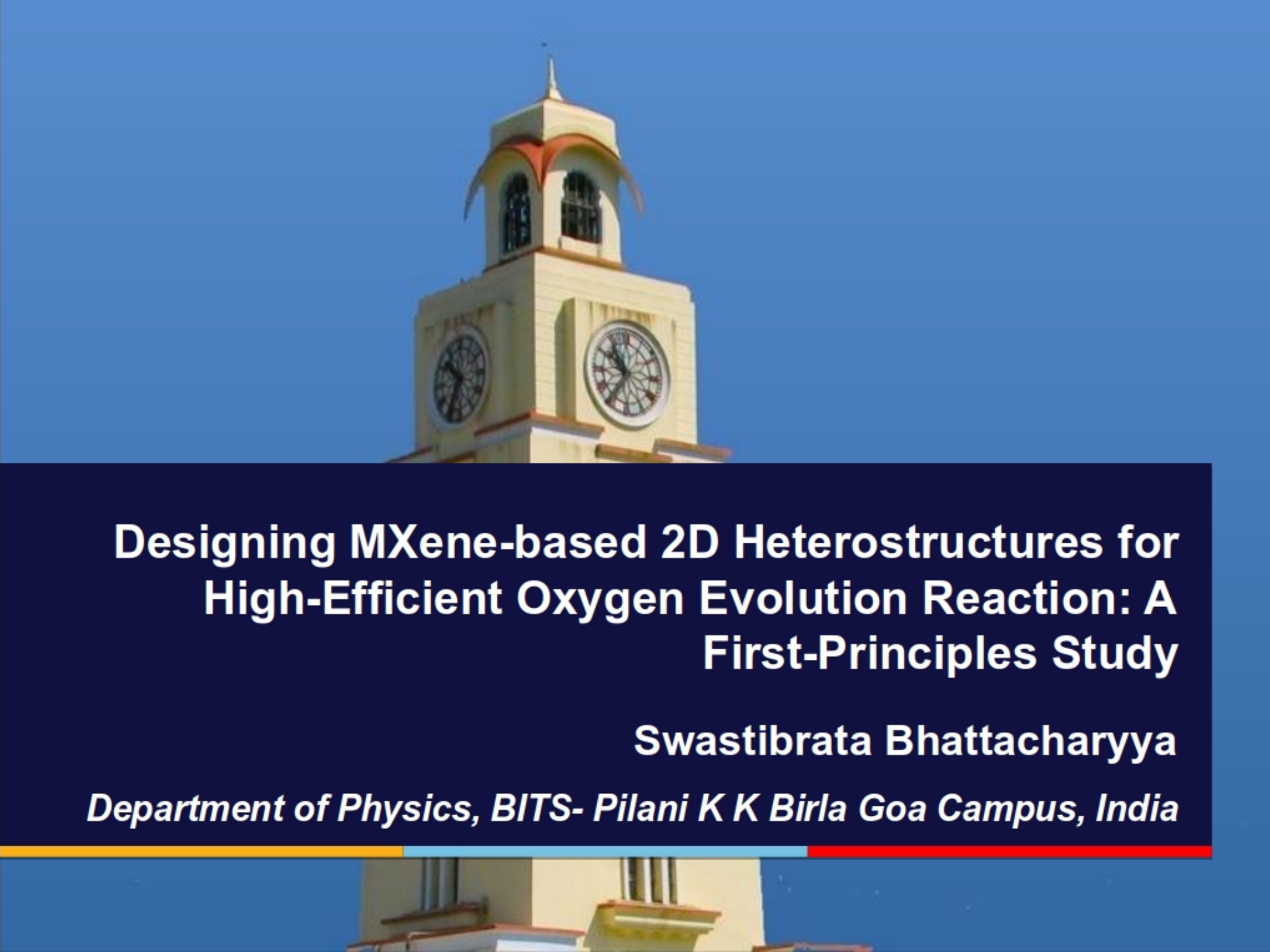


Designing MXene-based 2D Heterostructures for High-Efficient Oxygen Evolution Reaction: A First-Principles Study

Swastibrata Bhattacharyya

Department of Physics, BITS- Pilani K K Birla Goa Campus, India

Birla Institute of Technology & Science - Pilani

innovate achieve lead

- Established in 1964
- An Institute of Eminence
- Programs:
  BE, Msc(Hons), ME
  PhD

K. K. Birla Goa Campus

Established in 2004

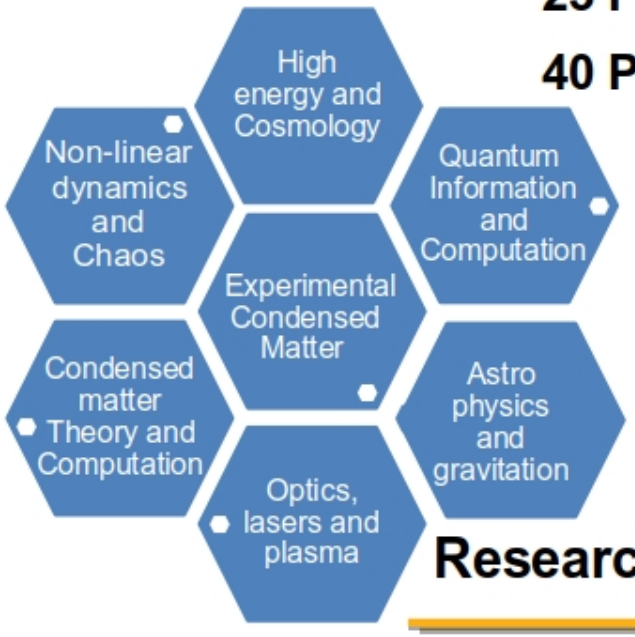
Department & Research Group

innovate achieve lead

Department of Physics

23 Faculties

40 PhD Scholars



Research areas

Research Group

Sarga P K
PhD Scholar

Sujit Satish Chaudhari
PhD Scholar

Zayid Ahmed
PhD Scholar

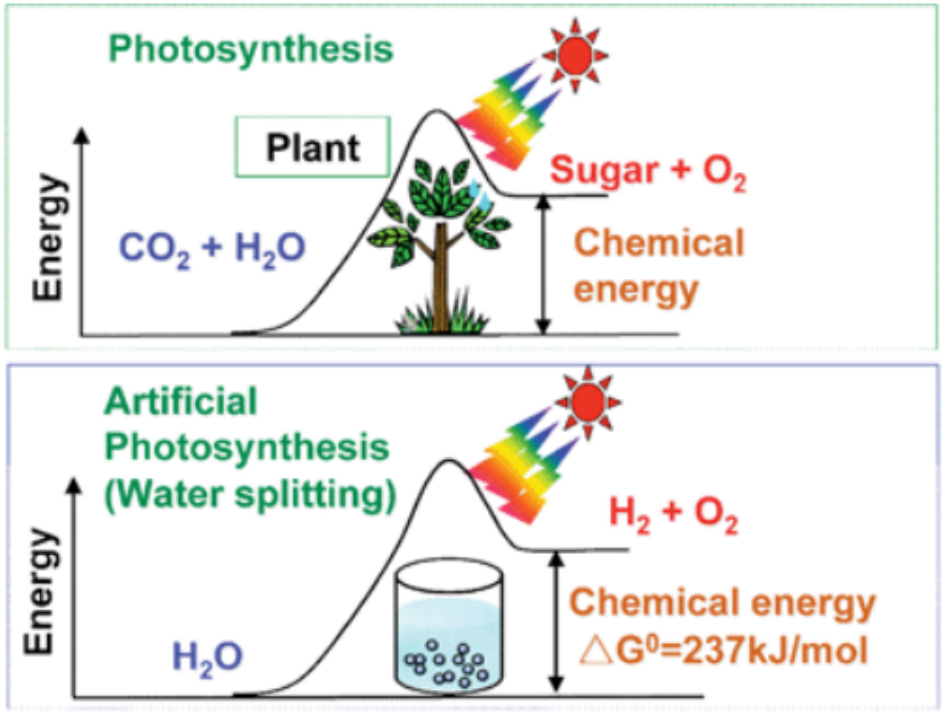
Simran Kanwar
PhD Scholar
(BITS-RMIT program)

Outlines

- Introduction: *2D materials and Photocatalysis*
- 2D van der Waals heterostructures
  - *MXene/BlueP*
  - *MXene/TMDC*
- Properties:
    - *Stability*
    - *Electronic properties*
    - *Optical properties*
    - *Gibbs free energy*
  - Application of strain

Photocatalysis

Photosynthesis by green plants and photocatalytic water splitting as an artificial photosynthesis



Chem. Soc. Rev. 2009, 38, 253-278

Potential applications:

- **solar energy harnessing and**
- **elimination of pollutants**

Photocatalysis Water splitting

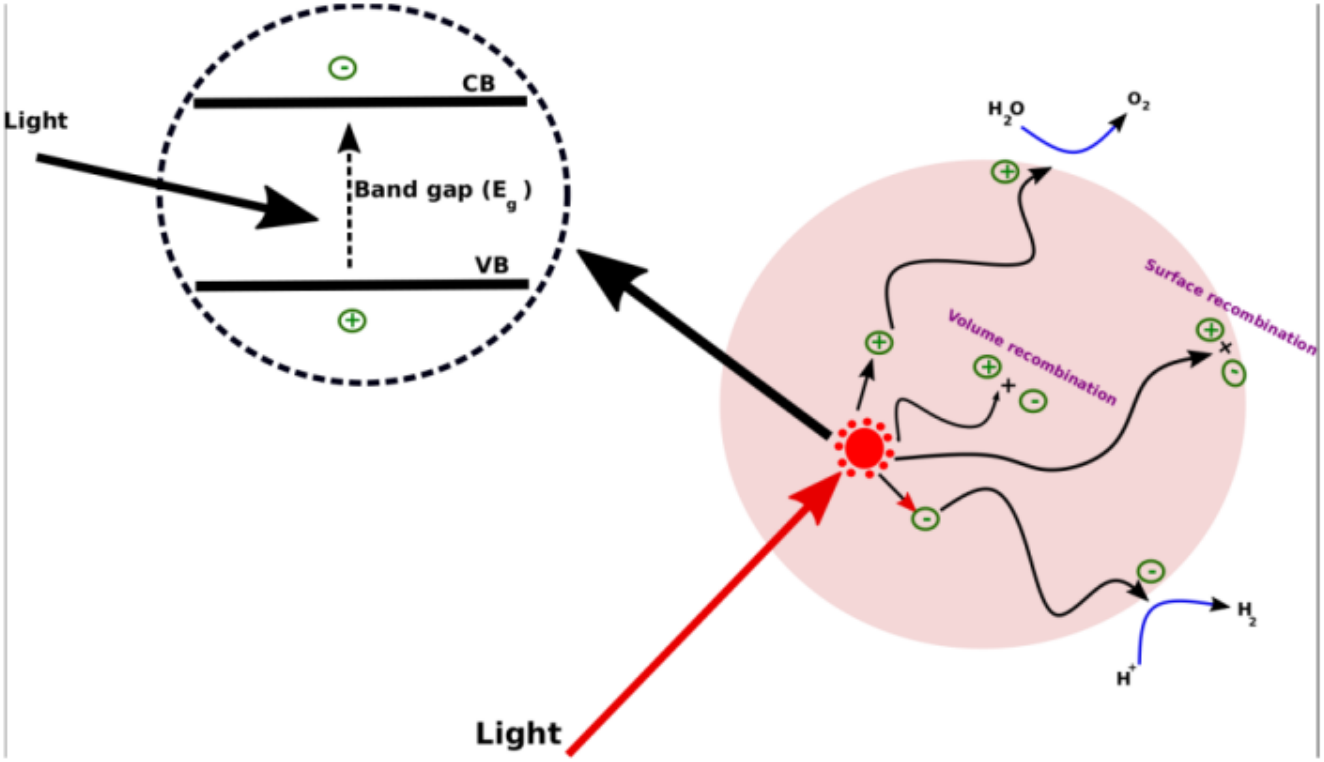
➔First experimental demonstration by Fujishima and Honda in 1972

➔Materials explored:

- **TiO_2, ZnO, $SrTiO_3$**
- **Two-dimensional (2D) materials**

(TMDCs, black phosphorene, MXene)

Photocatalysis



Photocatalysis Water spliting Challenges

- ➔Suitable band gap (>1.23 eV)
- ➔Mobility and Recombination Rate
- ➔Optical Properties
- ➔Reduction and oxidation capabilities
- ➔Low Gibbs free energy

The electrochemical redox potentials of water:

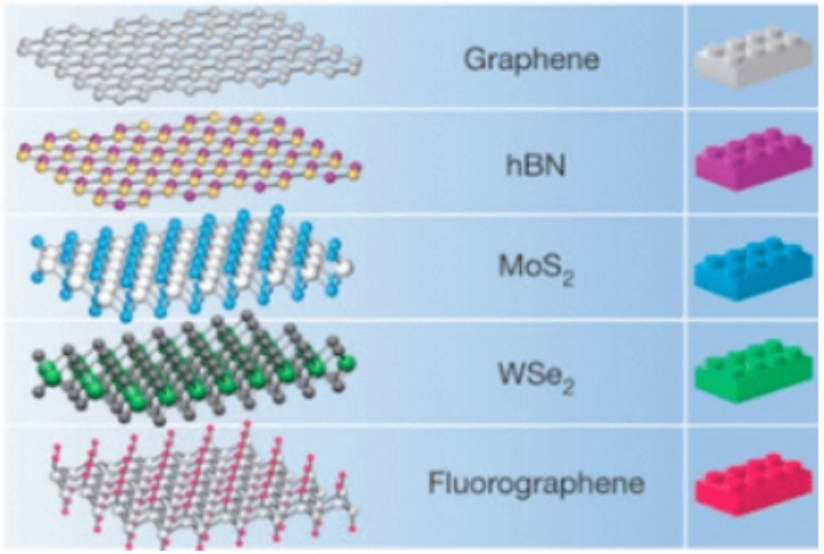
$E_{H+}/H_2 = -4.44 + (pH \times 0.059)$ eV

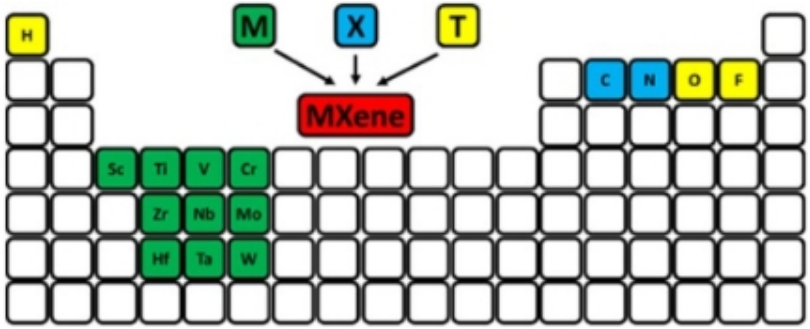
$E_{O2}/H_2O = -5.67 + (pH \times 0.059)$ eV

2D Materials

Properties

- Unique Electronic Properties
- Mechanical Strength
- Thermal Conductivity
- Optical Properties
- Energy Storage





Mxenes: Newest and most important family of 2D transition metal carbides, carbonitrides and nitrides

$M_{n+1}X_n$

Functionalized Mxenes: $M_{n+1}X_nT_x$

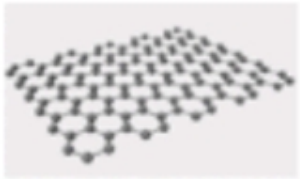
M = Transition Metal

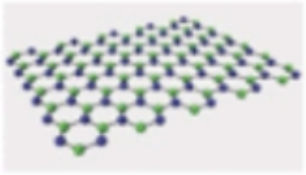
X= C or N T = O, F, OH

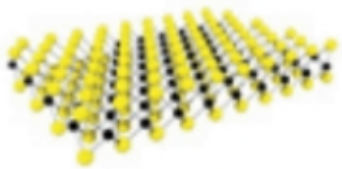
2D Materials

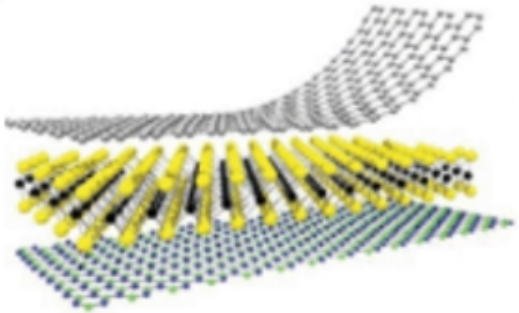
Improvement

- Strain Engineering
- Heterostructures
- Doping
- Chemical Functionalization
- Layer Number Control
- Defect Engineering

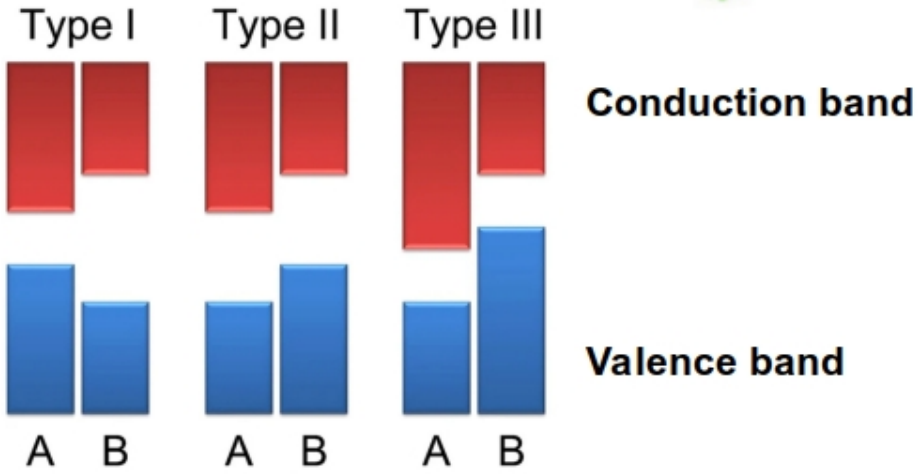

Graphene


h-BN


MoS_2



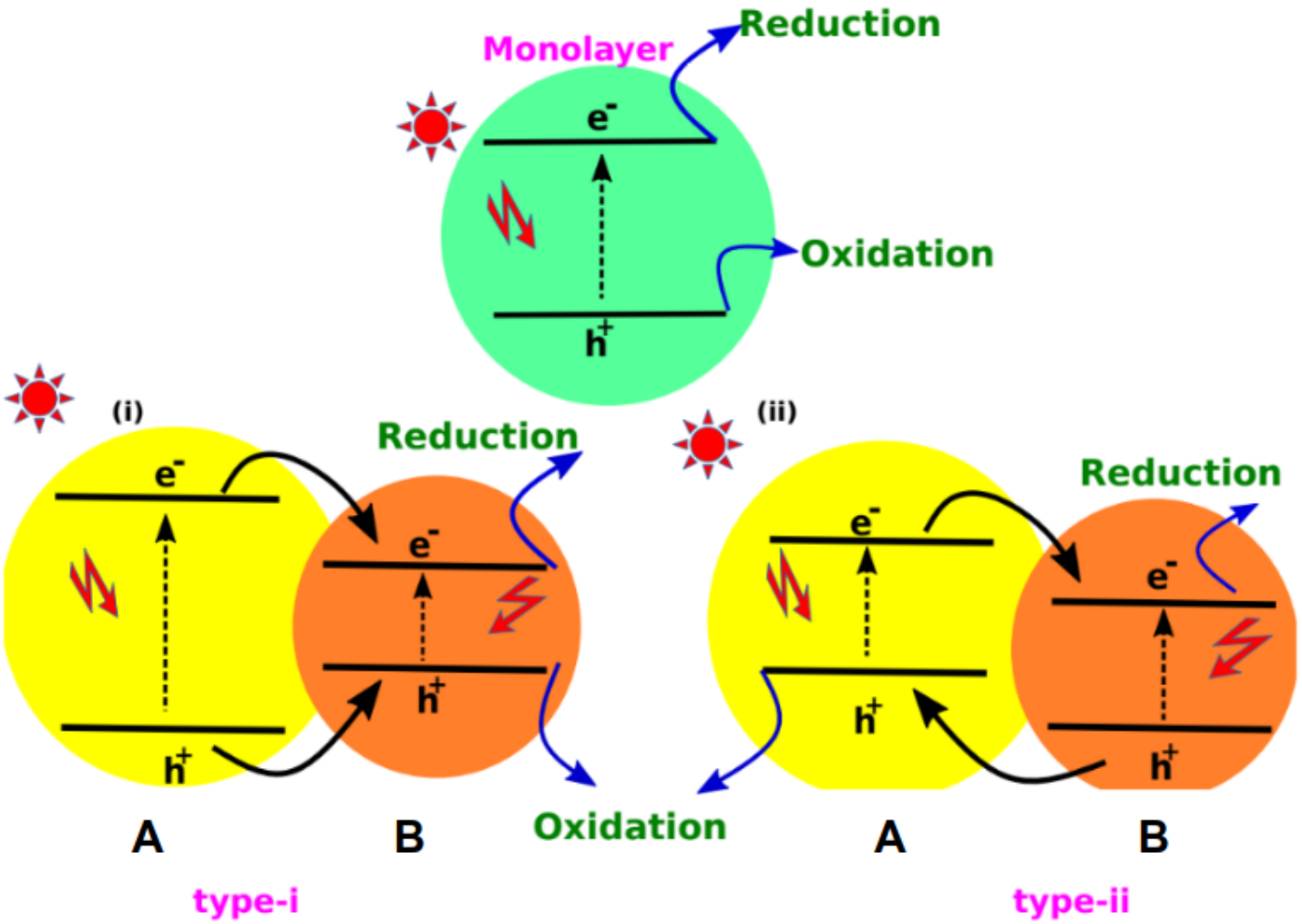
Van der Waals Heterostructure



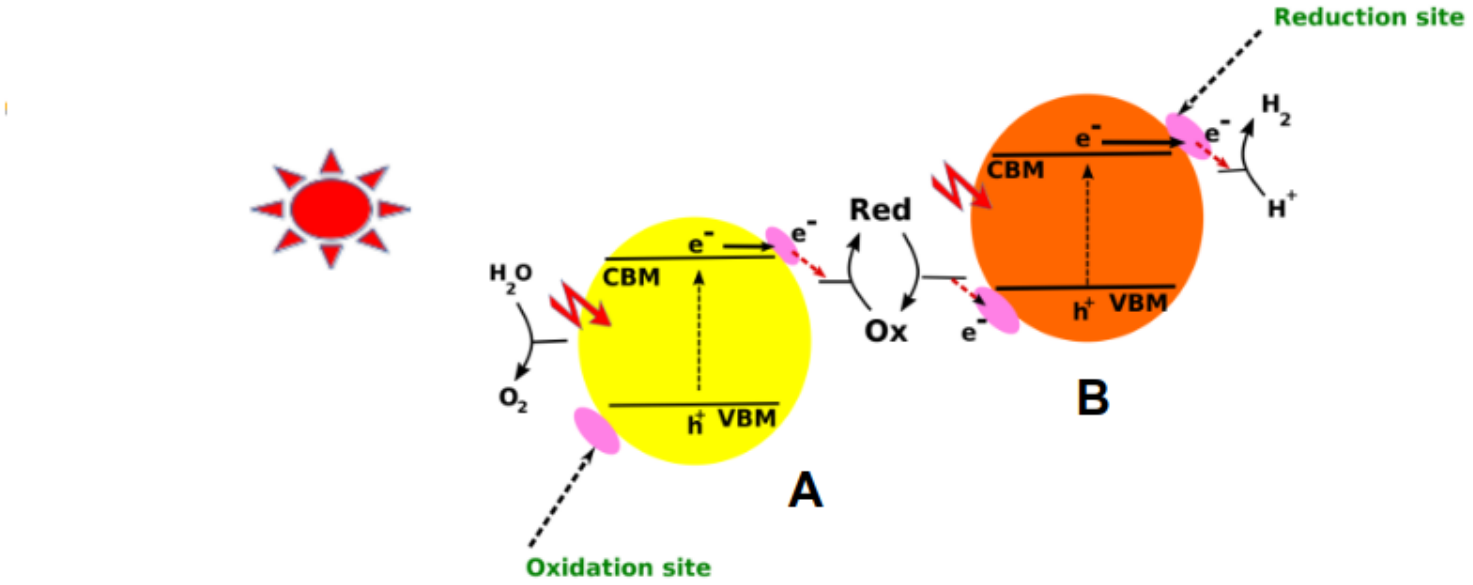
Conduction band

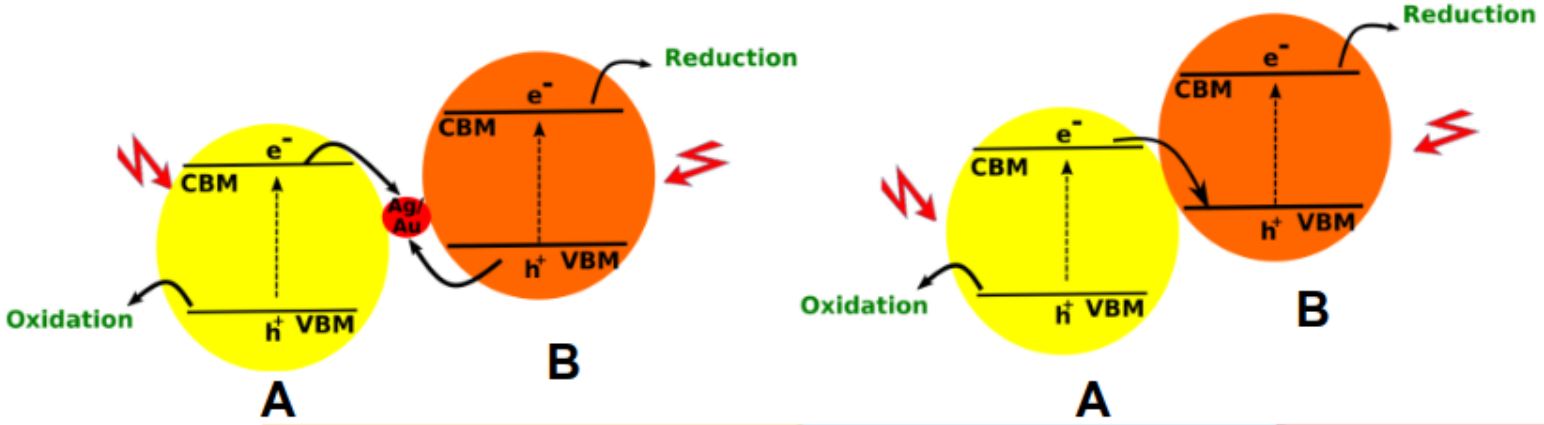
Valence band

Different types of photocatalyst

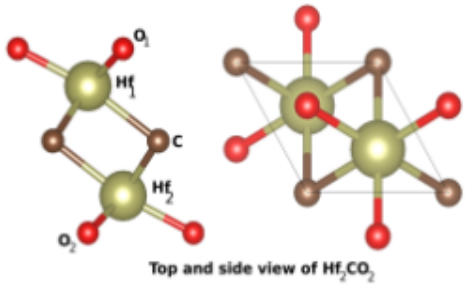


Z-Scheme

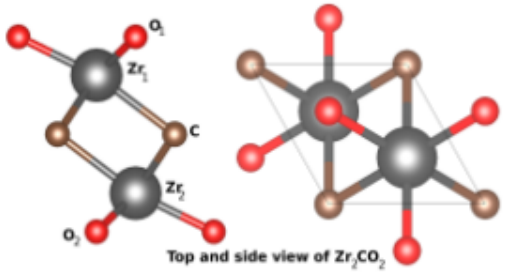

Reduction site
H2
e-
e-
CBM
H+
Red
e-
H2O
e-
CBM
Ox
h+ VBM
e-
O2
B
h+ VBM
A
Oxidation site


Reduction
e-
CBM
e-
Ag/
Au
CBM
h+ VBM
Oxidation
h+ VBM
B
A
Reduction
e-
CBM
e-
CBM
h+ VBM
Oxidation
h+ VBM
B
A

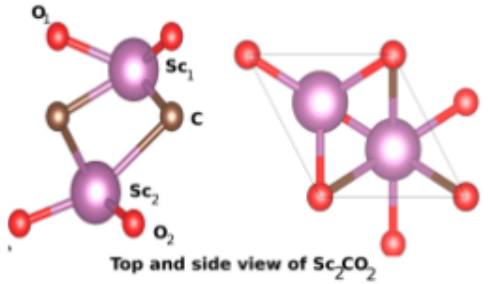
MXene and Blue phosphorene



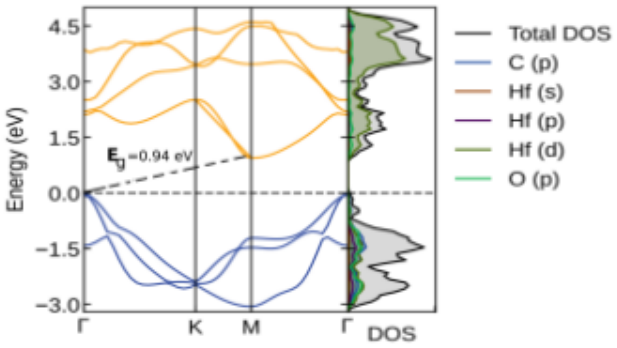
Top and side view of Hf_2CO_2

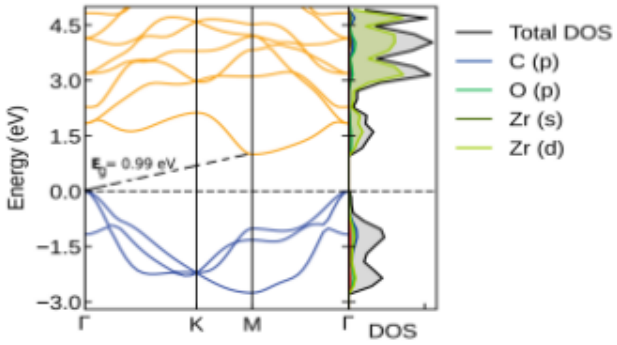


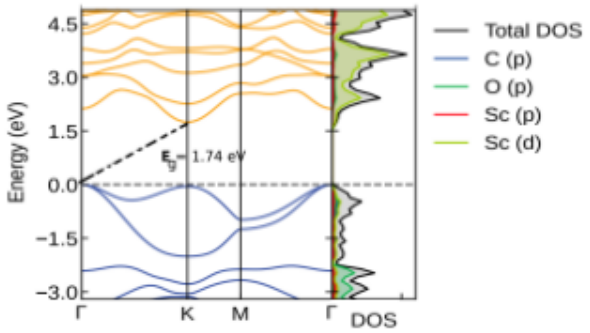
Top and side view of Zr_2CO_2



Top and side view of Sc_2CO_2

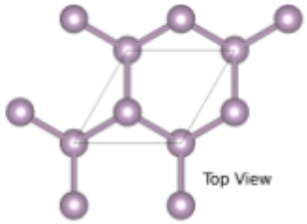




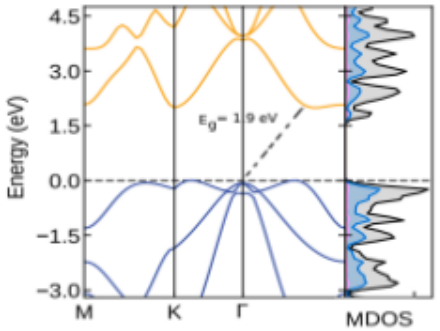


BlueP

Side View



Top View



Band structure and Density of States

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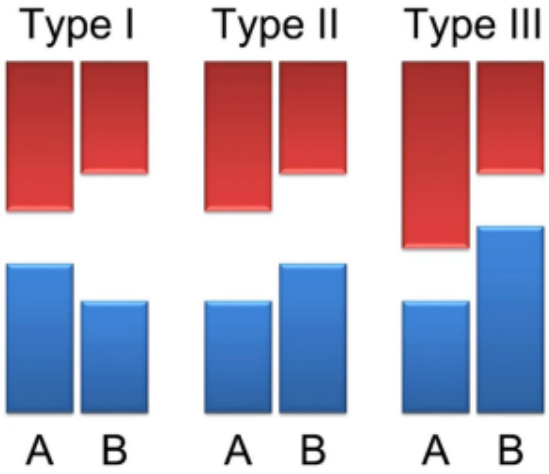
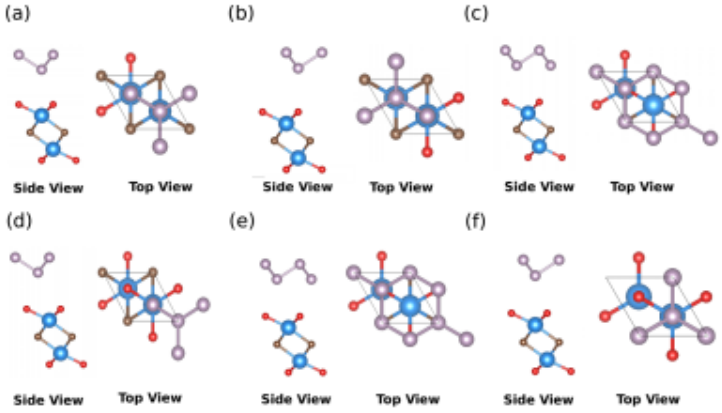
Heterostructures (MXene/blueP)





Different stacking

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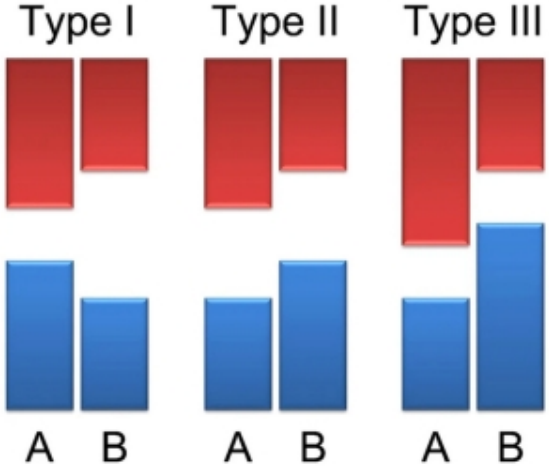
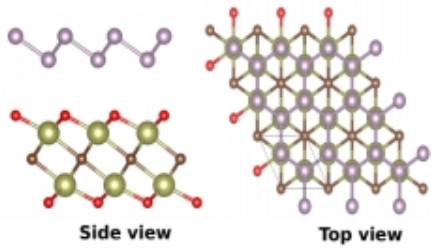
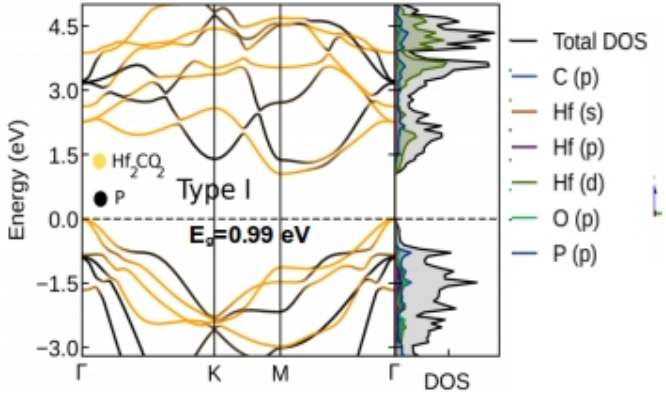
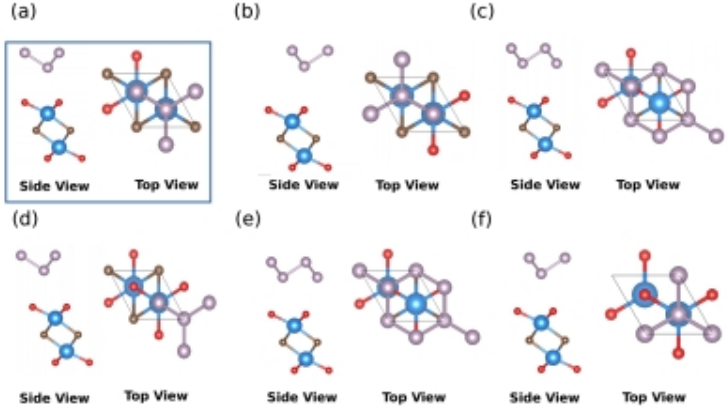
Heterostructures (MXene/blueP)



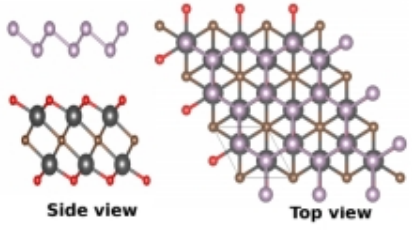


Hf_2CO_2/ BP

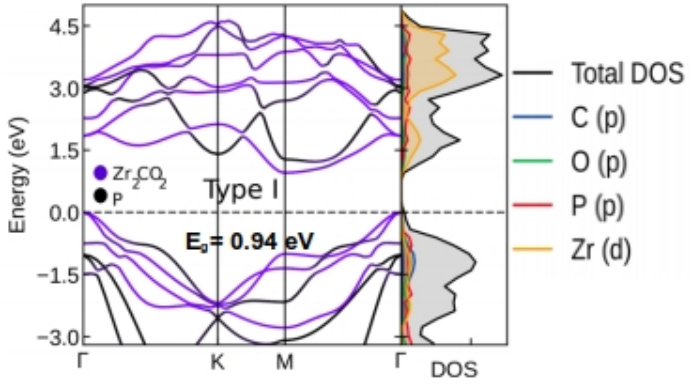




Different stacking



Zr_2CO_2/ BP



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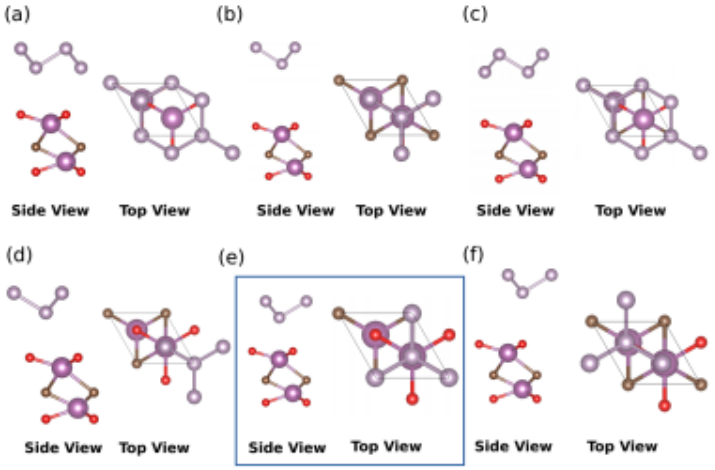
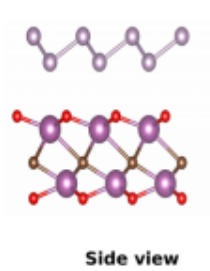
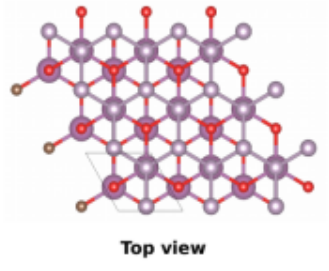
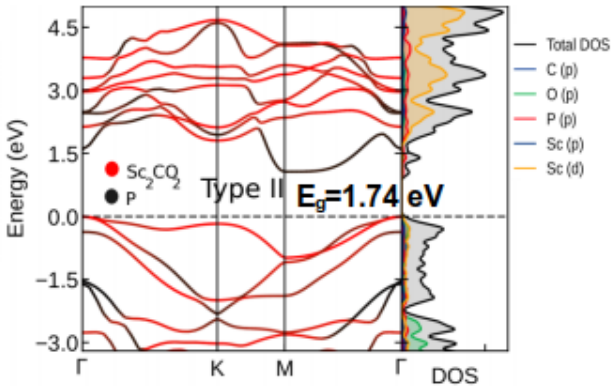
Heterostructures (MXene/blueP)







Sc_2CO_2 / BP

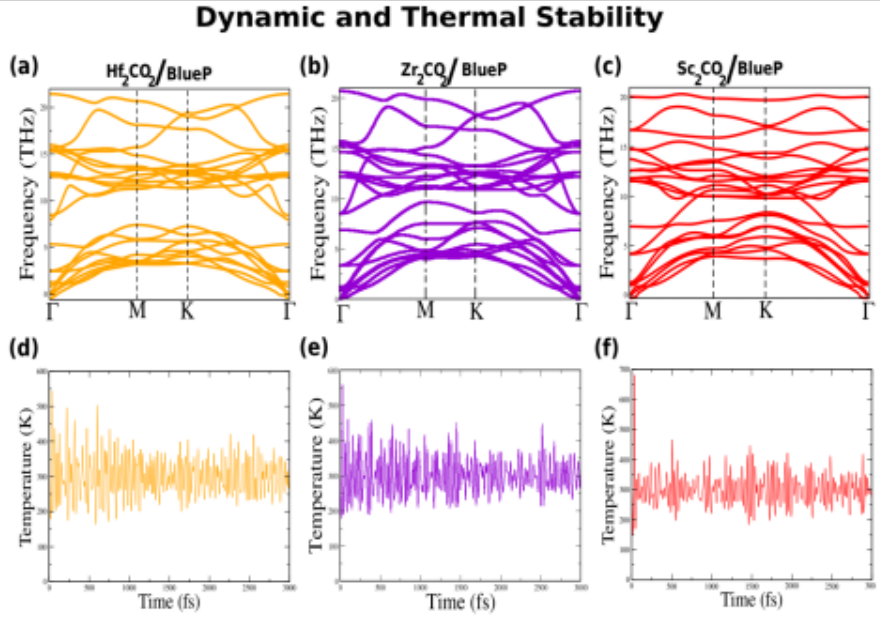


Different Stacking

Formation Energy, E_f (eV) $E_f = (E_{total} - (E_{MXene} + E_{blueP}))$

Heterostructure	a	b	c	d	e	f
Hf_2CO_2/blueP	**-0.434**	-0.408	-0.357	-0.342	-0.426	-0.413
Zr_2CO_2/blueP	**-0.451**	-0.428	-0.367	-0.370	-0.441	-0.419
Sc_2CO_2/blueP	-0.405	-0.333	-0.248	-0.248	**-0.418**	-0.324

Stability



Phonon band structure:

Absence of imaginary frequencies in the phonon spectra

Thermal stability at 300 K:

Convergence of temperature at the end of the simulation steps

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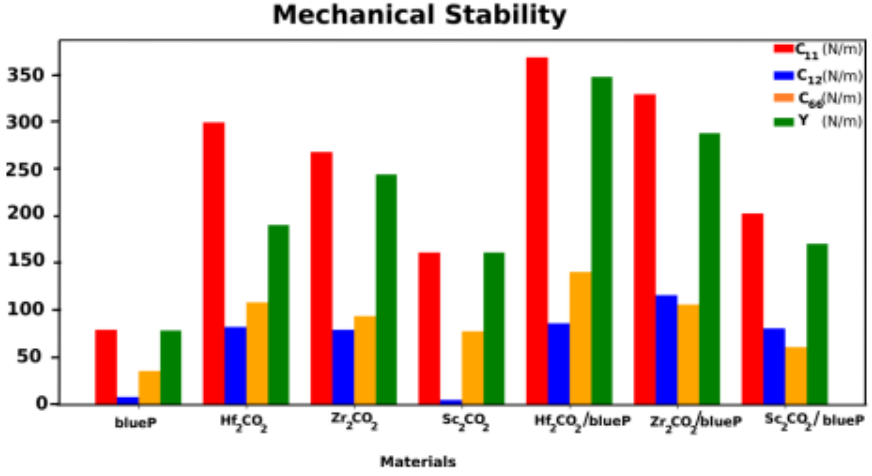
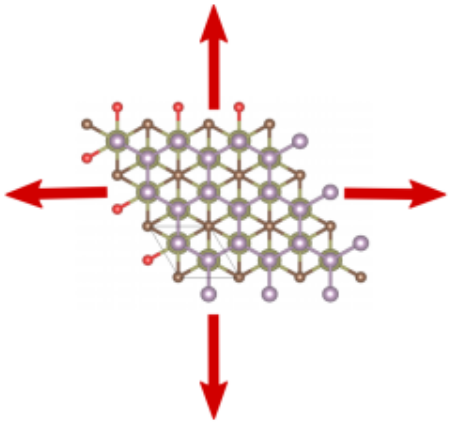


Elastic constants and Young's modulus:

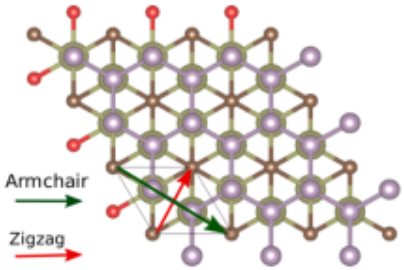
Meet the mechanical stability criteria ($C_{11} > 0$ and $C_{11} > |C_{12}|$)

Effect of external strain

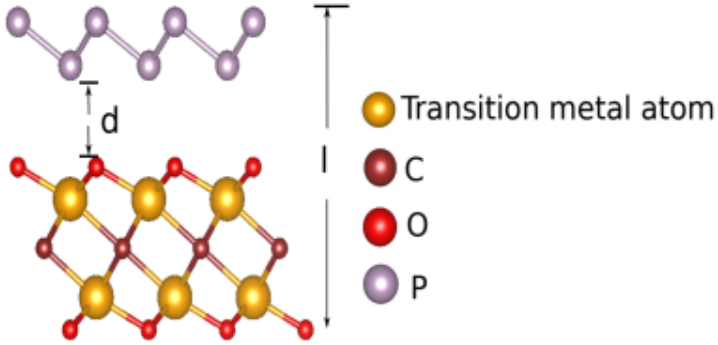
Biaxial strain

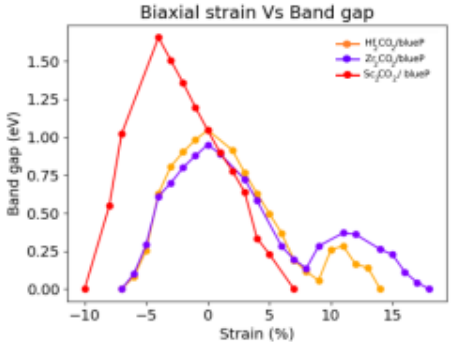


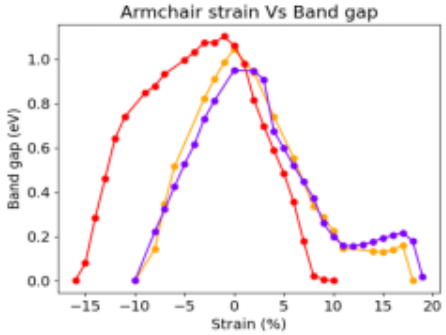
Uniaxial strain

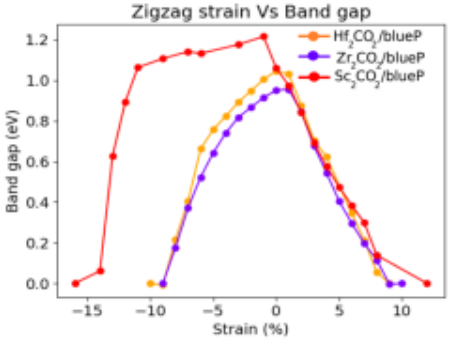


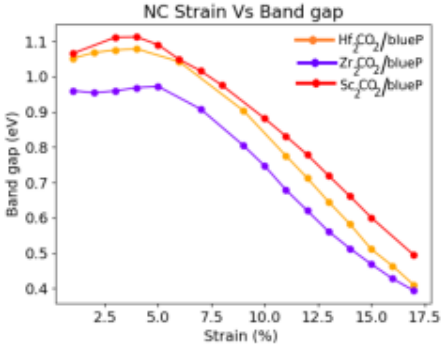
Normal compressive strain











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Effect of external strain

Heterostructure	Biaxial Strain	Armchair	Zigzag	N-C Strain
Hf_2CO_2/blueP	S-M (-7%,14%) type I-type II (-5%, 2%)	S-M(-10%) type I-type II (2%,-7%)	S-M (9%,-10%) type I-type II (1%,-6%)	type I-type II(8%)
Zr_2CO_2/blueP	S-M (-7%,18%) type I-type II (5%, 2%)	S-M (-10%) Type I-type II (6%,-9%)	S-M(10%.-9%) Type I-type II (4%,-7%)	type I-type II(7%)
Sc_2CO_2/blueP	S-M (-9%,6%) type II-type I(-7%)	S-M(10%,-16%) Indirect-direct(6%)	S-M(12%,-16%) Indirect-direct(6%)	Nill

Why type II is important?

type II hetrostructure shows promising potential for photocatalytic water splitting

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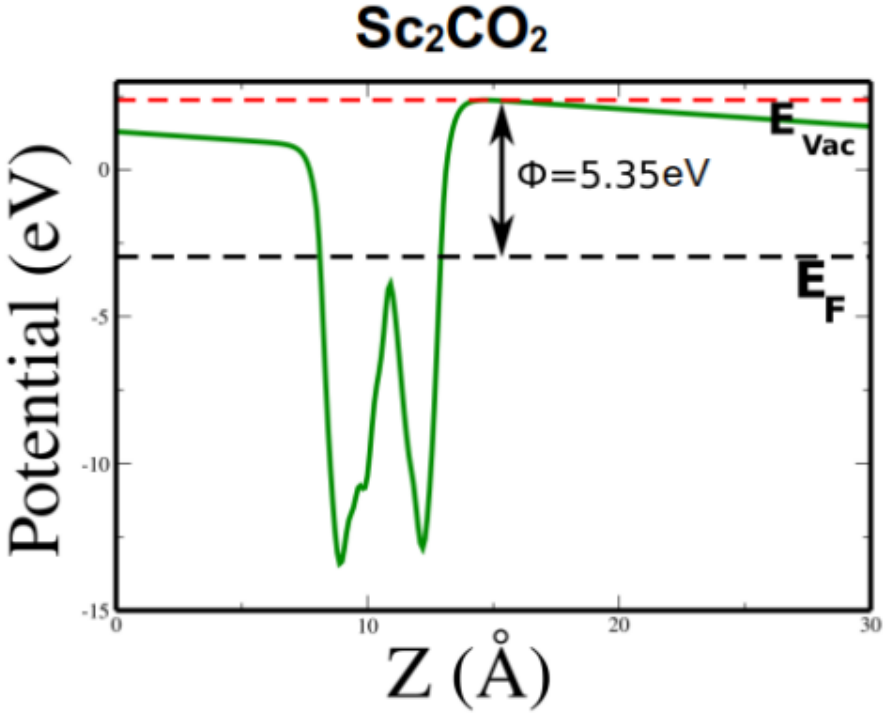
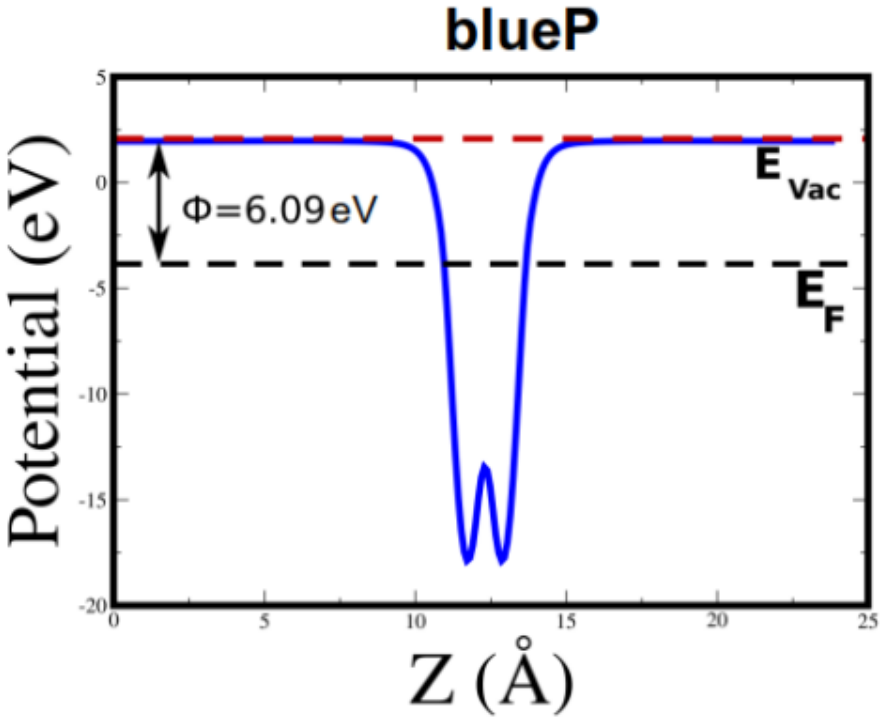
Electrostatic potential Sc_2CO_2 and blueP mololayers

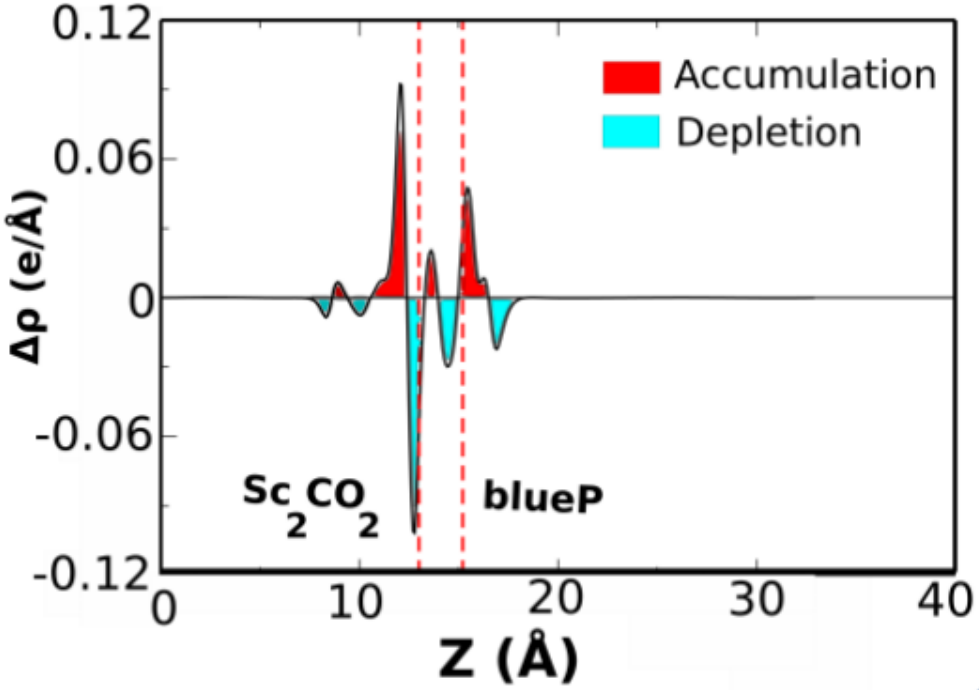


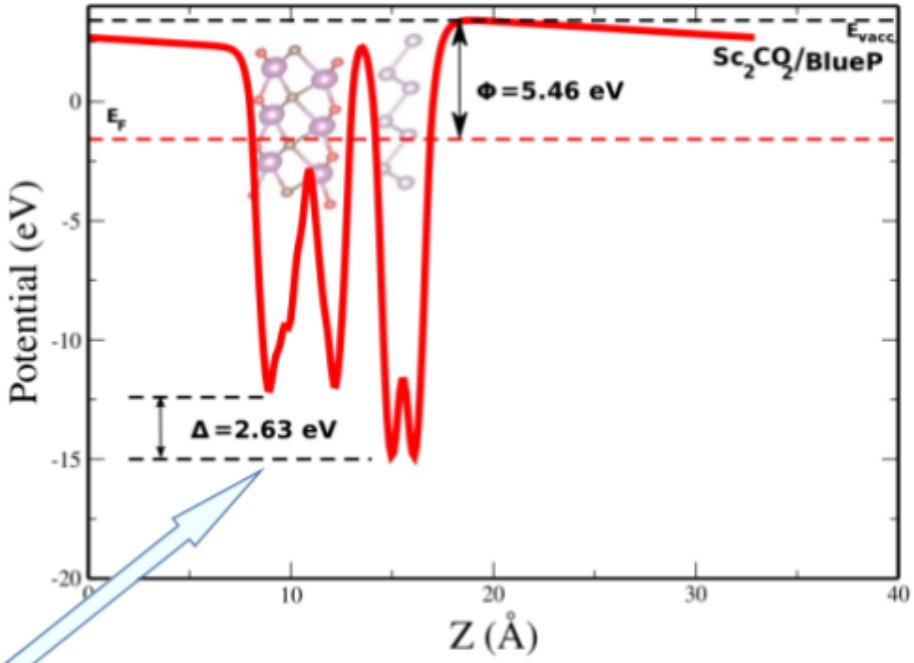


Direction of Built in Electric Field ⇨ **Sc_2CO_2 to blueP**

Charge seperation and Effective Potential

Sc_2CO_2/blueP heterostructure

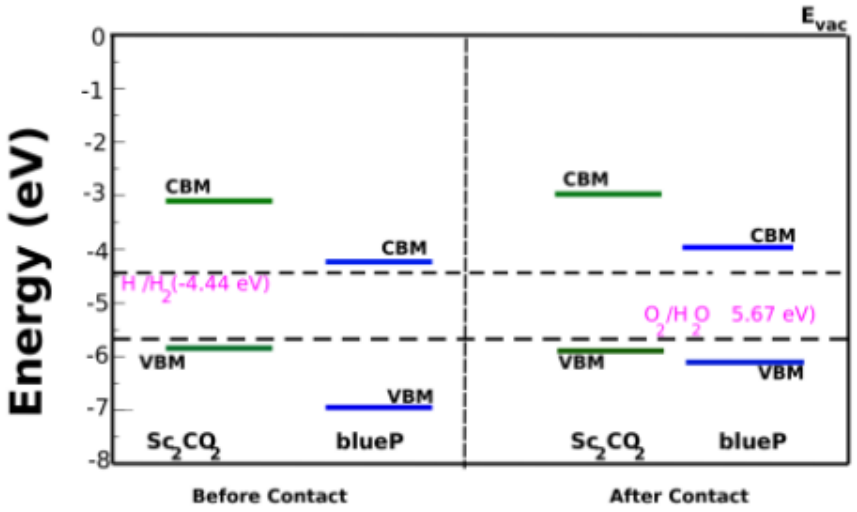




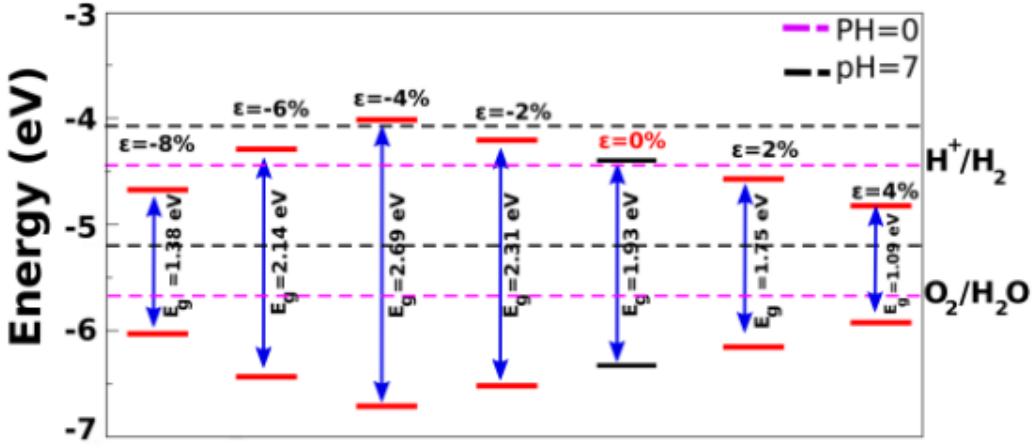
Strength of Build in Electric Field

Oxidation and Reduction Capabilities and effect of strain

Band Edge with respect to redox potential

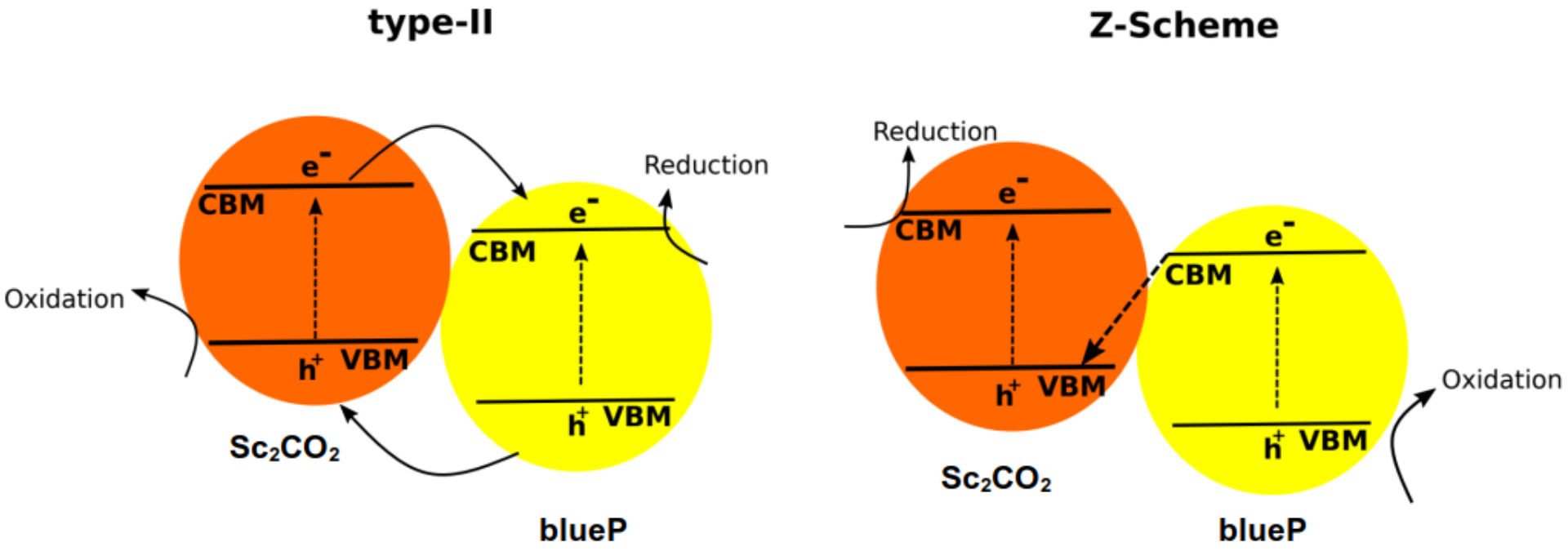


Without strain



With strain

Type-II or Z-scheme?



Charge Transfer Mechanism Identification

- **Built-in electric field direction:**
  The build in electric field indicates a Z-scheme charge transfer pathway.

- **Thermodynamic confirmation:**
  Gibbs free energy analysis is required to confirm the mechanism

Gibbs Free Energy

$$\Delta G=\Delta E+\Delta E(ZPE)-T\Delta S-neU$$

ΔE — Total energy difference from DFT

$\Delta E(ZPE)$ — Zero-point energy correction

$T\Delta S$ — Entropic contribution

n — electrons transferred

U — applied potential

Reaction mechanism for OER and HER

$$H_2O + * \rightarrow OH^* + H^+ + e^-$$

$$OH^* \rightarrow O^* + H^+ + e^-$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^-$$

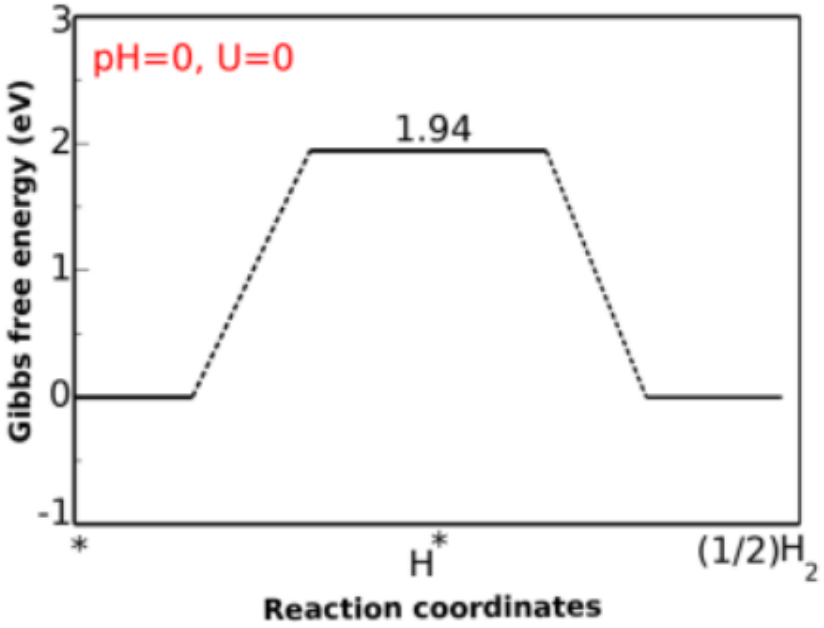
$$OOH^* \rightarrow * + O_2 + e^-$$

$$H^+ + e^- + * \rightarrow H^*$$

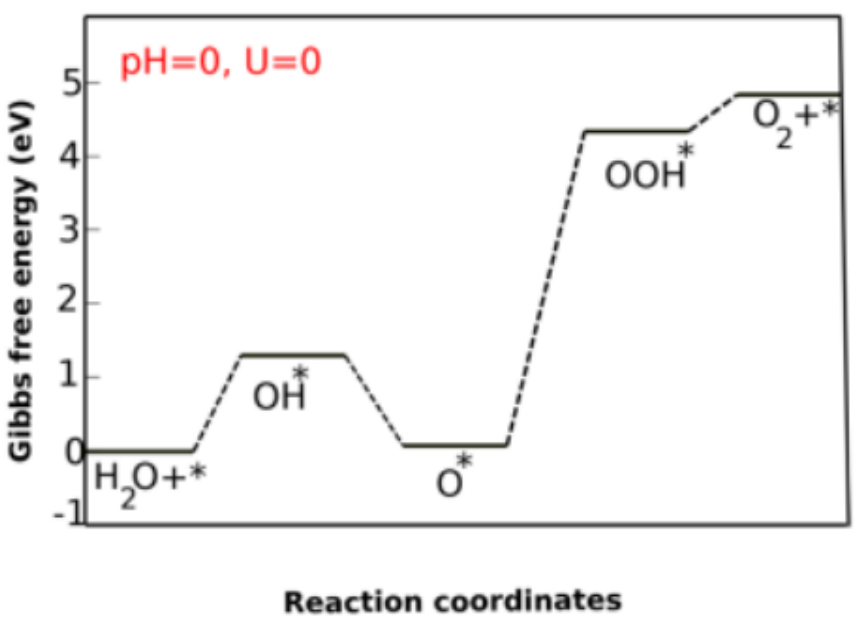
$$H^* + H^* \rightarrow H_2 + 2*$$

Gibbs Free Energy (Z-Scheme)

HER



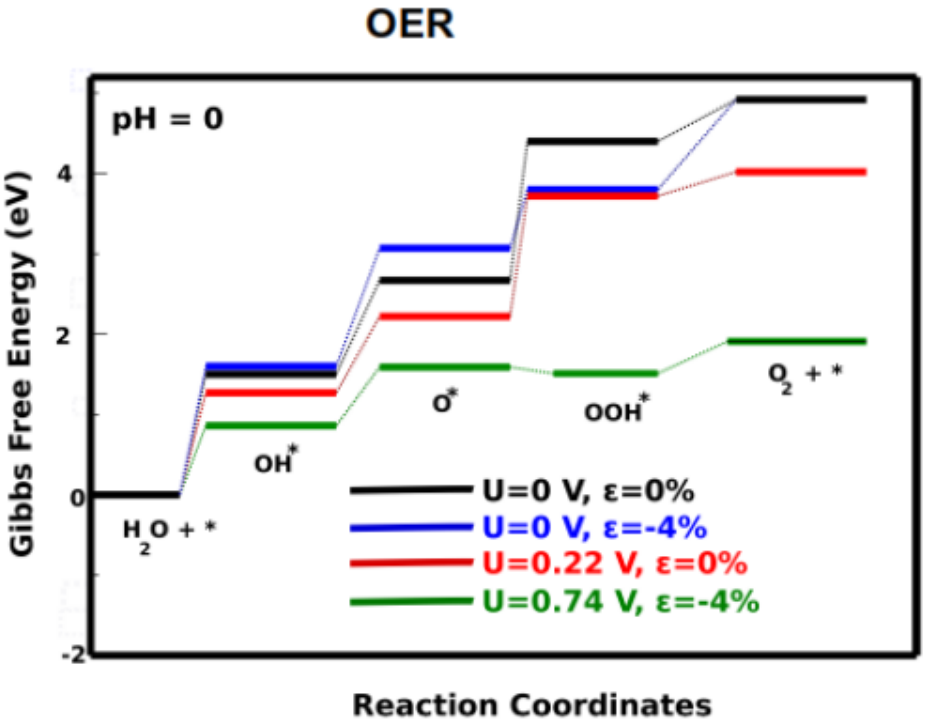
OER

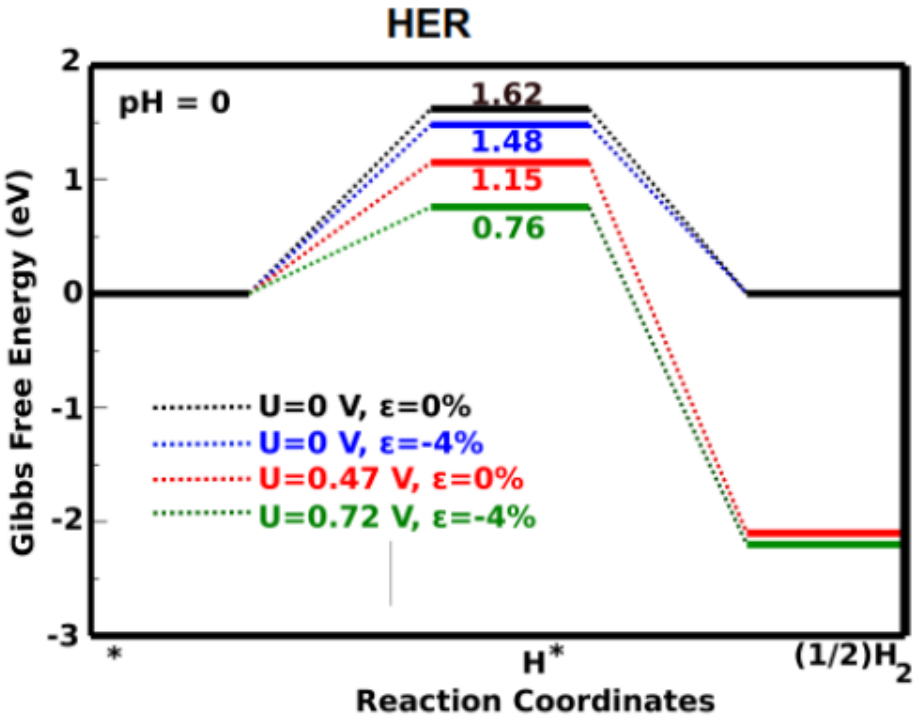


Rate limiting step **O** ⇨ **OOH**

Over Potential = 4.23 (eV)

Gibbs Free Energy (Type-II)

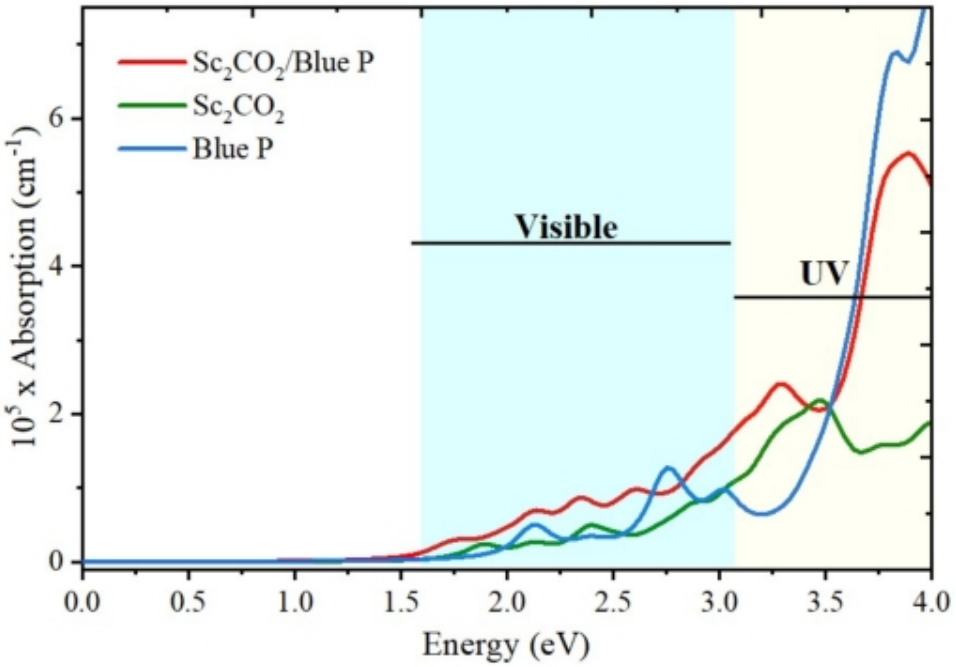


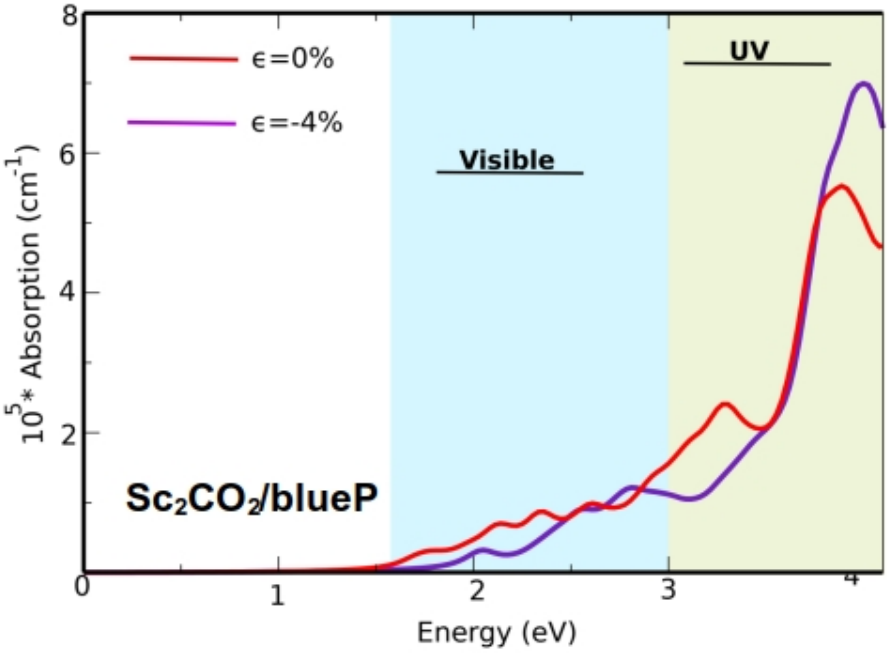


Over potential was found to be 0.50 V (Without strain)

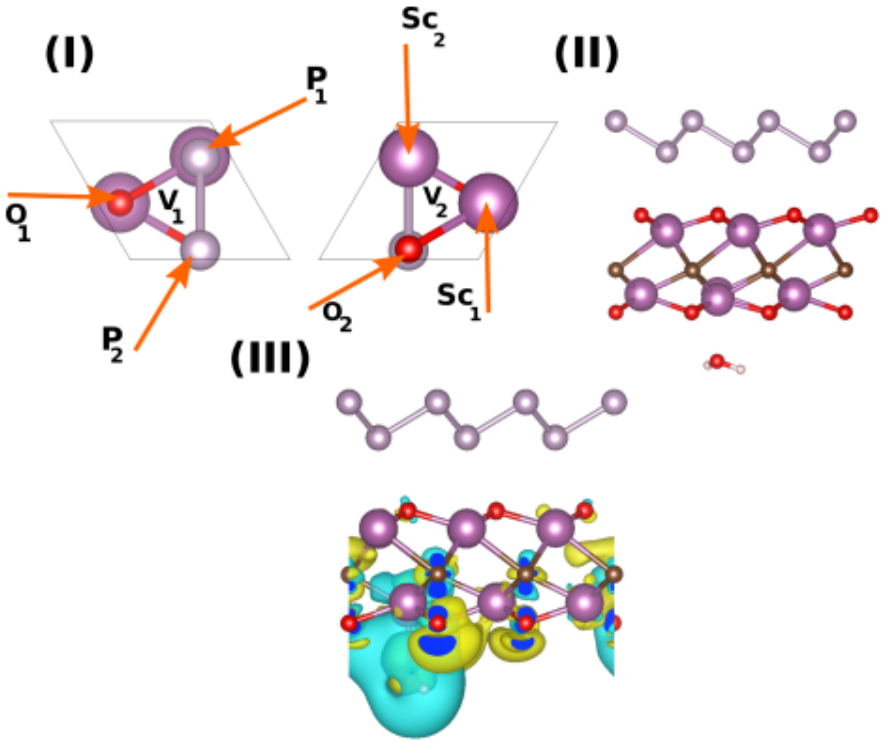
Over potential was found to be 0.37 V (With strain -4%)

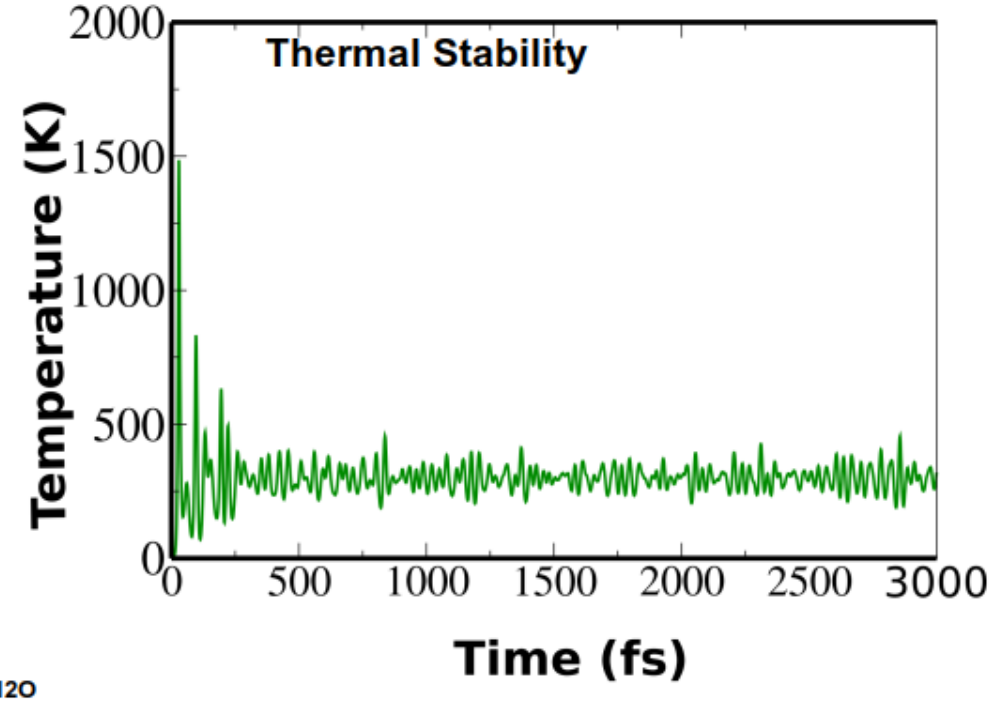
Optical properties





Water Stability



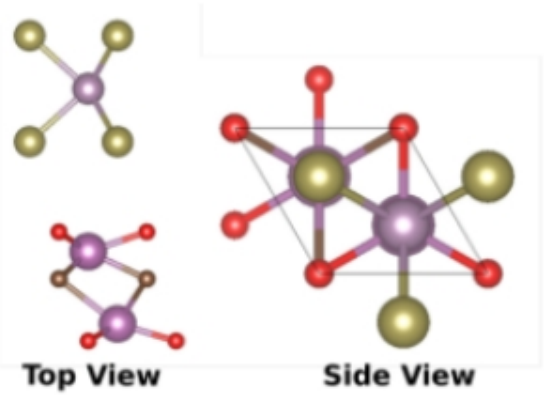


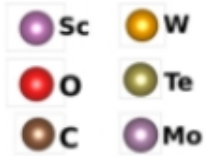
$E_{ads} = E_{H2O@Sc2CO2/blueP} - E_{Sc2CO2/blueP} - E_{H2O}$

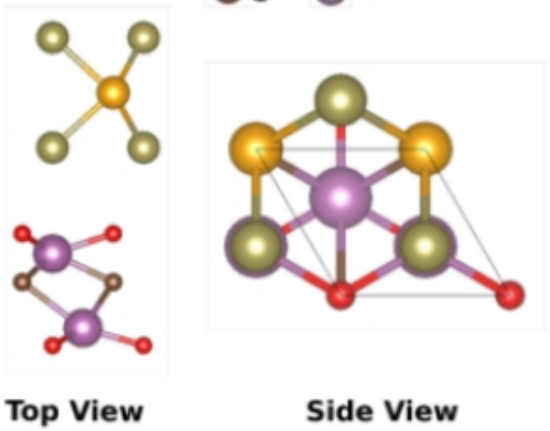
The most stable adsorption occurred when the water molecule was positioned below the Sc_2CO_2 layer at the Sc_2 site with an adsorption energy of -0.506 eV. A negative adsorption energy indicates an exothermic process, signifying a stronger interaction between the H_2O molecule and the photocatalyst surface.

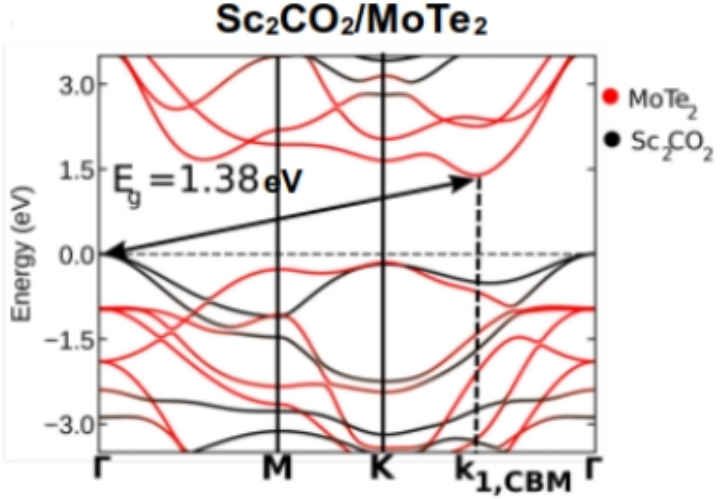
Sc_2CO_2/TMDC heterostructures

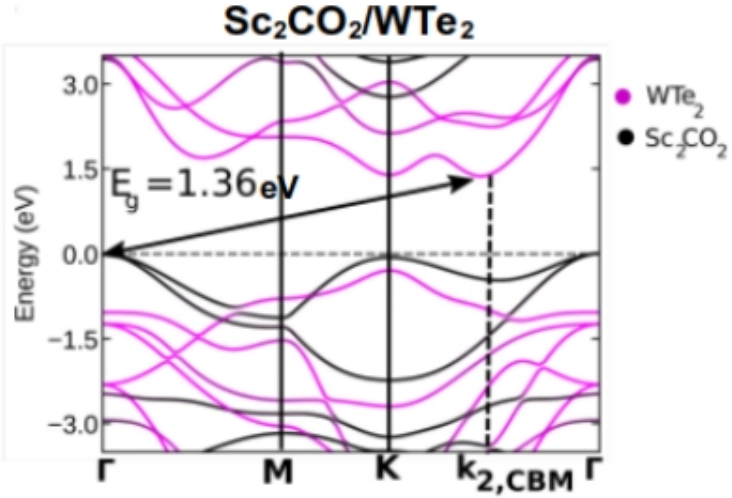
Sc_2CO_2/TMDC heterostructures



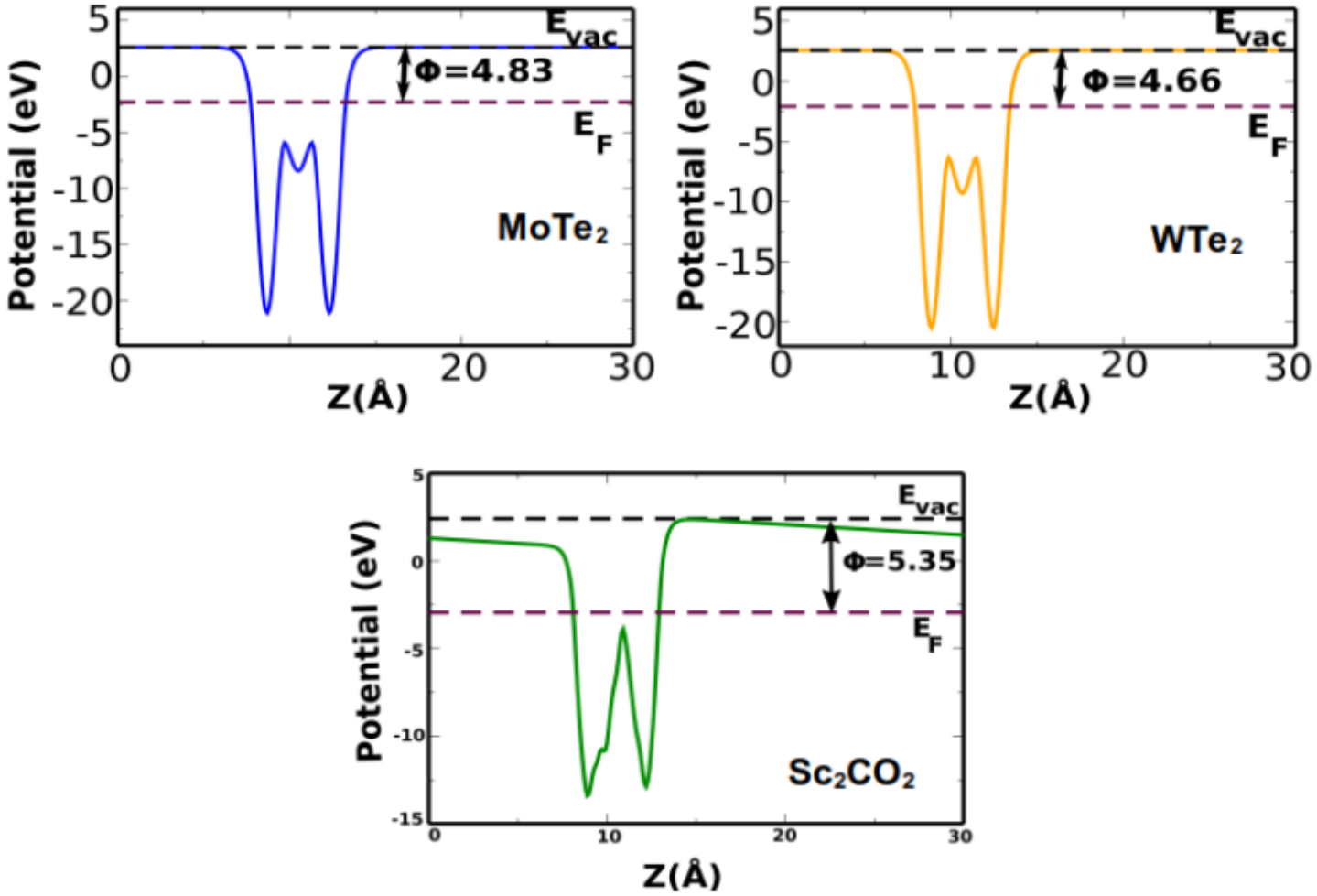






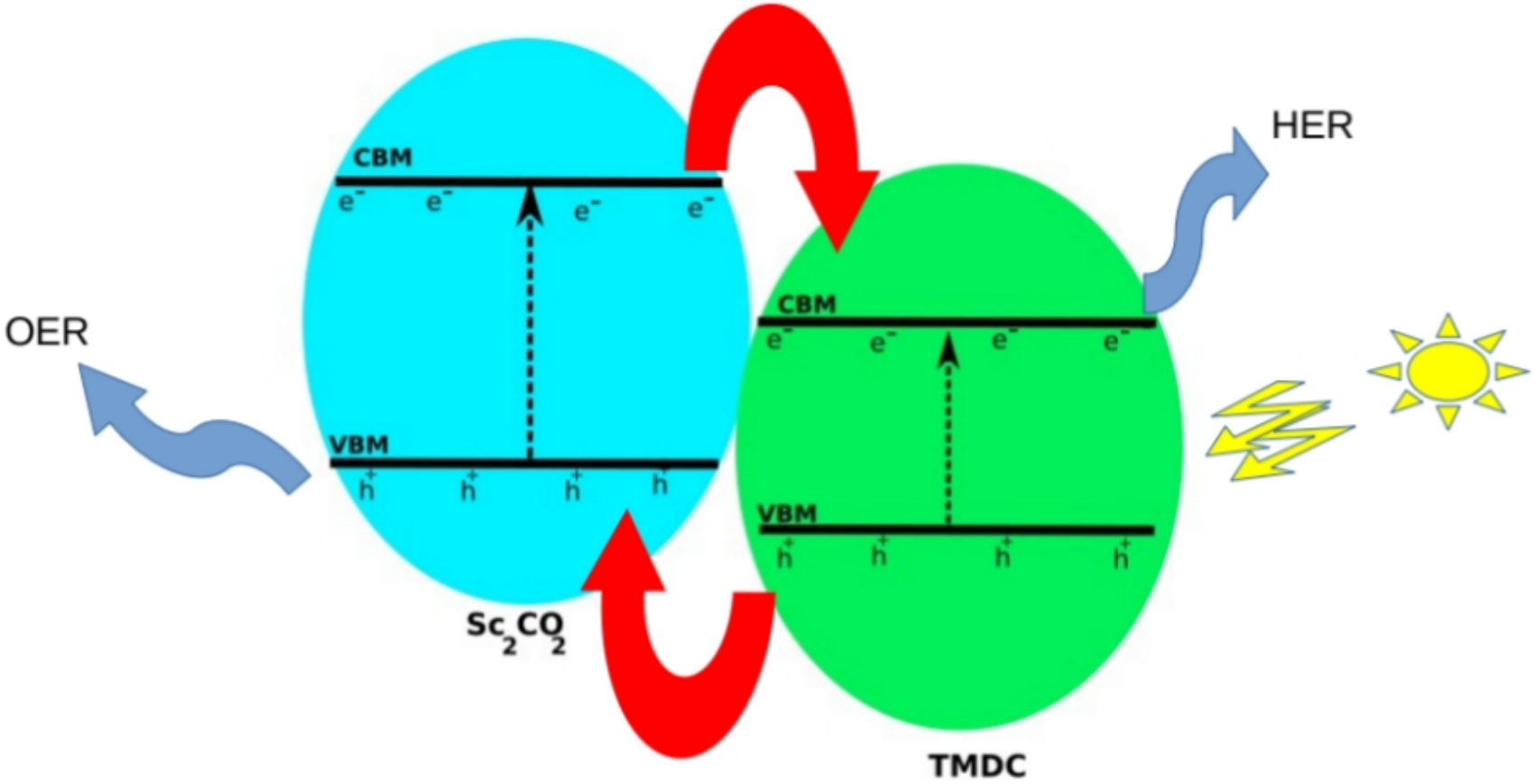


Electrostatic Potential

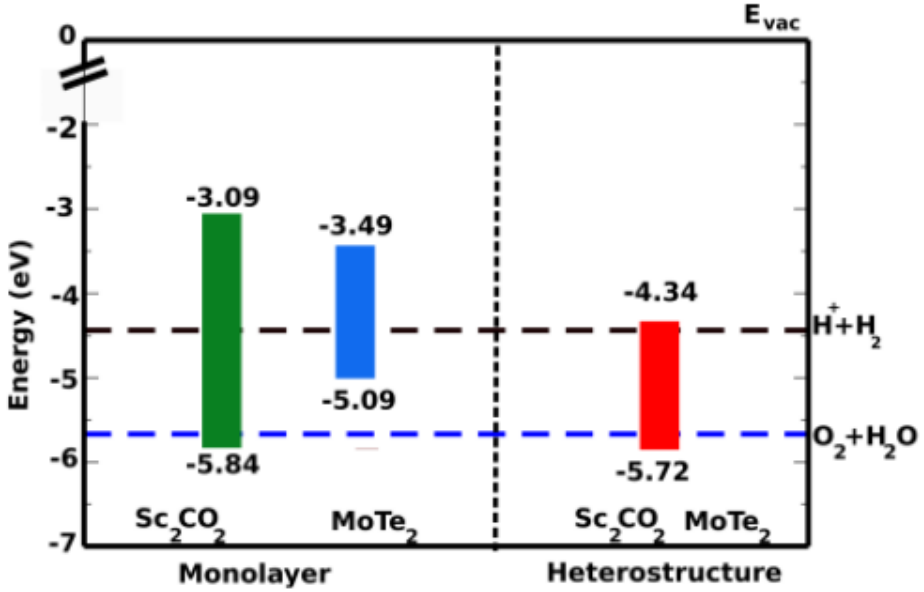


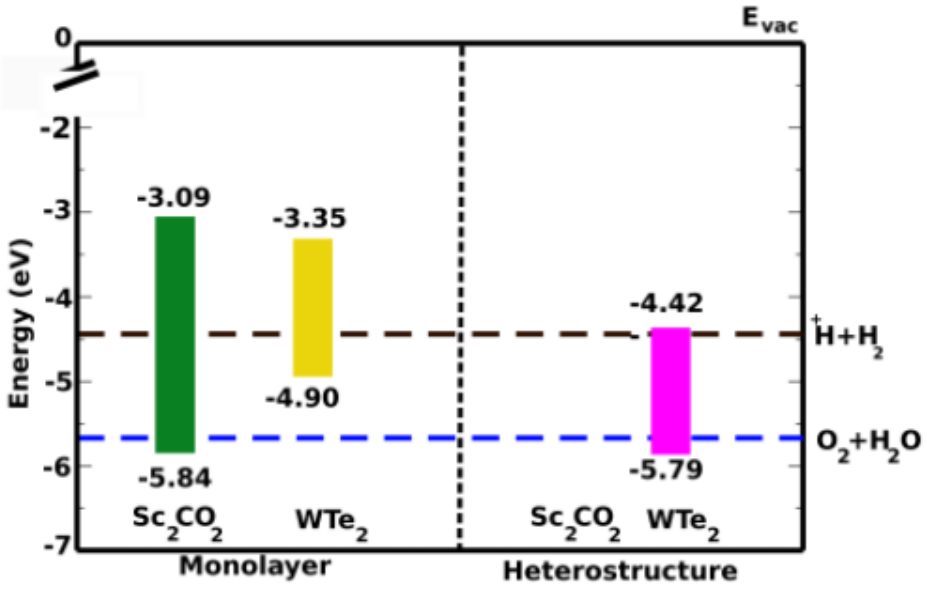
Direction of Build in electric field ⇨ TMDC to Sc_2CO_2

Type-II Mechanism



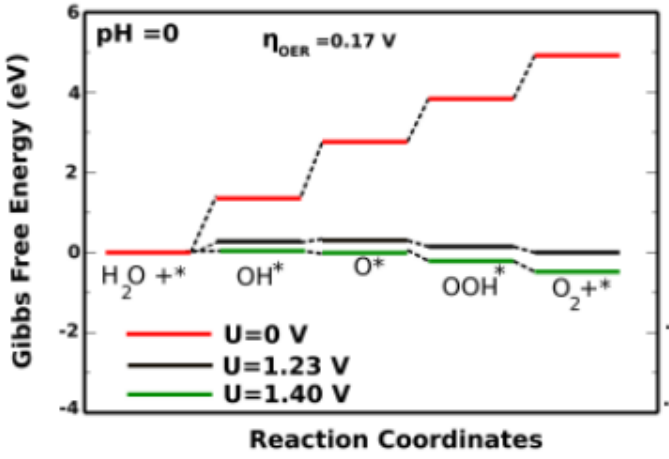
Oxidation and Reduction Capabilities



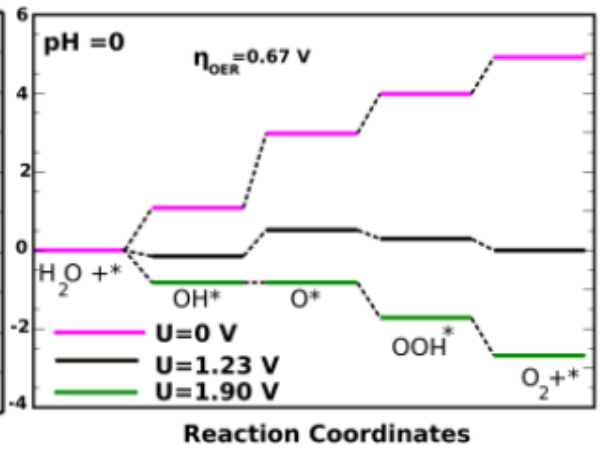


Gibbs Free Energy

OER

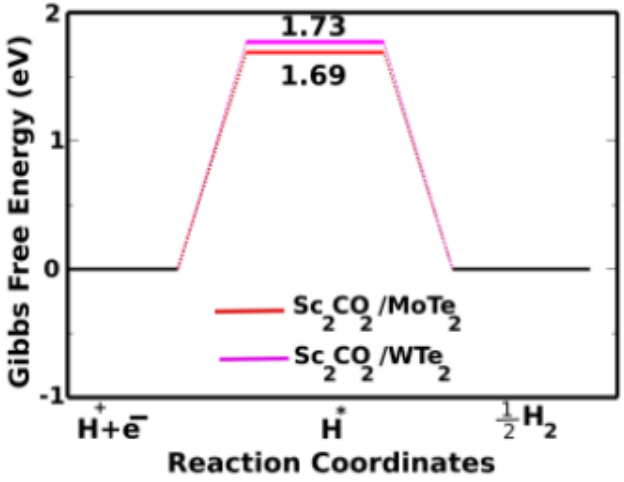


$Sc_2CO_2/MoTe_2$

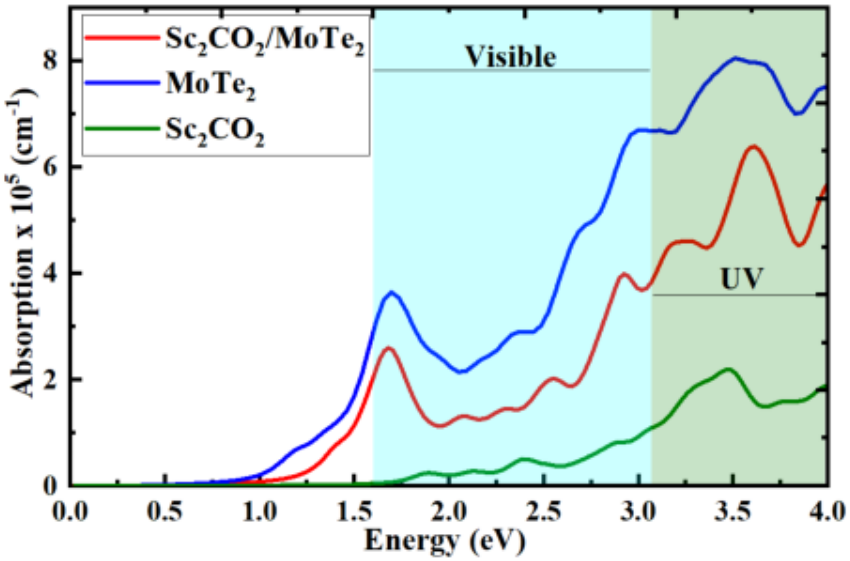


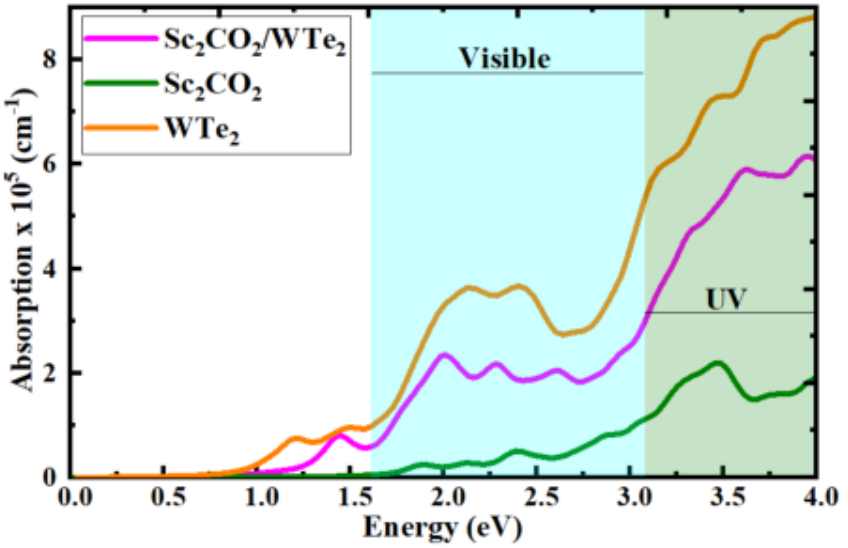
Sc_2CO_2/WTe_2

HER

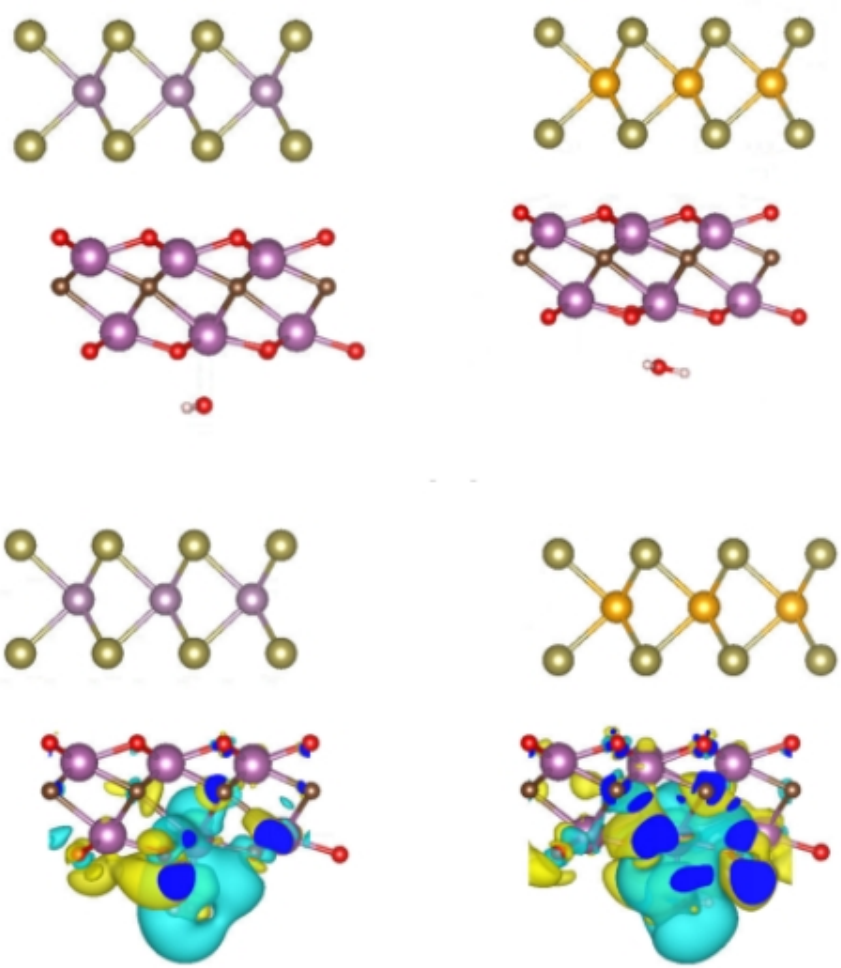


Optical properties





Water Stability



E_{ads} :

−0.607 eV for $Sc_2CO_2/MoTe_2$

−0.656 eV for Sc_2CO_2/WTe_2

A negative E_{ads} indicates an exothermic (thermodynamically favorable) adsorption.

$$E_{ads} = E_{H2O@Sc2CO2/TMDC} - E_{Sc2CO2/TMDC} - E_{H2O}$$

Summary

Mxene/Blue Phosphorene heterostructures:

- Hf_2CO_2/blueP and Zr_2CO_2/blueP exhibit type-I band alignment
- Sc_2CO_2/blueP exhibit type-II band alignment, favorable for charge separation.
- External strain induces type-I → type-II transitions, demonstrating tunable electronic properties.
- Gibbs free energy analysis of Sc_2CO_2/blueP indicates thermodynamically favorable HER/OER behavior within the type-II framework.
- Biaxial strain (−4%) reduces the overpotential for OER from 0.50 eV to 0.37 eV, enhancing catalytic efficiency.
- For HER, the Gibbs free energy change decreases from 1.62 eV to 0.72 eV under strain and Ue = 0.72 V.

Summary

MXene/TMDC heterostructures:

- $Sc_2CO_2/MoTe_2$ heterostructure demonstrates strong type-II photocatalytic characteristics
- Low overpotential of ~0.17 eV for OER

- Water adsorption is thermodynamically stable on all investigated heterostructures, indicating strong surface interaction and suitability for photocatalytic water splitting.
- Overall, MXene-based heterostructures provide a strain-tunable platform for efficient photocatalytic water splitting.

innovate achieve lead

BITS Pilani

Thank You