Exploring the Photoactive Properties of MXenes for Water Splitting

Diego Ontiveros, Francesc Viñes, Carme Sousa

Departament de Ciència de Materials i Química Física &
Institut de Química Teòrica i Computacional (IQTCUB),
Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028, Barcelona, Spain.

Universitat de Barcelona

Institut de Química Teòrica i Computacional
Universitat de Barcelona

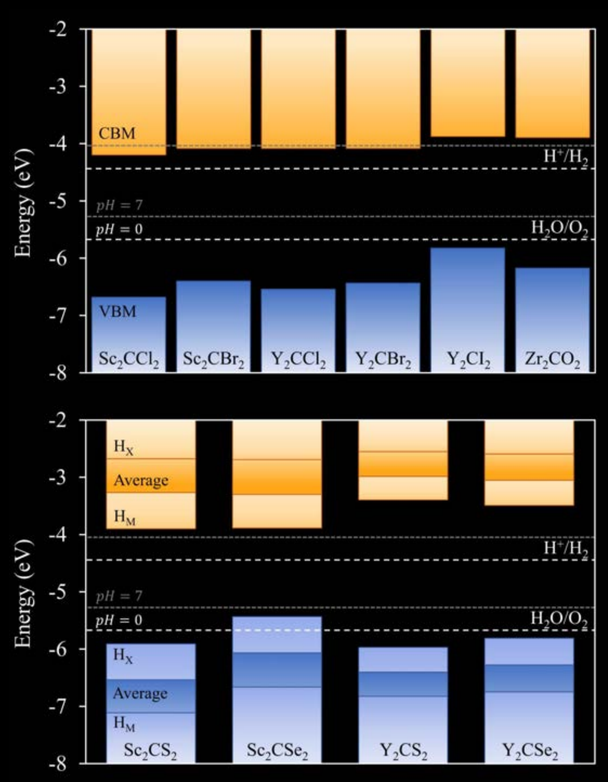
General Properties

- An effective photocatalyst needs good band alignment, efficient charge separation, minimal VBM/CBM overlap, anisotropic carrier mobilities, strong visible light absorption, and high solar-to-hydrogen (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 photocatalyze HER.
- H_{MX}: Janus → intrinsic $\vec{E} \rightarrow e^- - h^+$ separation.



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

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.[1,2]

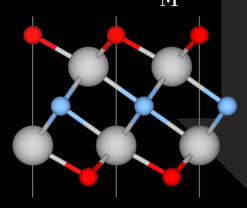
Objective: Explore the photoactive effectiveness of MXenes in the water splitting process, through different photocatalytic properties.

10 promising MXenes studied

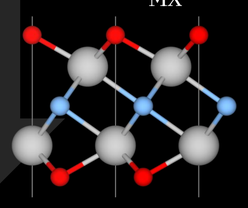
Sc_2CT_2, Y_2CT_2 (T = Cl, Br), Y_2CI_2, Zr_2CO_2

Sc_2CT_2, Y_2CT_2 (T = S, Se)

ABC H_M



ABC H_{MX}

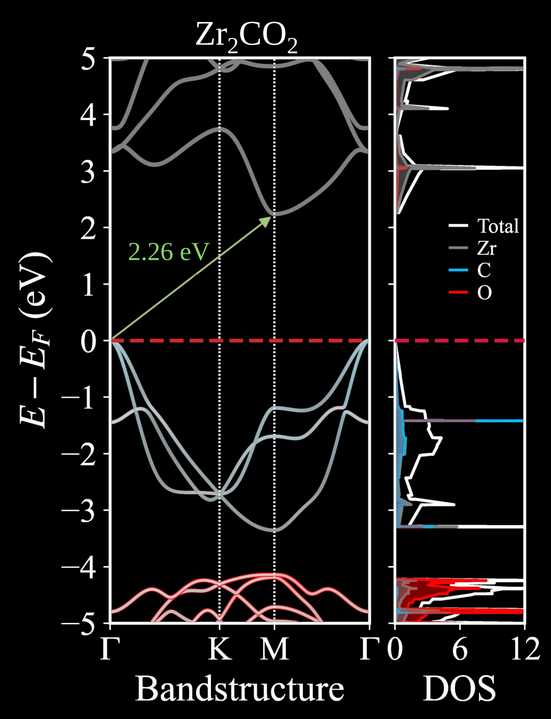


Methods: DFT with PBE0 hybrid functional for electronic structure and GW-BSE for optical properties.

MXenes Approved

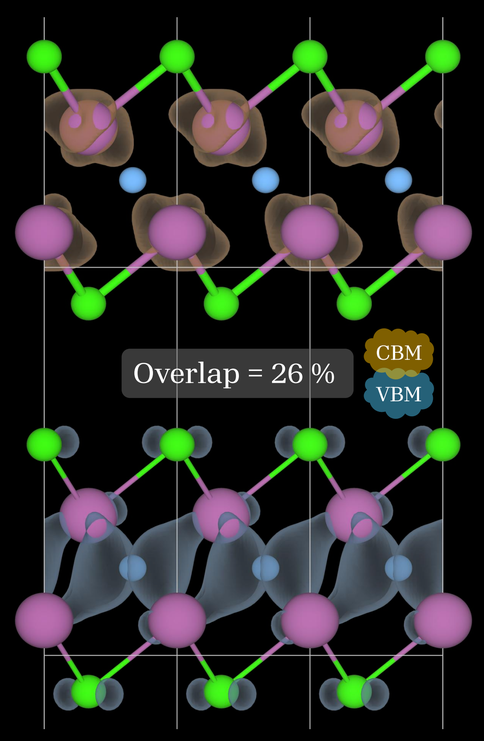
Electronic Structure

- Semiconductors E_g ≈ visible range.
- H_{MX} MXene structures: E_g ≈ 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.



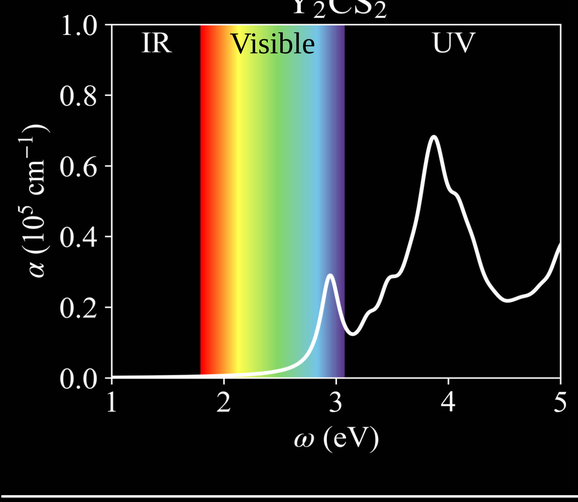
Charge Density

- 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

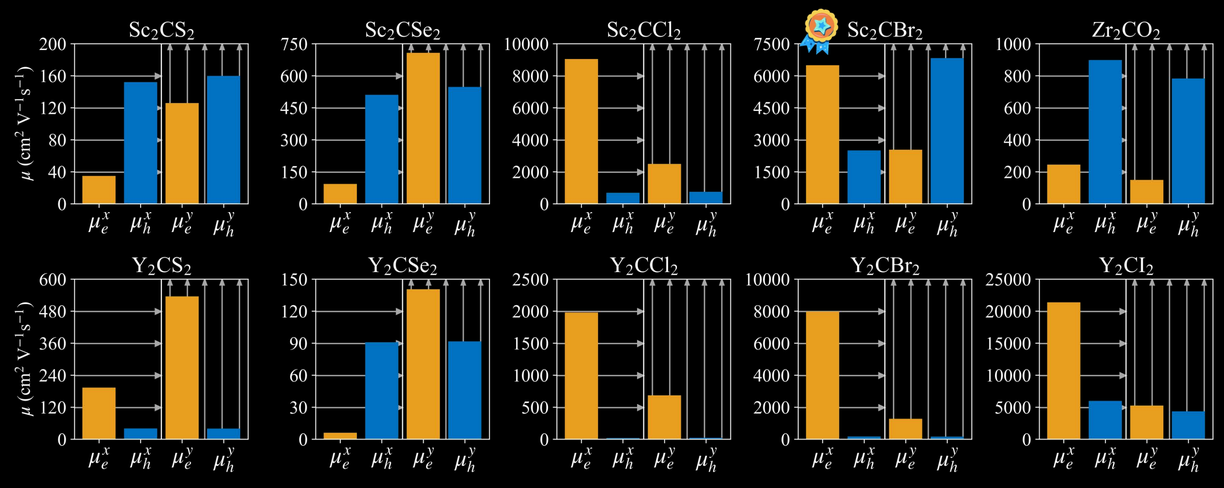
- H_M: Good optical absorption in visible range.
- H_{MX}: Optical absorption shifted to UV.
- E_{opt}(Y) < E_{opt}(Sc).
- BSE → Exciton → E_b ≈ 0.3 – 0.7 eV.
- STH efficiency:
  halide (11–23%) > chalcogen (1–3%).



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] D. Ontiveros, F. Viñes, C. Sousa, *J. Mater. Chem. A,* 2023, 11, 13754–13764.
[2] D. Ontiveros, S. Vela, F. Viñes, C. Sousa, *Energy Environ. Mater.*, 2024, 7, e12774.

diego.ontiveros@ub.edu

diegonti.github.io

Acknowledgments

PID2021-126076NB-I00
TED2021-129506B-C22

QHS-2023-2-0017
QHS-2023-3-0012

CEX2021-001202-M

Ac2216561

2021SGR00079