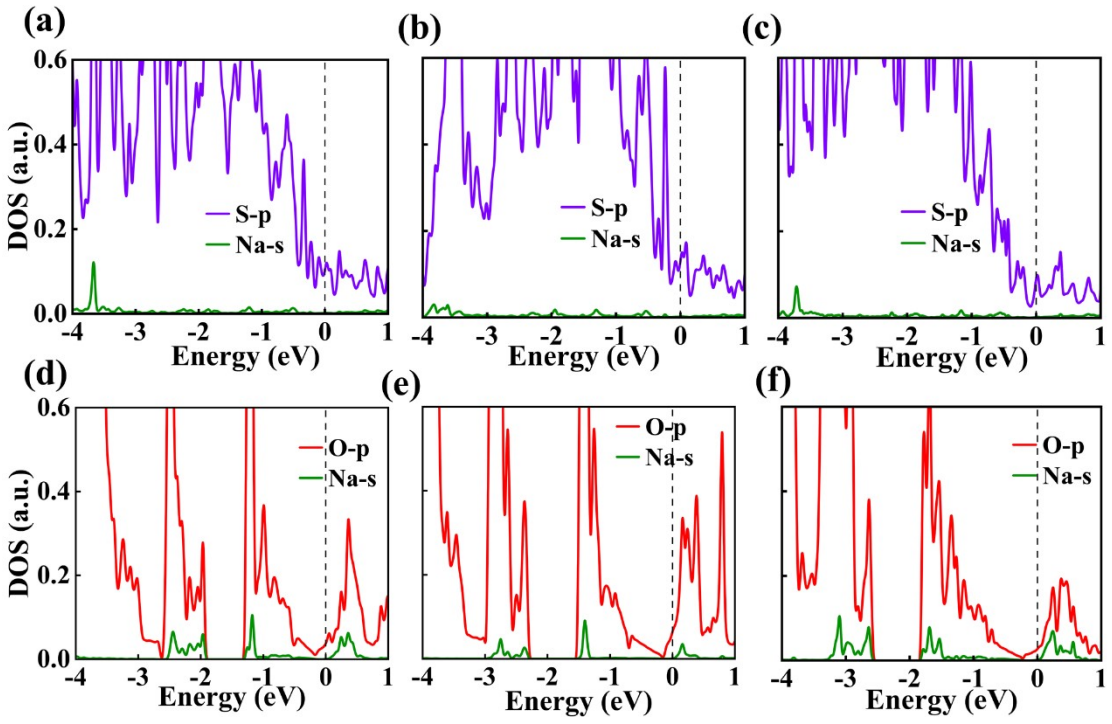


**Fig. S6.** (a-c) PDOS of the adsorbed Na atom and its surrounding S atom in $ZrTiCS_2$, $HfTiCS_2$, and $HfZrCS_2$, (d-f) PDOS of the adsorbed Na atom and its surrounding O atom in $VNbCO_2$, $VTaCO_2$, and $NbTaCO_2$. The Fermi level is set to zero.

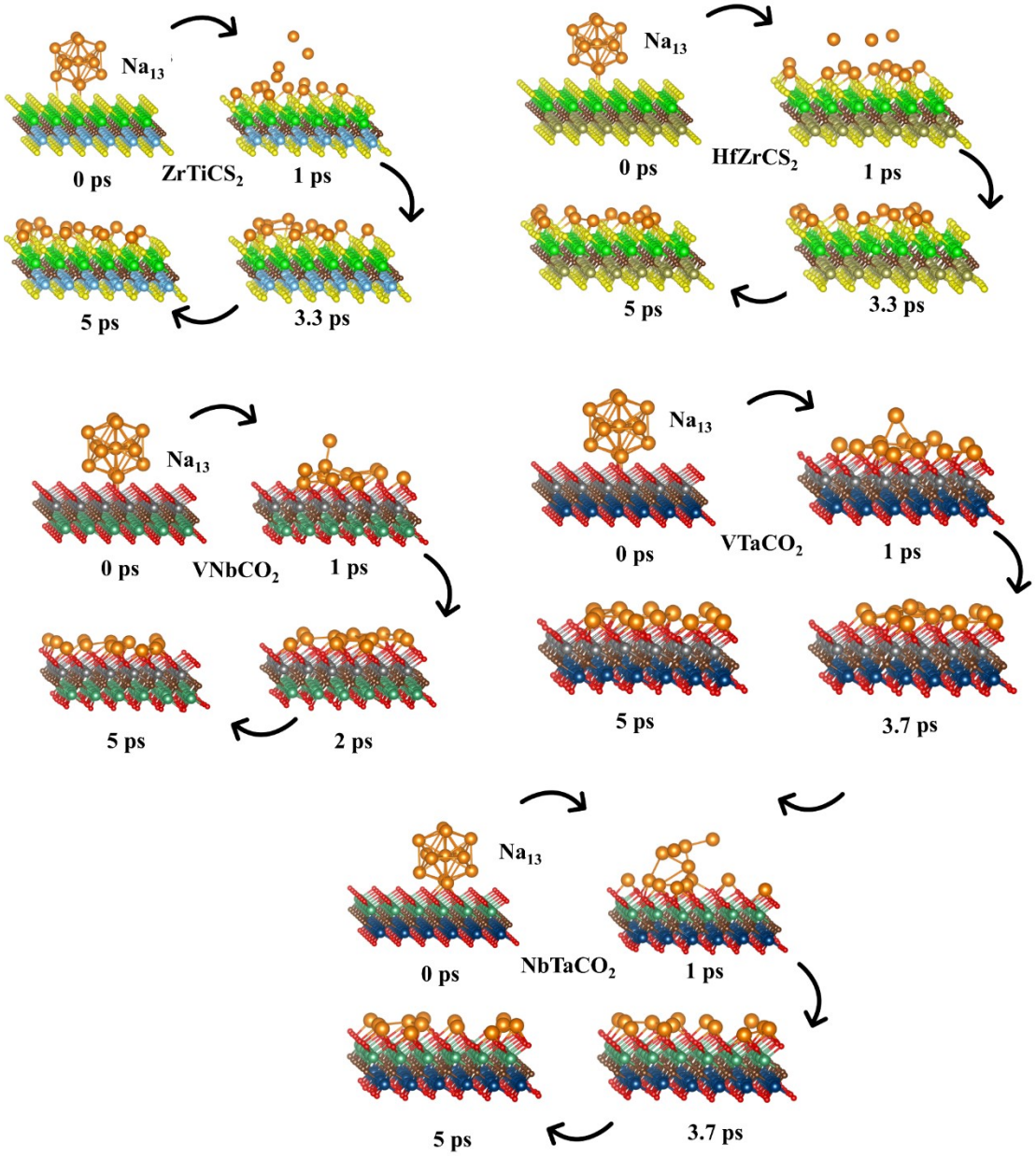


**Fig. S7.** Snapshots of AIMD simulations of $Na_{13}$ on $ZrTiCS_2$, $HfZrCS_2$, $VNbCO_2$, $VTaCO_2$, and $NbTaCO_2$ Janus Mxene at 300 K.

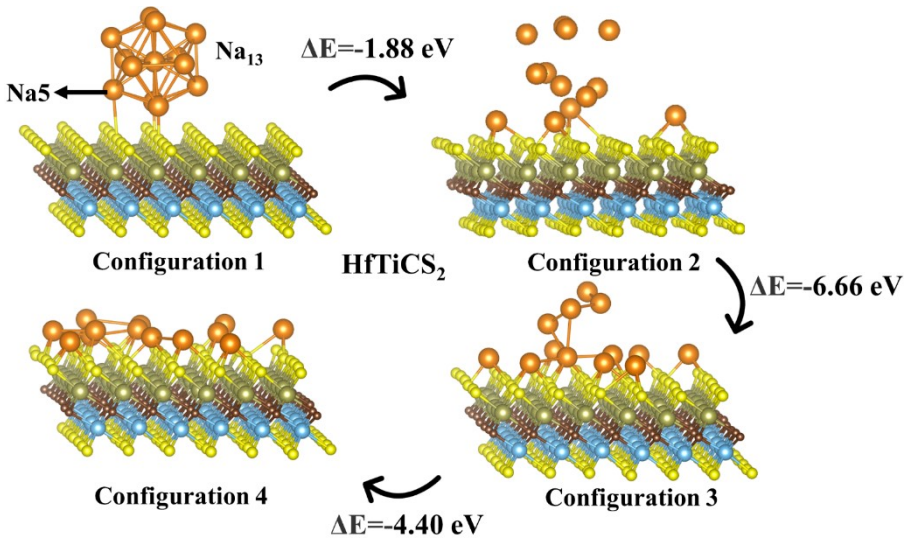


**Fig. S8.** The four-state structure of the $Na_{13}$ cluster on the $HfTiCS_2$ Janus MXene surface during the 3D-to-2D transition at 300 K.

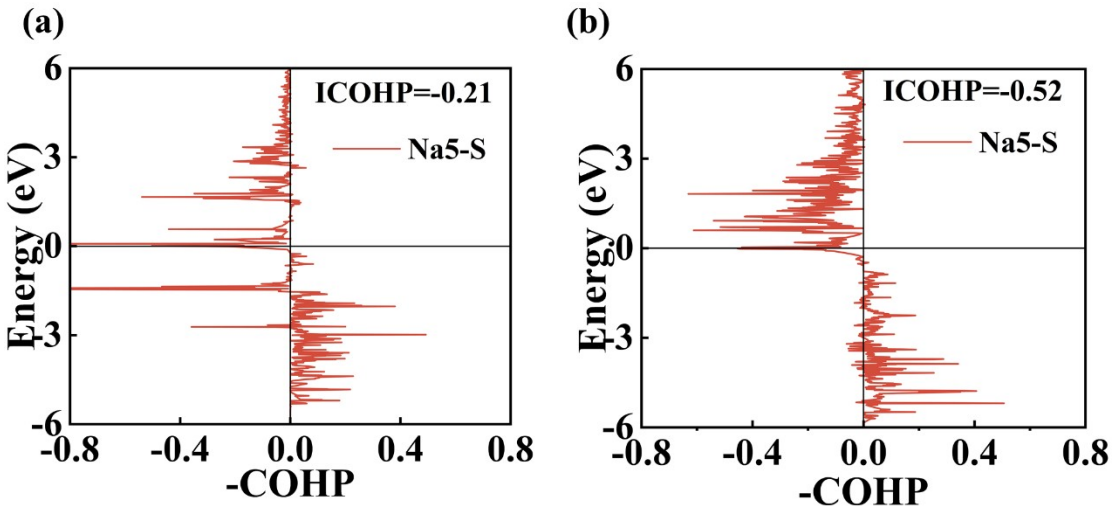


**Fig. S9.** (a) The COHP of Na5 atom within the $Na_{13}$ clusters in interacting with surface S atoms in configuration 1. (b) The COHP of Na5 atom within the $Na_{13}$ cluster in interacting with surface S atoms in configuration 4.

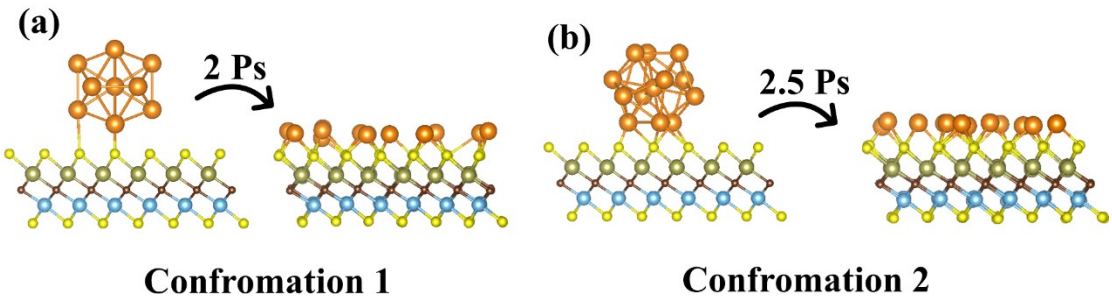


**Fig. S10**. Snapshots of AIMD simulations of different $Na_{13}$ conformations on $HfTiCS_2$ Janus MXene at 300 K.(a) Conformation 1. (b) Conformation 2.

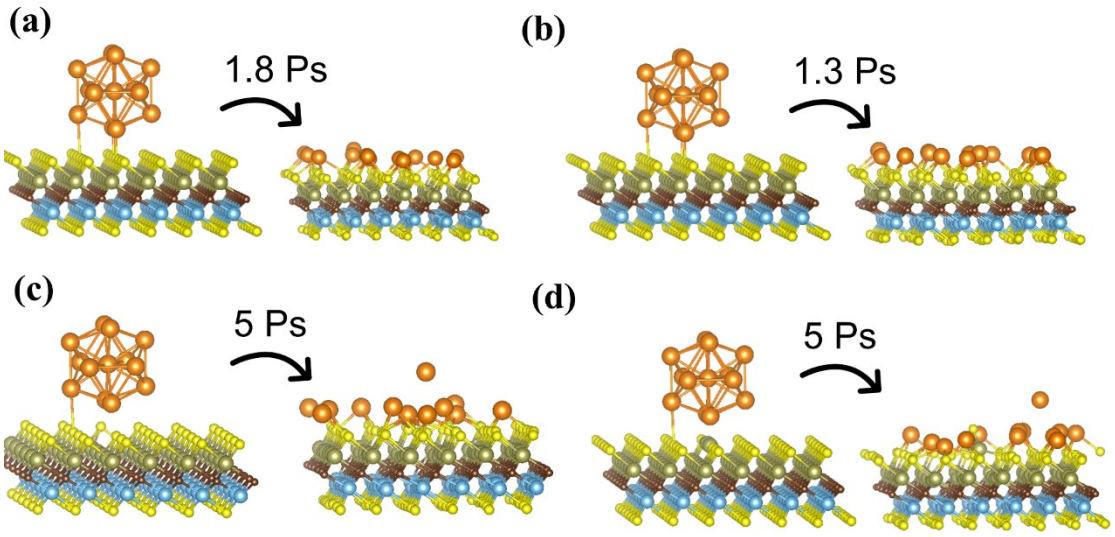


**Fig. S11.** (a) and (b) Snapshots of AIMD simulations of $Na_{13}$ on $HfTiCS_2$ Janus MXene at 400 K and 500K. (c) and (d) Snapshots of AIMD simulations of $Na_{13}$ on vacancy-defect and doped-defect $HfTiCS_2$ Janus MXene at 300 K

**Table S1.** Lattice parameter, lengths of M–C ($d_{M–C}$), M′–C ($d_{M'–C}$), M–S ($d_{M–S}$), and M′–S ($d_{M'–S}$) bonds of all $MM'CS_2$, $M_2CS_2$, and $M_2'CS_2$ MXenes are shown.

| | Lattice (Å) | $d_{M–C}$ (Å) | $d_{M'–C}$ (Å) | $d_{M–S}$ (Å) | $d_{M'–S}$ (Å) |
|---|---|---|---|---|---|
| $ZrTiCS_2$ | 3.31 | 2.33 | 2.26 | 2.53 | 2.41 |
| $HfTiCS_2$ | 3.29 | 2.31 | 2.26 | 2.50 | 2.41 |
| $ZrHfCS_2$ | 3.43 | 2.4 | 2.37 | 2.53 | 2.41 |
| $Ti_2CS_2$ | 3.16 | 2.19 | / | 2.40 | / |
| $Zr_2CS_2$ | 3.45 | 2.4 | / | 2.53 | / |
| $Hf_2CS_2$ | 3.41 | 2.37 | / | 2.51 | / |

**Table S2.** Lattice parameter, lengths of M–C ($d_{M–C}$), M′–C ($d_{M'–C}$), M–O ($d_{M–O}$), and M′–O ($d_{M'–O}$) bonds of All $MM'CO_2$, $M2CO_2$, and $M_2'CO_2$ MXenes are shown.

| | a (Å) | $d_{M–C}$ (Å) | $d_{M'–C}$ (Å) | $d_{M–O}$ (Å) | $d_{M'–O}$ (Å) |
|---|---|---|---|---|---|
| $VNbCO_2$ | 2.98 | 2.08 | 2.14 | 2.03 | 2.07 |
| $VTaCO_2$ | 2.99 | 2.09 | 2.13 | 2.03 | 2.08 |
| $NbTaCO_2$ | 3.08 | 2.22 | 2.15 | 2.11 | 2.1 |
| $V_2CO_2$ | 2.88 | 2.04 | / | 1.95 | / |
| $Nb_2CO_2$ | 3.10 | 2.19 | / | 2.09 | / |
| $Ta_2CO_2$ | 3.12 | 2.19 | / | 2.1 | / |

**Table S3.** Binding energies (unit: eV) of Na-adatom on Janus MXenes at different sites. The largest binding energies were highlighted.

| | $E_{T1}$ | $E_{H1}$ | $E_{H2}$ | $E_{T2}$ | $E_{h1}$ | $E_{h2}$ |
|---|---|---|---|---|---|---|
| $ZrTiCS_2$ | -2.08 | -2.62 | **-2.63** | -1.98 | -2.50 | -2.50 |
| $HfTiCS_2$ | Unstable | -2.47 | **-2.51** | -1.94 | -2.49 | -2.46 |
| $ZrHfCS_2$ | Unstable | -2.47 | **-2.52** | -1.89 | -2.43 | -2.46 |
| | $E_{T3}$ | $E_{H3}$ | $E_{H4}$ | $E_{T4}$ | $E_{h3}$ | $E_{h4}$ |
| $VNbCO_2$ | -2.59 | **-3.09** | -3.01 | -1.53 | -1.93 | -2.01 |
| $VTaCO_2$ | -2.29 | **-2.79** | -2.71 | -0.88 | -1.27 | -1.35 |
| $NbTaCO_2$ | -2.06 | **-2.54** | -2.43 | -0.88 | -1.25 | -1.34 |

**Table S4.** The alteration in the charge state of M (M′) atom following the formation of S-terminated MXenes

| | $\Delta Q_m$ (\|e\|) | $\Delta Q_{m'}$ (\|e\|) |
|---|---|---|
| $ZrTiCS_2$ | -1.83 | -1.63 |
| $HfTiCS_2$ | -1.89 | -1.62 |
| $ZrHfCS_2$ | -1.88 | -1.90 |
| $Ti_2CS_2$ | -1.64 | / |
| $Zr_2CS_2$ | -1.89 | / |
| $Hf_2CS_2$ | -1.92 | / |

**Table S5.** The alteration in the charge state of M (M′) atom following the formation of O-terminated MXenes

| | $\Delta Q_m$ (\|e\|) | $\Delta Q_{m'}$ (\|e\|) |
|---|---|---|
| $VNbCO_2$ | -1.66 | -2.07 |
| $VTaCO_2$ | -1.66 | -2.16 |
| $NbTaCO_2$ | -1.85 | -2.21 |
| $V_2CO_2$ | -1.75 | / |
| $Nb_2CO_2$ | -2.05 | / |
| $Ta_2CO_2$ | -2.13 | / |

**Table S6.** Calculated electric charge transferred (ΔQ) from Na-adatom to Janus MXenes surface.

| | $\Delta Q_m$ **(\|e\|)** |
|---|---|
| $ZrTiCS_2$ | 0.886 |
| $HfTiCS_2$ | 0.885 |
| $ZrHfCS_2$ | 0.882 |
| $VNbCO_2$ | 0.911 |
| $VTaCO_2$ | 0.910 |
| $NbTaCO_2$ | 0.909 |

**Table S7.** The distance (H) between the adsorbed Na atom and the M transition metal layer in various Janus MXenes

| | H (Å) |
|---|---|
| $VNbCO_2$ | 2.750 |
| $VTaCO_2$ | 2.760 |
| $NbTaCO_2$ | 2.830 |
| $ZrTiCS_2$ | 3.430 |
| $HfTiCS_2$ | 3.540 |
| $ZrHfCS_2$ | 3.510 |

**Table S8.** Binding energy (eV) of Na clusters with different structures and Janus MXenes

| | Configuration 1 | Configuration 2 | Configuration 3 | Configuration 4 |
|---|---|---|---|---|
| $ZrTiCS_2$ | -0.13 | -0.72 | -1.19 | -1.21 |
| $HfTiCS_2$ | -0.12 | -0.77 | -1.11 | -1.12 |
| $ZrHfCS_2$ | -0.11 | -0.78 | -1.18 | -1.20 |
| $VNbCO_2$ | -0.20 | -0.83 | -1.13 | -1.23 |
| $VTaCO_2$ | -0.22 | -0.92 | -1.11 | -1.12 |
| $NbTaCO_2$ | -0.14 | -0.78 | -0.89 | -0.92 |

**Table S9.** The average charge ($\Delta Q$) transferred to the surface of Janus MXenes by a single Na atom within the $Na_{13}$ cluster.

| | Configuration 1 | Configuration 2 | Configuration 3 | Configuration 4 |
|---|---|---|---|---|
| $ZrTiCS_2$ | 0.22 | 0.47 | 0.59 | 0.73 |
| $HfTiCS_2$ | 0.21 | 0.42 | 0.55 | 0.77 |
| $ZrHfCS_2$ | 0.21 | 0.45 | 0.60 | 0.82 |
| $VNbCO_2$ | 0.22 | 0.42 | 0.61 | 0.76 |
| $VTaCO_2$ | 0.22 | 0.48 | 0.63 | 0.74 |
| $NbTaCO_2$ | 0.22 | 0.41 | 0.52 | 0.74 |