Theoretical studies in solar energy materials

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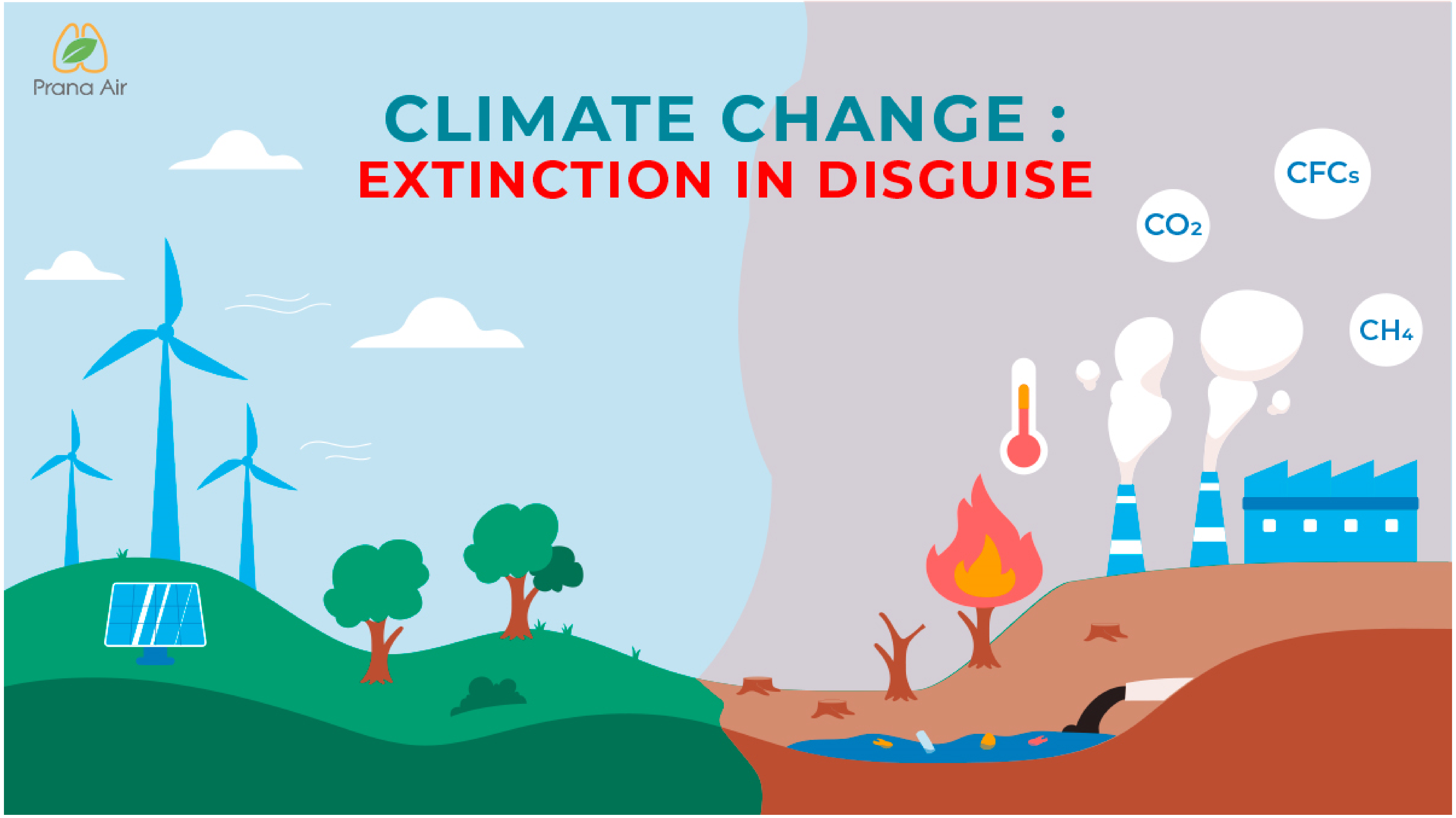
MIEM, HSE University

NATIONAL RESEARCH UNIVERSITY

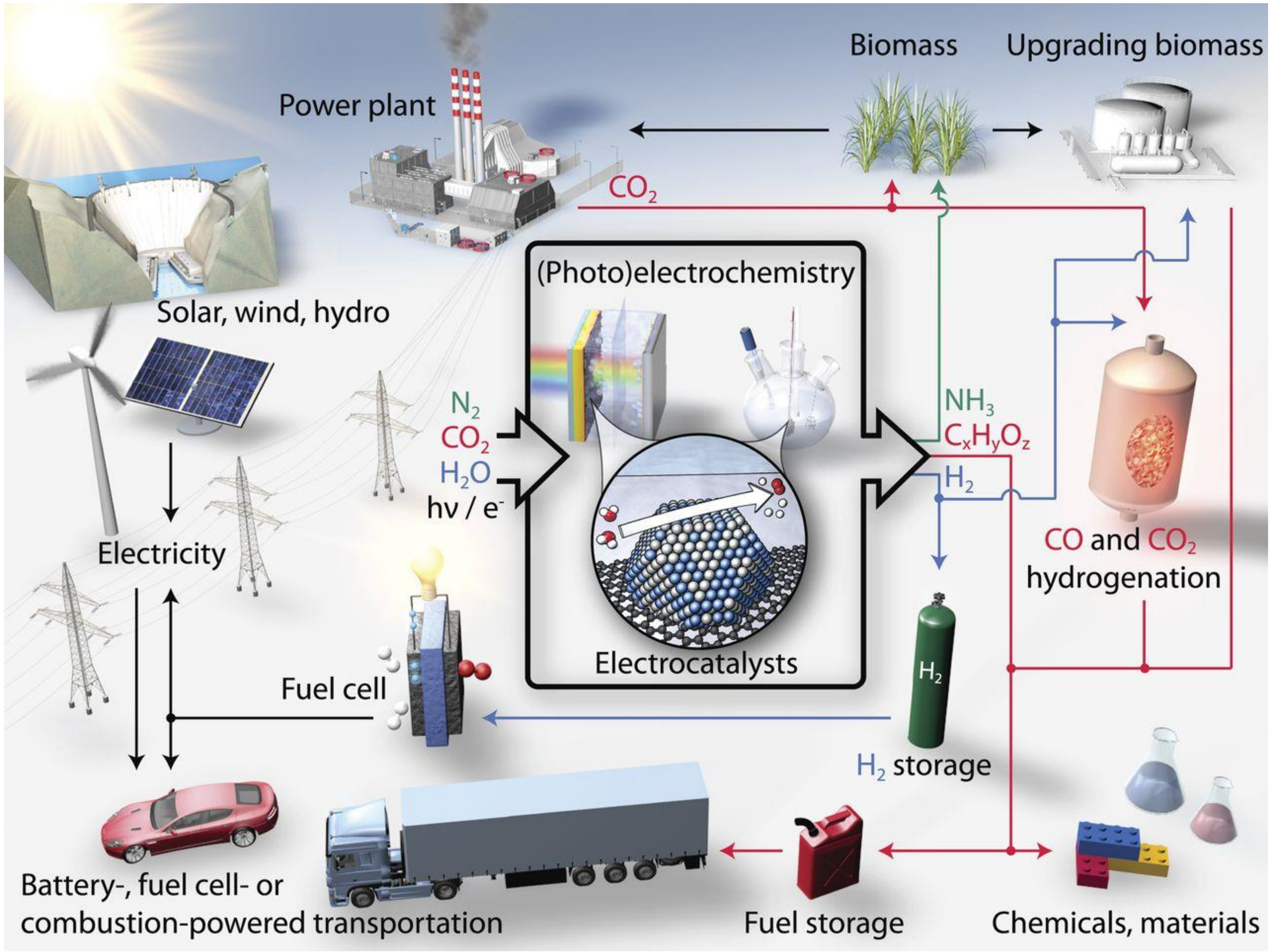
OUTLINE

1. The background of solar energy utilization
2. How theoretical approaches contribute to these topics
3. Our collaborative work on solar energy materials
4. Our theoretical work on perovskites

THE USAGE OF FOSSIL FUELS

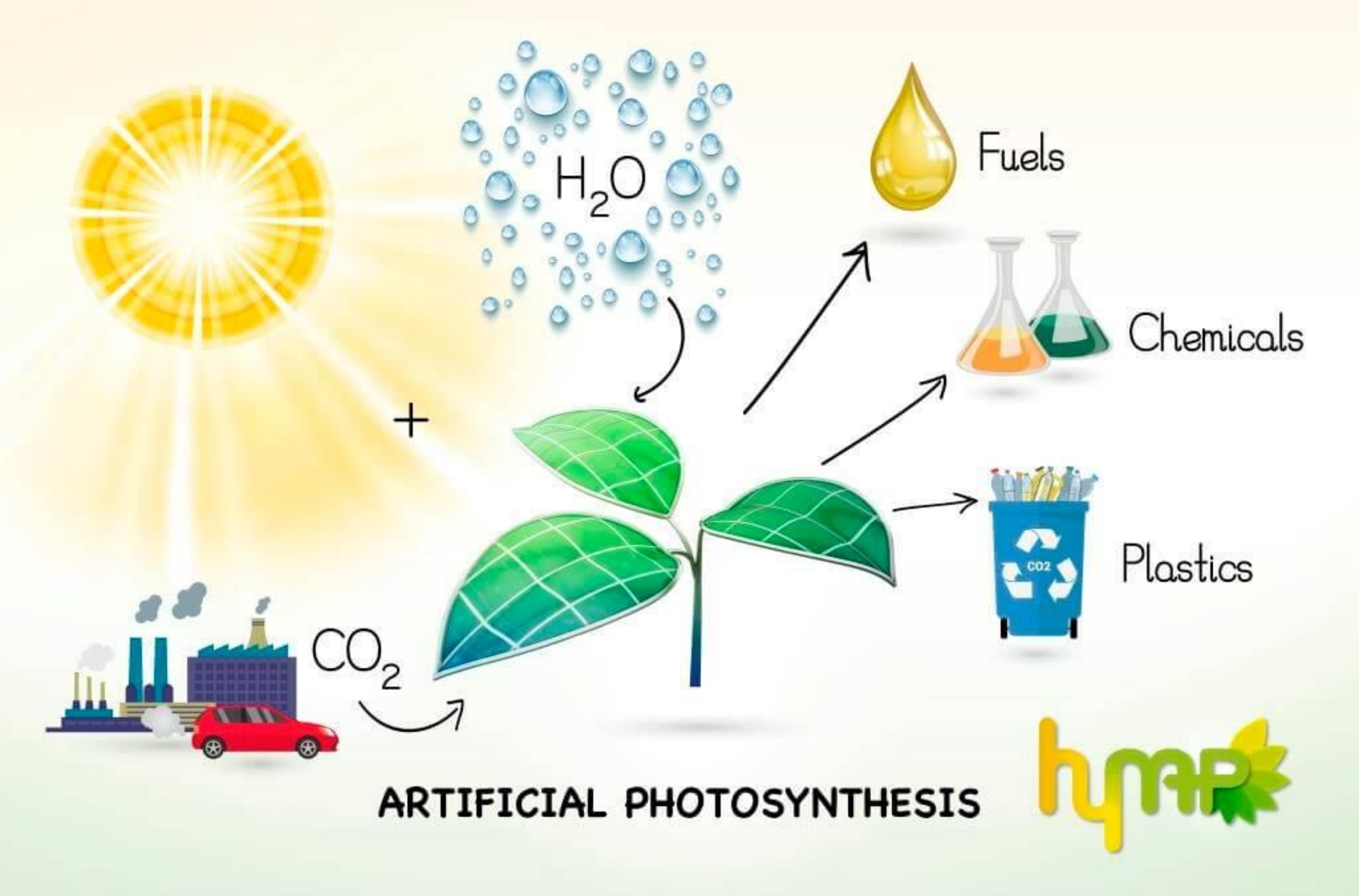


A ROADMAP OF RENEWABLE ENERGY INDUSTRY: COMPATIBLE WITH FOSSIL FUELS



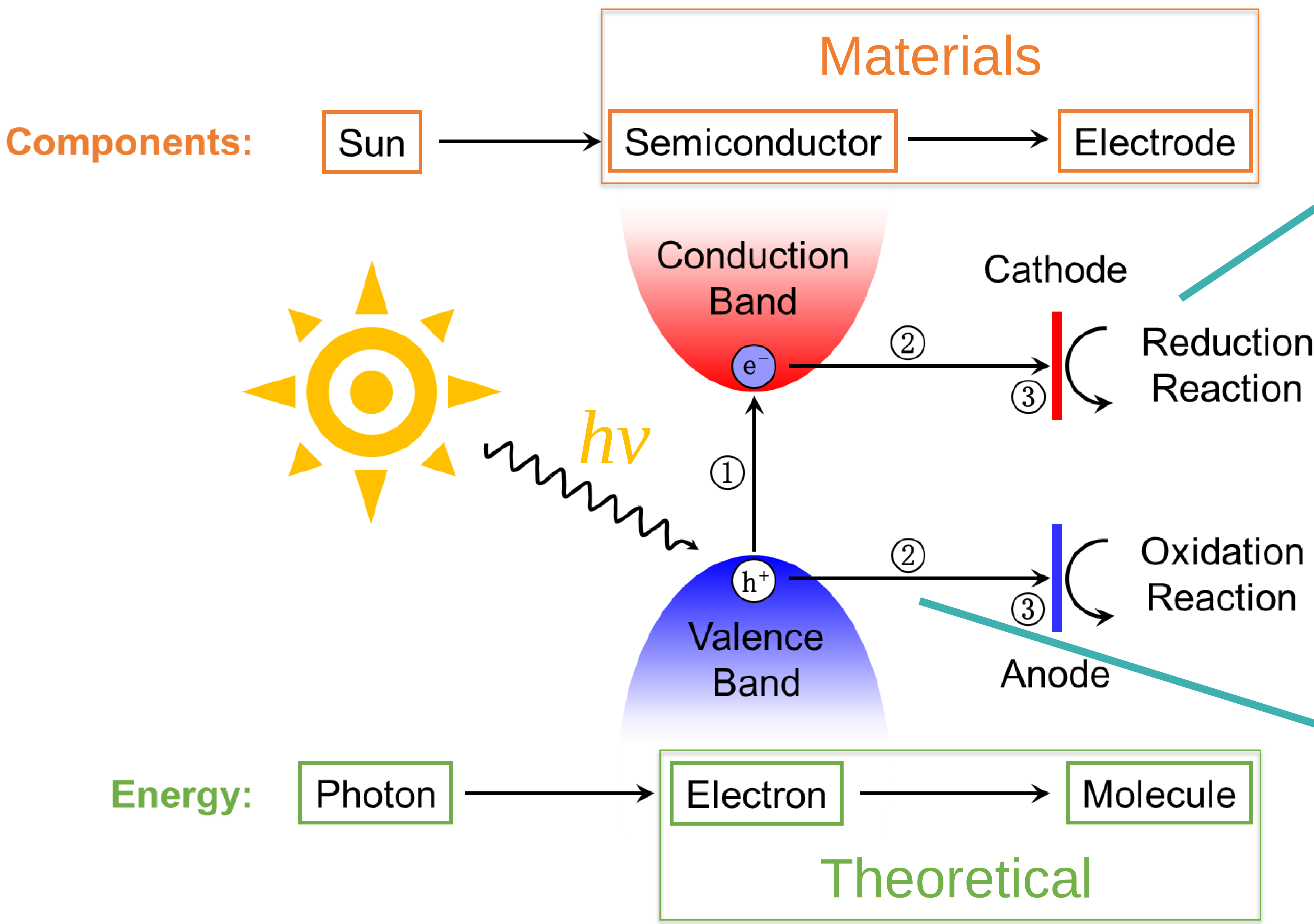
Seh Z W, Kibsgaard J, Dickens C F, et al. Science, 2017, 355(6321): eaad4998.

ARTIFICIAL PHOTOSYNTHESIS

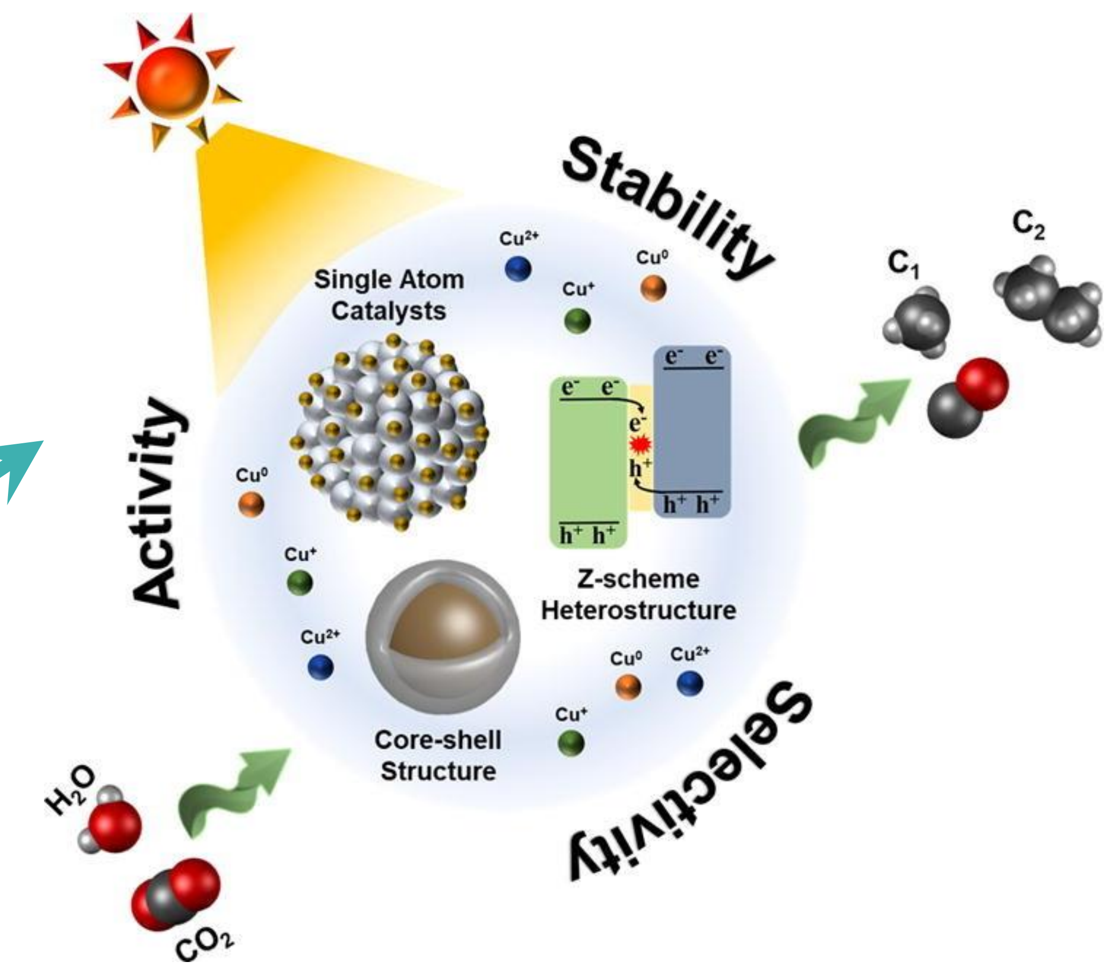


https://www.globalengineering.info/artificial-photosynthesis/

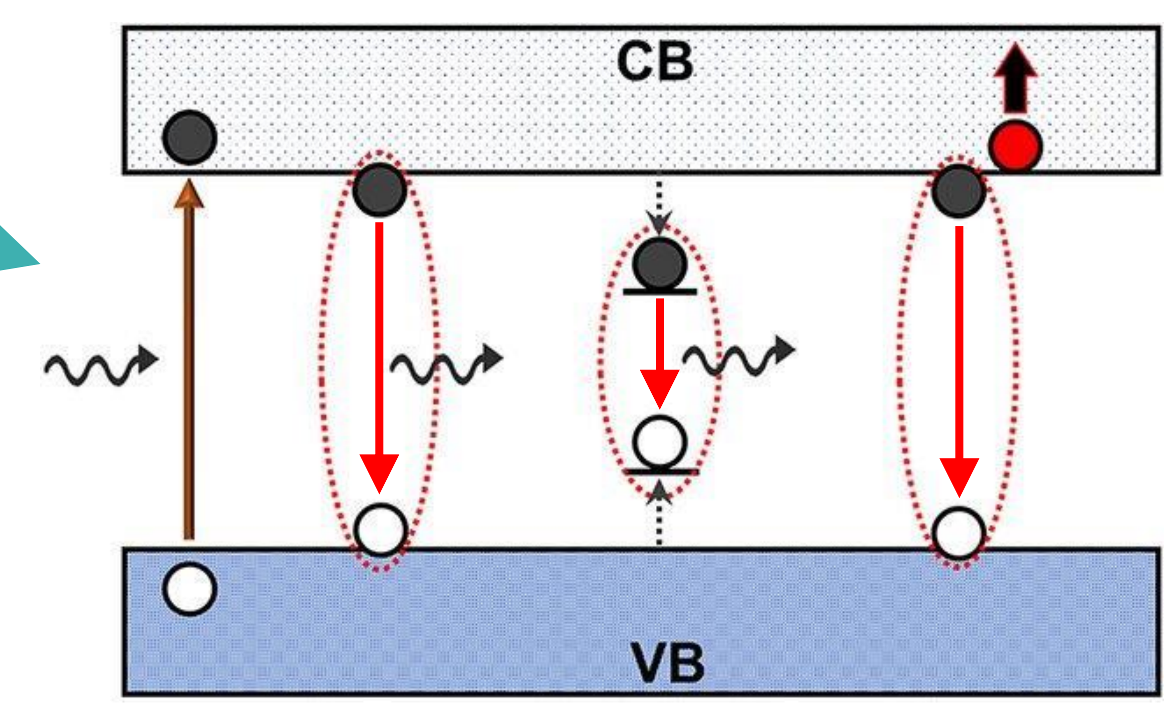
THEORETICAL ANALYSIS



Energy loss: Overpotential, selectivity



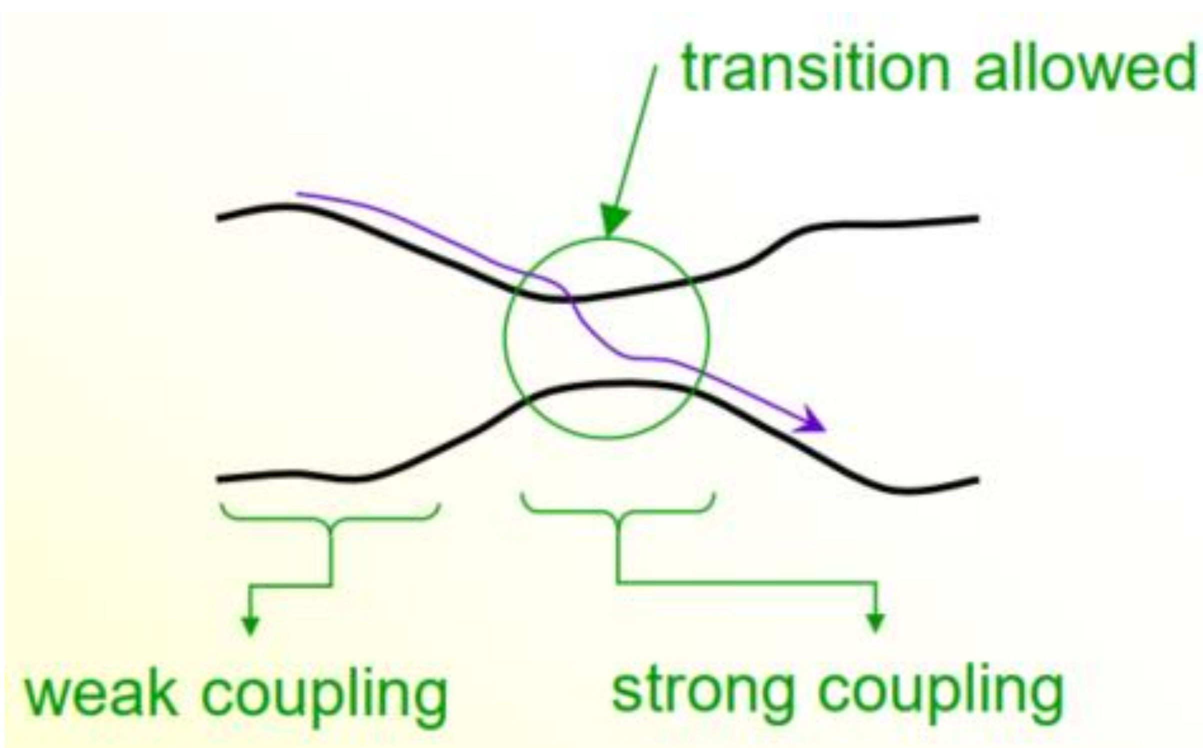
Energy loss: Carrier recombination



https://doi.org/10.1016/j.cej.2021.131579, https://doi.org/10.1515/nanoph-2020-0484

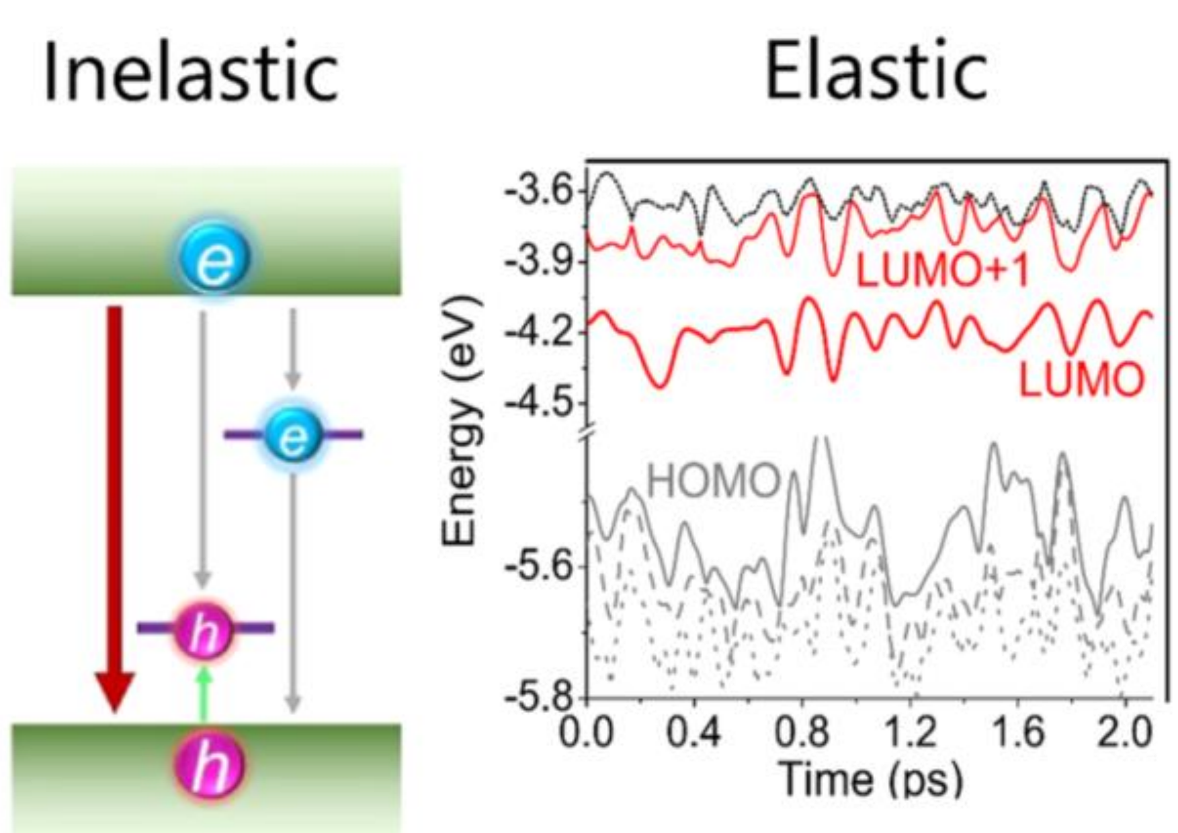
THEORETICAL ANALYSIS

Carrier recombination

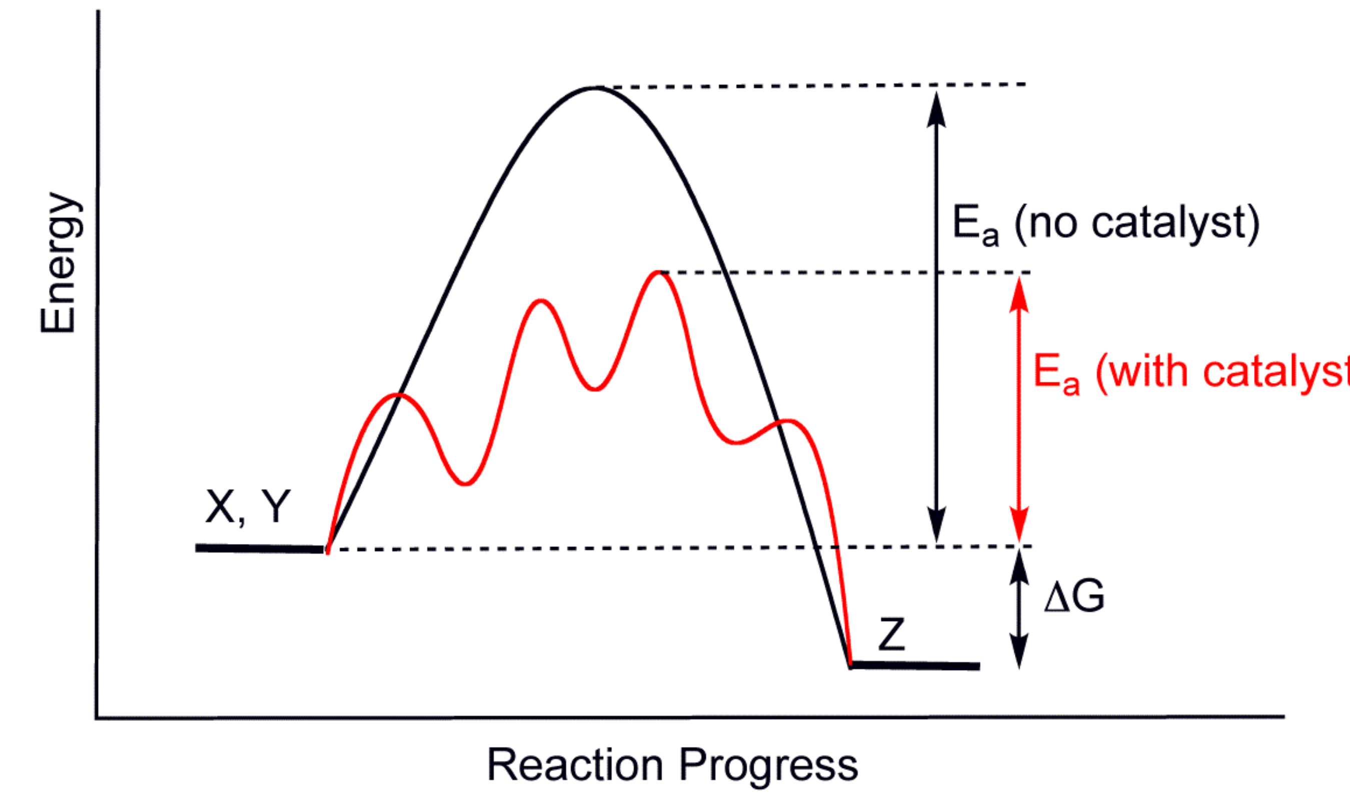


Non-adiabatic molecular dynamics

Electronic structure

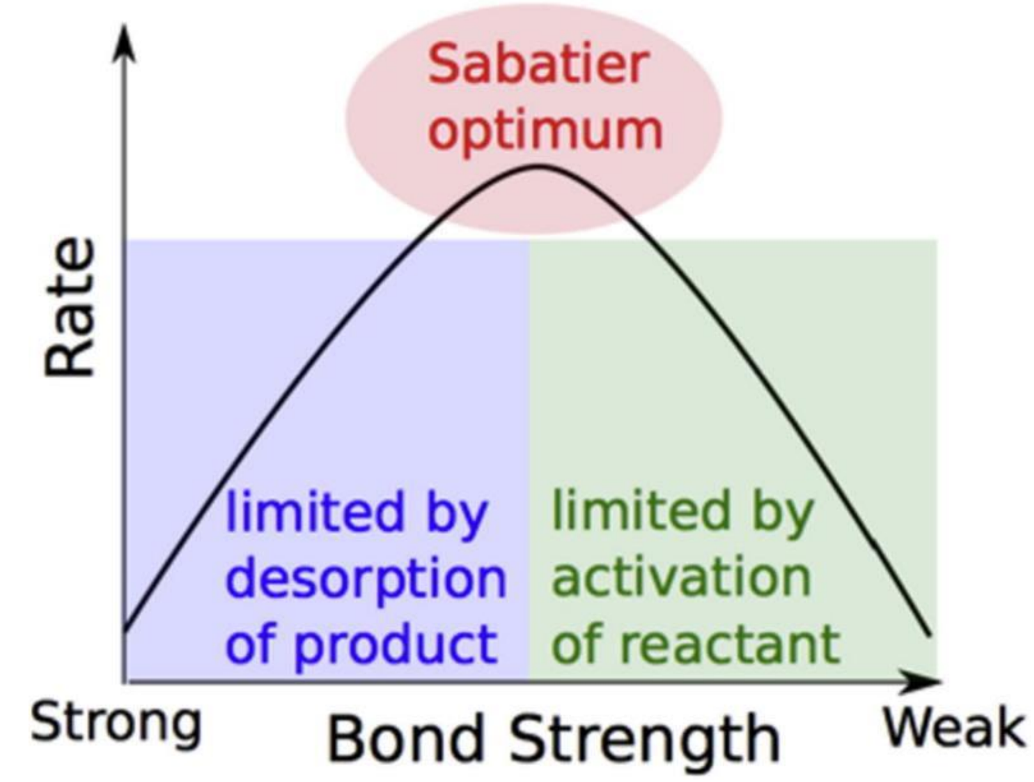


Catalytic reaction



Thermodynamics models

Total energy



https://doi.org/10.1021/acs.accounts.1c00525, Wikipedia, https://doi.org/10.1016/j.jcat.2014.12.033

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SCHRÖDINGER EQUATION

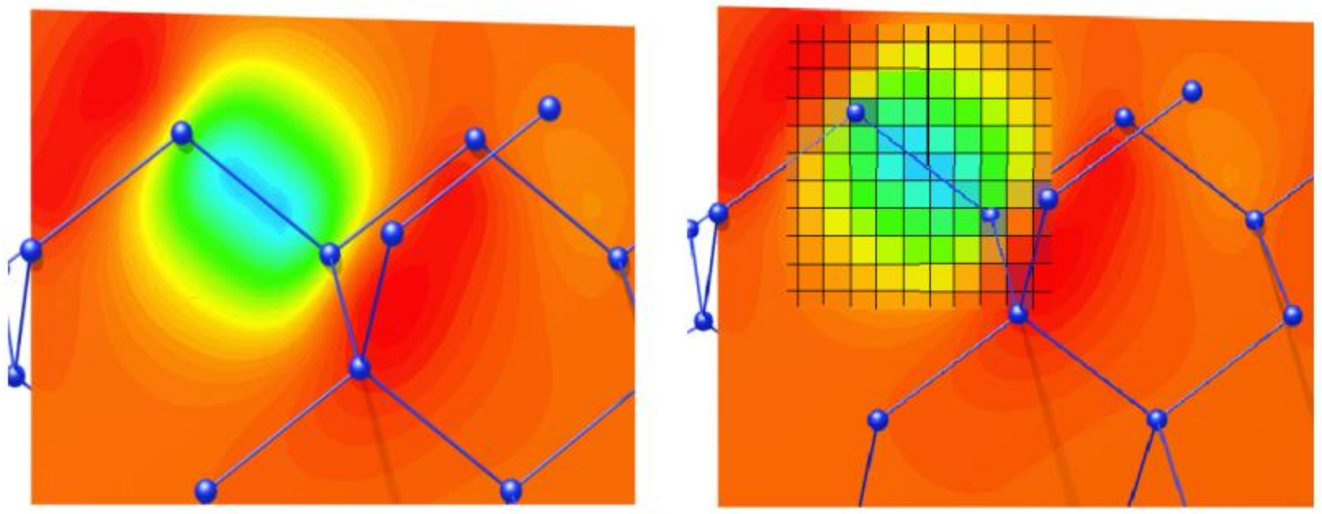
The Many-Body Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\left(-\frac{1}{2}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

For instance, many-body WF storage demands are prohibitive:

$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ $\quad$ $(\#\text{grid points})^N$



5 electrons on a 10×10×10 grid ~ 10 PetaBytes !

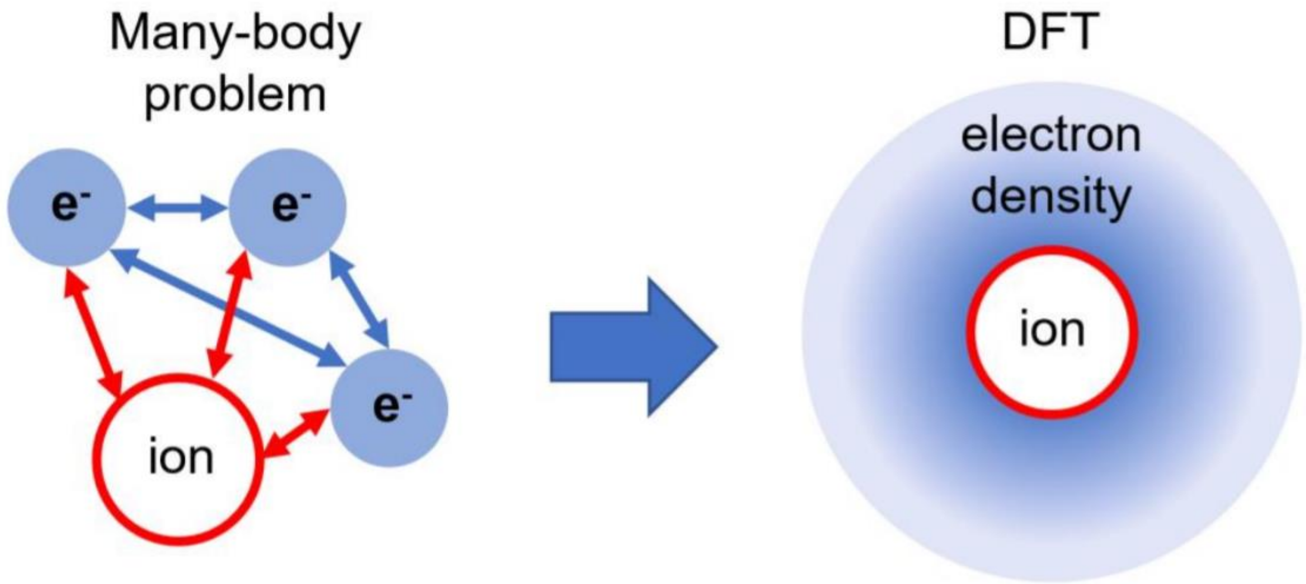
A solution: map onto “one-electron” theory:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\}$$

Erwin Schrödinger
Nobel Prize in Physics
(1933)

https://www.vasp.at/wiki/images/5/5d/VASP_lecture_Basics.pdf

DENSITY FUNCTIONAL THEORY



Hohenberg-Kohn-Sham DFT

Map onto “one-electron” theory:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \ldots, \psi_N(\mathbf{r})\} \qquad \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i)$$

Total energy is a functional of the density:

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\mathrm{xc}}[\rho] + E_Z[\rho] + U[Z]$$

The density is computed using the one-electron orbitals:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

The one-electron orbitals are the solutions of the Kohn-Sham equation:

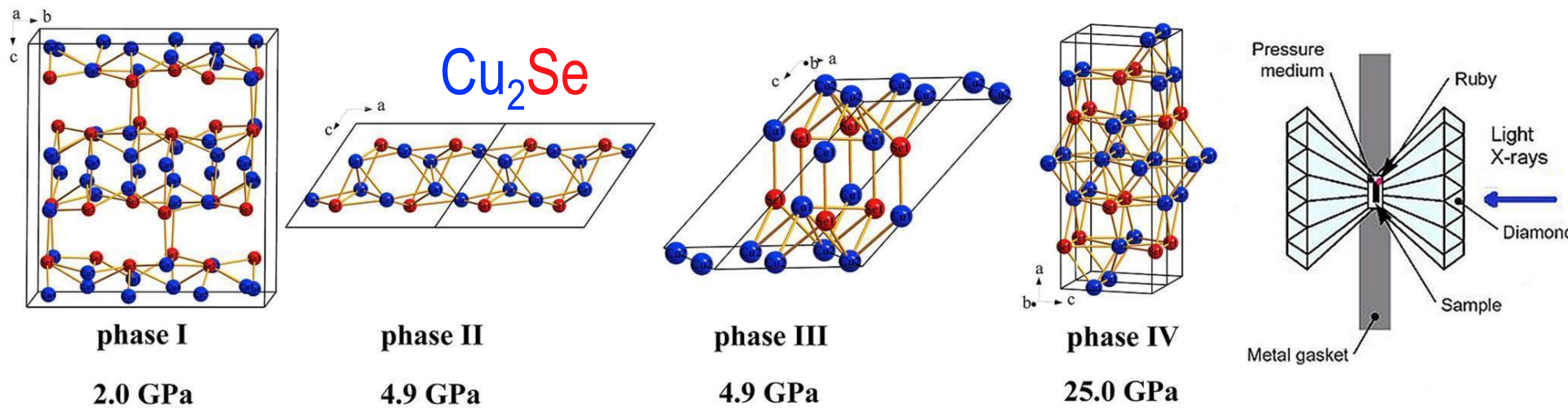
$$\left(-\frac{1}{2}\Delta + V_Z(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Walter Kohn
Nobel Prize in Chemistry
(1998)

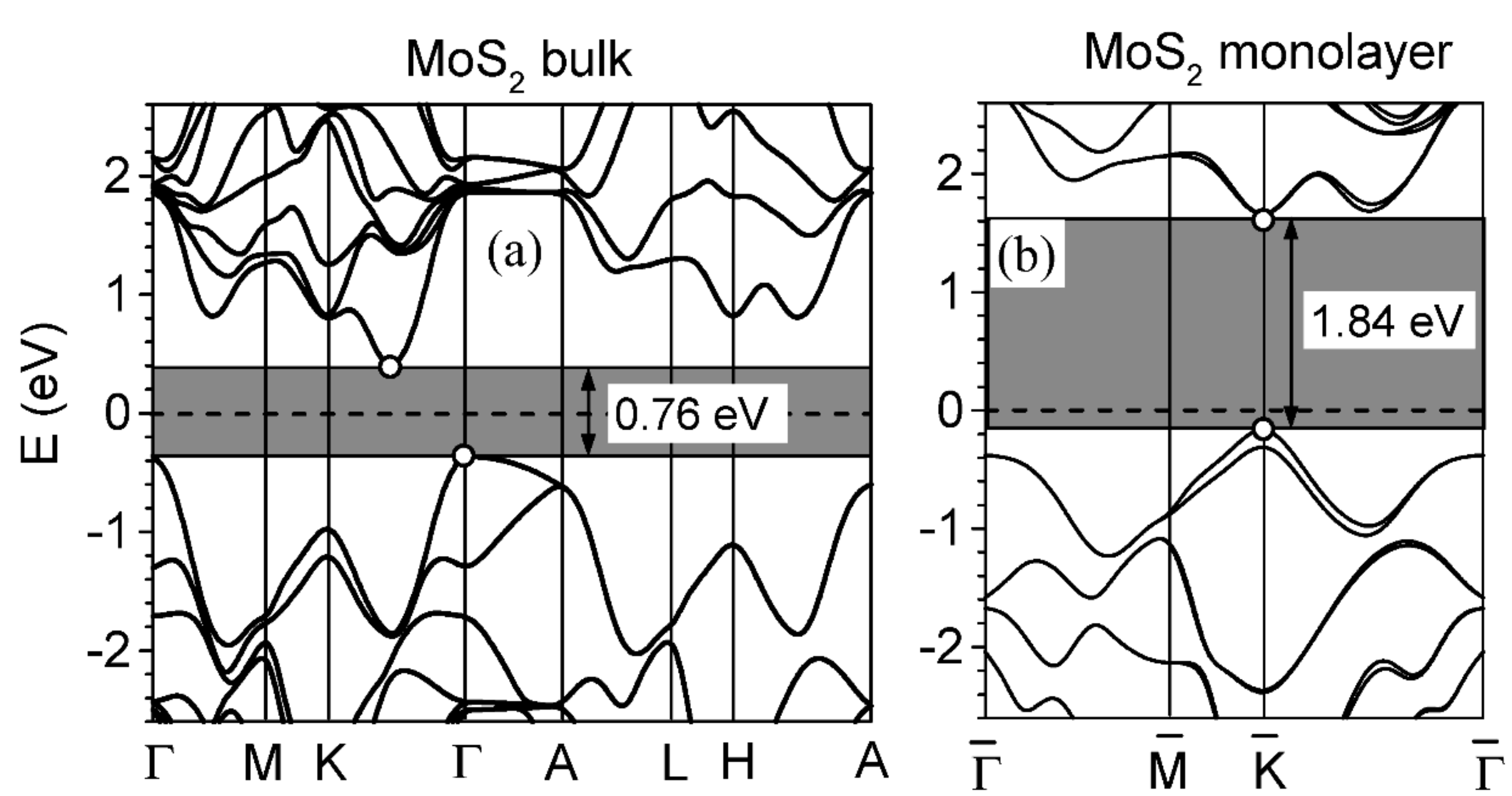
https://www.vasp.at/wiki/images/5/5d/VASP_lecture_Basics.pdf

WHAT CAN DFT DO?

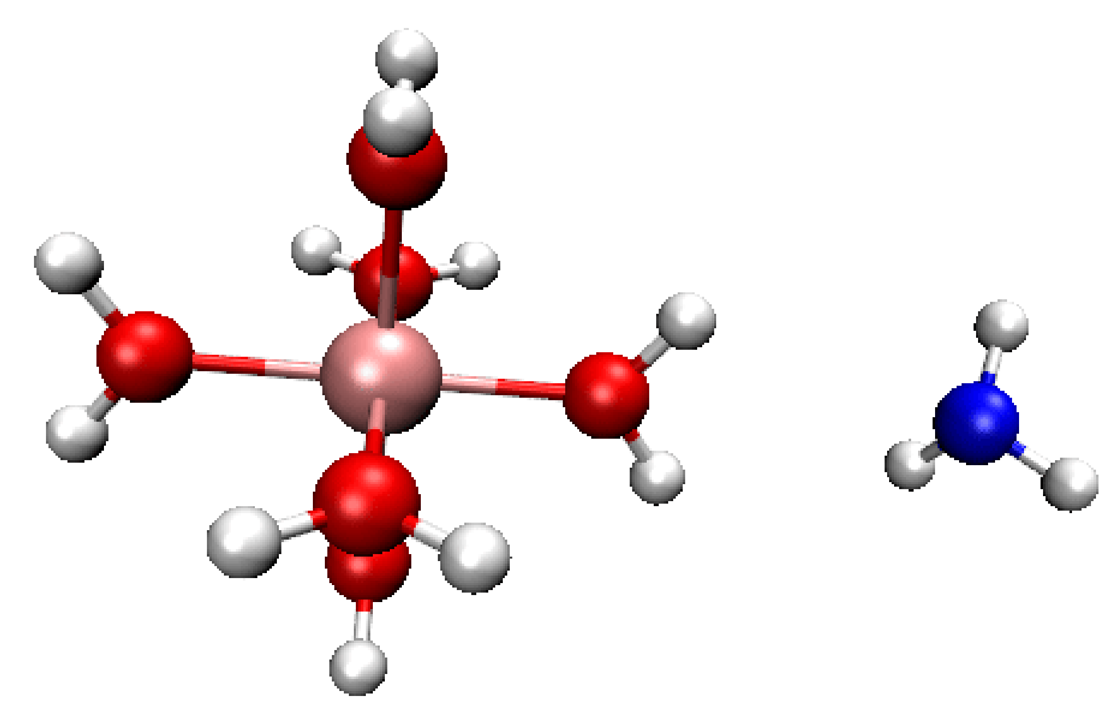
Structure prediction (total energy)



Band structure (energy level)



Molecular dynamics (force)



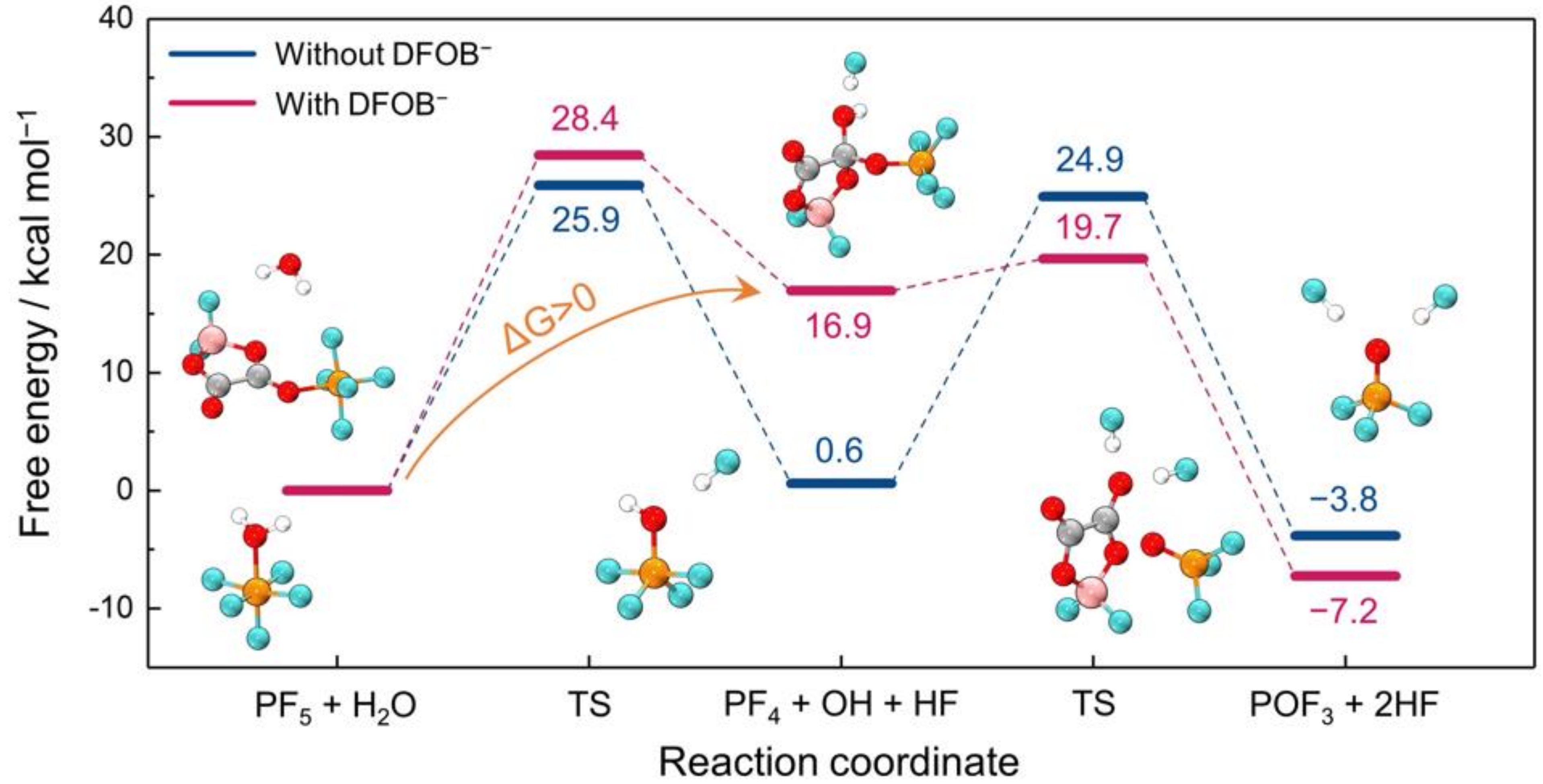
$[Al(H_2O)_6]^{3+} + NH_3 \longrightarrow [Al(H_2O)_5(OH)]^{2+} + NH_4^+$

ADVANCED APPLICATIONS OF DFT

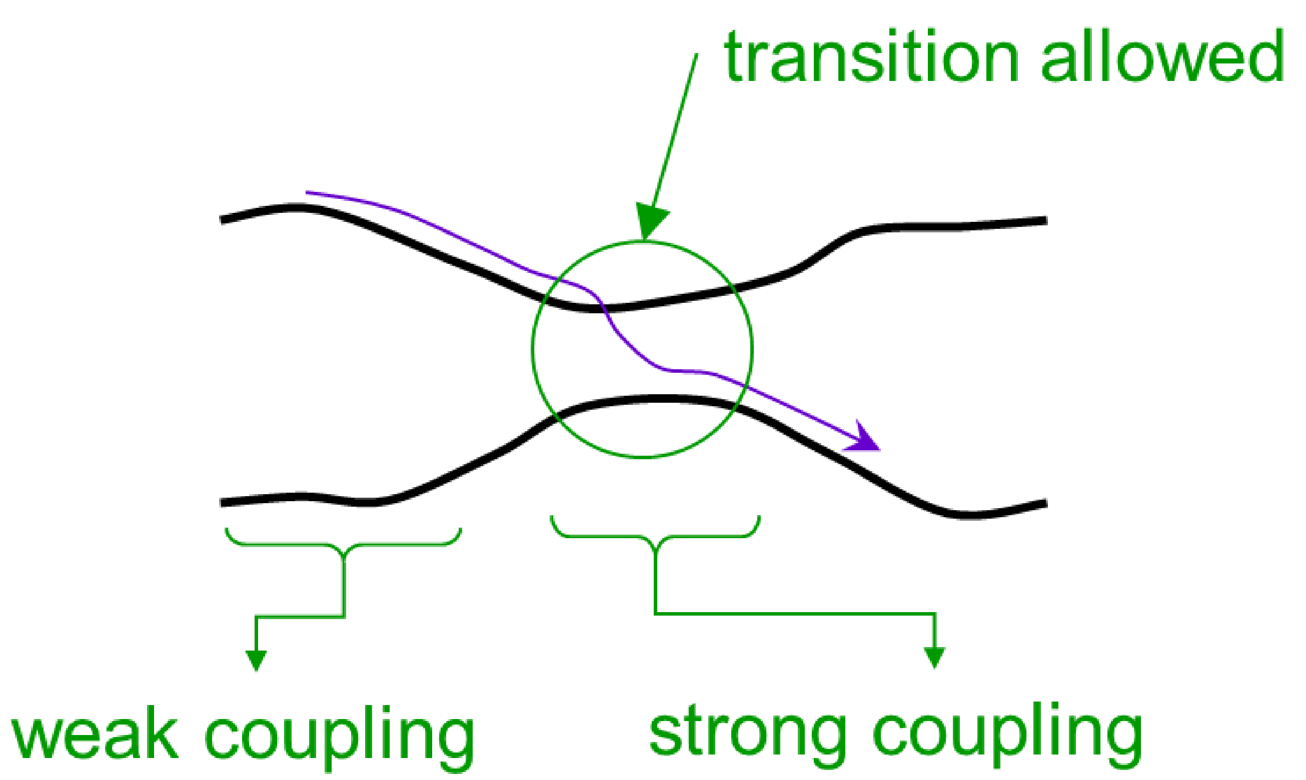
DFT + thermal corrections => free energy for reaction

$$U(0) = H(0) = G(0) = \varepsilon_{\text{ele}} + \text{ZPE}$$
$$U(T) = \varepsilon_{\text{ele}} + U_{\text{corr}}(T)$$
$$H(T) = \varepsilon_{\text{ele}} + H_{\text{corr}}(T)$$
$$G(T) = \varepsilon_{\text{ele}} + G_{\text{corr}}(T)$$

$$U_{\text{corr}} = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{ele}}$$
$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{ele}}$$
$$C_{\text{V}} = C_{\text{V,trans}} + C_{\text{V,rot}} + C_{\text{V,vib}} + C_{\text{V,ele}}$$

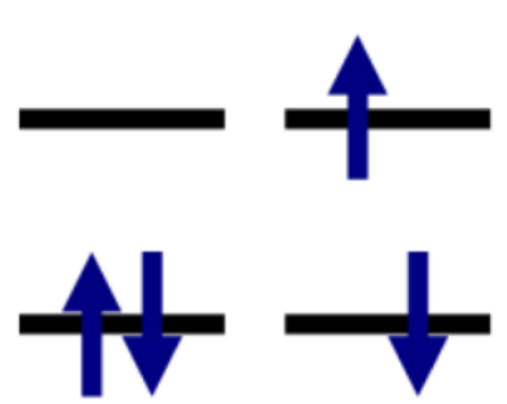


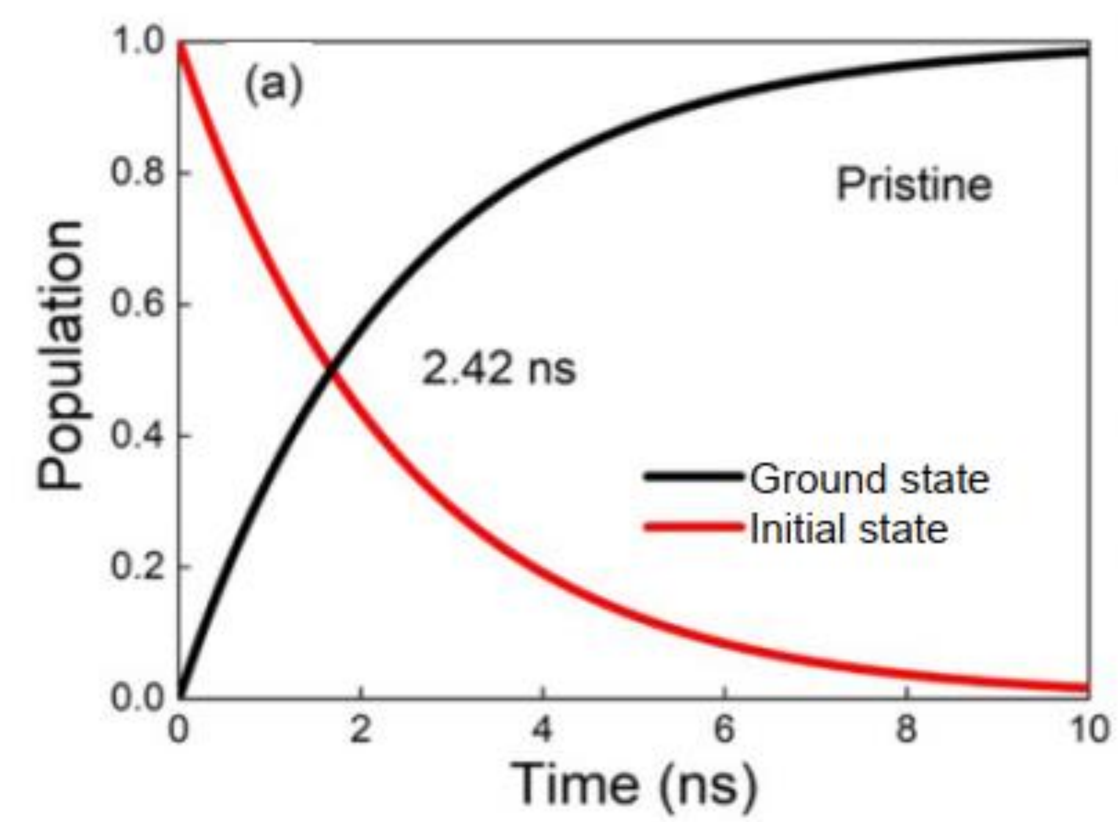
DFT + nonadiabatic molecular dynamics => carrier recombination



Non-adiabatic coupling (scalar)

$$\boldsymbol{d}_{jk} \cdot \dot{\boldsymbol{R}} = \langle \psi_j | \nabla_{\boldsymbol{R}} | \psi_k \rangle \cdot \dot{\boldsymbol{R}} = \frac{\langle \psi_j | \nabla_{\boldsymbol{R}} \hat{H} | \psi_k \rangle}{\varepsilon_k - \varepsilon_j} \cdot \dot{\boldsymbol{R}}$$





QUANTUM MECHANICS CALCULATIONS

Schrödinger equation

$H\ \Psi = E\ \Psi$

+

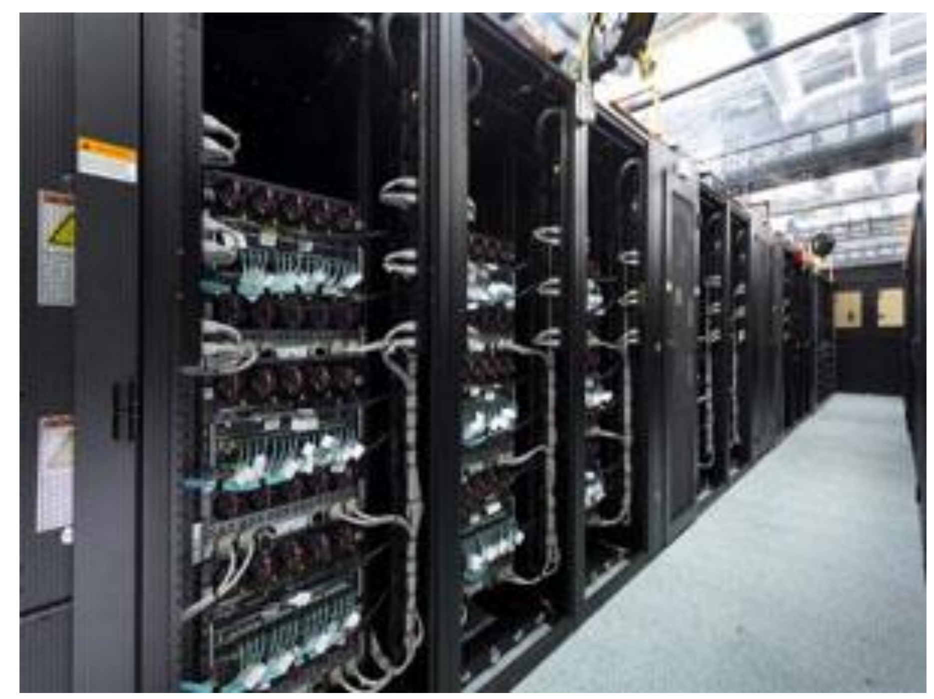
DFT

$E(\boldsymbol{r}) \rightarrow E[\rho(\boldsymbol{r})]$

+

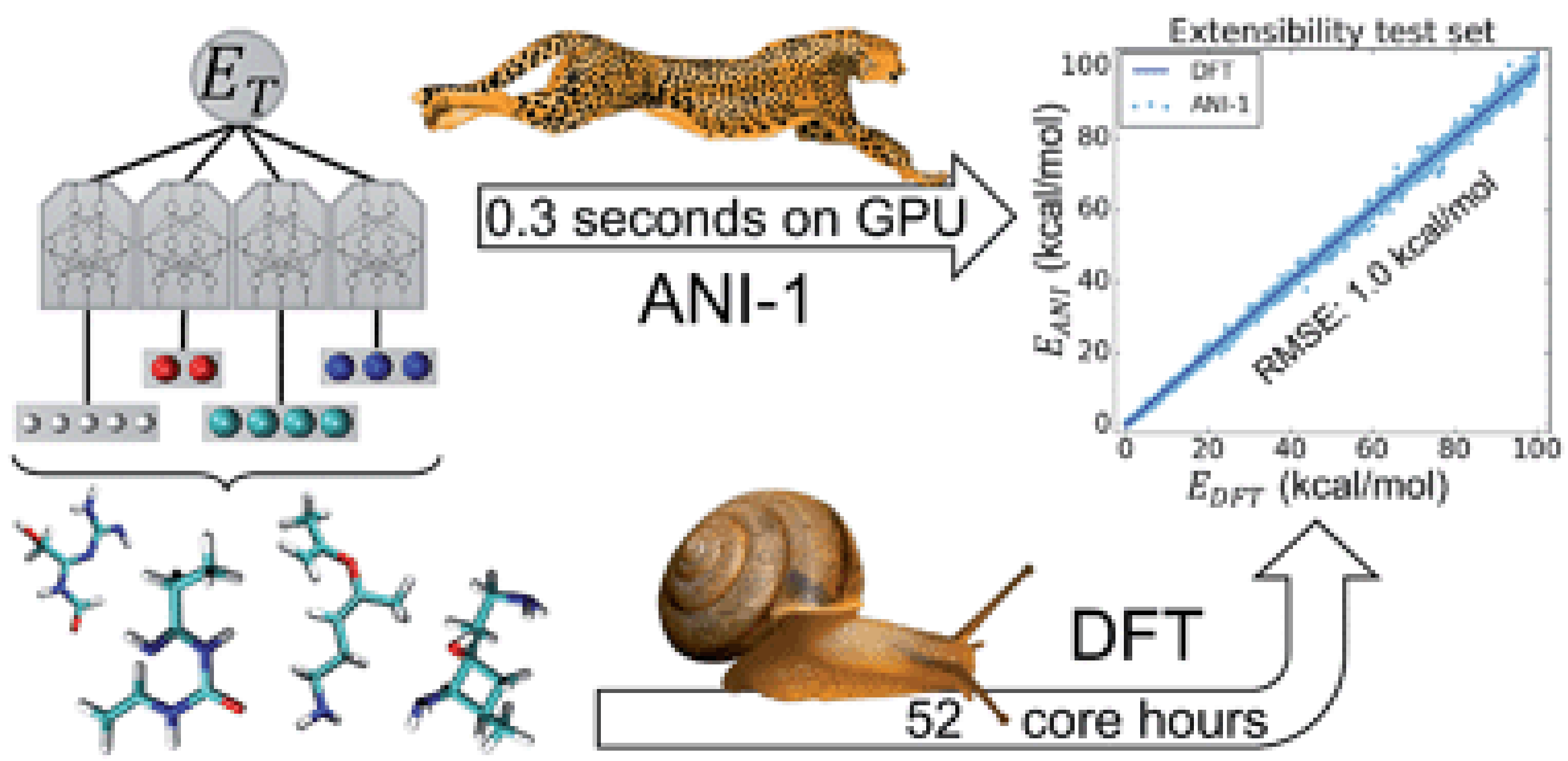
High-performance computer

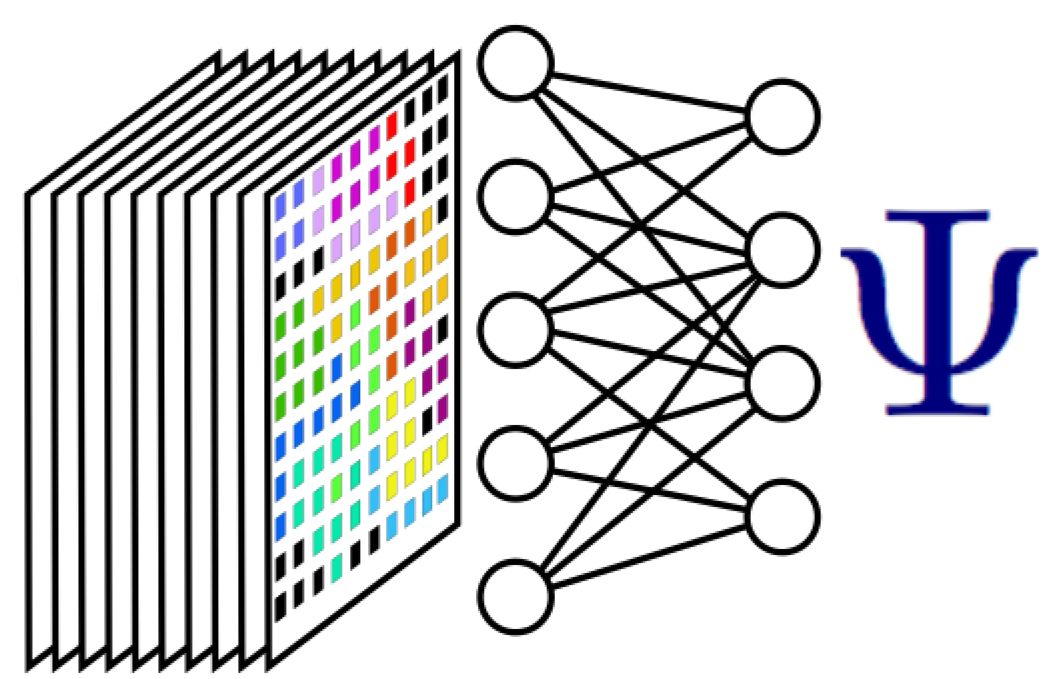
Multicore parallel



Machine learning

+





Chem. Sci., 2017,8, 3192-3203

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DFT + EXPERIMENTS:
PHOTOCATALYSIS WITH MG-DOPED ZNO

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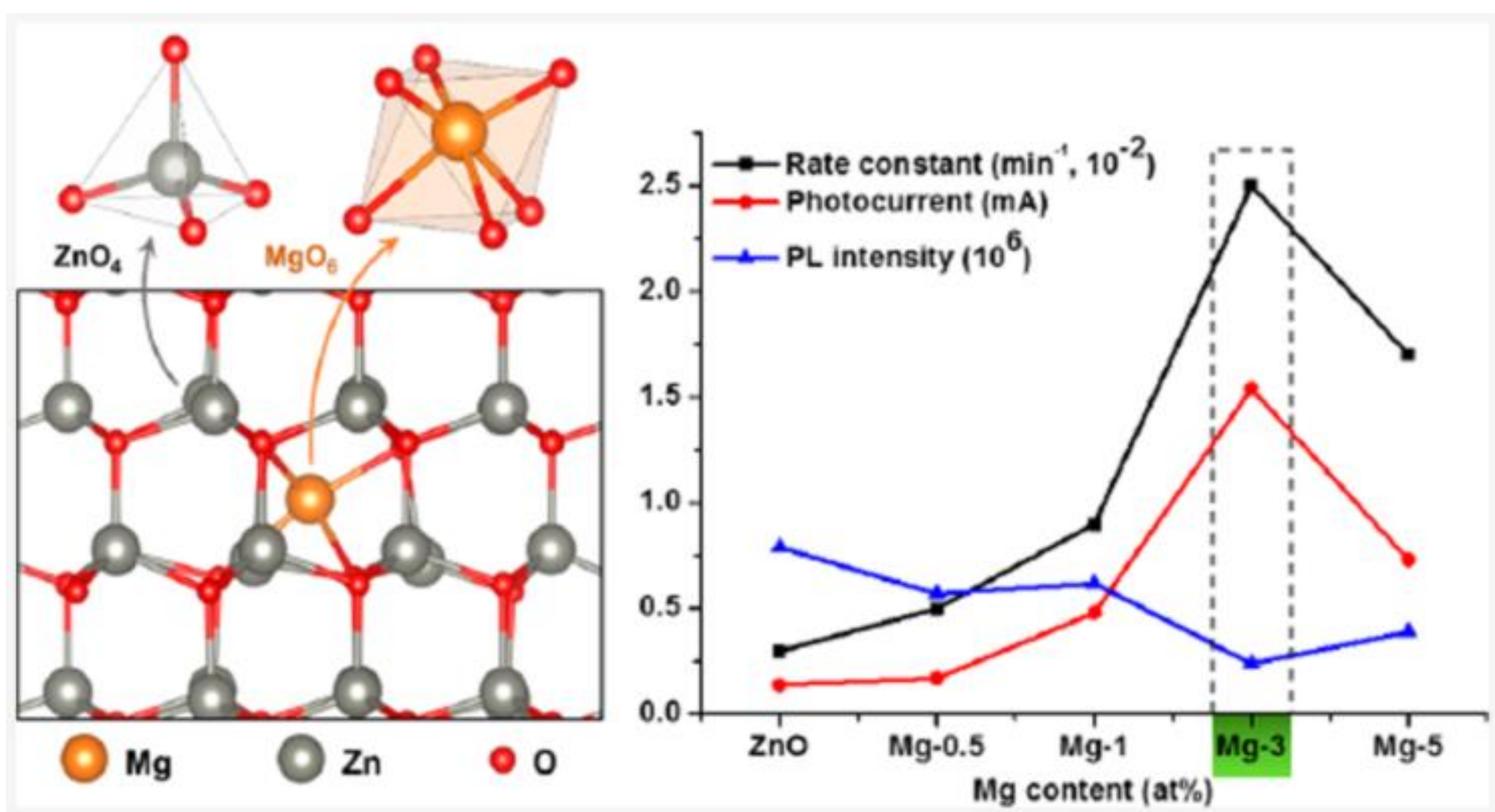
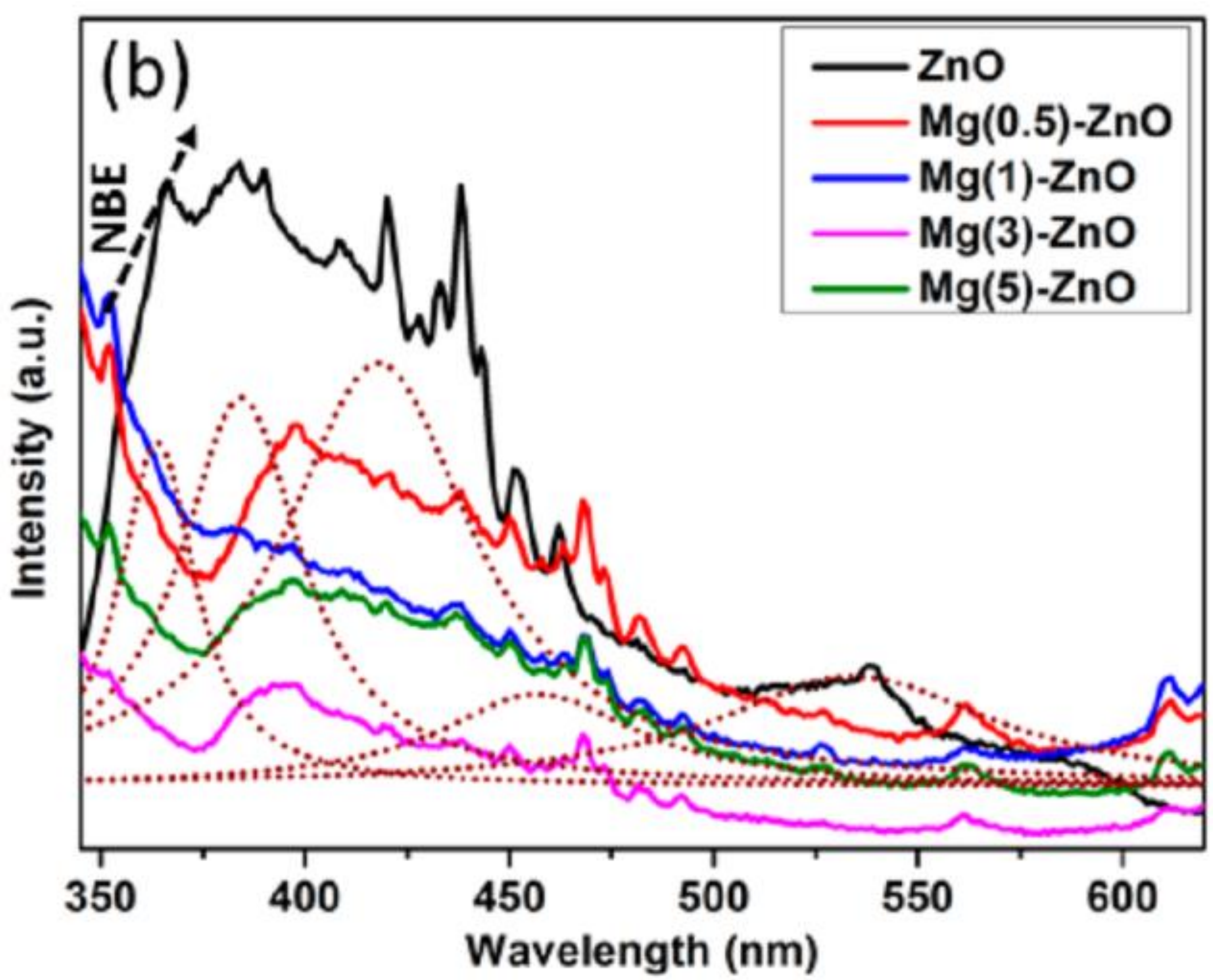
Enhancement of Photocatalytic and Photoelectrochemical Performance of ZnO by Mg Doping: Experimental and Density Functional Theory Insights

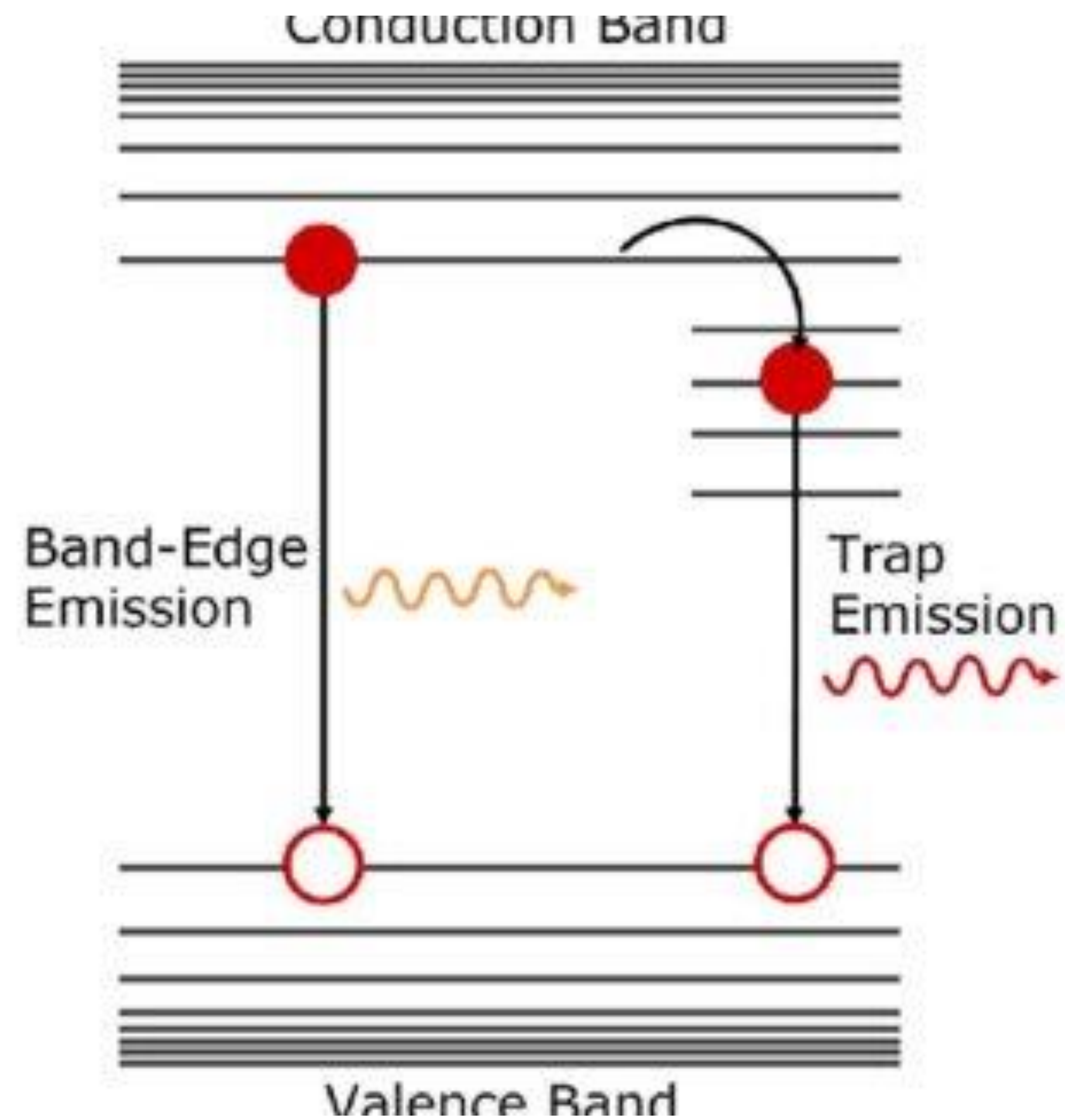
Abinash Das, Dongyu Liu, Riu Riu Wary, Andrey S. Vasenko, Oleg V. Prezhdo,* and Ranjith G. Nair*



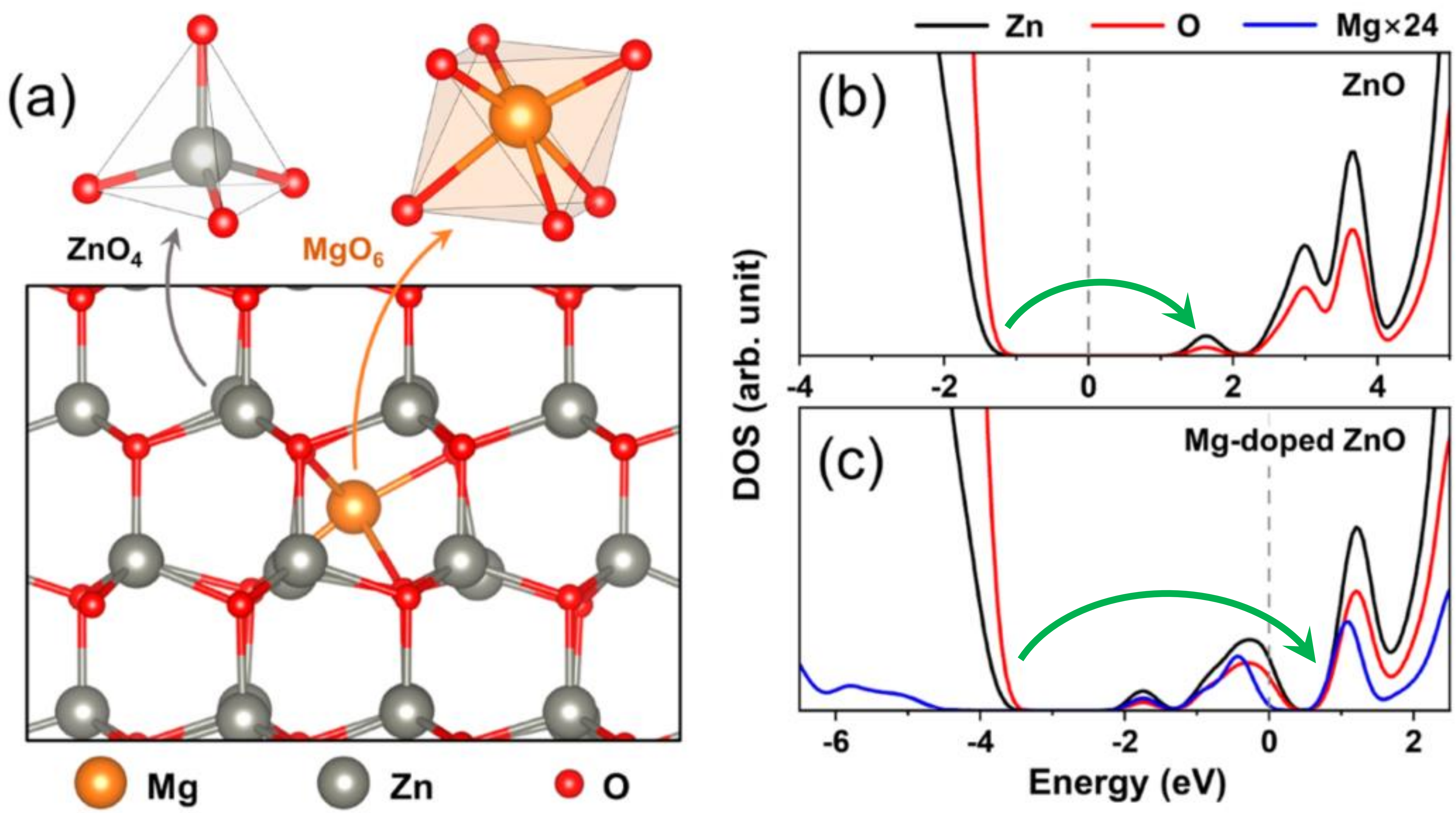
PHOTOLUMINESCENCE SPECTRA

Near band-edge emission





ELECTRONIC STRUCTURE



DFT + EXPERIMENTS: PHOTOCATALYSIS WITH MN-DOPED ZNO

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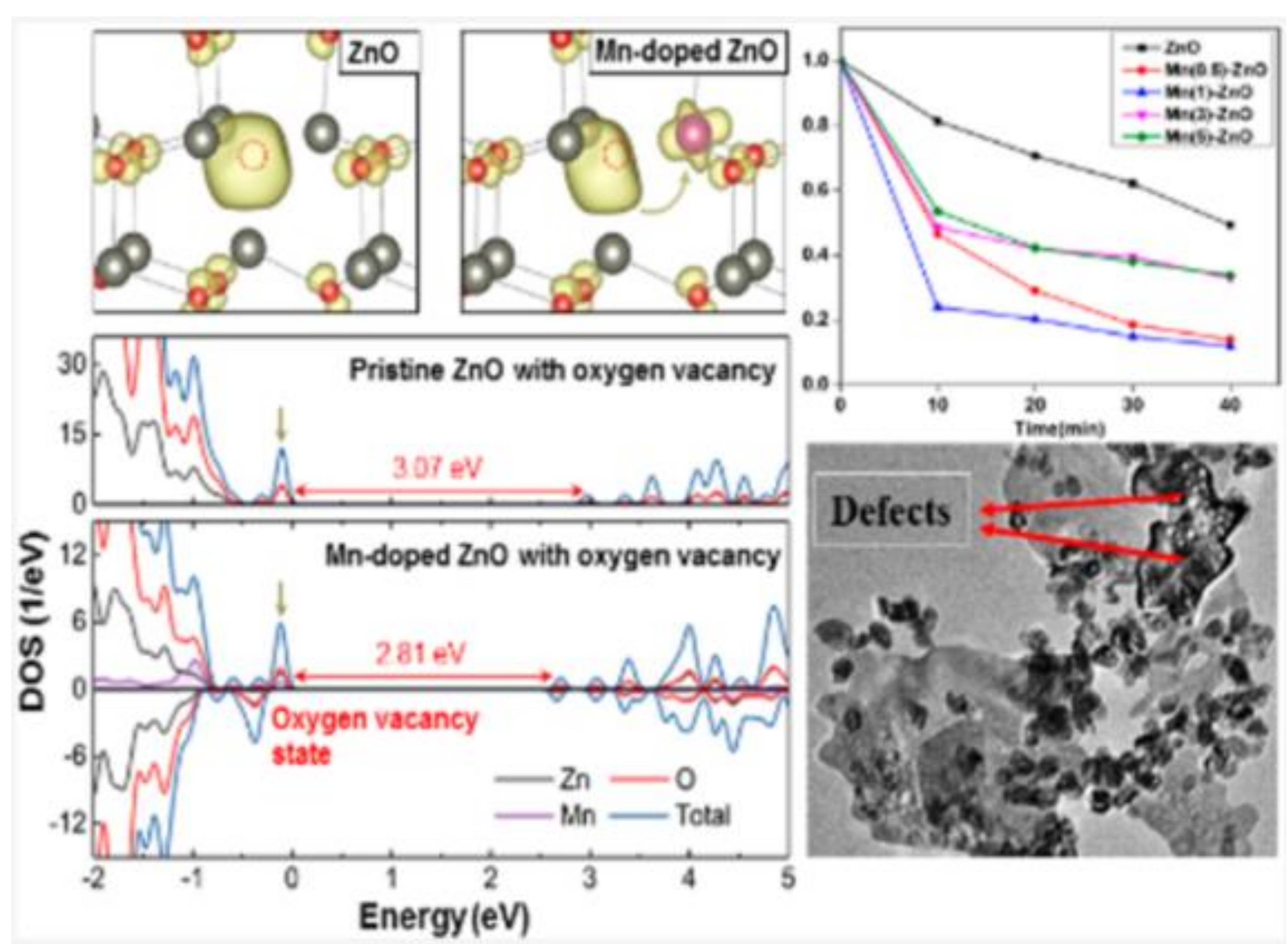
Letter

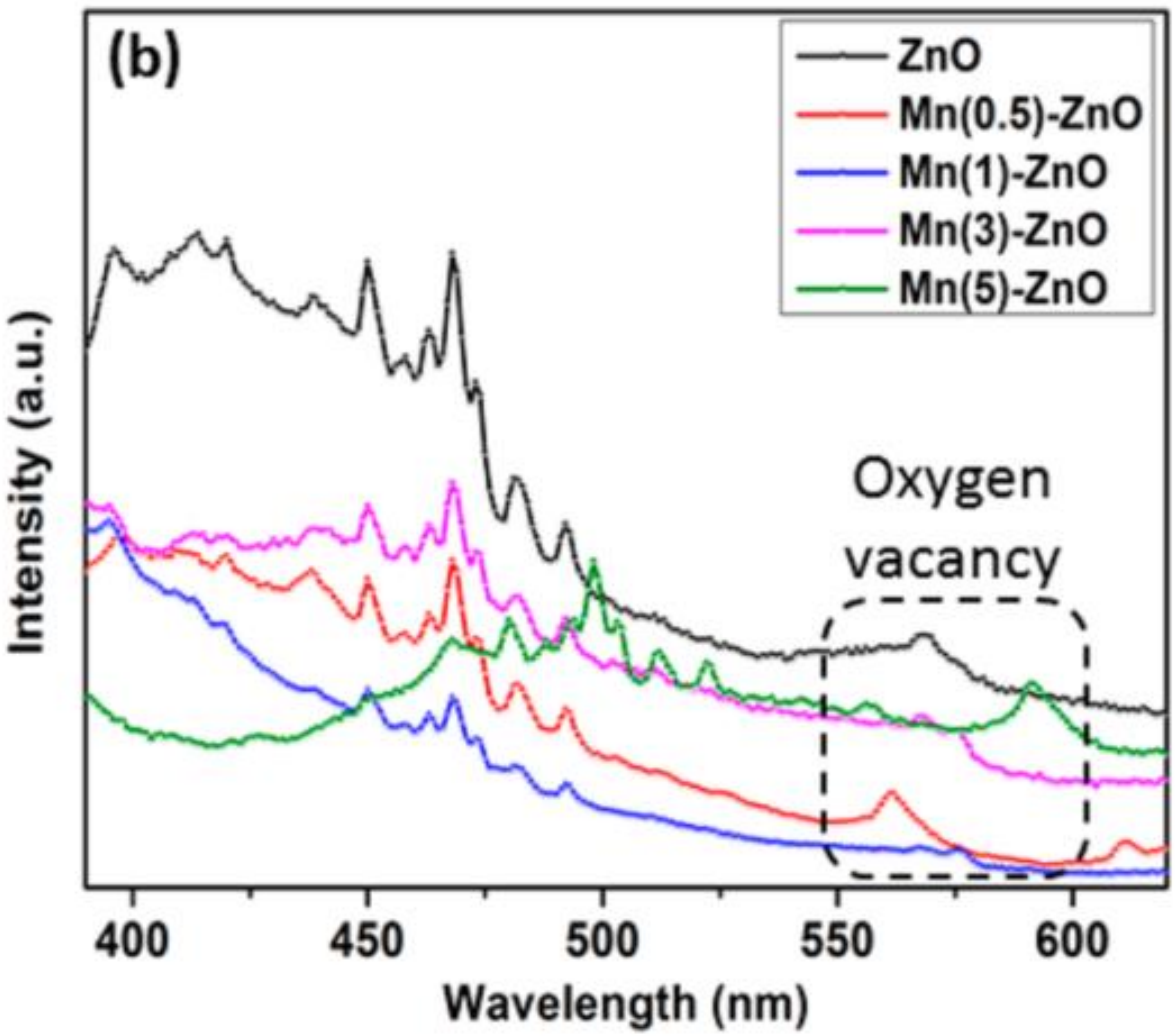
Mn-Modified ZnO Nanoflakes for Optimal Photoelectrochemical Performance Under Visible Light: Experimental Design and Theoretical Rationalization

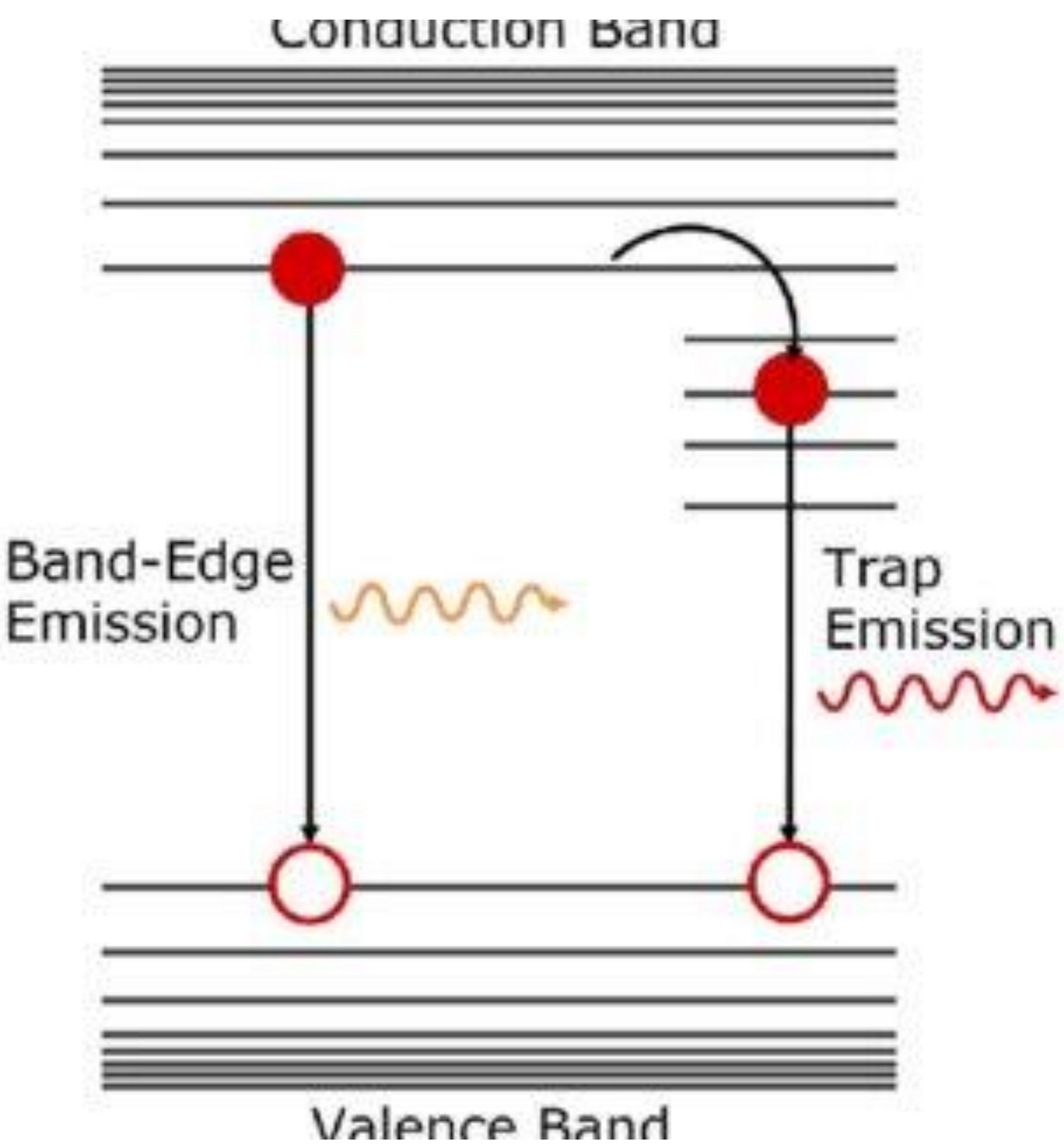
Abinash Das, Dongyu Liu, Riu Riu Wary, Andrey S. Vasenko, Oleg V. Prezhdo,* and Ranjith G. Nair*



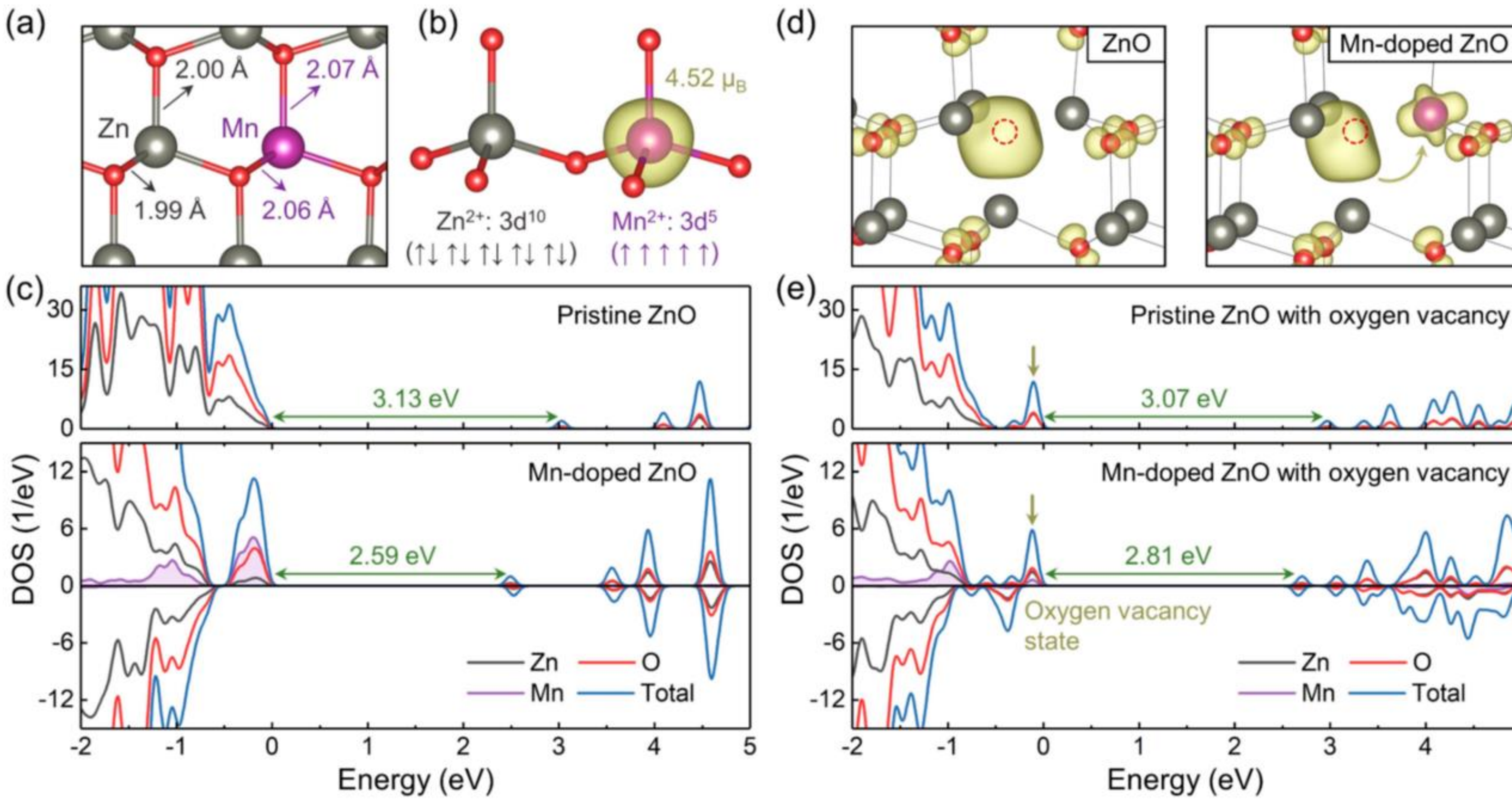
OXYGEN VACANCIES IN ZNO

PL





ELECTRONIC STRUCTURE



DFT + EXPERIMENTS: CO2 REDUCTION ON CU-DOPED ZNO

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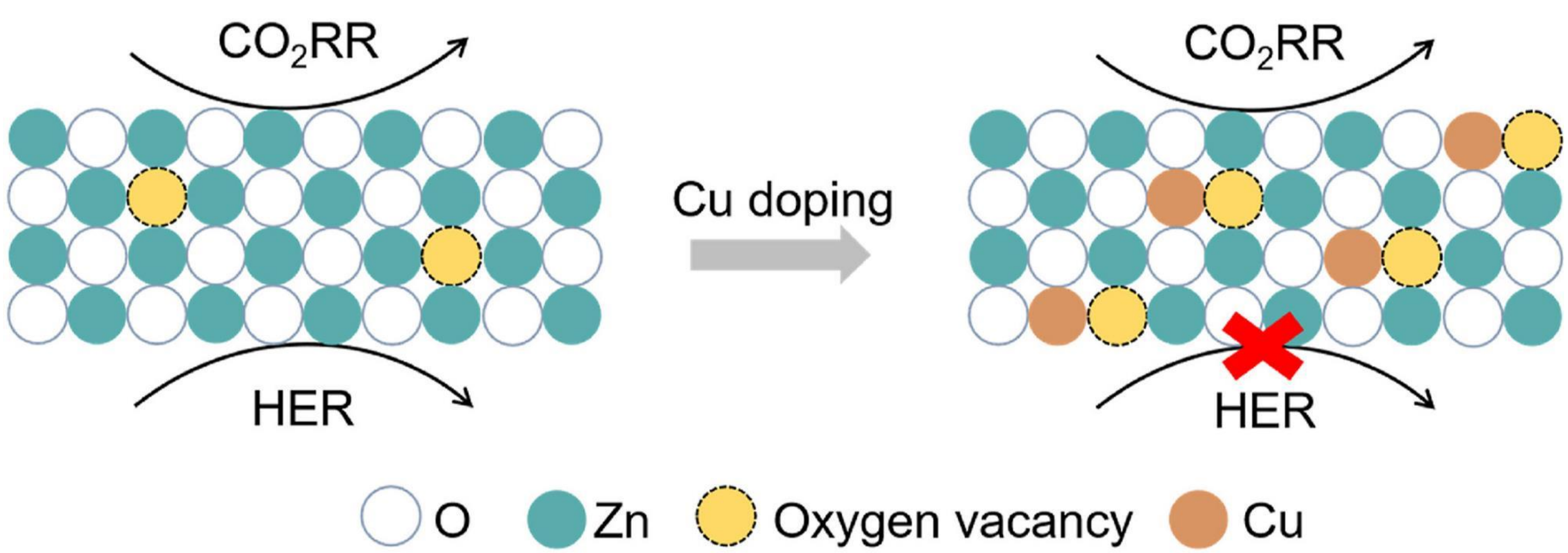
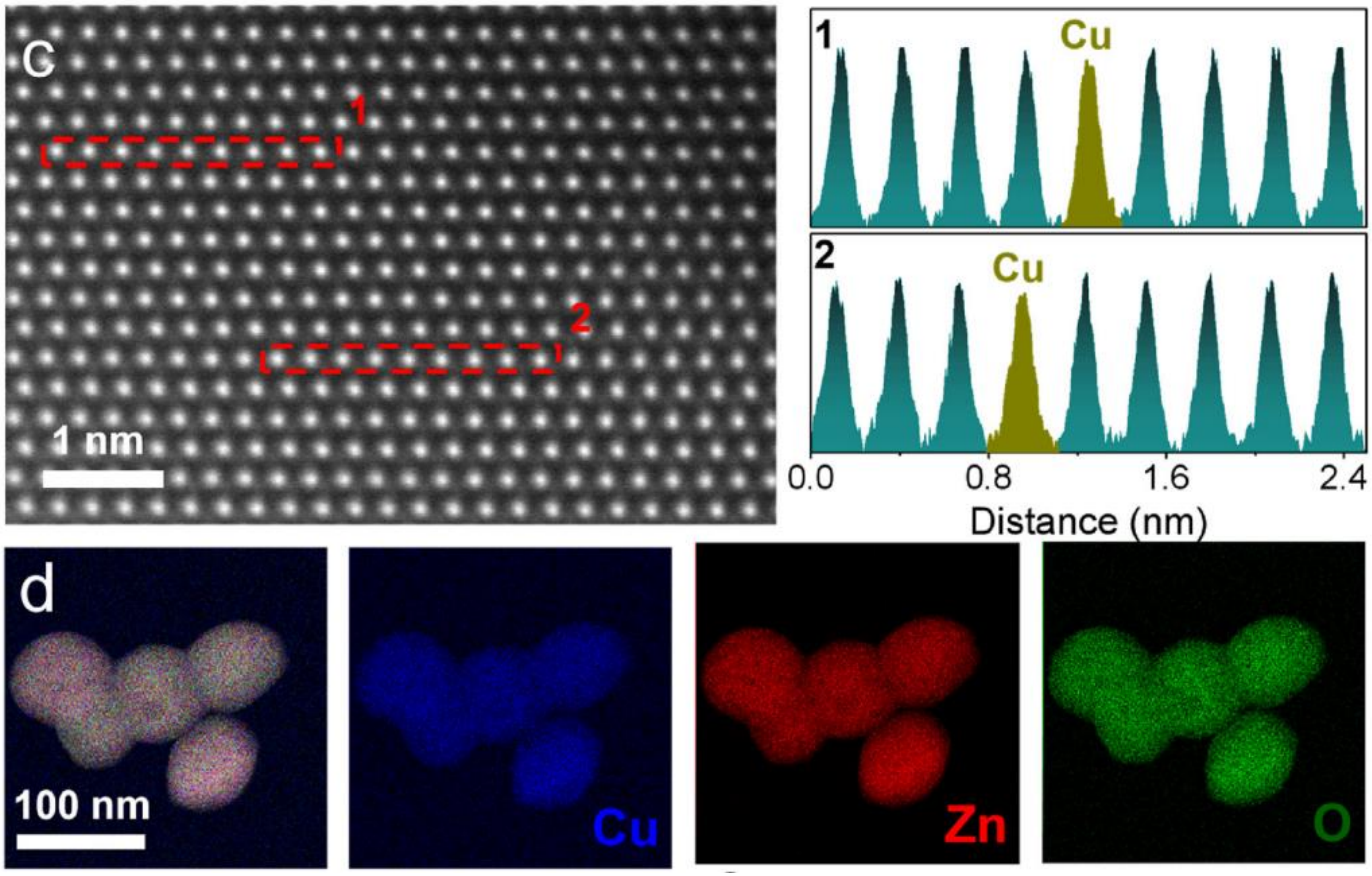
Research Paper

Tuning the local electronic structure of oxygen vacancies over copper-doped zinc oxide for efficient CO_2 electroreduction

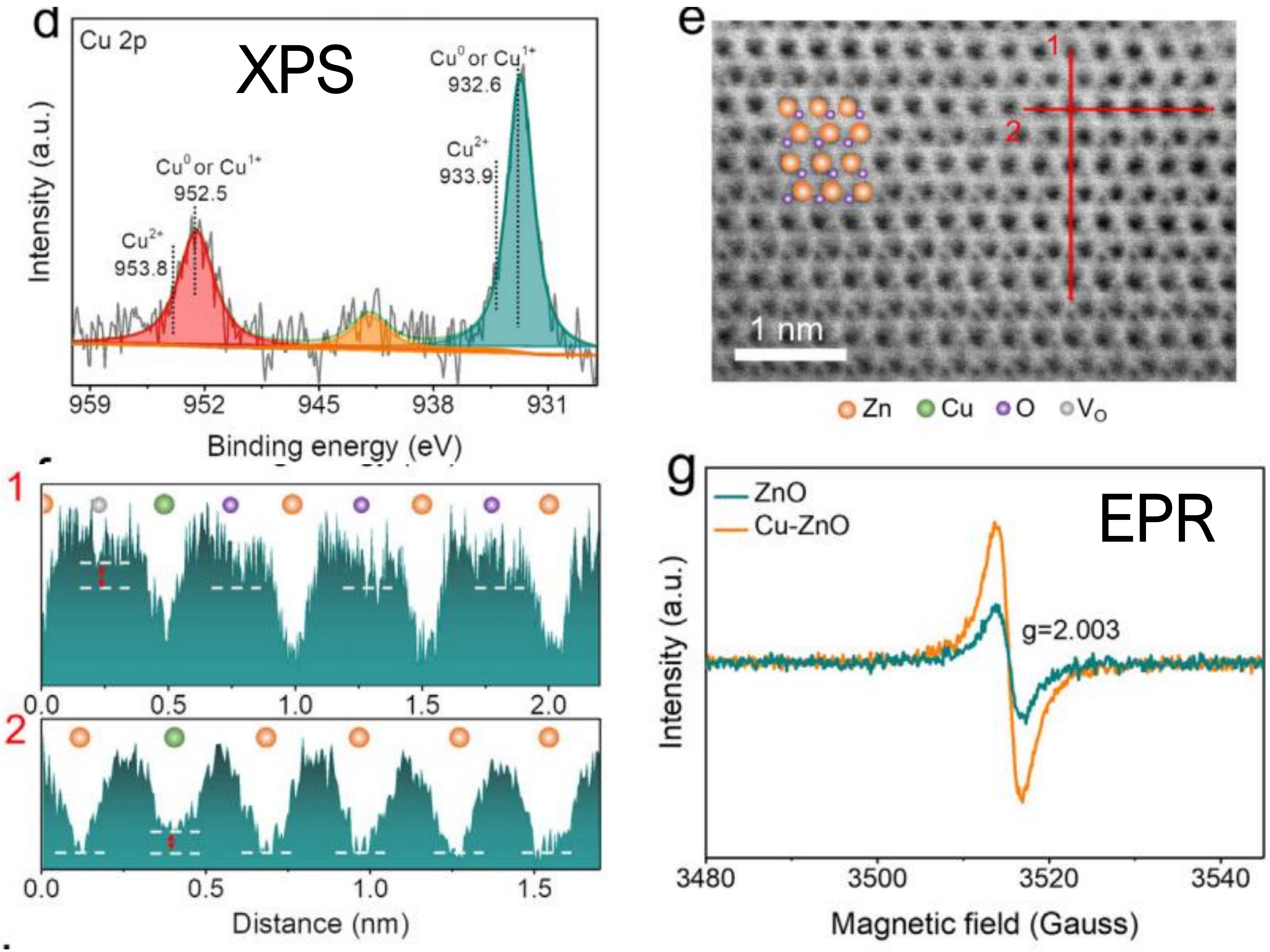
Ke Wang [a,1], Dongyu Liu [b,c,1], Limin Liu [a,1], Jia Liu [d], XiaoFei Hu [a], Ping Li [e], Mingtao Li [b], Andrey S. Vasenko [c], Chunhui Xiao [a,*], Shujiang Ding [a]



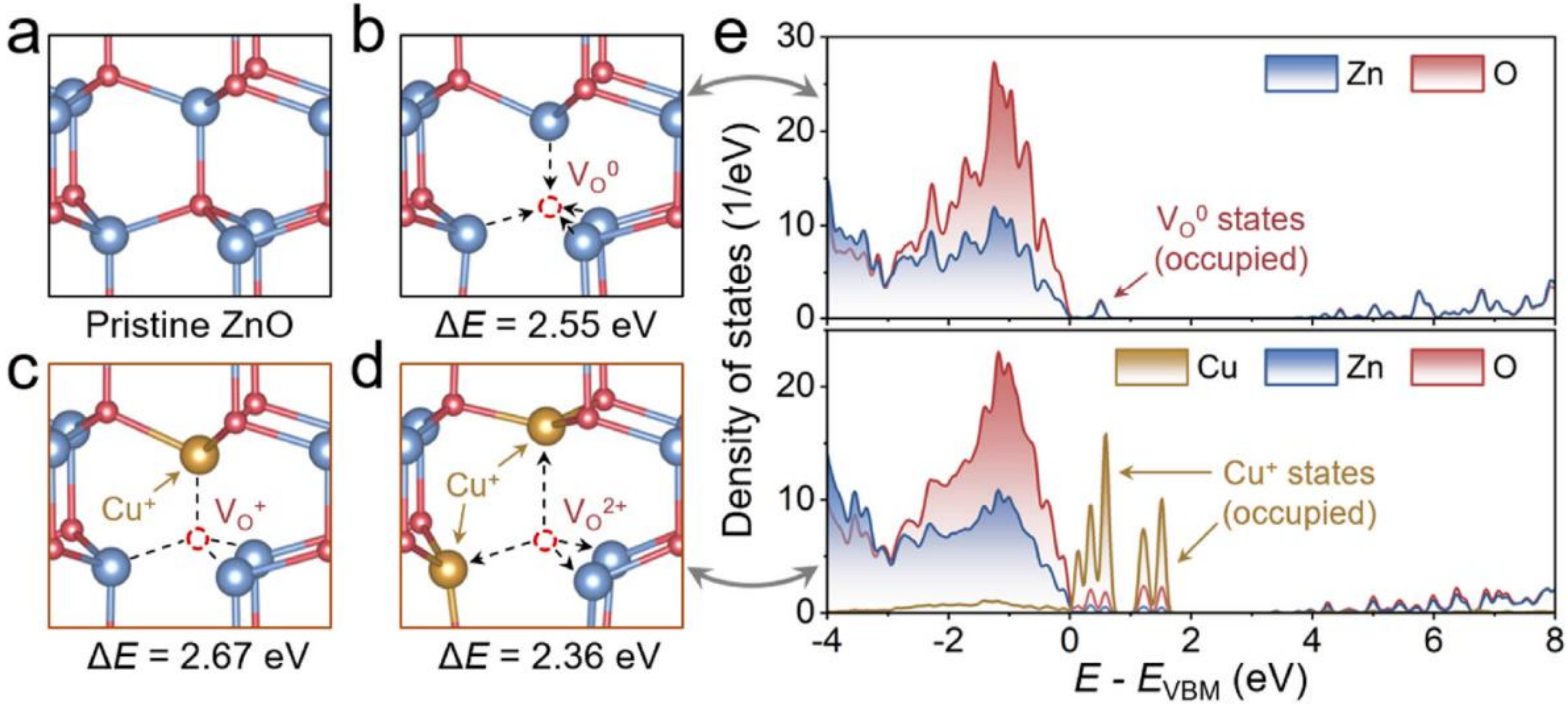
DFT + EXPERIMENTS: CU DOPING



DFT + EXPERIMENTS: CU AND OXYGEN VACANCY



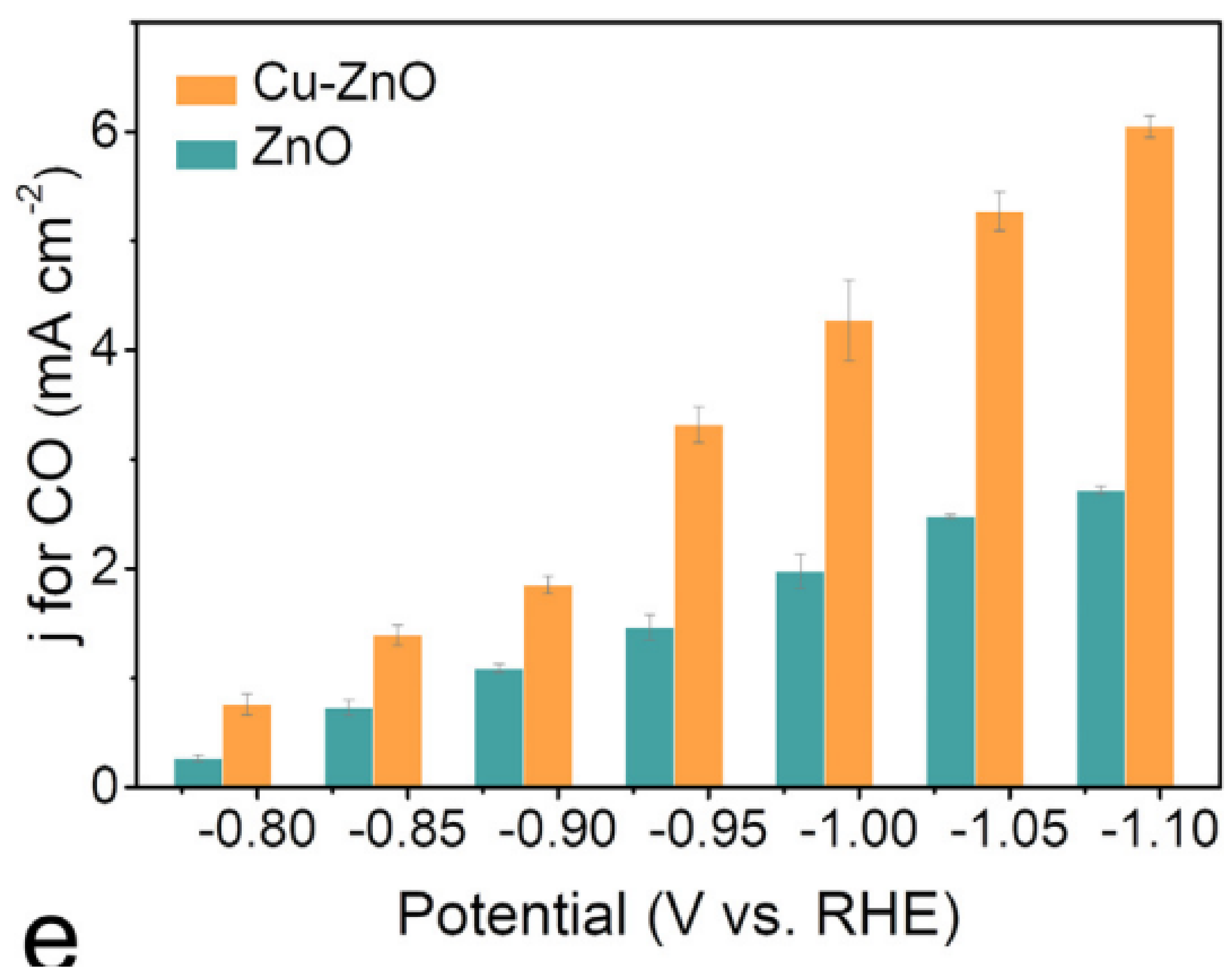
DFT + EXPERIMENTS: CU AND OXYGEN VACANCY



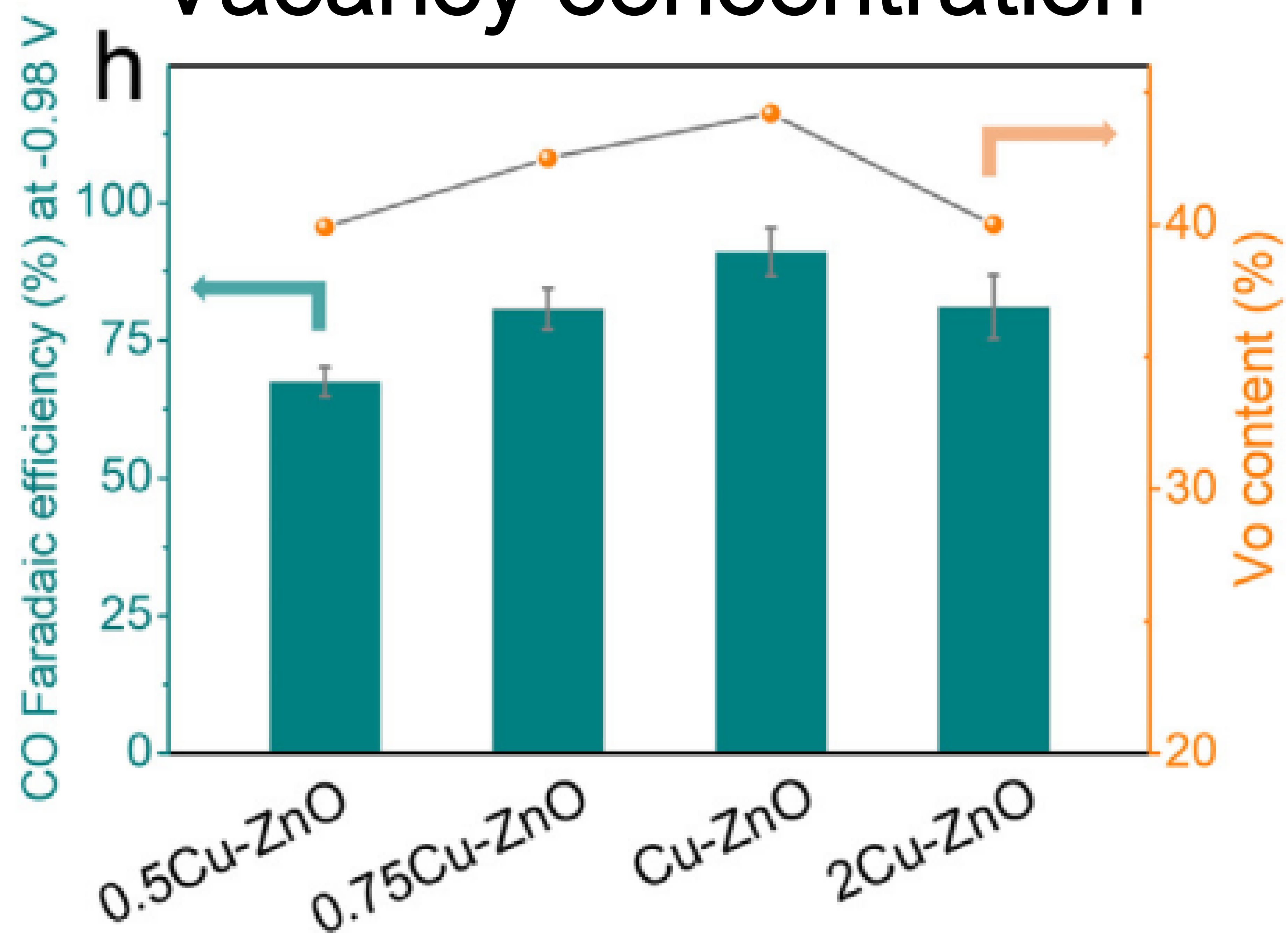
Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

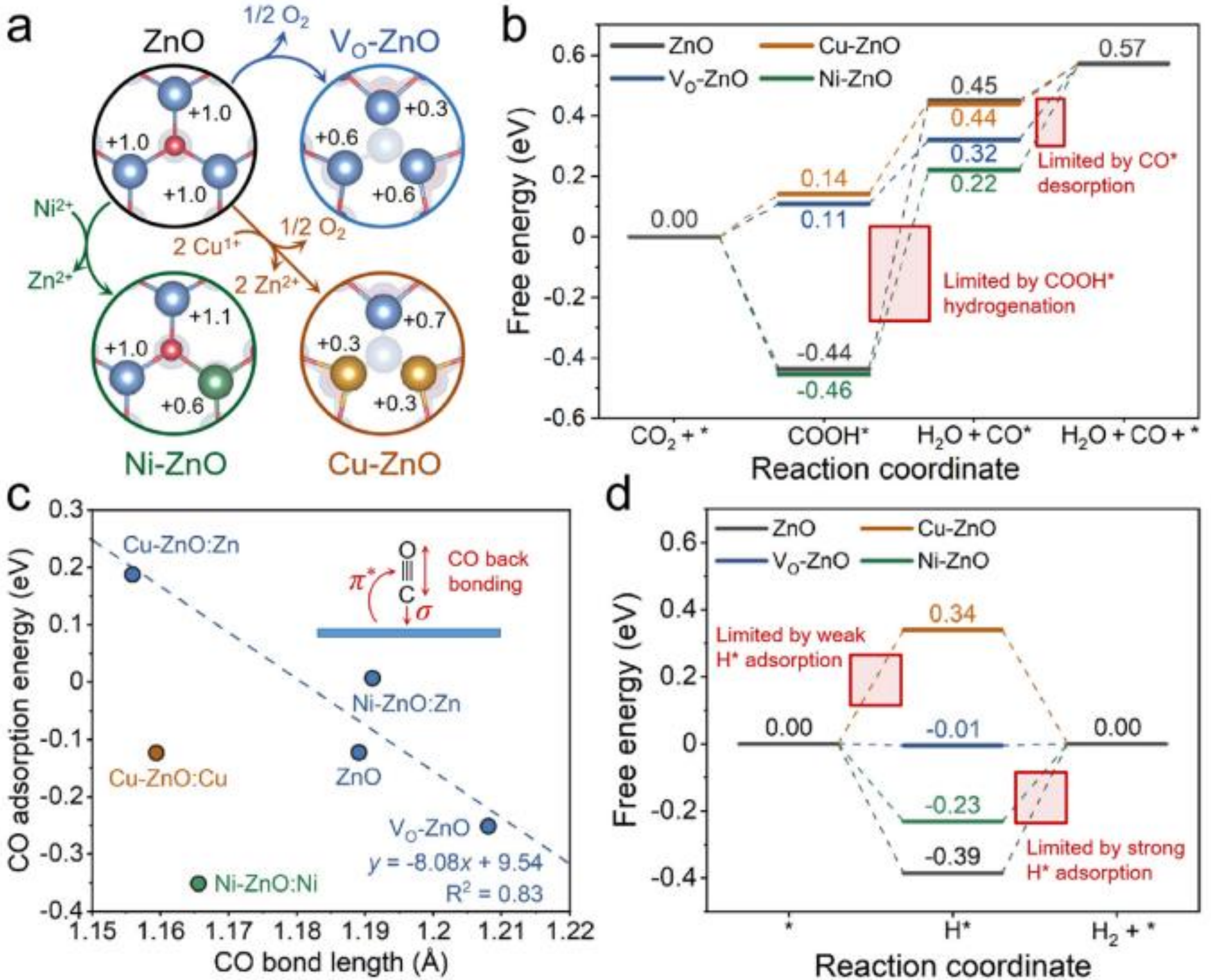
DFT + EXPERIMENTS: CO2RR PERFORMANCE

Activity



Vacancy concentration





a
ZnO
1/2 O$_2$
V$_O$-ZnO
+1.0
+1.0
+1.0
+0.3
+0.6
+0.6
Ni^{2+}
Zn^{2+}
1/2 O$_2$
2 Cu^{1+}
2 Zn^{2+}
+1.1
+1.0
+0.6
+0.7
+0.3
+0.3
Ni-ZnO
Cu-ZnO
b
ZnO
Cu-ZnO
V$_O$-ZnO
Ni-ZnO
0.57
0.45
0.44
0.32
0.22
0.14
0.11
0.00
-0.44
-0.46
Limited by CO* desorption
Limited by COOH* hydrogenation
Free energy (eV)
CO$_2$ + *
COOH*
H$_2$O + CO*
H$_2$O + CO + *
Reaction coordinate
c
Cu-ZnO:Zn
CO back bonding
π^*
σ
Ni-ZnO:Zn
Cu-ZnO:Cu
ZnO
V$_O$-ZnO
Ni-ZnO:Ni
$y = -8.08x + 9.54$
$R^2 = 0.83$
CO adsorption energy (eV)
CO bond length (Å)
d
ZnO
Cu-ZnO
V$_O$-ZnO
Ni-ZnO
0.34
Limited by weak H* adsorption
0.00
-0.01
0.00
-0.23
-0.39
Limited by strong H* adsorption
Free energy (eV)
*
H*
H$_2$ + *
Reaction coordinate

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THEORETICAL WORK ON PEROVSKITES: CS2AGBIBR6

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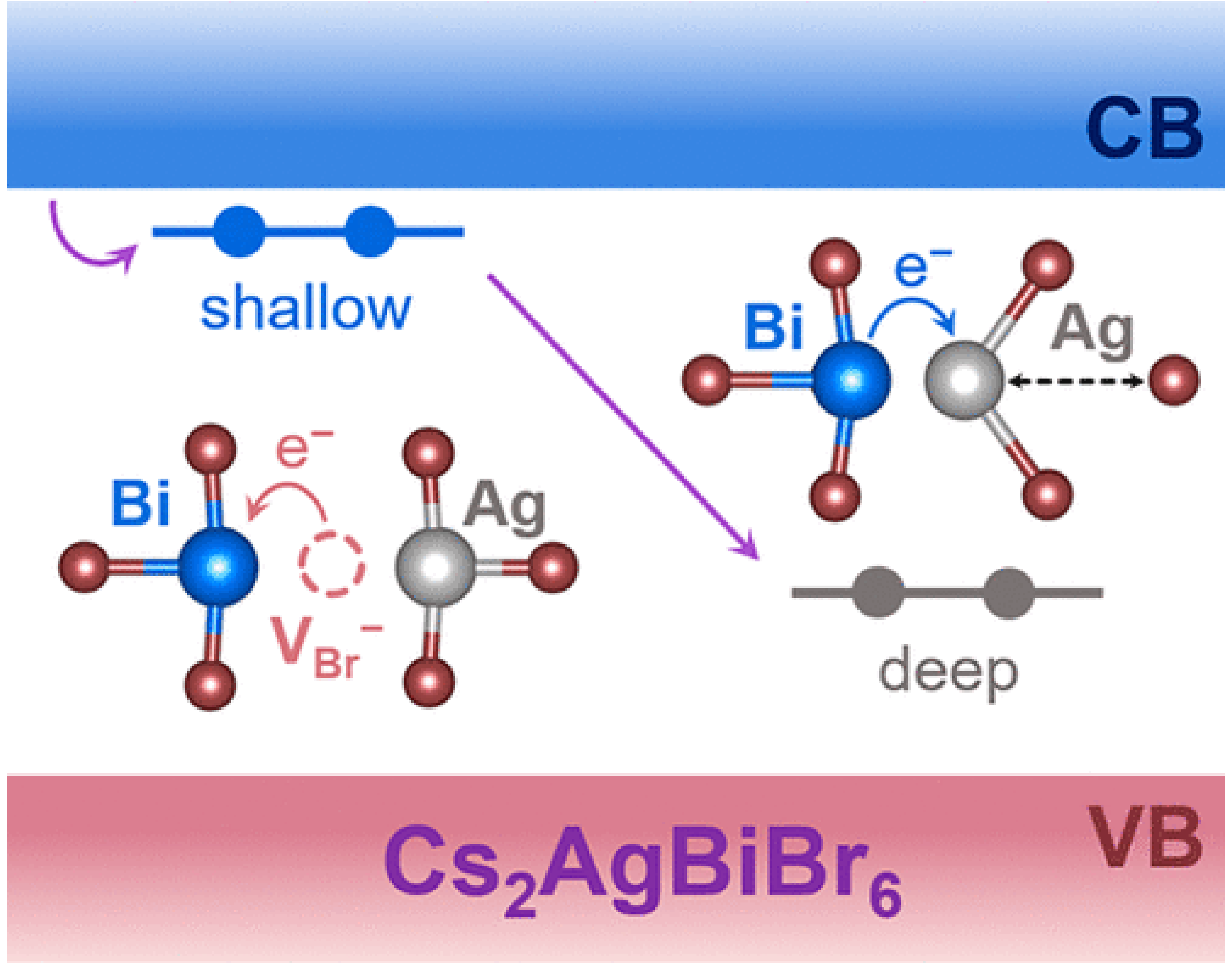
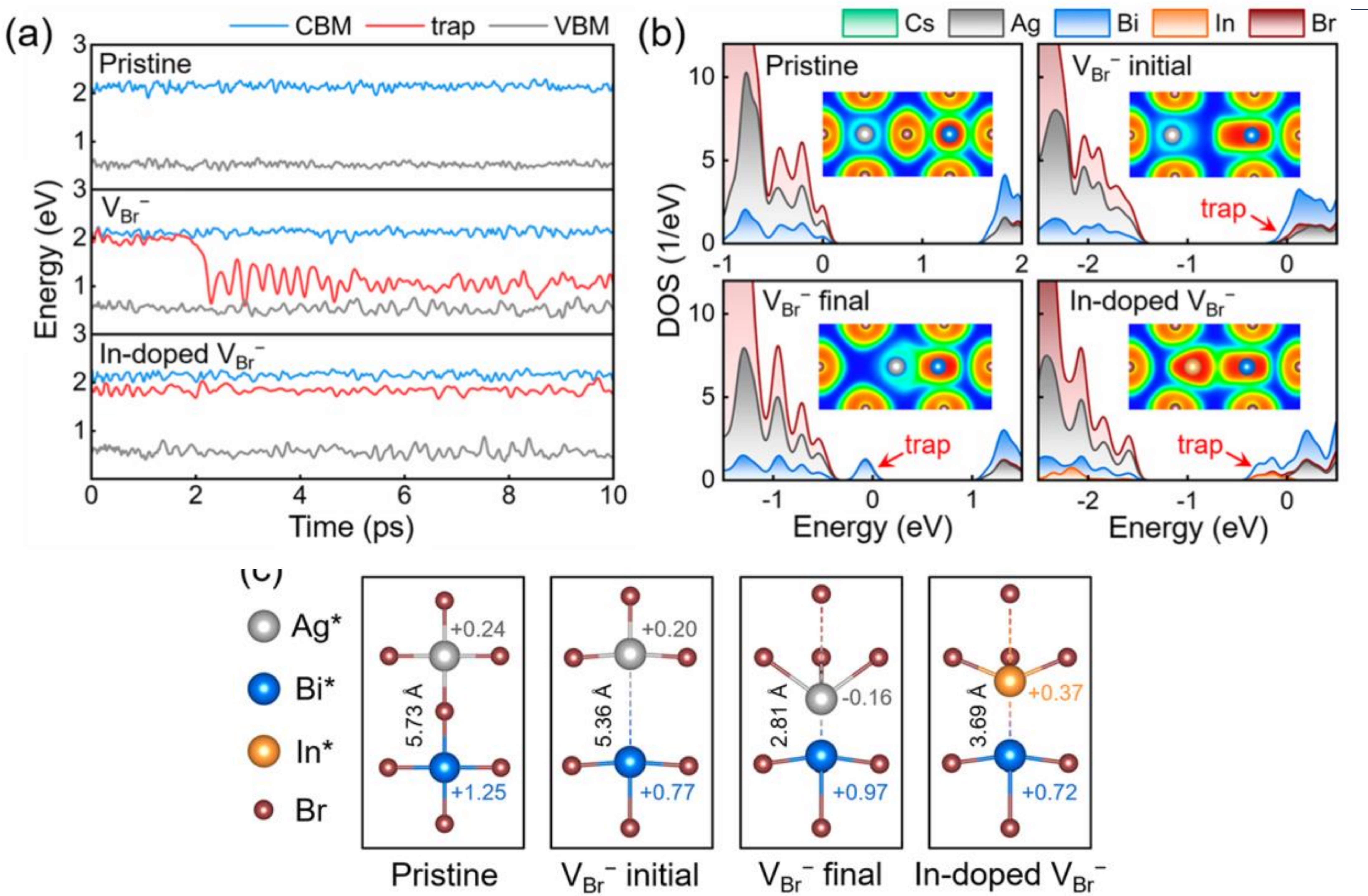
Letter

Ag–Bi Charge Redistribution Creates Deep Traps in Defective $Cs_2AgBiBr_6$: Machine Learning Analysis of Density Functional Theory

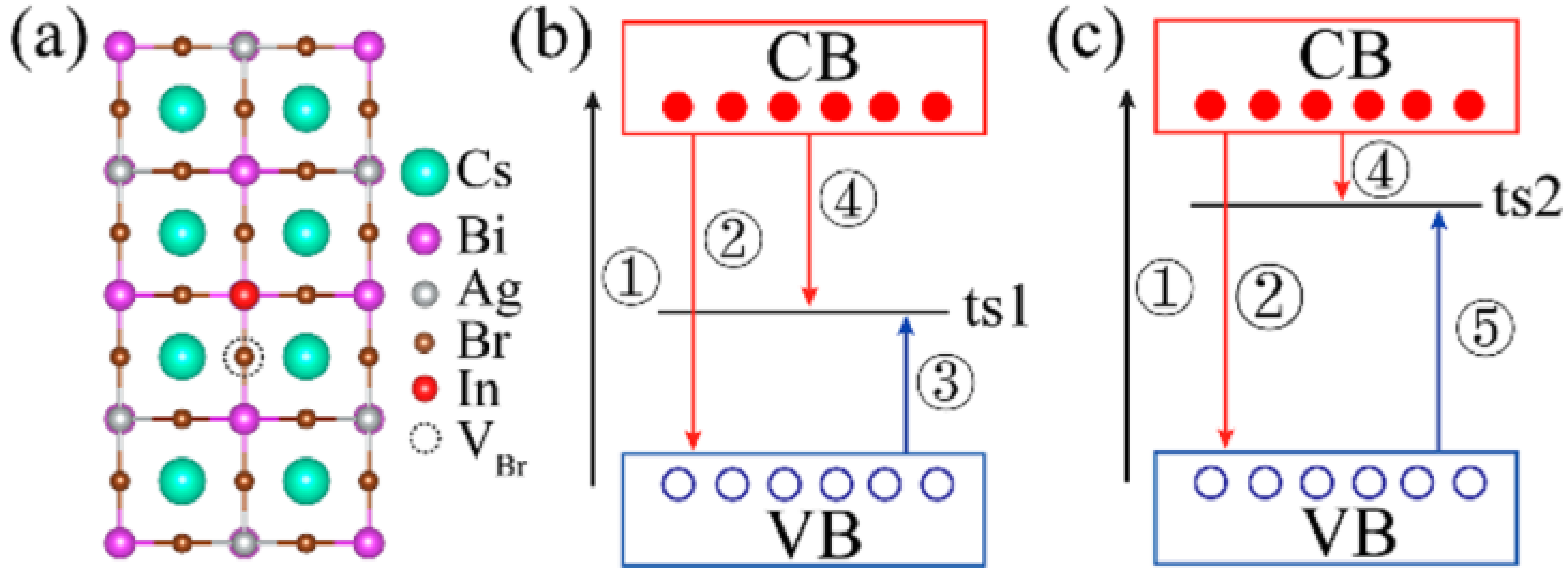
Dongyu Liu, Carlos Mora Perez, Andrey S. Vasenko,* and Oleg V. Prezhdo*

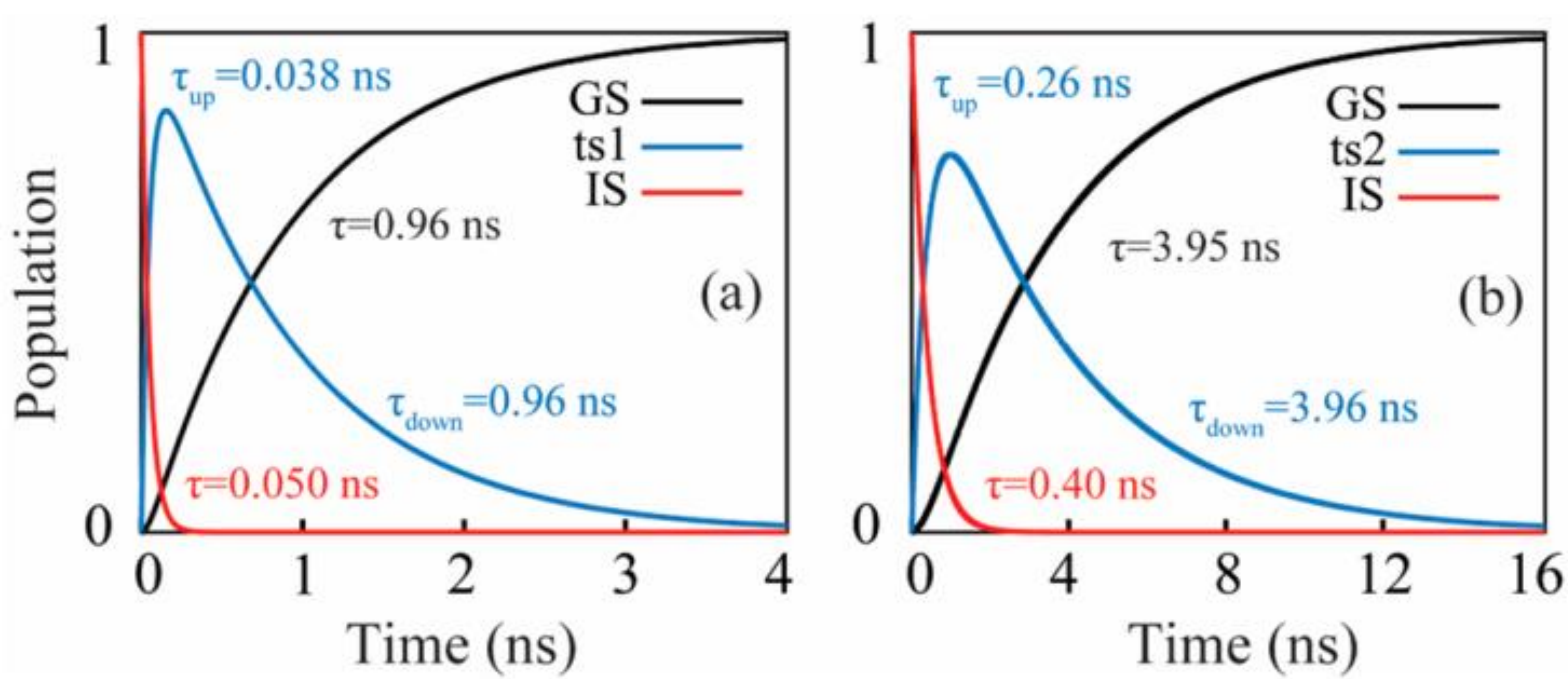


AG-BI INTERACTION



CARRIER RECOMBINATION DYNAMICS





THEORETICAL WORK ON PEROVSKITES: CSPBBR3 GRAIN BOUNDARY

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Cite this: *Nanoscale*, 2023, **15**, 285

Grain boundary sliding and distortion on a nanosecond timescale induce trap states in $CsPbBr_3$: *ab initio* investigation with machine learning force field†

Dongyu Liu,[a] Yifan Wu,[b] Andrey S. Vasenko *[a,c] and Oleg V. Prezhdo *[b,d]

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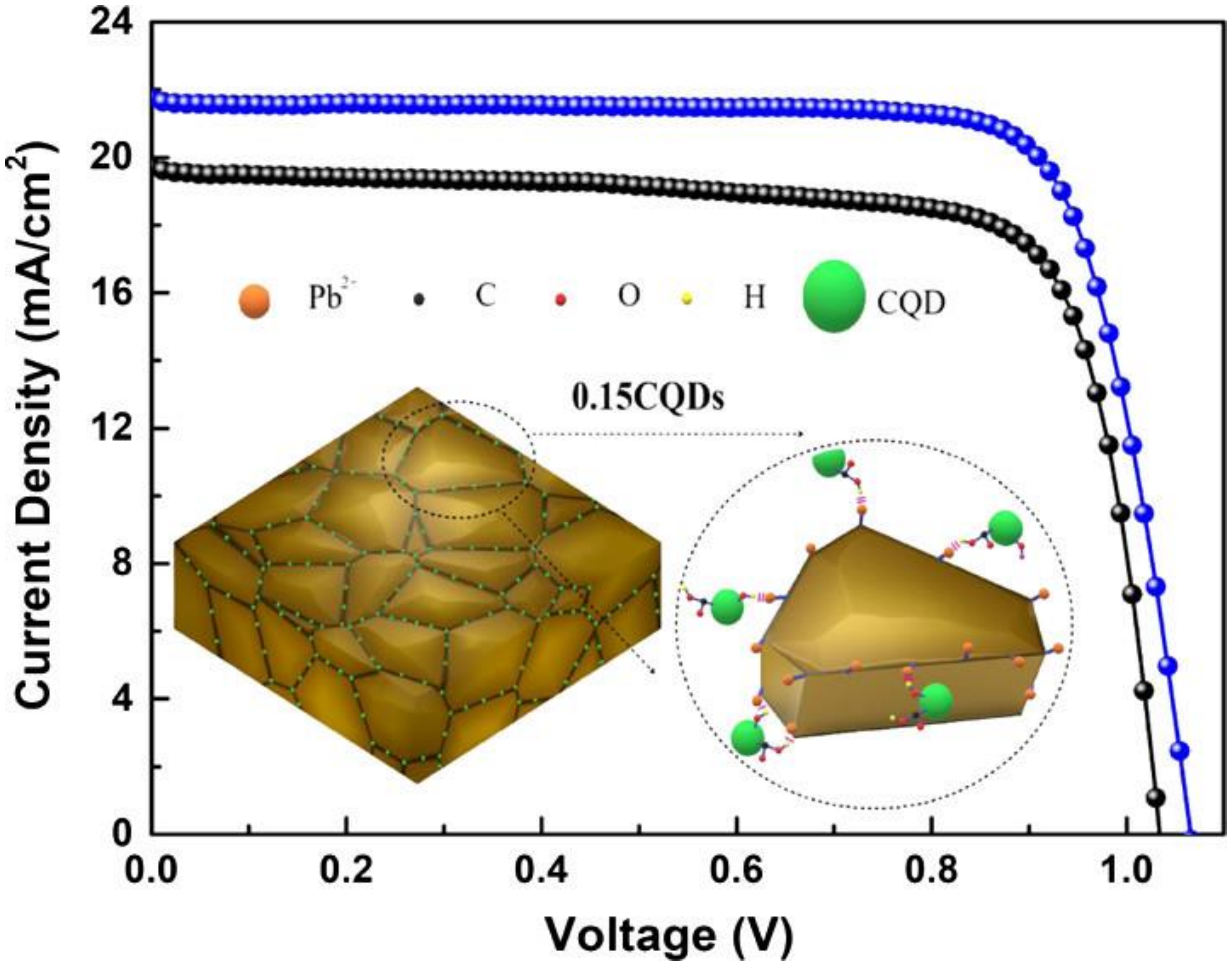
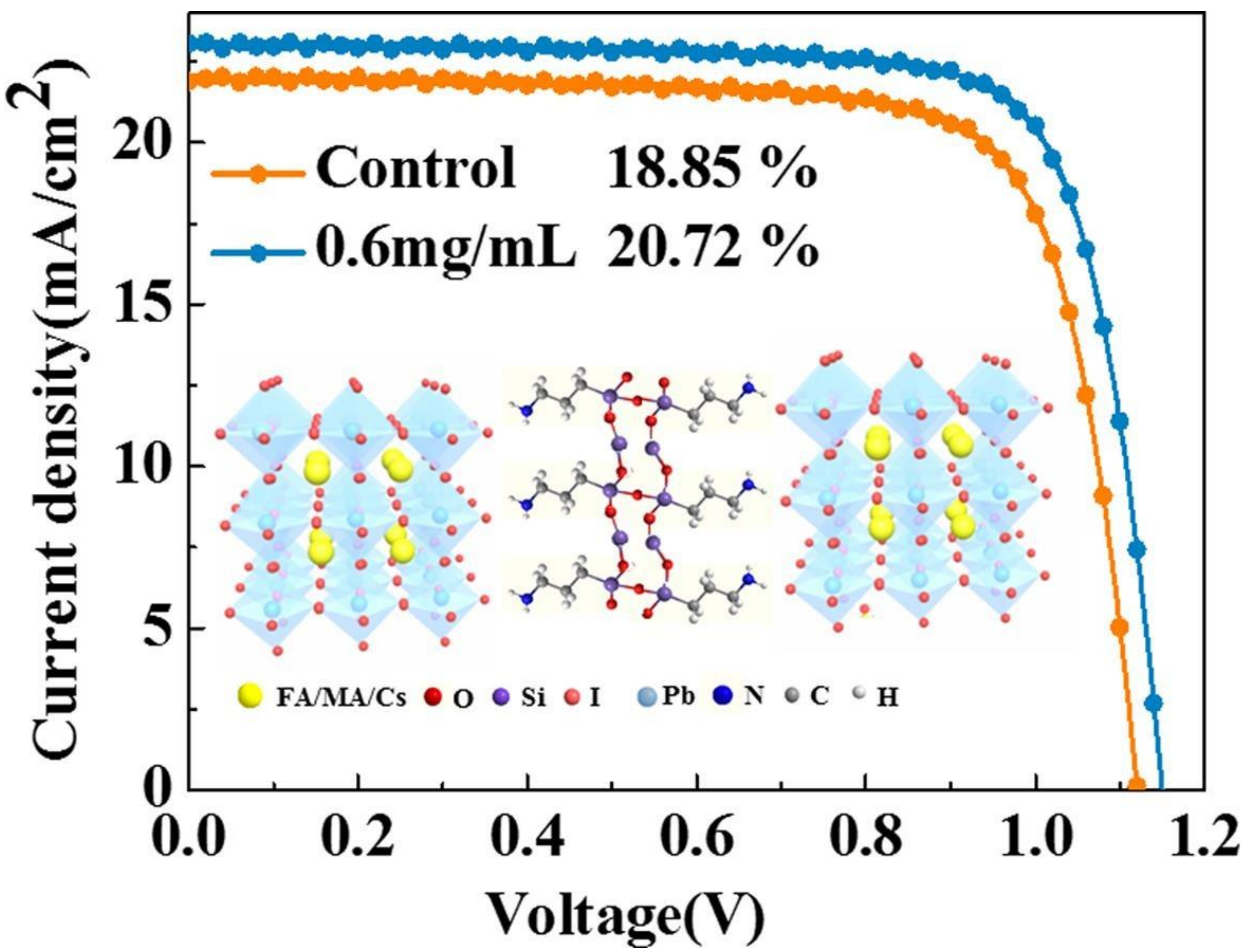
Article

Compression Eliminates Charge Traps by Stabilizing Perovskite Grain Boundary Structures: An Ab Initio Analysis with Machine Learning Force Field

Dongyu Liu, Yifan Wu, Mikhail R. Samatov, Andrey S. Vasenko, Evgueni V. Chulkov,*
and Oleg V. Prezhdo*

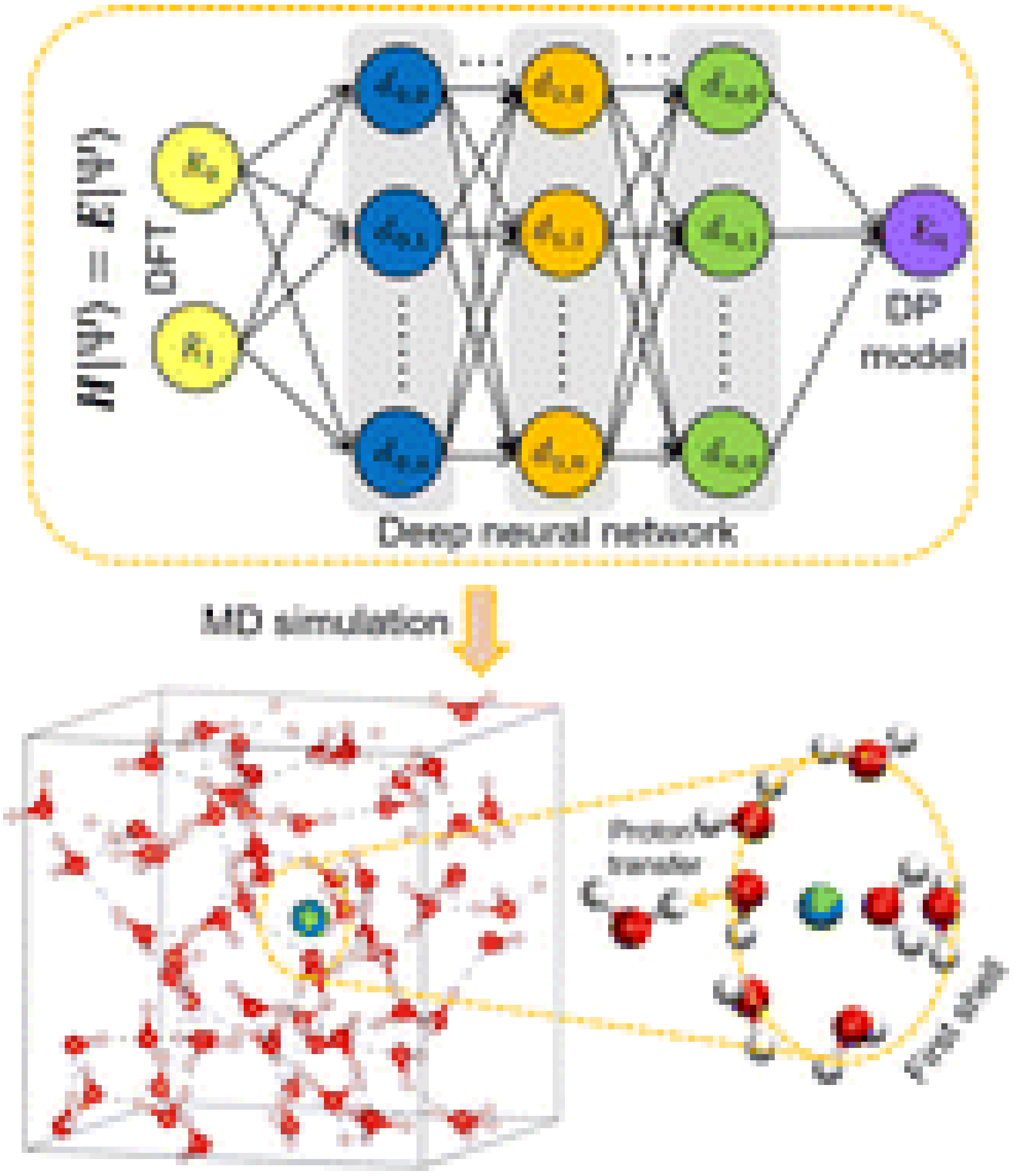
PEROVSKITE GRAIN BOUNDARY

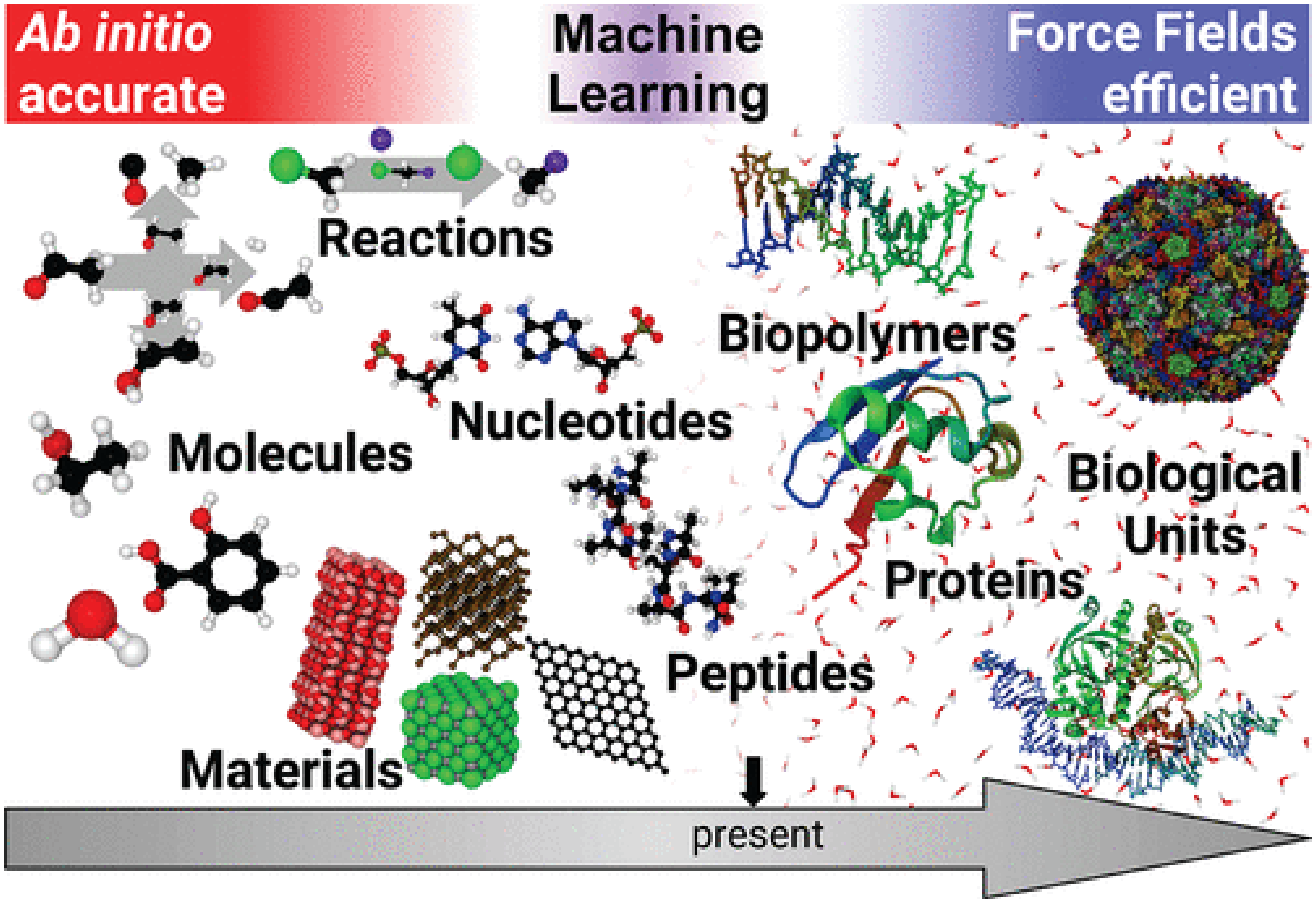




ACS Appl. Mater. Interfaces 2019, 11, 3, 3044–3052, https://doi.org/10.1016/j.solener.2021.06.001

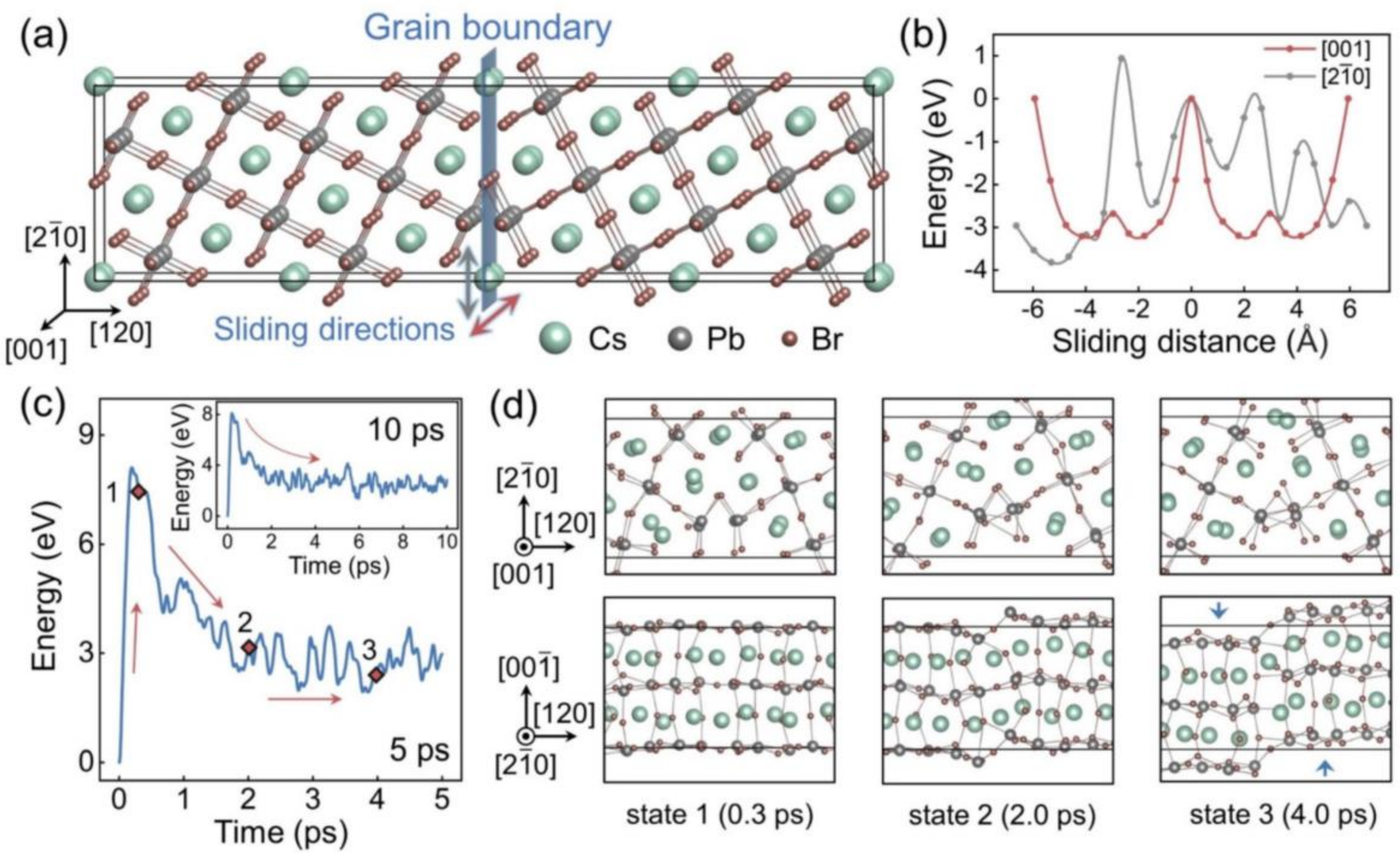
ML FORCE FIELDS





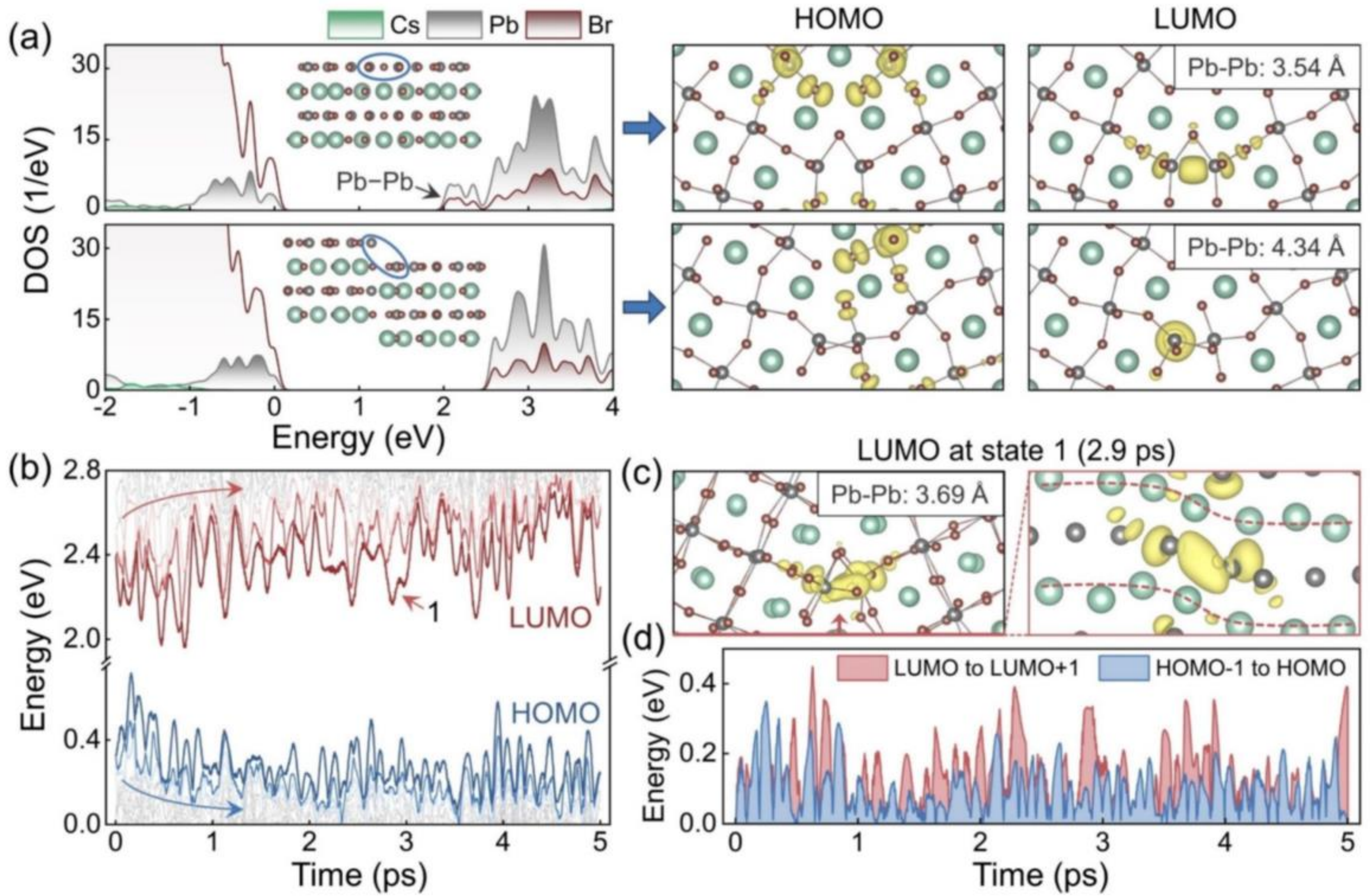
Phys. Chem. Chem. Phys., 2023,25, 983-993, Chem. Rev. 2021, 121, 16, 10142–10186

GB SLIDING

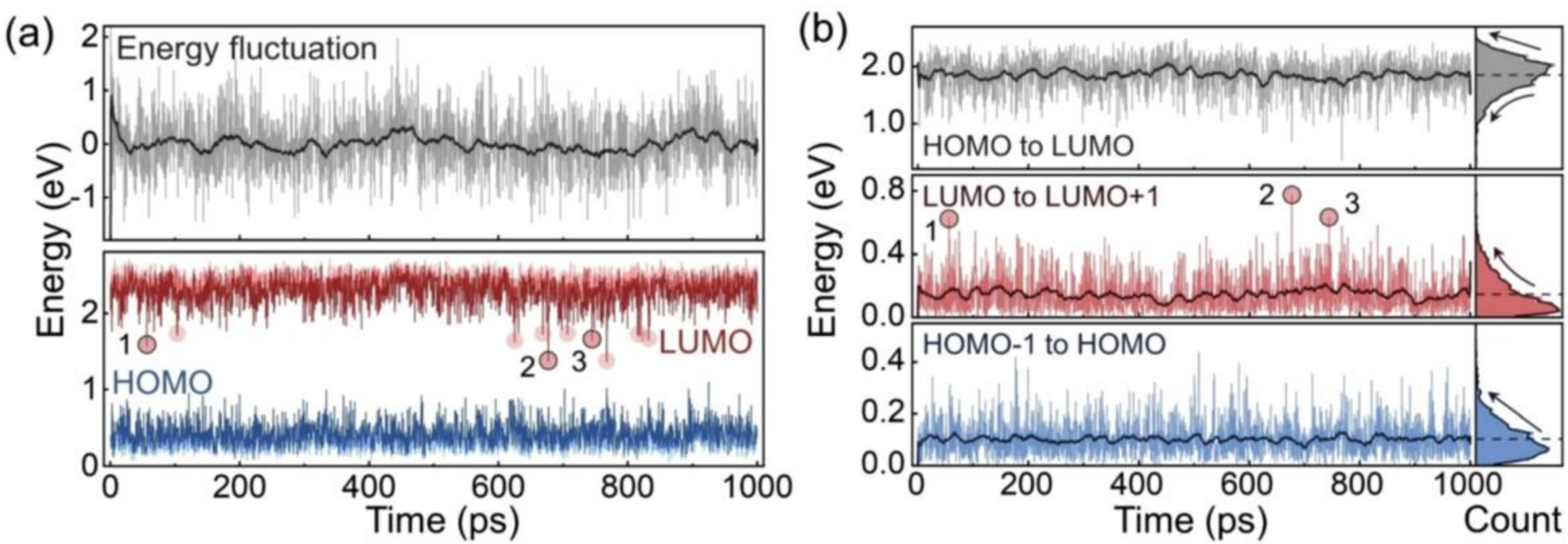


(a)
Grain boundary
[2$\bar{1}$0]
[001]
[120]
Sliding directions
Cs
Pb
Br
(b)
[001]
[2$\bar{1}$0]
Energy (eV)
Sliding distance (Å)
(c)
Energy (eV)
Time (ps)
10 ps
5 ps
(d)
[2$\bar{1}$0]
[120]
[001]
[00$\bar{1}$]
[120]
[2$\bar{1}$0]
state 1 (0.3 ps)
state 2 (2.0 ps)
state 3 (4.0 ps)

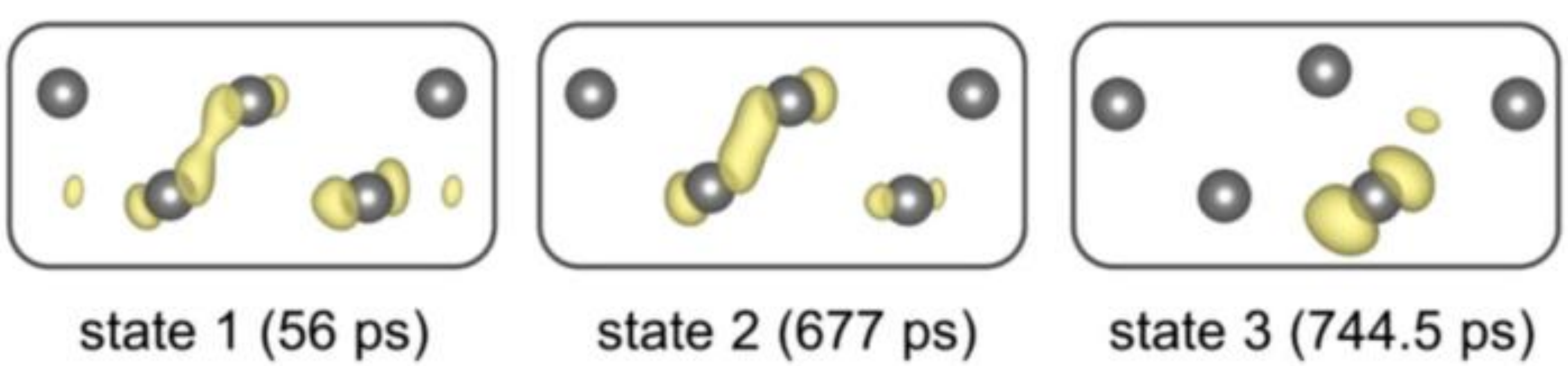
IMPACT OF SLIDING AND DISTORTION



IMPACT OF SLIDING AND DISTORTION

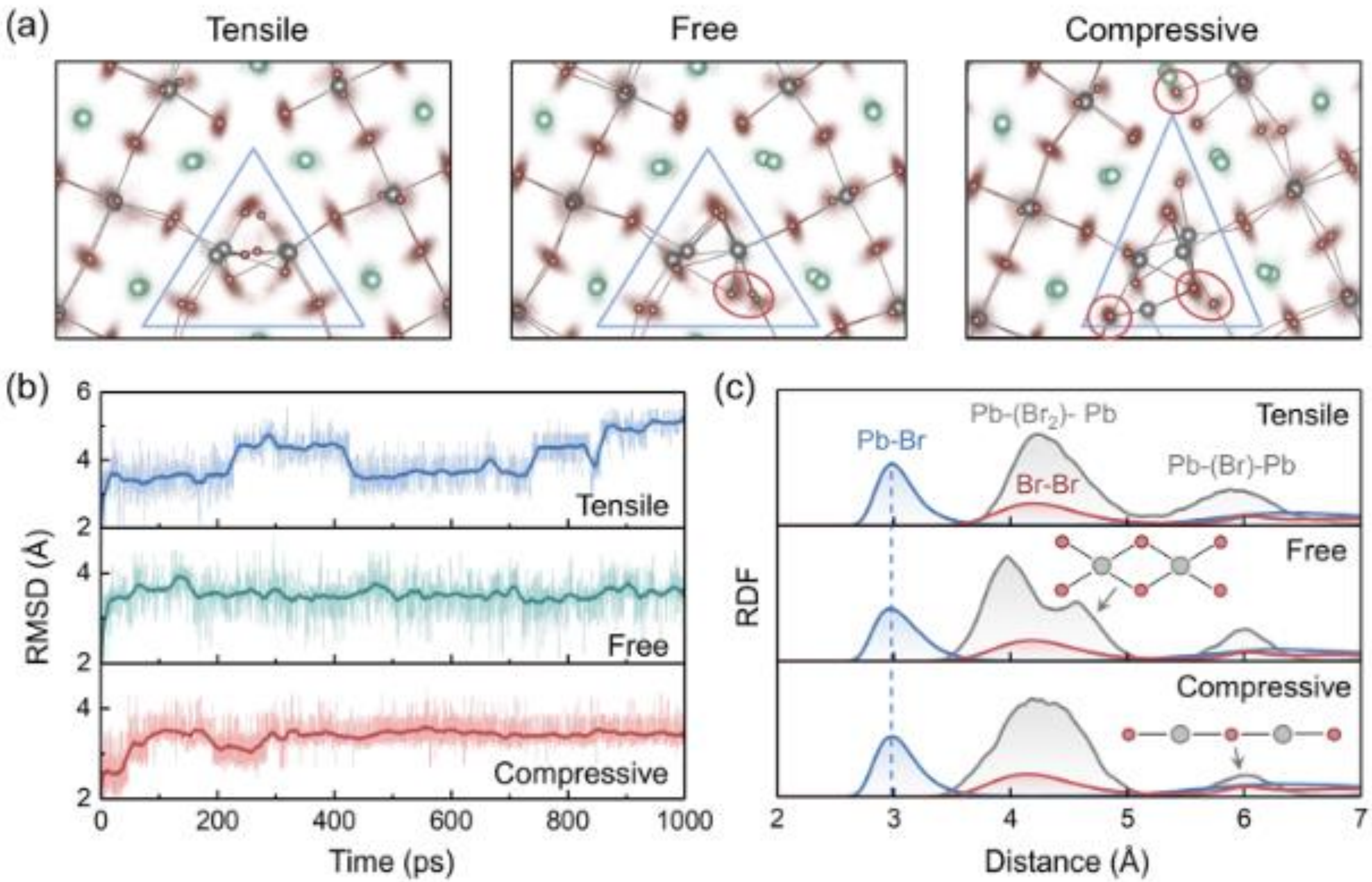


(c)

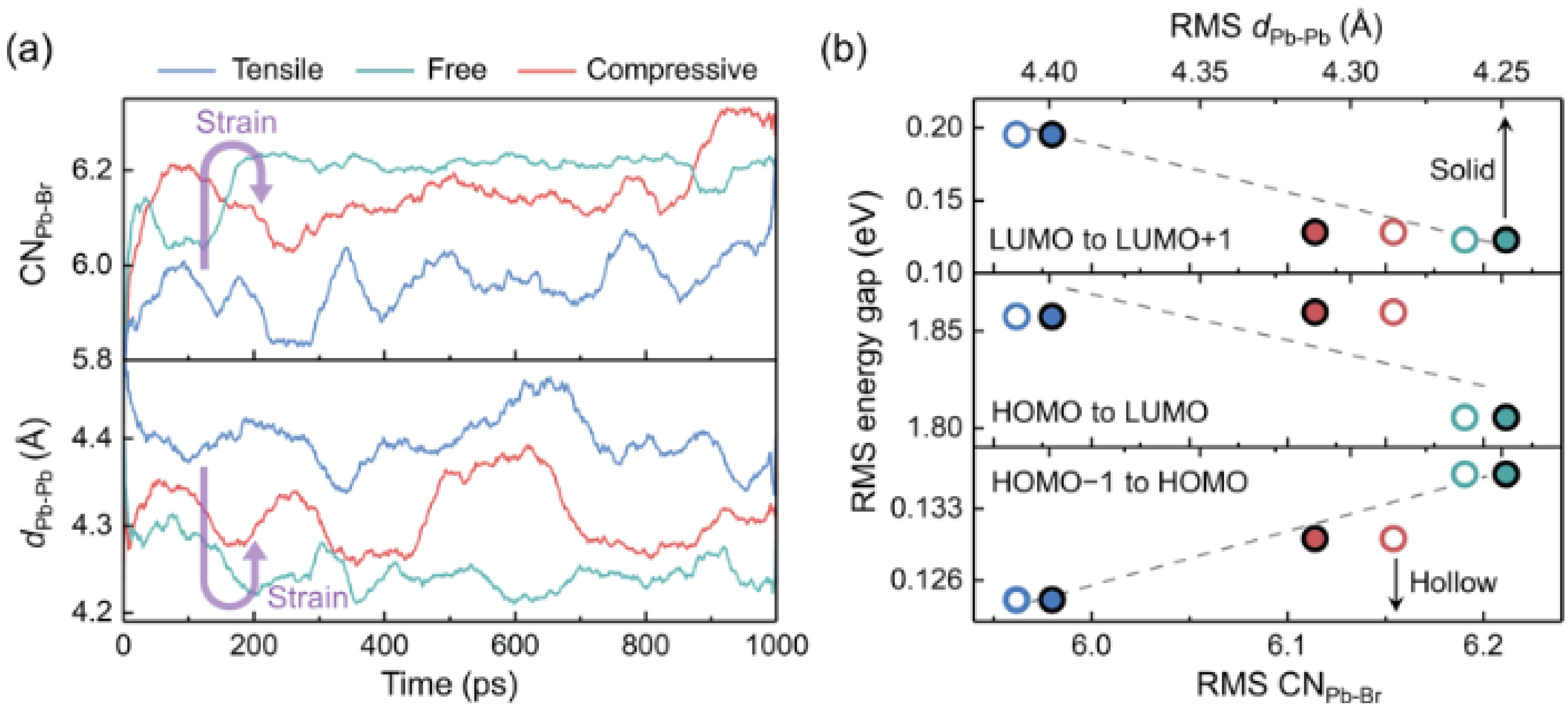


state				
1	4.64	3.88	4.81	3.99
2	4.70	3.67	4.82	3.87
3	4.18	4.76	4.04	5.07

STRAIN SUPPRESSES DISTORTION



STRAIN SUPPRESS DISTORTION



Any Questions?