Exploring the Photoactive Properties of MXenes for Water Splitting

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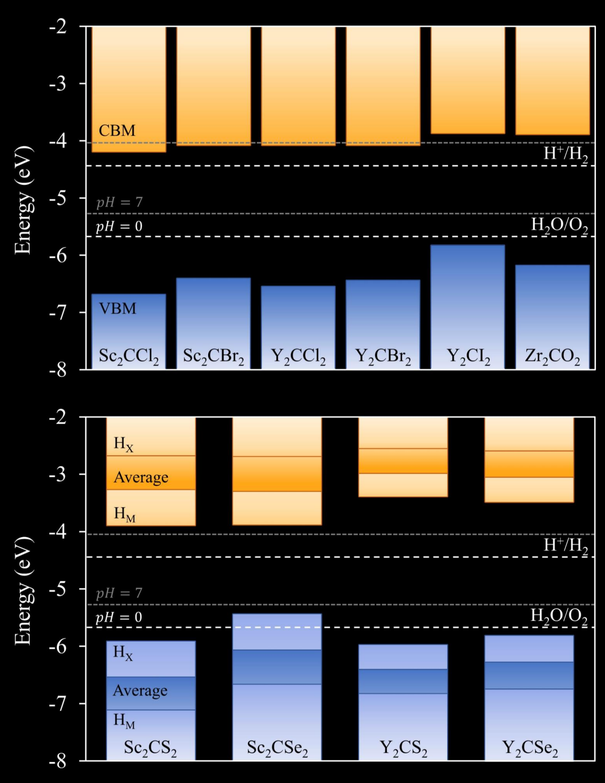
General Properties:

- An effective photocatalyst needs good band alignment, efficient charge separation, minimal VBM/CBM overlap, anisotropic carrier mobilities, strong visible light absorption, and high STH efficiency.
- Cohesive energy, phonons → energetical and dynamical stability.

MXene	E_{coh} (eV/at.)	E_g^{PBE0} (eV)	E_{opt} (eV)	Overlap (%)	η_{STH} (%)
Zr_2CO_2	-7.68	2.26	2.87	27.9	2.5
Sc_2CS_2	-5.52	3.23	3.34	35.2	0.9
Y_2CS_2	-5.52	3.42	2.93	38.5	2.7
Sc_2CSe_2	-5.16	2.75	3.15	31.9	1.4
Y_2CSe_2	-5.17	3.21	2.99	34.5	2.3
Sc_2CCl_2	-5.41	2.48	2.30	26.2	11.0
Y_2CCl_2	-5.42	2.44	1.89	31.7	21.3
Sc_2CBr_2	-5.09	2.31	2.31	27.1	10.9
Y_2CBr_2	-5.13	2.36	1.85	30.7	22.6
Y_2CI_2	-4.77	1.94	1.79	25.2	12.2

Band Alignment

- *pH* = 0: ✓ band alignment for all cases, excepting Sc_2CSe_2 (on H_X surface).
- *pH* = 7: Some halide-terminated MXenes become unable to photocatalyzed HER.
- H_{MX}: Janus → intrinsic $\vec{E} \rightarrow e^-/h^+$ separation.



MXenes[1] $(M_{n+1}X_nT_x)$

M = Transition Metal (Groups 3 – 6)
X = C or N n = 1 – 4
T = Termination (Groups 16 – 17)

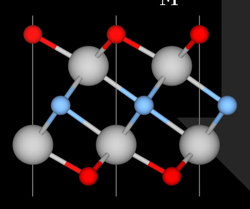
Promising candidates for photocatalysing the water splitting process and produce clean H_2.[2,3]

Objective: Explore the photoactive effectiveness of MXenes in the water splitting process, through different photocatalytic properties.

10 promising MXenes studied

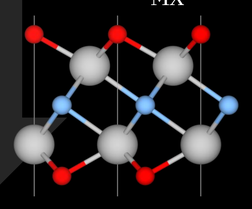
Sc_2CT_2, Y_2CT_2 (T = Cl, Br), Y_2CI_2, Zr_2CO_2

ABC H_M



Sc_2CT_2, Y_2CT_2 (T = S, Se)

ABC H_{MX}

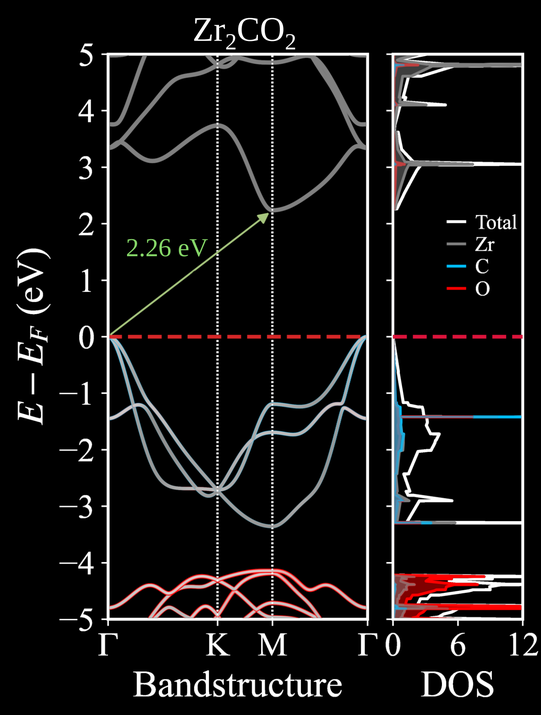


Methods: DFT with PBE0 hybrid functional for electronic structure and GW-BSE for optic properties.

MXenes Approved

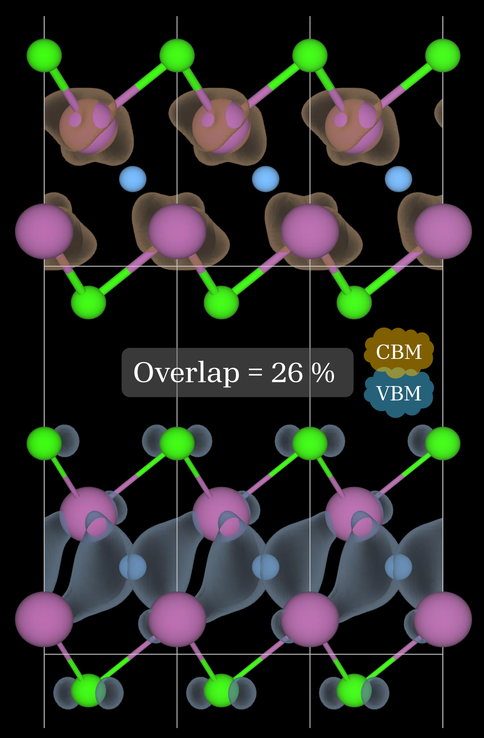
Electronic Structure:

- Semiconductors $E_g \approx$ visible range.
- H_{MX} MXene structures: $E_g \approx$ UV.
- Indirect Γ→M (H_M) or Γ→K (H_{MX}) transitions.
- VB → C and M atoms, and T at lower energies.
- CB → *d* orbitals of M.



Charge Density:

- Overlap(VBM, CBM) ≈ 25 – 38 %.
- H_M: VBM → *p*(C) orbitals, CBM → M layers.
- H_{MX}: VBM → H_X face, CBM → M-C layers.
  ↳ asymmetry in charge distribution.



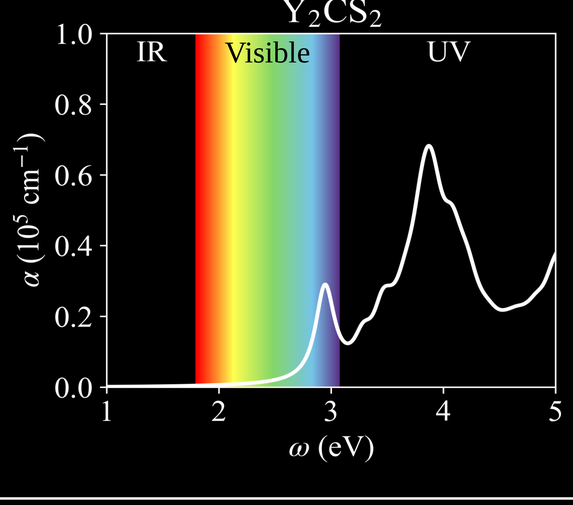
Optical Absorption

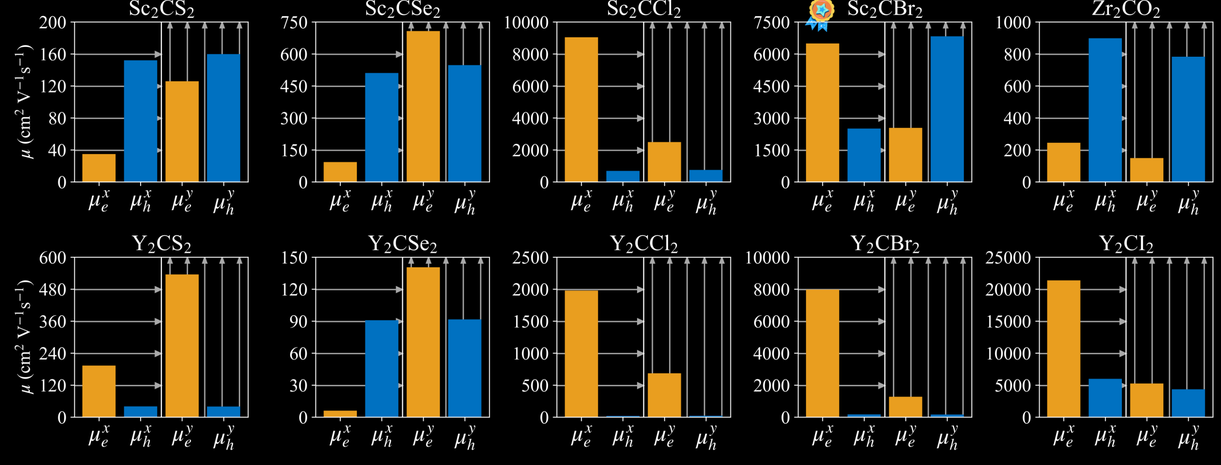
- H_M: Good optical absorption in visible range.
- H_{MX}: Optical absorption shifted to UV.
- E_{opt}(Y) < E_{opt}(Sc).
- BSE → Exciton → $E_b \approx 0.3 – 0.7$ eV.
- STH efficiency:
  halide (11–23%) > chalcogen (1–3%).

Charge Carrier Mobility:

- Along x (*zigzag* ⟋⟍⟋) and y (*armchair* ⟍⟋⟍).
- Anisotropic electron carrier mobility, $\mu_e^x \neq \mu_e^y$.
- H_{MX}: $\mu_e^x < \mu_e^y$, H_M: $\mu_e^x > \mu_e^y$.
- Isotropic hole carrier mobility, $\mu_h^x \approx \mu_h^y$.

↳ ! Except for Sc_2CBr_2 → Asymmetric anisotropy both in e and h (charge separation ✓)





CONCLUSIONS ✓

The photoactive potential of a group of 10 MXenes has been deeply explored using DFT calculations, showcasing robust stability, high charge carrier mobilities, strong visible light absorption, and promising solar-to-hydrogen efficiency. These features make them leading candidates for efficient water splitting photocatalysis, with H_M structures generally outperforming H_{MX} structures.

REFERENCES

[1] *Adv. Mater.* 2011, *23*, 4248–4253.
[2] *J. Mater. Chem. A*, 2023, *11*, 13754–13764 .
[3] *Energy Environ. Mater.*, 2024, *0*, e12774.

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