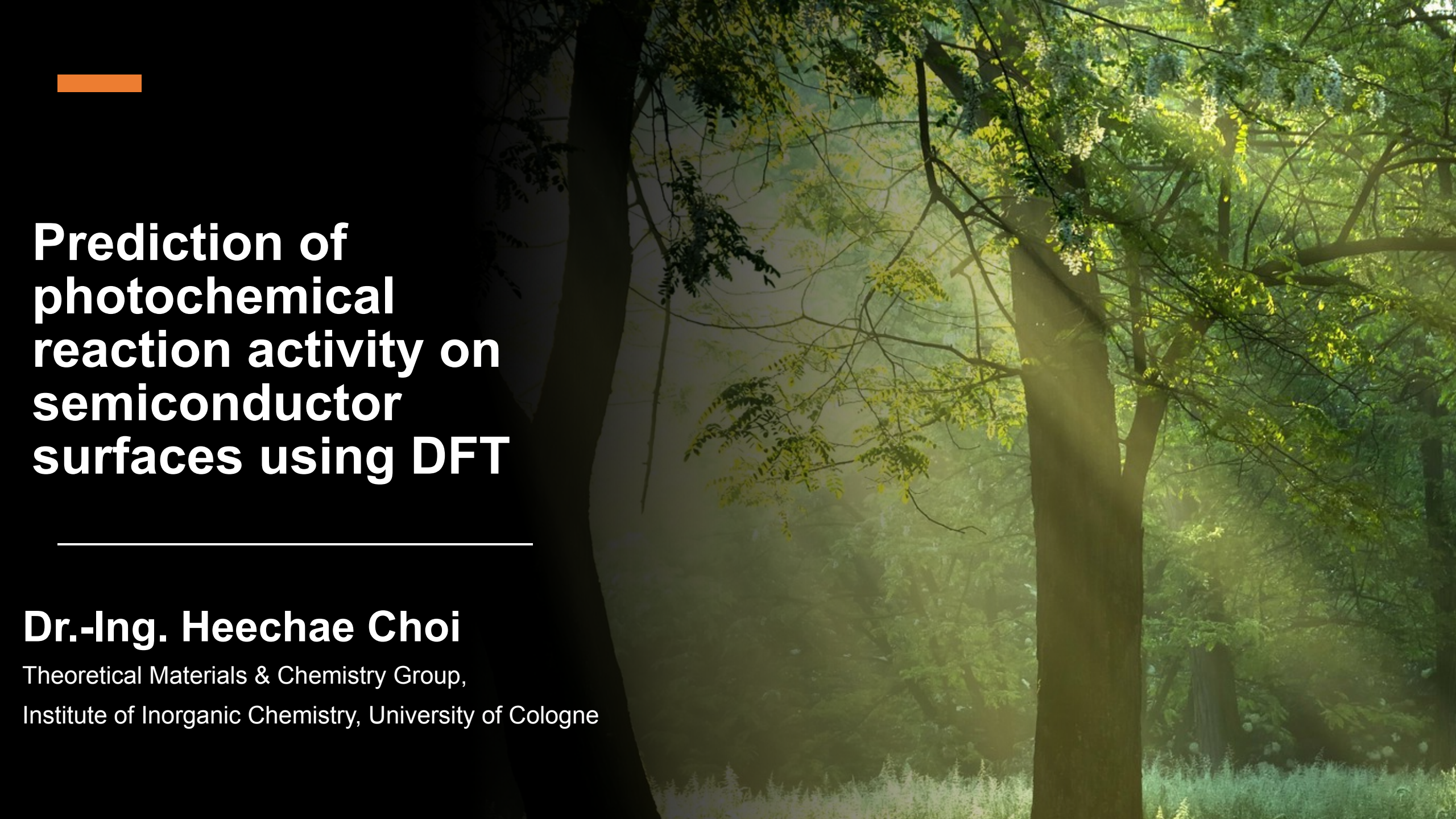
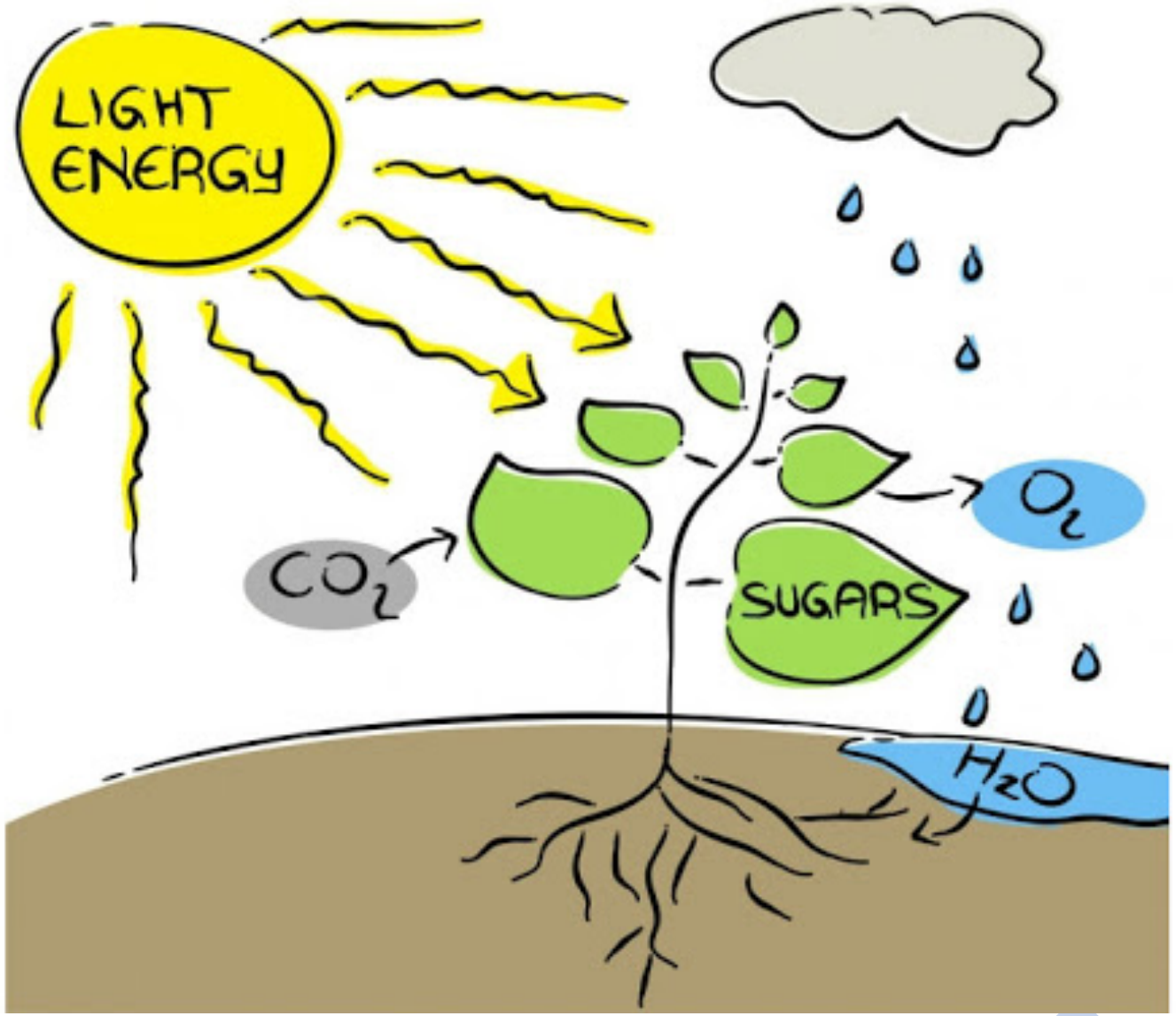
Prediction of photochemical reaction activity on semiconductor surfaces using DFT



Dr.-Ing. Heechae Choi

Theoretical Materials & Chemistry Group,

Institute of Inorganic Chemistry, University of Cologne



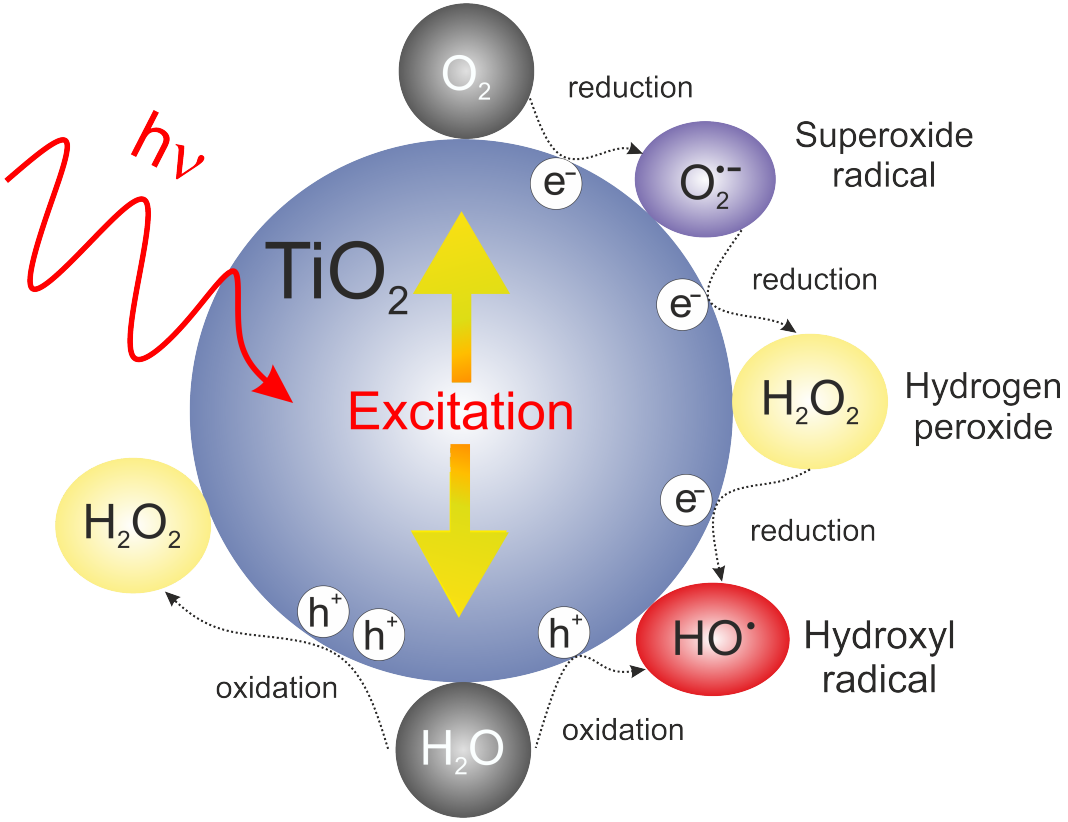
http://www.earthtimes.org/energy/photosynthesis-dream-renewable-energy/1956/

Index

- Photochemical reaction
- Adsorption theory correction for semiconductor
- Activity predictions for photochemical reactions
- Examples
  - P-type CeO_2
  - Reduced n-type TiO_2

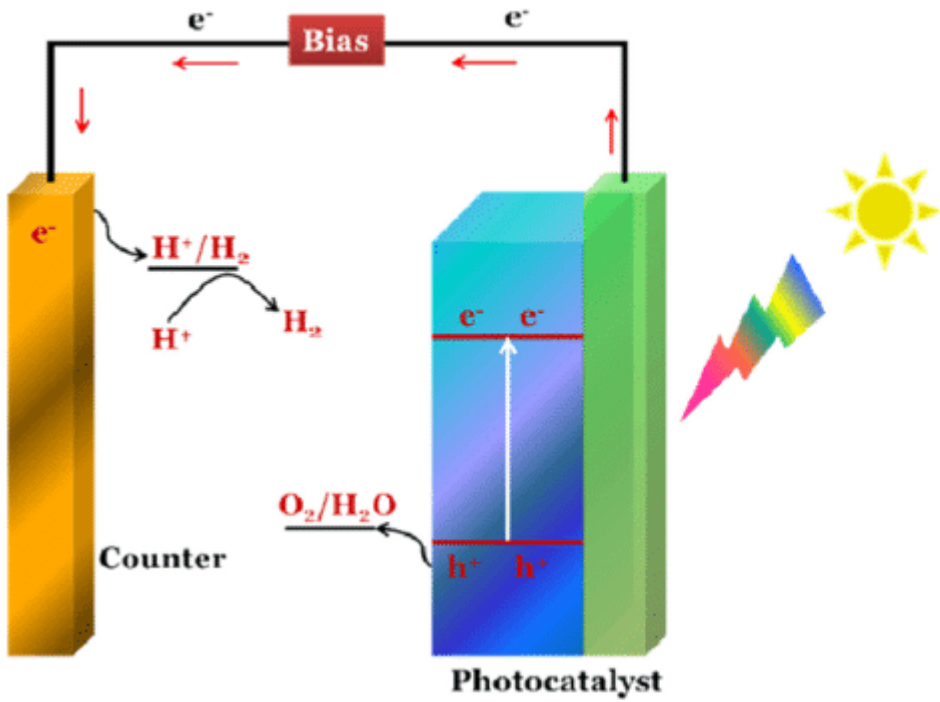
Photochemical reactions

Photocatalysis



http://fotokataliza.pl/

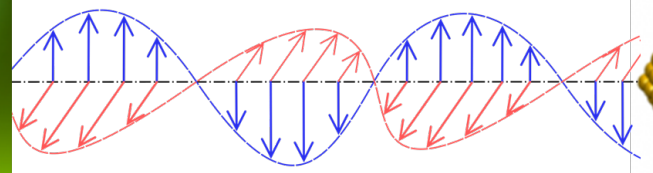
Photoelectrochemistry



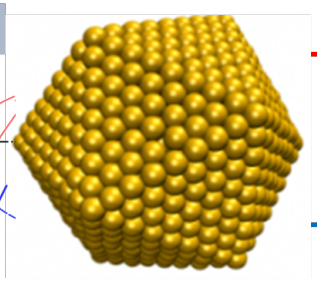
J. Electrochem. Sci. Technol. 2016, 7, 1.

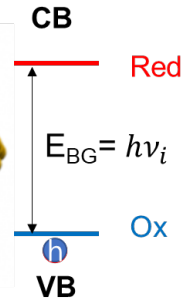
Photochemical reaction is complicated

Light = EM wave = e-h generation

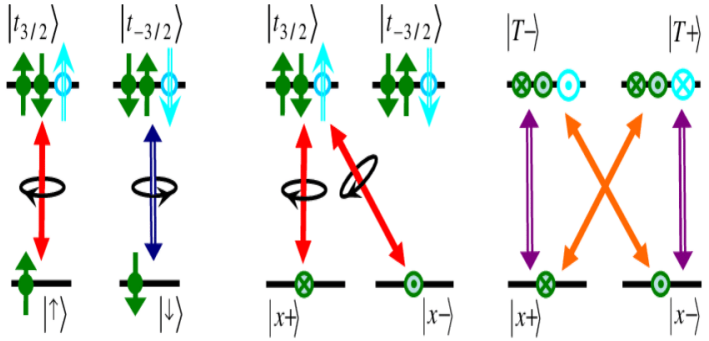


$$E = \sum_i D(\nu_i) h\nu_i$$



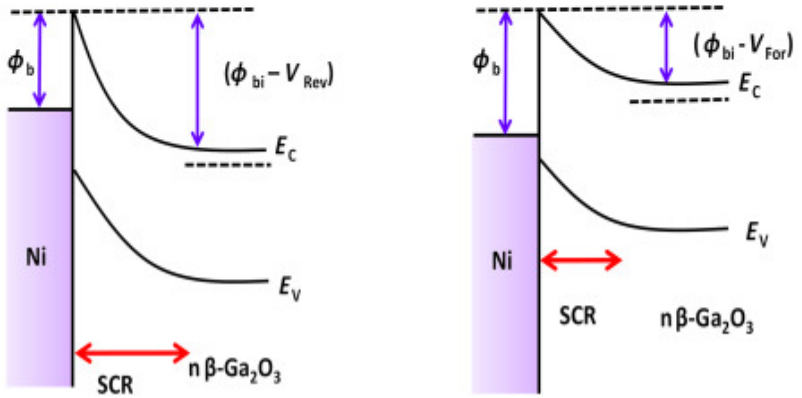


1) Optical transition



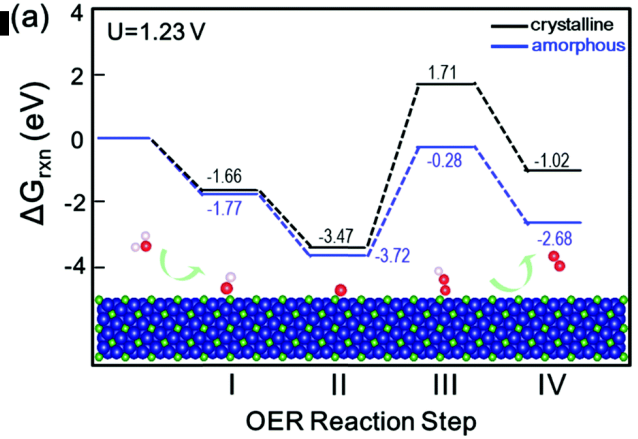
R.-B. Liu, et al., Adv. Phys. 2010, 59, 703.

2) Charge transport



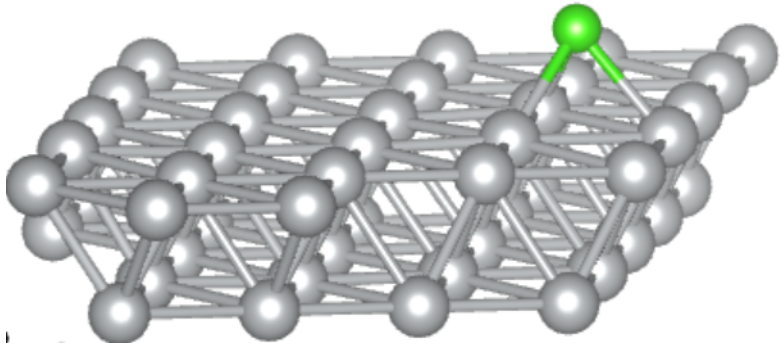
https://www.sciencedirect.com/topics/engineering/metal-semiconductor-junction

3) Catalytic reaction

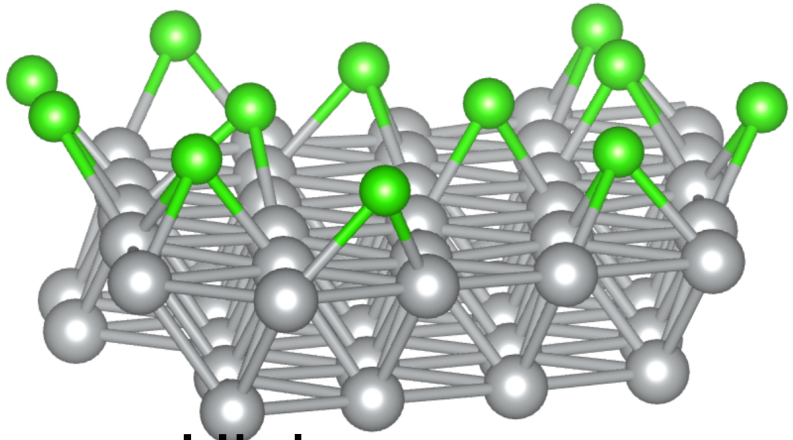


H.Han, H.Choi, et al., EES 2019, 12, 2443.

Metal vs semiconductors

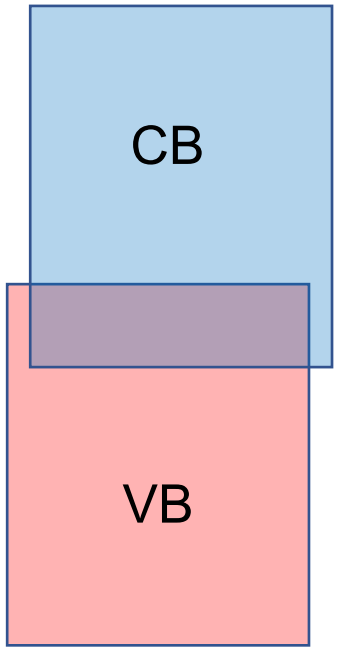


Low coverage



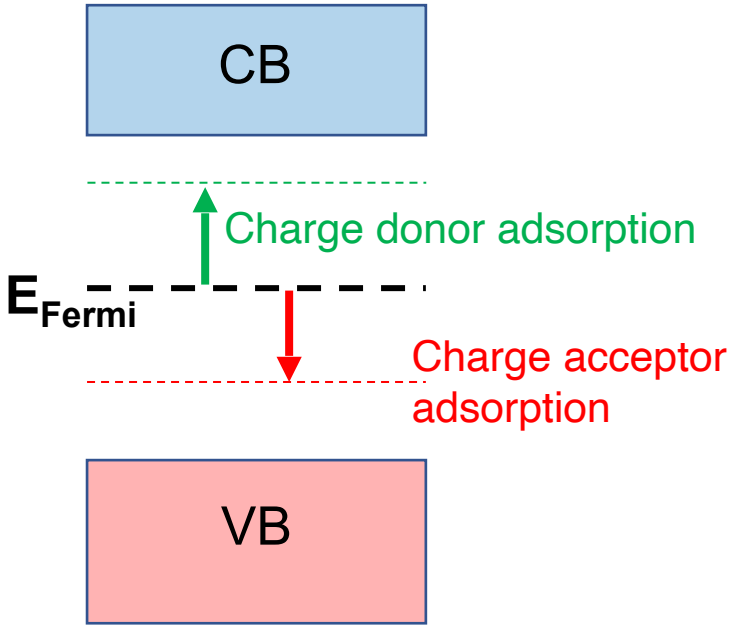
High coverage

Metal



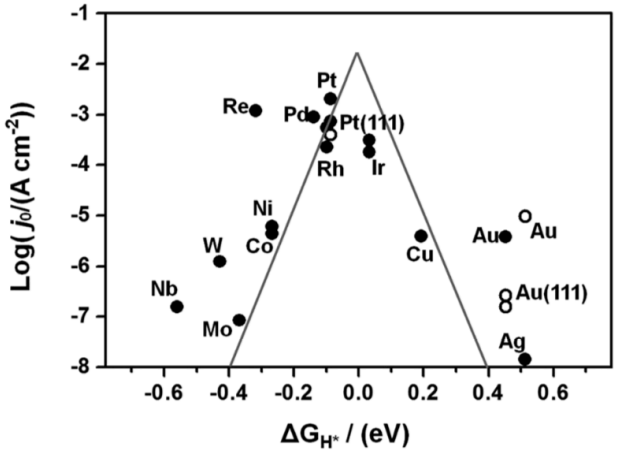
E_{ad} = constant

Semiconductor

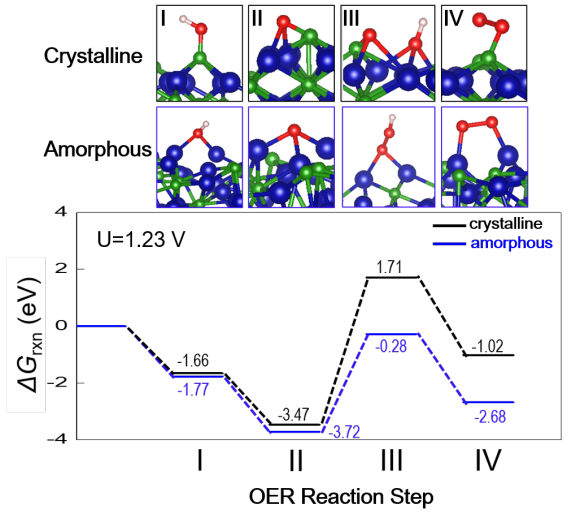


$E_{ad} = f(\theta)$

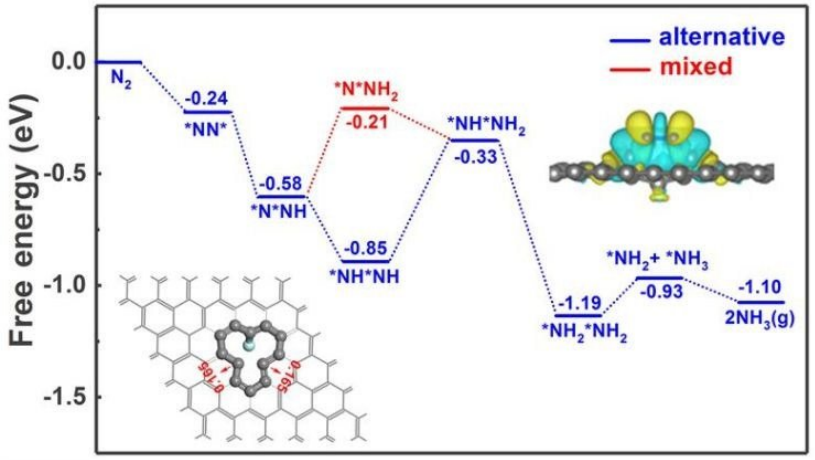
General modeling & DFT approach



M. Zeng et al., *J. Mater. Chem. A* (2015)

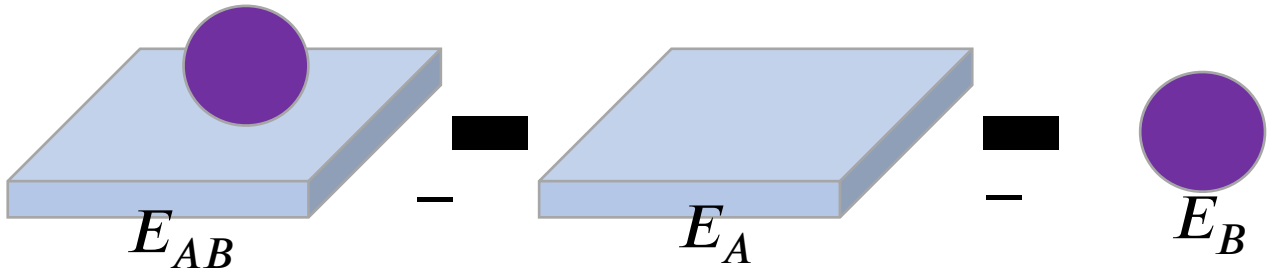


H.Han, H.Choi, et al., *EES* 2019



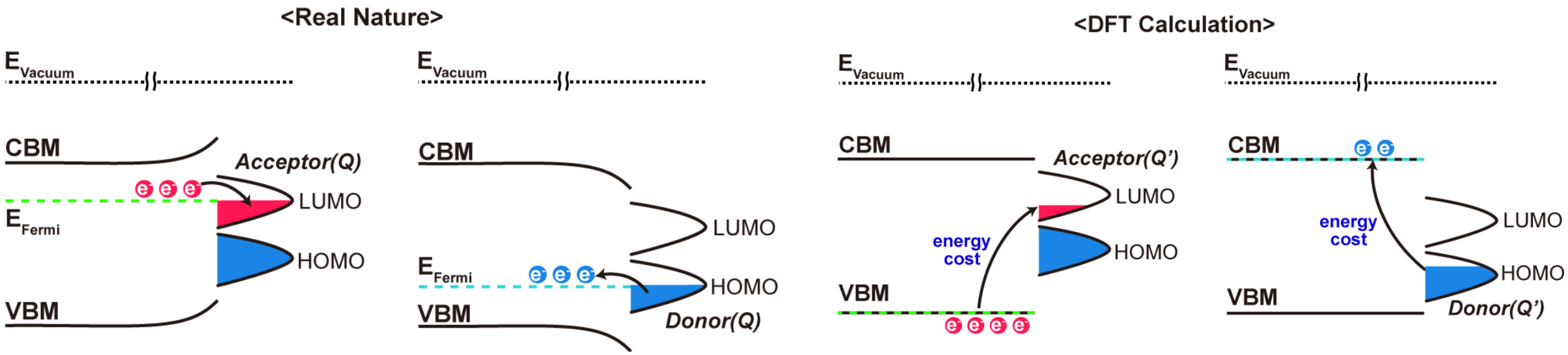
J. Zhao, et al., *Chem. Commun.* 2019

DFT calculation



$$\Delta G = \Delta E + \Delta ZPE - T\Delta S - neU - ln10 \times pH \cdots$$

Correction of adsorption energy calculations for semiconductors



Needs a new theoretical scheme!!

Corrections for theoretical photochemical reaction prediction

1. Fermi-level-dependency of adsorption energy

2. Coverage-depdency of adsorption energy

Fermi level dependent adsorption energy

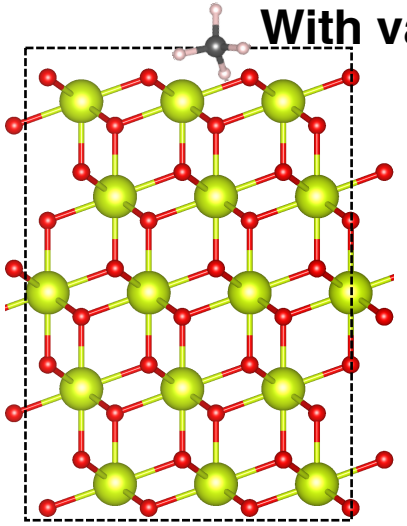
$$\Delta G = (E_{substrate+adsorbate} - E_{substrate} - E_{adsorbate}) + q(\varepsilon_F + E_{VBM}) + E_{iso} - E_{per} + q\Delta V$$

For varying Fermi level Correction energy

<For varying Fermi level>

$$q(\varepsilon_F + E_{VBM})$$

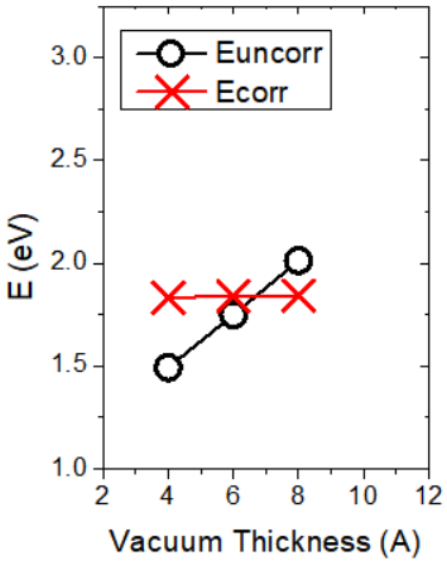
With varying q

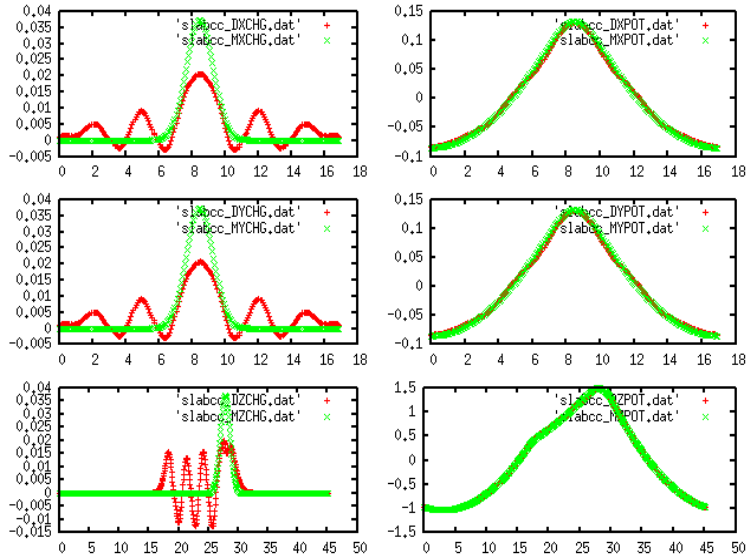


$CeO_2(111)$

<Correction energy>

$$E_{corr} = E_{iso} - E_{per} + q\Delta V$$



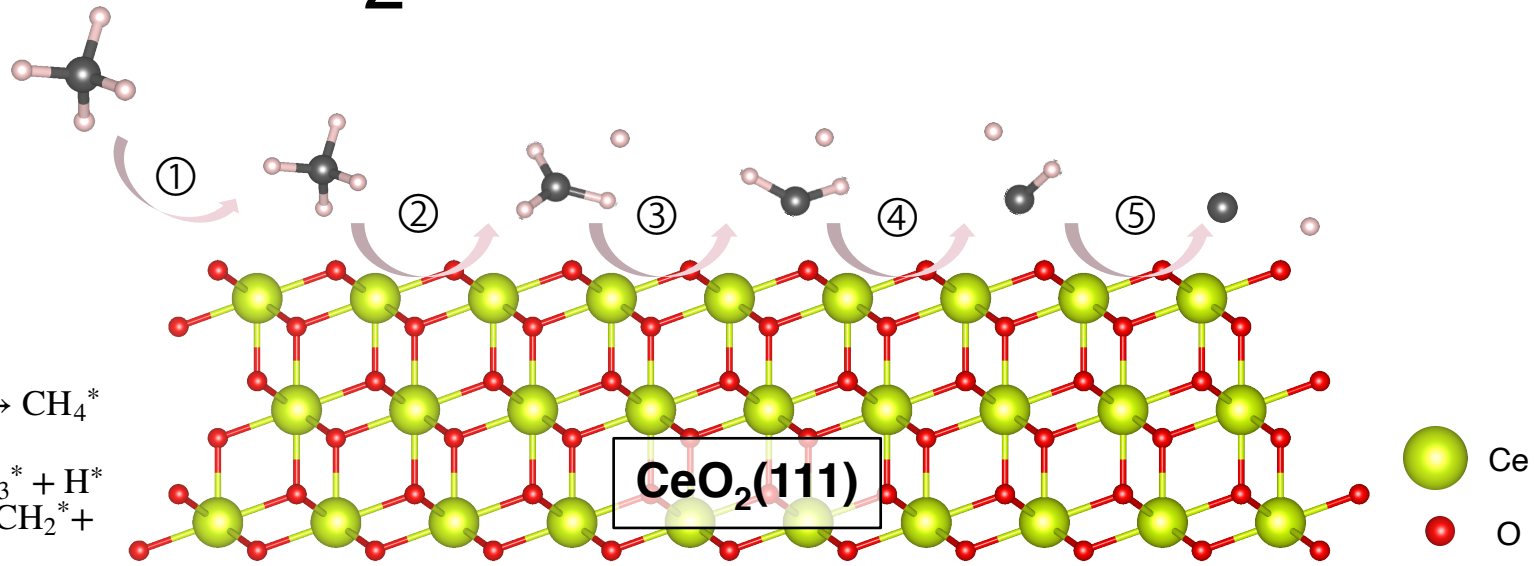


Modeled charge

Fitted ΔV

q : charged state

Example1. CeO_2



① $CH_4(g) \leftrightarrow CH_4^*$

②

$CH_4^* \leftrightarrow CH_3^* + H^*$

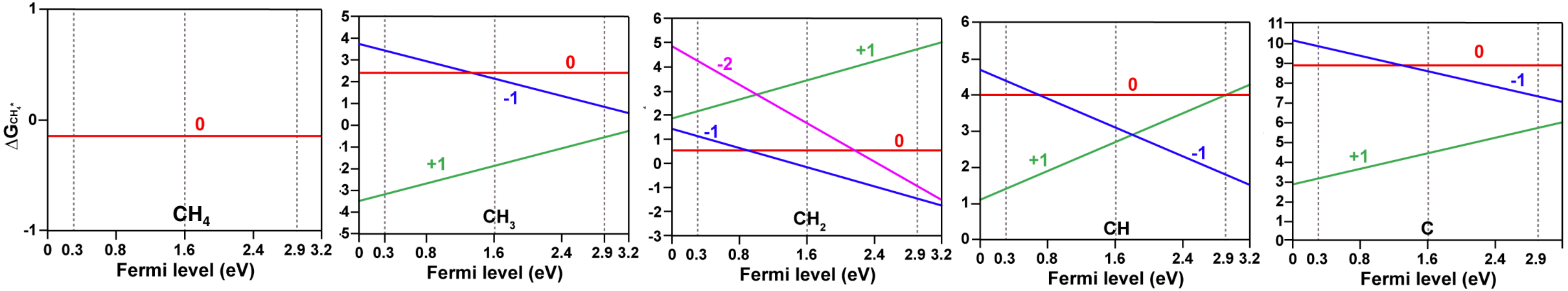
③ $CH_3^* \leftrightarrow CH_2^* + H^*$

④

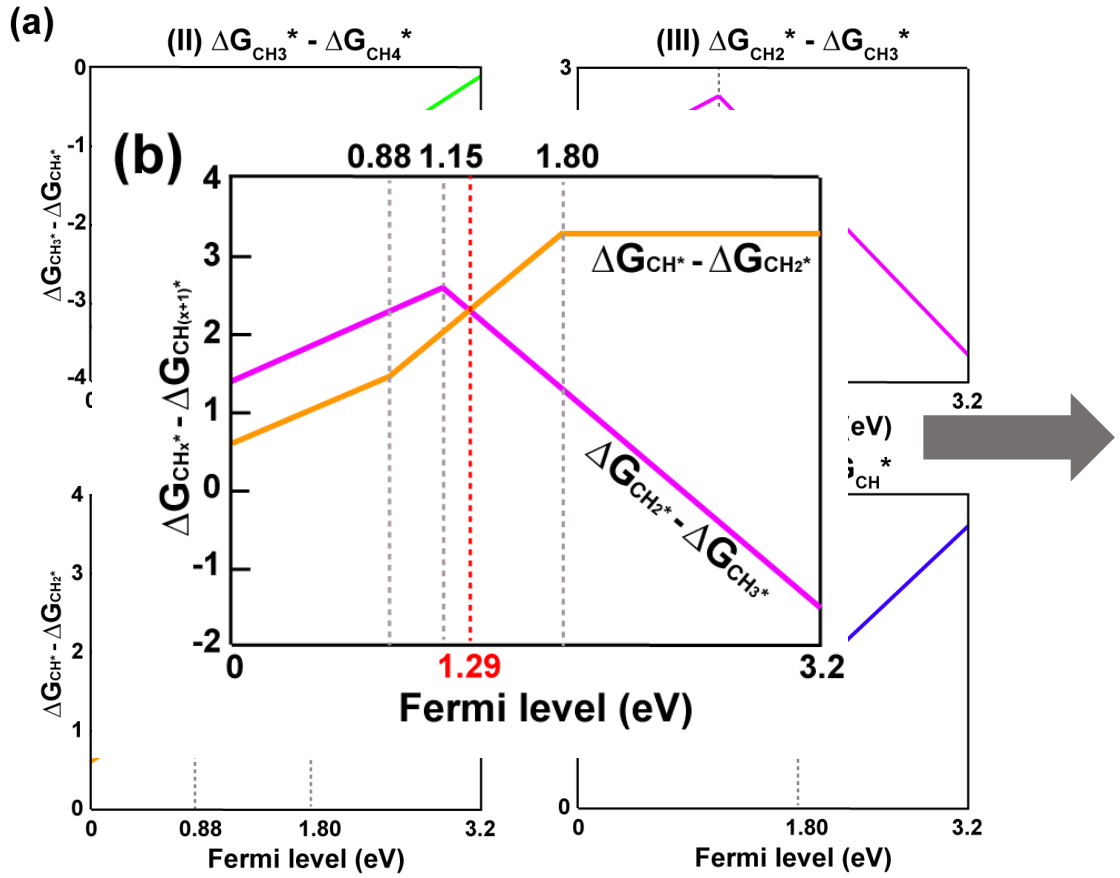
$CH_2^* \leftrightarrow CH^* + H^*$

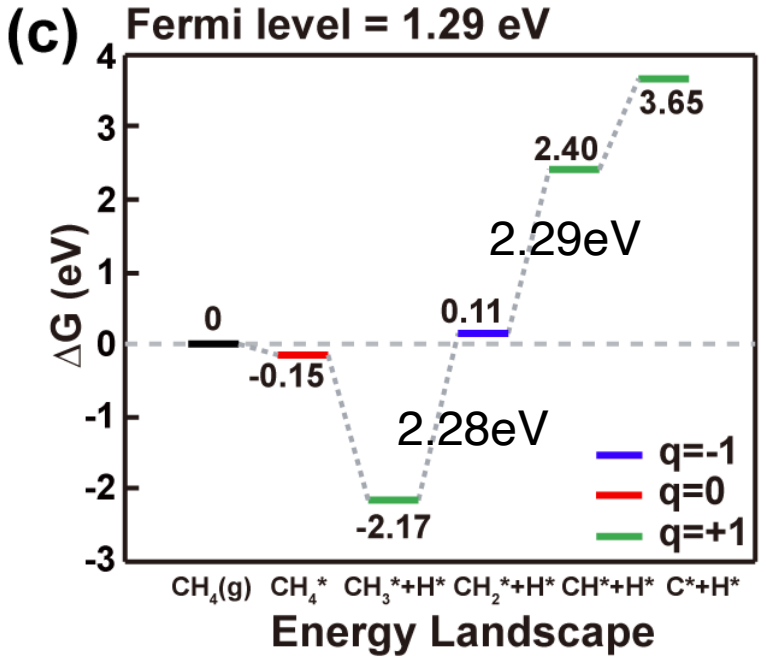
⑤ $CH^* \leftrightarrow C^* + H^*$

Band gap ≈ 3.2 eV



Example1. CeO_2



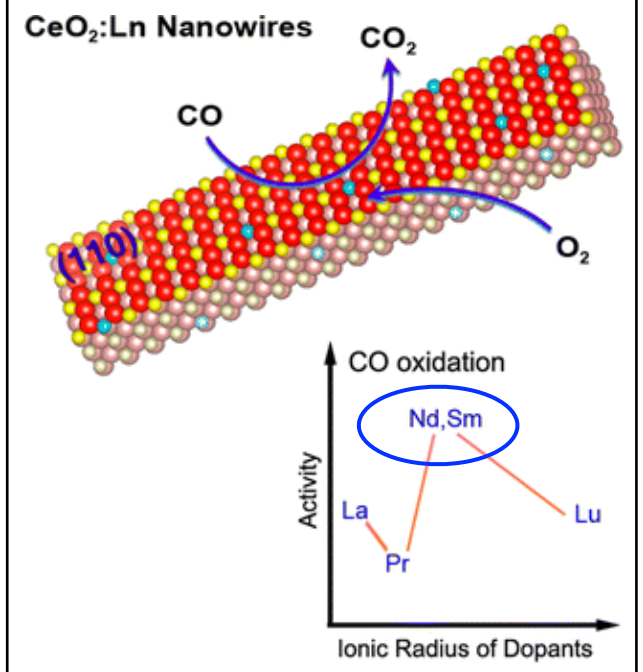


"p-type dopants are beneficial!"

Example1. CeO_2

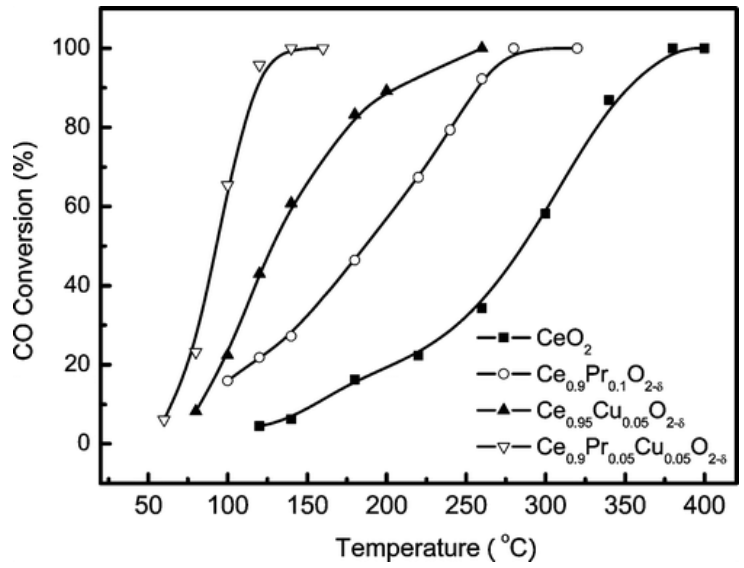
Examples of P-type dopants

Nd, Sm doping



J. Am. Chem. Soc. 2013, 135, 40, 15191–15200

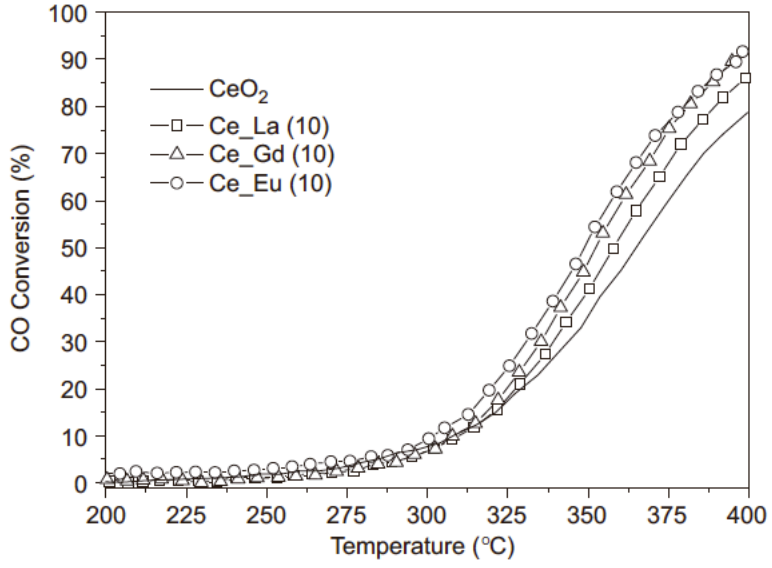
Pr, Cu doping



Compared to the pure CeO_2, the $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ catalyst was more active, while the $Ce_{0.95}Cu_{0.05}O_{2-\delta}$ catalyst was more active than the $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ catalyst.

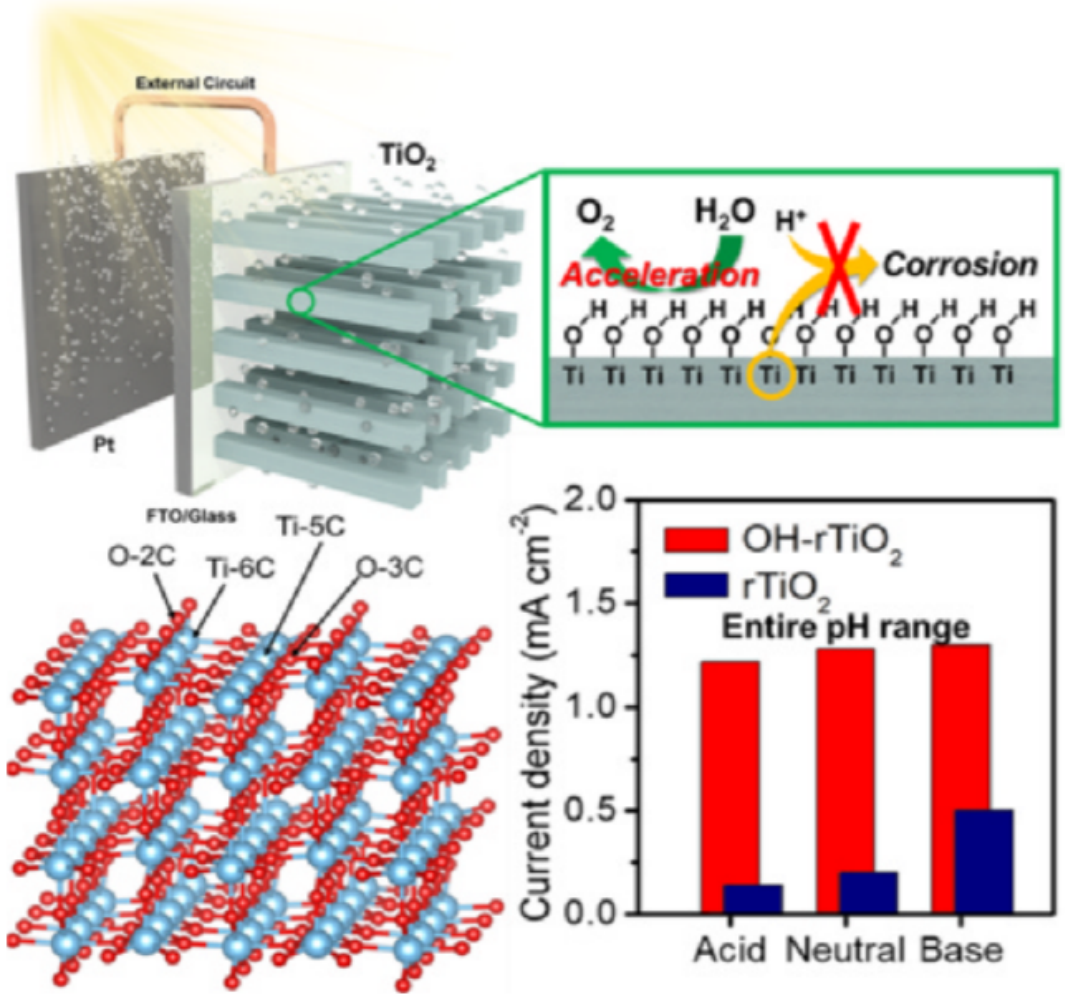
J. Phys. Chem. C 2008, 112, 38, 15045–15051

La, Gd, Eu doping



J. Ke, J. W. Xiao, W. Zhu, H. Liu, R. Si, Y. W. Zhang, C. H. Yan, *J. Am. Chem. Soc.* **2013**, *135*, 15191–15200.
Z. Y. Pu, X. S. Liu, A. P. Jia, Y. L. Xie, J. Q. Lu, M. F. Luo, *J. Phys. Chem. C* **2008**, *112*, 15045–15051.
W. Y. Hernández, O. H. Laguna, M. A. Centeno, J. A. Odriozola, *J. Solid State Chem.* **2011**, *184*, 3014–3020.

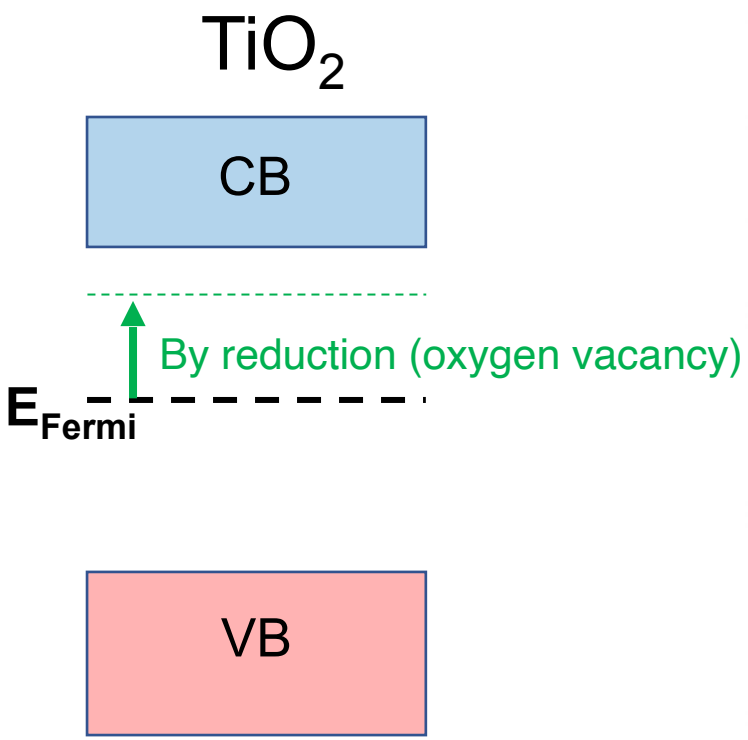
Example2. TiO_2

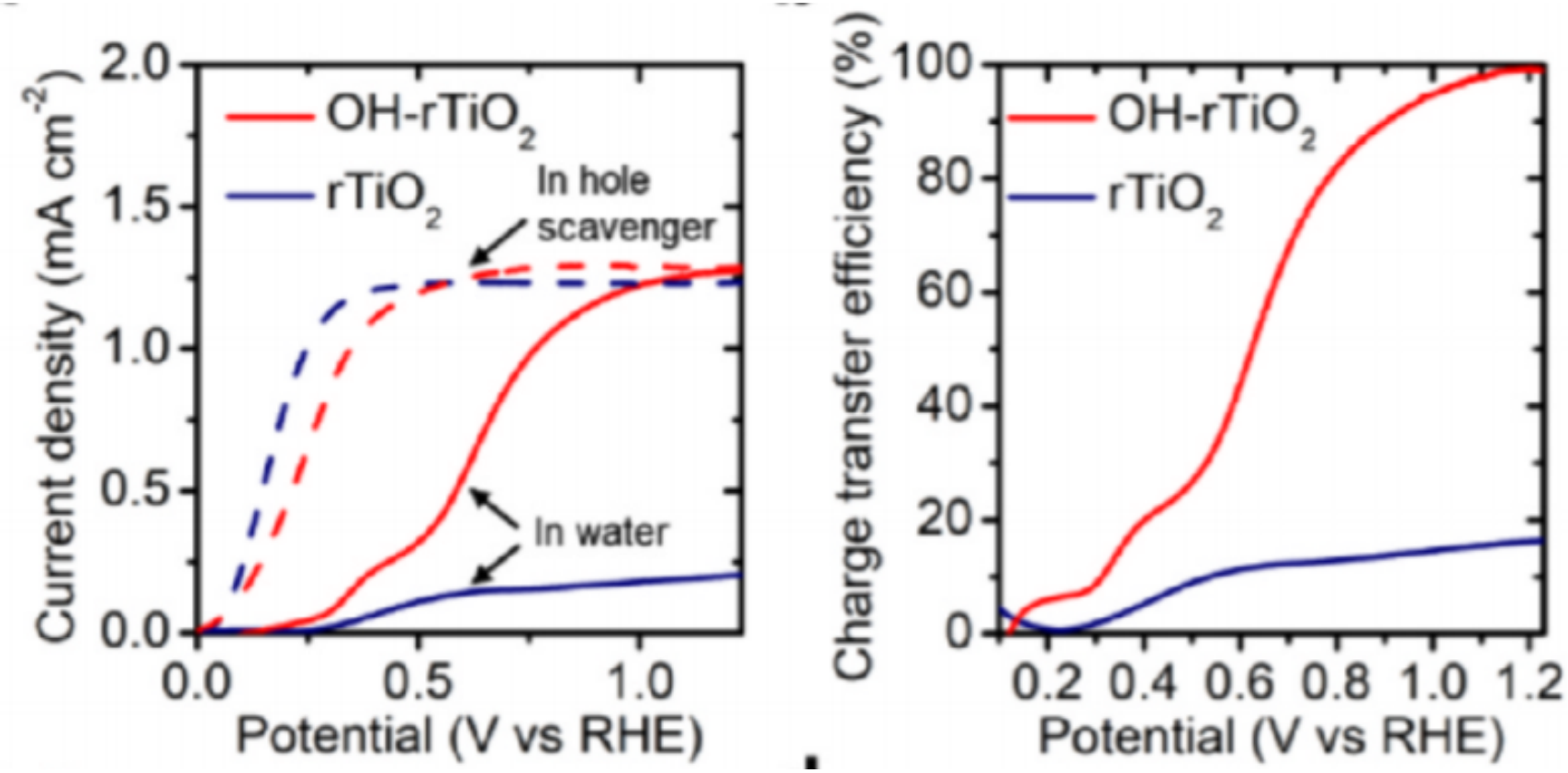


- Why reduction (more oxygen vacancy) on TiO_2 makes better photoelectrochemical water splitting activity?
- Why reduction make the water splitting performance ***less*** pH-dependent

H.Choi*, J. K. Kim*, J. H. Park*, et al., Chem. Eng. J. 2020, 126929.

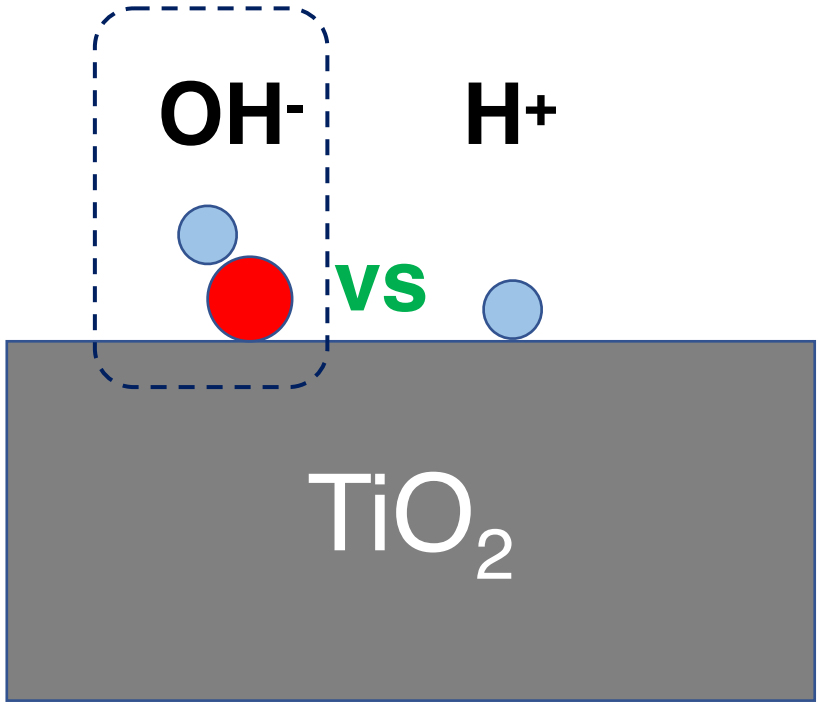
Example2. TiO_2

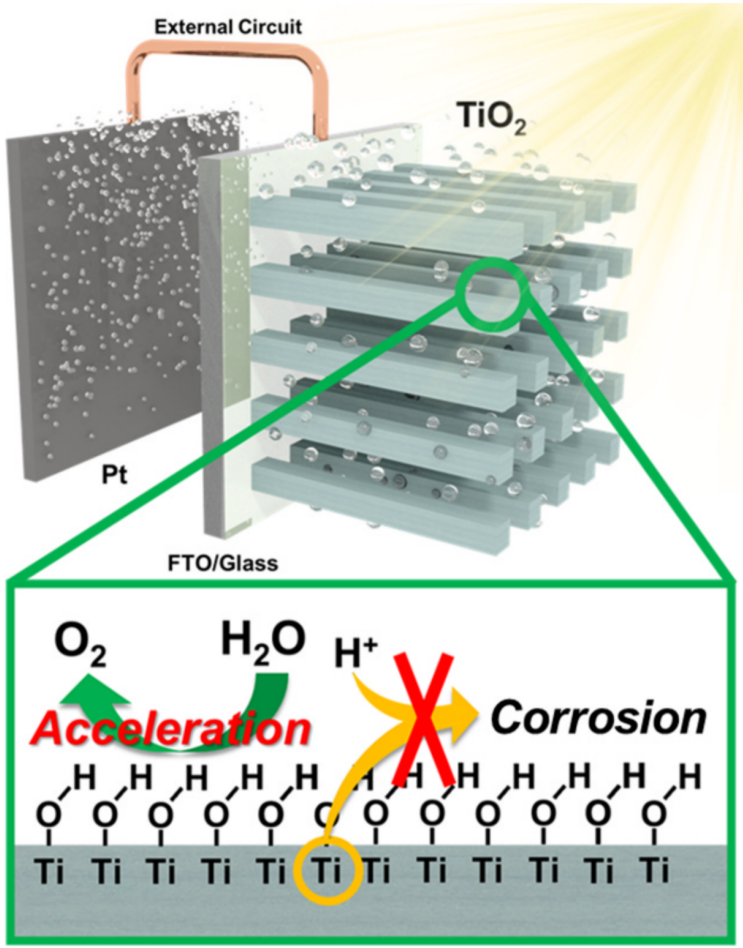


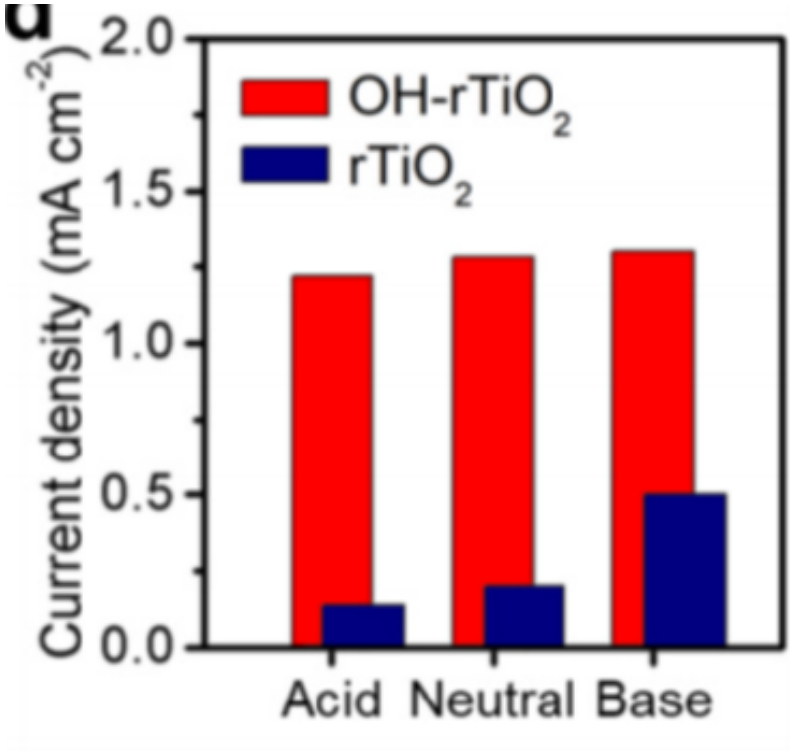


H.Choi*, J. K. Kim*, J. H. Park*, et al., Chem. Eng. J. 2020, 126929.

Example2. TiO_2







H.Choi*, J. K. Kim*, J. H. Park*, et al., Chem. Eng. J. 2020, 126929.

Adsorption energy correction

Fermi level variation:

$$\Delta G = (E_{substrate+adsorbate} - E_{substrate} - E_{adsorbate}) + q(\varepsilon_F + E_{VBM}) + E_{iso} - E_{per} + q\Delta V$$

For varying Fermi level Correction energy

pH-variation in water:

Modified model for aqueous H^+ ion adsorption

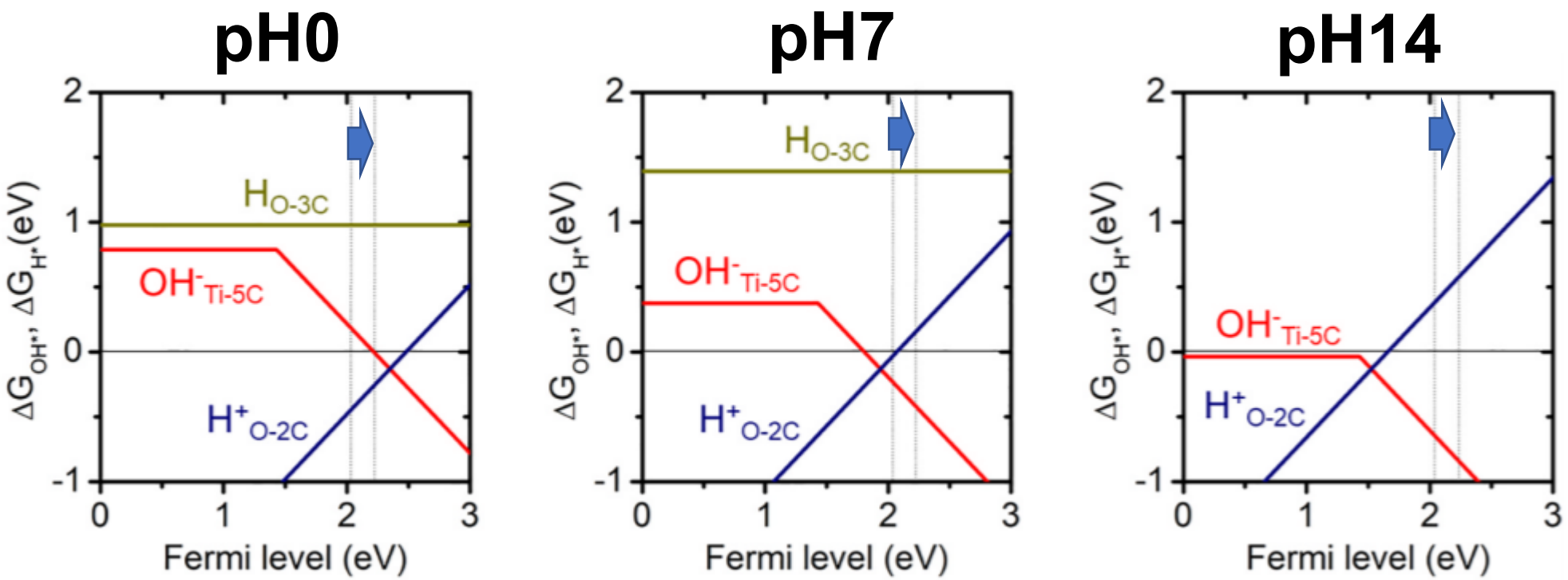
$$K = \frac{[Substate - H*]}{[Substrate*][H^+]} = \frac{\theta}{(1-\theta)10^{-pH}} \Rightarrow \theta = \frac{K10^{-pH}}{1 + K10^{-pH}}$$

$$\mathrm{pH} = -\log_{10}[H^+]$$

Adsorption energy

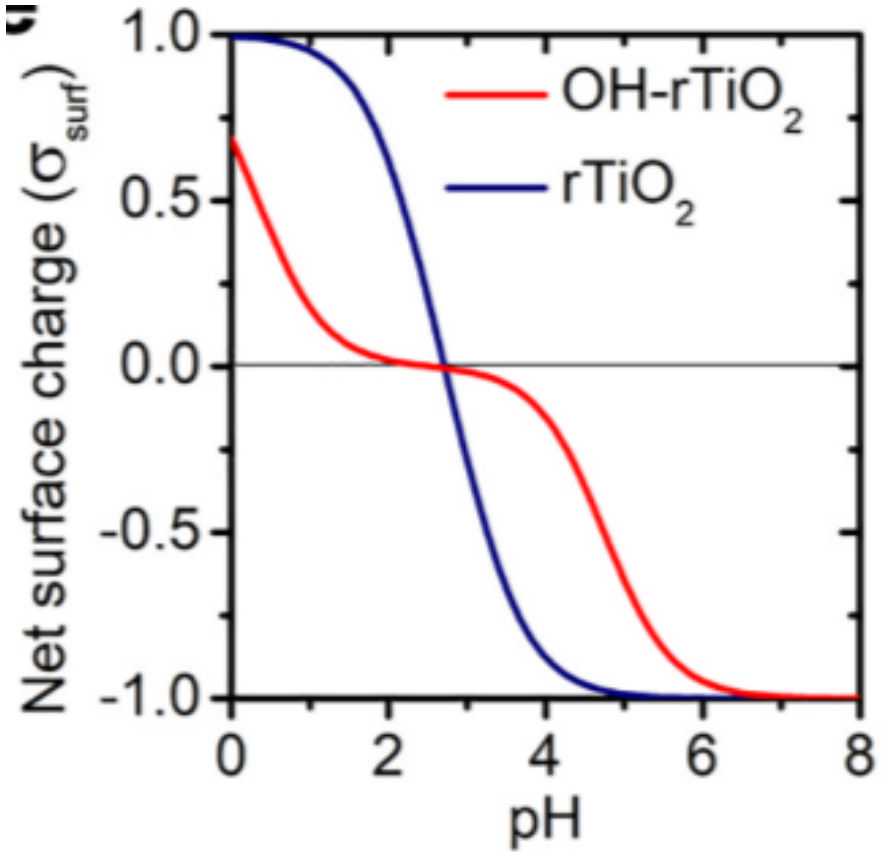
$$\theta_{OH^-} = \frac{\exp\left\{-\frac{(\Delta G^0_{OH*} - 0.059pH)}{kT}\right\}}{\left[1 + \exp\left\{-\frac{(\Delta G^0_{OH*} - 0.059pH)}{kT}\right\}\right]}$$

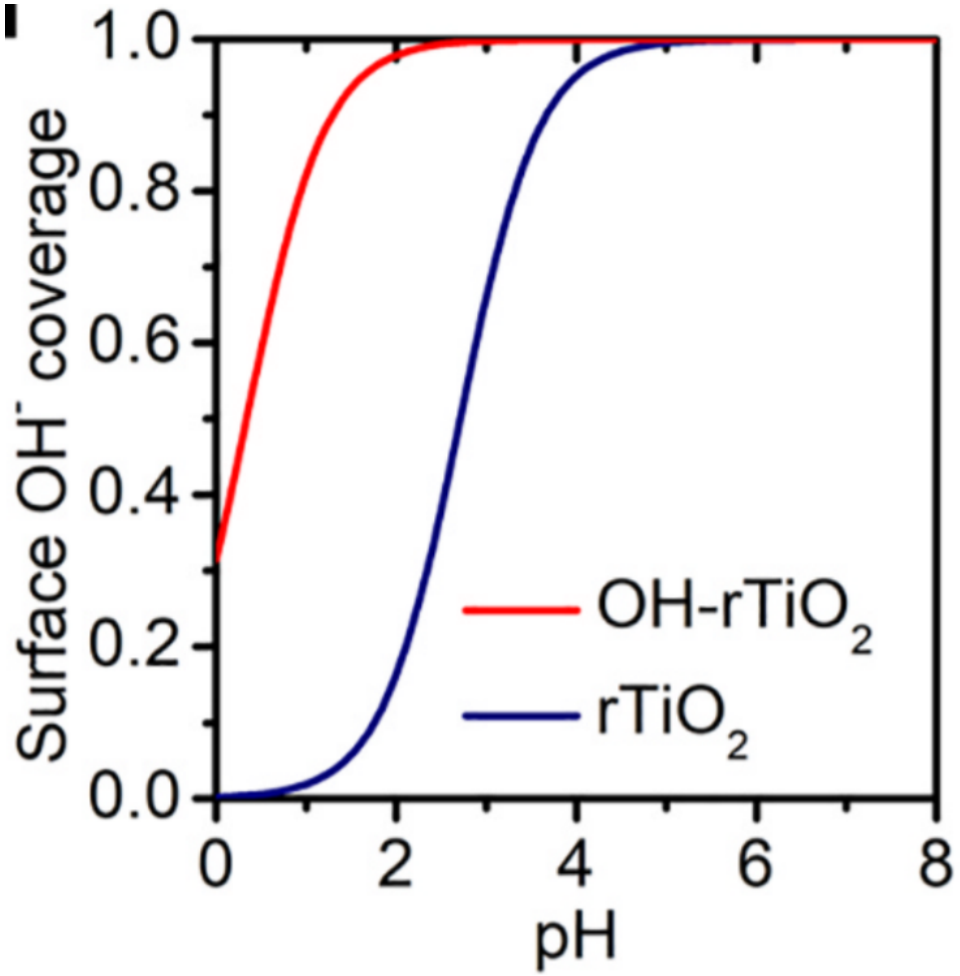
$$\theta_{H^+} = \frac{\exp\left\{-\frac{(\Delta G^0_{H*} + 0.059pH)}{kT}\right\}}{\left[1 + \exp\left\{-\frac{(\Delta G^0_{H*} + 0.059pH)}{kT}\right\}\right]}$$



pH-dependency

$$\sigma_{\text{surf}} = q(\theta_{H^+} - \theta_{OH^-})$$





Conclusion

- Photochemical reaction activities on semiconductor surfaces have not been successfully predicted or analyzed.
- Surface reaction activity on semiconductors could be well predicted and explained with modified model: Fermi-level-dependent adsorption energy
- Considering the potential difference of band levels and redox levels, photoexcitation effects can be expressed in accurate reaction pathway prediction.