Quantum simulation on the TiO_2-related reactions for solar cell application

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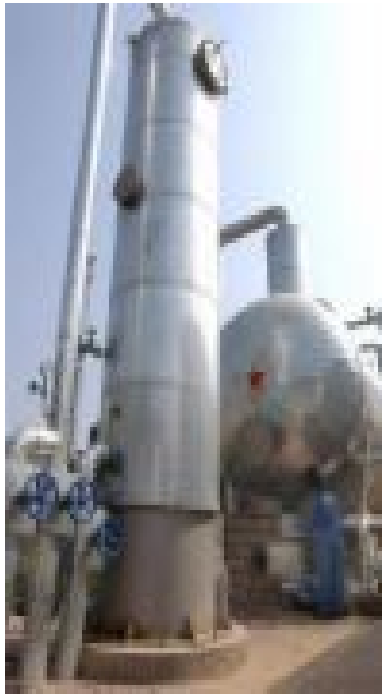
Summer Workshop on Nanoscale Meterials
August 15th, 2008

Introduction

Energy crisis

Greenhouse effect

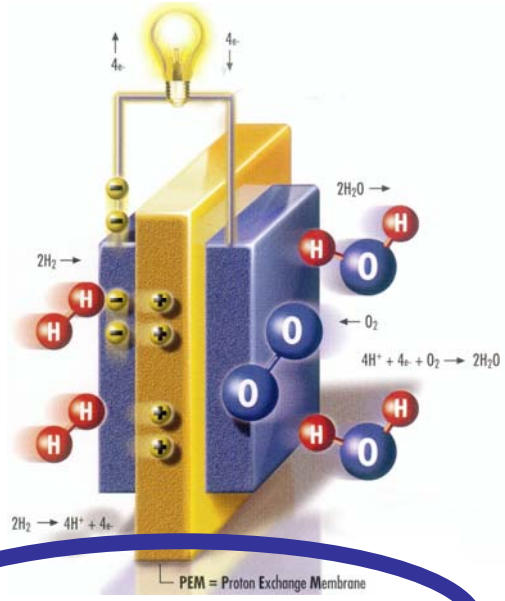


根據IEA國際能源署最新資料統計結果：

- 石油僅剩下40年
- 天然氣僅剩62年
- 煤炭剩216年
- 原子能鈾70年

石化燃料僅剩無幾，尋找新能源迫在眉睫

water power



Fuel cell

bioenergy

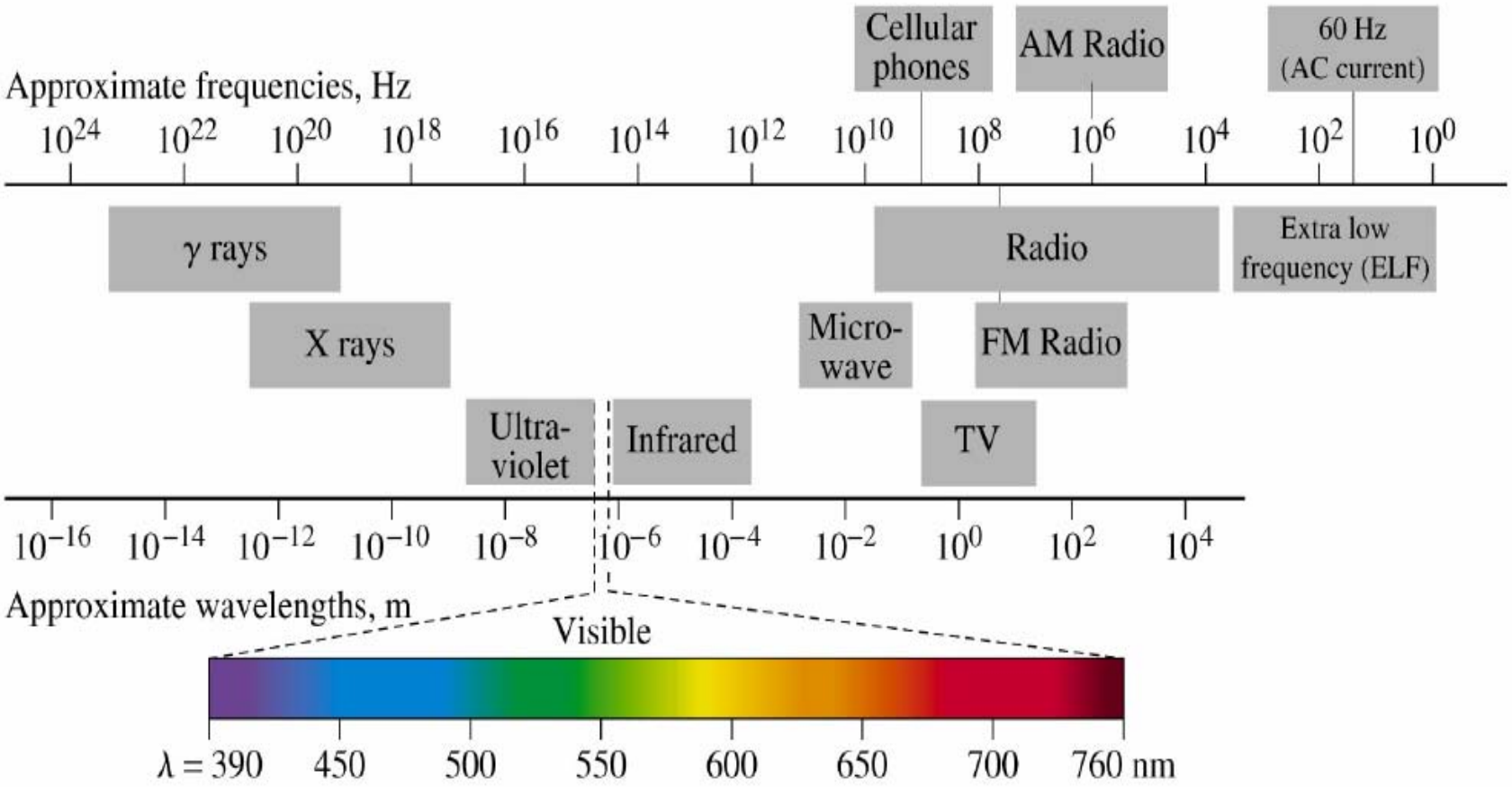
solar energy

Renewable Energy

wind power

最有淺力的綠色能源—太陽能電池

- 太陽所傳到地球大氣層的總能量每年達1.55×10^{15}百萬度之多。其中大約35%被反射回太空去，18%被大氣層所吸收，47%到達地面。單就到達地面的那一部份來說，假設，只轉換地球表面0.1%的太陽能為電能，設轉變率5%，每年發電量可達5.6×10^{12}度，**相當於目前世界上能耗的40倍之多**，太陽能電池無疑是當今最有淺力的綠色能源。

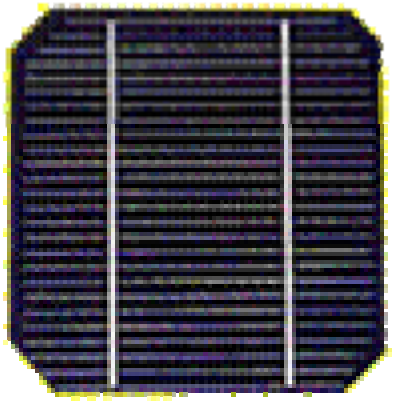

Approximate frequencies, Hz
10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0}
Cellular phones
AM Radio
60 Hz (AC current)
γ rays
X rays
Ultra-violet
Infrared
Micro-wave
Radio
FM Radio
TV
Extra low frequency (ELF)
10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4}
Approximate wavelengths, m
Visible
λ = 390 450 500 550 600 650 700 760 nm

太陽的輻射光譜

- **種類：**

太陽能電池的種類有單晶矽、多結晶矽、薄膜太陽能電池（非晶矽）三大類。

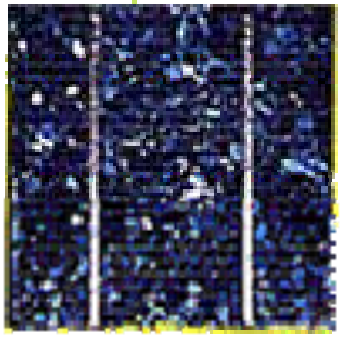
◎單晶矽太陽能電池：



單晶矽的組成原子均按照一定的規則，週期性地排列，它的製作方法是把99.99%矽金屬熔融於石英坩堝中，然後拉晶，在經過修角、切片等後續修飾動作，即可形成一單晶矽碇。

光電轉換效率最高，壽命最長，為主流太陽能電池。

◎多晶矽太陽能電池：



多晶矽電池的光電轉換效率較單晶矽低，但因製程步驟較簡單，成本亦低廉，較單晶矽電池價格便宜20%，因此一些低功率的電力應用系統均採用多晶矽太陽電池。

◎薄膜（非矽晶）太陽能電池：

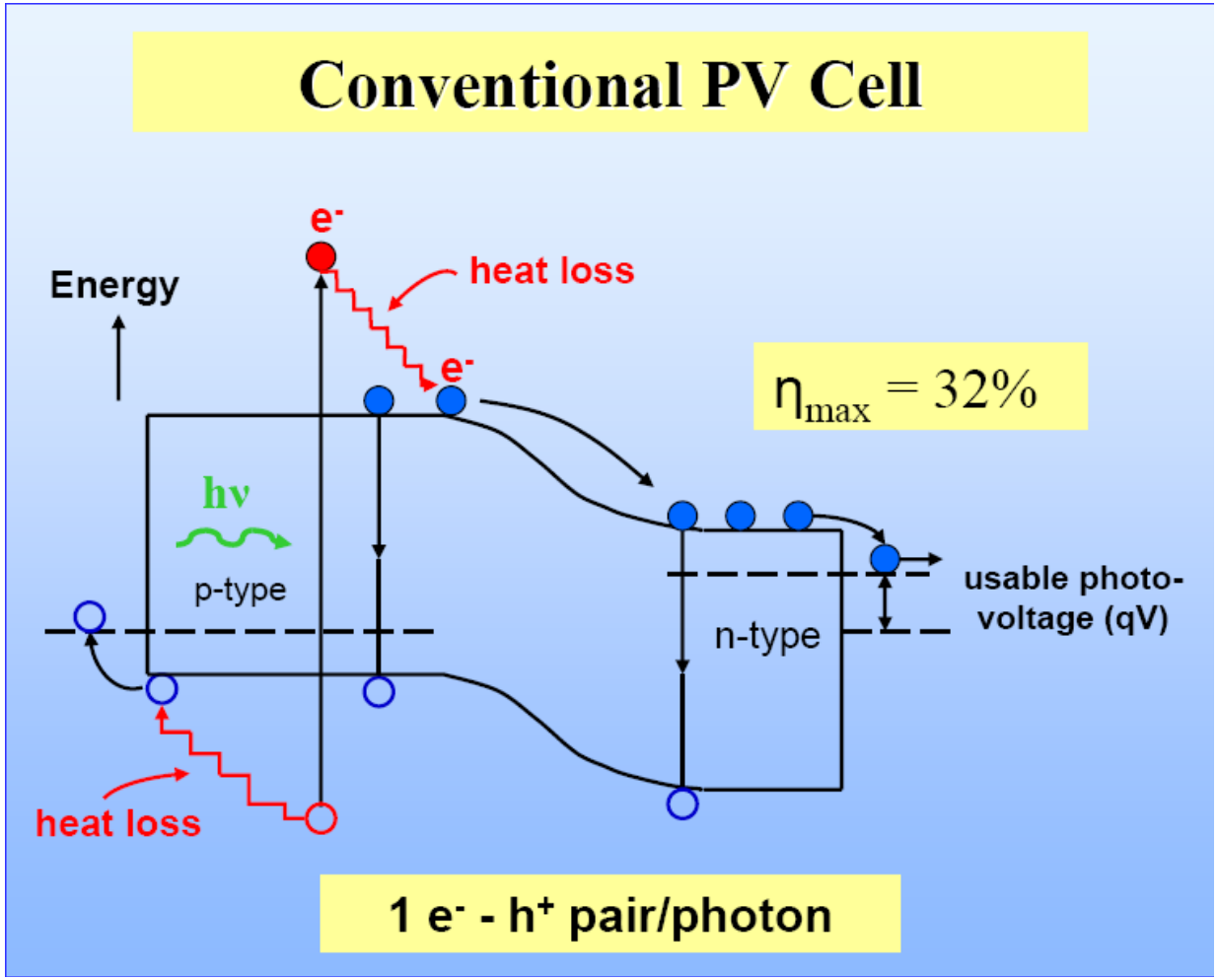
在玻璃等基板上附著厚度約1um左右之薄膜。此薄膜對光的吸收性比矽強好幾倍，所以只需要薄薄的一層就可以把光子的能量有效地吸收，且不需要使用昂貴的結晶矽基板，而用較便宜的玻璃、陶瓷或是金屬等基板，如此不僅可以節省大量的材料成本，也使得製作大面積的太陽電池成為可能（結晶矽太陽電池的面積受限於矽晶圓的尺寸），但壽命最短。

太陽電池種類及其用途

種　類	理論轉換效率%	成本	耐用性	主要用途
砷化鎵太陽電池	27	很高	佳	太空用
單晶矽太陽電池	23	高	佳	太空獨立電源 與中央發電系統用
多晶矽太陽電池	20	低	佳	獨立電源用
非晶矽太陽電池	14	低	普通	民生用品消費性產品
硫化鎘－碲化鎘 太陽電池	16-17	低	佳	民生用品消費性產品
多元化合物太陽電池	16-17	低	佳	民生用品消費性產品

History of solar cell

No.1 solar cell



Phys. Today. **2007**, *3*, 37

No.2 solar cell--GaAs

Advantage

1.photo absorption

2.low cost

3.made easily

Disadvantage

1.defect-----Staebler-Wronski effect

也就是光引發的非穩定性（light-induced instability）問題。也就是，非晶矽太陽電池第一次曝光，其效率便馬上減少10 至20%。

No.3 Dye Sensitized Solar Cell

1.Light adsorption

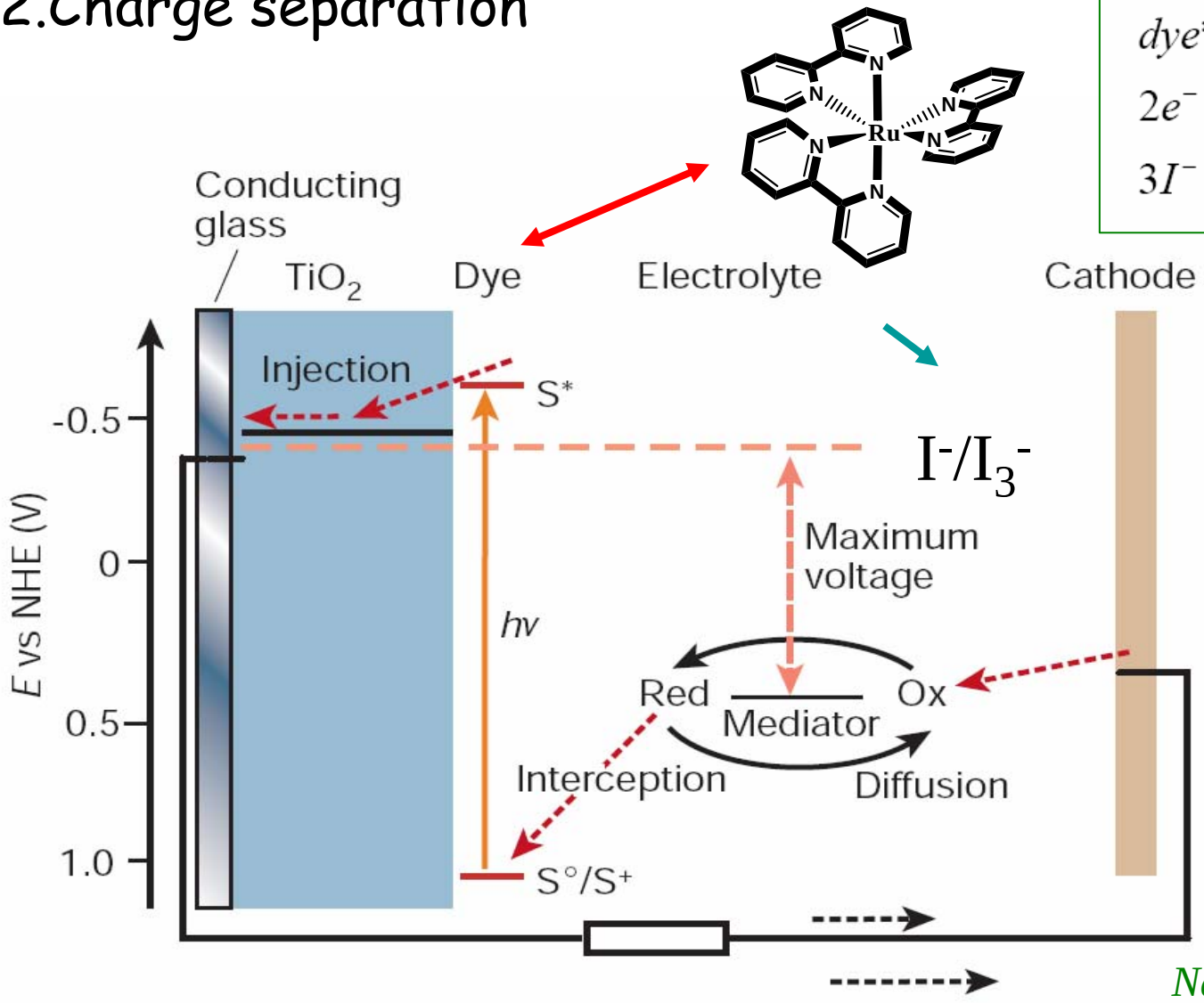
2.Charge separation

$$dye + h\nu \rightarrow dye*$$

$$dye* \rightarrow dye^{+} + e^{-}(TiO_2)$$

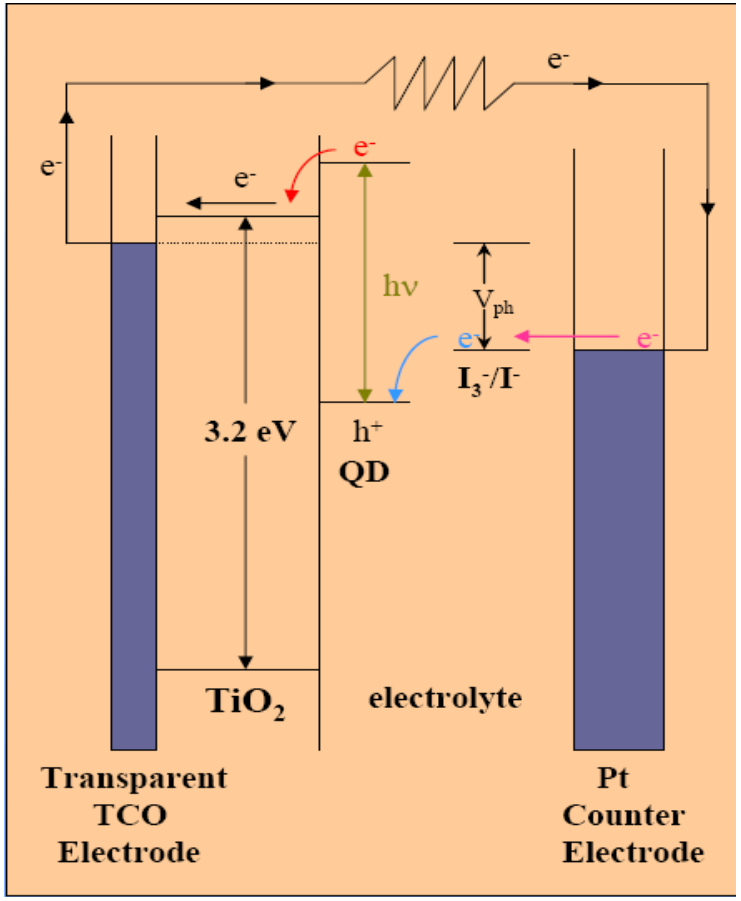
$$2e^{-} + I_3^{-} \rightarrow 3I^{-}$$

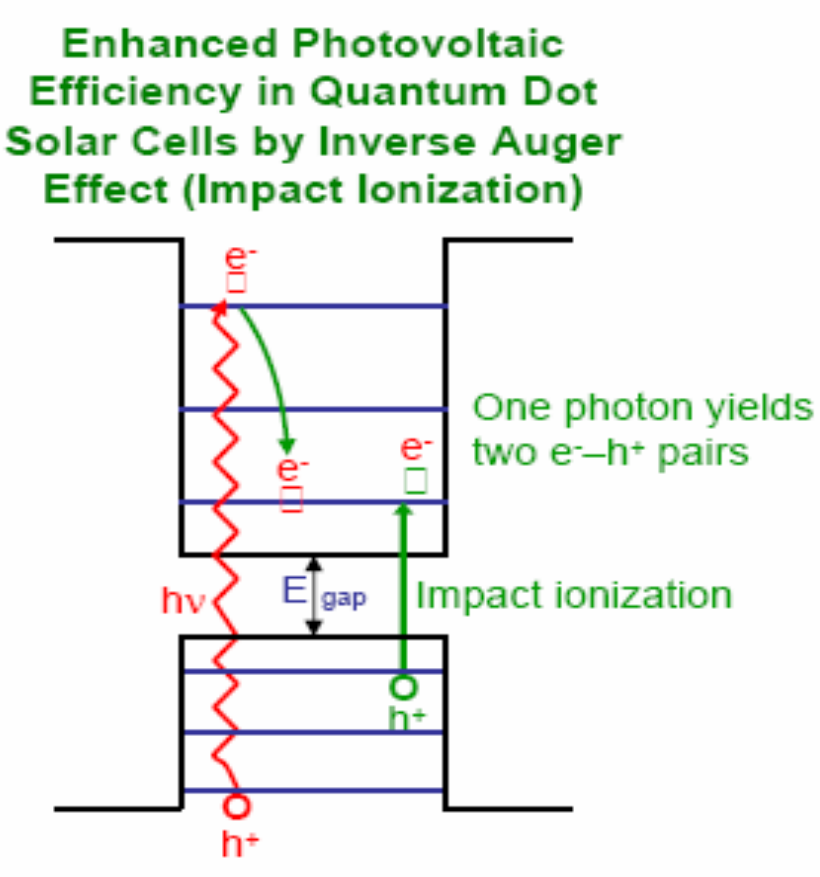
$$3I^{-} + dye^{+} \rightarrow I_3^{-} + dye$$



Nature. **1991**, *353*, 737.

Quantum Dots Sensitized Solar Cell

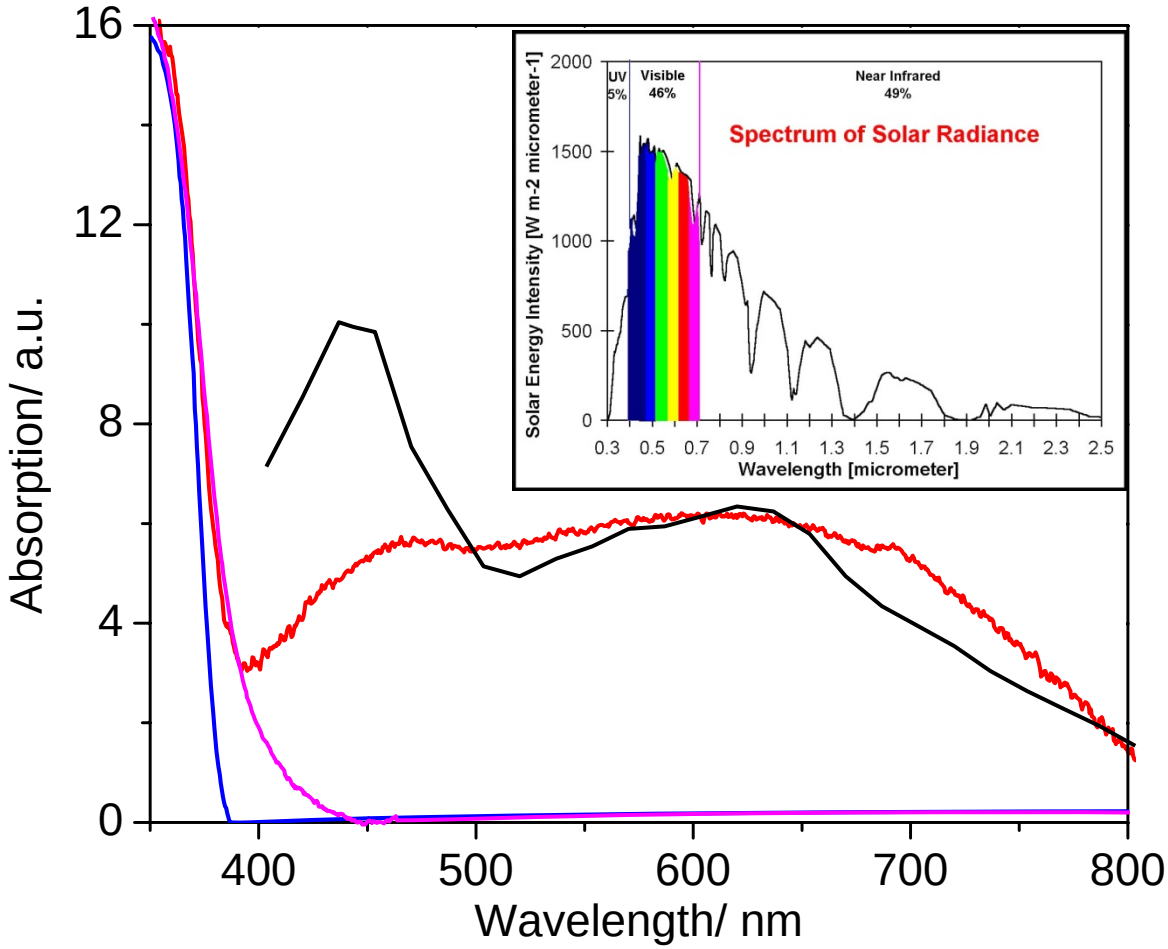




Physica E. **2002,** 14, 115

UV Visible Spectra

- **TiO_2 film:** absorption from 370 nm due to the 3.2-eV band gap
- **N-doped TiO_2 film:** red-shift to 430 nm, related to the mixing between N 2p and O 2p states.
- **InN/TiO_2 film:** a broad band absorption in 390 ~ 800 nm, resulted from polycrystalline InN films
- **Black dye:** a broad band adsorption in the visible range



Black dye: Nazeeruddin, M. K.; Pechy, P.; Graetzel, M. *Chem. Comm.,* **18** 1705, (1997)
N-doped TiO_2: Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science,* **293**, 269 (2001)
Solar spectrum: Lawrence Berkeley National Laboratory, Environment Energy Technology Division, http://eetd.lbl.gov

一、Quantum Simulations of Solar Energy

$(InN)_x/OY(O)O/TiO_2$ (Y=B and P)

1. Adsorption Configurations and Reactions of $X(OH)_3$ [X= B, P] on TiO_2 Surface

-$InN/OY(O)O/TiO_2$ (Y=B and P)

2. InN/Linker/TiO_2 related calculations

-An anchoring group, linker, between two nanoparticles, plays a critical role in their physical as well as electronic connections

3. Adsorption and Reaction of H_2O_2 and H_2S on TiO_2 Surface

-Hydrogen peroxide is a potential TiO_2 hydroxylation agent

-Hydrogen sulfide is an efficient precursor for metal sulfide thin-film preparation.

VASP

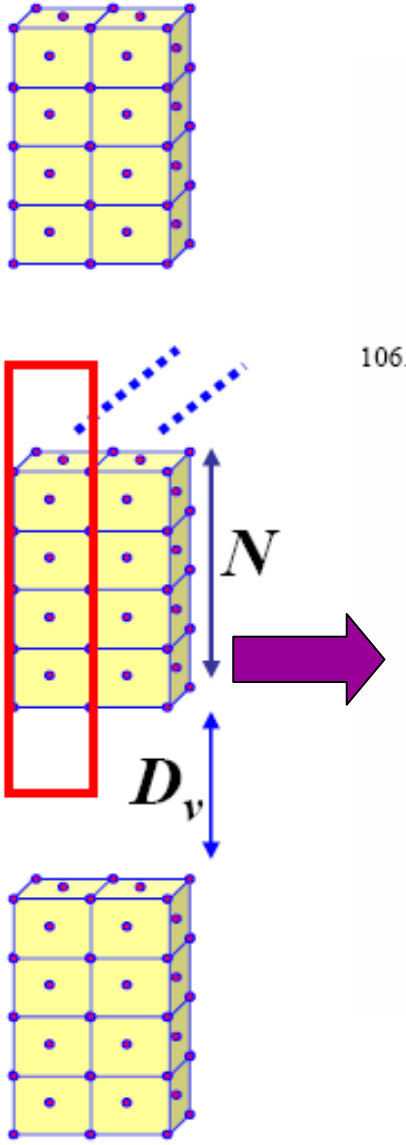
- **Total energies have been calculated by using ultrasoft pseudopotentials. The exchange-correlation function was GGA of the PW91 formulation.**
- **Monkhorst-Pack k-point 6x6x1 and 600eV cutoff energy.**
- **Vacuum space: 15 Å**

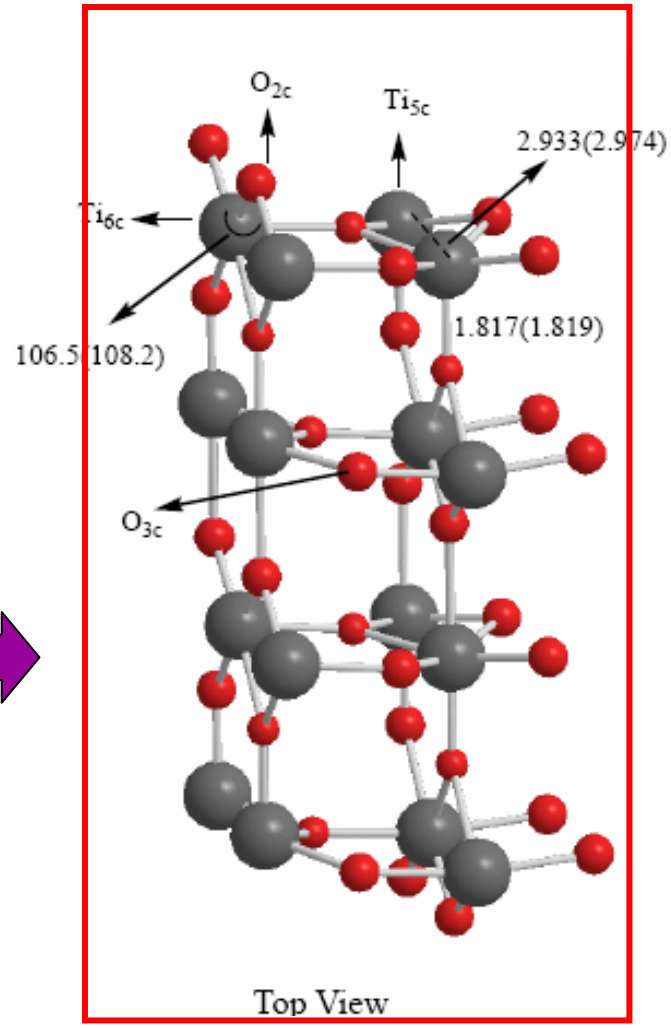
Adsorption energy in kcal/mol
$\triangle$Ead = - [Eproducts - Ereactants]
= -[E(surface + adsorbate) - Esurface - Eadsorbate]

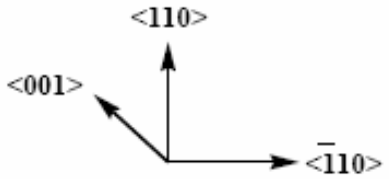
Experimental and calculated lattice parameters (Å) of TiO_2.

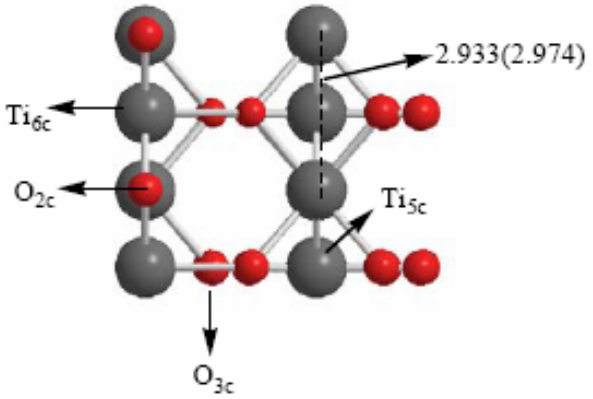
	Anatase (101)			Rutile (110)		
	this work	experimental	theoretical	this work	experimental	theoretical
a	3.785	3.782	3.882 (3.785)	4.593	4.594	4.640(4.595)
c	9.739	9. 502	9.690 (9.715)	2.933	2.958	2.988(2.959)
u	0.201	0.208	0.208 (0.206)	0.296	0.305	0.305

TiO_2 (110) rutile



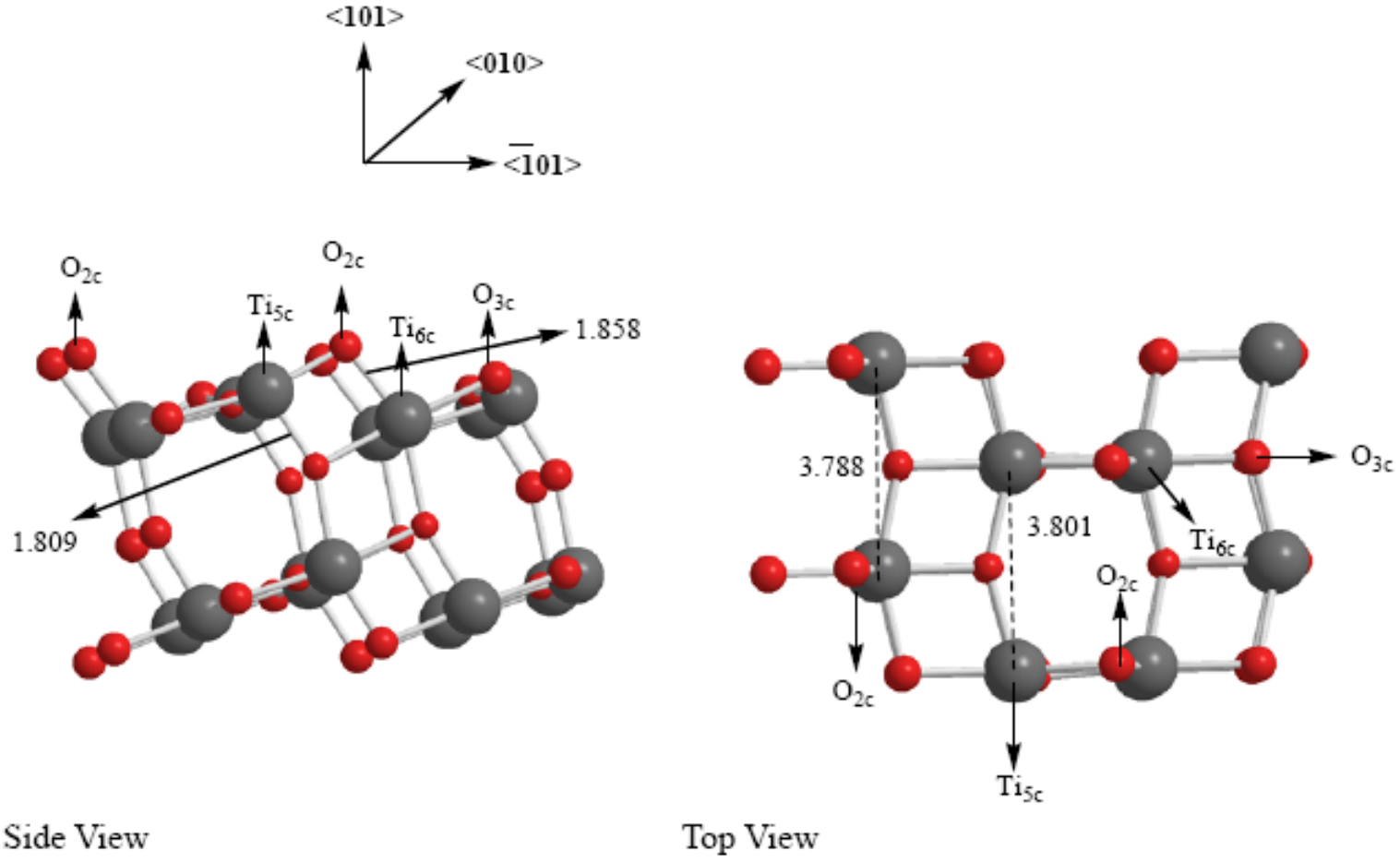






D_v (Vacuum space): 15 Å

TiO_2 (101) anatase

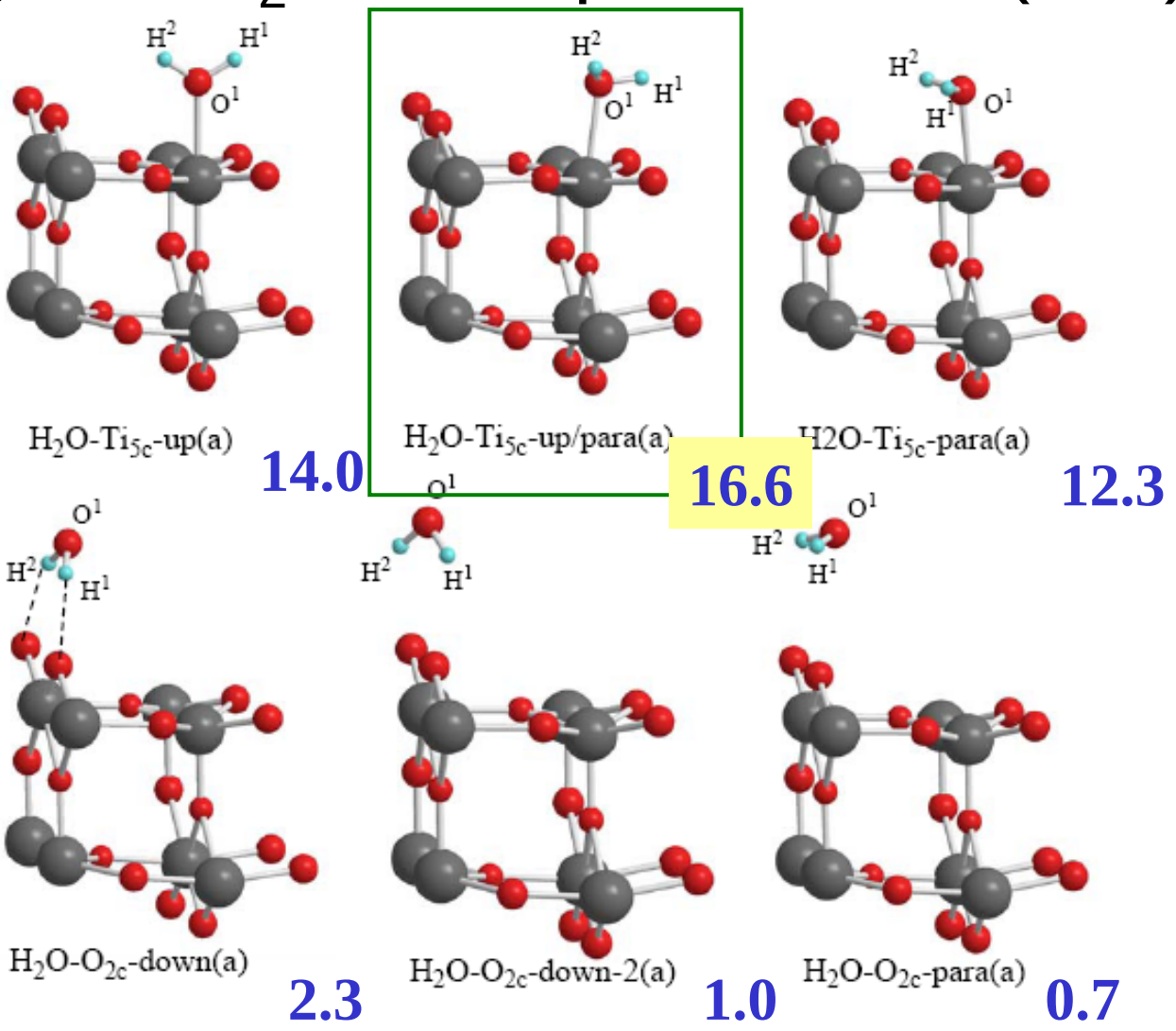


Side View

Top View

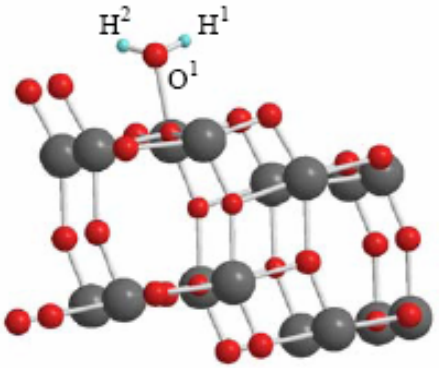
D_v (Vacuum space) : 15 Å

Testing with H_2O adsorption-Rutile (110) Surface

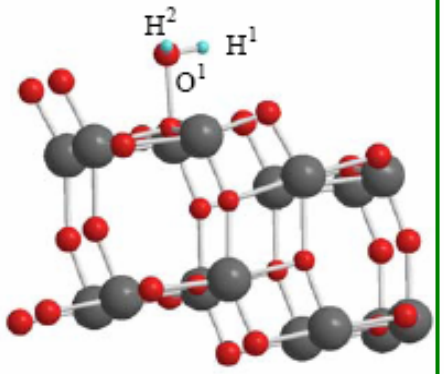


Adsorption energy (E_{ads}) ➡ $E_{ads} = -[E_{total} - (E_{slab} + E_{molecule})]$

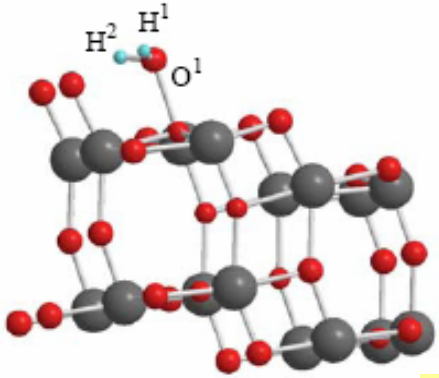
Testing with H_2O adsorption -Anatase (101) Surface



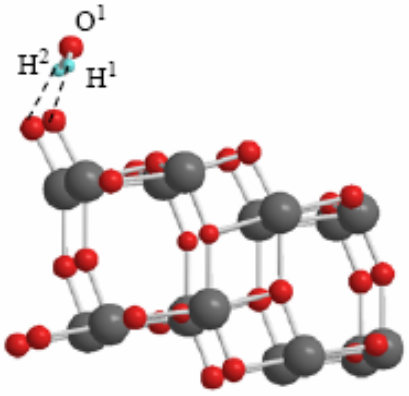
H_2O-Ti_{5c}(a) **12.1**



H_2O-Ti_{5c}-pararight(a) **10.5**



H_2O-Ti_{5c}-paraleft(a) **15.7**



H_2O-O_{2c}-down (a) **1.9**

On rutile surface

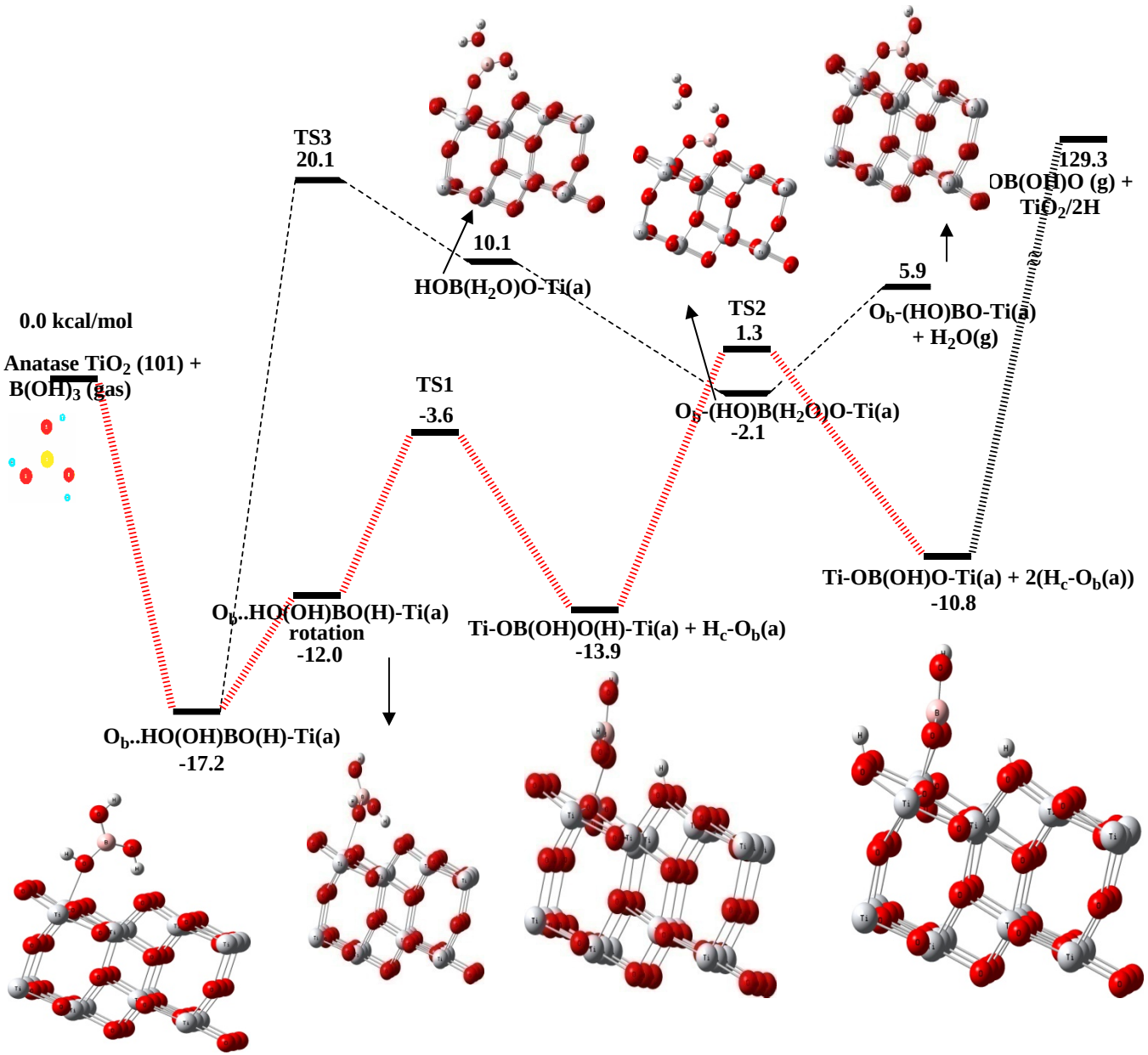
14.8~17.1 kcal/mol

On anatase surface

16.6 ~17.1 kcal/mol

Herman, G. S.; Dohnalek, Z.; Ruzycki, N.; Diebold, U. *J. Phys. Chem. B* **2003**, *107*, 2788.

Adsorption/Decomposition of $B(OH)_3$ on Anatase TiO_2 (101)



Adsorption Energy (kcal/mol):

Ti-OB(OH)O(H)-Ti(a) = 74.9

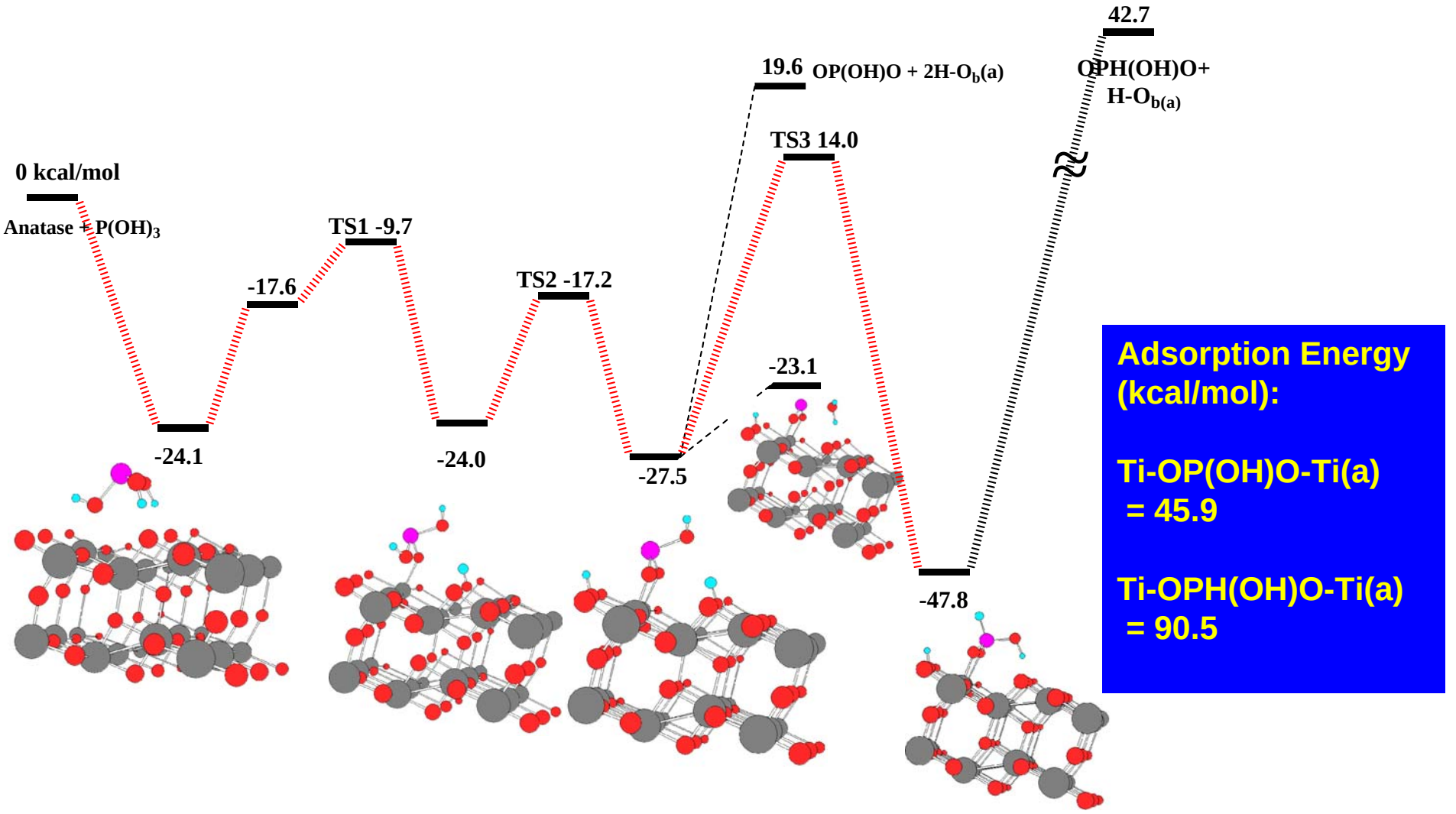
Ti-OB(OH)O-Ti(a) = 140.1

O_b-B(OH)O-Ti(a) = 44.1

The HOB(O)O<Ti_2 binding is very strong when compare with HOP(O)O<Ti_2 and is a good linker for InN and TiO_2.

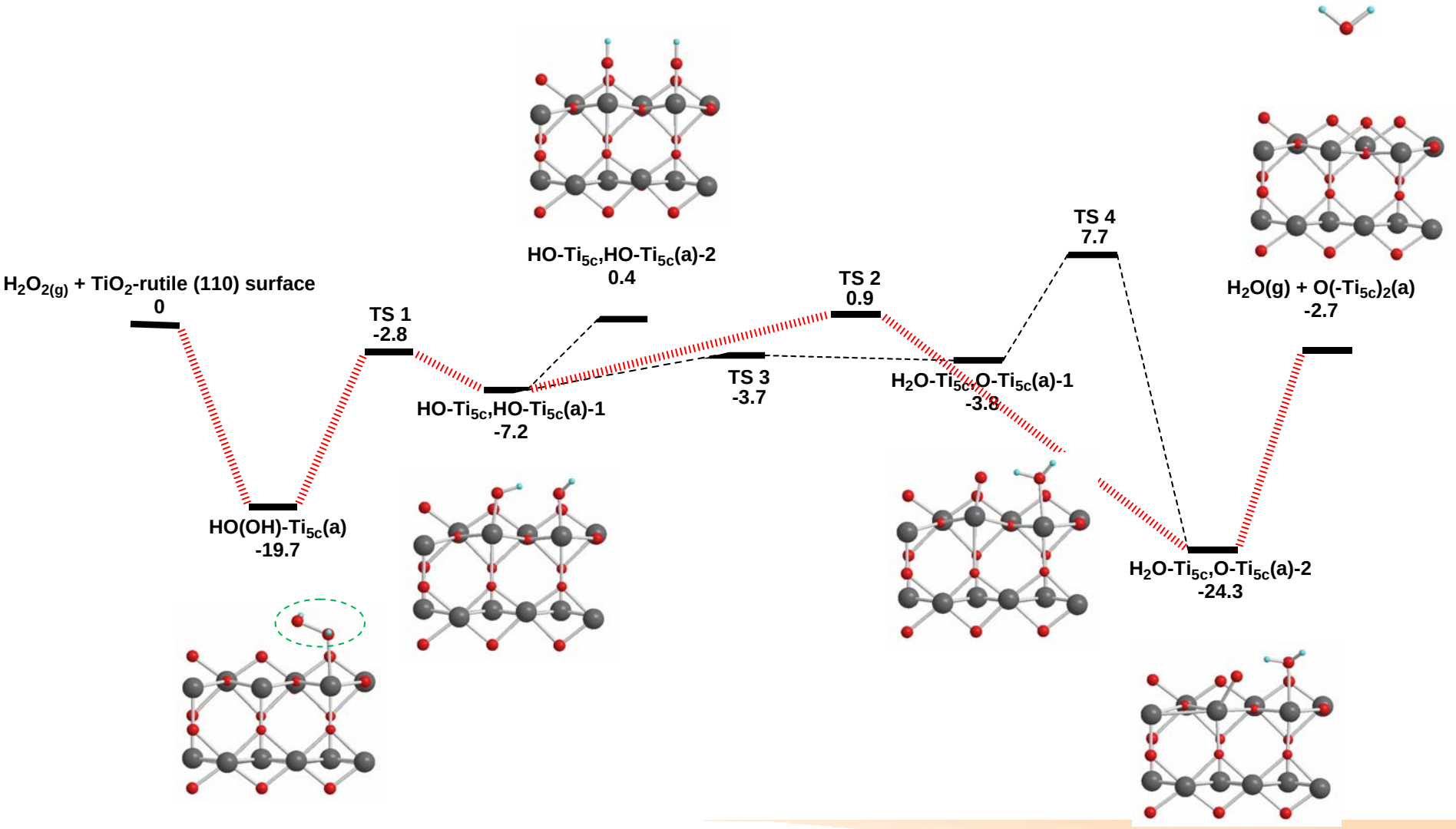
➢Neighboring H(a) enhances adsorption energies.

Adsorption/Decomposition of $P(OH)_3$ on Anatase TiO_2 (101)

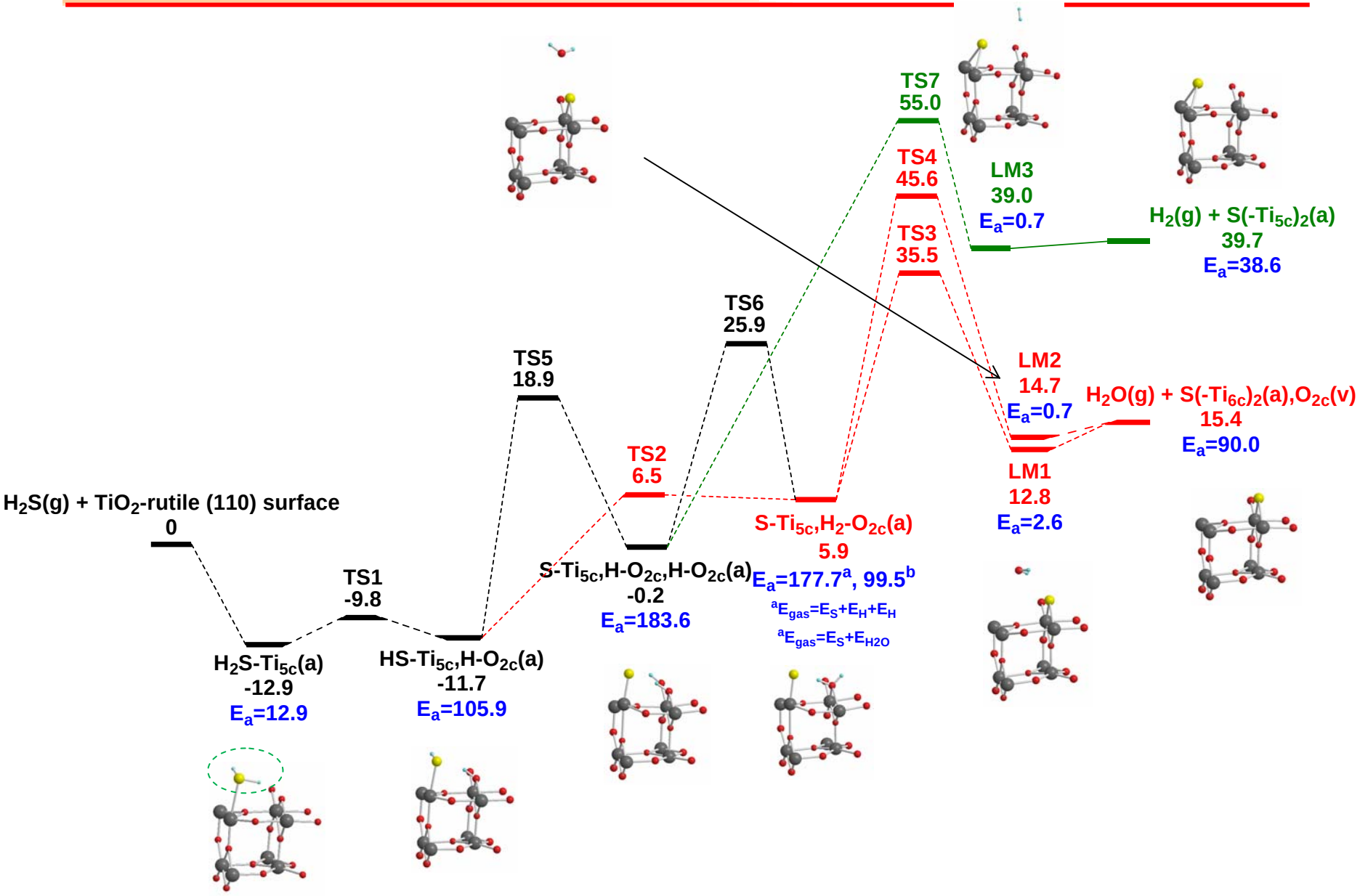


➢ Ti-OB(OH)O-Ti adsorbates can be employed as strong linkers between semiconductor quantum dots such as InN and TiO2 nanoparticles.

PES of H_2O_2 on TiO_2-rutile (110) Surface



PES of H_2S on TiO_2-rutile (110) Surface



Rate Constant：$H_2S(g)+TiO_2\text{-rutile}\rightarrow TS_3\rightarrow H_2O(g)+S(-Ti_{6c})_2(a),O_{2c}(v)$ $k=1.486\times10^{-14}\exp(-37.272/RT)$

Hydrogen effect
- adsorption energy

Table 3-3(c) Adsorption Energies (kcal/mol) for some Species Calculated at the PW91 Level

Species	Without Hydrogen Effect	With Hydrogen Effect[E]	
Rutile/Ti_{5c}-ON(O)O-Ti_{5c}H-O_{2c} (a)	12.0	58.7	68.9[H]
Anatase/Ti_{5c}-ON(O)ON(O)O-Ti_{5c}(a)	6.6	56.7	
H_2S-Ti_{5c}(a)[F]	12.9	9.3	
HS-Ti_{5c}(a)	12.2	42.4	
H_2O-Ti_{5c}(a)	19.9	16.8	
HO-Ti_{5c}(a)	40.7	77.3	
Ti_{5c}-OB(OH)O-Ti_{5c}(a)[G]	53.8	134.6	

[E] The adsorption surface is considered with one hydrogen adsorbed on the O_{2c} site.

$E_{ads} = -[E_{total/H} - (E_{slab/H} + E_{molecule})]$

[F] Hunag W. F., Chen H. T. and Lin M.C.

[G] Raghunath P. and Lin M.C.

[H] The adsorption energy is considered with two hydrogen adsorbed on the O_{2c} site.

Hydrogen effect is more significant in radical molecule than non-radical molecule.

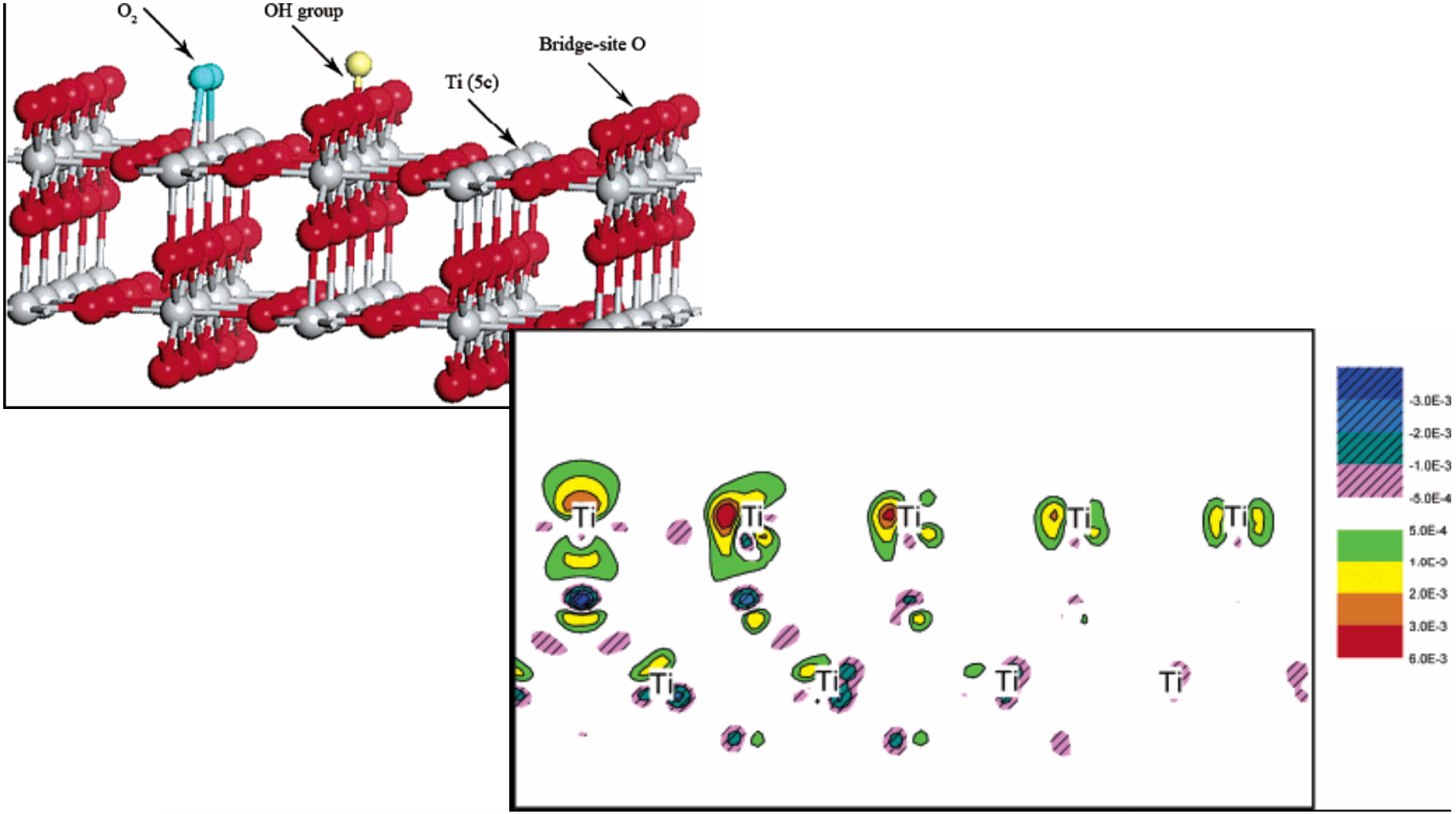
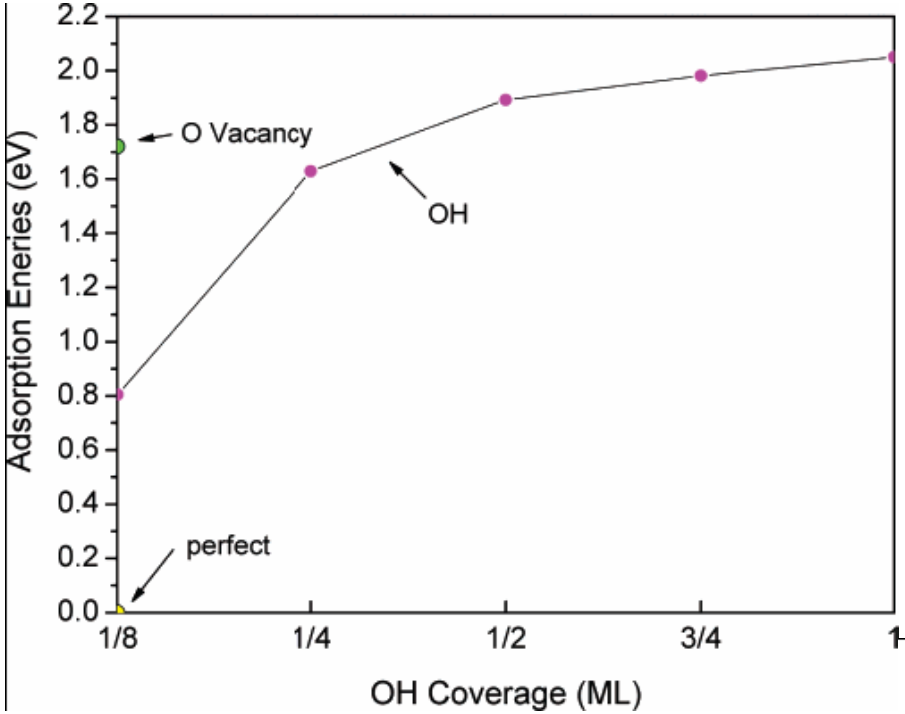
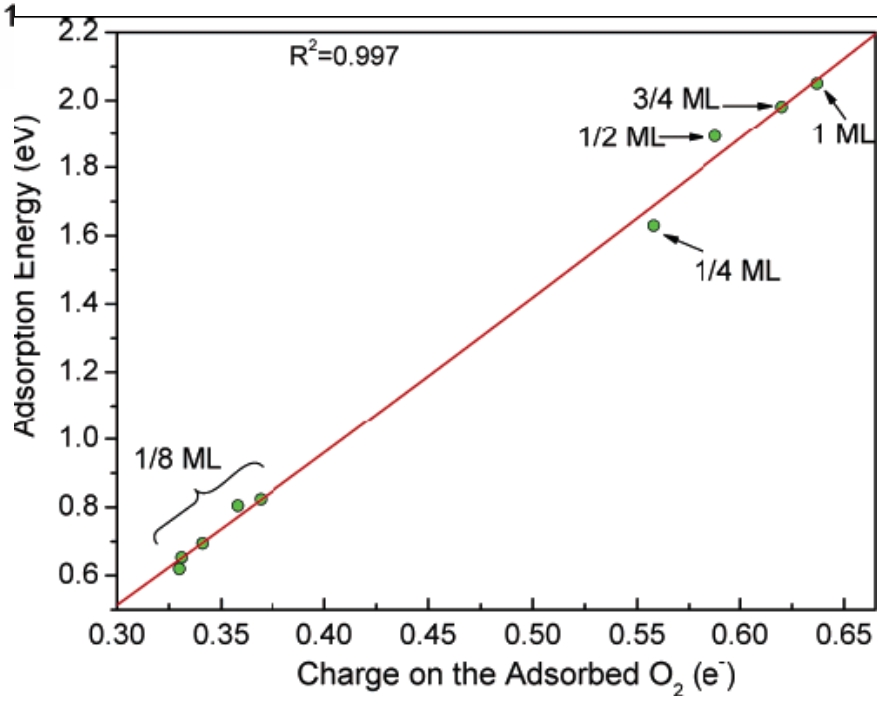


Table 1. Calculated Adsorption Energies with Different Distances between O_2 and OH Using P(1×8) Unit Cell

distances (Å)	3.32	4.93	7.48	10.22
adsorption energies (eV)	0.82	0.69	0.65	0.62

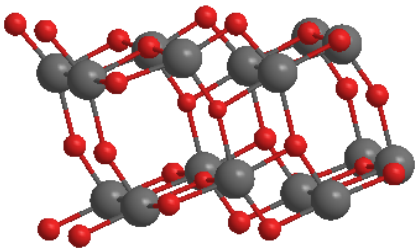
Liu, L. M. et al. J. Am. Chem. Soc.; 2006; 128; 4017.

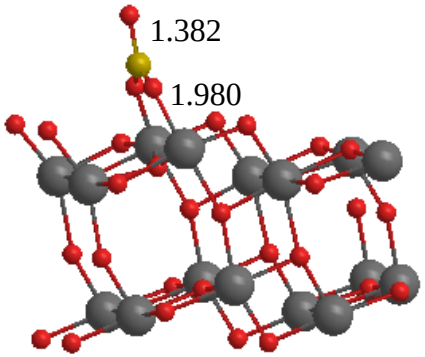

Adsorption Eneries (eV)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
O Vacancy
OH
perfect
1/8
1/4
1/2
3/4
1
OH Coverage (ML)


R²=0.997
3/4 ML
1/2 ML
1 ML
1/4 ML
1/8 ML
Adsorption Energy (eV)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
Charge on the Adsorbed O2 (e-)

Strategy:

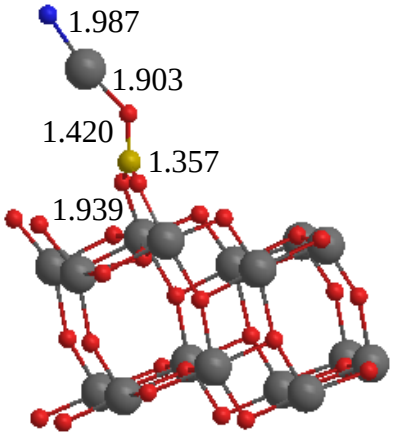
$(InN)_x$ absorbed on **YO_3-TiO_2 surfaces, Y=B, P**





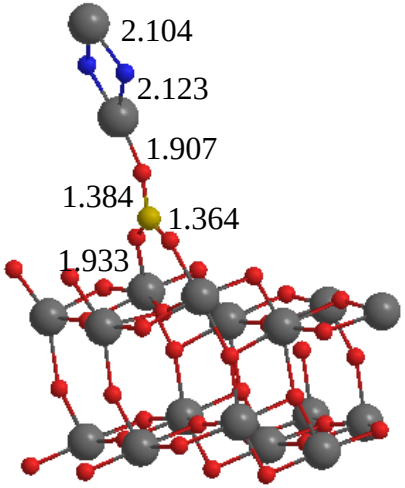
E_{ad}= 56.9 kcal/mol

(29.2 for -OP(O)O-)



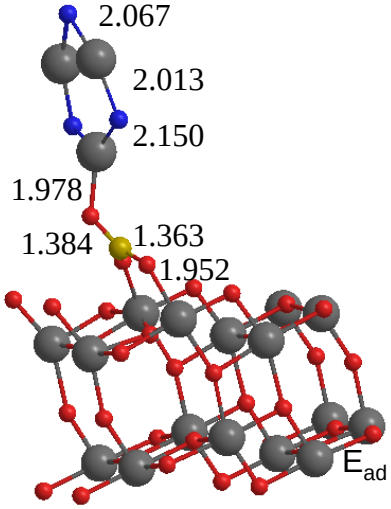
E_{ad} of InN= 69.2 kcal/mol

(52.4)



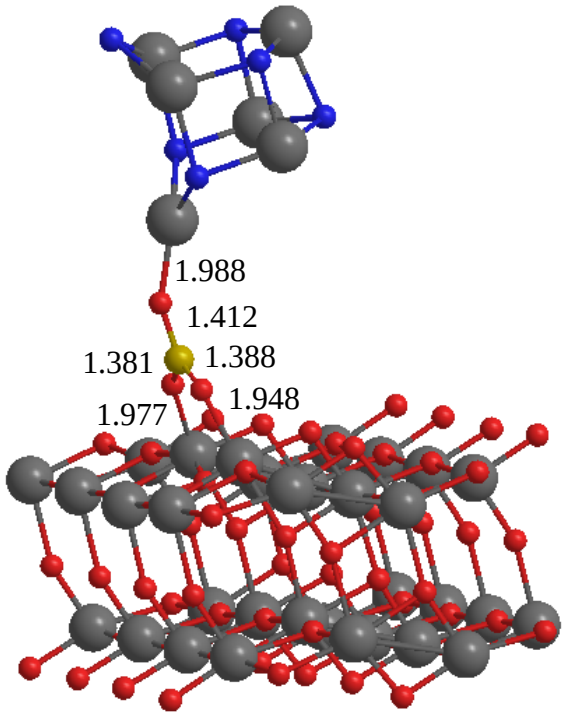
E_{ad} of InN= 72.8 kcal/mol

(56.2)



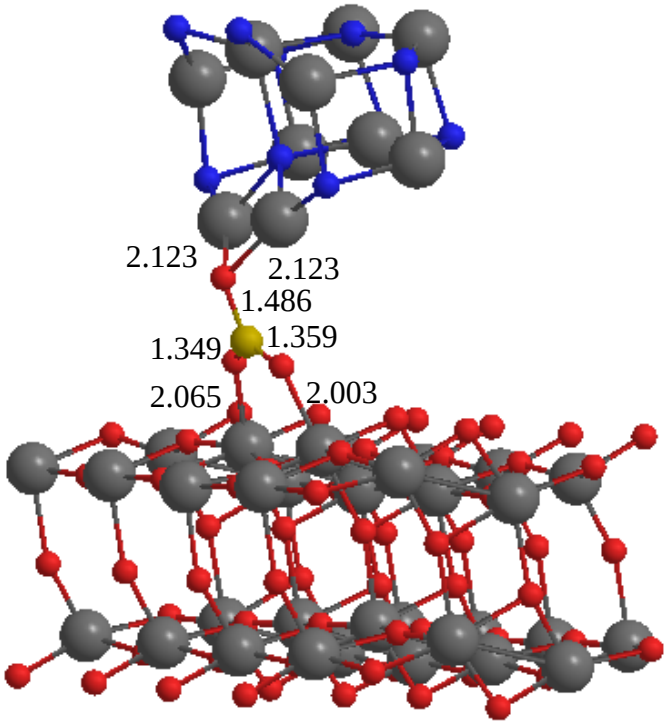
E_{ad} of InN= 79.9 kcal/mol

(64.9)



E_{ad} of InN= 97.2 kcal/mol

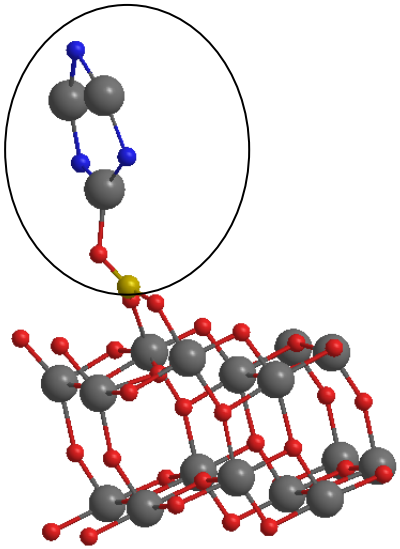
(92.1)



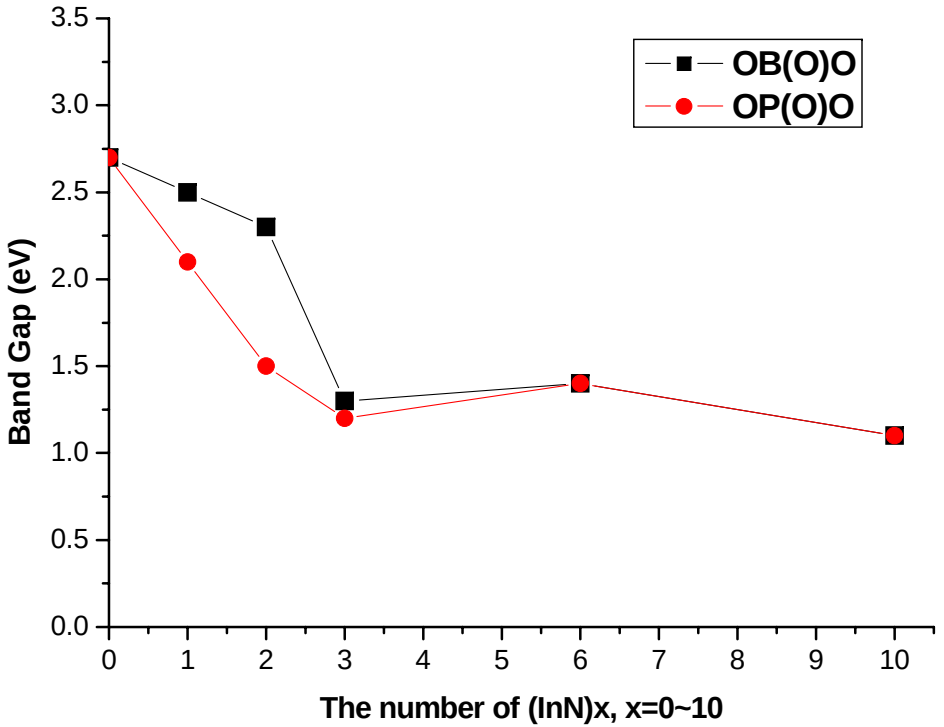
E_{ad} of InN= 104.1 kcal/mol

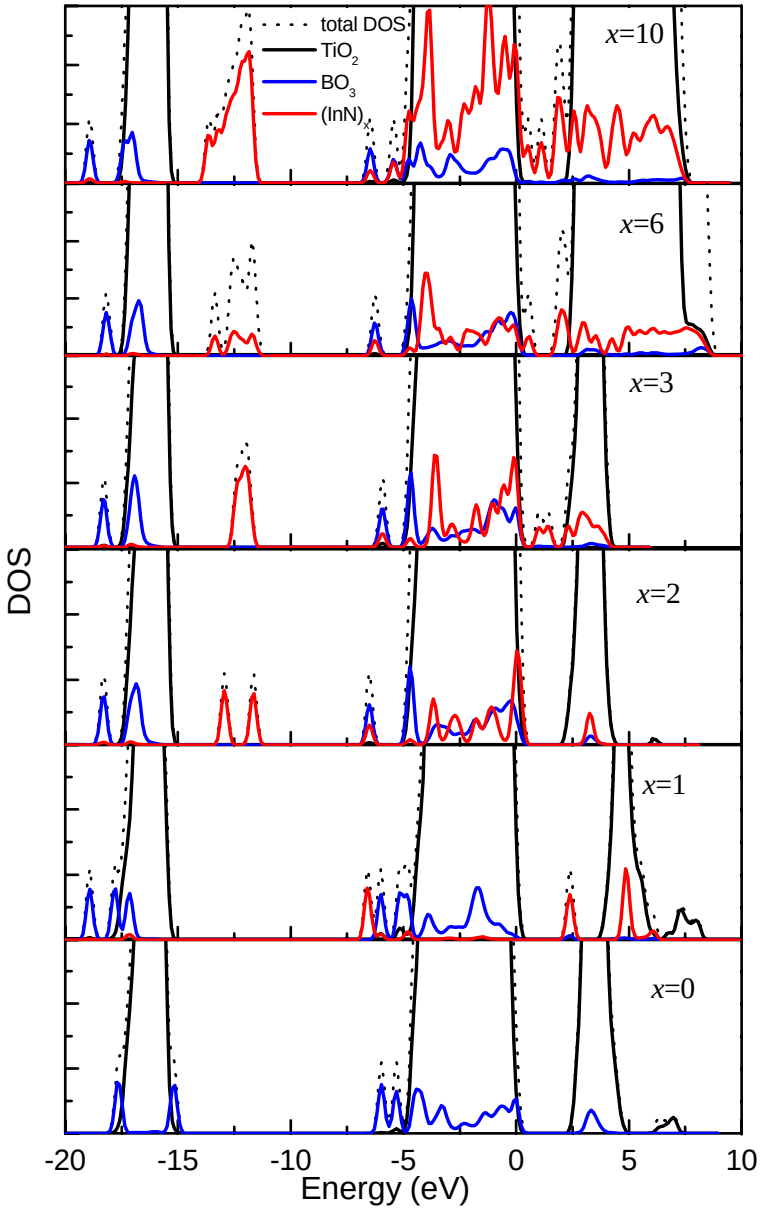
(96.9)

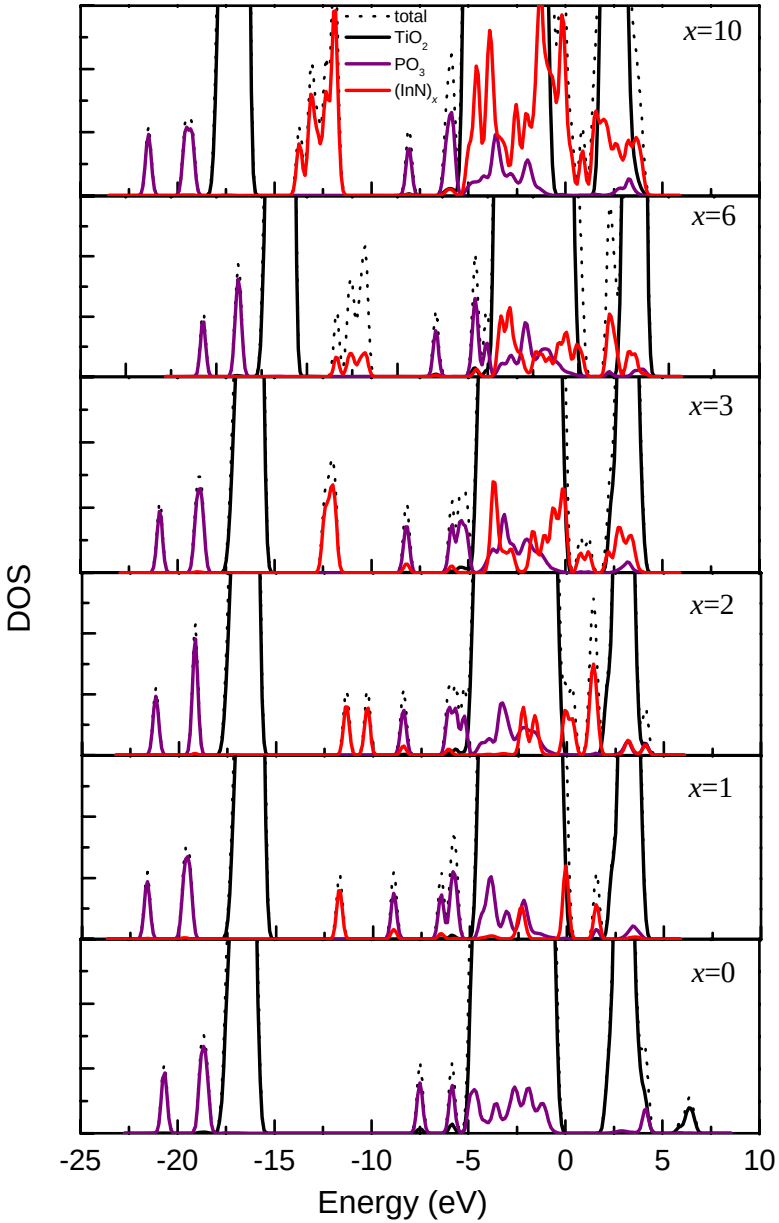
$(InN)_x$, x=0~10



$(InN)_x$-O*Y*(O)O-anatase TiO_2,
Y=B, P







• The presence of the –OB(O)O– density of state localizes slightly above the upper edge of the valence band.

Table for Bader Charge Analyses for (InN)x-OY(O)O-TiO_2 anatase surface, Y=B, P

x	Ti	OB(O)O	(InN)x	Ti	OP(O)O	(InN)x
	2.46, 2.46			2.46, 2.46		
0	2.47, 2.53	-0.49		2.52, 2.52	-0.69	
1	2.52, 2.52	-2.08	1.3	2.49, 2.49	-1.09	0.96
2	2.52, 2.52	-1.97	2.13	2.50, 2.50	-1.06	1.61
3	2.52, 2.52	-1.84	1.07	2.50, 2.50	-1.02	0.79
6	2.52, 2.52	-1.99	2.00	2.50, 2.50	-1.07	1.09
10	2.52, 2.52	-2.56	2.41	2.49, 2.49	-0.97	1.05

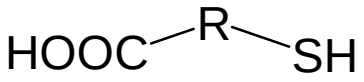
Conclusions:

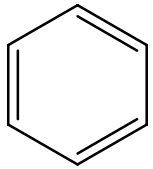
By analyzing the density of states (DOS), the presence of the –OB(O)O– density of state localizes slightly above the upper edge of the valence band, while the –OP(O)O– density of state localizes below the upper edge of the valence band.

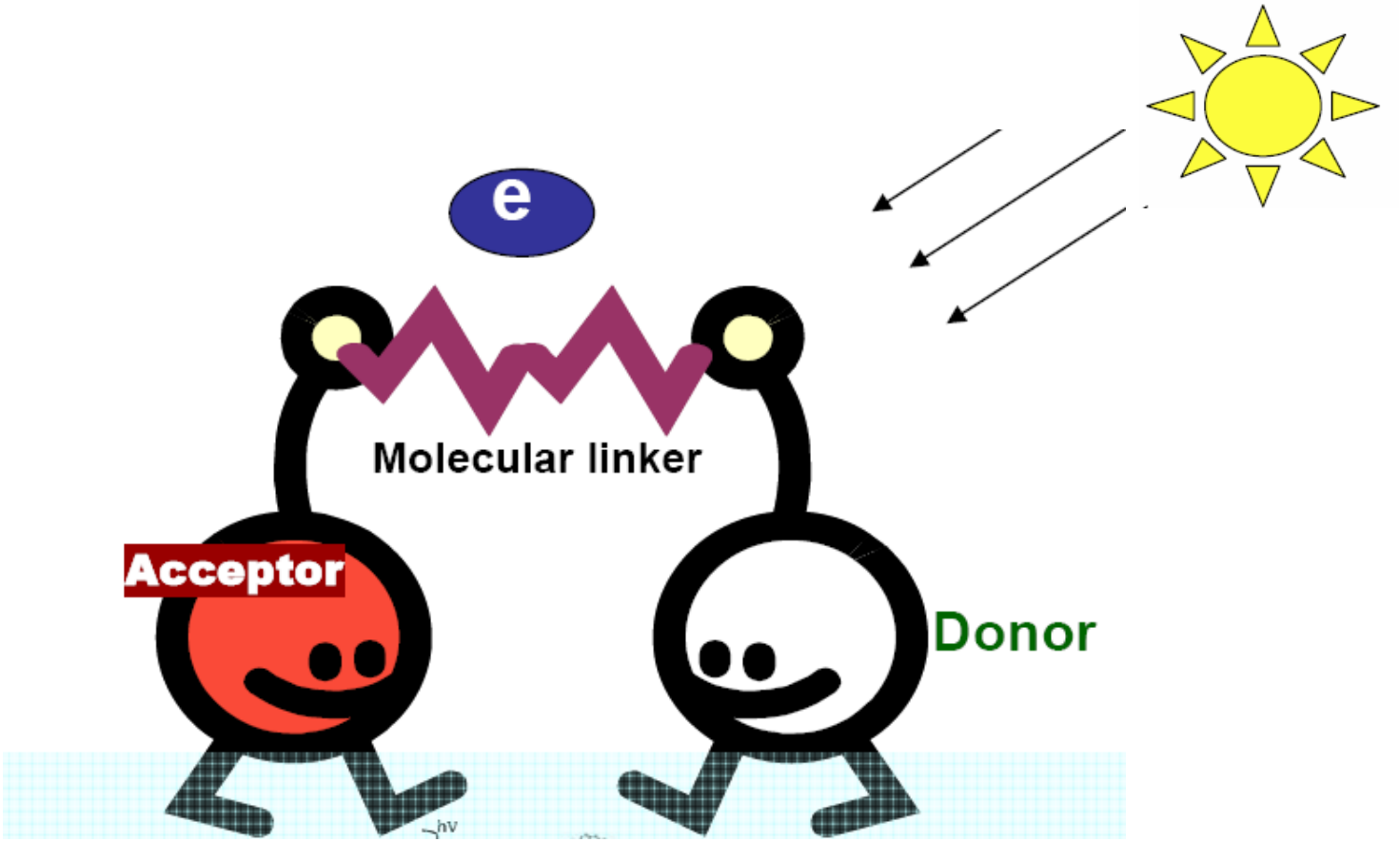
We also found that the overlap of the $(InN)_x$ states and the –OB(O)O– states in the valence band, which facilitating the electron transfer between InN and TiO_2 surface, is more significant than that of the $(InN)_x$ states and the –OY(O)O– states.

The Bader charge analyses show that the more electron density (1.5~2.0 *e*) is transferred from InN to the –OB(O)O– linker, but less (~0.4 *e*) is transferred to the –OP(O)O– linker.

The other idea linker molecules:



R=  , CH_2, $(CH_2)_x$

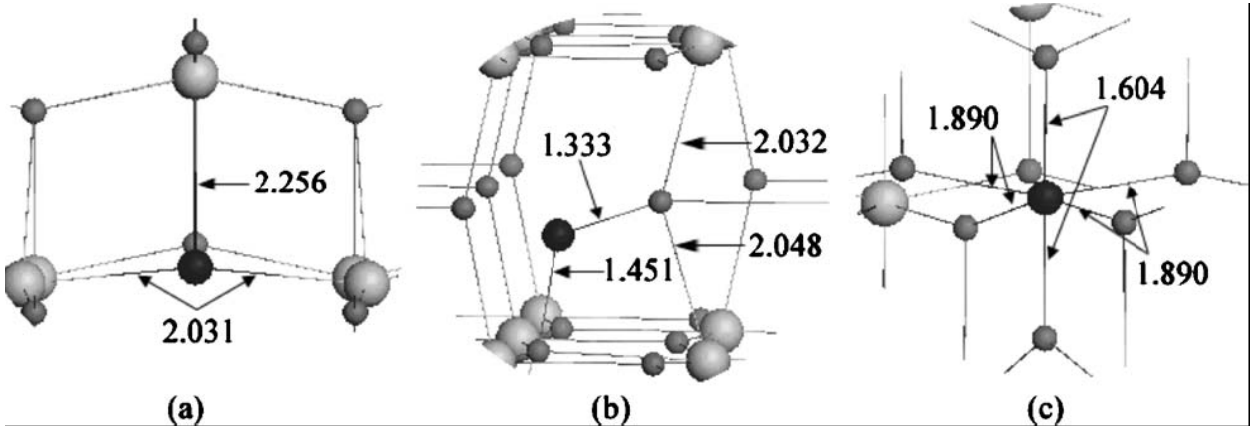


The other idea on doped TiO_2

1. Nonmetal-doped TiO_2, substituting oxygen with B, N, P, S or F to enhance its photocatalytic activity.

Application to InN-linkers-nonmetal-doped TiO_2.

Physical Review B, **2007**, 195201 and *JPCC*, **2007**, on website.



substitutional B atom to O | interstitial B in TiO_2 cell | substitutional B atom to Ti

2. Metal-doped TiO_2, substituting Ti with Cr, Fe, V….

Acknowledgement:

Thank the Institute of Nuclear Energy Research (INER) for the founding of this project (962001 INER 0028)

Co-worker:
C.Y. Chang, W. F. Hunag, P. Raghunath and M. C. Lin

~节能减碳~

~Thank you for your attention~