Electronic Supplementary Information

$YTaNO_2$ Janus MXene as an Optimal Electrocatalyst for the Hydrogen Evolution Reaction

Latifa Bettadj,[†] Reda M. Boufatah,[†] Tarik Ouahrani,[‡] Chewki Ougherb,[‡] Ángel Morales-García,[¶] Michael Badawi,[§] and Daniel Errandonea[*,‖]

[†]*Laboratoire de Physique Théorique, Université de Tlemcen, BP 119, 13000, Algeria*

[‡]*Ecole Supérieure en Sciences Appliquées, ESSA-Tlemcen, BB 165 RP Bel Horizon, Tlemcen 13000, Algeria.*

[¶]*Departament de Ciéncia de Materials i Química Física & Institut de Química Teórica i Computacional (IQTCUB), Universitat de Barcelona, c/Martí i Franquès 1-11, 08028 Barcelona, Spain*

[§]*Université de Lorraine, CNRS, L2CM, F-54000 Nancy, France*

[‖]*Departamento de Física Aplicada - Instituto de Ciencia de Materiales, Matter at High Pressure (MALTA) Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, 46100, Valencia, Spain*

E-mail: daniel.errandonea@uv.es

Spin Configurations and Stability of Y–M–N–O_2, M = Cr and V MXenes

For both Y–Cr–N–O_2 and Y–V–N–O_2 Janus MXenes, several magnetic configurations were systematically investigated to determine the magnetic ground state. The calculations were performed using a 2×2×1 supercell to allow for possible antiferromagnetic ordering.

Spin-polarized DFT calculations were carried out for the following configurations:

- **Non-magnetic (NM):** all atoms initialized with zero magnetic moment.
- **Ferromagnetic (FM):** all transition metal atoms (Cr or V) initialized with parallel spins.
- **Antiferromagnetic 1 (AFM1, $+-+-$):** transition metal atoms arranged in an alternating up and down spin pattern along one direction of the supercell.
- **Antiferromagnetic 2 (AFM2, $++--$):** transition metal atoms arranged in blocks of parallel spins with alternating signs along the supercell

Despite these initial spin arrangements, the results summarized in Table S1 show that for both Cr- and V-based MXenes, all configurations relax to a vanishing total magnetic moment. The FM configuration, which initially imposed parallel spins, and the AFM configurations, which imposed alternating spin patterns, both converge to essentially the same total energy as the NM state. This behavior arises because the transition metal atoms in these Janus MXenes experience strong hybridization with neighboring atoms (Y, N, and O) and a delocalized electronic structure, which quenches local magnetic moments. Consequently, magnetic ordering is not energetically favorable. Therefore, the ground state of these Y–M–N–O_2 MXenes is confirmed to be **non-magnetic**, and no stable ferromagnetic or antiferromagnetic ordering exists under the tested conditions.

Table S1 Total energies (E_{total}) obtained from spin-polarized DFT calculations for different magnetic configurations of Y–M–N–O_2 Janus MXenes (M = Cr, V). All energies are given in eV per unit cell.

System	Magnetic configuration	E_{total} (eV)
Y–Cr–N–O_2	NM	−167.62742079
	FM	−167.62742092
	AFM1	−166.57275466
	AFM2	−166.57275466
Y–V–N–O_2	NM	−170.13765847
	FM	−170.13765870
	AFM1	−169.70165214
	AFM2	−169.70165214

Stability of the studies structures

In order to assess the effect of transition metal substitution, we compared a hypothetical $YMNO_2$ MXene with the reference Y-based MXene (without transition metal replacement). In the pristine Y-based structure, yttrium ($4d^15s^2$) exhibits a relatively large atomic radius (180 pm) and low electronegativity, resulting in long Y–C bonds and a moderately flexible lattice. This softness can facilitate distortions when the surface is functionalized with NO_2 groups, which impose strong electron-withdrawing effects.

In contrast, introducing an M transition metal (M = Ta, Hf, Mo, etc.) into the Y layer modifies the local bonding environment:

- The M atom reduces the average atomic radius of the TM layer, better matching the C–C in-plane distances.
- For 5d metals such as Ta or Hf, the extended d orbitals enhance hybridization with both C and O/N atoms from the NO_2 group, thereby stabilizing the structure.
- The mechanical rigidity increases due to stronger metallic and covalent bonding, reducing the amplitude of surface reconstructions.

For $YMNO_2$ with M =Hf or Ta, the lattice remains stable upon relaxation, indicating that the balance between Y (large radius, ionic character) and M (optimal radius, strong

d-orbital hybridization) is favorable. Conversely, using smaller 3d metals (e.g., V, Cr) in $YMNO_2$ tends to create local strain due to mismatch with Y, leading to distortions and possible phonon instabilities. The pure Y-based MXene shows flexibility but reduced stability upon NO_2 functionalization. Substitution with an optimal transition metal such as Hf or Ta in $YMNO_2$ enhances both electronic bonding and mechanical integrity, mitigating the destabilizing effects of NO_2 adsorption.

Table S2 Optimized lattice parameter a, interlayer width d, and relative stacking energy ΔE for the six Y_2NO_2 stacking configurations.

Configuration	a (Å)	d (Å)	ΔE (eV)
ABC_{HM}	3.510	4.758	0
ABC_{HMX}	3.525	4.697	0.196
ABC_{HX}	3.476	4.913	0.617
ABA_{H}	3.489	4.971	0.281
ABA_{HMX}	3.516	4.821	0.586
ABA_{HX}	3.484	4.983	0.848

Table S3 Elastic constants C_{ij} ($\mathrm{N\,m^{-1}}$), Young's modulus Y_{2D} ($\mathrm{N\,m^{-1}}$), Poisson's ratio (ν), and shear modulus G of $YHfNO_2$ and $YTaNO_2$.

Material	C_{11}	C_{12}	C_{66}	Y_{2D}	ν	G
$YHfNO_2$	124.0	58.0	33.0	96.8	0.47	33.0
$YTaNO_2$	205.0	60.0	72.5	187.4	0.29	72.5

Thermal stability of the studied structures

To further evaluate the thermal stability of the cell of $3\times3\times1$ of the Janus MXenes $YHfNO_2$ and $YTaNO_2$, ab initio molecular dynamics (AIMD) simulations were carried out at finite temperature. As shown in Fig. S4(a,b), the temperature fluctuations remain well controlled around the target value throughout the entire simulation time, confirming the reliability of the Nosé–Hoover thermostat and the numerical stability of the AIMD runs. The corresponding total energy profiles displayed in Fig. S4(c,d) exhibit moderate and bounded oscillations without any systematic drift, which is a clear signature of thermodynamic equilibrium and structural robustness.

Notably, $YHfNO_2$ presents relatively regular and continuous oscillations in its total energy, indicating the preservation of its structural framework during the simulation. However, despite this apparent dynamical stability, $YHfNO_2$ shows more pronounced energy fluctuations compared to $YTaNO_2$, highlighting a stronger sensitivity to thermal effects. These fluctuations are likely associated with the asymmetric Janus configuration and the mass and bonding contrast between Hf- and Y-terminated surfaces, which enhance lattice vibrations at finite temperature. In contrast, $YTaNO_2$ exhibits slightly smoother energy variations, suggesting a comparatively higher resistance to thermal perturbations.

Overall, the AIMD results demonstrate that both Janus MXenes remain thermally stable within the simulated temperature range, with no indication of bond breaking or structural collapse. The observed differences in energy fluctuation amplitudes underline the role of metal composition in governing the finite-temperature dynamical response, which is an

important factor for the practical application of Janus MXenes under realistic operating conditions.

To assess the thermal stability of Y-based Janus MXenes ($YCrNO_2$, $YMoNO_2$, $YNbNO_2$, $YVNO_2$, $YScNO_2$, $YWNO_2$, and $YZrNO_2$), additional AIMD simulations at 300 K were performed (Fig. S5 and Fig. S6). All structures exhibit pronounced temperature (>100 K) and energy (up to ∼2.0 eV) fluctuations over 5 ps, indicating severe thermal and structural instability. Among them, $YNbNO_2$ shows the strongest instability, while $YCrNO_2$ displays comparatively reduced, though still insufficient, stability.

Table S4 Lattice parameters (a (Å)), adsorption energy (E_{ads} (eV)), and Gibbs free energy (ΔG_{H^*} (eV)) of the studied J-MXene and Y_2NO_2 MXene

Material	a (Å)	E_{ads} (eV)	ΔG_{H^*} (eV)
Y_2NO_2	3.53	-1.12	-1.356
$YScNO_2$	3.43	-0.73	-0.971
$YTiNO_2$	3.27	-0.58	-0.819
$YVNO_2$	3.24	-0.88	-1.119
$YCrNO_2$	3.26	-0.73	-0.971
$YZrNO_2$	3.41	0.55	0.315
$YNbNO_2$	3.32	0.44	0.205
$YMoNO_2$	3.35	-0.23	-0.466
$YHfNO_2$	3.37	0.64	0.396
$YTaNO_2$	3.32	0.24	-0.001
$YWNO_2$	3.35	0.44	0.204

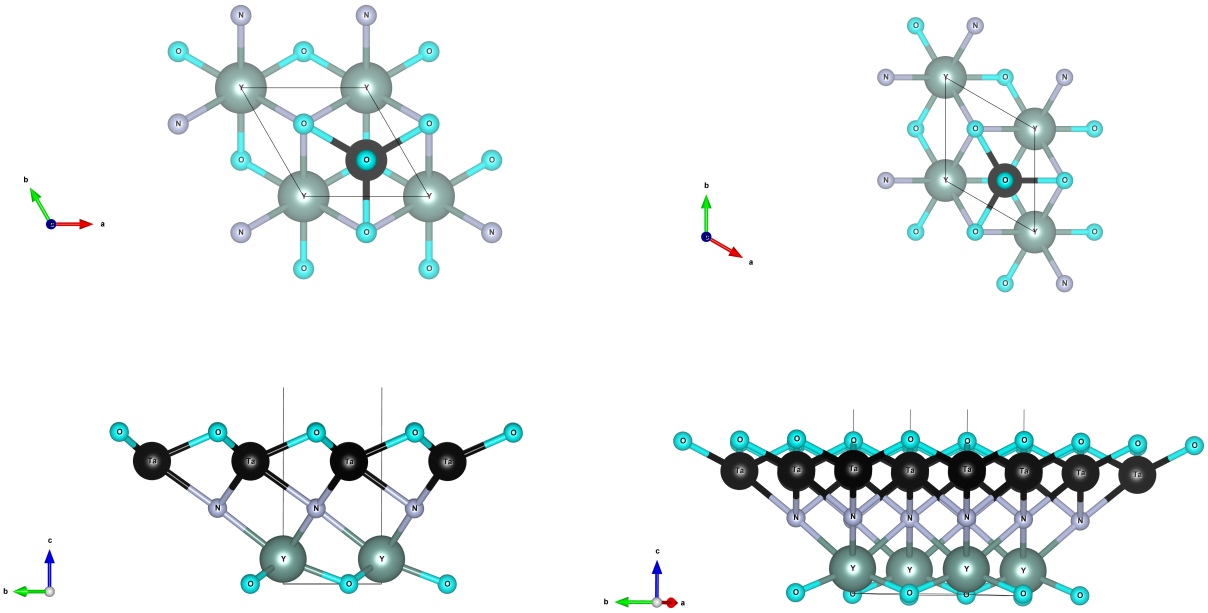

Figure S1 Top, side, and perspective views of the Janus ABC_{HMX} configuration of Y–M–N–O_2 MXenes. The structure exhibits an intrinsic out-of-plane asymmetry induced by the distinct chemical terminations on the two surfaces. Black spheres denote the transition metal atom M in the Y–M–N–O_2 framework, where M = Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. The different views highlight the atomic stacking sequence, surface terminations, and the broken mirror symmetry characteristic of Janus MXenes.

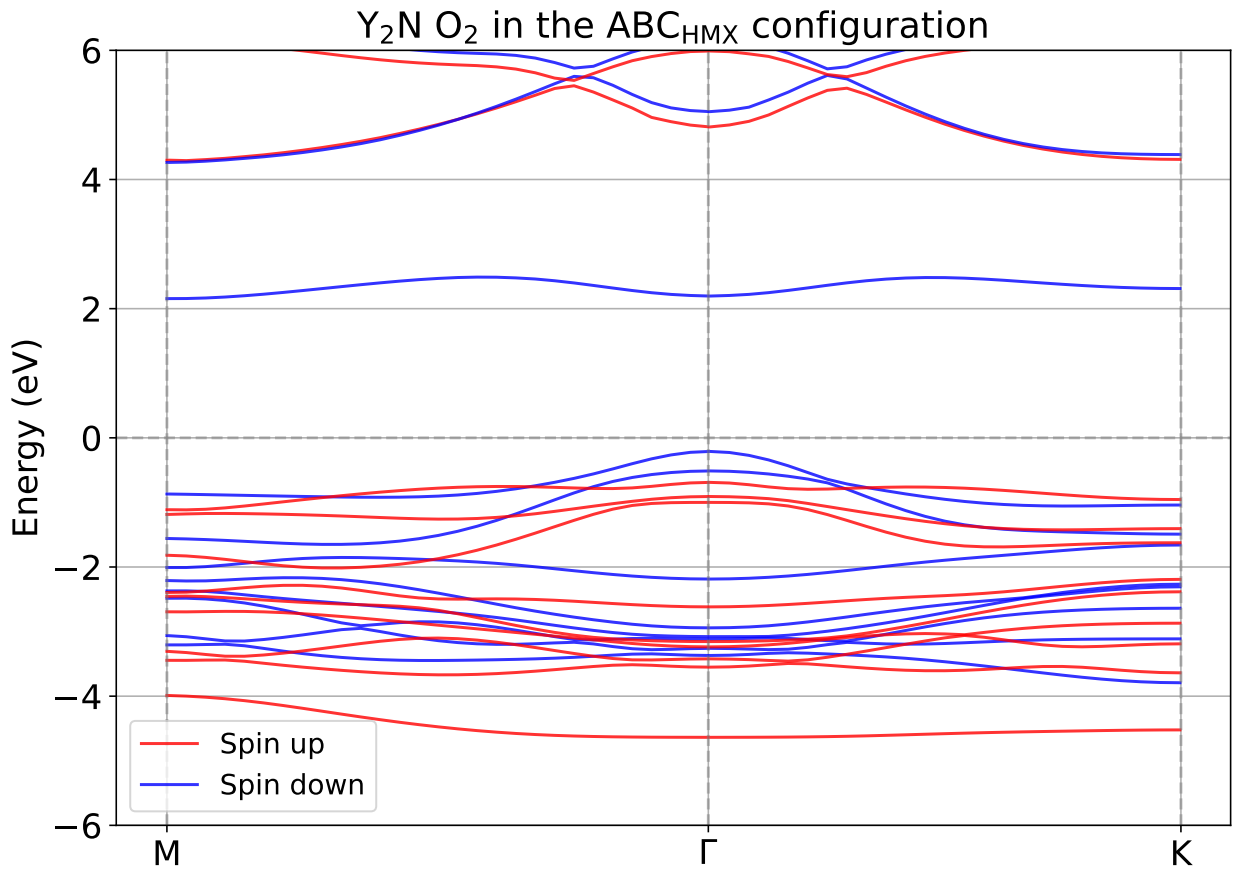

Figure S2 (Color online) Spin-polarized electronic band structure of Y_2N O2 in the ABC_{HMX} configuration at HSE level. The red and blue lines correspond respectively to the spin-up and spin-down channels. The Fermi level is set to zero. The band structure is plotted along the high-symmetry path M–Γ–K of the Brillouin zone, with the corresponding k-points indicated by vertical dashed lines.

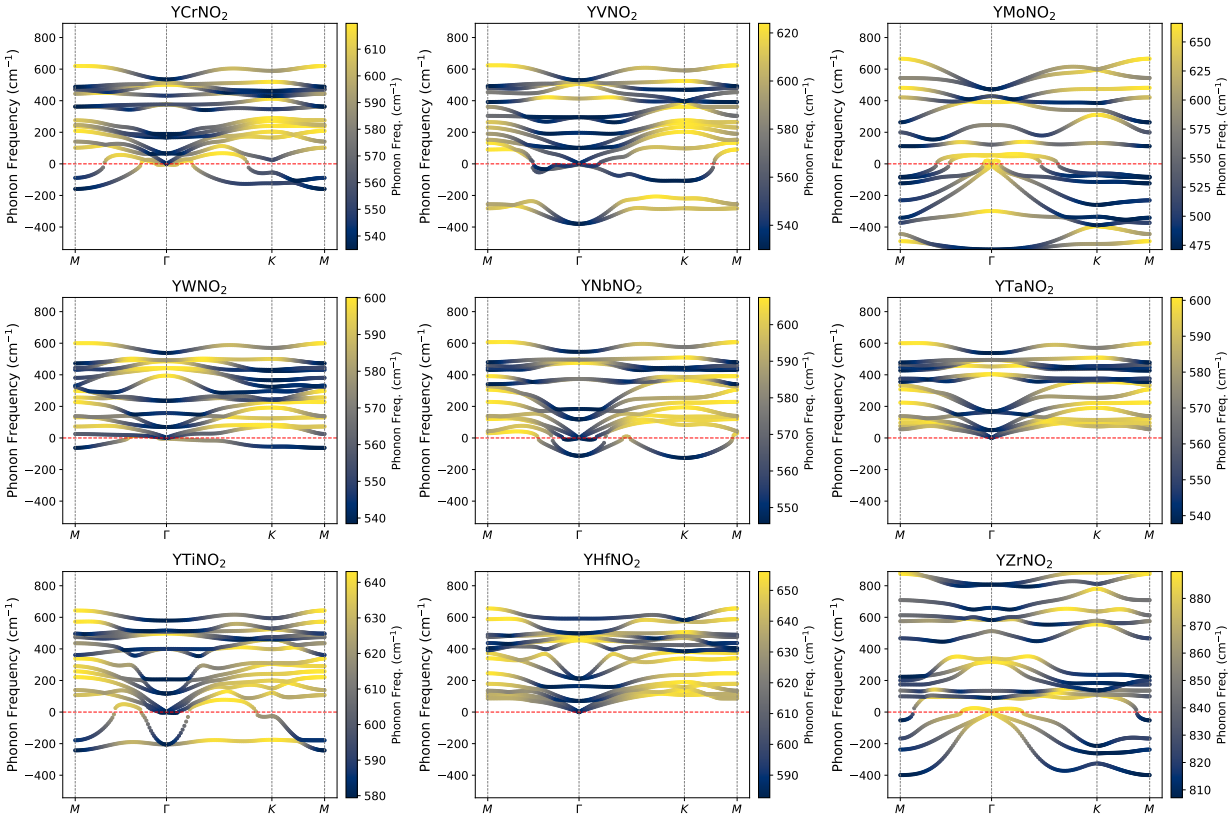

Figure S3 (Color online) Phonon dispersion plot of the studied Janus MXene and Y_2NO_2 MX

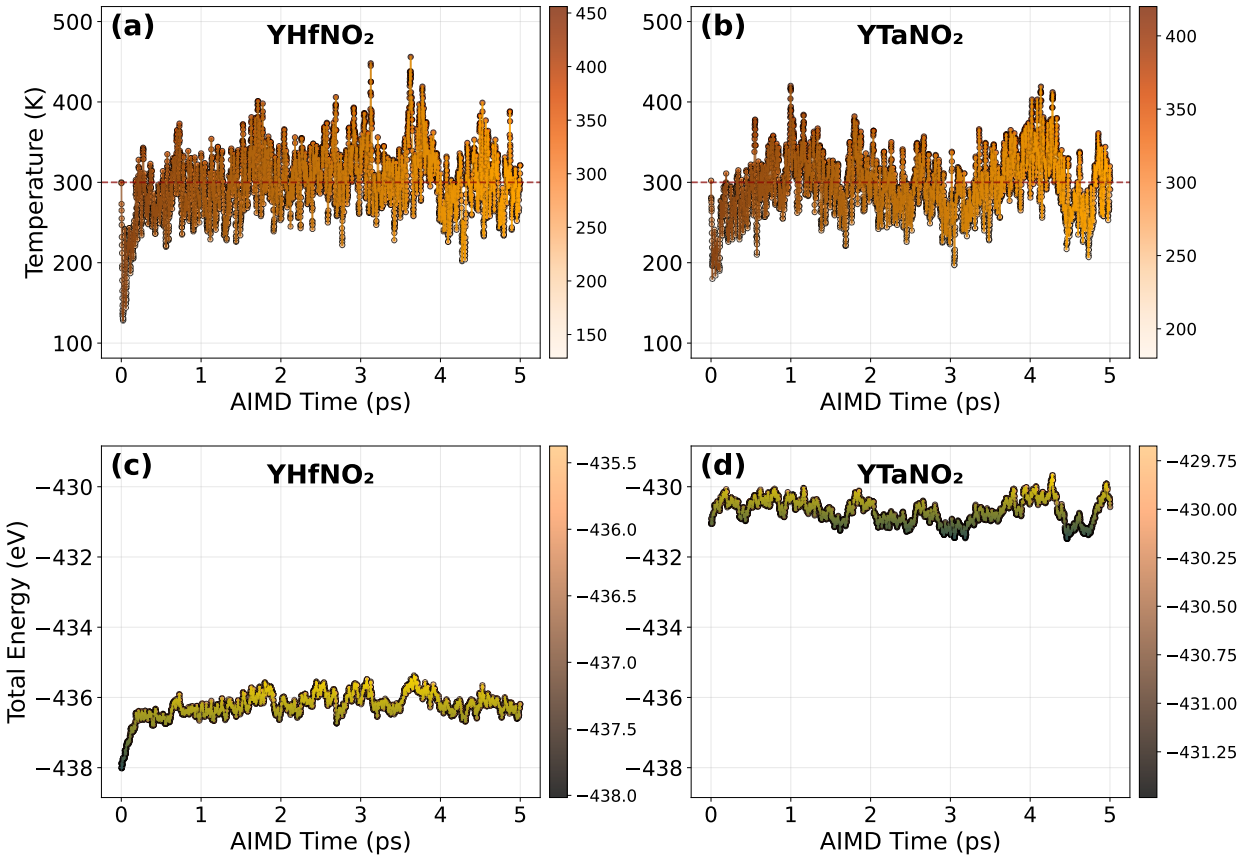

Figure S4 Ab initio molecular dynamics (AIMD) simulations performed for the Janus MXenes $YHfNO_2$ and $YTaNO_2$ to assess their thermal stability. Panels (a) and (b) show the time evolution of the temperature during the AIMD trajectories for $YHfNO_2$ and $YTaNO_2$, respectively, indicating that the target temperature is well maintained throughout the simulation. Panels (c) and (d) display the corresponding total energy fluctuations as a function of simulation time. Both systems exhibit bounded energy oscillations without any abrupt drift, suggesting the absence of structural degradation or phase transition within the simulated time scale. Despite the relatively regular oscillatory behavior observed for $YHfNO_2$, noticeable energy fluctuations are still present, reflecting its sensitivity to thermal effects at finite temperature.

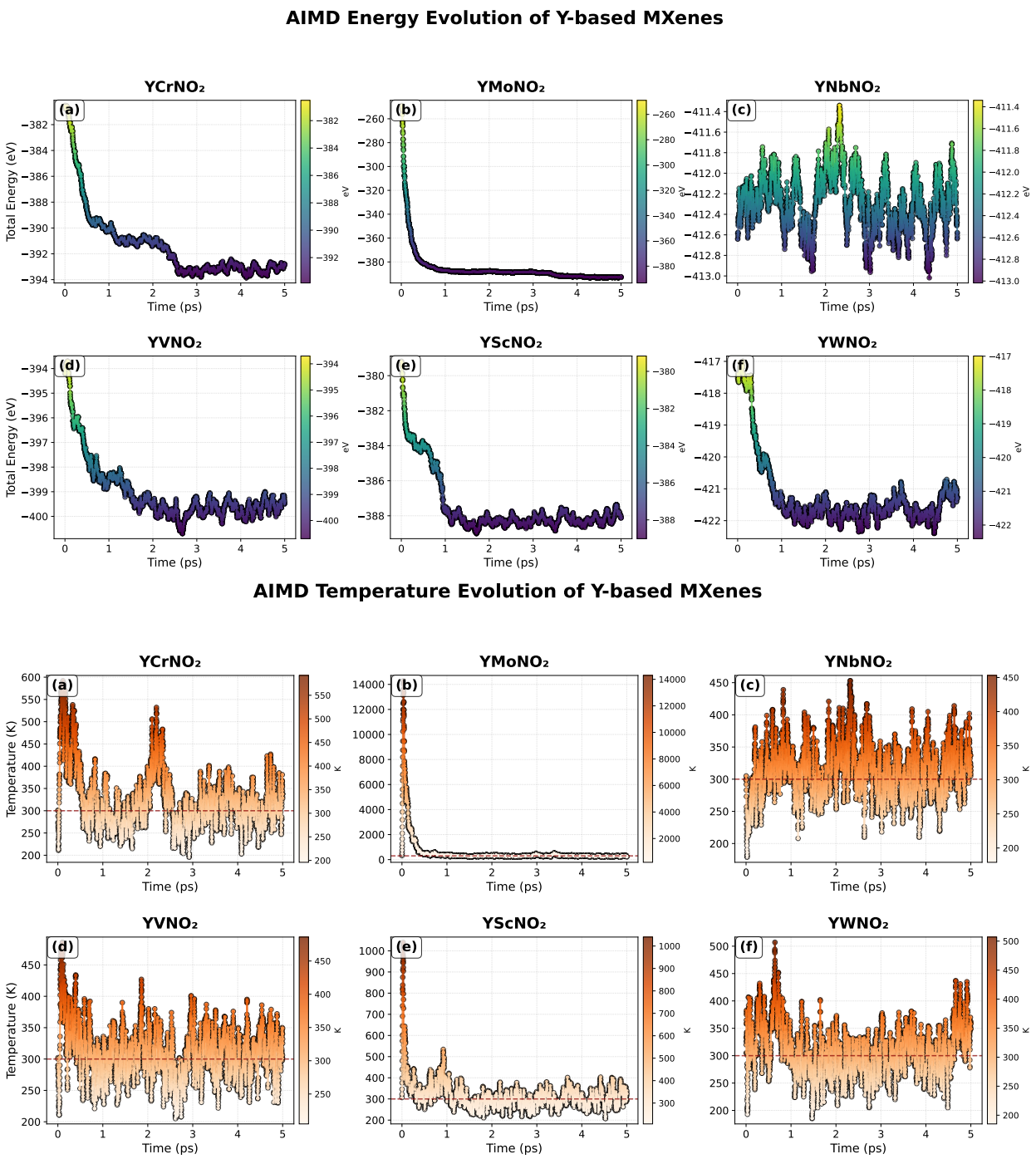

Figure S5 Time evolution of the total energy and temperature obtained from *ab initio* molecular dynamics (AIMD) simulations at 300 K for Janus Y-based MXenes: $YCrNO_2$, $YMoNO_2$, $YNbNO_2$, $YVNO_2$, $YScNO_2$, and $YWNO_2$. Pronounced energy drifts and large temperature fluctuations, frequently exceeding 100 K and in some cases reaching extreme values, indicate poor thermal stability. Among the investigated systems, $YNbNO_2$ exhibits the most severe instability, whereas $YCrNO_2$ shows comparatively reduced, yet still insufficient, stability, highlighting the intrinsic thermodynamic instability of NO_2-terminated Y-based Janus MXenes at room temperature.

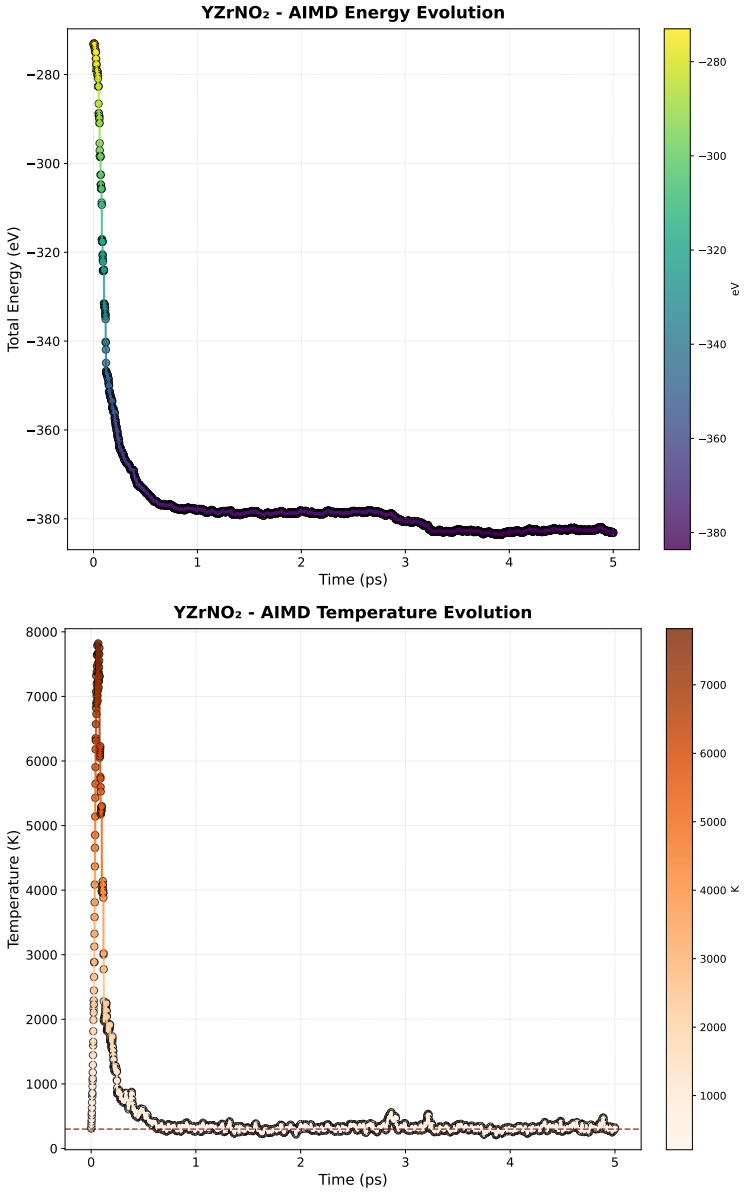

Figure S6 Time evolution of the total energy and temperature obtained from *ab initio* molecular dynamics (AIMD) simulations at 300 K for Janus Y-based MXenes: $YZrNO_2$

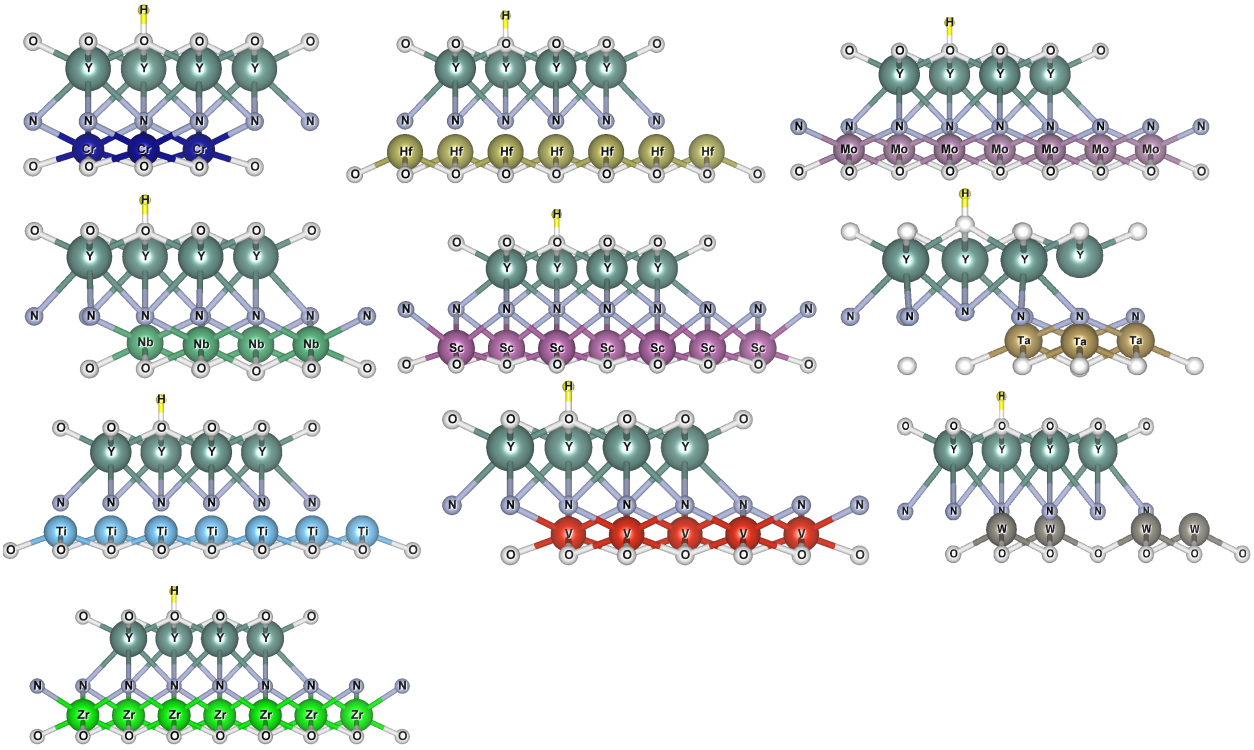

Figure S7 (Color online) Relaxed atomic configurations of hydrogen adsorption on layered $YMNO_2$ Janus MXenes for a broad range of transition-metal constituents (M = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W). For each composition, the most stable H adsorption geometry is obtained after full structural relaxation within DFT.

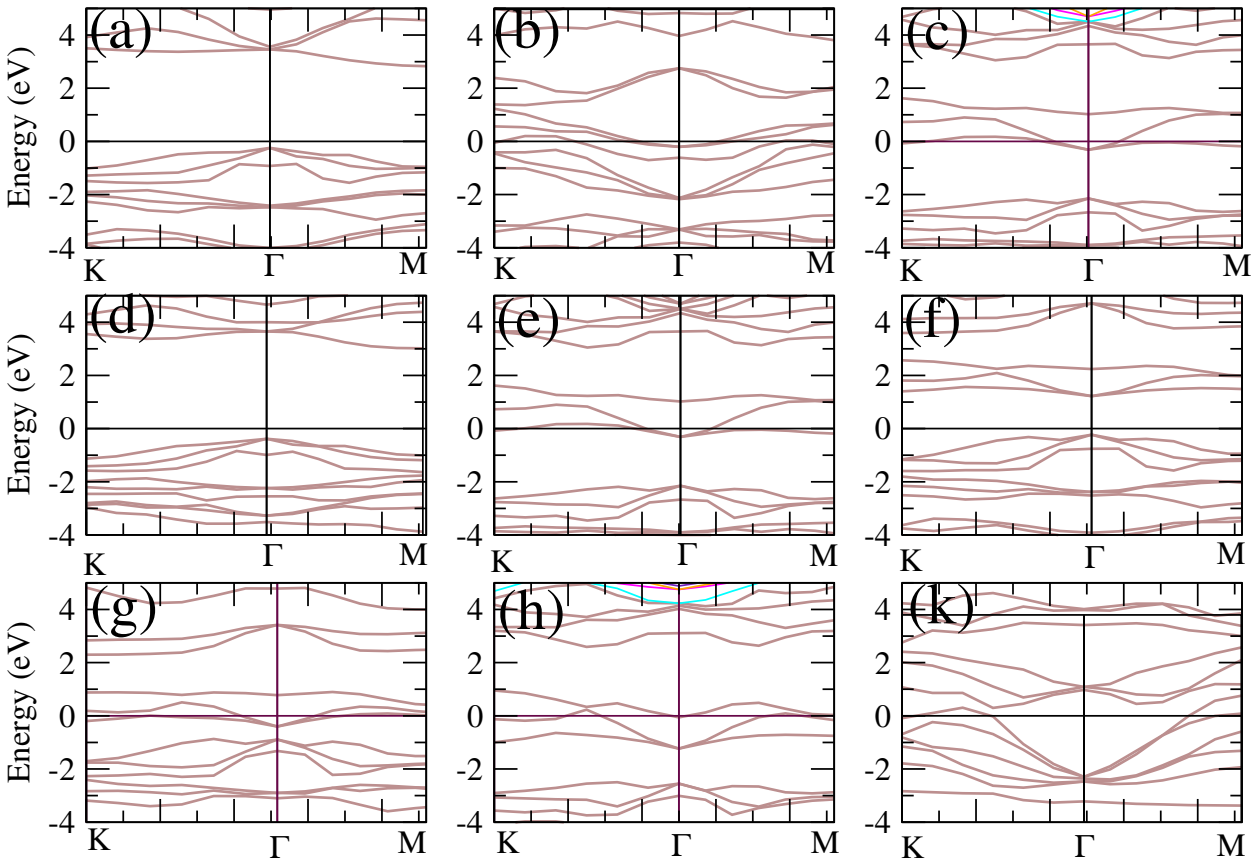

Figure S8 (Color online) band structure of (a) $YHfNO_2$, (b) $YMoNO_2$, (c) $YNbNO_2$, (d) $YScNO_2$, (e) $YTaNO_2$, (f) $YTiNO_2$, (g) $YVNO_2$, (h) $YWNO_2$, (k) $YZrNO_2$ Janus MXenes.

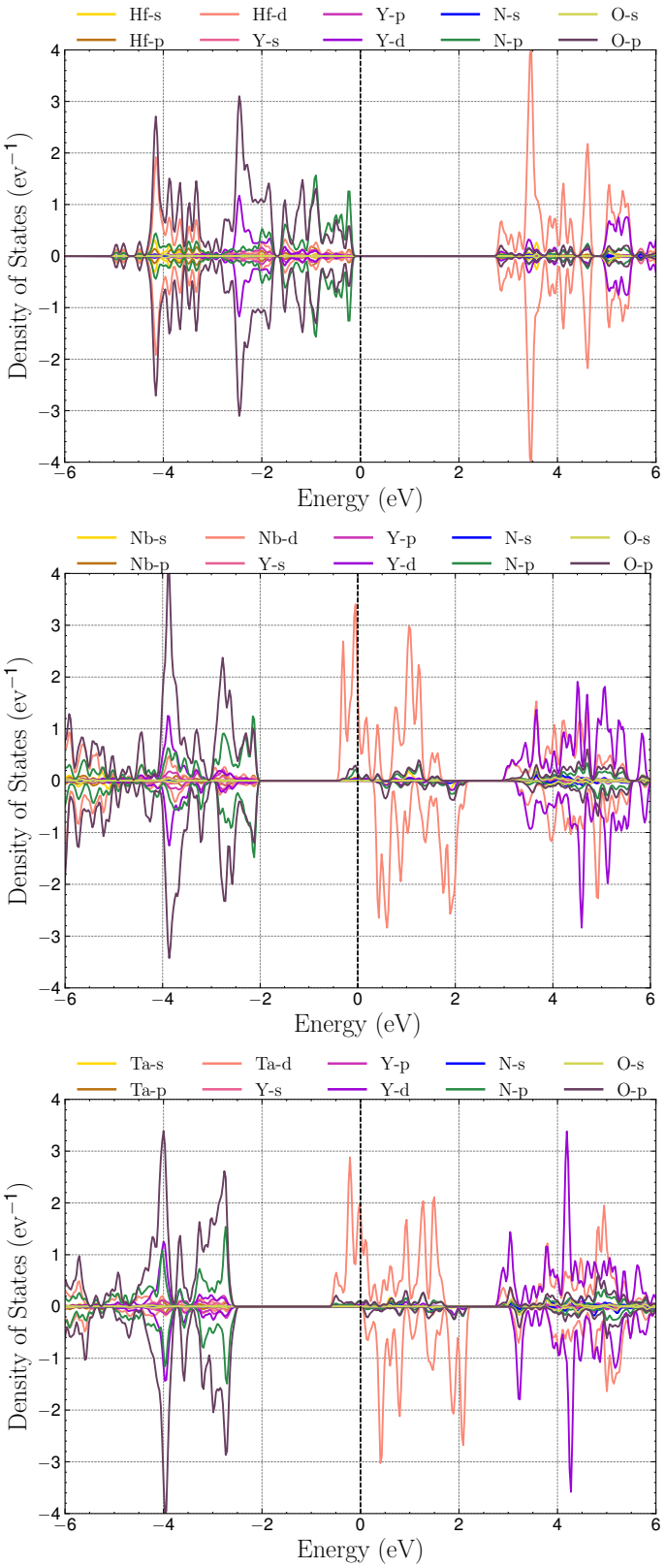

Figure S9 Partial densities of state of the (top): $YHfNO_2$, (middle): $YNbNO_2$ and (bottom):$YTaNO_2$

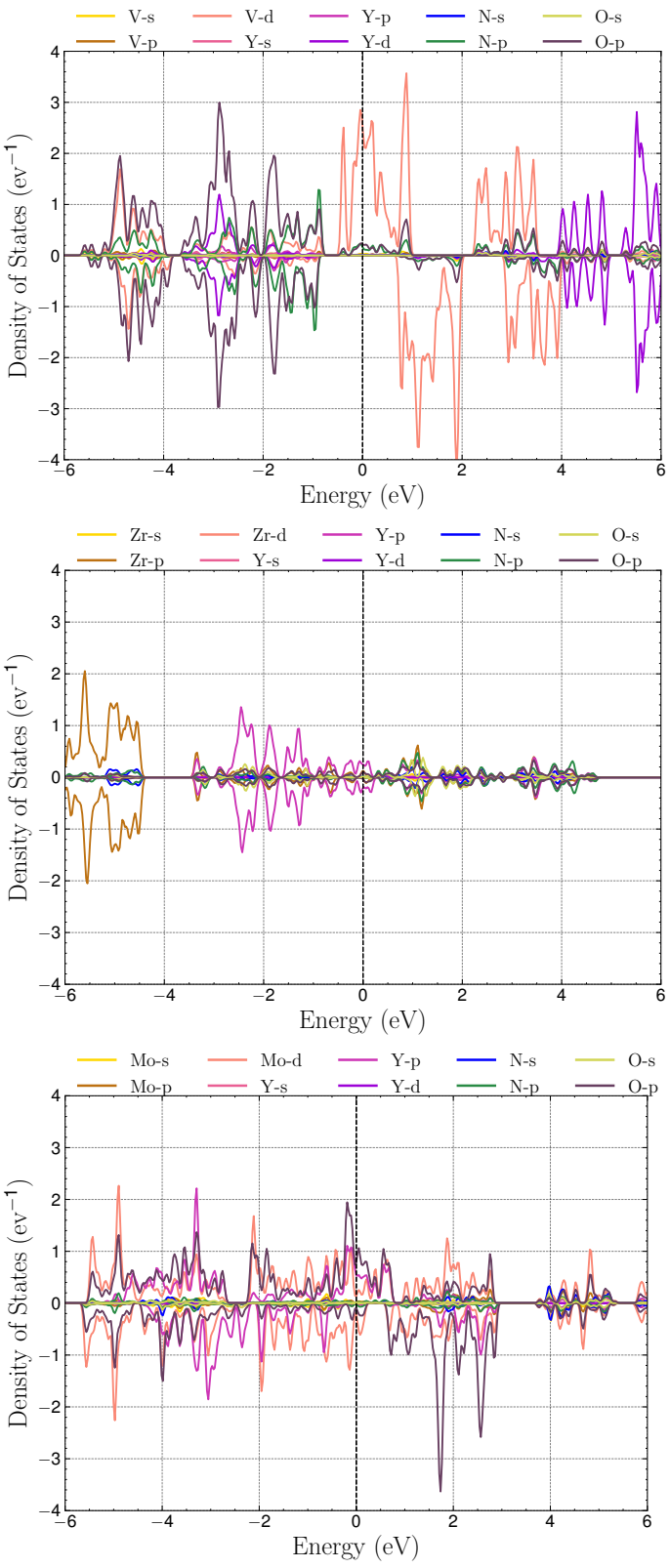

Figure S10 Partial densities of state of the (top): $YVNO_2$, (middle): $YZrNO_2$ and (bottom):$YMoNO_2$

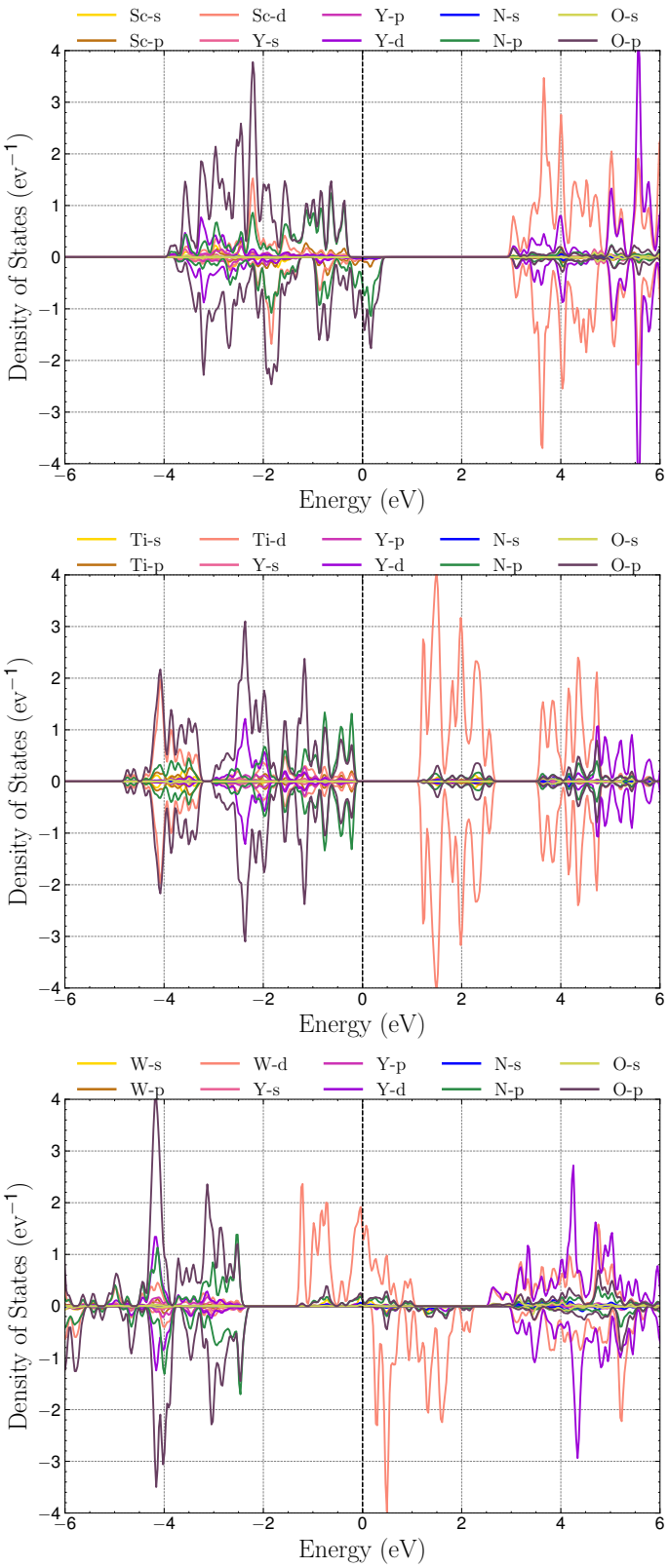

Figure S11 Partial densities of state of the (top): $YScNO_2$, (middle): $YTiNO_2$ and (bottom):$YWNO_2$

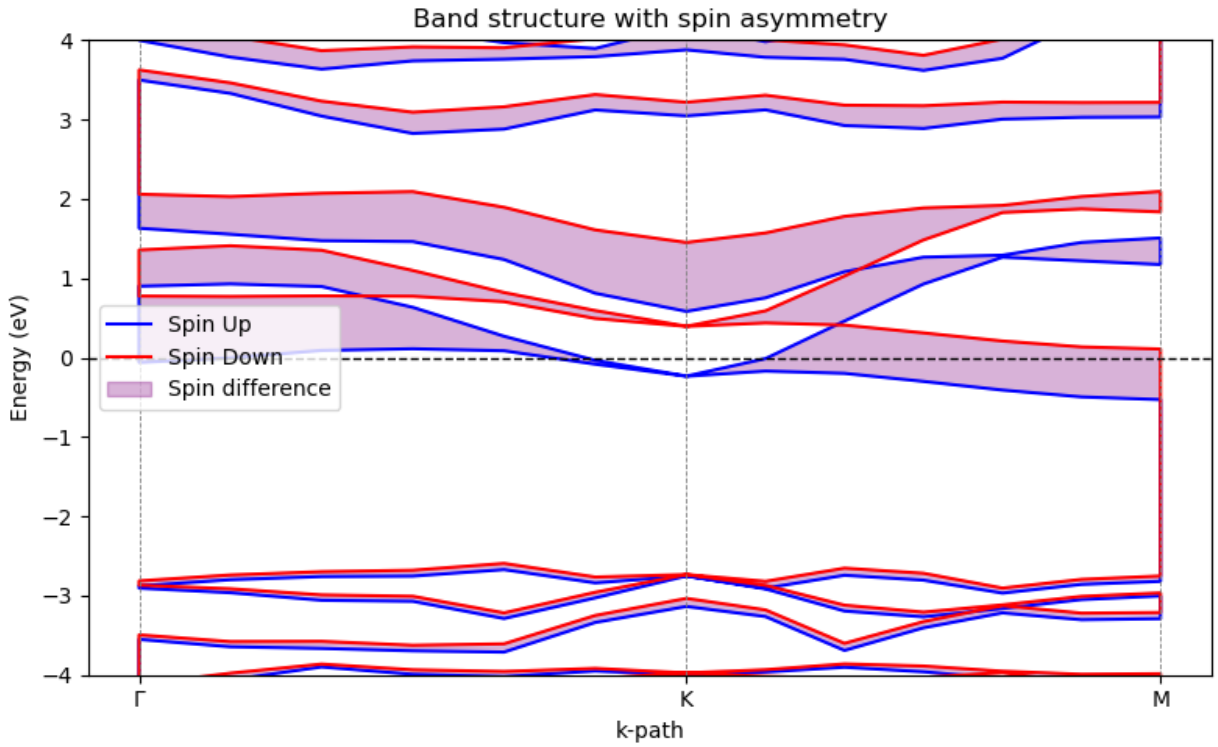

Figure S12 (Color online) Spin polarized band structure of the $YTaNO_2$ janus MXene, the difference between the spin up and down channels is highlighted with the mauve color