Production of Hydrogen Using Titania Based Photocatalysts

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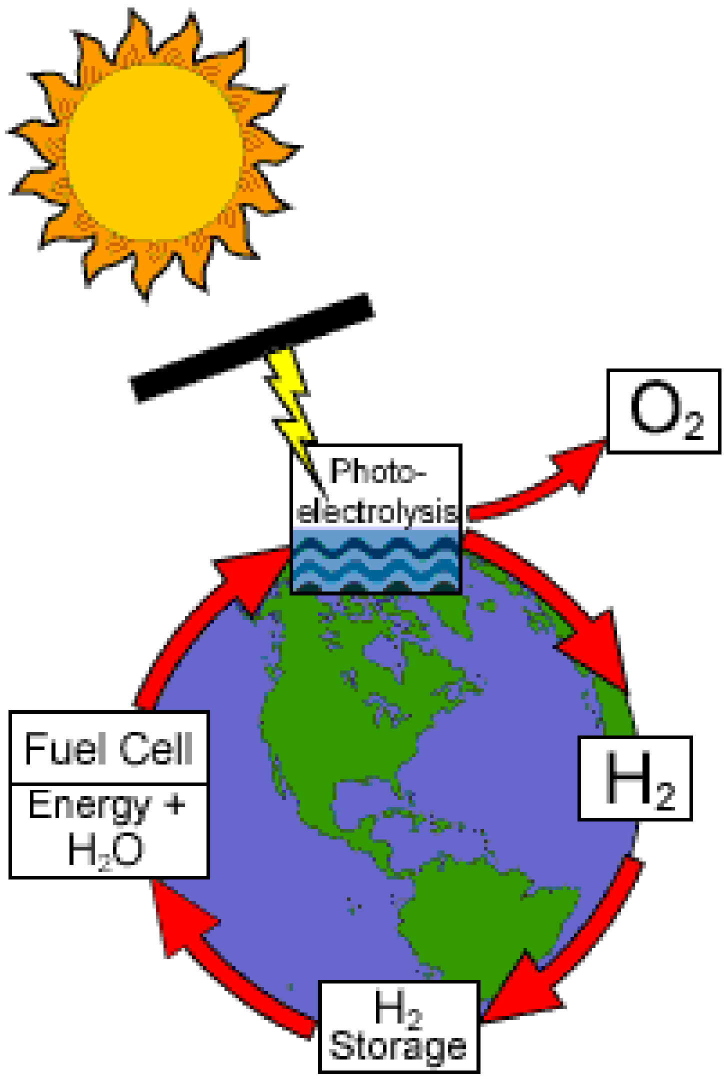
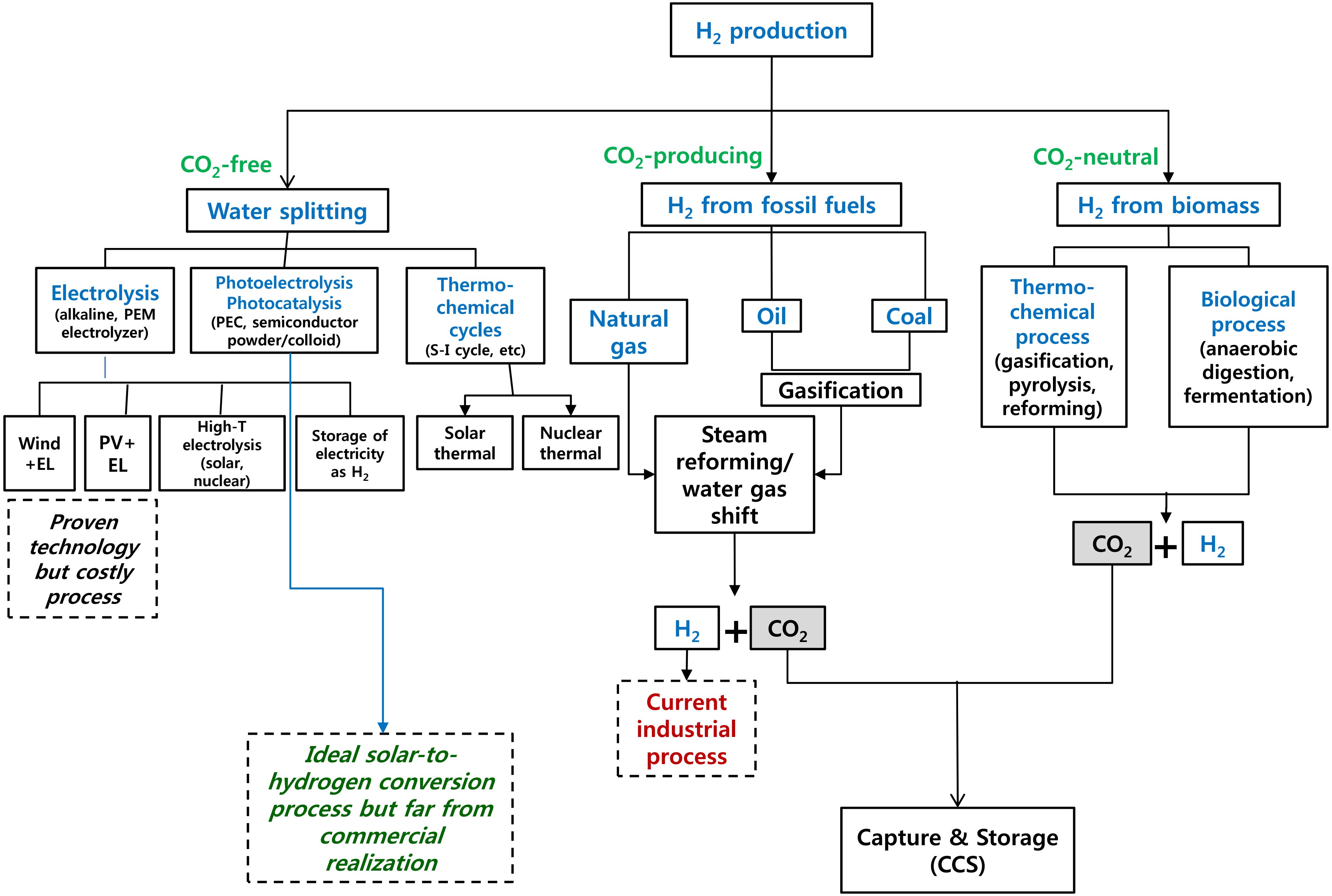
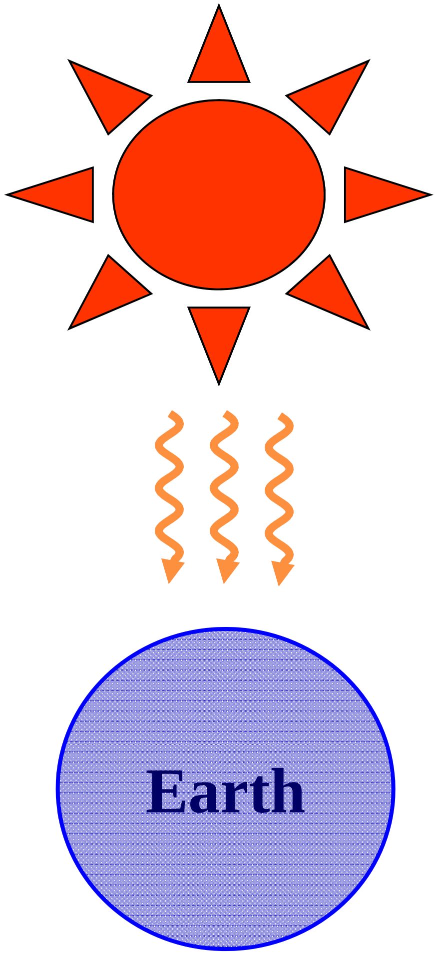
Solar Energy Based Hydrogen Economy





H_2 production
CO_2-free
CO_2-producing
CO_2-neutral
Water splitting
H_2 from fossil fuels
H_2 from biomass
Electrolysis (alkaline, PEM electrolyzer)
Photoelectrolysis Photocatalysis (PEC, semiconductor powder/colloid)
Thermo-chemical cycles (S-I cycle, etc)
Natural gas
Oil
Coal
Gasification
Thermo-chemical process (gasification, pyrolysis, reforming)
Biological process (anaerobic digestion, fermentation)
Wind +EL
PV+ EL
High-T electrolysis (solar, nuclear)
Storage of electricity as H_2
Solar thermal
Nuclear thermal
Steam reforming/ water gas shift
Proven technology but costly process
H_2 + CO_2
CO_2 + H_2
Current industrial process
Ideal solar-to-hydrogen conversion process but far from commercial realization
Capture & Storage (CCS)

Solar Energy



Global need
13 TW

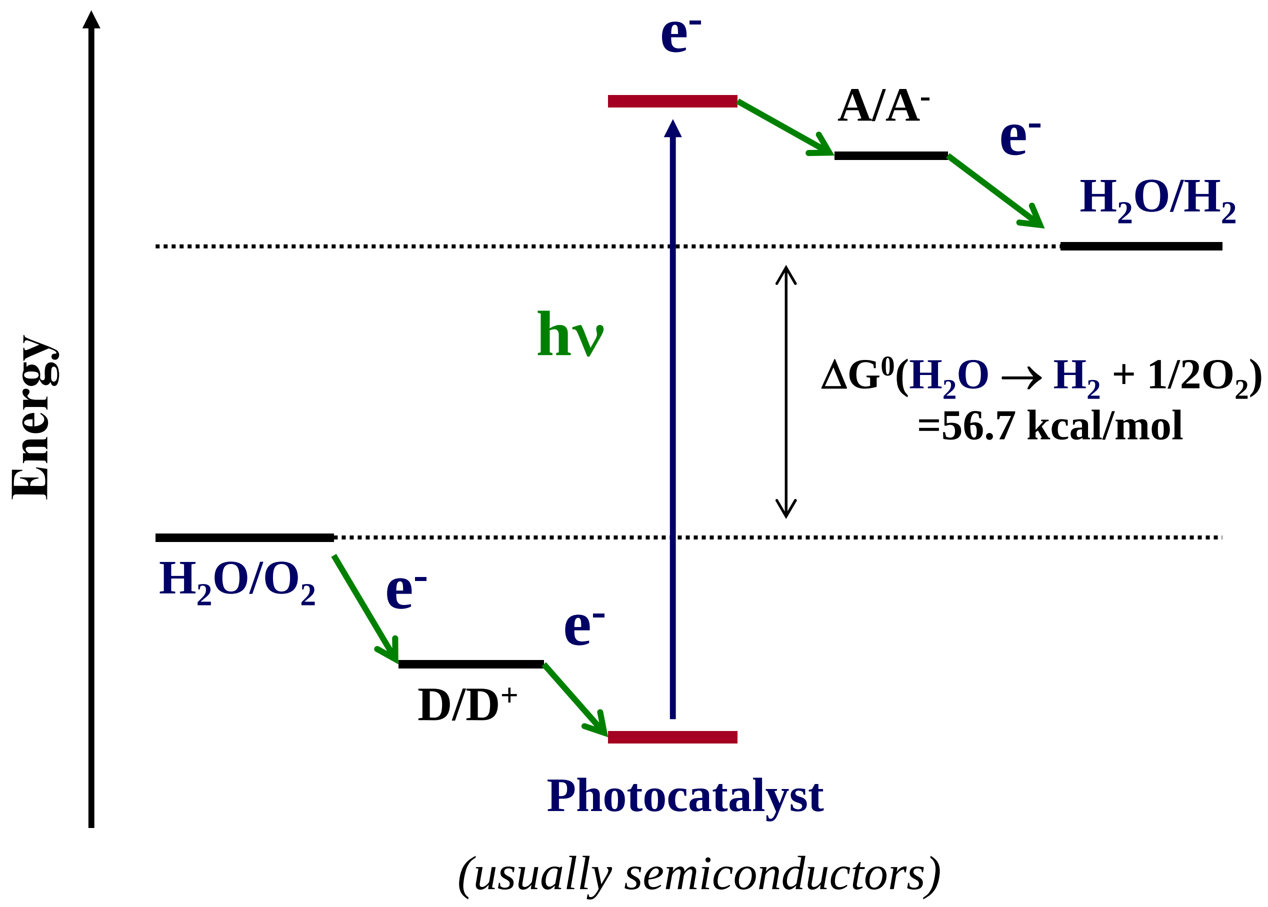
Solar Energy
1.2×10^5 TW

(10,000 x Current world demands)

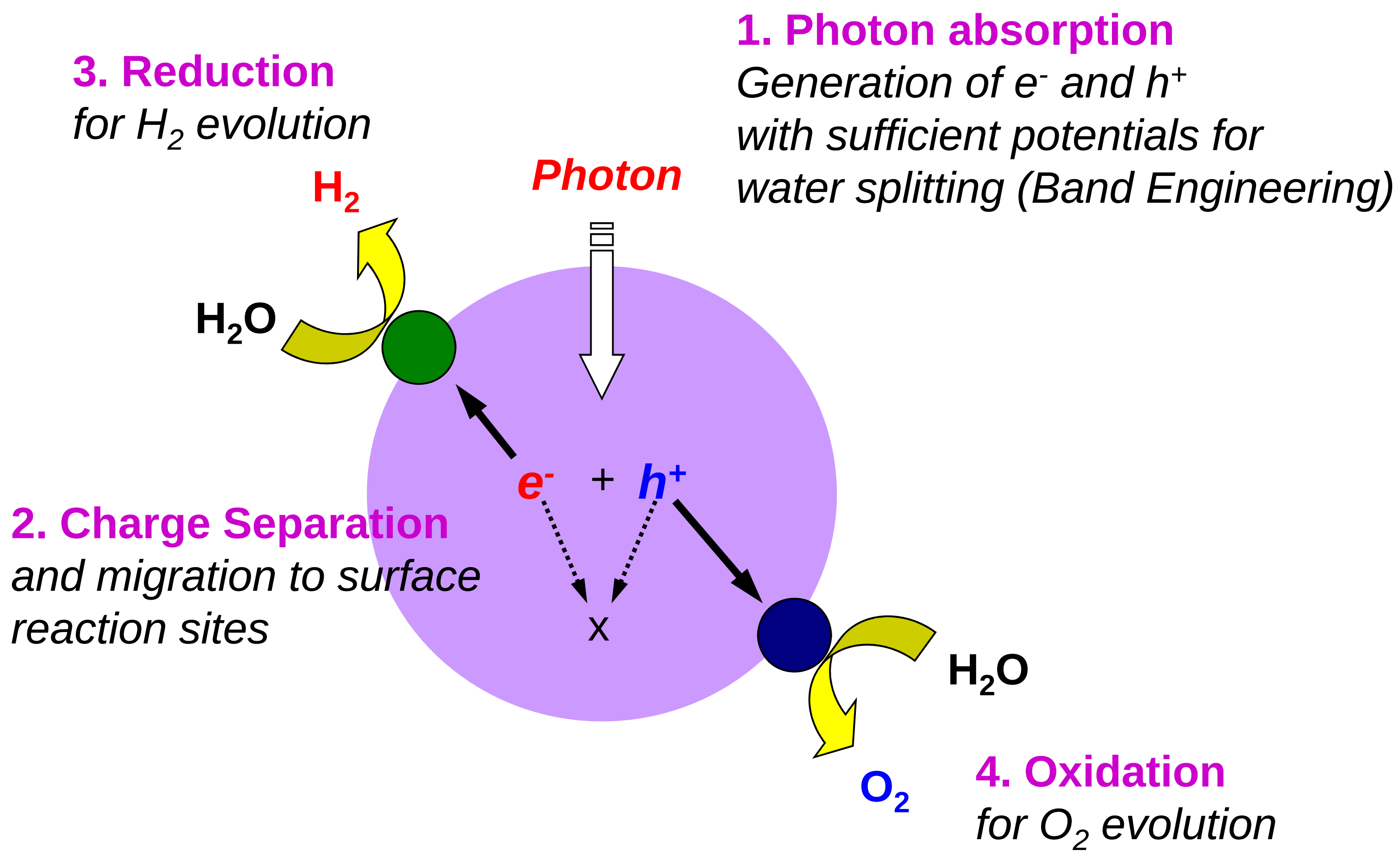
- *Abundant*
- ***Environment-friendly** energy source*
- *Safe and Clean*

~ 0.1% of the Earth's surface
(5 times as big as South Korea)
+
~ 10% conversion efficiency

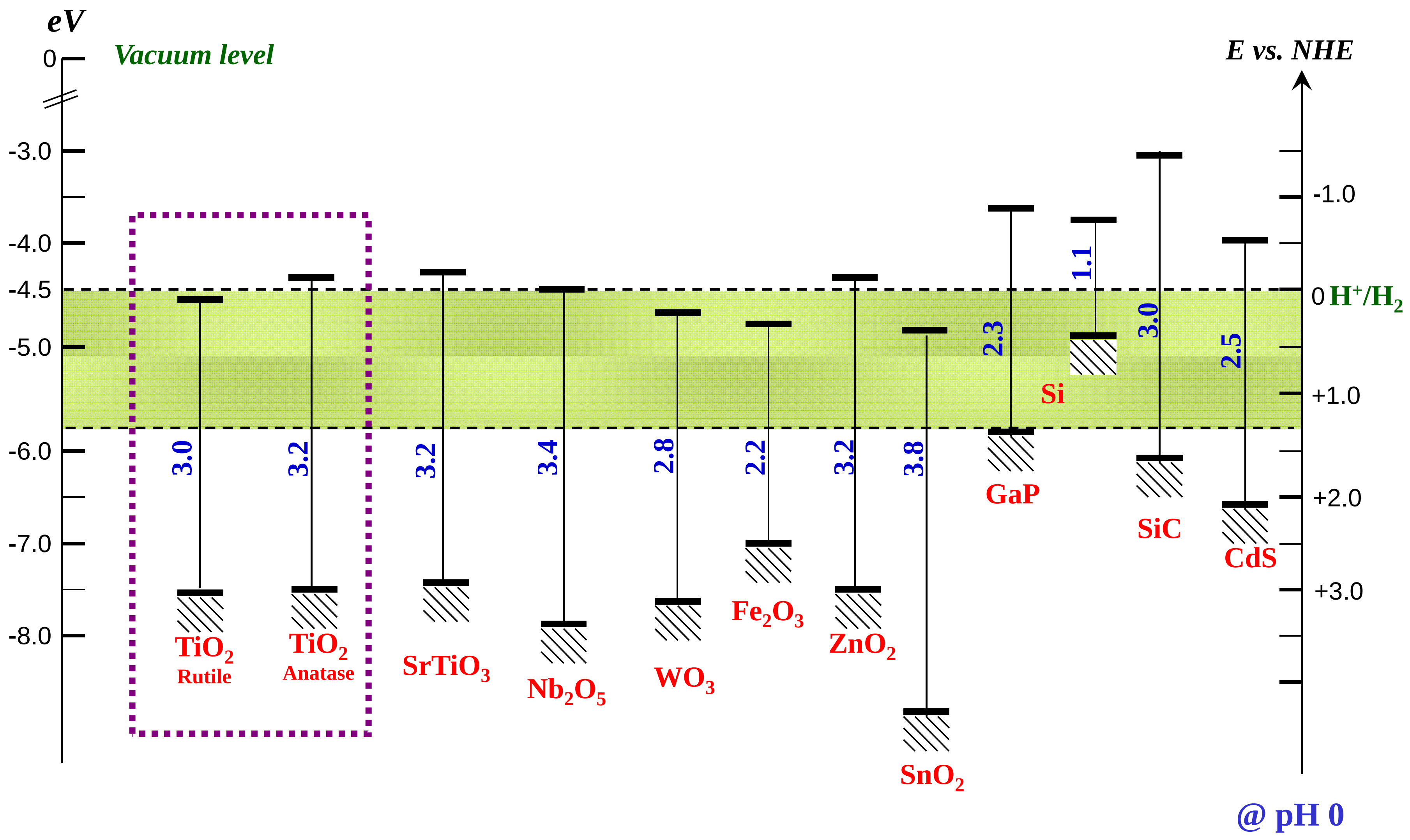
Photocatalysis as a mean of solar energy conversion



Water Splitting
on a Photocatalyst Particle



Band Gap Positions in Various Semiconductors



Common Strategies for Developing Visible Light Photocatalysts

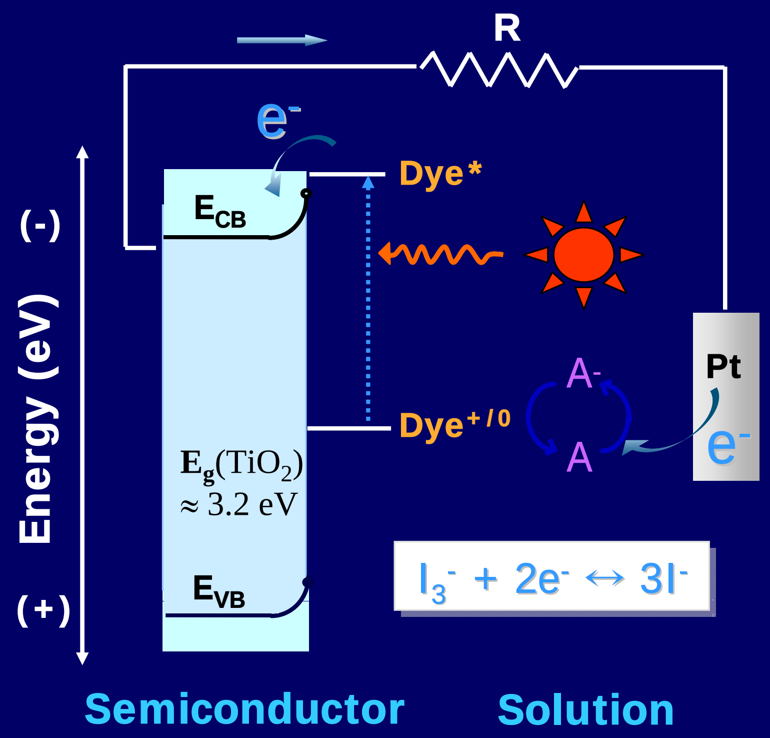
1. **Impurity Doping in Wide Band-gap Oxide Semiconductors**
   - transition metal ions (cations)
   - nitrogen, carbon (anions)

2. **Sensitization of Wide Band-gap Oxide Semiconductors**
   - organometallic complexes (*e.g.,* ruthenium bipyridyl derivatives)
   - organic dyes
   - inorganic quantum dots (*e.g.,* CdS)

3. **Nanohybrid Systems**
   (metal oxides & chalcogenides, metal nanoparticles, organic & inorganic sensitizers, polymers, etc.)

Dye-Sensitized TiO_2 Solar Cell

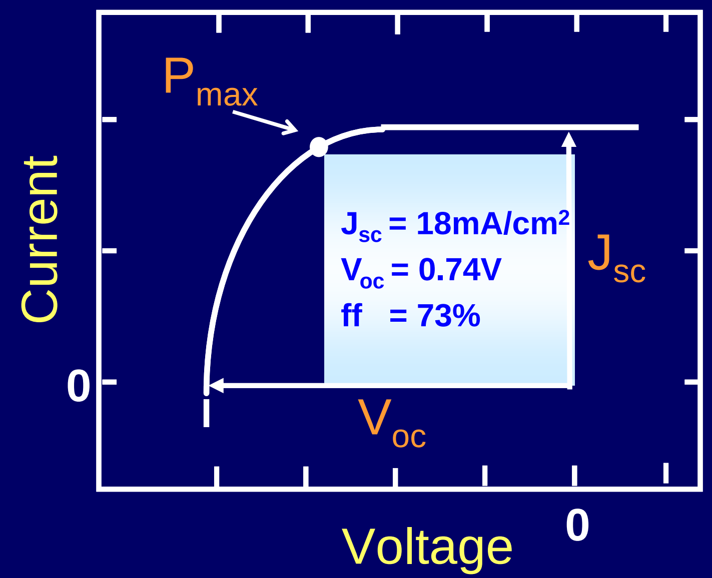
Schematics of DSSC



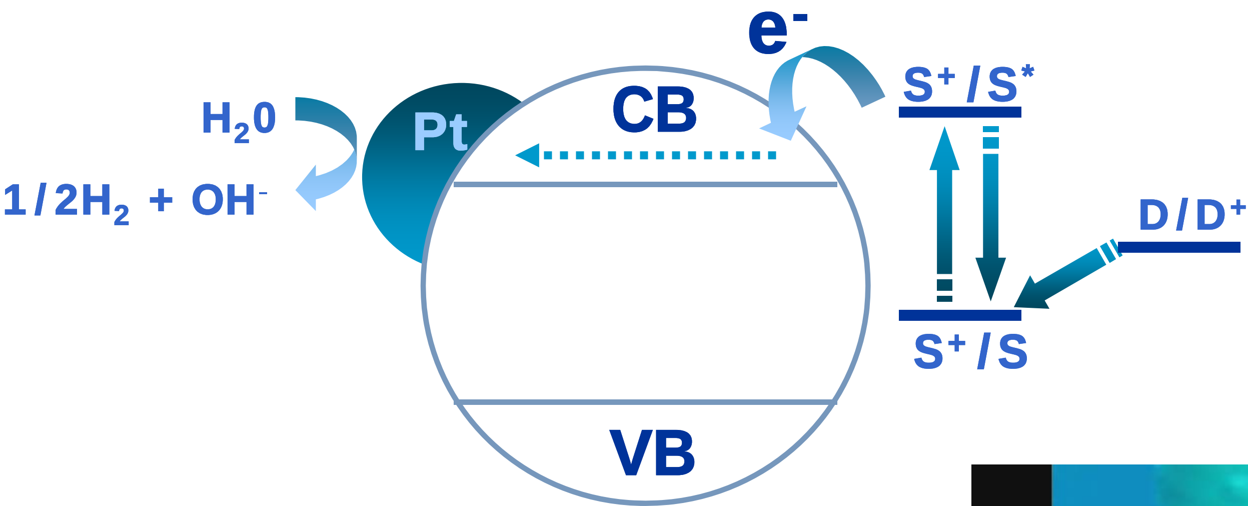
Performance of DSSC

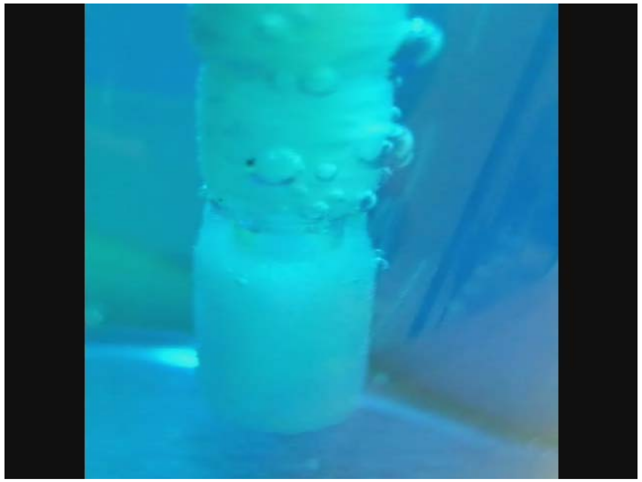
J_{sc} : short circuit current
V_{oc}: open circuit voltage
ff : fill factor

$$ff = \frac{\quad}{J_{sc} \times V_{oc}}$$



H_2 Production on Dye-Sensitized TiO_2





$2H^+ + 2e^- \longrightarrow H_2$ (E_0 = -0.41 V) (1)

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (E_0 = +0.82 V) (2)

$H_2O \longrightarrow H_2 + 1/2O_2$ (ΔG = 1.23 V) (3)

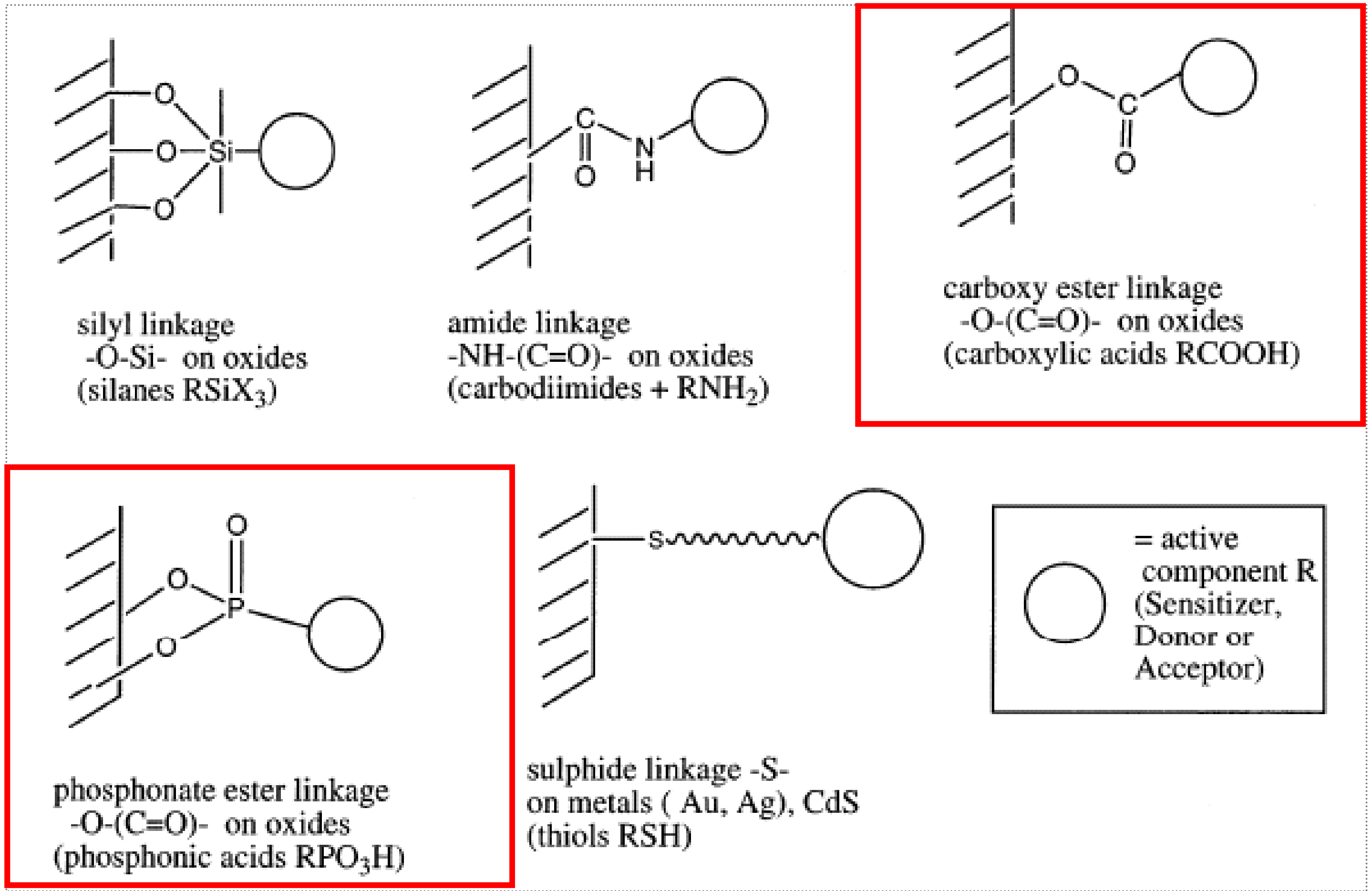
Hydrogen Production with Dye-Sensitized TiO_2

Controlling/Modifying Interfacial Properties :

- Sensitizer anchoring mode
- Ion-exchange resin coating
- Barrier layer coating
- Hybridization with carbon nanotubes

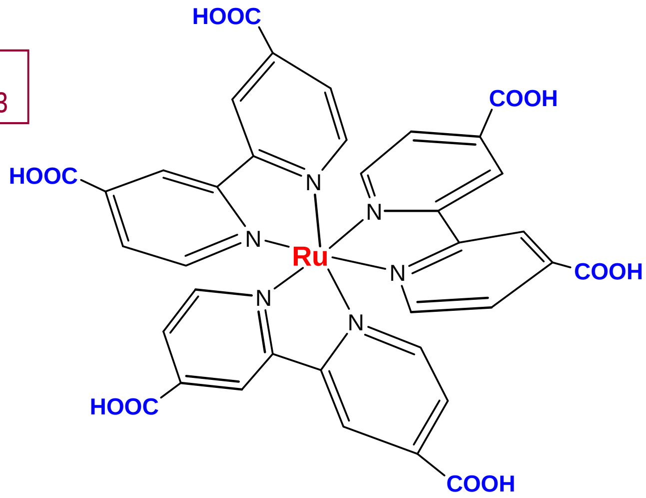
- Non-Ruthenium Dye sensitized systems

Anchoring Group



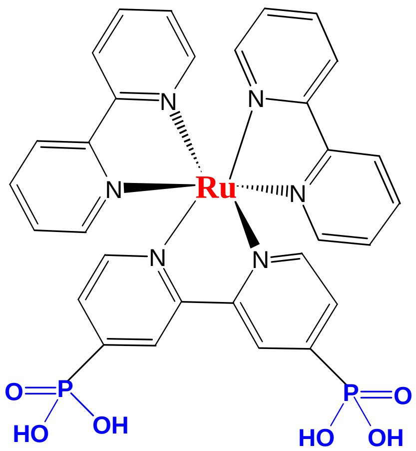
Different ways of anchoring molecules on surfaces

$c\text{-}Ru^{III}L_3$

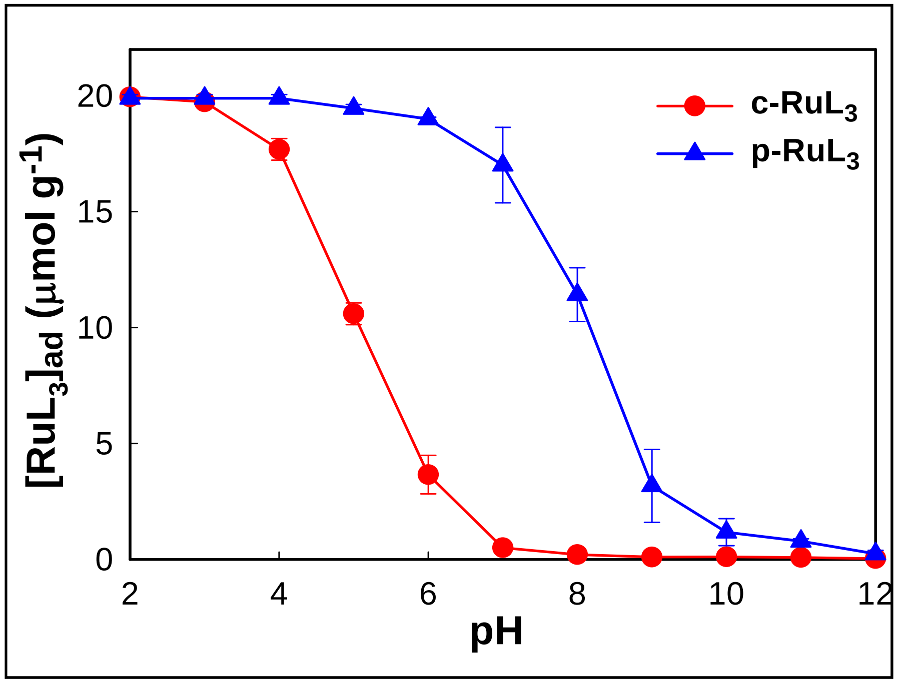


Tris(4,4'-dicarboxy-2,2'-bipyridyl) Ruthenium(II)

$p\text{-}Ru^{III}L_3$



(Bpy)$_2$(4,4'-bis(phosphonato)-2,2'-bipyridyl) Ruthenium(II)



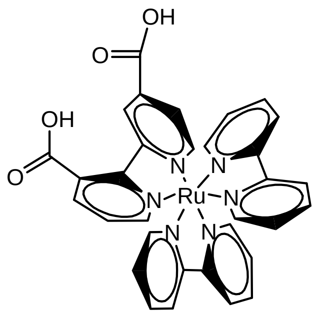
pH-dependent adsorption of the Ru-sensitizer on TiO_2

($[TiO_2]$ = 0.5 g/L, $[RuL_3]$ = 10 μM)

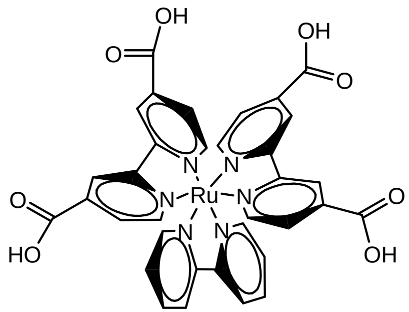
Bae *et al., J. Phys. Chem. B* **2004**, *108, 14903*

Anchoring Groups in Ru-Sensitizers

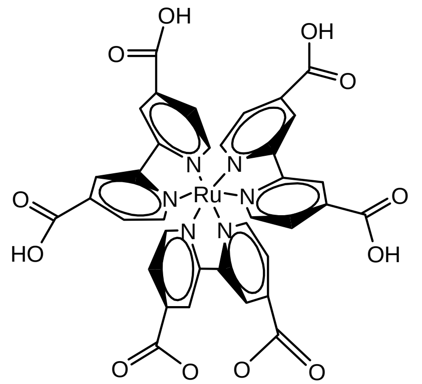
Carboxyl



C2

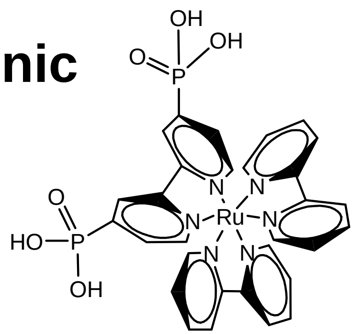


C4

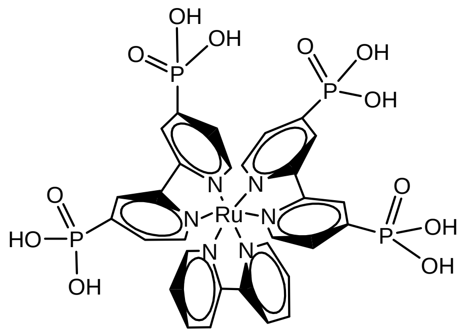


C6

Phosphonic



P2



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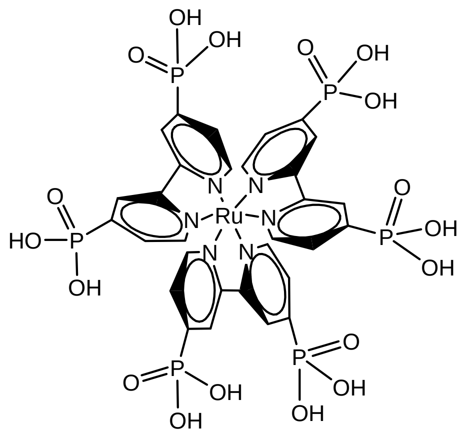
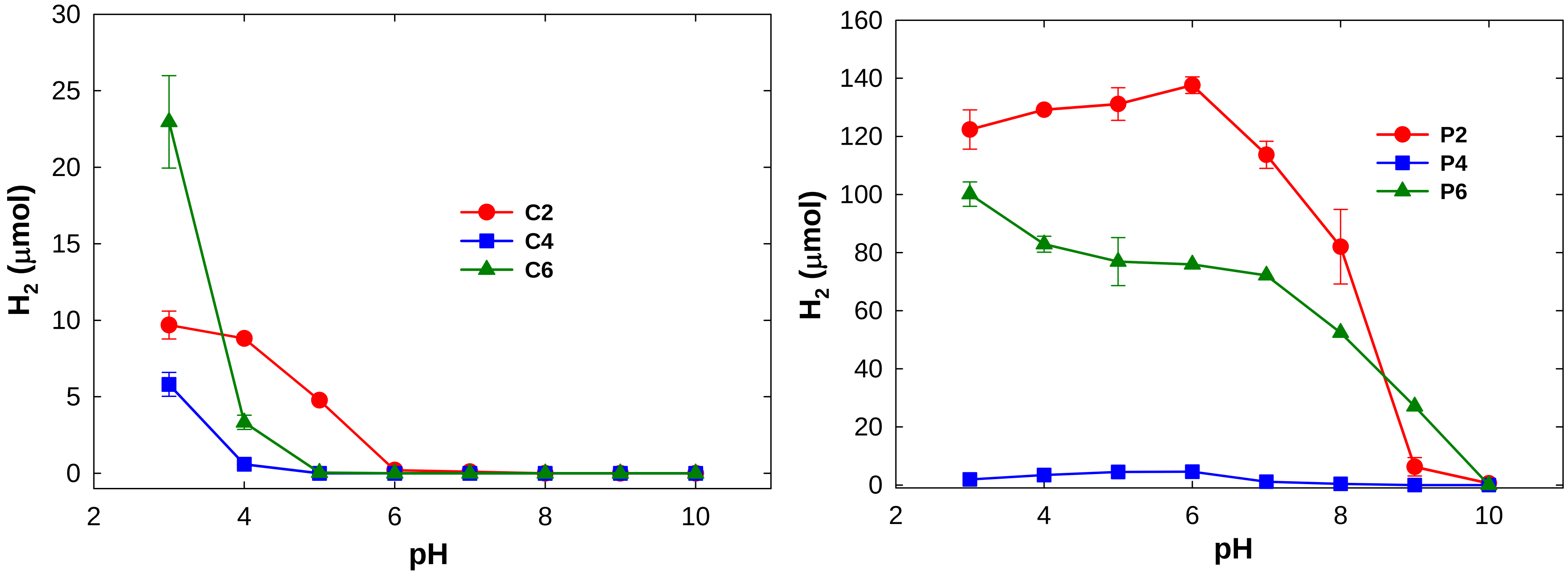


P6

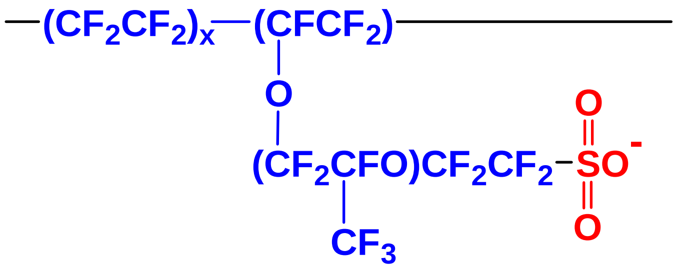
Anchoring Group Effect: pH-dependent Hydrogen Production on $Ru^{II}/Pt-TiO_2$ under Visible-light Illumination



$[Pt/TiO_2]$ = 0.5 g/L; $[RuL_x]_i$ = 10 μM; [EDTA] = 10 mM; λ > 420 nm

(Bae and Choi, *J. Phys. Chem. B* **2006**, *110*, 14792)

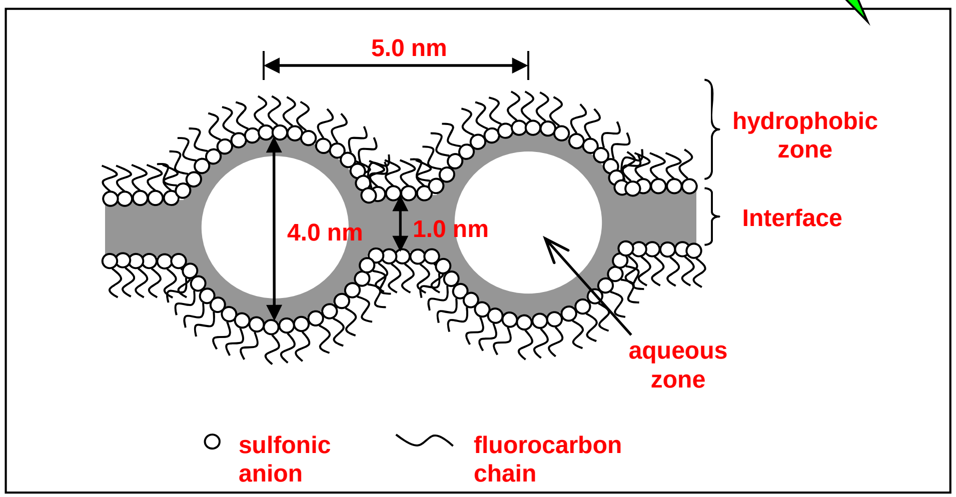
TiO_2 Surface Modification with Nafion

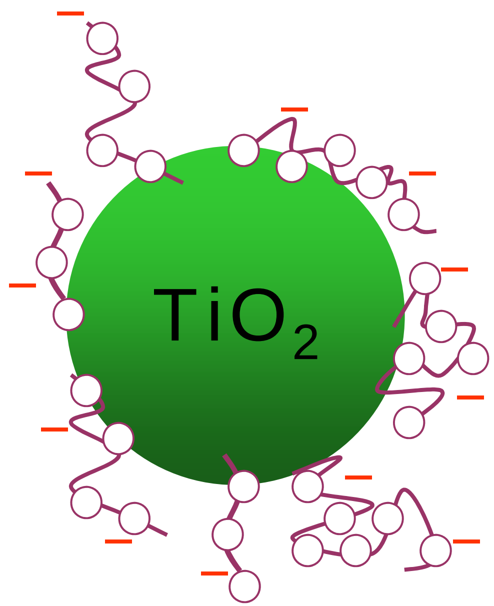


Monomer unit of nafion

Cation-exchanger

Stable against photocatalytic oxidation

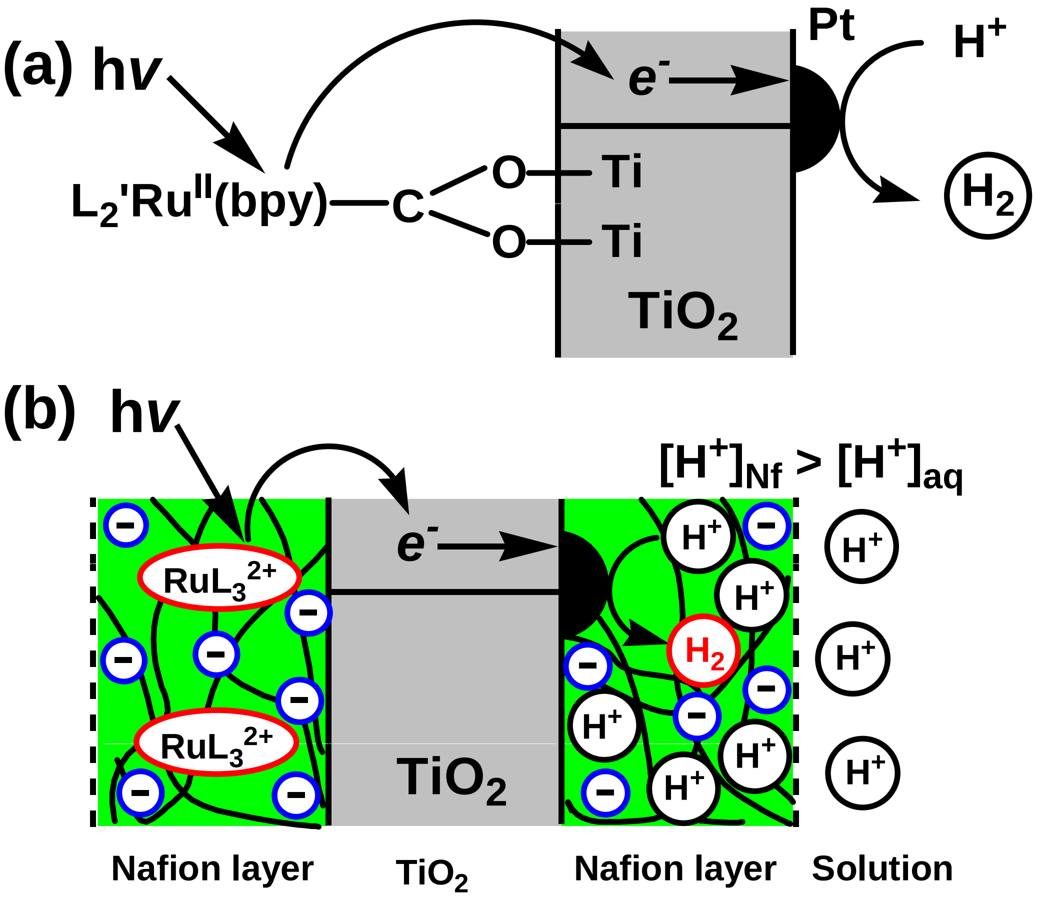


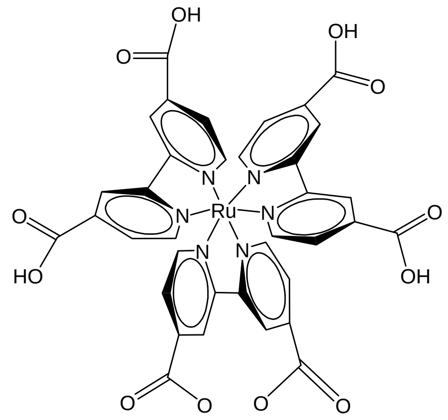


Nafion-Coated TiO_2 Particle

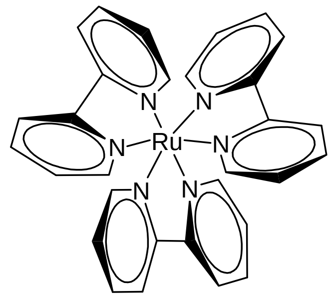
(H. Park and W. Choi, *J. Phys. Chem. B* **2005**, *109*, 11667)

$Ru(dcbpy)_3$-TiO_2 vs. $Ru(bpy)_3^{2+}$/Nafion/TiO_2



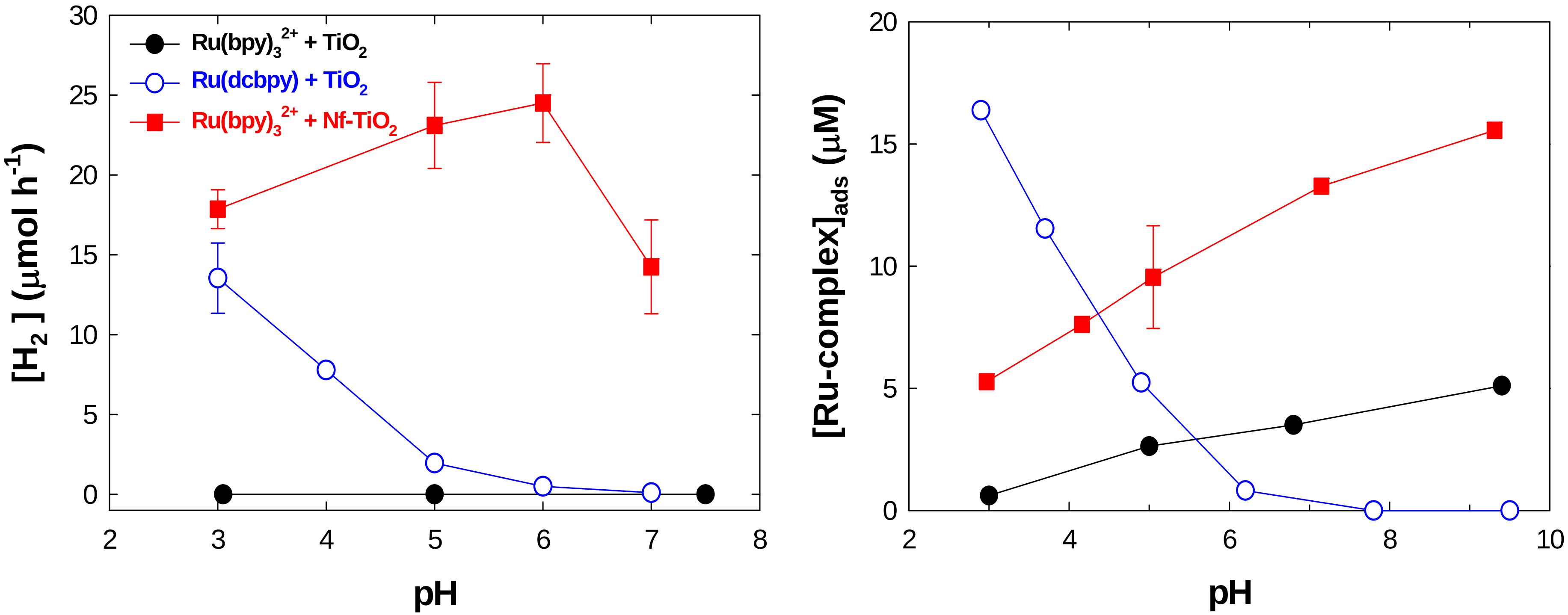


$Ru^{II}(dcbpy)_3$



$Ru^{II}(bpy)_3^{2+}$

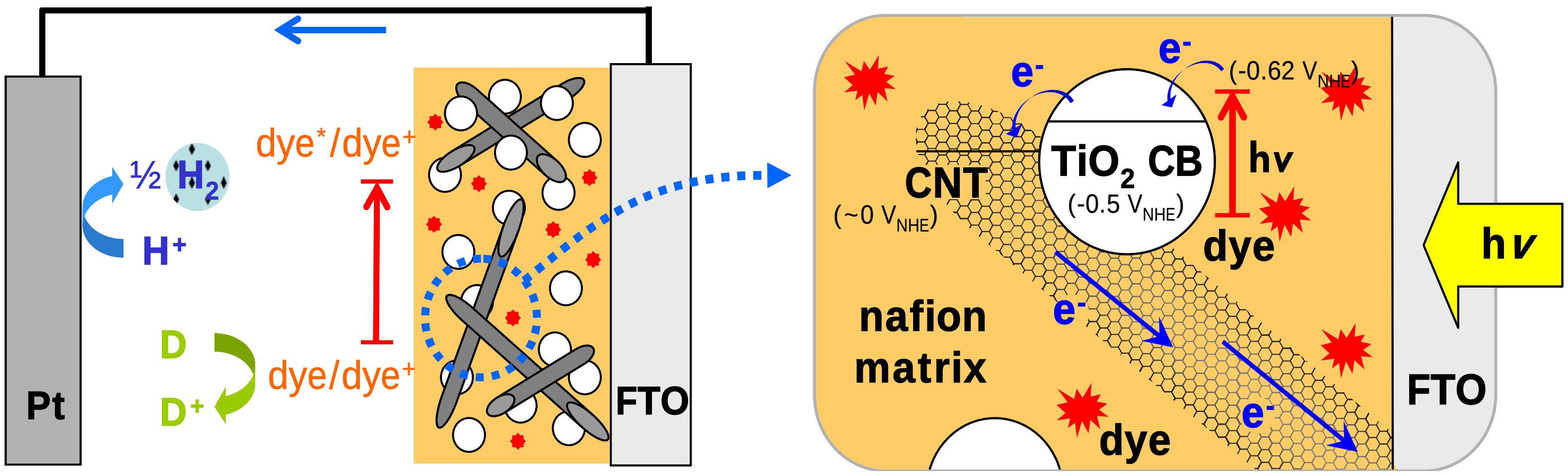
Photo-sensitized H_2 Production in two anchoring systems



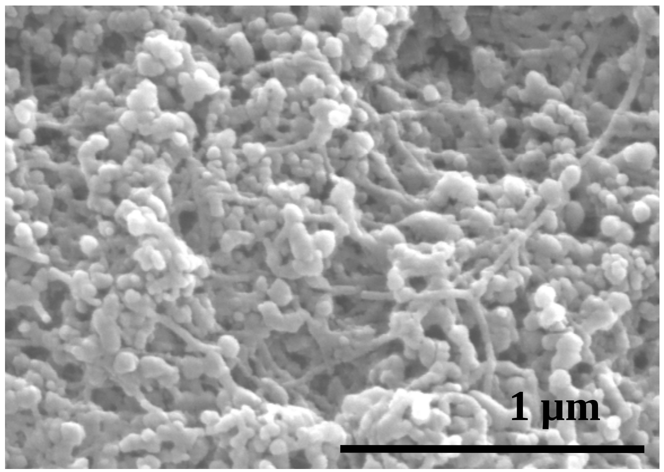
(H. Park and W. Choi, *Langmuir* **2006**, *22*, 2906)

Photoelectrochemical Hydrogen Production

Carbon Nanotube Assisted Generation of Hydrogen in Dye-Sensitized Photoelectrochemical Cell under Visible Light

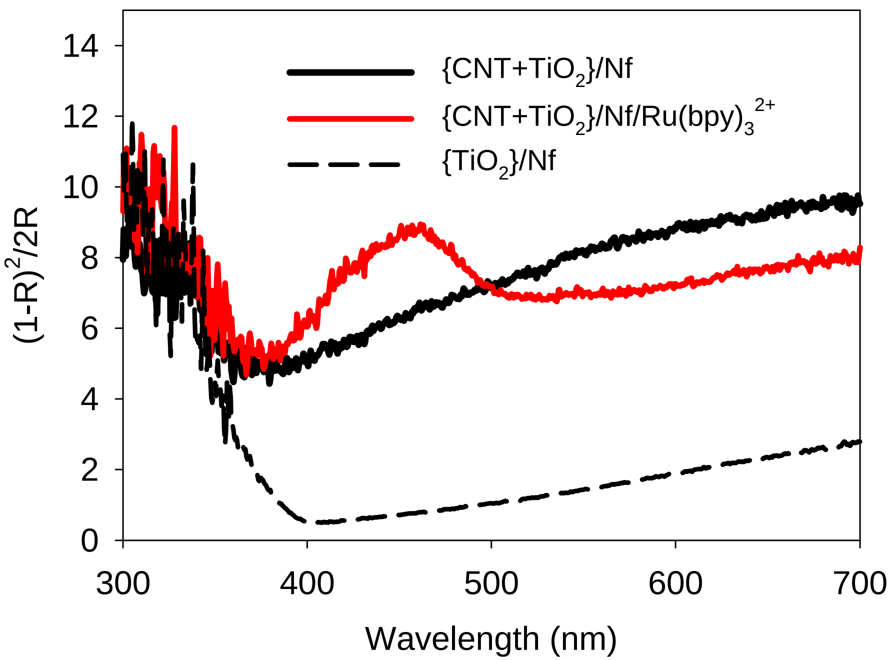


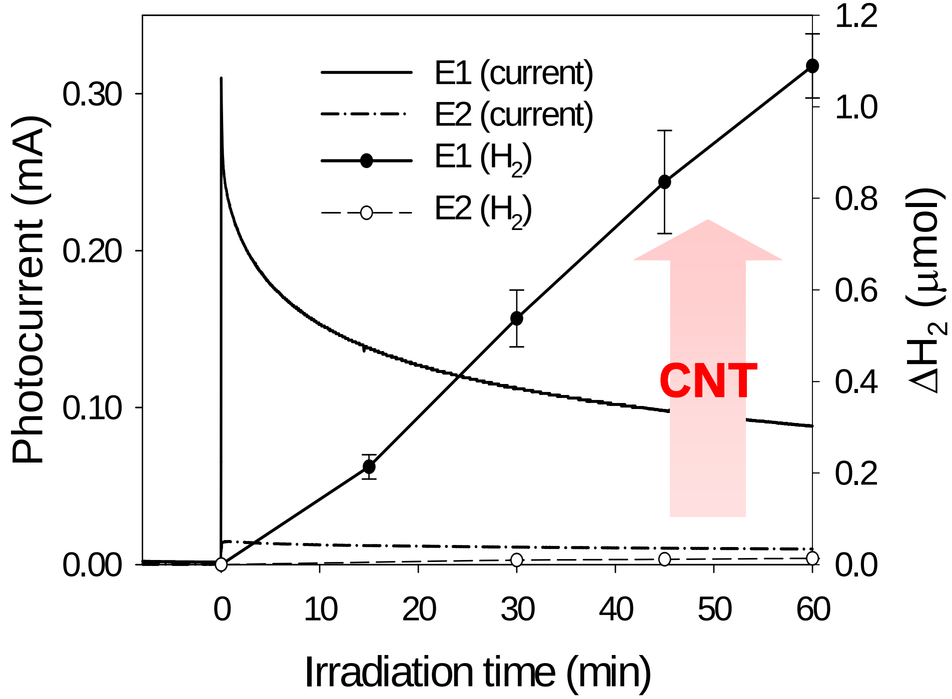
TiO$_2$/Nafion/CNT/Dye electrode



(J. Park and W. Choi, *J. Phys. Chem. C* **2009**, *113*, 20974)

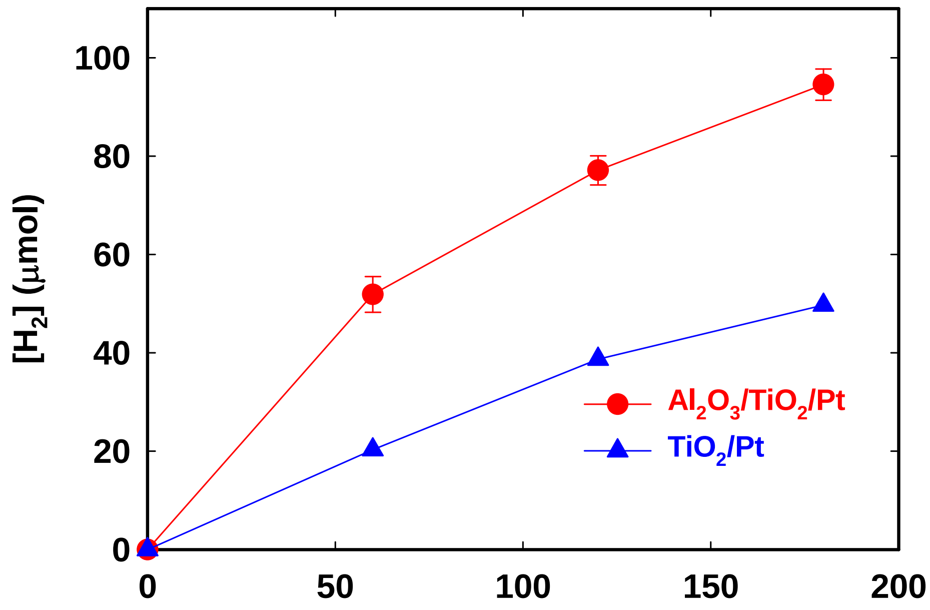
Photoelectrochemical Hydrogen Production

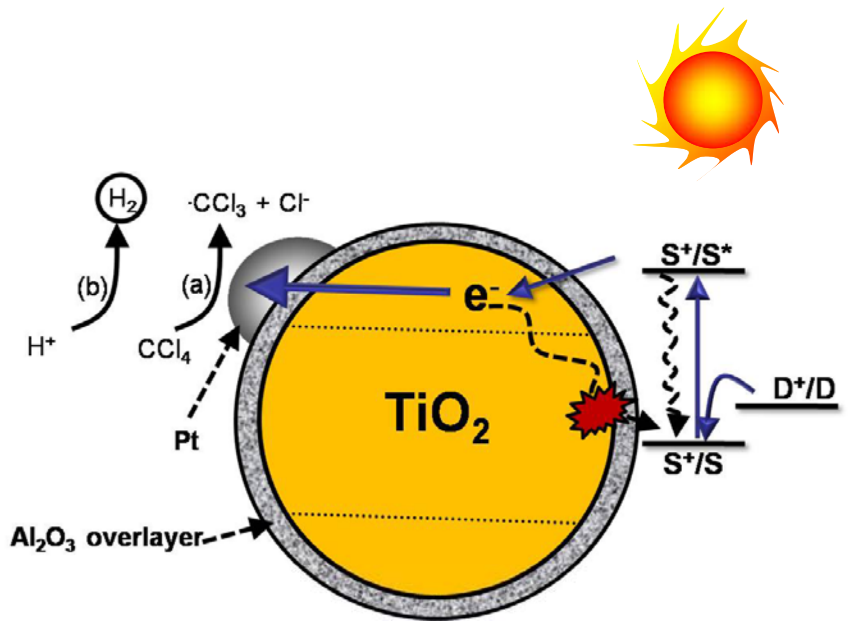


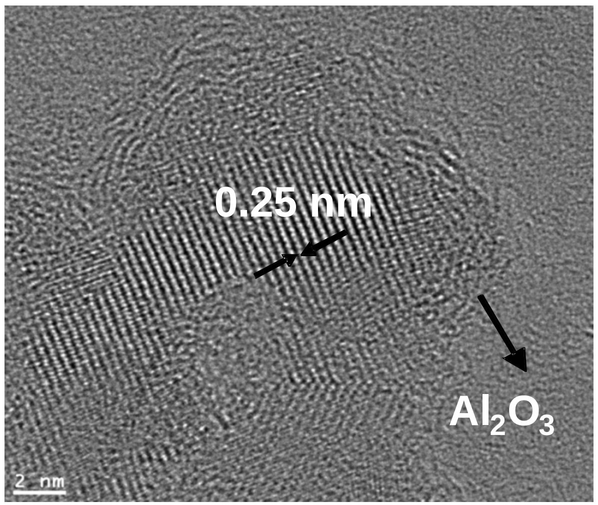


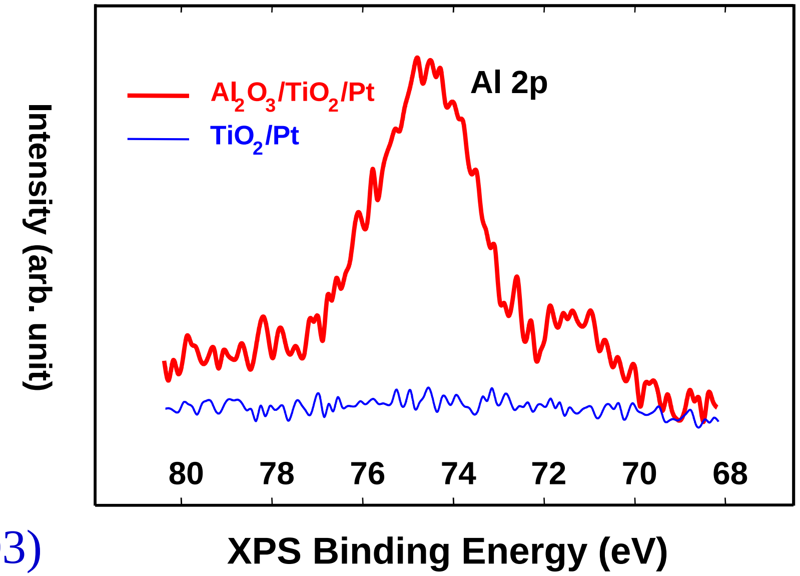
E1: TiO_2/Nf/RuL_3 with CNT
E2: without CNT

Dye-Sensitized TiO_2 with Thin Overcoat of Al_2O_3



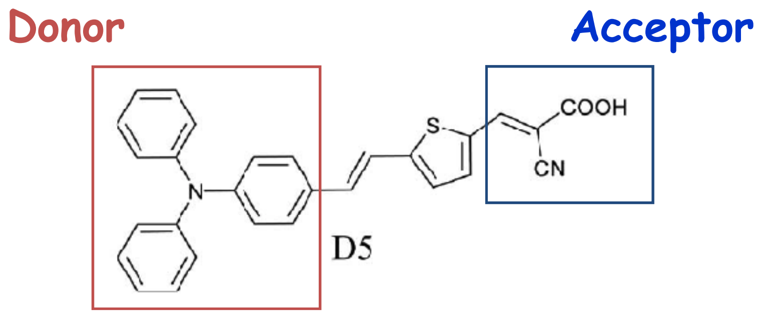




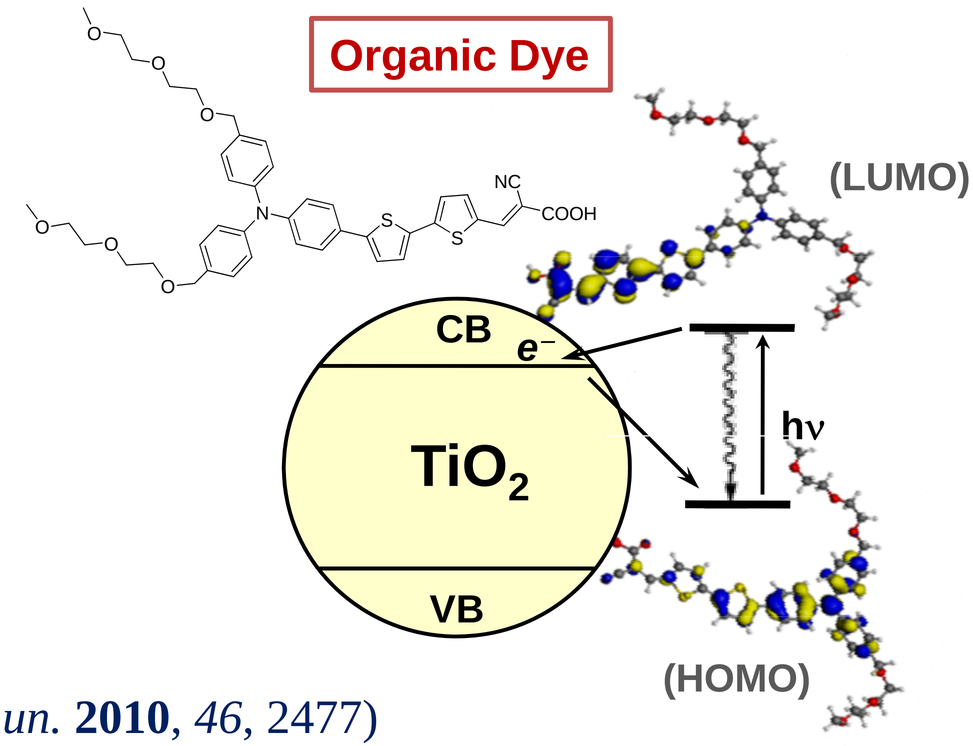


(W. Kim et al., *J. Phys. Chem. C* **2009**, *113*, 10603)

Organic Dye



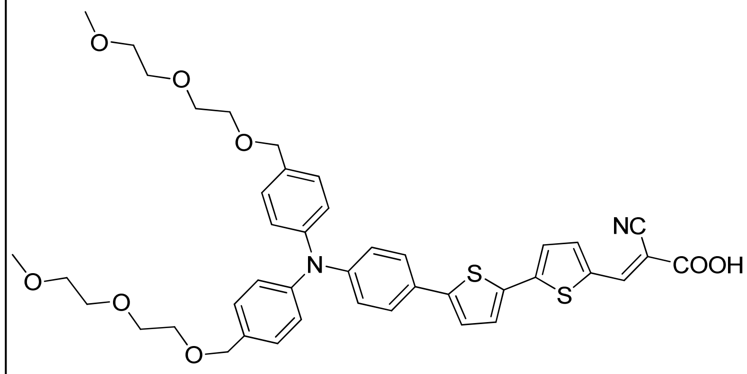
Strong Intra-molecular Charge Transfer



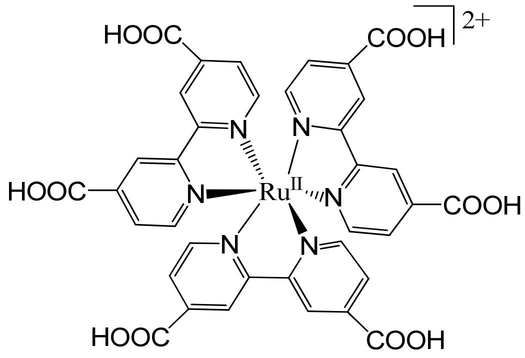
(Y. Park et al., *Chem. Commun.* **2010**, *46*, 2477)

Organic Dye vs. Ru-complex Dye

Organic-dye (OD)



Ru-dye (RuL_3)



Dye	λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	ΔE (V)	$E^0(dye/dye^{\cdot+})$ (V_{NHE})	$E^0(dye^*/dye^{\cdot+})$ (V_{NHE})
OD	445	24500	2.45	1.35	-1.0
RuL_3[c]	465	19500	2.20	1.39	-0.81

Metal-free organic dye sensitizers

Low-cost production

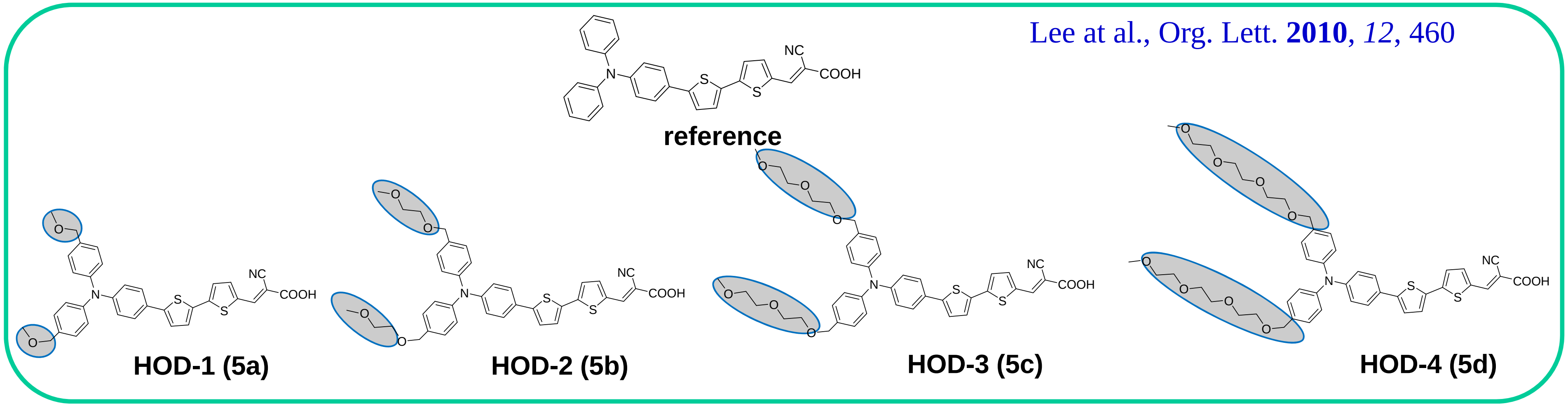
High visible light absorption

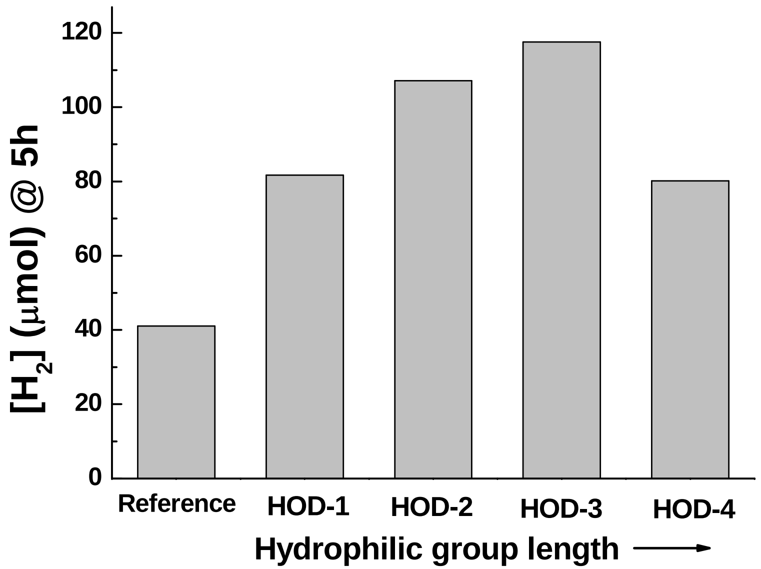
Facile molecular design

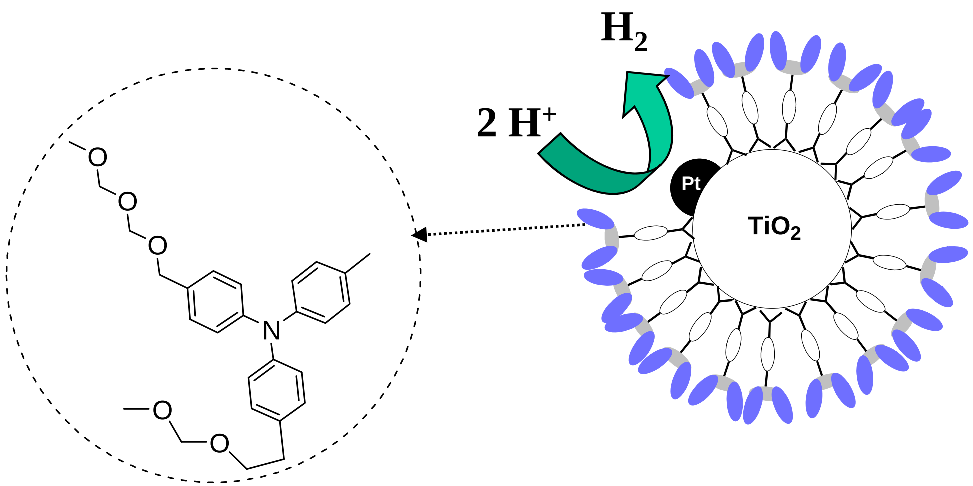
H_2 Production using a Dye Sensitized TiO_2 System

Hydrophilicity of Organic Dyes

Lee at al., Org. Lett. **2010**, *12*, 460





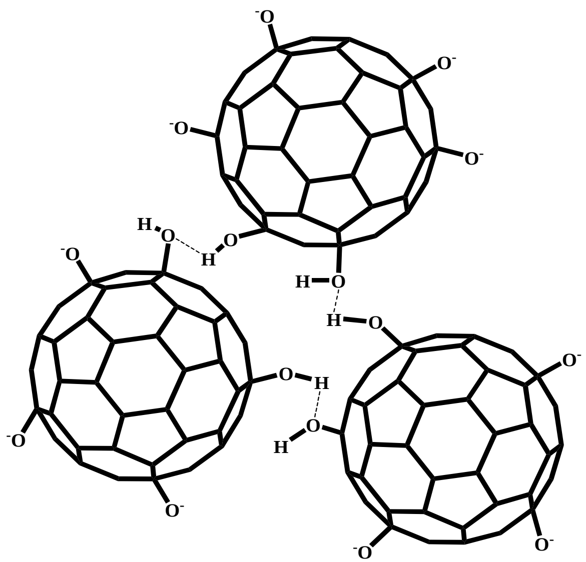


Enhanced proximity of proton source to the reduction center (Pt)

[Dye/Pt/TiO_2]= 10 μmol/g, [EDTA] = 10 mM, [Cat] =1g/L , pH_0=3, λ>420nm

Fullerol/TiO_2 Charge Transfer Mediated Visible Light Photocatalysis

Fullerol ($C_{60}(OH)_x$)

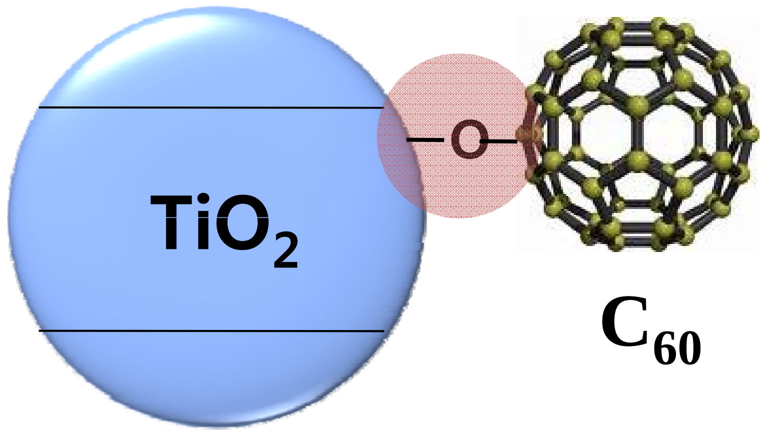


Water Soluble !

- Polyhydroxylate water-soluble form of the fullerene C_{60}

-$C_{60}(OH)_x(ONa)_y$ (x+y=24) y generally around 10-15

$C_{60}(OH)_x$ / TiO_2

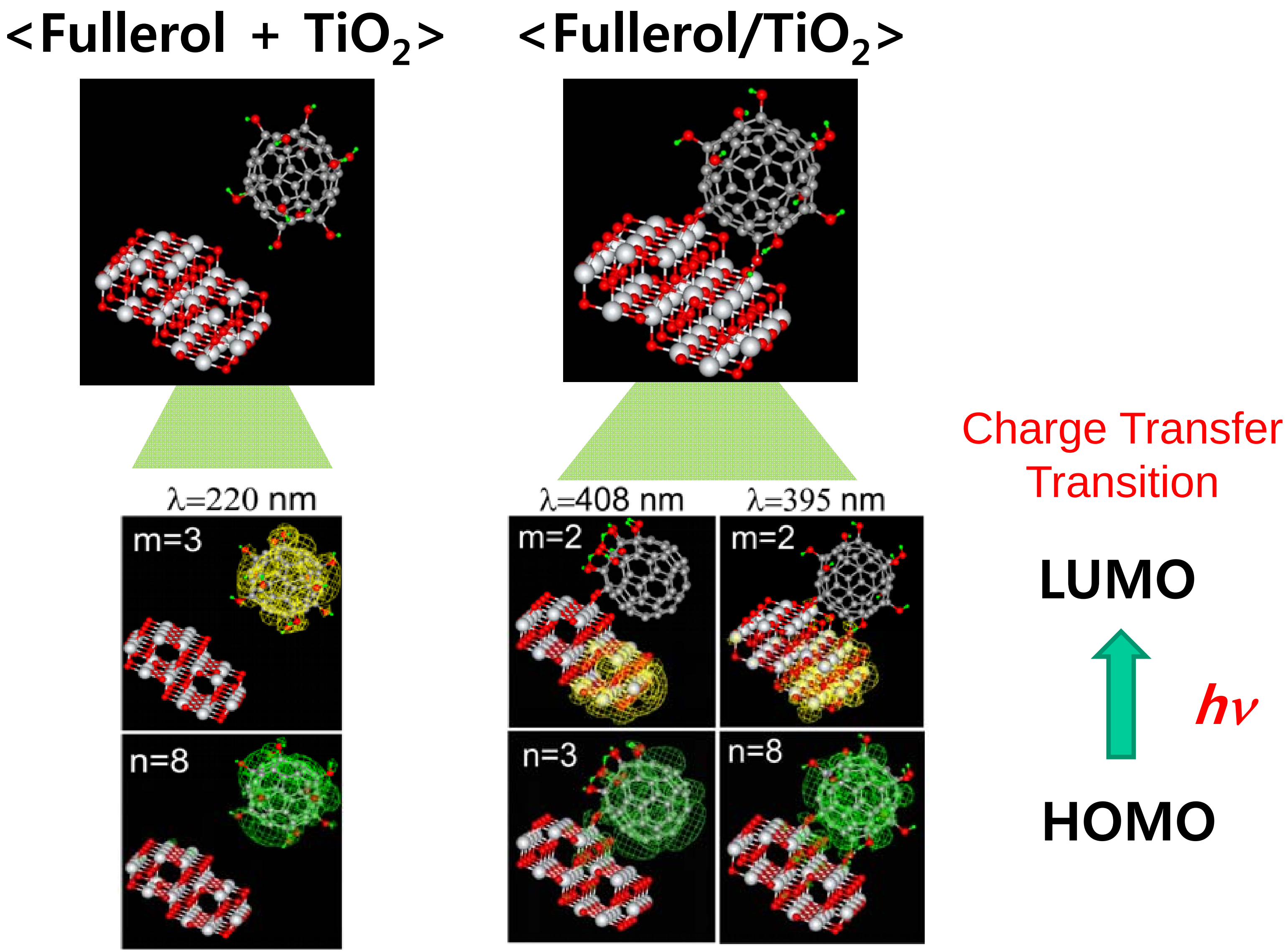


Surface-Complex Formation

Ligand(C_{60}) to Metal (Ti) charge transfer (LMCT)

Visible light activity

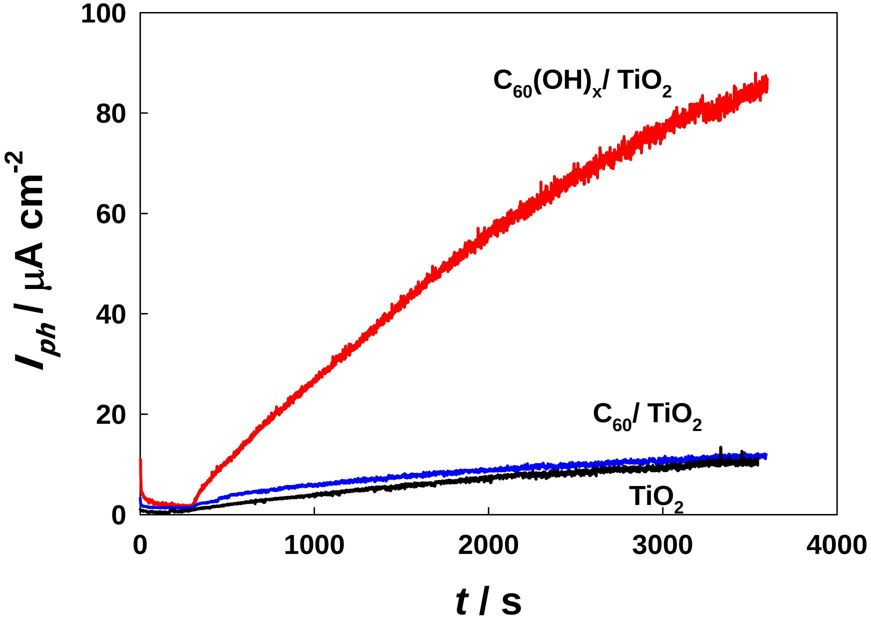
Theoretical Calculation of Fullerol/TiO_2 Complex

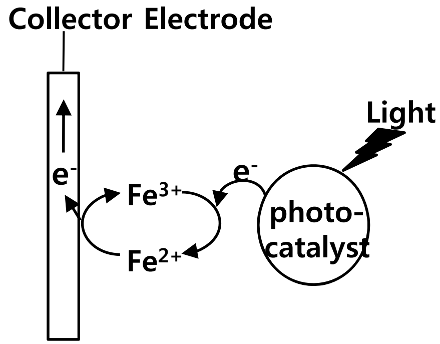


•These absorption spectra are calculated using intermediate neglect of differential overlap (INDO) model parameterized for spectroscopy at the configuration interaction (CI) level of theory (ZINDO/S-CIS)

Photocatalytic Activity of Fullerol/TiO_2

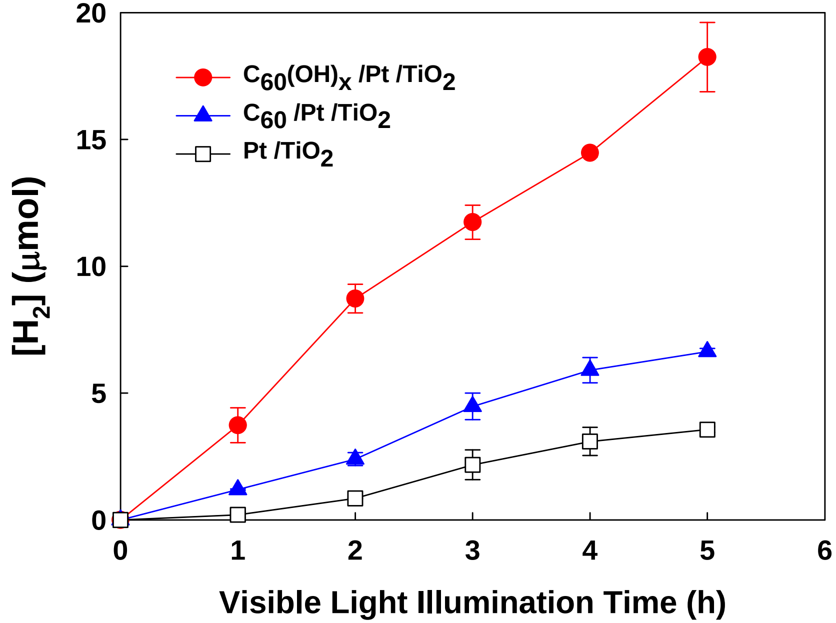
Photocurrent





[Fe^{3+}] = 1 mM, [$LiClO_4$] = 0.1 M, pH 1.8, [Cat]=1g/L, λ>420nm,E= 0.7 V, RE: Ag/AgCl, CE: Graphite rod, WE: Pt plate

H_2 Production



[EDTA] = 10 mM, [Cat] =1g/L, pH_0=3, λ>420nm

Y. Park et al., *Chem. Eur. J.* **2009**, *15*, 10843

Conclusions

- Dye-sensitized TiO_2 nanoparticles can be modified in various ways for H_2 production.
- The hydrogen production on dye-sensitized TiO_2 is critically influenced by the kind of surface anchoring groups of the dye.
- Nafion-coated TiO_2 can anchor non-derivatized ruthenium bipyridyl complexes via ion exchange for efficient hydrogen production.
- The presence of alumina overcoat on TiO_2 enhanced the efficiency of dye-sensitization for hydrogen production.