MXenes as Photocatalytic Materials for Water Splitting

UNIVERSITAT DE BARCELONA

Diego Ontiveros, Francesc Viñes, Carme Sousa

Institut de Química Teòrica i Computacional (IQTCUB),
Departament de Ciència de Materials i Química Física, Universitat de Barcelona.

Institut de Química Teòrica i Computacional
UNIVERSITAT DE BARCELONA

Global Warming | Environmental Pollution

Need for *green* fuels

Hydrogen (H_2)

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

M = Transition Metal (Groups III – VI)
X = C or N **n** = 1–3
T = Termination (*p*-block: O, F, OH, H, S, Cl)

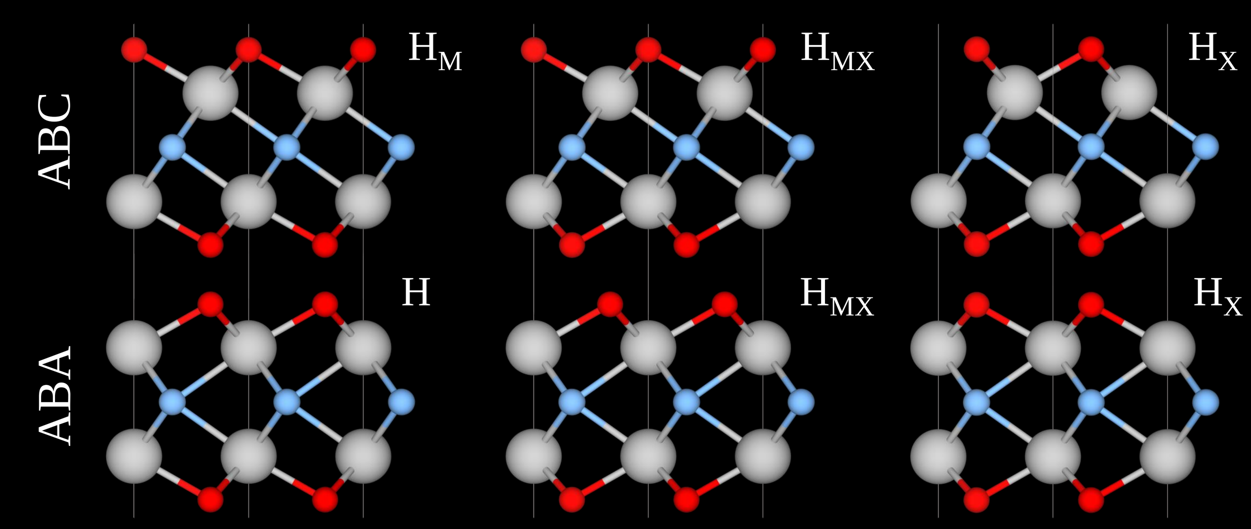
Semiconductors when adding a termination.[2]
Good candidates for photocatalysing the water splitting process and produce clean H_2.[3]

Sustainable source of H_2:
Water Splitting
$2\ H_2O \rightarrow 2\ H_2 + O_2$

Problem: Requires large amounts of energy

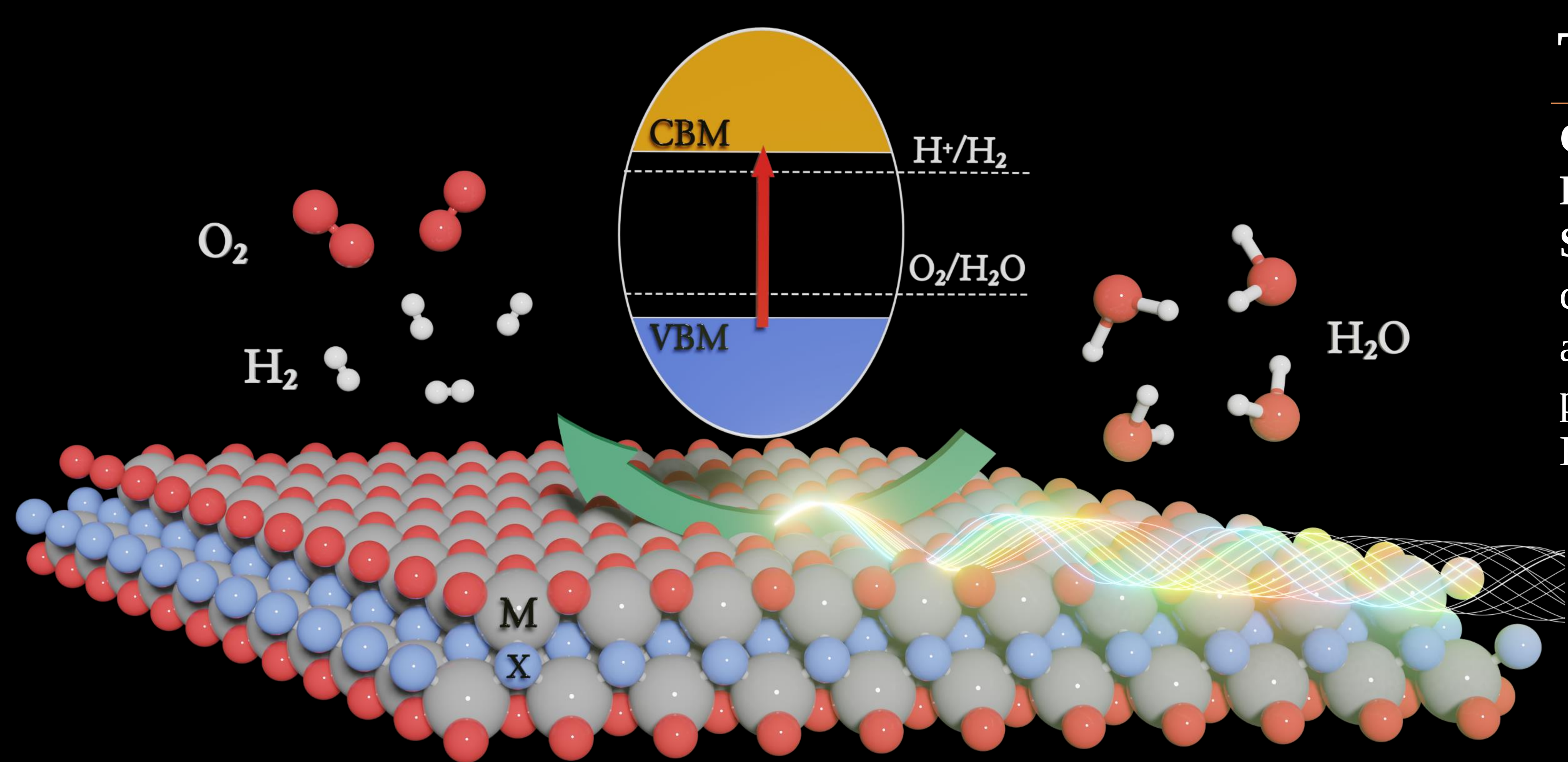
Solution: Sunlight as energy source

Photocatalysis



OBJECTIVES

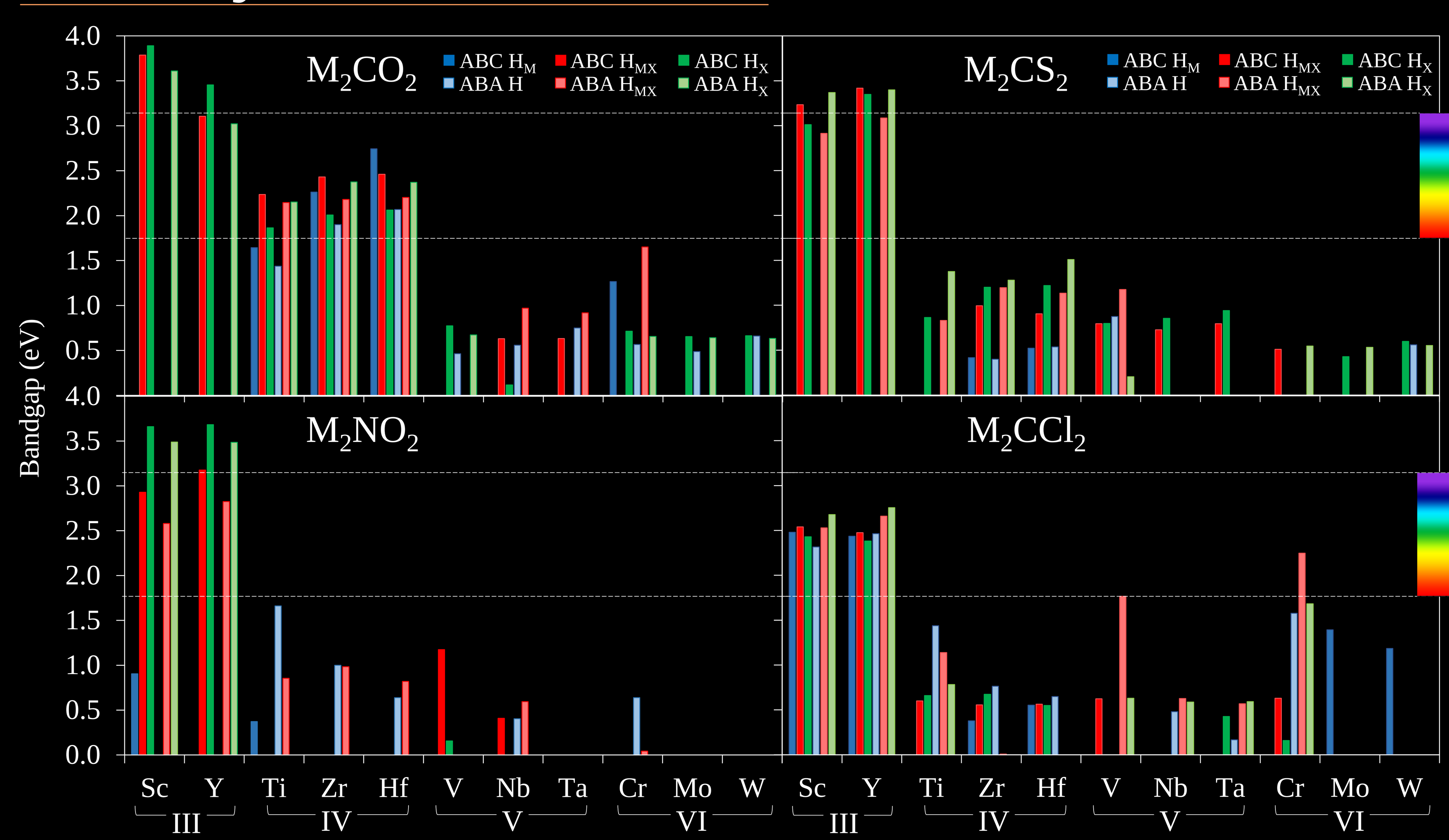
Modify and design the bandgap of MXenes by varying their composition (M, X, T), width (n), stacking and termination position, to find potential photoactive candidates for water splitting using solar light.



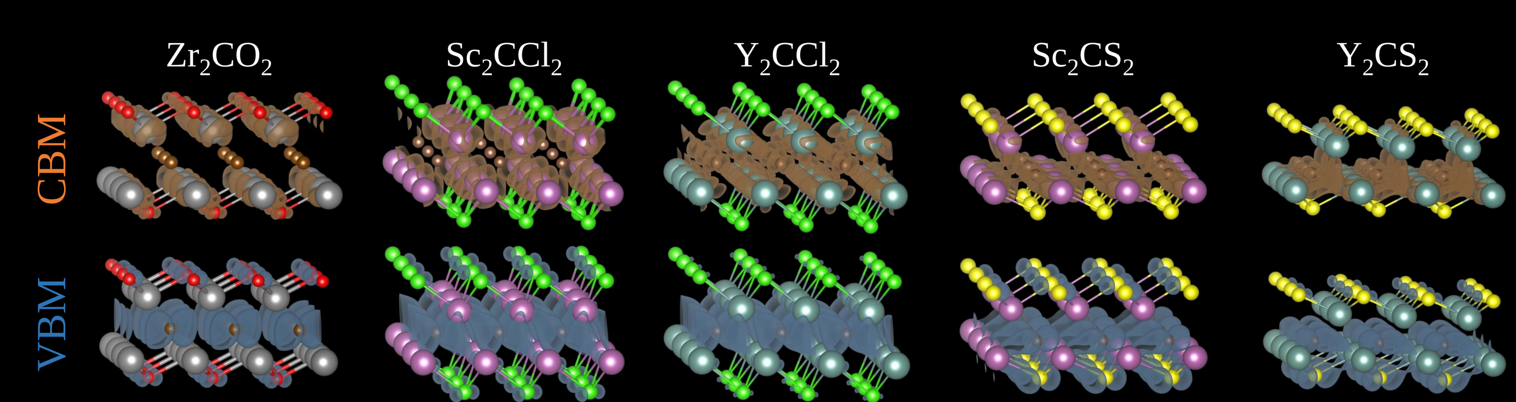
TOOLS

Computational Method: DFT
Functionals: PBE and PBE0
Structures: periodic slab models, considering two stackings (ABC and ABA) and three termination positions for each stacking (H_M/H, H_{MX} and H_X)

Density of States

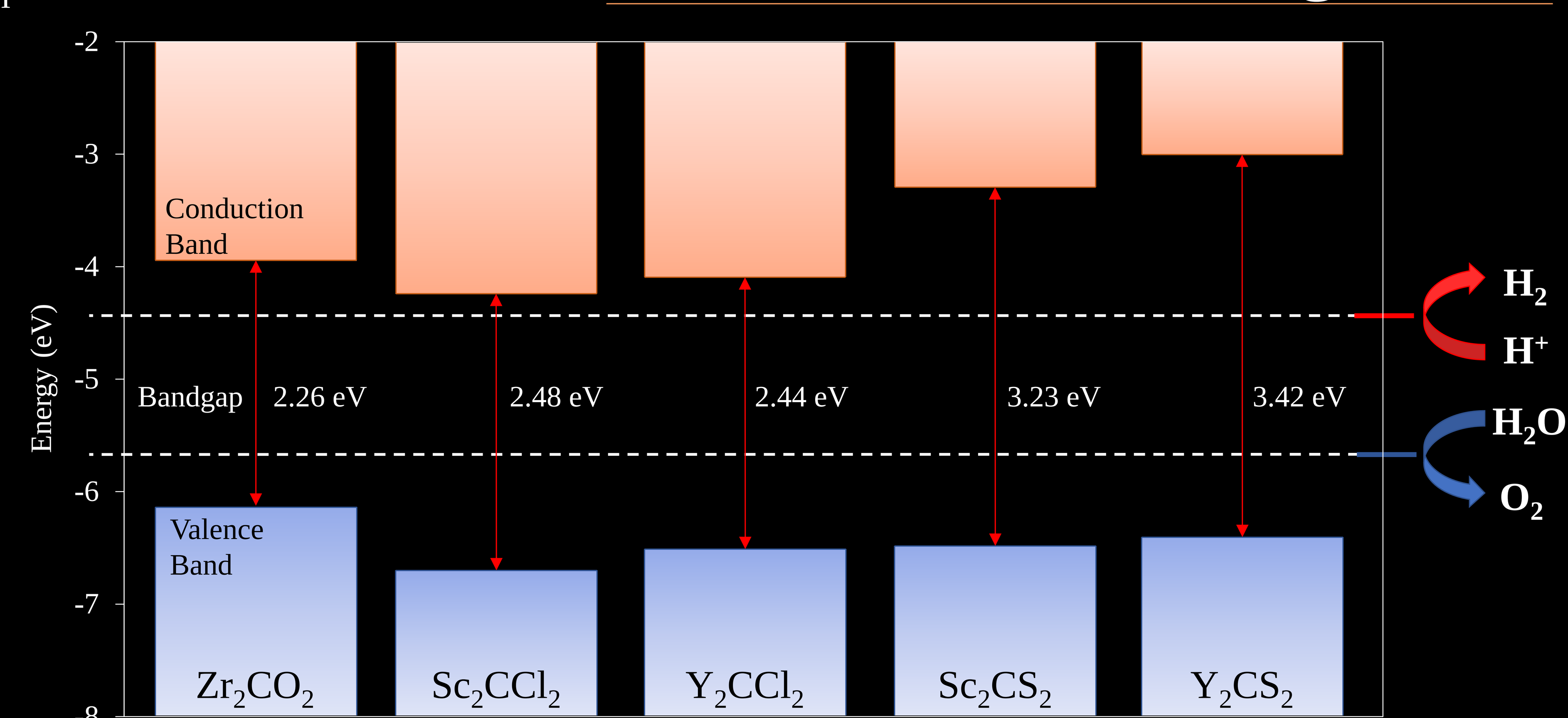


- 6 different structures for each terminated MXene are considered (2376 in total).
- Group III and IV MXenes with n = 1 → large bandgaps, in the visible region.
  → The most promising cases for being photoactive materials with sunlight.
- C-MXenes → more semiconducting cases and larger bandgaps than N-MXenes.
- Pristine MXenes → metallic properties (not photoactive).
- MXenes n = 2, 3 → Increasing the amount of "bulk" tends to make them metallic.



Band Alignment

- The band alignment with respect to the half-reaction potentials has been studied for the most promising photoactive cases ($E_g > 1.23$ eV).
- The ideal cases will be those that, in addition to having a suitable band alignment, are the most stable structure among the six considered.
- Several structures from Groups III and IV exhibit correct alignments.
- The cases of Zr_2CO_2, Sc_2CCl_2, Y_2CCl_2, Sc_2CS_2, and Y_2CS_2 fulfill these optimal conditions, which allows us to propose them as potential candidates for the photocatalytic water splitting.
- These systems exhibit an indirect bandgap and a significant charge density separation between the valence band maximum and conduction band minimum (VBM and CBM), promoting the separation of generated charges.



CONCLUSIONS

Based on DFT calculations, MXenes with n = 1, X = C, M = Groups III and IV, and T = O, S, Cl, especially Zr_2CO_2, Sc_2CCl_2, Y_2CCl_2, Sc_2CS_2, and Y_2CS_2, exhibit a visible range bandgap, optimal for solar light absorption, and band edges that exceed the half-reaction potentials of water splitting, suitable for photocatalysing the process and generating green H_2.

REFERENCES

[1] *Adv. Mater*. 2011, *23*, 4248–4253.
[2] *Adv. Funct. Mater*. 2013, *23*, 2185–2192.
[3] *J. Mater. Chem. A* 2016, *4*, 11446–11452.

diegonti.doc@gmail.com github.com/diegonti