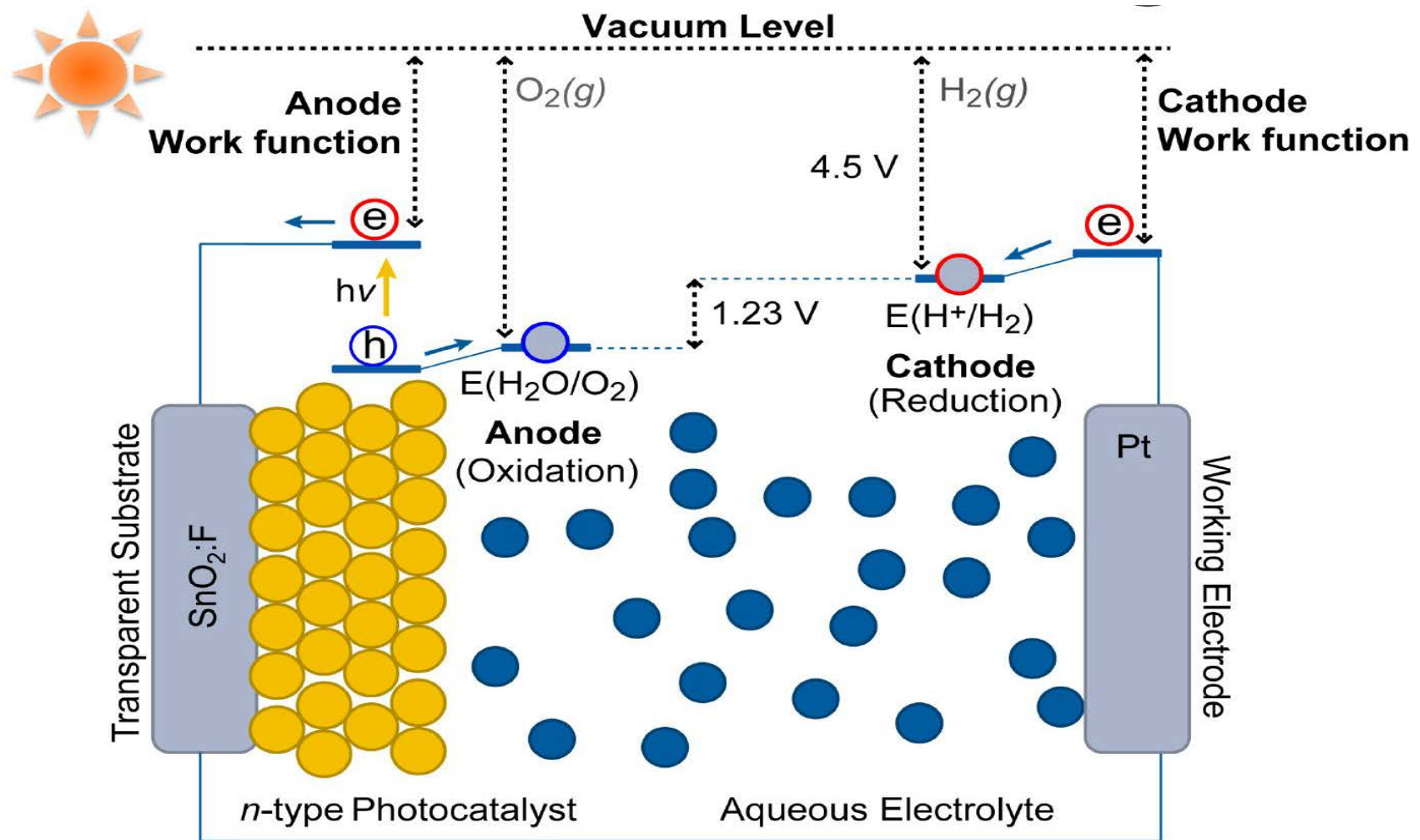




Mechanism and activity of water oxidation on TiO_2 -based materials

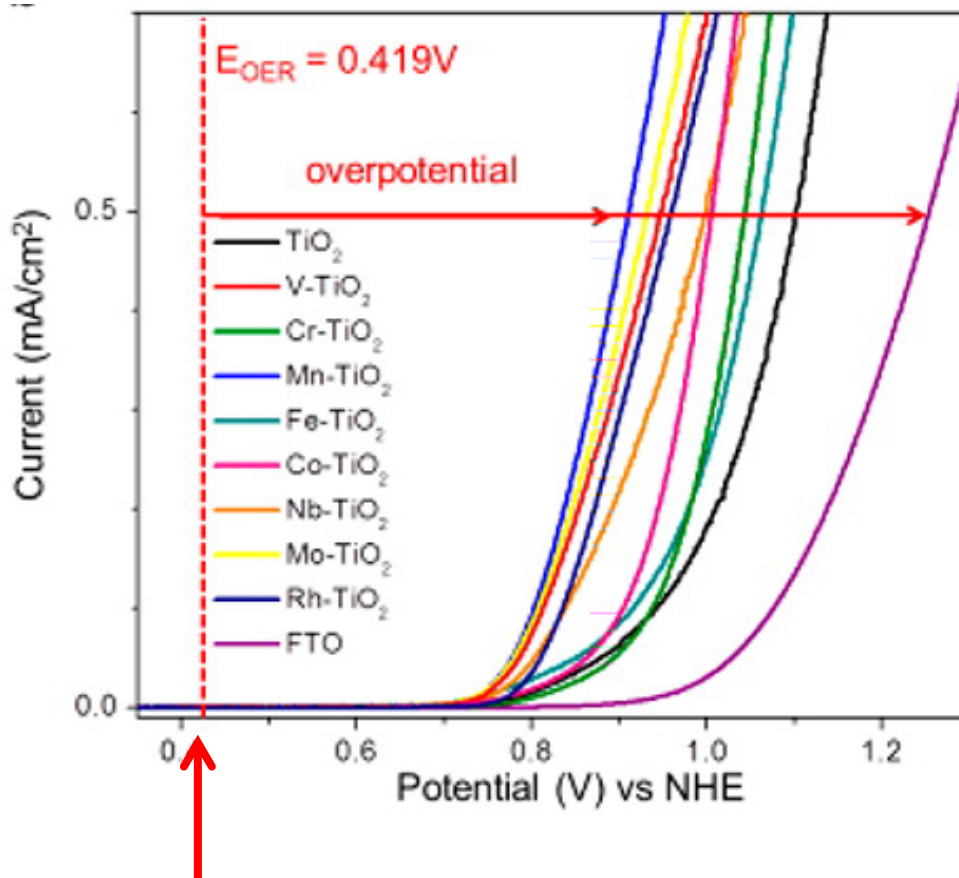
Jia Chen, Jun Hee Lee, Ye Fei Li, AS
Department of Chemistry, Princeton University

Scheme for Photoelectrochemical Water Splitting



TiO_2 abundant and very stable

OER Overpotential on Transition-Metal-Doped TiO₂ Nanowires

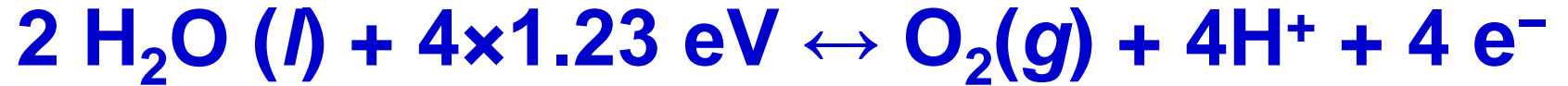


Thermodynamic redox potential for water oxidation at pH = 13.6

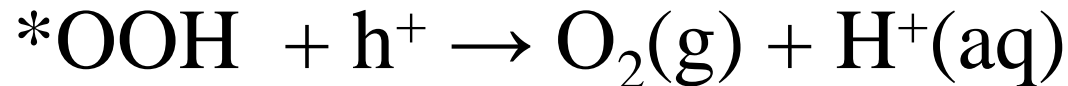
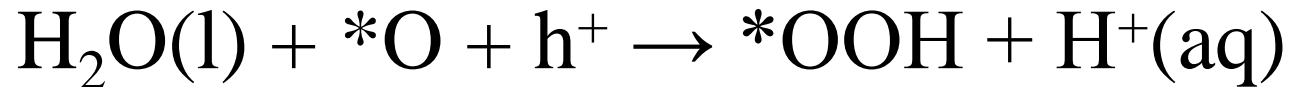
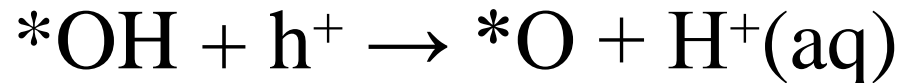
Outline

- TiO_2 is widely used b/c cheap and very stable; yet not very efficient
- TiO_2 modifications \Rightarrow TiO_2 /Ferroelectric Heterostructures
- Try to understand detailed kinetics first!

Oxygen Evolution Reaction – (a)

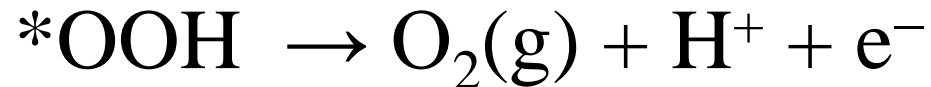


4 PCET steps



Oxygen Evolution Reaction – (b)

Practical scheme used in periodic calculations

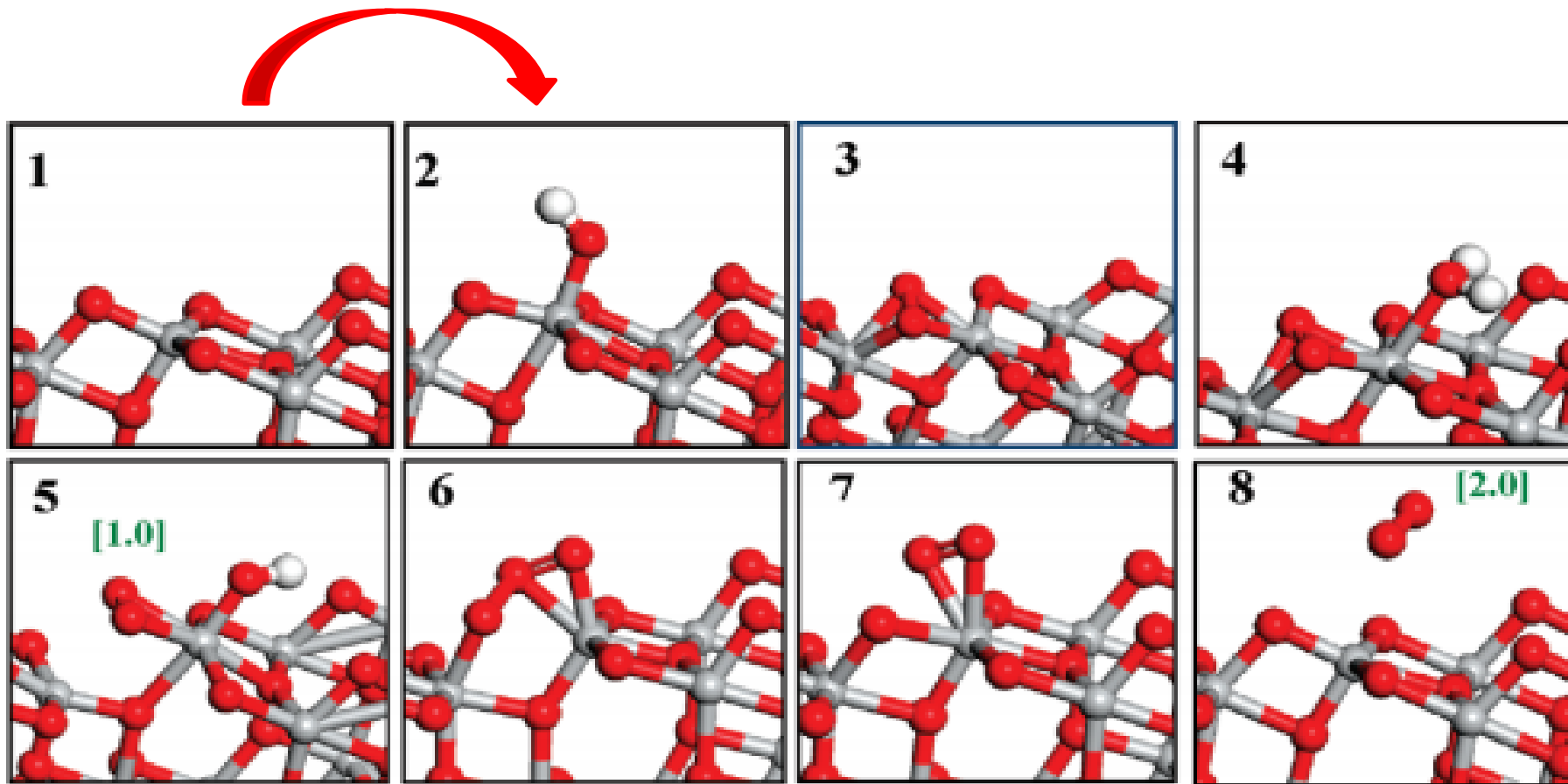


Compute $\Delta G_1 - \Delta G_4$

SHE: $\text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{H}_2$ at $U=0$ & $\text{pH}=0$

Energetics pathway of the OER on anatase (101)

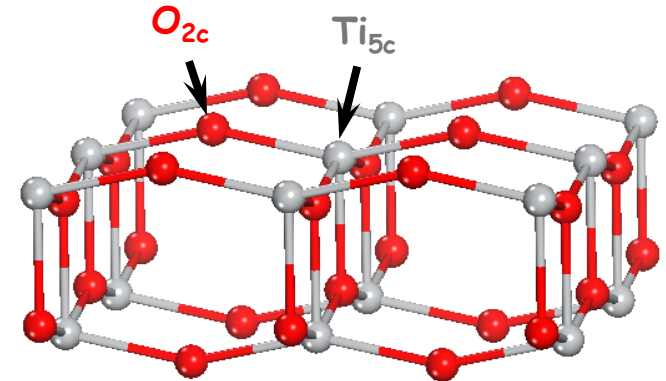
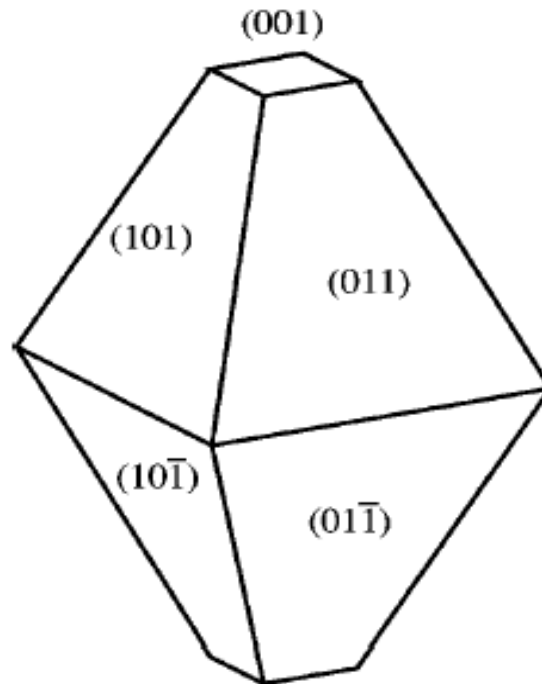
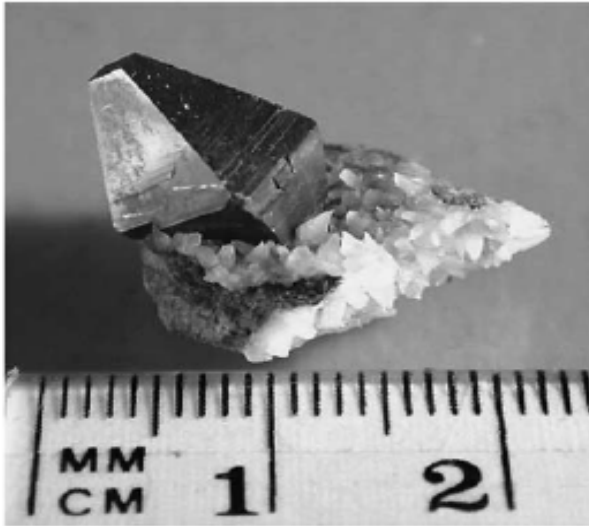
Rate determining step



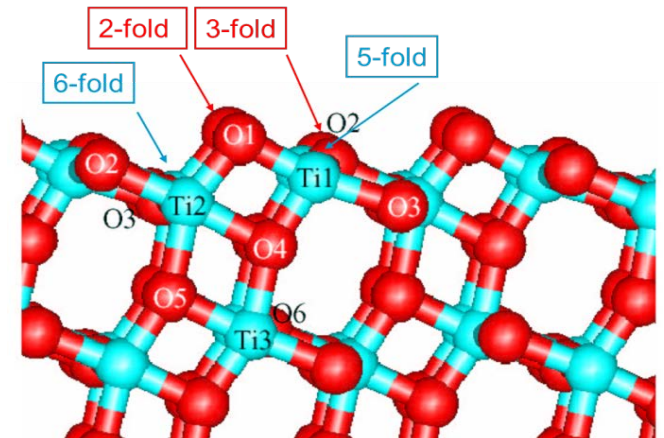
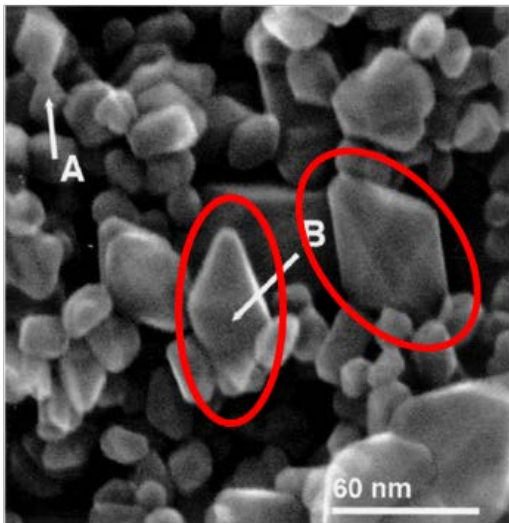
Y.-F. Li, Z.-P Liu, W. Gao and L. Liu, *J. AM. CHEM. SOC.*, 132, 13008.

First proton coupled electron transfer of water oxidation at the interface of water with photoexcited TiO_2 anatase (101)

TiO₂ anatase surface

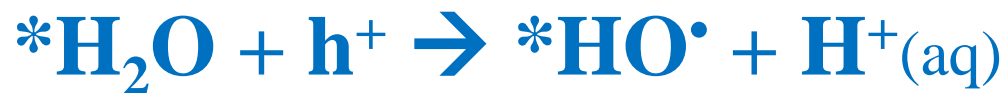


minority (001)

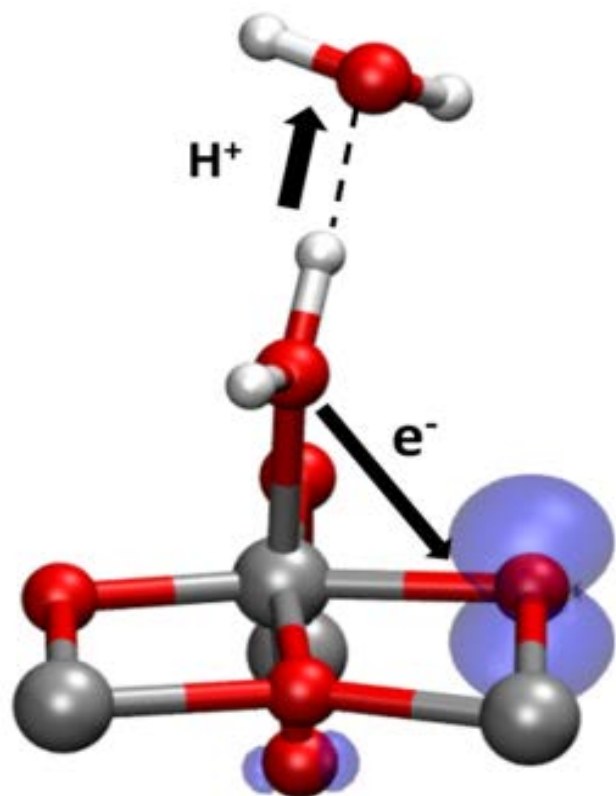


majority (101)

Rate determining step: first proton release



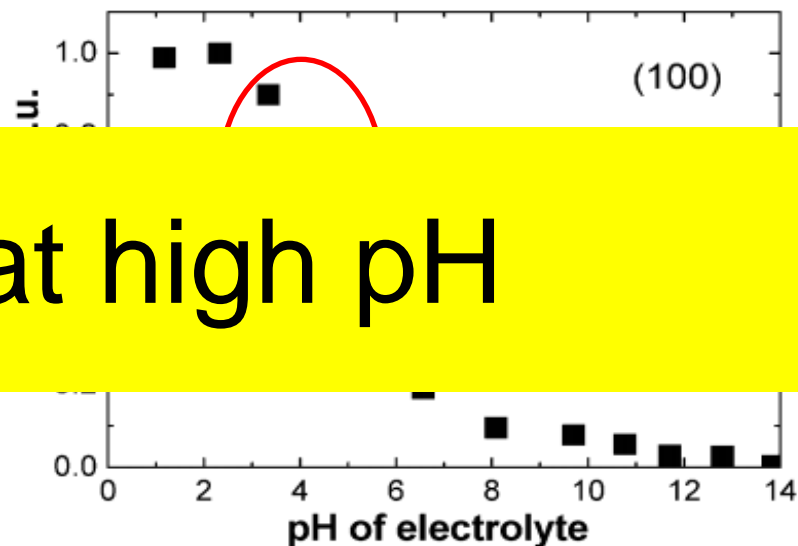
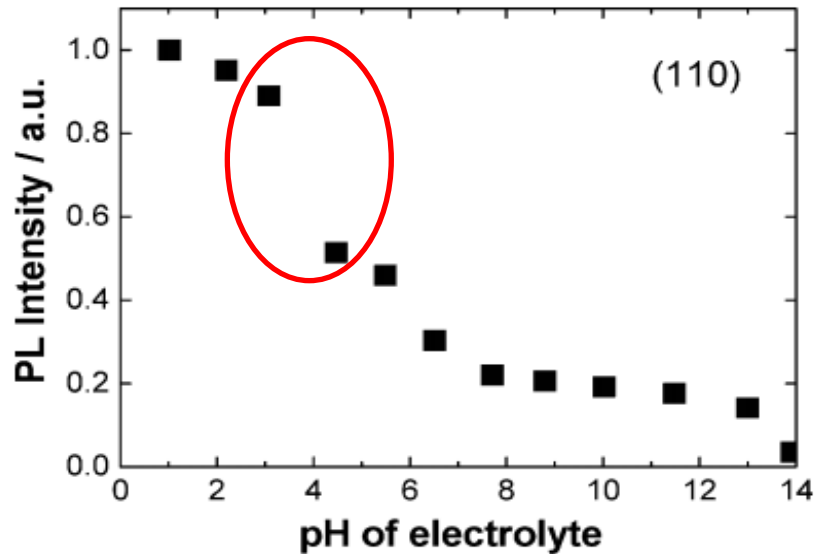
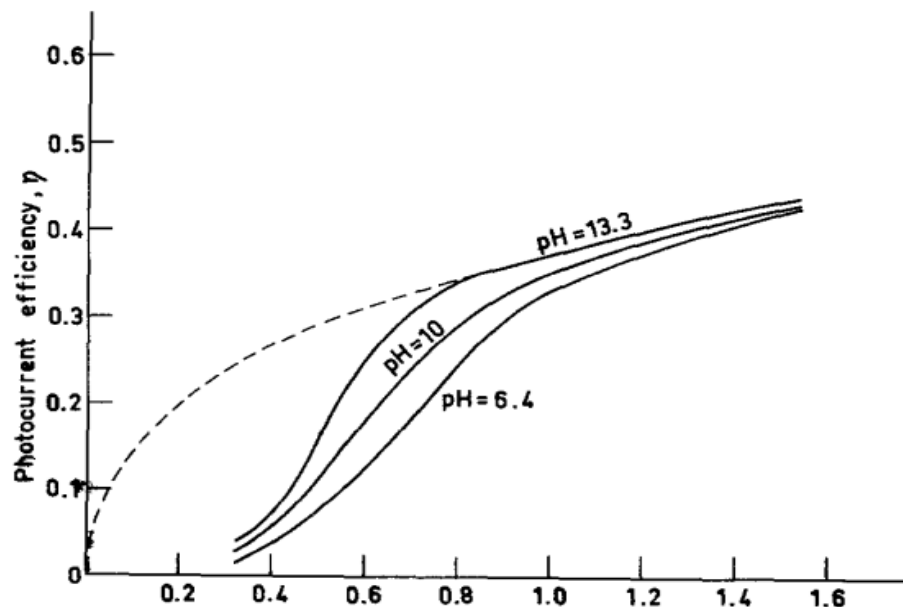
What about kinetics?



General interest

Specific issues

Influence of pH for OER on TiO₂



OER is faster at high pH

Overpotential's dependence on pH



$$\Delta G/e \text{ (pH)} = \Delta G^0/e - 0.059\text{eV pH}$$

$$E_{\text{O}_2/\text{H}_2\text{O}} = E^0_{\text{O}_2/\text{H}_2\text{O}} - 0.059\text{eV pH}$$

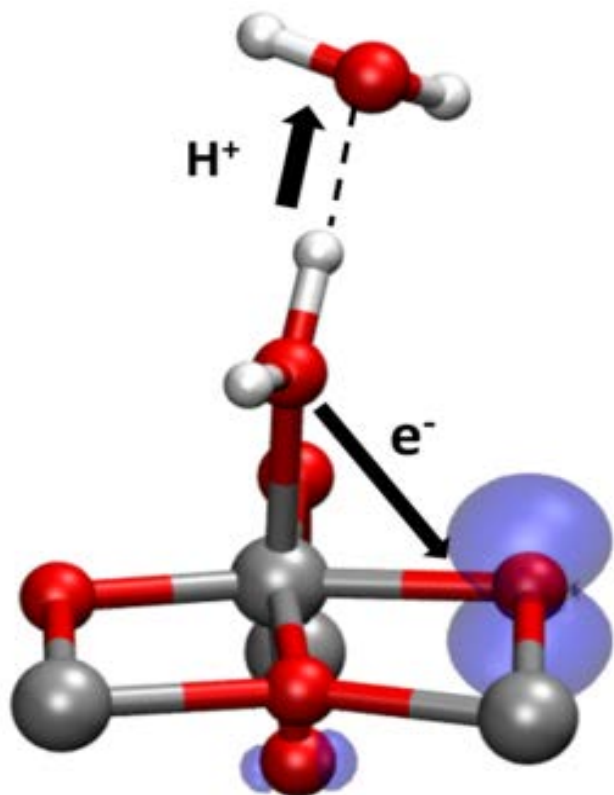
Theoretical analysis of energetics predicts the onset overpotential to be independent of pH

$$\eta(\text{pH}) = \Delta G(\text{pH})/e - E_{\text{O}_2/\text{H}_2\text{O}} = \Delta G^0/e - E^0_{\text{O}_2/\text{H}_2\text{O}} = \text{constant}$$

Rate determining step: first proton release



How to deal with the kinetics?



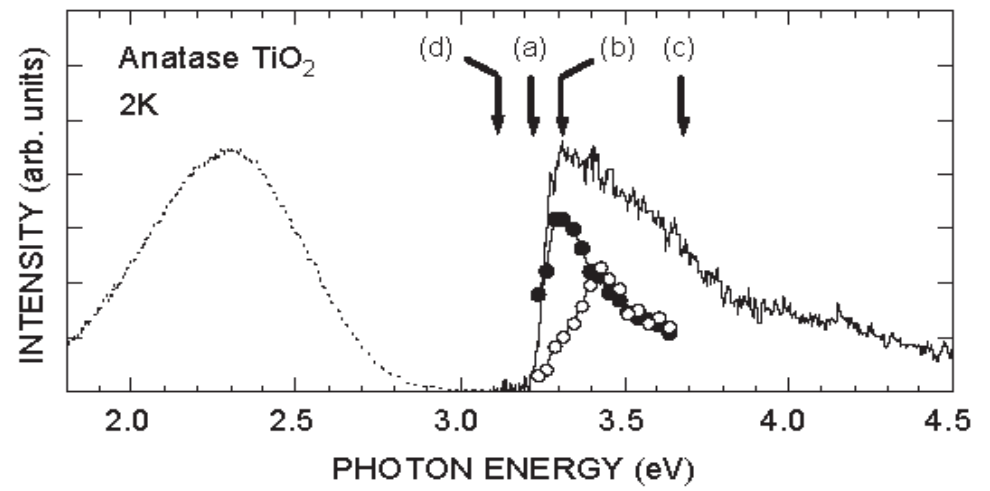
Difficulties:

- (i) **Localized hole**
- (ii) Solvation effect
- (iii) Reaction coordinate for proton coupled electron transfer

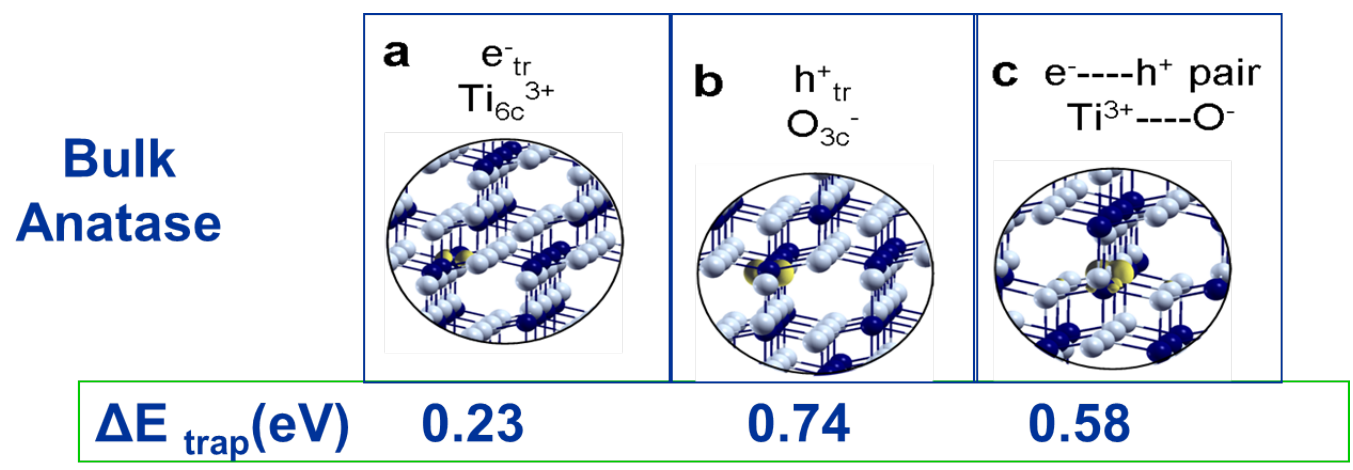
➤ Experimental evidence of self-trapped excitons/ holes in TiO_2

Luminescence band from self trapped (triplet) excitons in anatase TiO_2

Watanabe & Hayashi, J. Lumin. (2005)

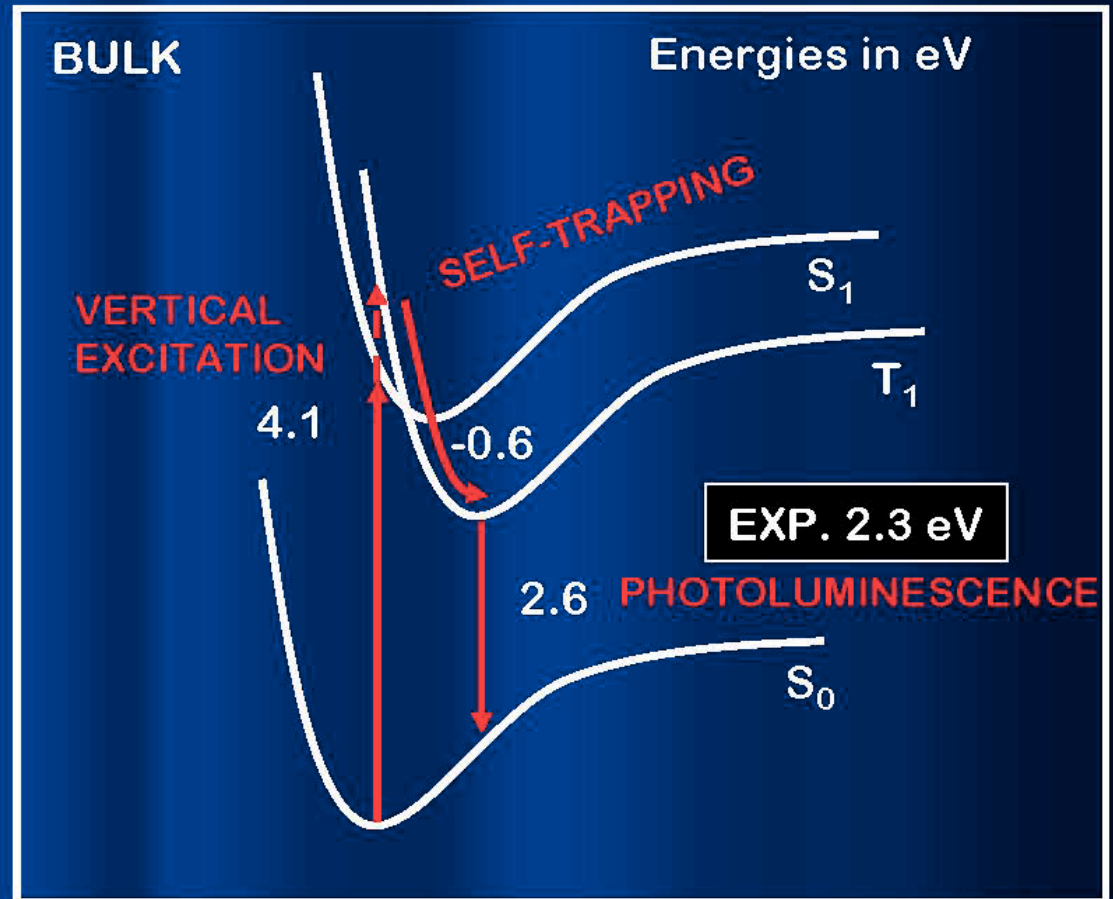
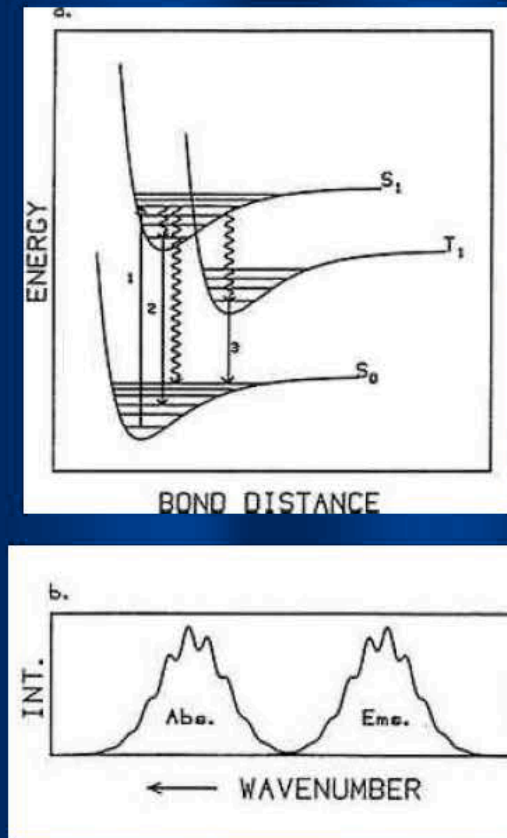


➤ Self-trapped polarons well described by hybrid functionals*



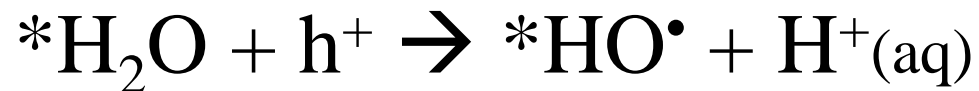
* C. Di Valentin, AS, JPC Lett. 2, 2223 (2011)

SCHEMATIC REPRESENTATION OF BULK ANATASE TiO_2 SPECTROSCOPY

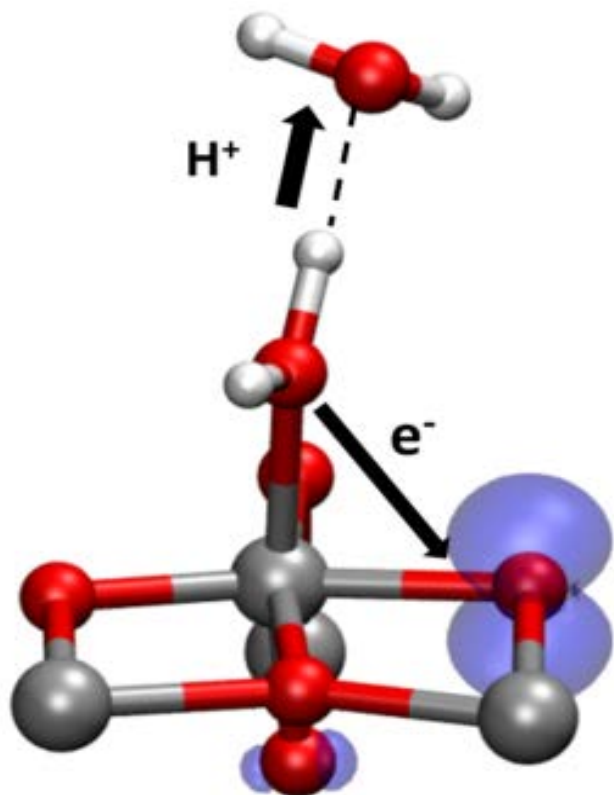


Order-N **PBE0** hybrid functional based on Maximally
Localized Wannier Functions implemented in Car-Parrinello
Molecular Dynamics in Quantum-Espresso.

Rate determining step: first proton release



How to deal with kinetics?



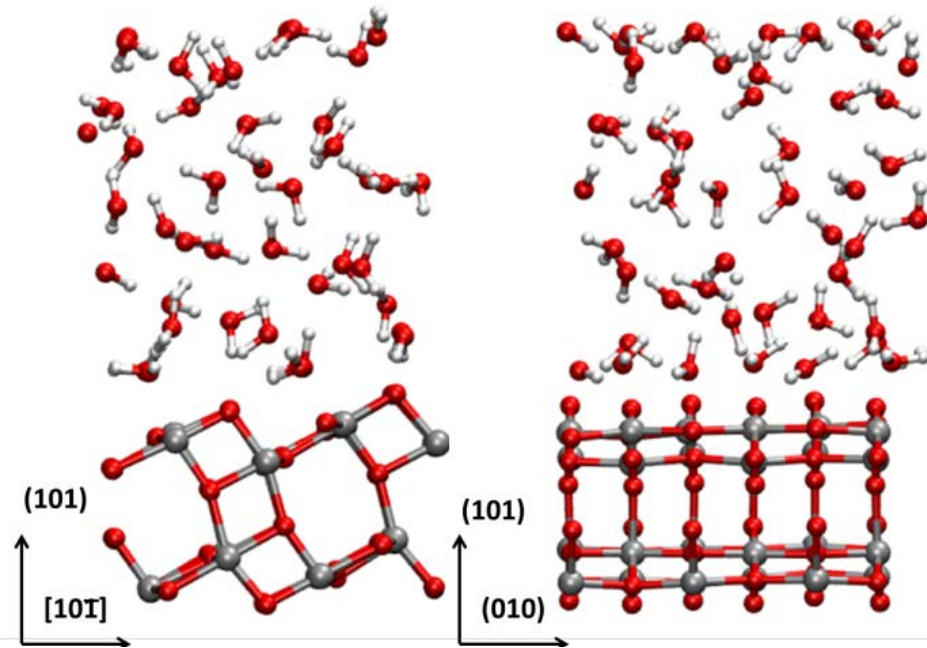
Difficulties:

(i) Localized hole

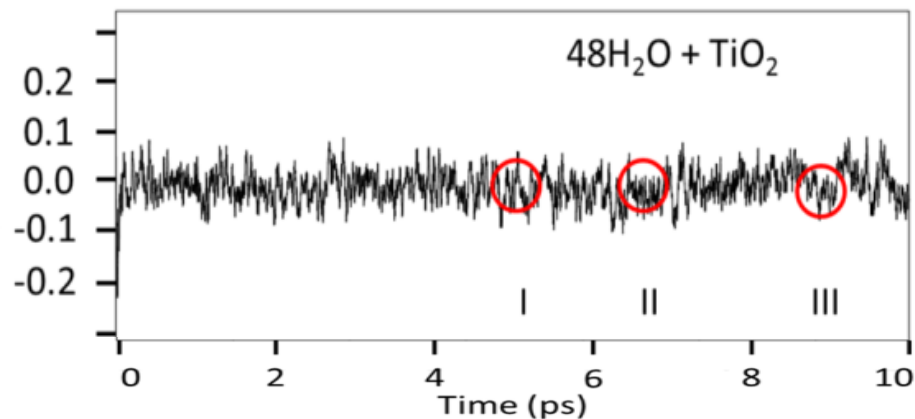
(ii) **Solvation effect**

(iii) Reaction coordination for proton coupled electron transfer

Solvation effect



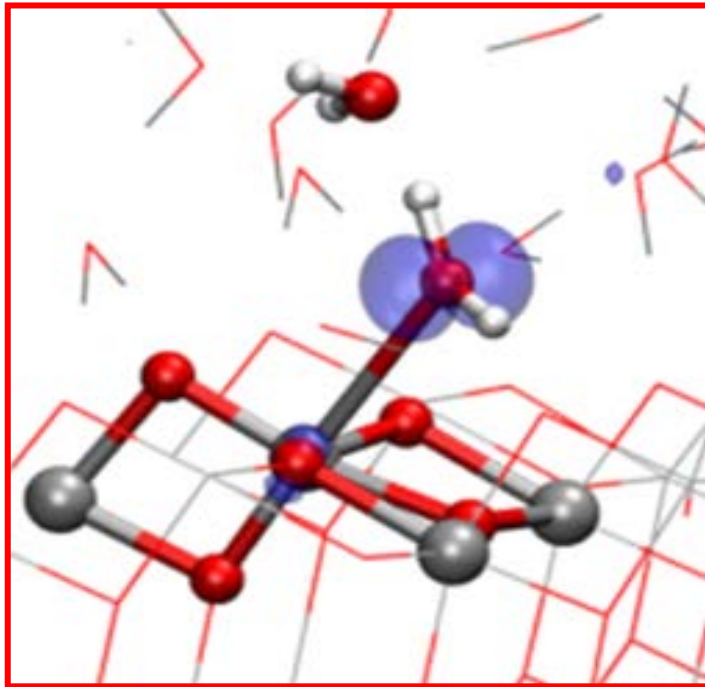
System size:
24 TiO₂ units +48 H₂O



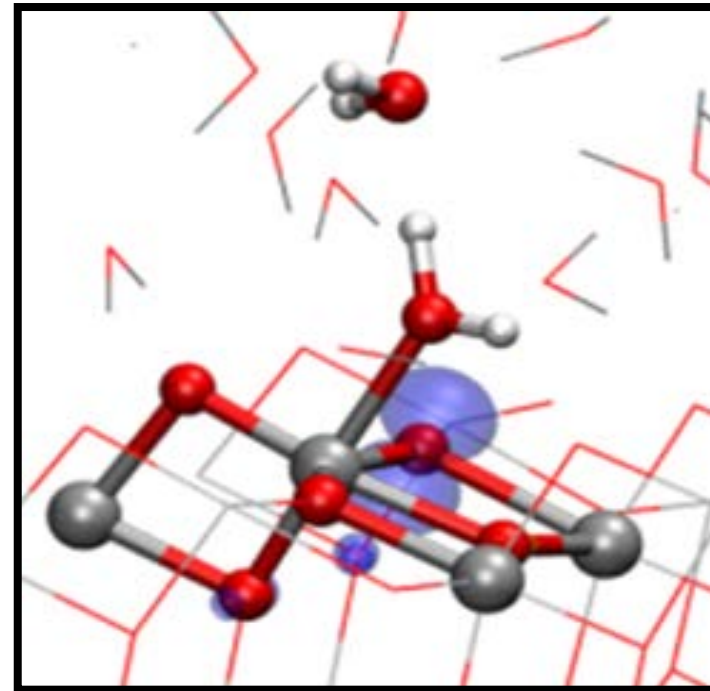
- (i) 10ps CPMD, 330K, PBE;
- (ii) Select three snapshots; (iii)
- Add a hole then relax with PBE0.

Relaxed system

Water-hole state



Surface-hole state

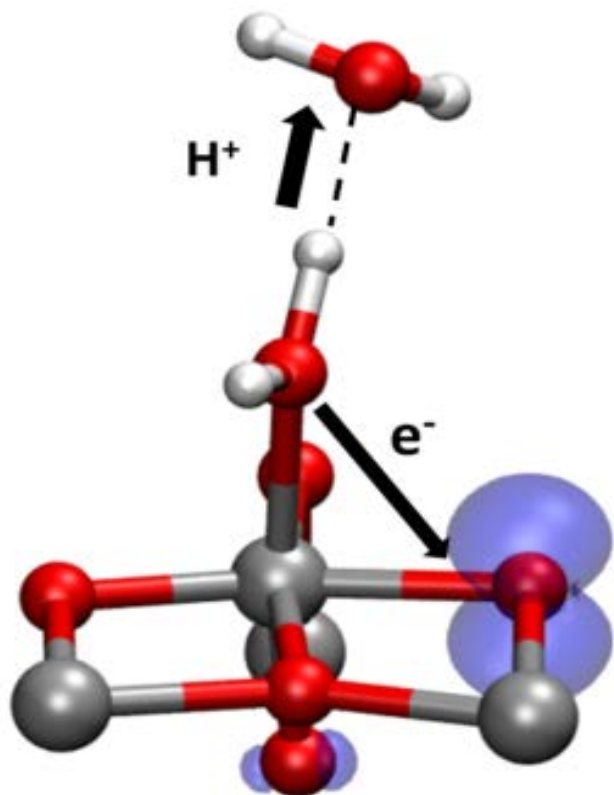


Spin density plot

Rate determining step: first proton release



How to deal with the kinetics?



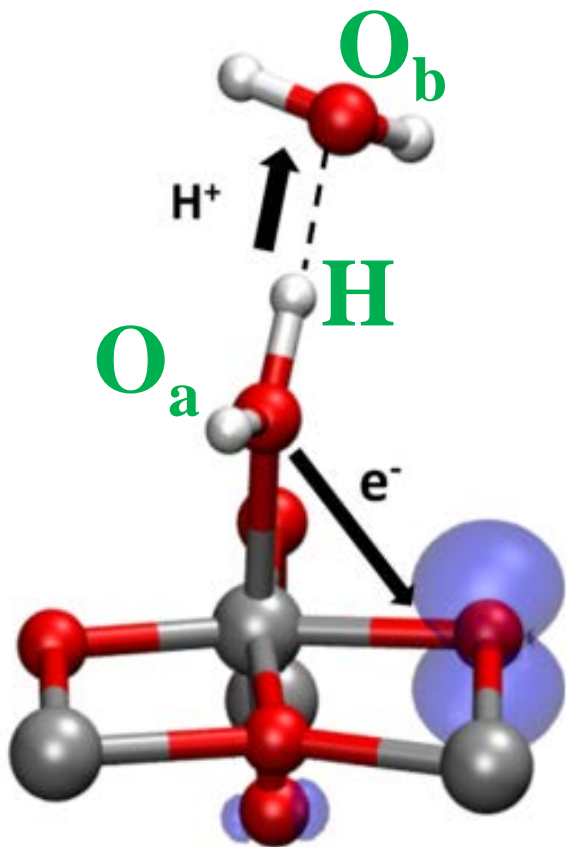
Difficulties:

(i) Localized hole

(ii) Solvation effect

(iii) **Reaction coordinate for proton coupled electron transfer**

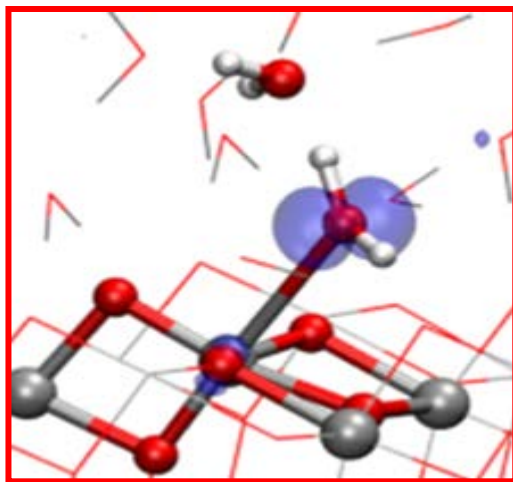
Reaction Coordinate for Proton Coupled Electron Transfer



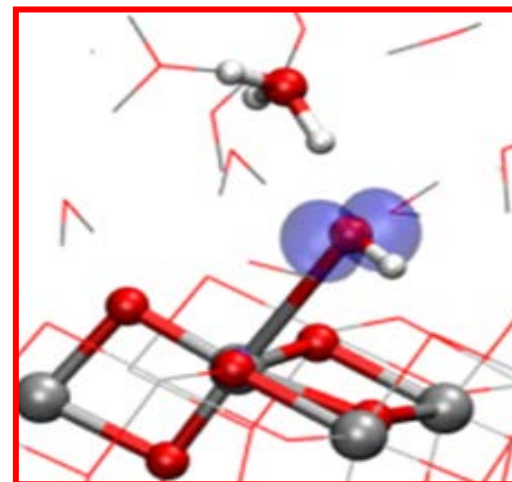
Difference between the distances of the proton to two water oxygens

$$\Delta d = d(O_a-H) - d(O_b-H)$$

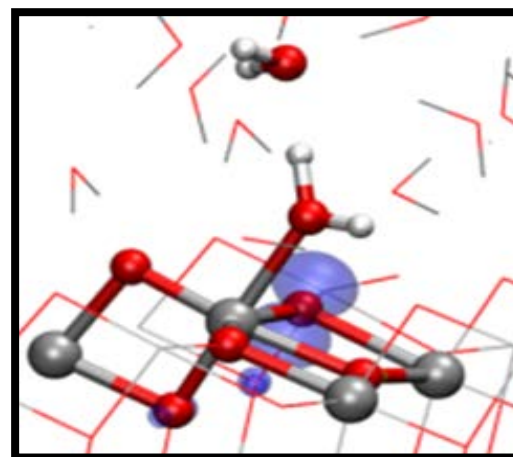
Water-hole state



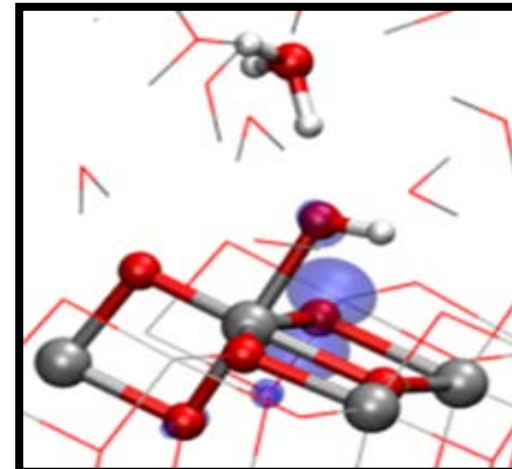
PT



Surface-hole state



PT

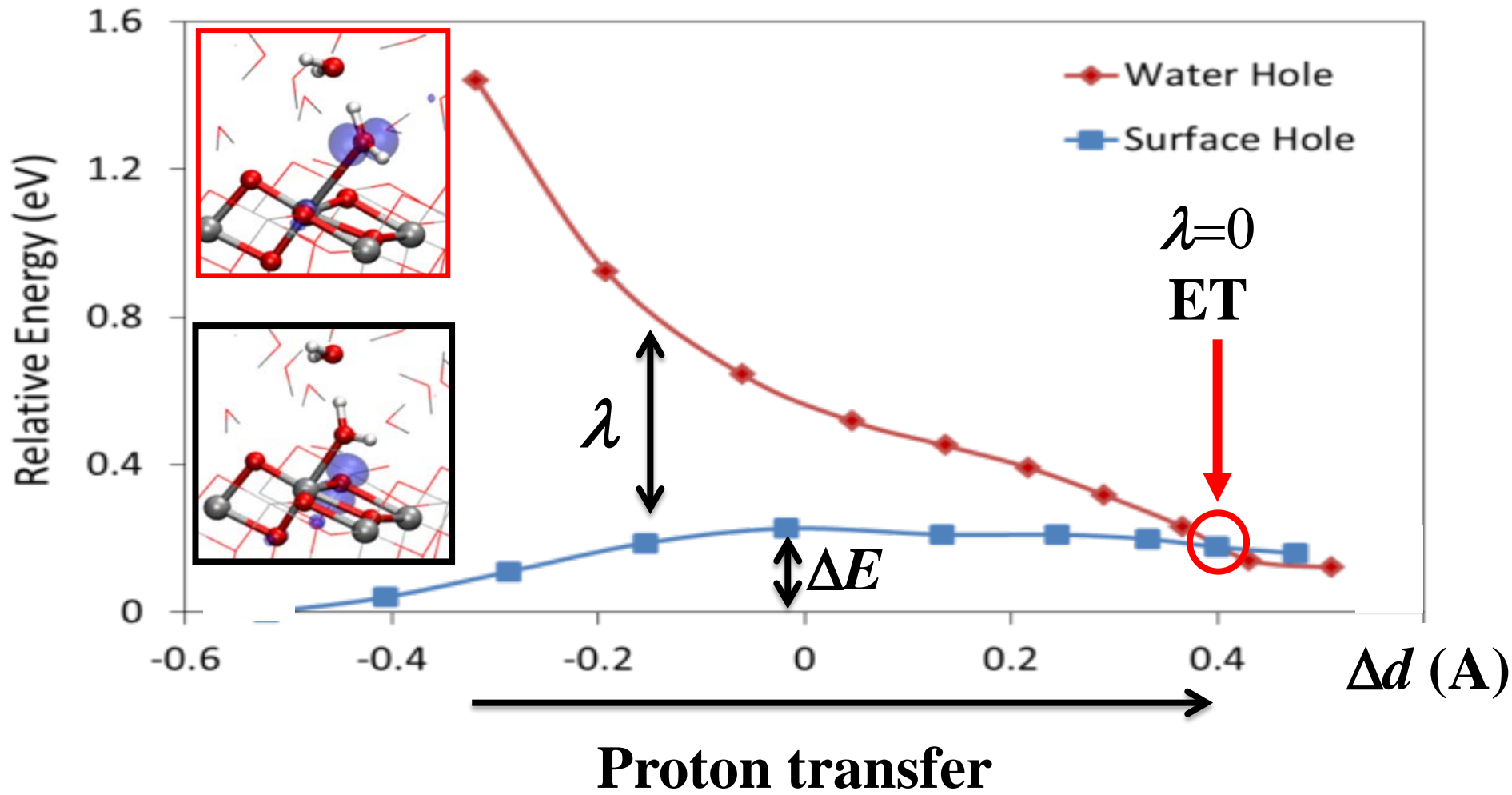


$\Delta d \sim -0.5$

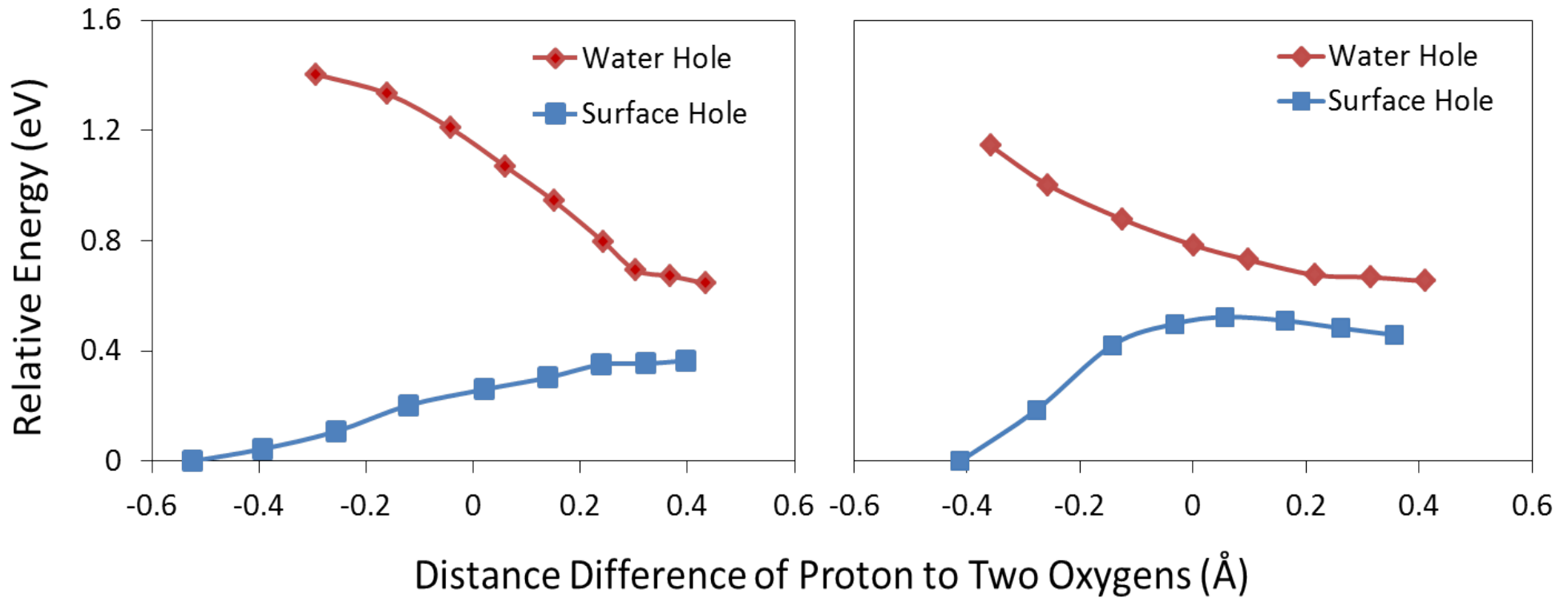
$\Delta d \sim +0.5$

Reaction Coordinate (Δd)

Potential Energy Surfaces



Additional snapshots

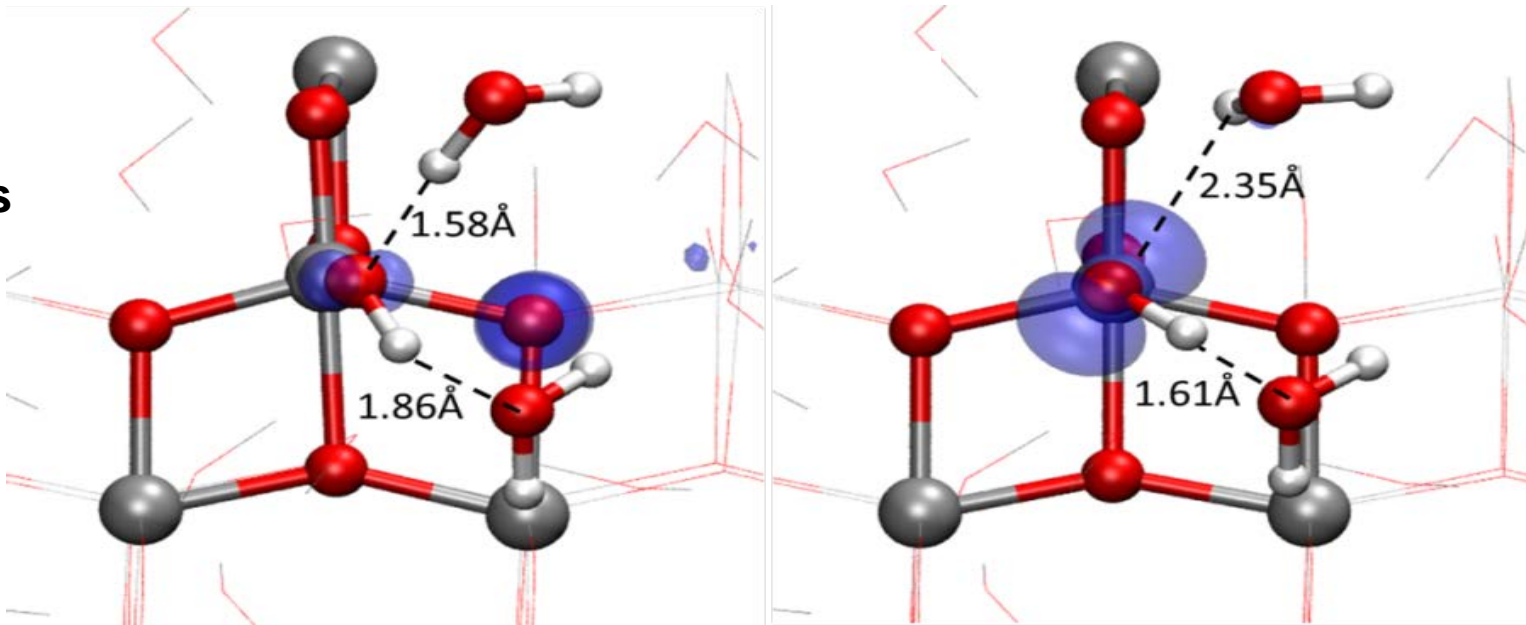


PCET likely sequential:



Why PT first?

Top views

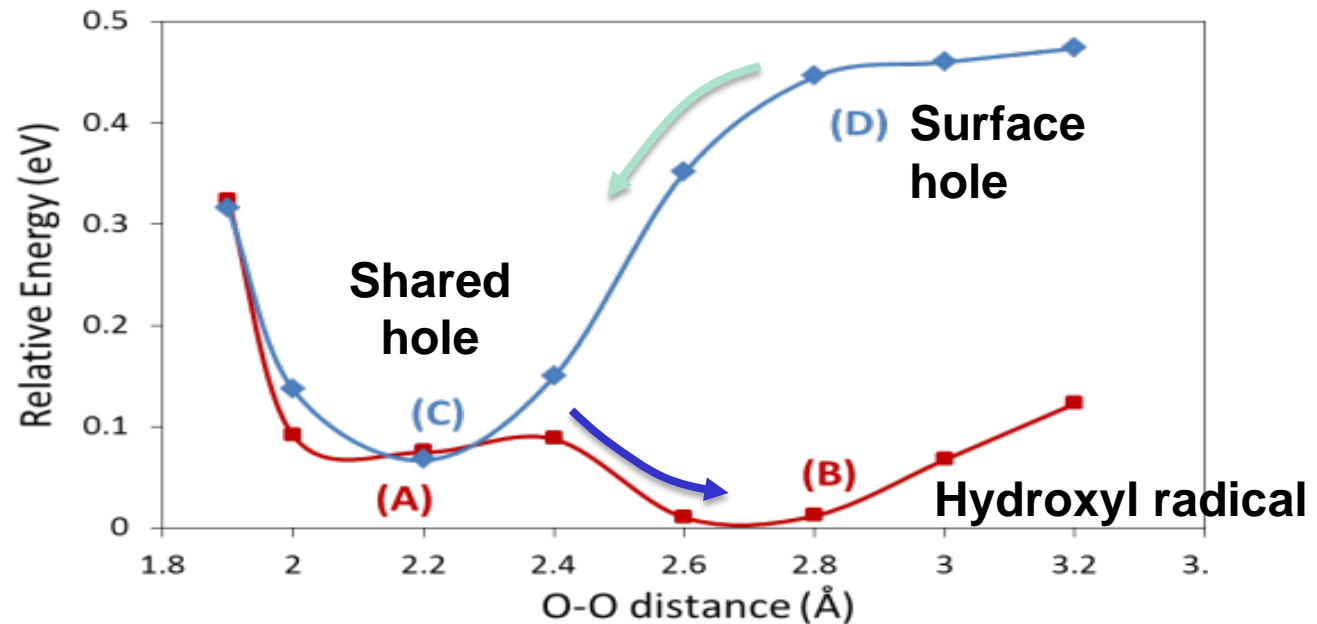
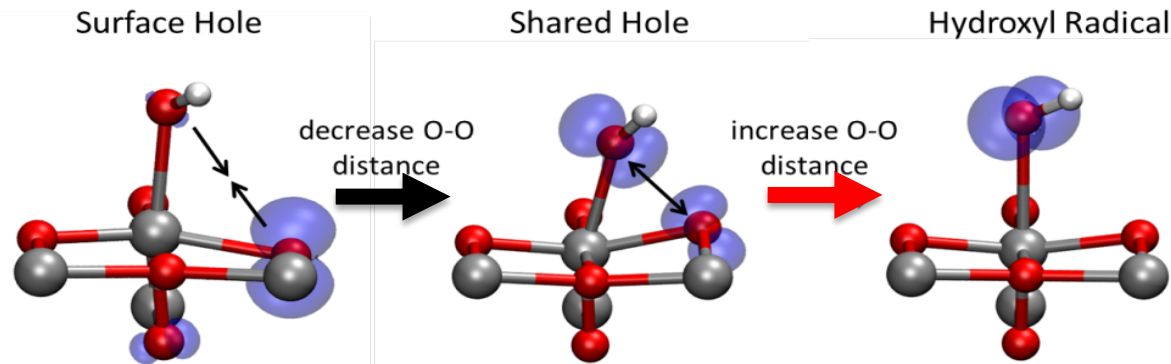


OH⁻ & surface hole
OH⁻ accepts H-bond

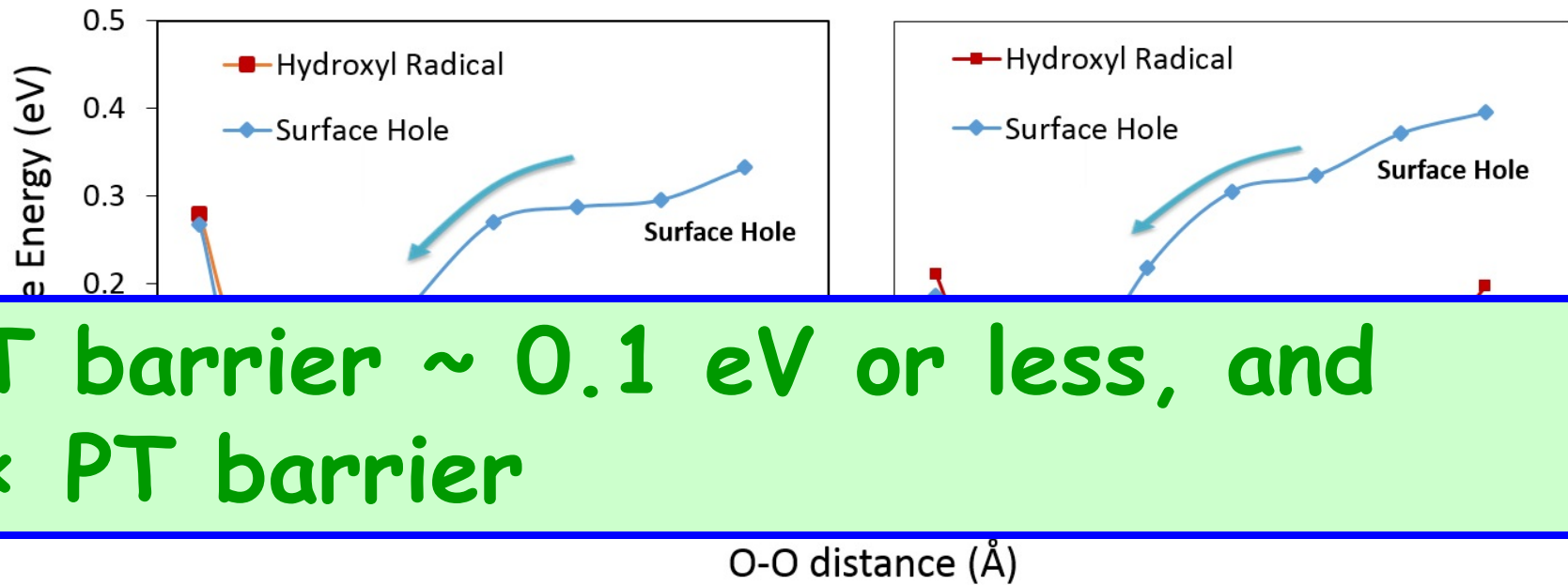
OH radical
donates H-bond

Kinetics of $*\text{OH}^- + \text{h}^+ \rightarrow *\text{OH}\cdot$

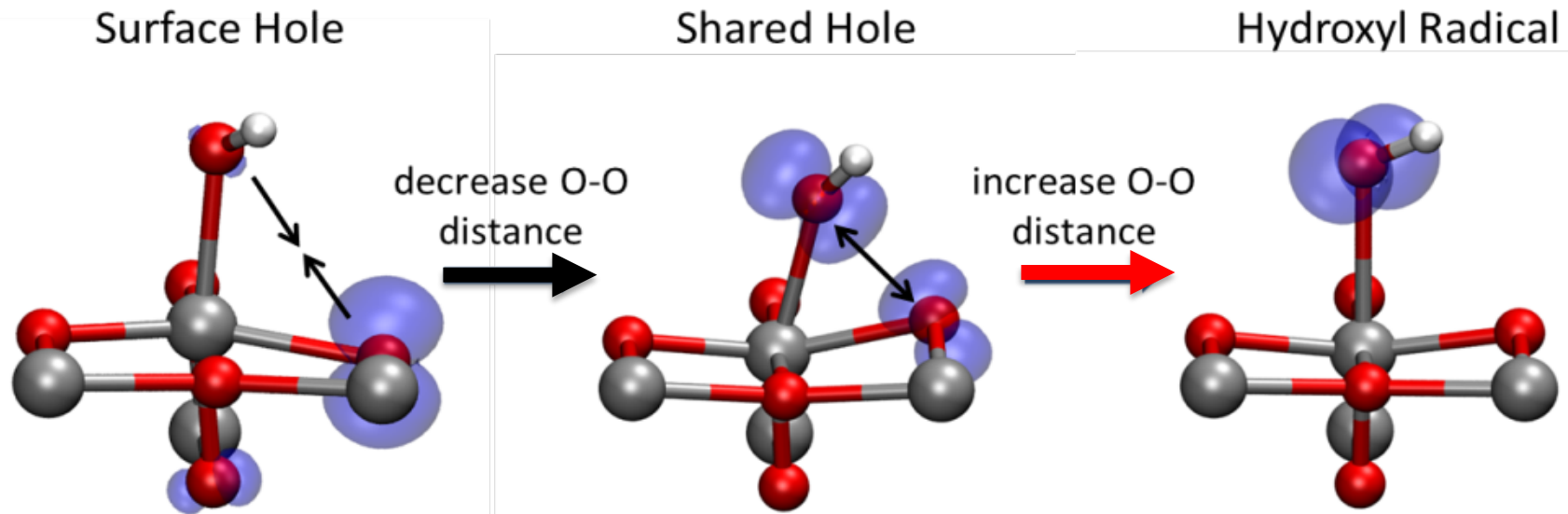
$O_w - O_{\text{surf}}$ distance is used as reaction coordinate



Additional snapshots



ET barrier ~ 0.1 eV or less, and
 \ll PT barrier



Partial summary

$$\text{pH} < \text{pzc}$$

PT occurs first: $*\text{H}_2\text{O} \rightarrow *\text{OH}^- + \text{H}^+ (\text{aq})$

ET is next: $*\text{OH}^- + \text{h}^+ \rightarrow *\text{OH}^\bullet$

PT barrier in the range 0.2- 0.5 eV

$$\text{pH} > \text{pzc}$$



ET barrier ~ 0.1 eV

\Rightarrow OER faster at high pH

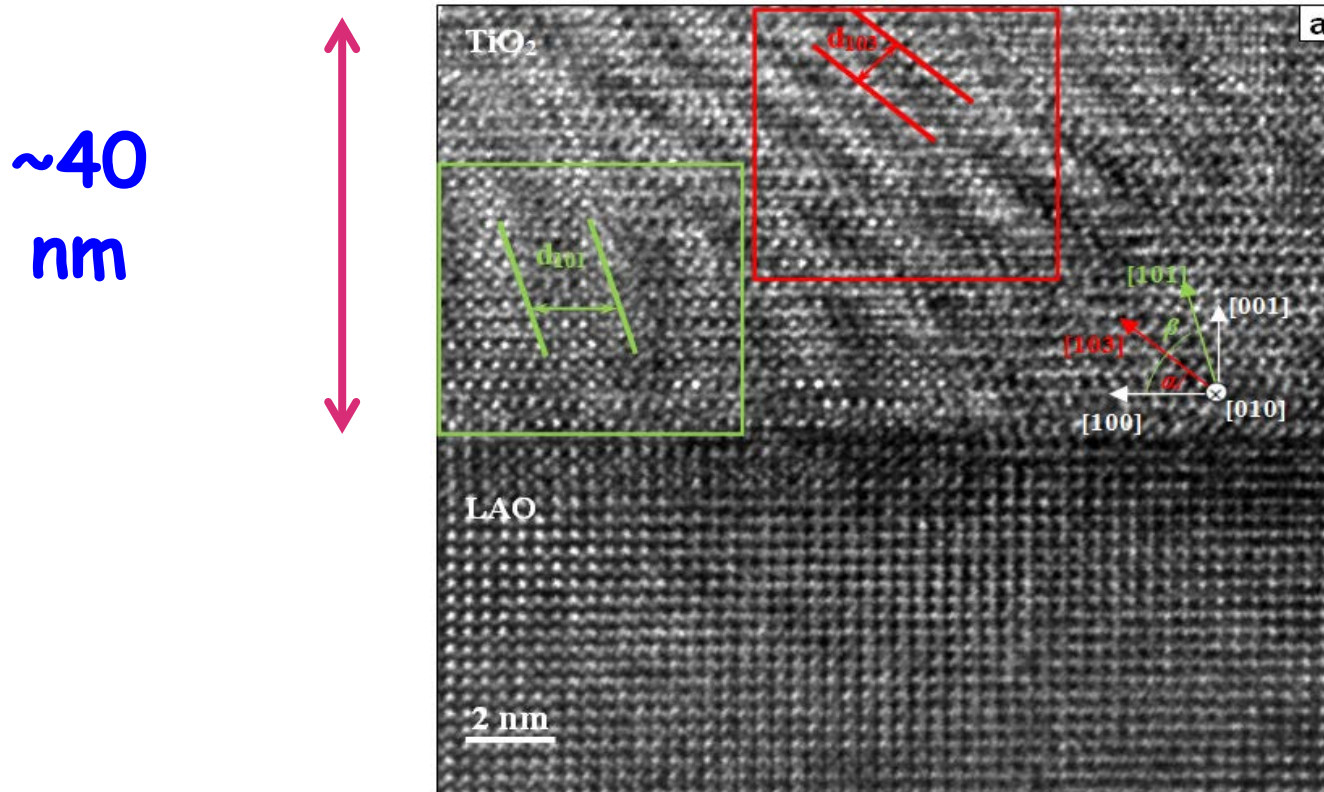
Polaronic effects essential to make transfer possible

TiO₂ modification via nano-structuring

TiO₂/SrTiO₃ heterostructures for
water oxidation

Jun Hee Lee & AS

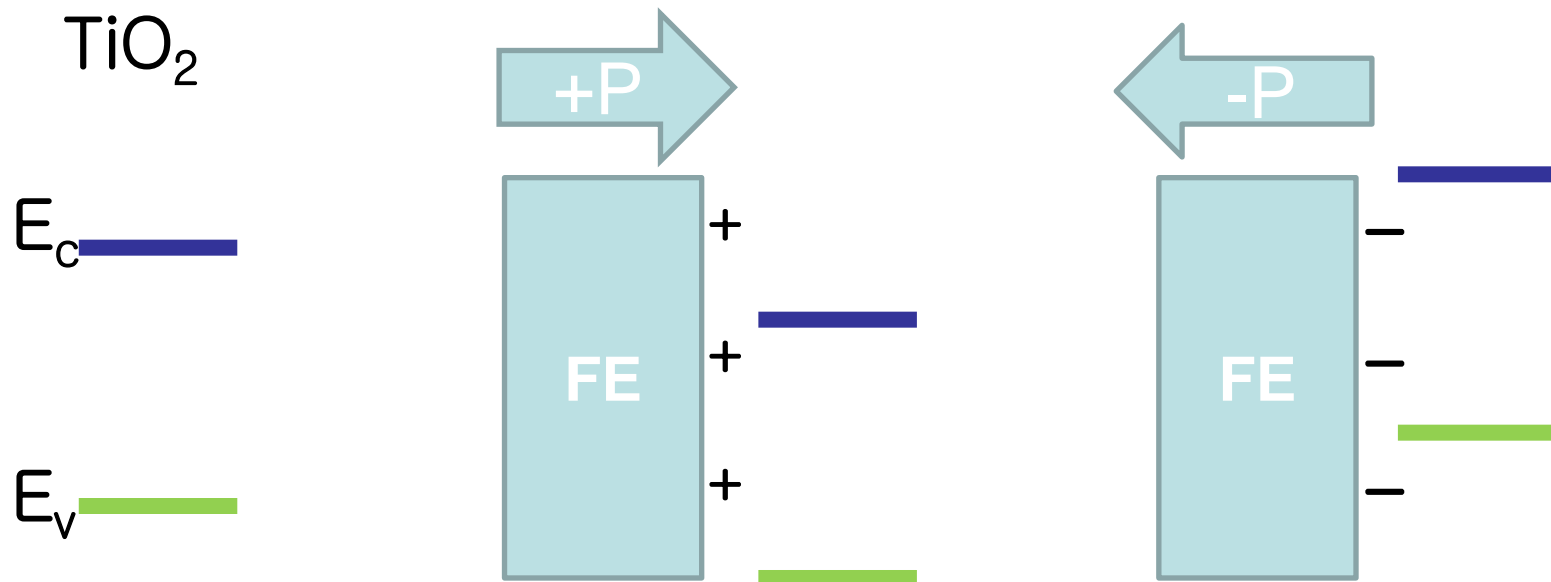
Anatase $\text{TiO}_2(001)$ can be grown epitaxially on LAO and STO



HRTEM image of TiO_2/LAO interfacial region taken in the $[010]$ zone axis of the film.

semiconductor/ferroelectric heterostructures

QUALITATIVELY



- Interface dipole can shift electron band energy positions & affect the surface chemistry (see e.g. work by Rohrer & co.)

More relevant for chemistry applications: Core-shell particles

Journal

J. Am. Ceram. Soc., 95 [4] 1414–1420 (2012)

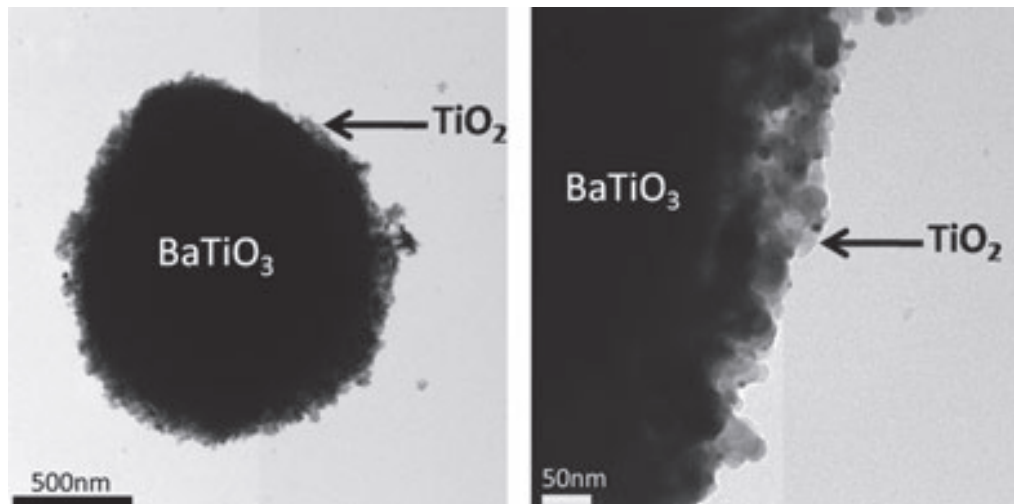
DOI: 10.1111/j.1551-2916.2012.05076.x

© 2012 The American Ceramic Society

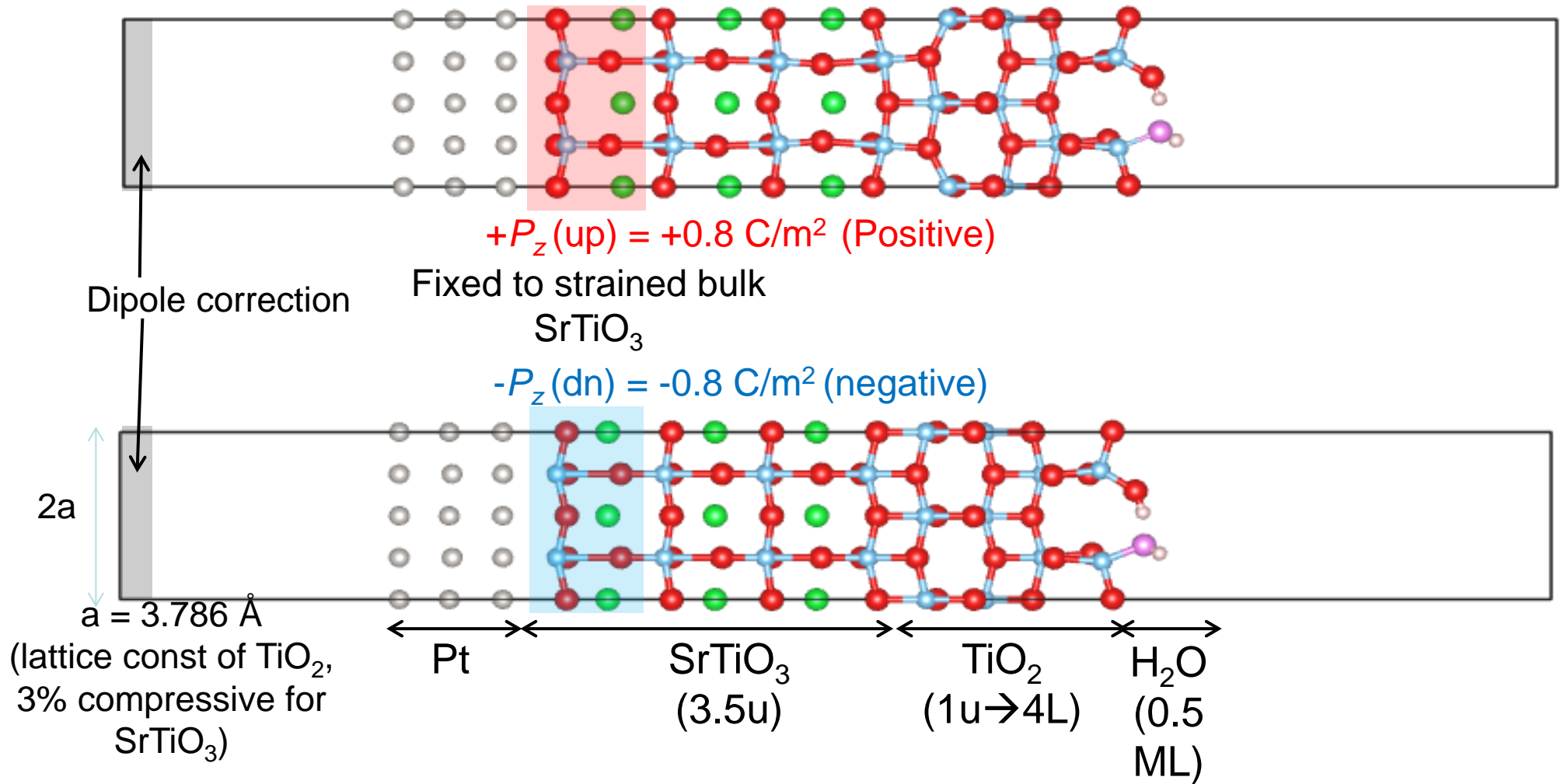
Heterostructured Ceramic Powders for Photocatalytic Hydrogen Production: Nanostructured TiO_2 Shells Surrounding Microcrystalline $(\text{Ba,Sr})\text{TiO}_3$ Cores

Li Li, Gregory S. Rohrer, and Paul A. Salvador[†]

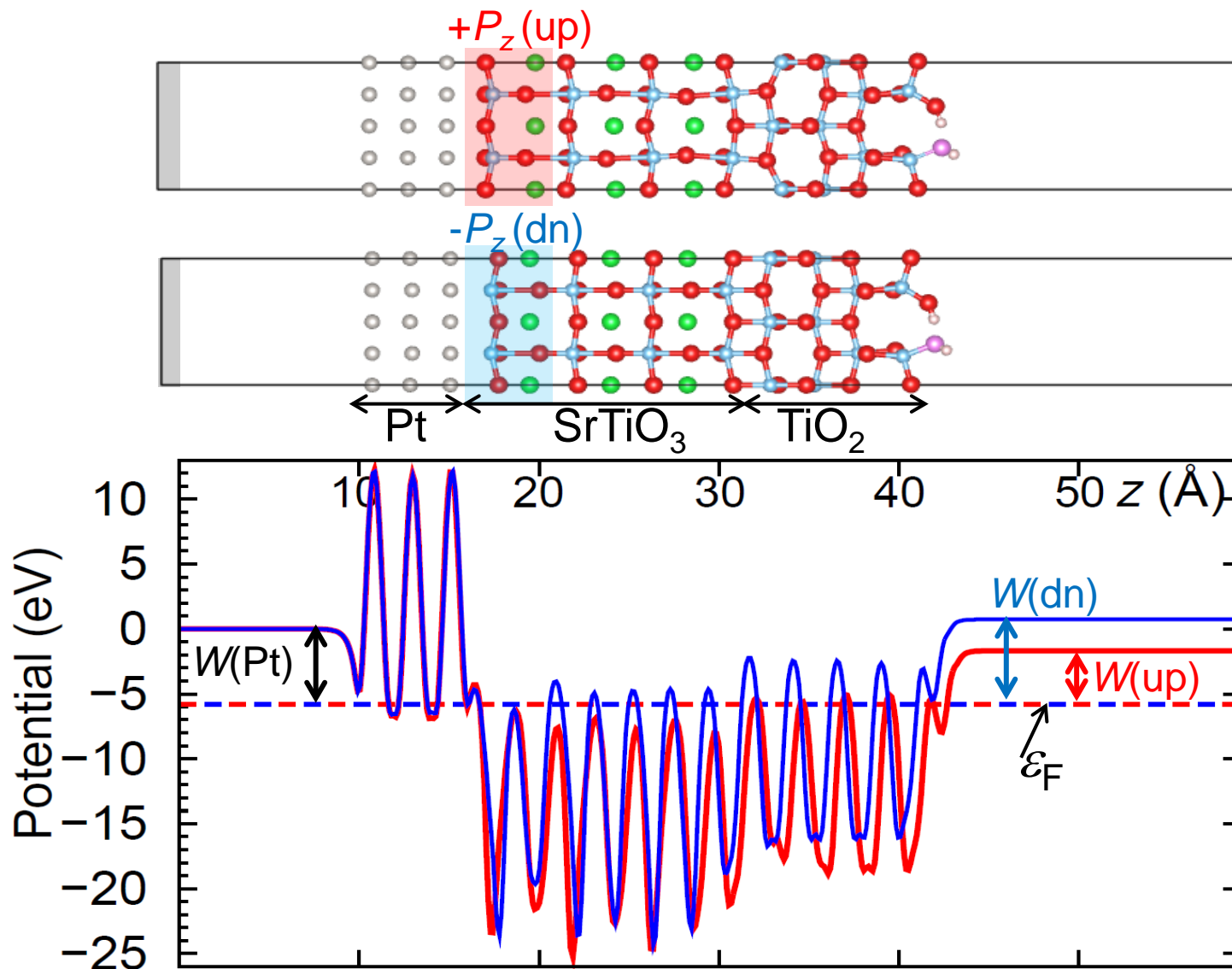
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213



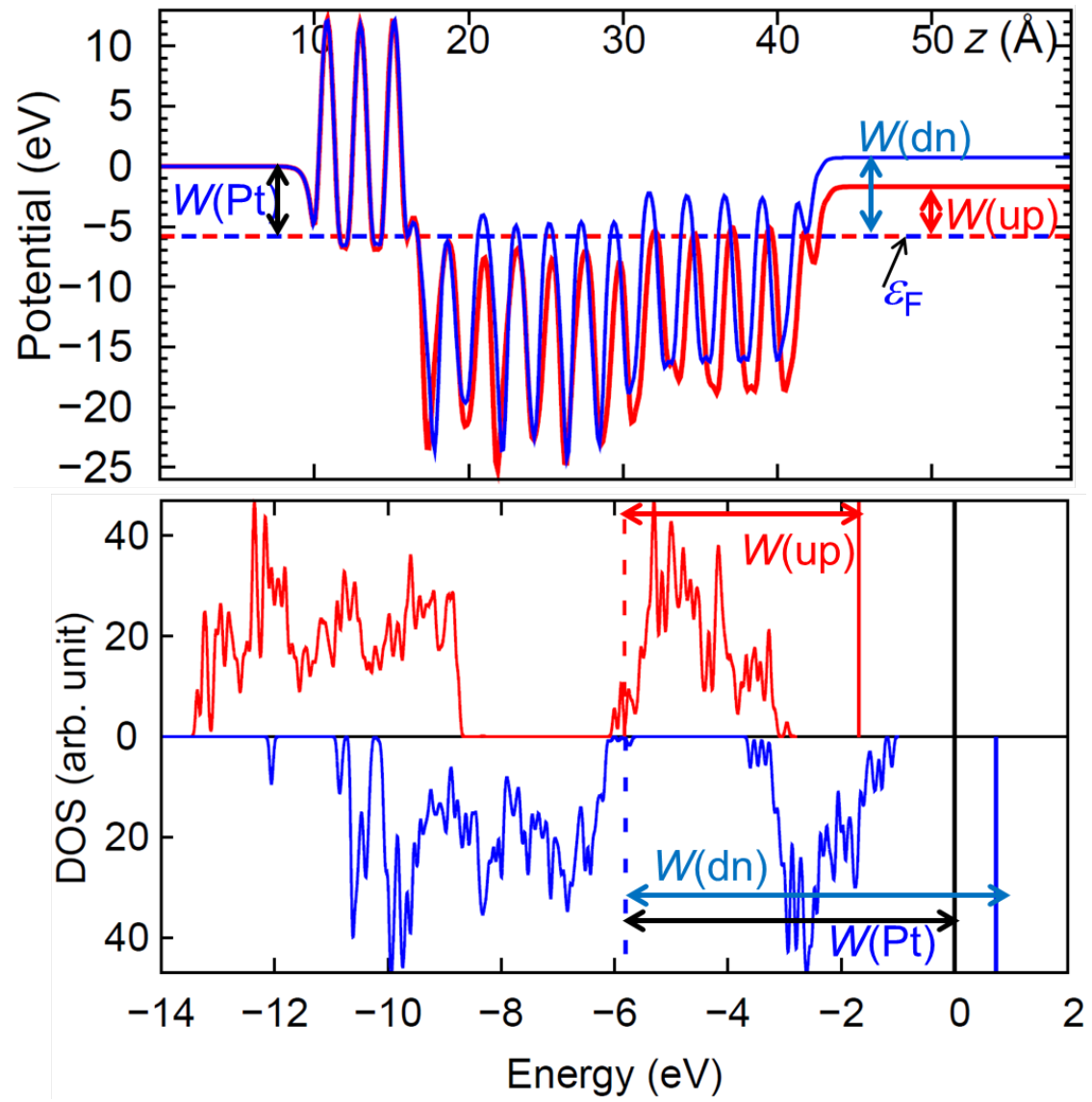
Computational model: Anatase TiO₂(001)/STO



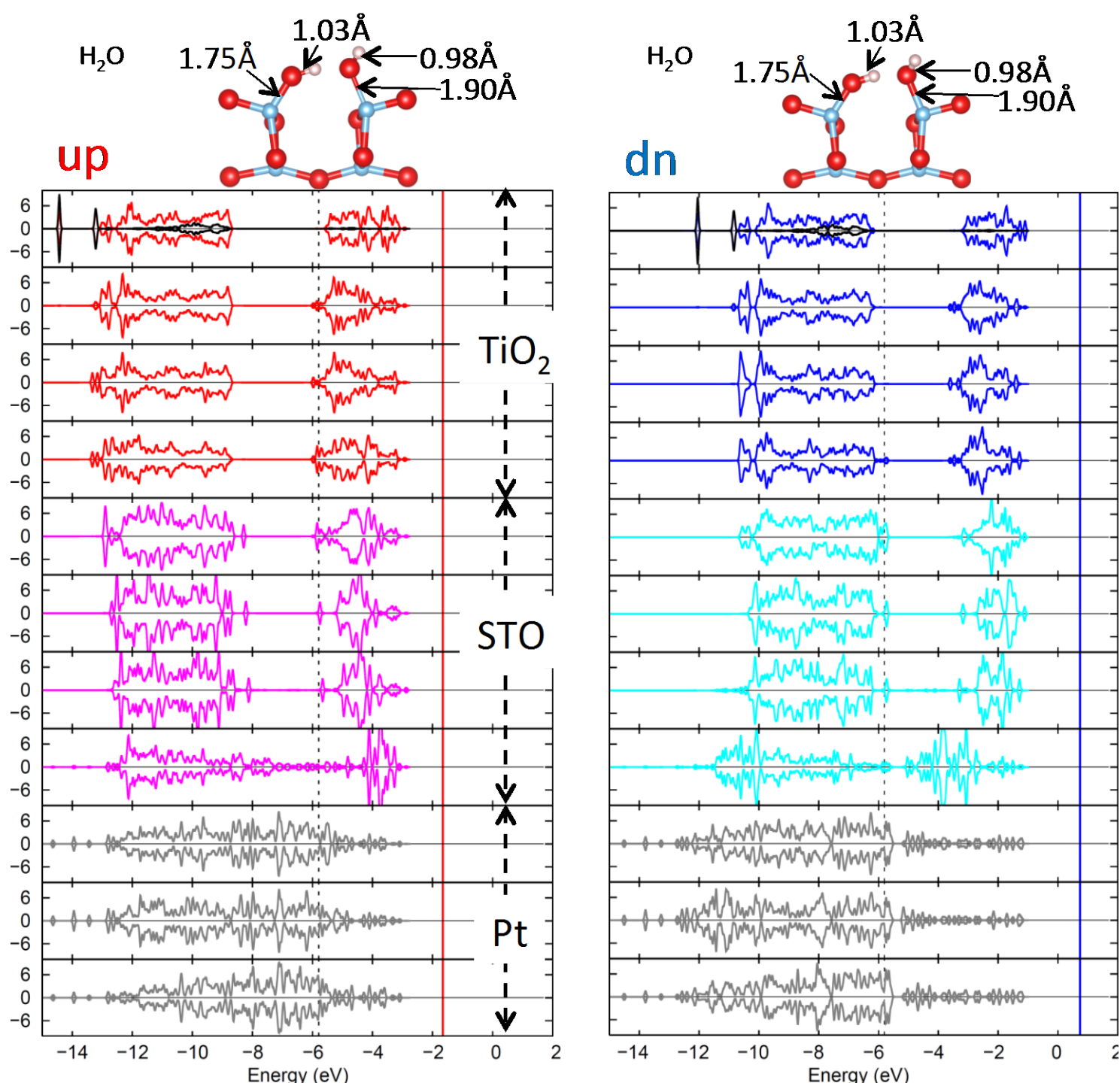
Hartree potential shift



Substrate polarization shifts the work-function

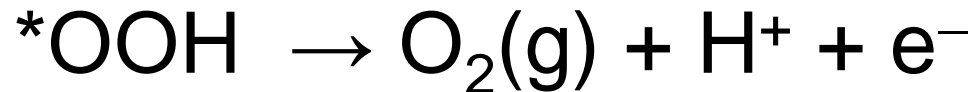


Layer-resolved DOS – Structure 1



Oxygen Evolution Reaction – (b)

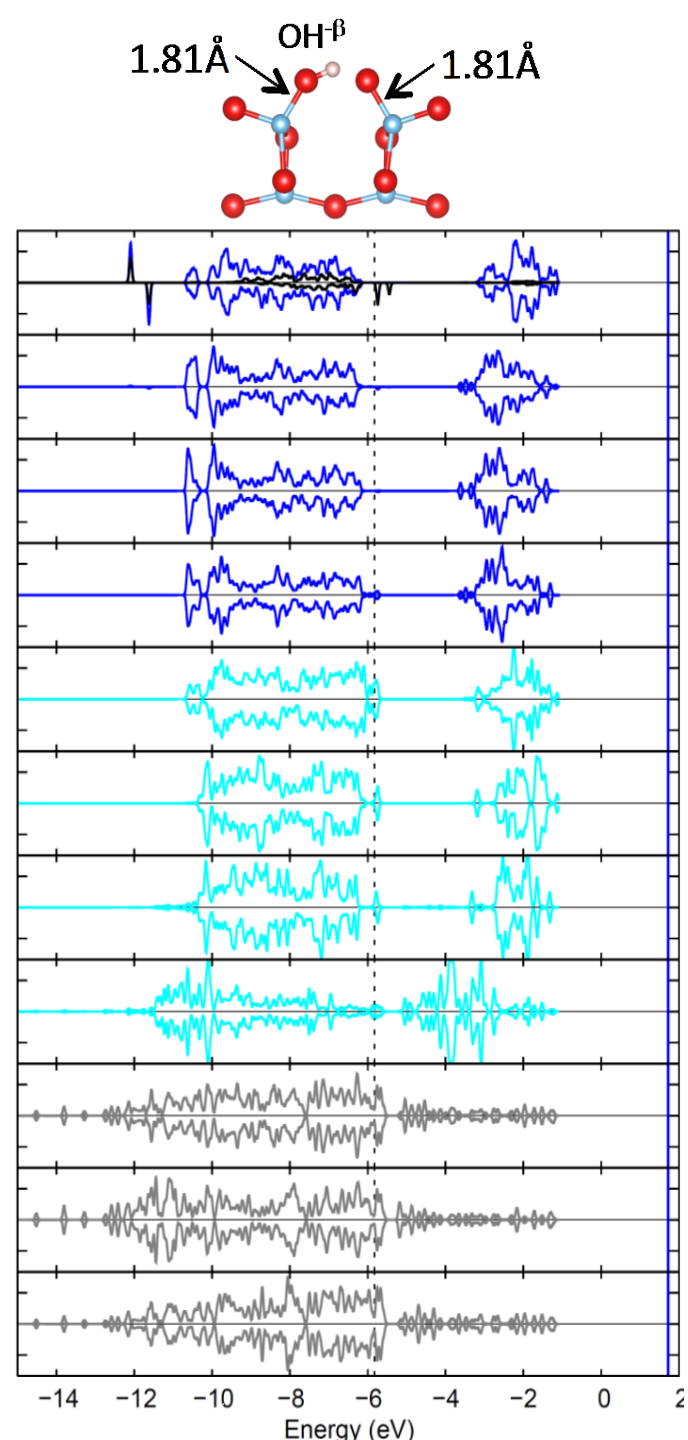
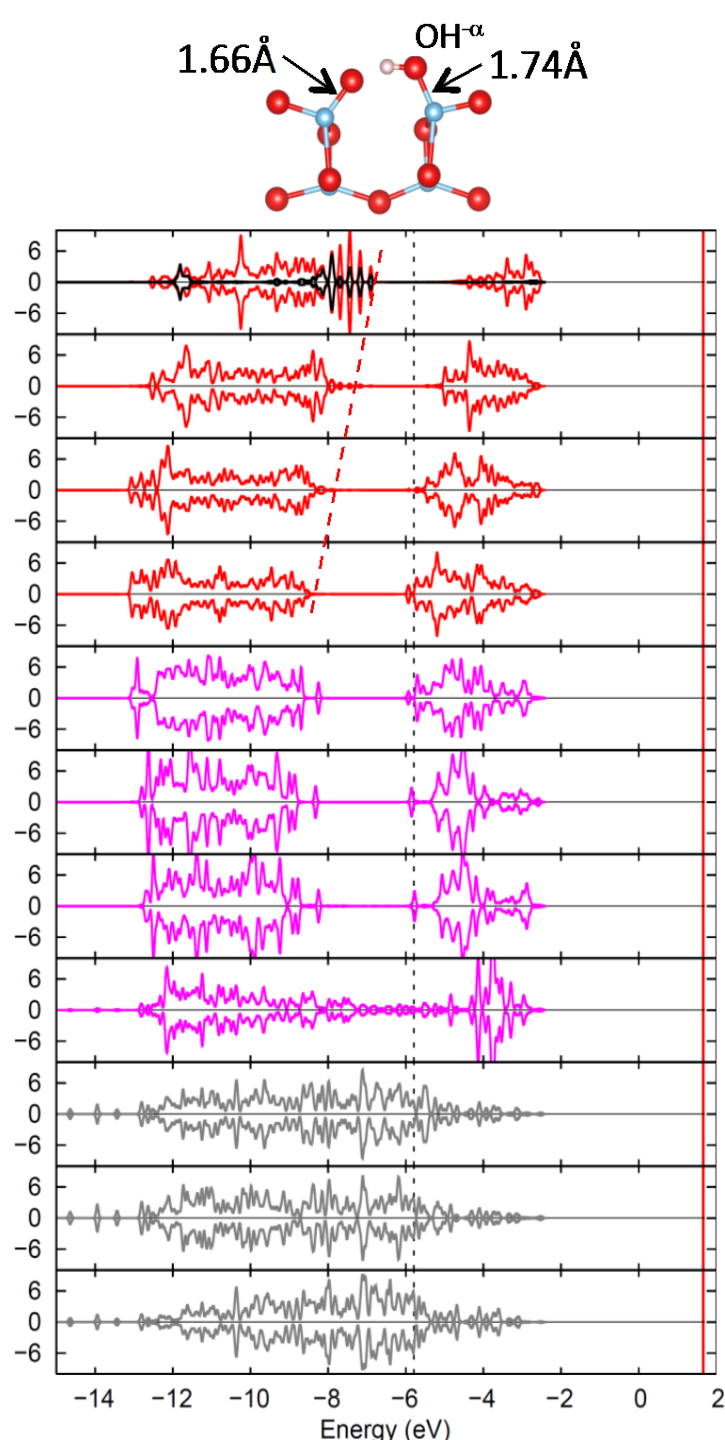
Practical scheme used in periodic calculations



Compute $\Delta G_1 - \Delta G_4$

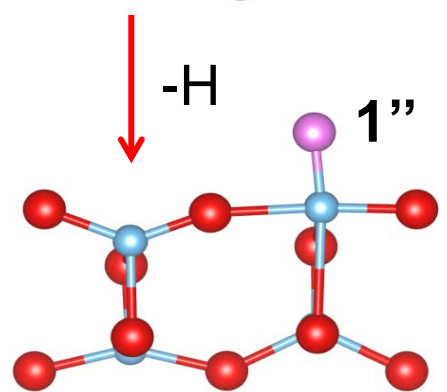
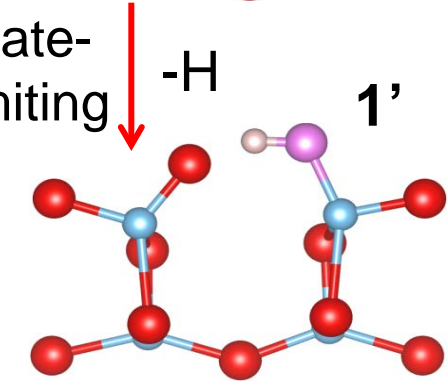
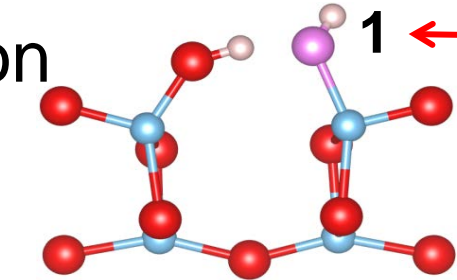
SHE: $\text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{H}_2$ at $U=0$ & $\text{pH}=0$

**Layer-
resolved
DOS –
Structure 1'**

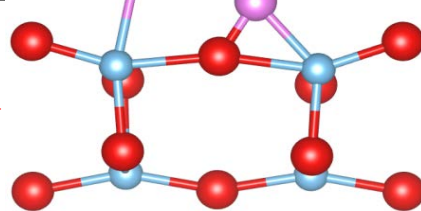
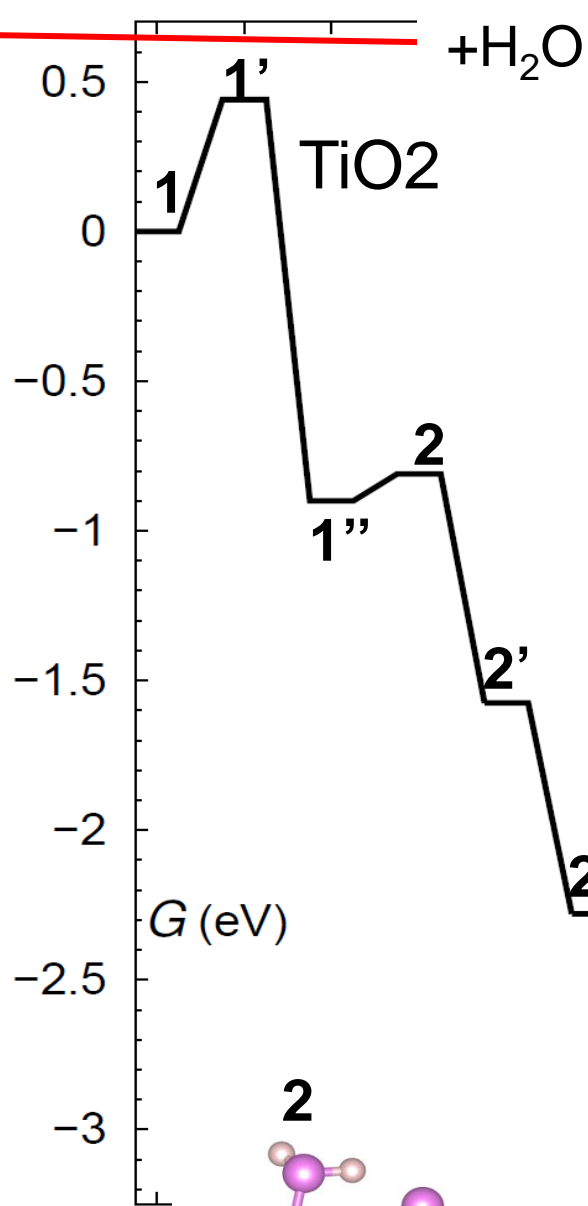


OER on
 TiO_2

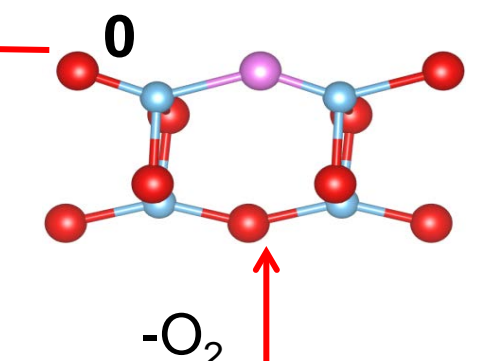
Rate-
limiting



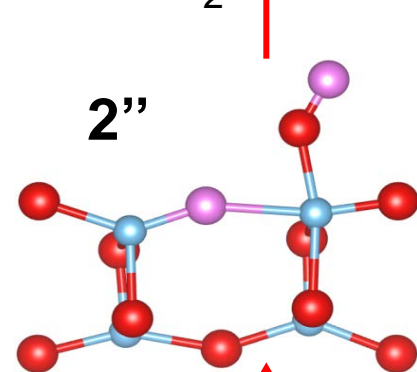
+ H_2O



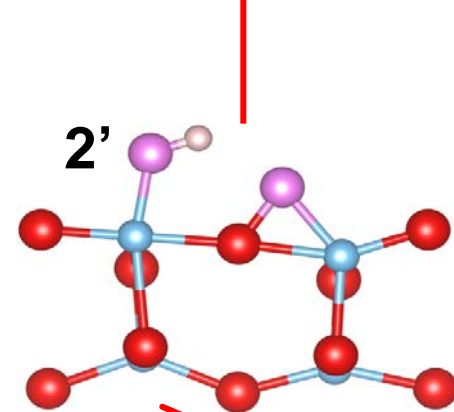
-H



- O_2

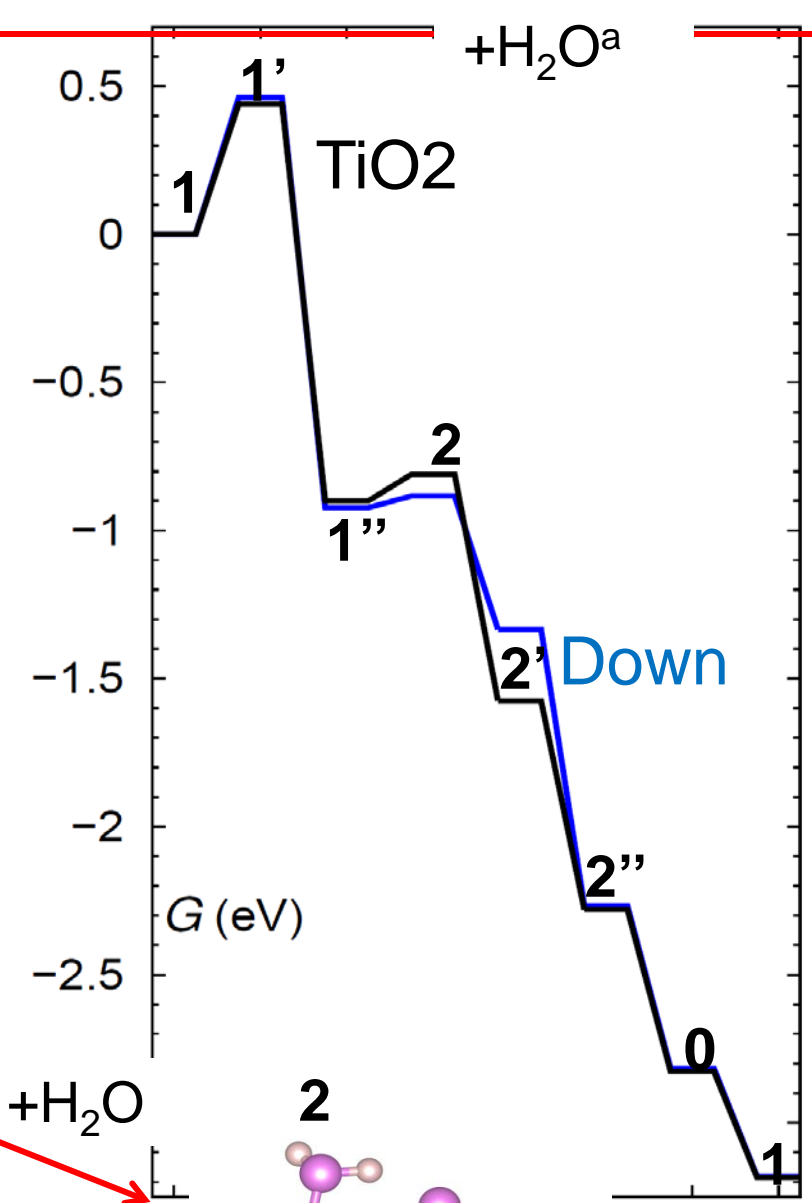
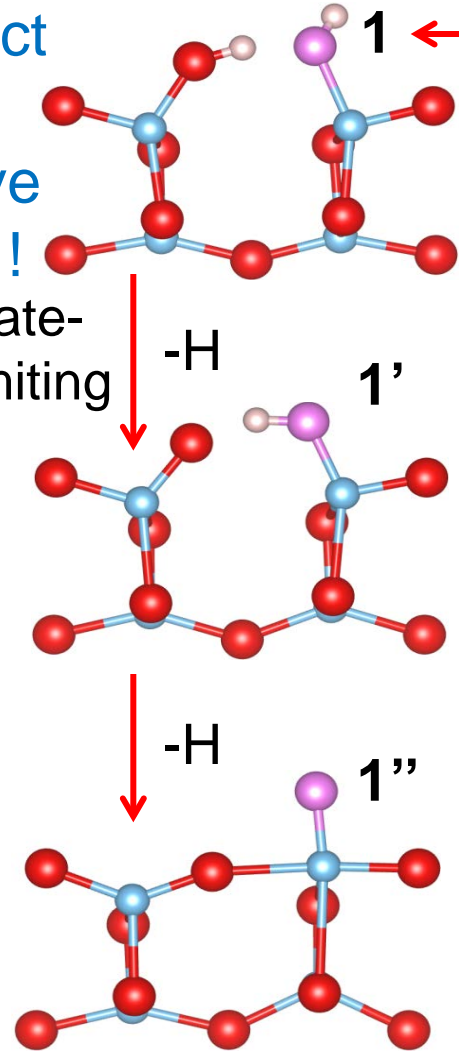


-H

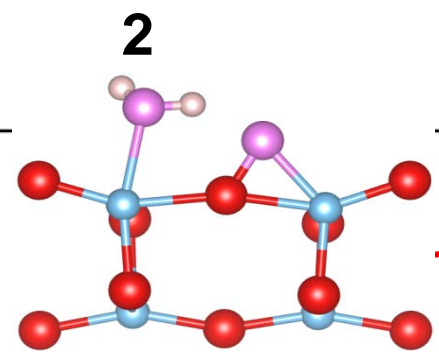


No effect from negative dipole!

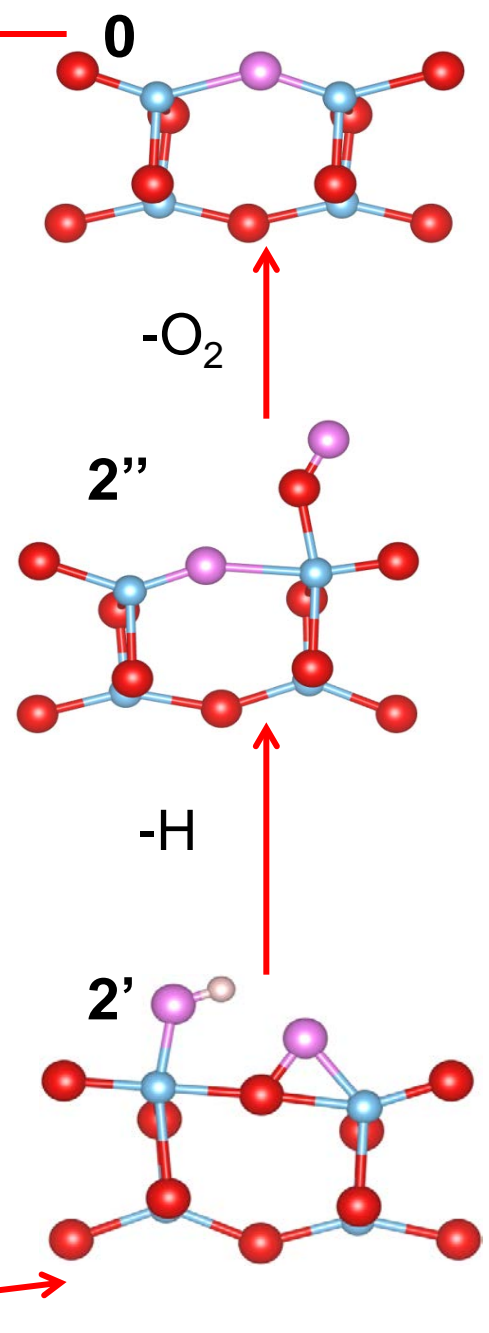
rate-limiting

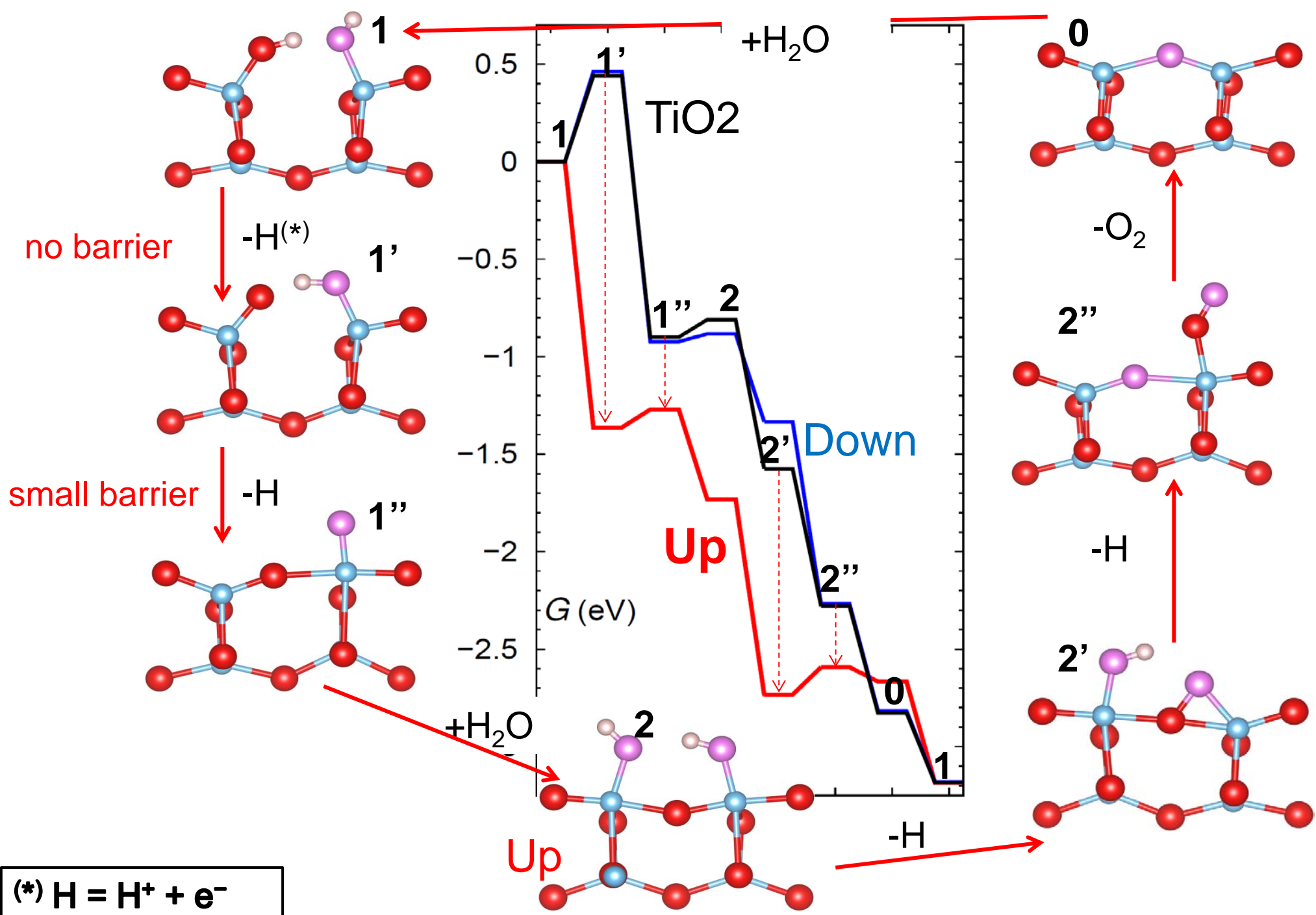


+H₂O

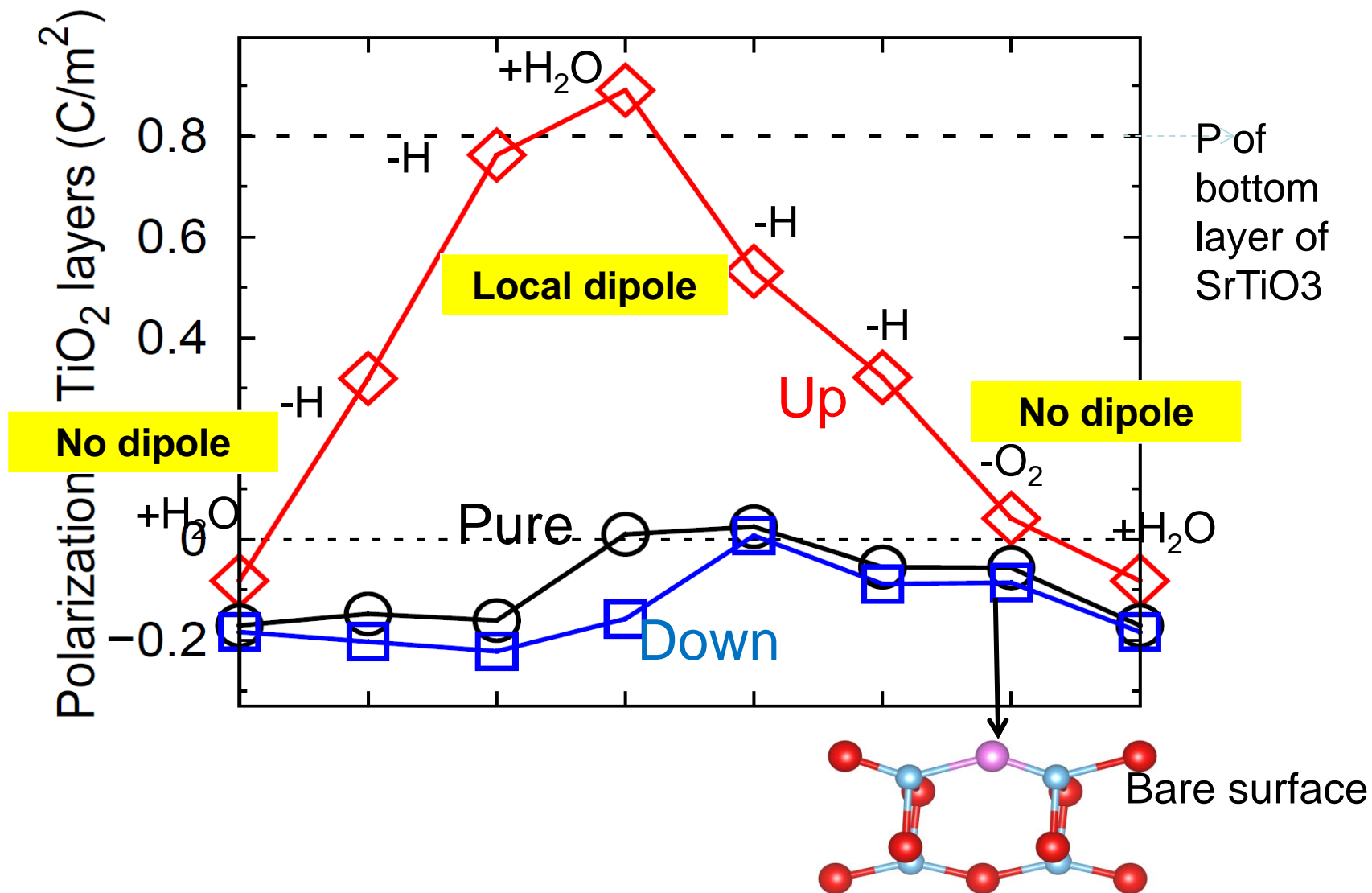


-H

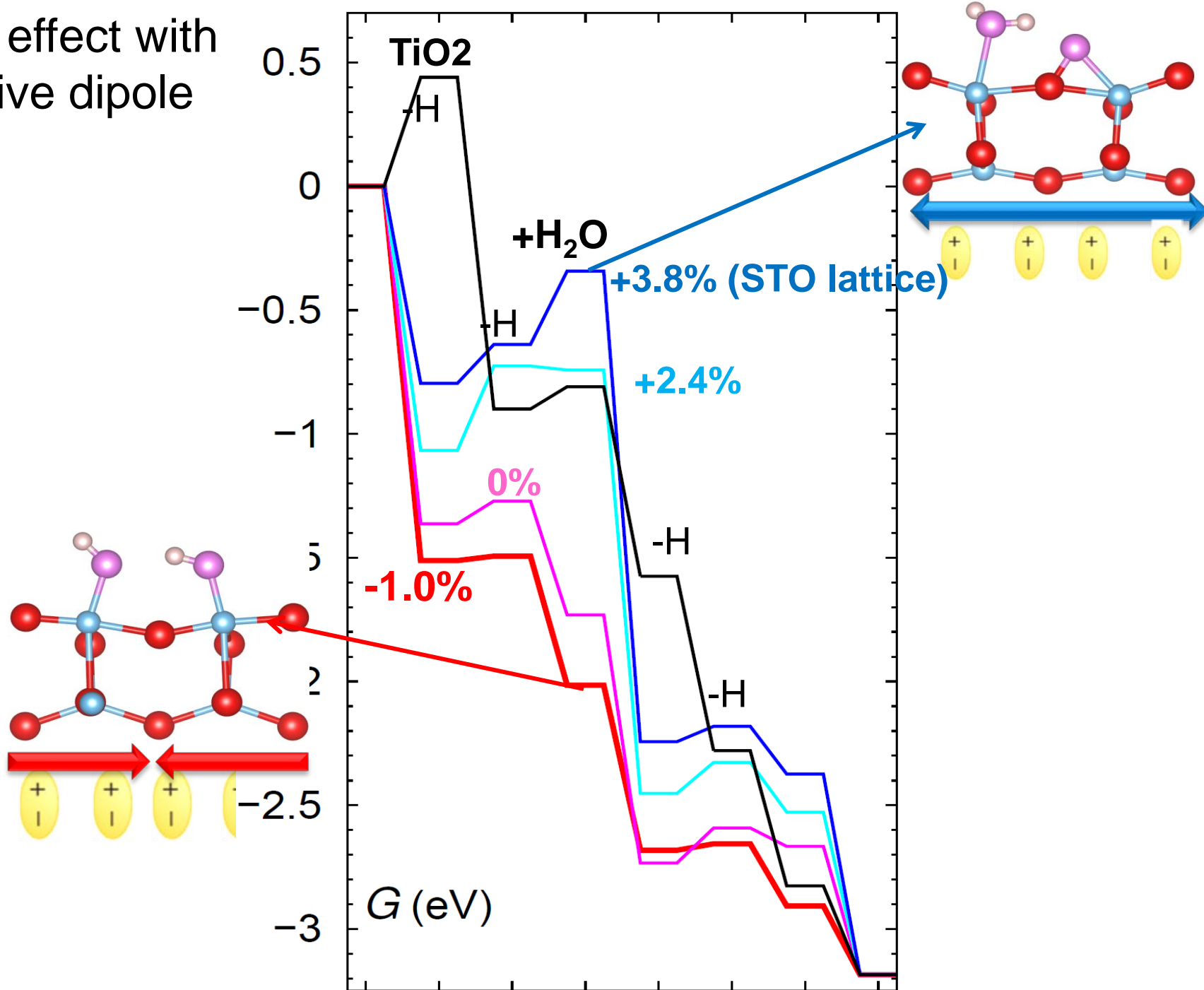


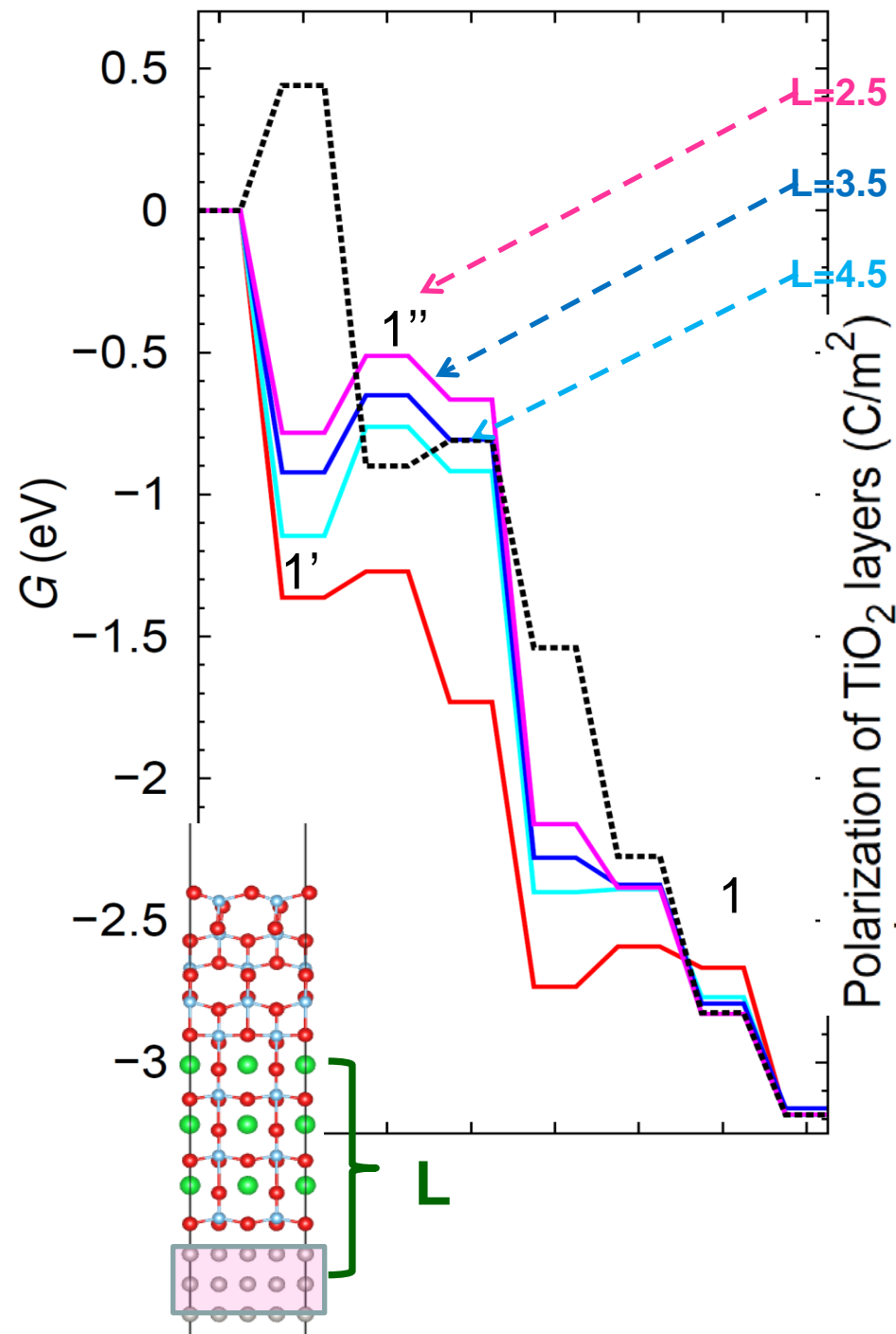


Dynamically Induced polarization of TiO₂ layers



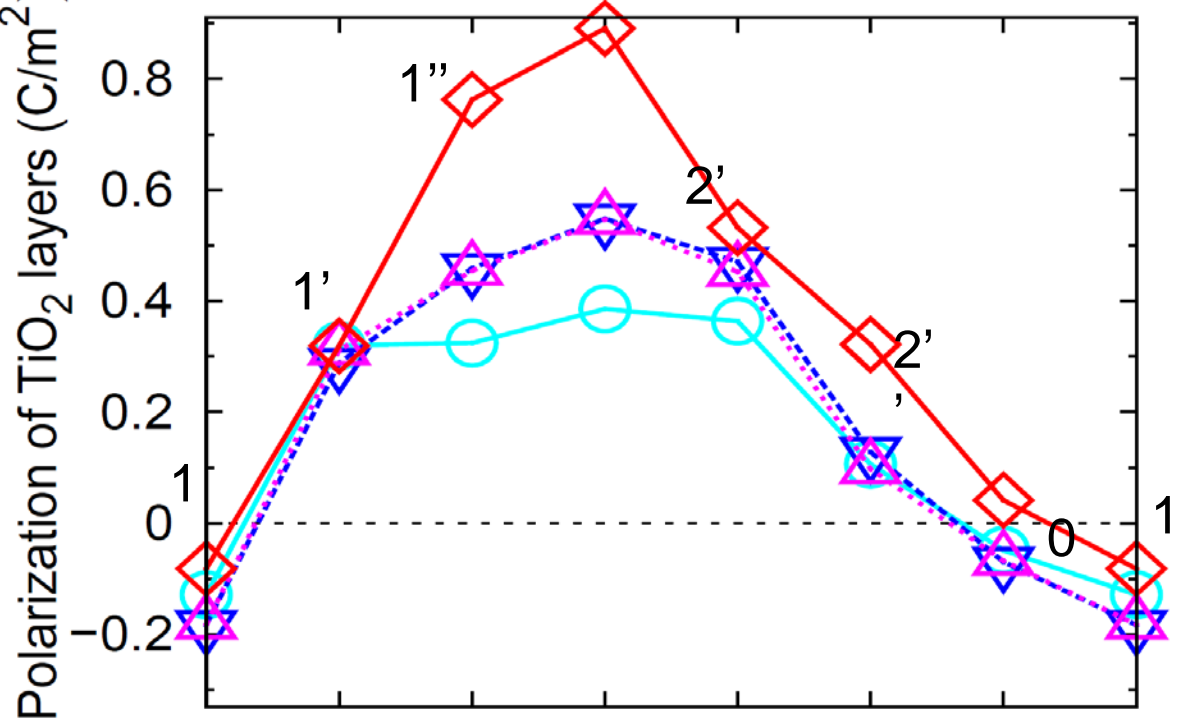
Strain effect with positive dipole



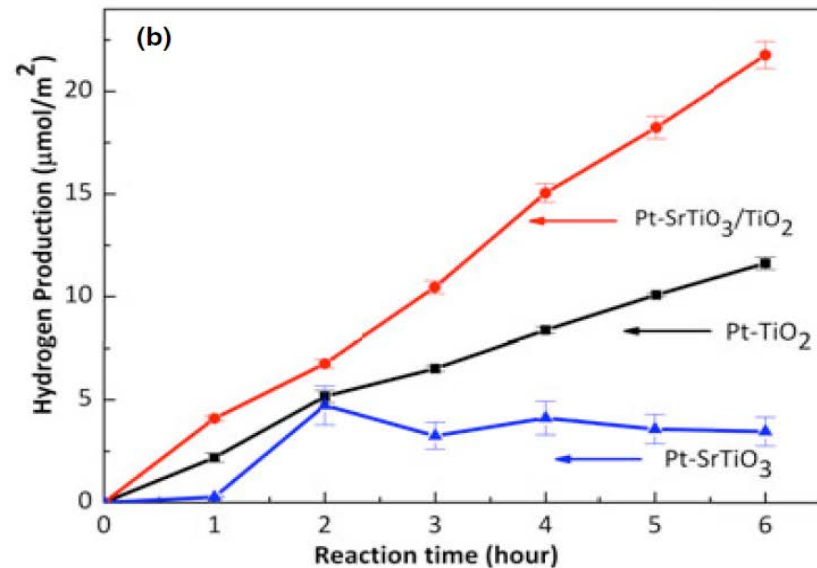
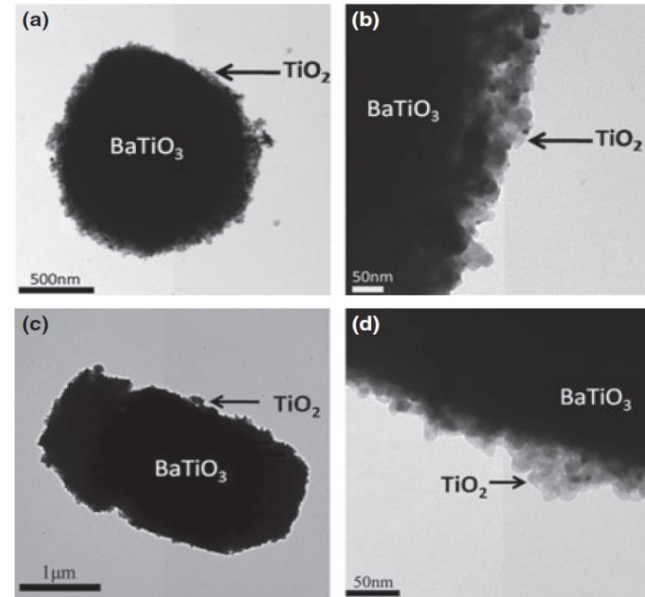
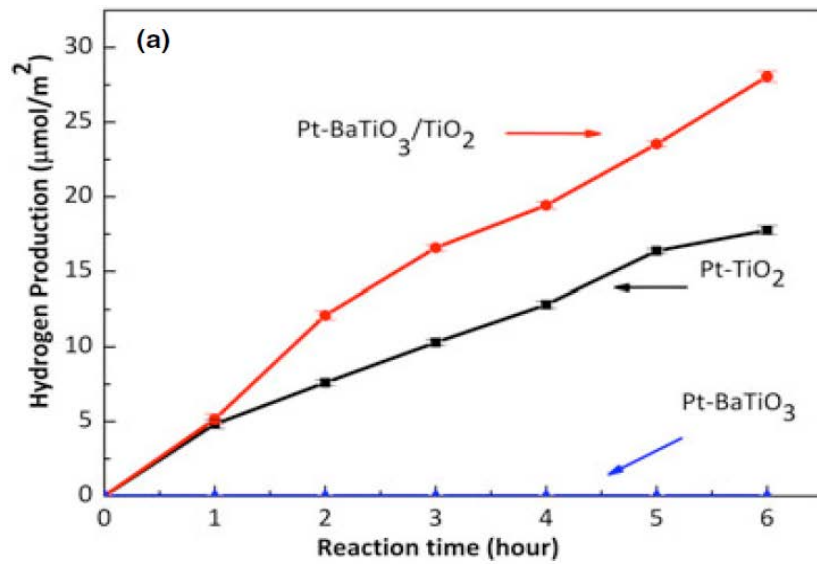


Catalysts on high-K

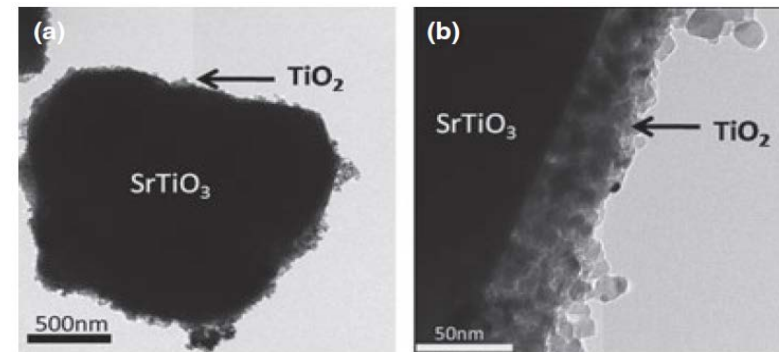
Overcome the rate-limiting step even without built-in P.



Recent experimental work



Li *et al.*, J. Am. Ceram. Soc. (2012)



Summary & Conclusions

➤ Many open questions!

- more realistic models: larger surface area, water environment, defects(?)
- beyond GGA
- Add real holes/electrons
- ...
- Expts: Single crystal monodomain