Higher School of Economics

Photocatalytic CO_2 reduction and excited state carrier dynamics

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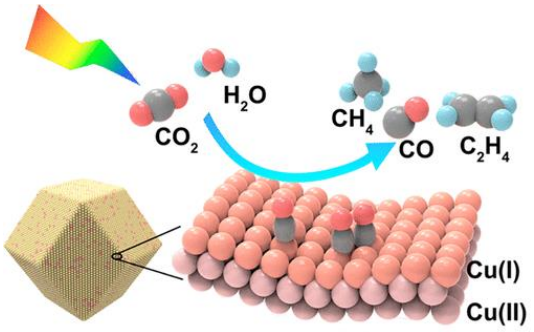
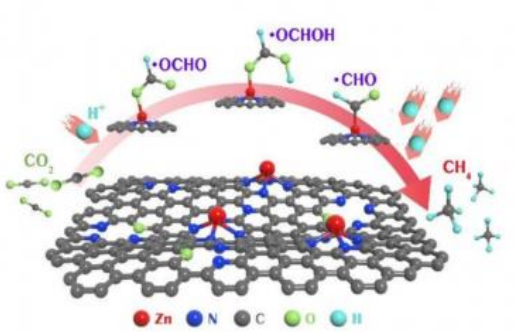
Outline

1. Photocatalytic CO_2 reduction: Ferroelectric polarization and single-atom catalyst synergistically promoting CO_2 photoreduction in $Ag@CuBiP_2Se_6$ system

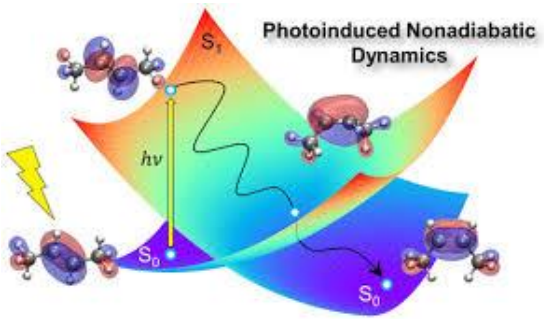
2. Excited state carrier dynamics: Electronic structural properties and carrier dynamics behaviors in $CuBiP_2Se_6/C_2N$ heterostructure



J. Am. Chem. Soc. 2021, 143, 7, 2984–2993



J. Am. Chem. Soc. 2020, 142, 29, 12563–12567



Chem. Rev. 2020, 120, 4, 2215–2287

Research background

Carbon dioxide

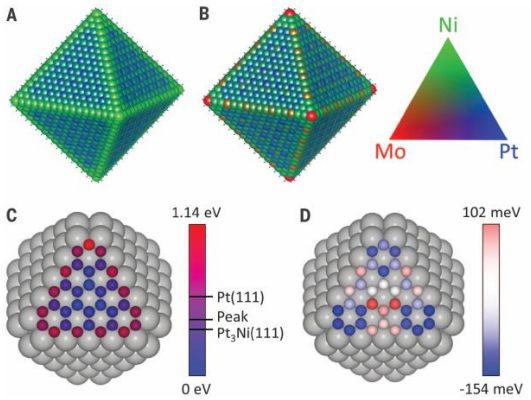
greenhouse effect

Serious carbon dioxide emissions

extreme weather

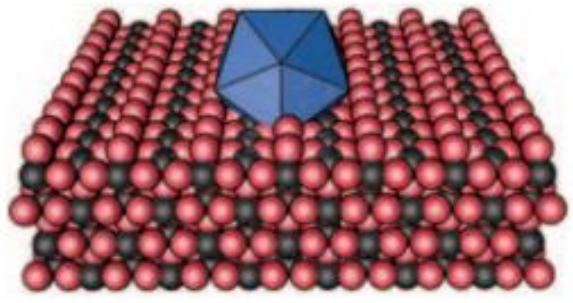
Research background

Precious metals

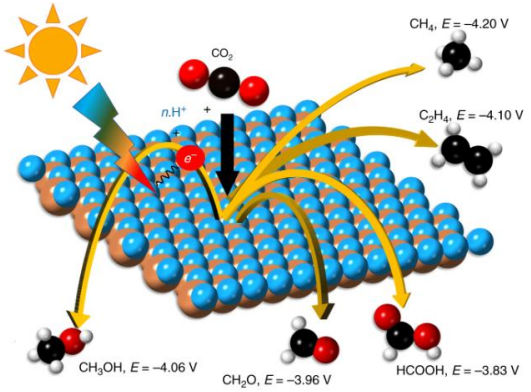


Science, 2015, 348(6240)

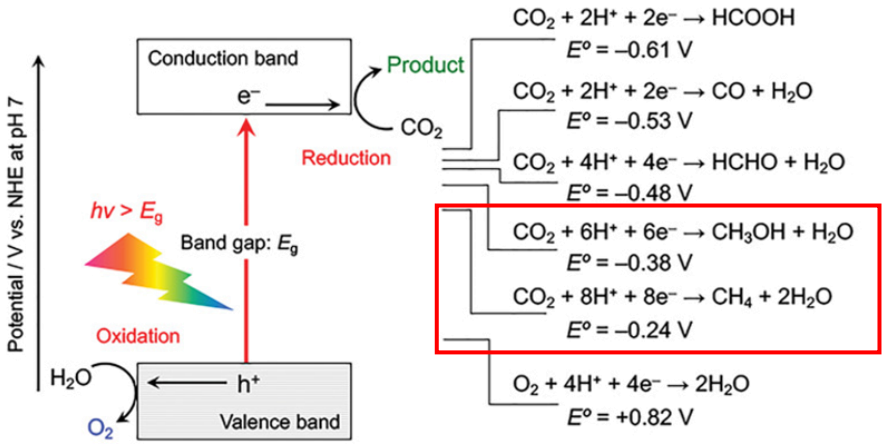
Advanced two-dimensional materials



Science, 2017, 355



Nature. Comm. 2019, 10, 443



Adv. Mater. 2019, 31, 1808205

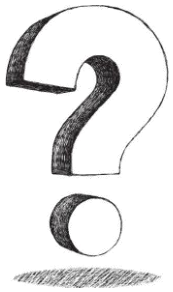
- Photocatalysis technology is considered as an effective way to alleviate energy crisis and environmental pollution.

- Based on these catalysts, the CO_2 can be converted into other chemical fuels, such as methane (CH_4) and carbinol (CH_3OH)

Challenges

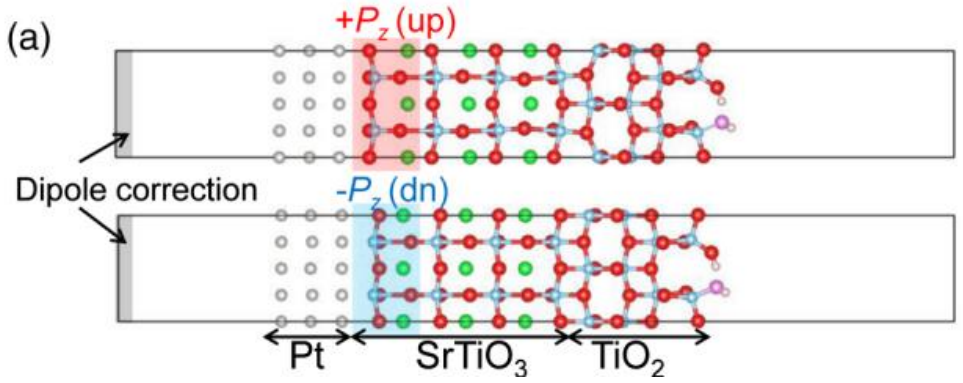
$$CO_2 + xH^+ + e^- \rightarrow CH_xO_y$$

- The ultrafast recombination of photogenerated electron-hole pairs
- Thermodynamically stable and structure inert of CO_2
- High C=O activation energy of ~750 kJ mol^{-1}
- Multiple proton coupled electron transfer process
- A wide variety of products with complex intermediates

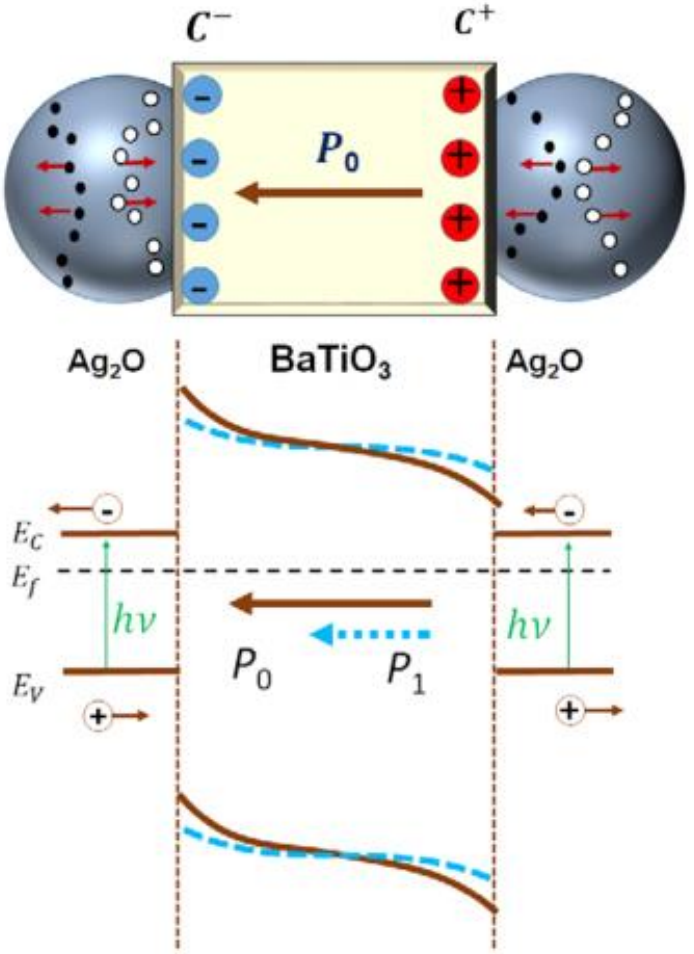


- Low energy conversion efficiency!
- Poor selectivity of reduction products!

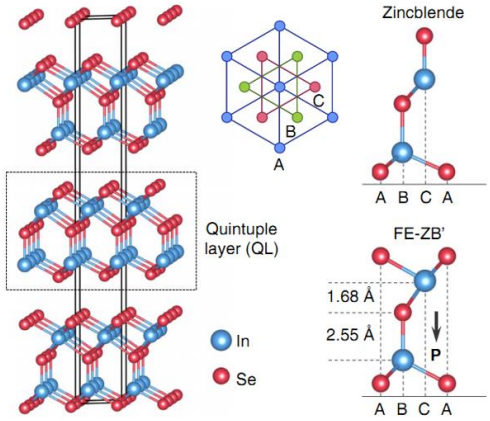
Research motivation



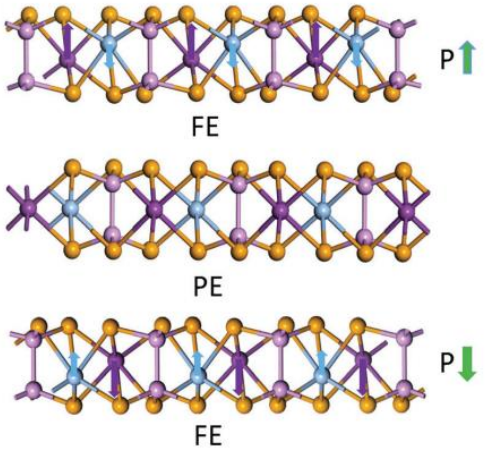
Phys . Rev. Lett. 2014,112, 196102



Nano Lett. 2015, 15, 2372 − 2379



Nature. Comm. 8, 14956 (2017)



Nanoscale, 9,8427 (2017)

- However, the coupling mechanism between ferroelectricity and photocatalysis remains unclear.

Ferroelectric polarization and single-atom catalyst synergistically promoting CO_2 photoreduction

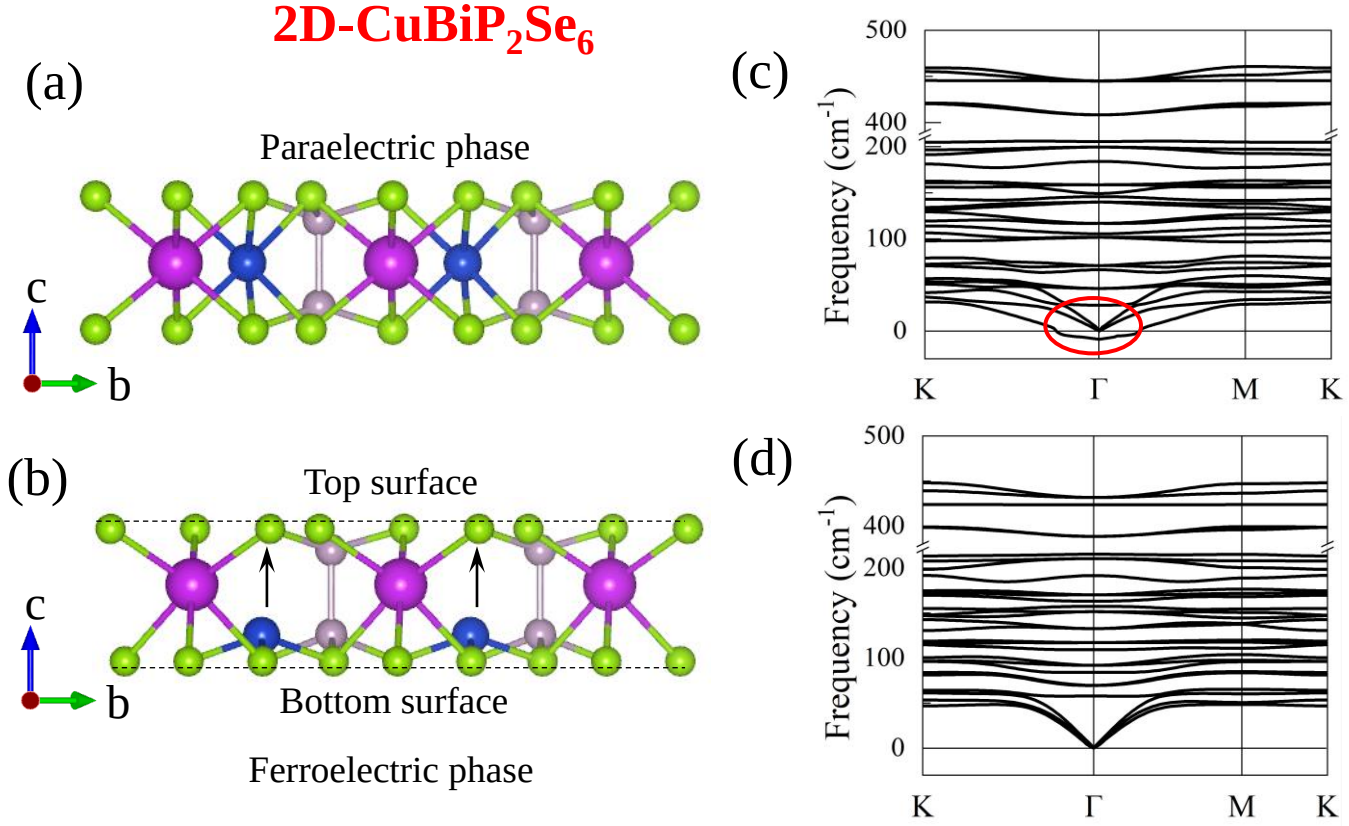
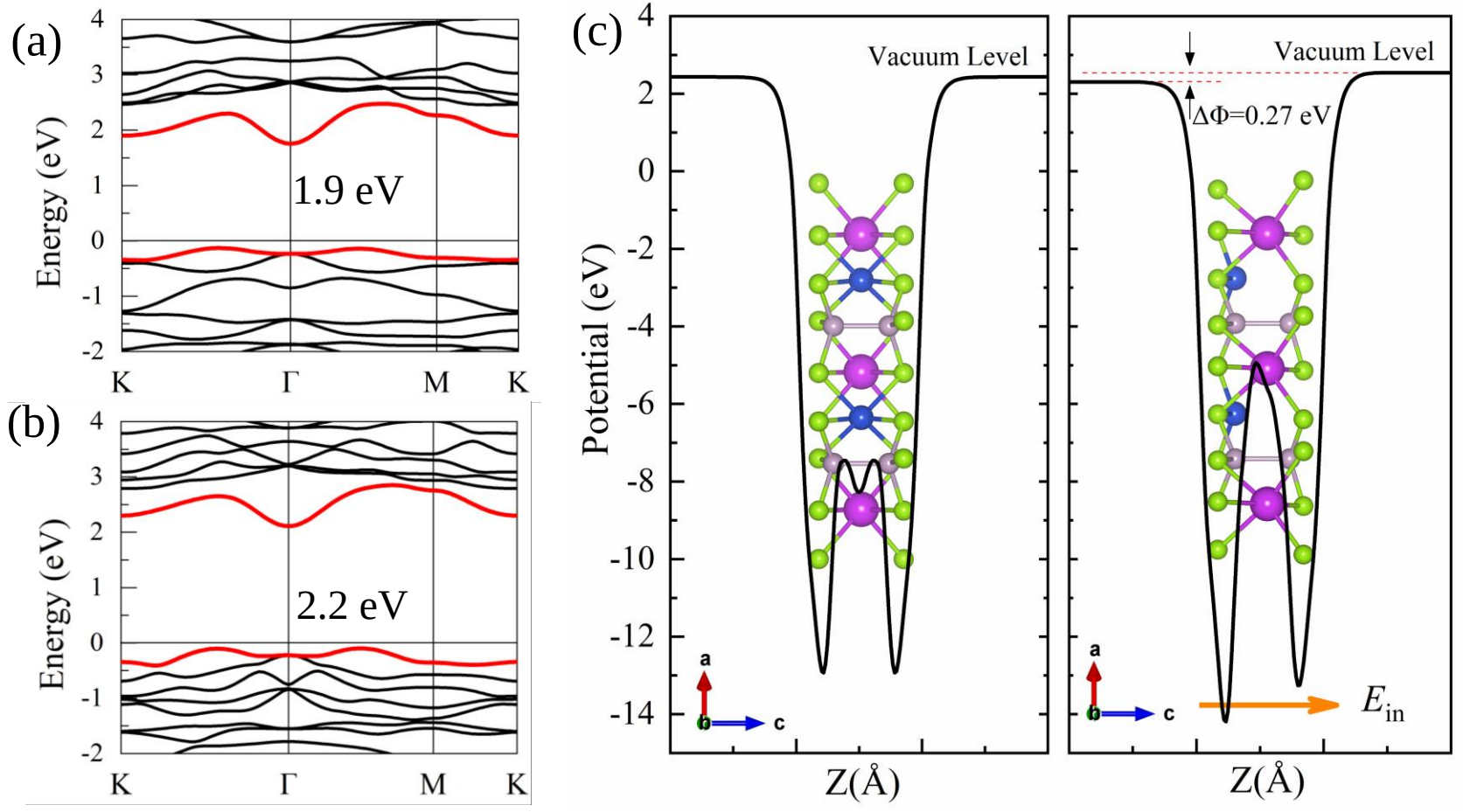


Table 1. Equilibrium lattice constants and space groups of 2D-$CuBiP_2Se_6$

	a (Å)	b (Å)	c (Å)	α	β	γ	Space group
PE-phase	6.54	6.54	25.00	90.00°	90.00°	120.00°	$R\bar{3}$
FE-phase	6.55	6.55	25.00	90.00°	90.00°	120.00°	$P3$

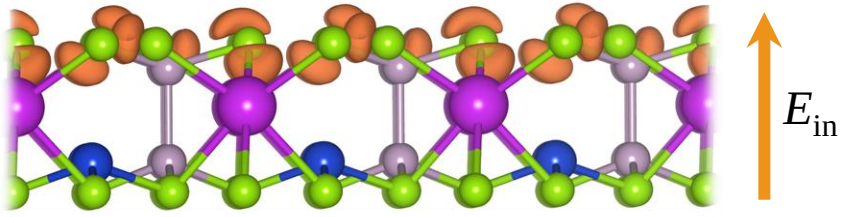
Electronic structure



- The PE and FE phases exhibit suitable bandgap and excellent semiconductor properties.
- The breaking of the inversion symmetry of the FE structure results in potential difference (ΔΦ) between the two surfaces, and cause an internal electric field.

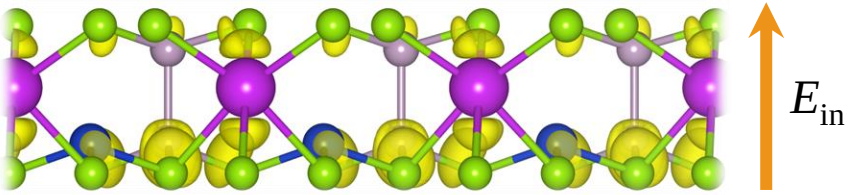
Carrier separation and CO_2 activation

(a) VBM holes



Partial charge density distribution

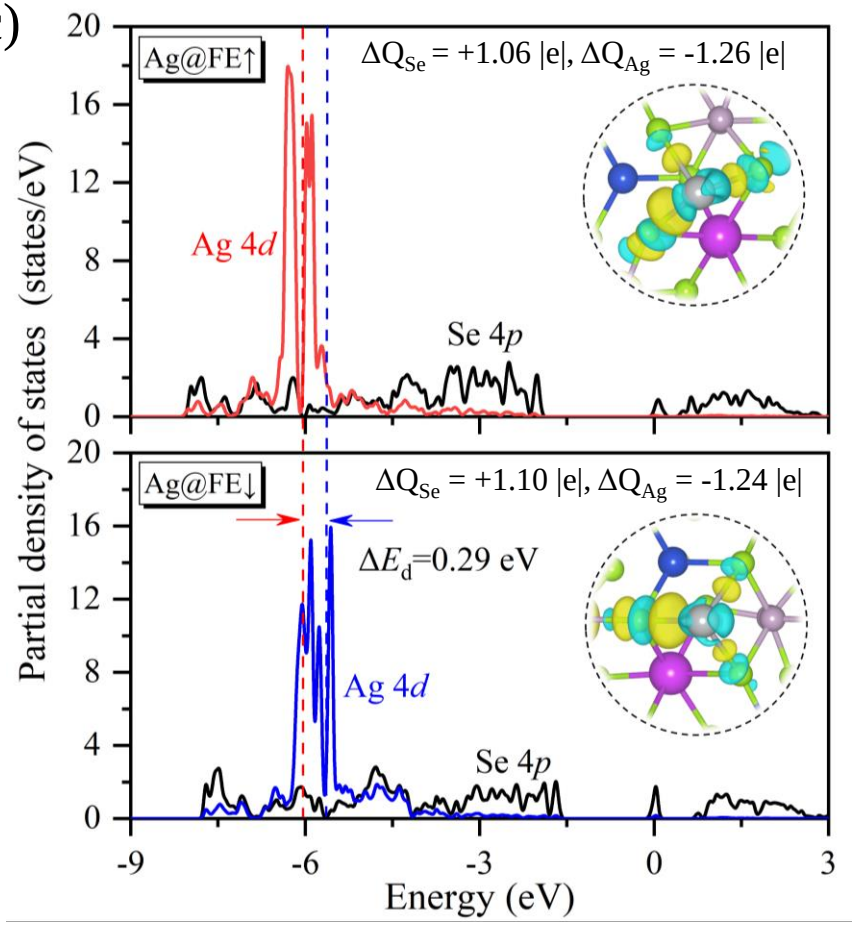
(b)



CBM electrons

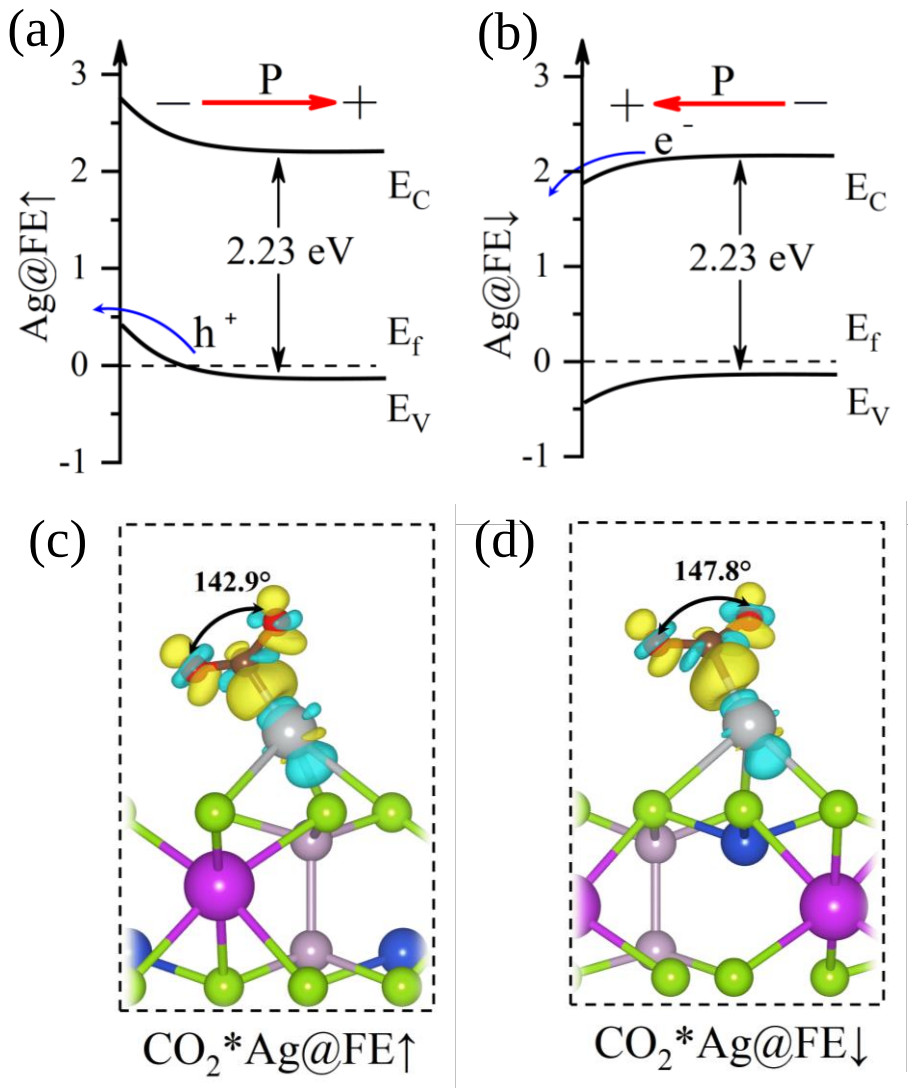
The isosurface value was set to 0.006 eÅ $^{-3}$

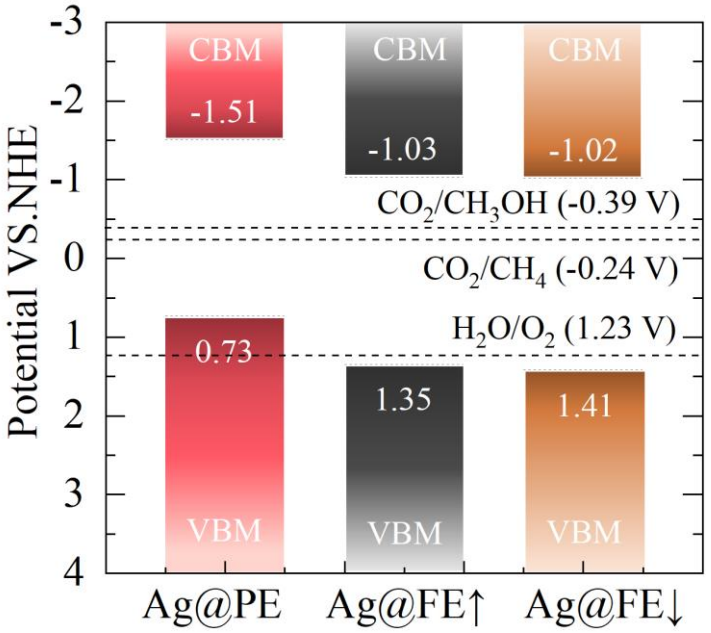
(c)



- Photogenerated carriers will transfer in the opposite direction, and the holes tend to accumulate on the top surface, while the electrons tend to accumulate on bottom surface.

Electronic structure and band edge position





@NHE电位:

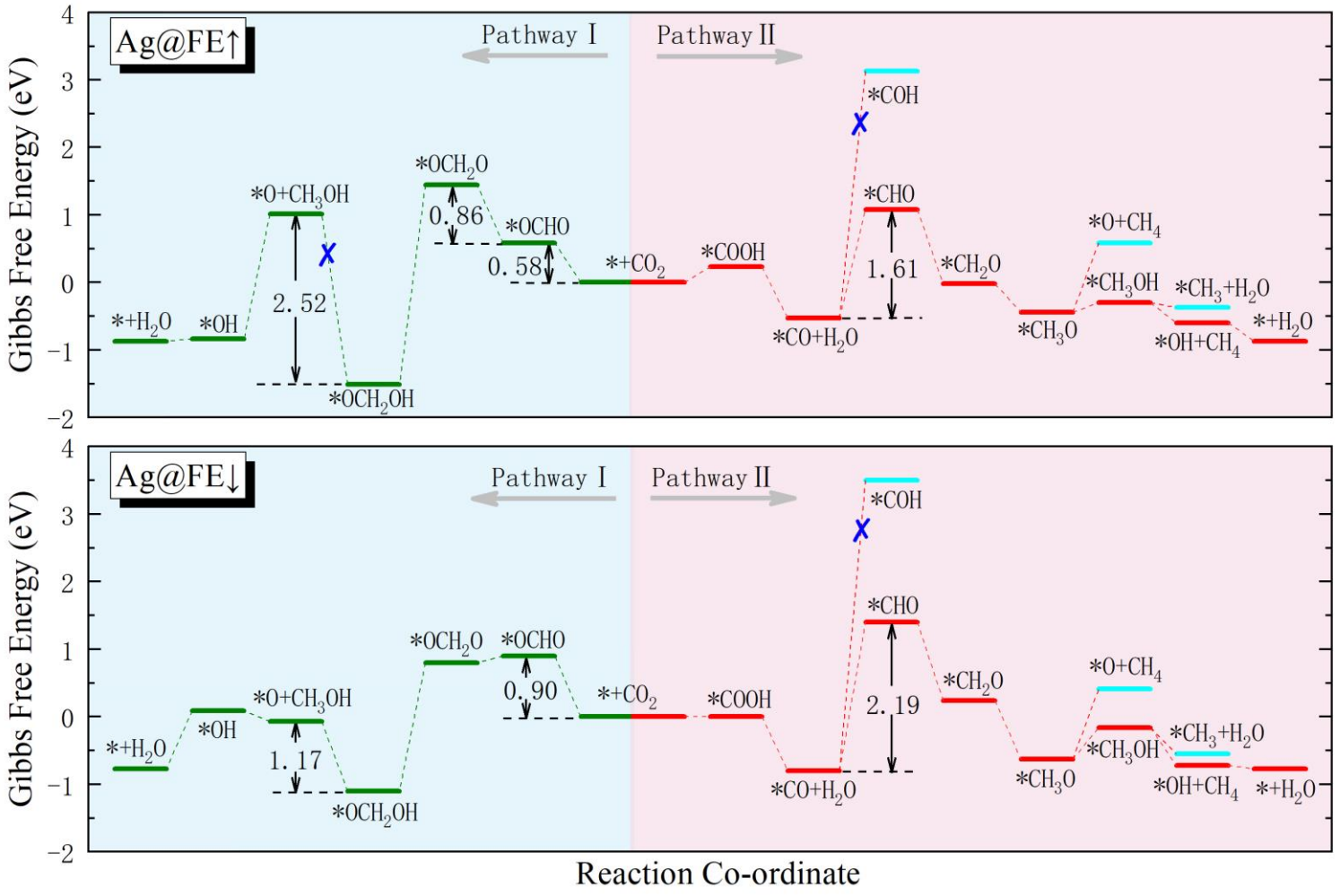
$H_2O \rightarrow O_2$ = 1.23 V;

$CO_2 \rightarrow CH_4$ = -0.24 V;

$CO_2 \rightarrow CH_3OH$ = -0.39 V;

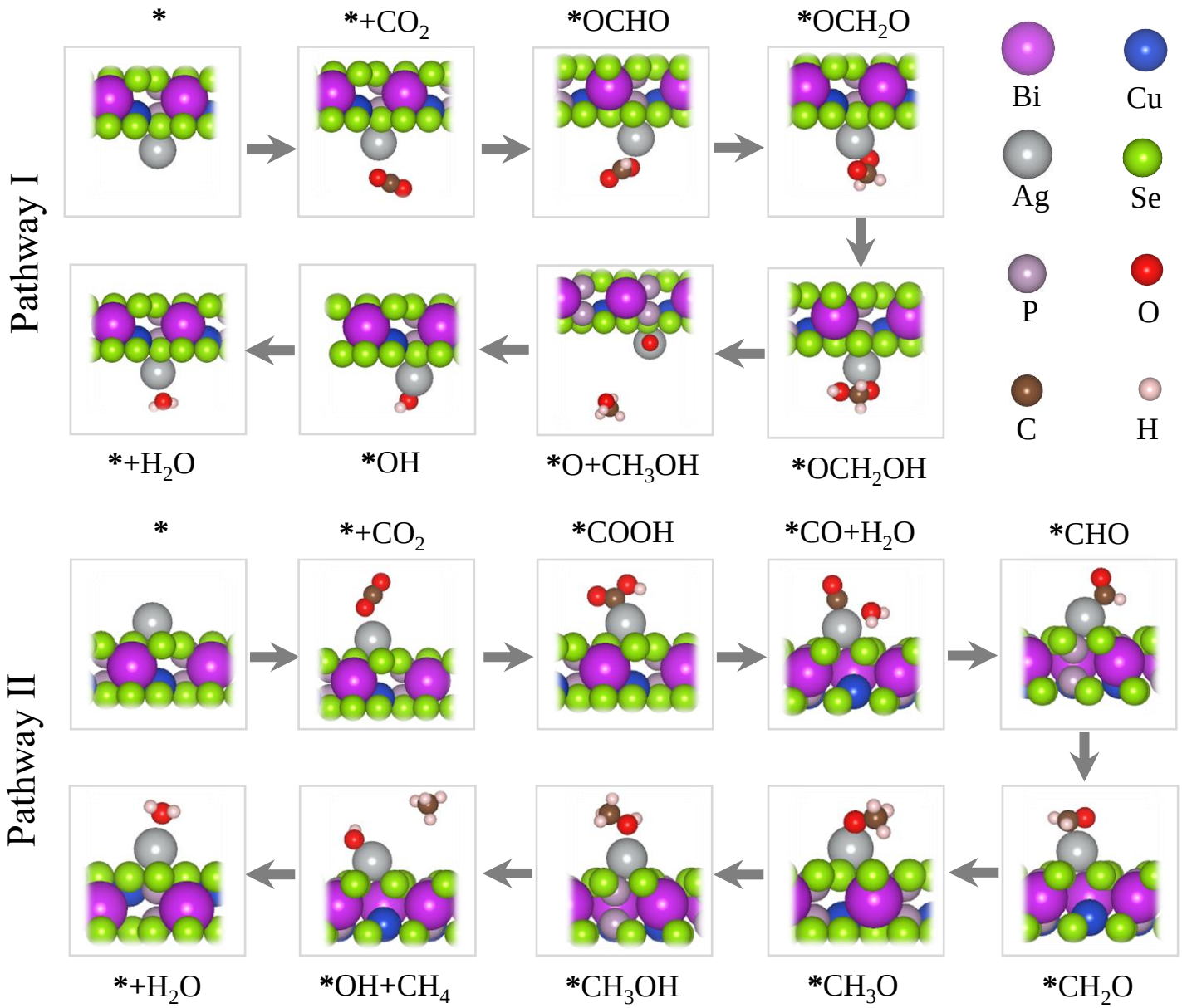
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$ (activation)

Different reaction pathways for CO_2 reduction



- Interestingly, we found that switching ferroelectric polarization can regulated the reaction path and the final product.

Optimized configurations of the intermediates



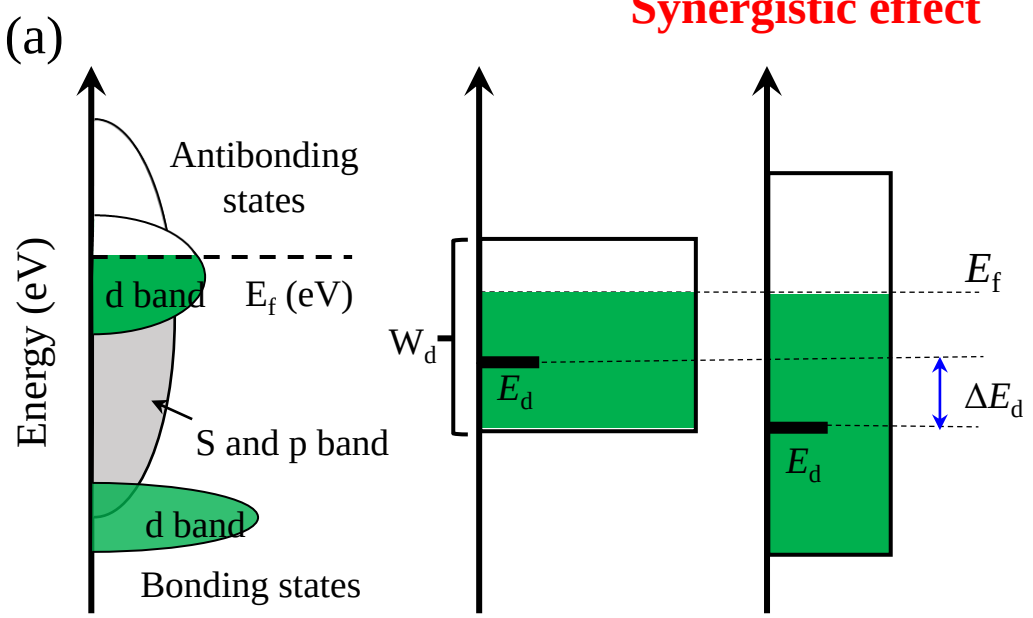
Some key information of the intermediate

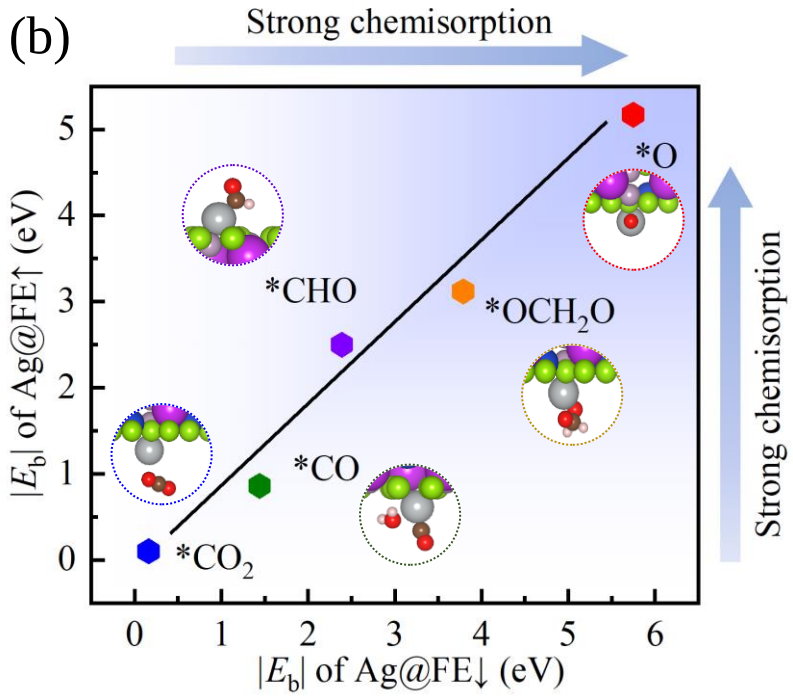
Table 2. Binding energy (E_b), charge transfer (ΔQ), average bond length ($d_{Ag\text{-}Se}$ or $d_{Ag\text{-}IP}$), and *d*-band center (E_d)

	E_b (eV)	ΔQ_{Se} (e)	ΔQ_{Ag} (e)	ΔQ_{IP} (e)	$d_{Ag\text{-}Se}$ (Å)	$d_{Ag\text{-}IP}$ (Å)	E_d (eV)
CO_2*Ag@FE↑	-0.10	1.08	-1.38	0.29	2.84	1.70	-5.85
CO_2*Ag@FE↓	-0.16	1.08	-1.34	0.28	2.87	1.94	-4.69
CO*Ag@FE↑	-0.86	1.12	-1.40	0.11	2.81	2.05	-6.58
CO*Ag@FE↓	-1.44	1.16	-1.38	0.14	2.94	2.09	-5.46
CHO*Ag@FE↑	-2.39	1.01	-1.21	0.16	2.95	2.13	-4.55
CHO*Ag@FE↓	-2.50	1.01	-1.21	0.19	2.81	2.12	-4.84
OCH_2O*Ag@FE↑	-3.12	0.78	-1.46	0.64	3.21	2.09	-4.18
OCH_2O*Ag@FE↓	-3.79	0.95	-1.45	0.66	3.37	2.28	-4.03
O*Ag@FE↑	-5.17	0.32	-1.40	0.89	2.81	2.14	-5.81
O*Ag@FE↓	-5.75	0.31	-1.43	0.87	3.05	2.21	-4.10

d-band center and binding energy

Synergistic effect

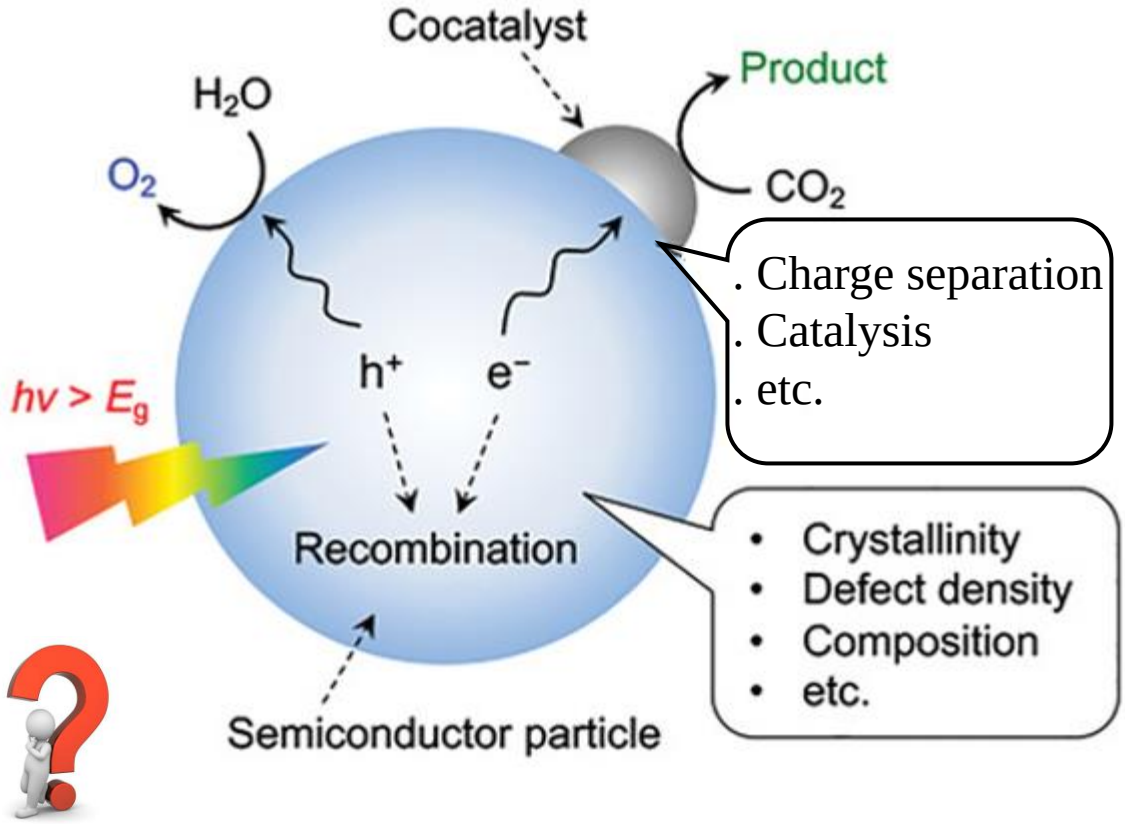




Bond length → Strong coupling → W_d → E_d → Weak chmisorption

- Switching ferroelectric polarization can cause some microscopic changes, especially in the average bond length and *d*-band center.
- The bottom surface can provide more electrons to the intermediate and make it easier to be reduction.

Photoexcited Carrier Dynamic



The entire photocatalytic reaction involves three steps:

(I) Photogenerated carriers.

(II) Carriers separate and transfer from the inside to the surface of the photocatalyst.

(III) The electrons reduce CO_2 into value-added fuels and chemicals, and holes oxidize sacrificial reagents.

- Among them, Step-II is the most critical step, which is also a key factor restricting the efficiency. Therefore, it is very important to explore the carrier transfer and recombination mechanism to improve the photocatalytic efficiency.

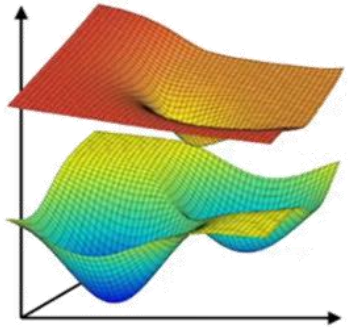
Calculation method

b-initio VASP package ienna imulation

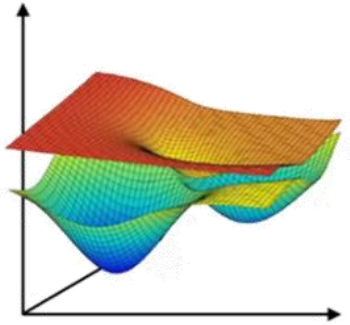
Virtual NanoLab

accelrys MATERIALS STUDIO

Non-adiabatic Molecular Dynamics (NAMD)



波恩-奥本海默 近似



Beyond 波恩-奥本海默 近似

非绝热动力学, 电子和原子核相互间强耦合

Non-Adiabatic MD & Real-Time TDDFT

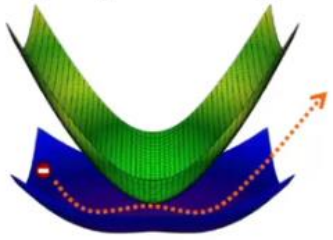
pyxaid

Python e**X**tension of **Ab** **I**nitio **D**ynamic (**PYXAID**)

University of Southern California, Prof. Oleg V. Prezhdo

- 平均场 Mean field (MF):

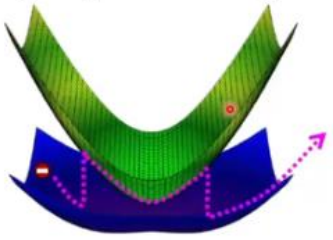
$$\frac{\partial|\psi\rangle}{\partial t}=\frac{\mathbf{H}|\psi\rangle}{i\hbar} \qquad m_i\ddot{x}_i=-\frac{\partial\langle\psi|\mathbf{H}|\psi\rangle}{\partial x_i}$$



Ehrenfest Dynamics
Ehrenfest, Z. Phys. 45, 445 (1927)

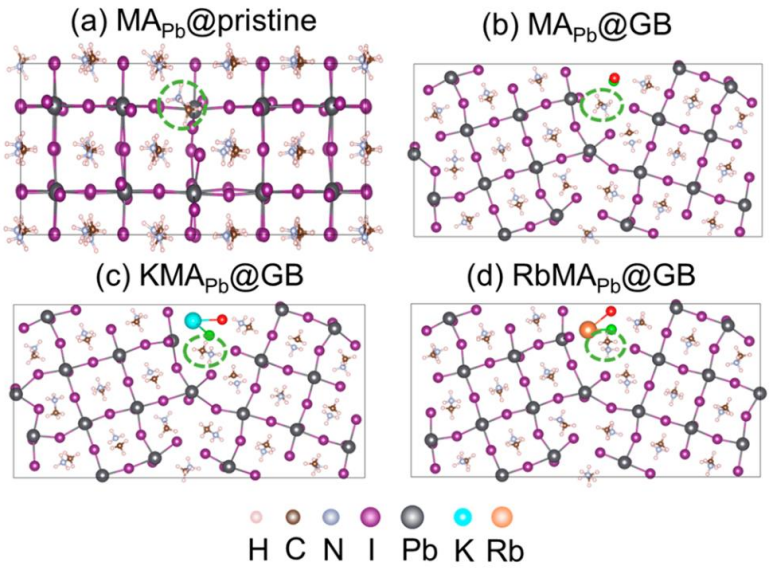
- 面跳跃 Surface hopping (SH):

$$\frac{\partial|\psi\rangle}{\partial t}=\frac{\mathbf{H}|\psi\rangle}{i\hbar} \qquad m_i\ddot{x}_i=-\frac{\partial\langle\psi_k|\mathbf{H}|\psi_k\rangle}{\partial x_i}$$

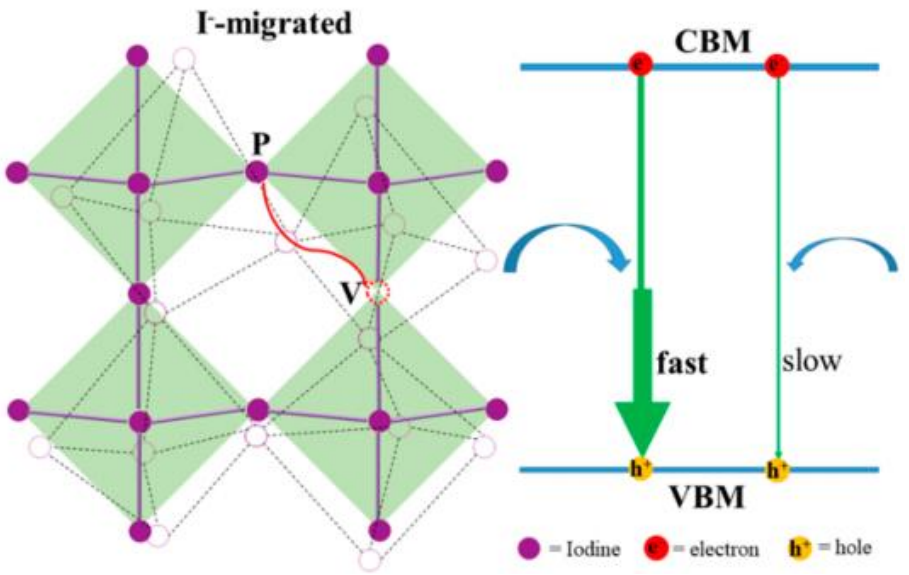


Surface Hopping
Tully, J. Chem. Phys. 93, 1061 (1990)

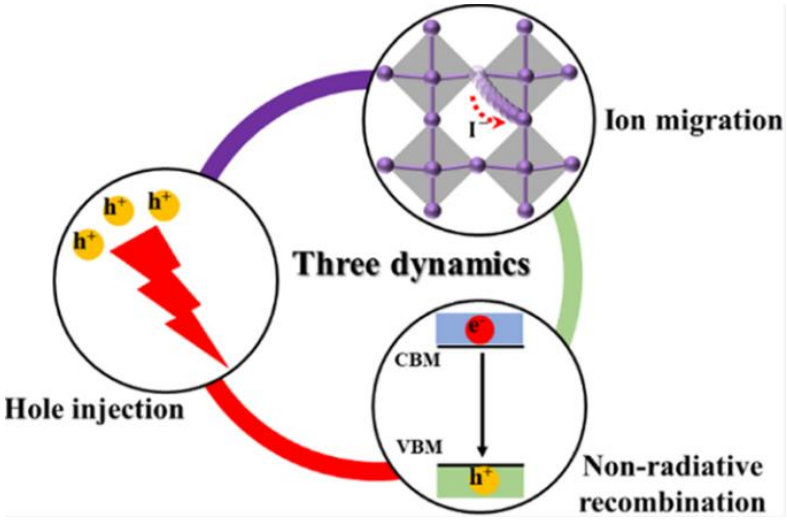
Calculation method



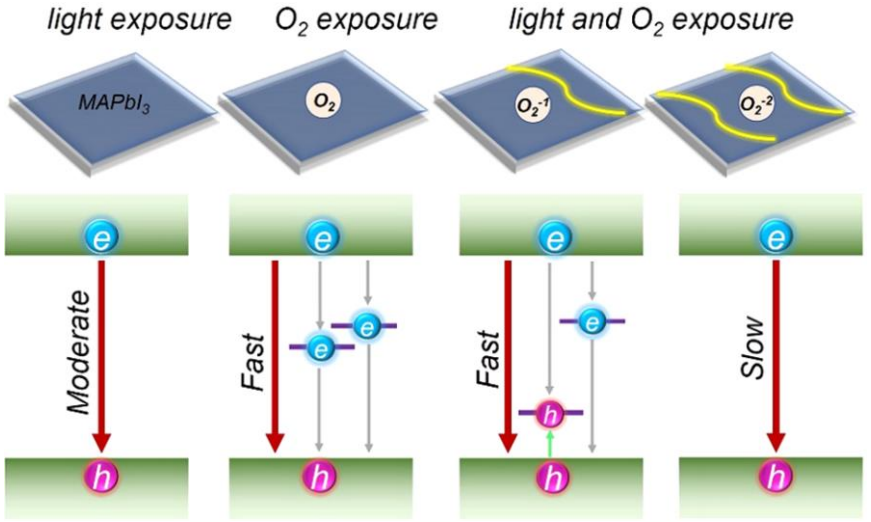
ACS Energy Lett. 2020, 5, 3813−3820



J. Am. Chem. Soc. 2020, 142, 3060−3068



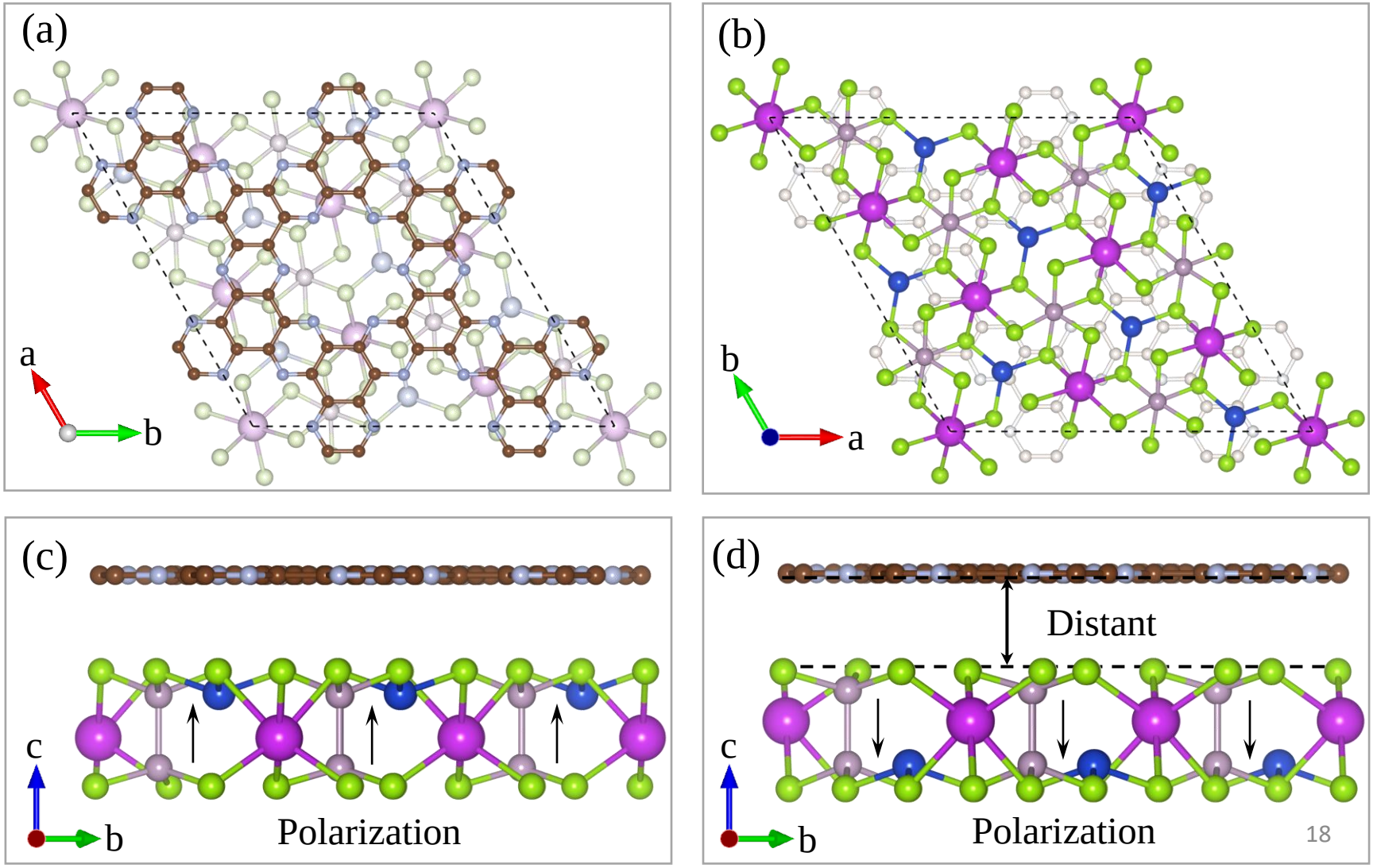
J. Am. Chem. Soc. 2022, 144, 6604−6612



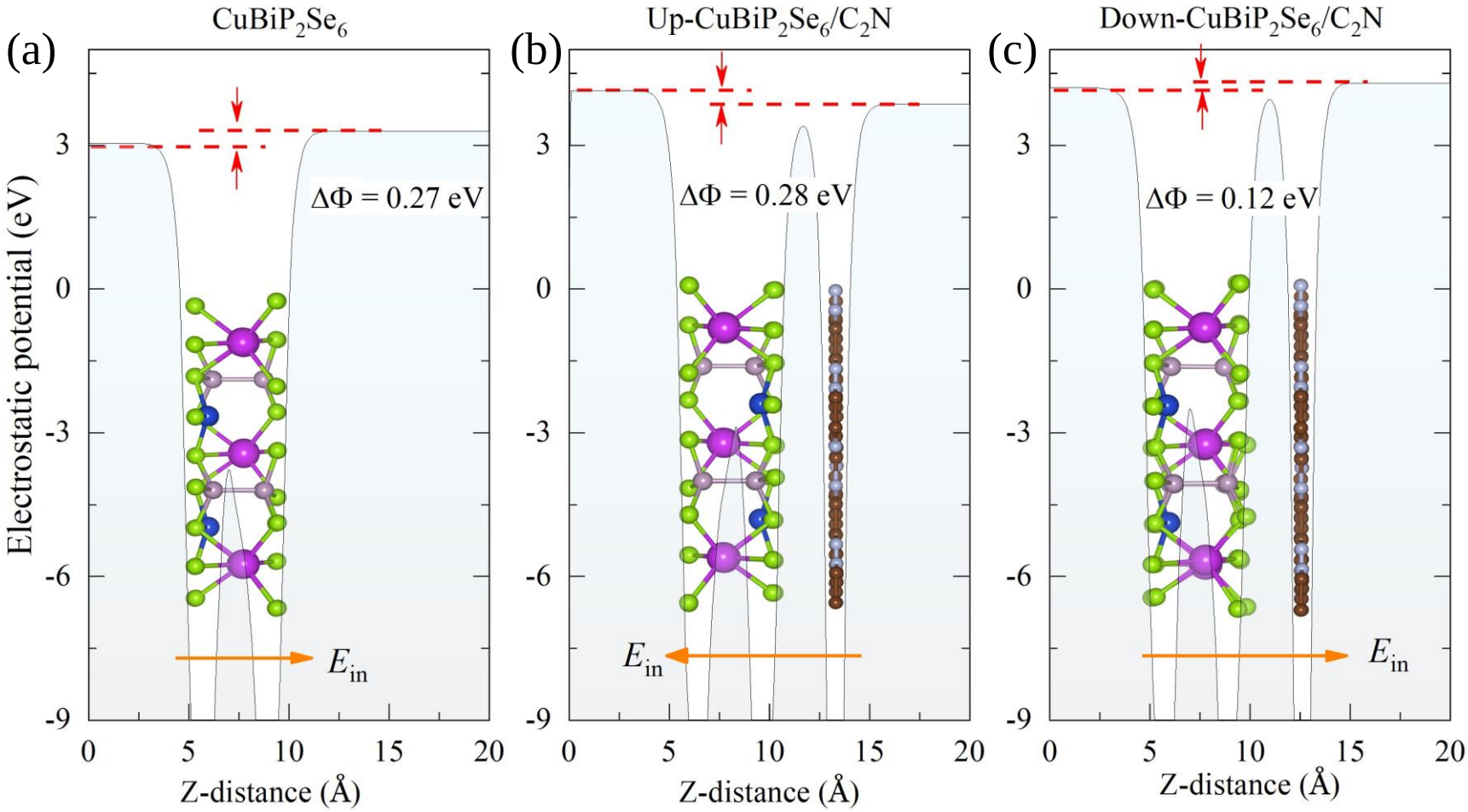
J. Am. Chem. Soc. 2020, 142, 14664−14673

Improved carrier separation by ferroelectric polarization in $CuBiP_2Se_6/C_2N$ heterostructure: a non-adiabatic molecular dynamics study

$CuBiP_2Se_6/C_2N$ heterostructure

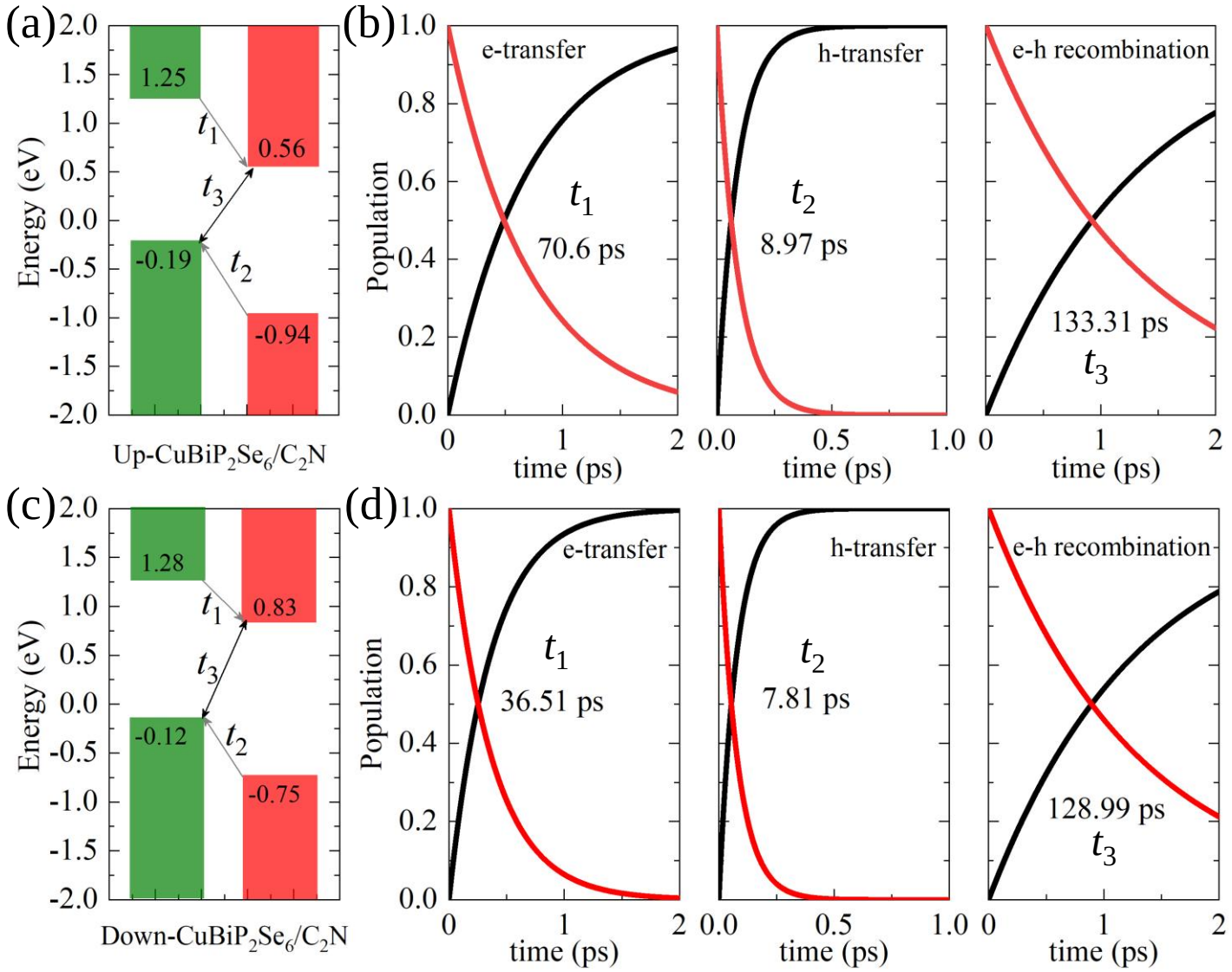


Average electrostatic potential



- The intrinsic polarization result in an electrostatic potential difference (ΔΦ) between the two surfaces within the heterostructure.

Band alignment and transfer mechanism



- **type-II:**

$t_1 < t_3$

$t_2 < t_3$

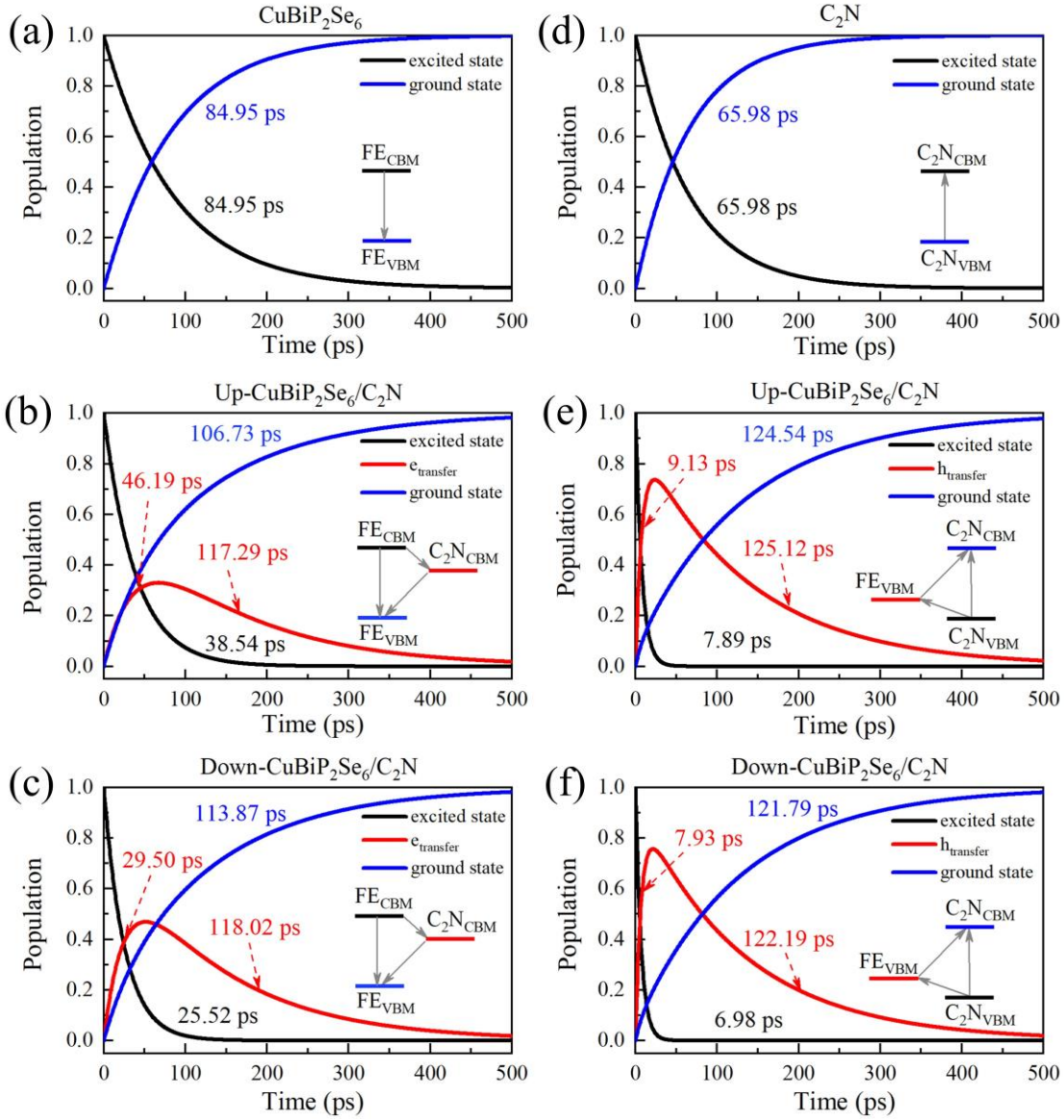
Can avoid the quantum annihilation process

- **Z-scheme:**

$t_1 > t_3$

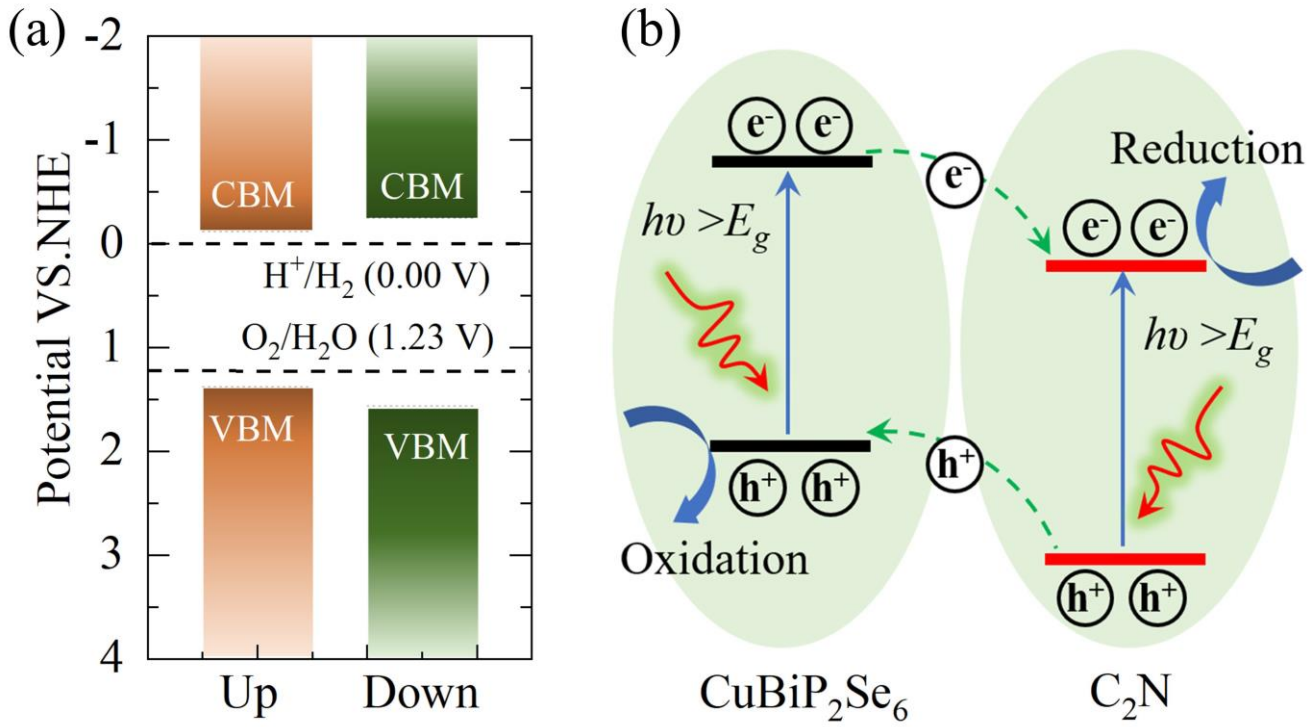
$t_2 > t_3$

Charge transfer and recombination dynamics



- We found that the carrier lifetime can be increased from ~70 ps to ~120 ps by constructing heterostructure.
- Small overlap of the wave functions between VBM and CBM

Band edge position and schematic diagram



- In summary, due to the $CuBiP_2Se_6/C_2N$ heterostructure has a suitable band edge potential, efficient type-II transfers mechanism and long carrier lifetime. We believe that $CuBiP_2Se_6/C_2N$ heterostructure may be an excellent photocatalysts for water splitting.

Summary

- We have revealed the microscopic relationship between ferroelectricity and photocatalytic performance in the $Ag@CuBiP_2Se_6$ system.
- We have proposed strategies to optimize the photocatalytic reaction path and control the final products by switching the ferroelectric polarization.
- We have elucidated the excited state carrier transfer and recombination mechanism in $CuBiP_2Se_6/C_2N$ heterostructure.

Acknowledgements

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Prof. Jiang Zeng (Hunan University, Formal analysis)

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Group Members:

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Dr. Yueshao Zheng (Hunan University, Formal analysis)

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Thank you for your time and attention today!