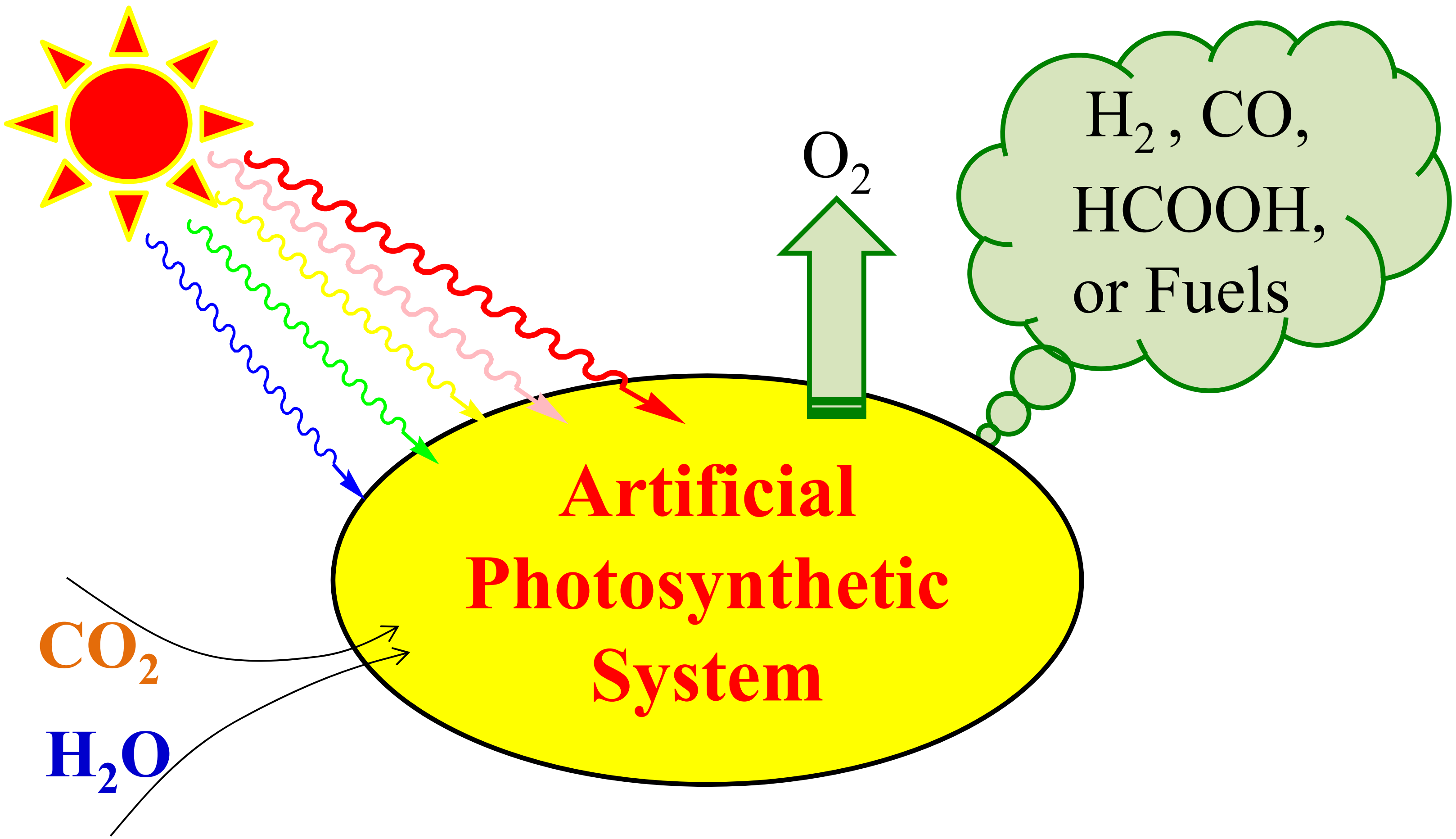
진공학회 @오션리조트여수/오동도홀; August 21th, 2013

Chemical Aspect of Artificial Photosynthesis

강상욱

Department of Material Chemistry
Sejong 2511, Korea University

Targets of Artificial Photosynthesis

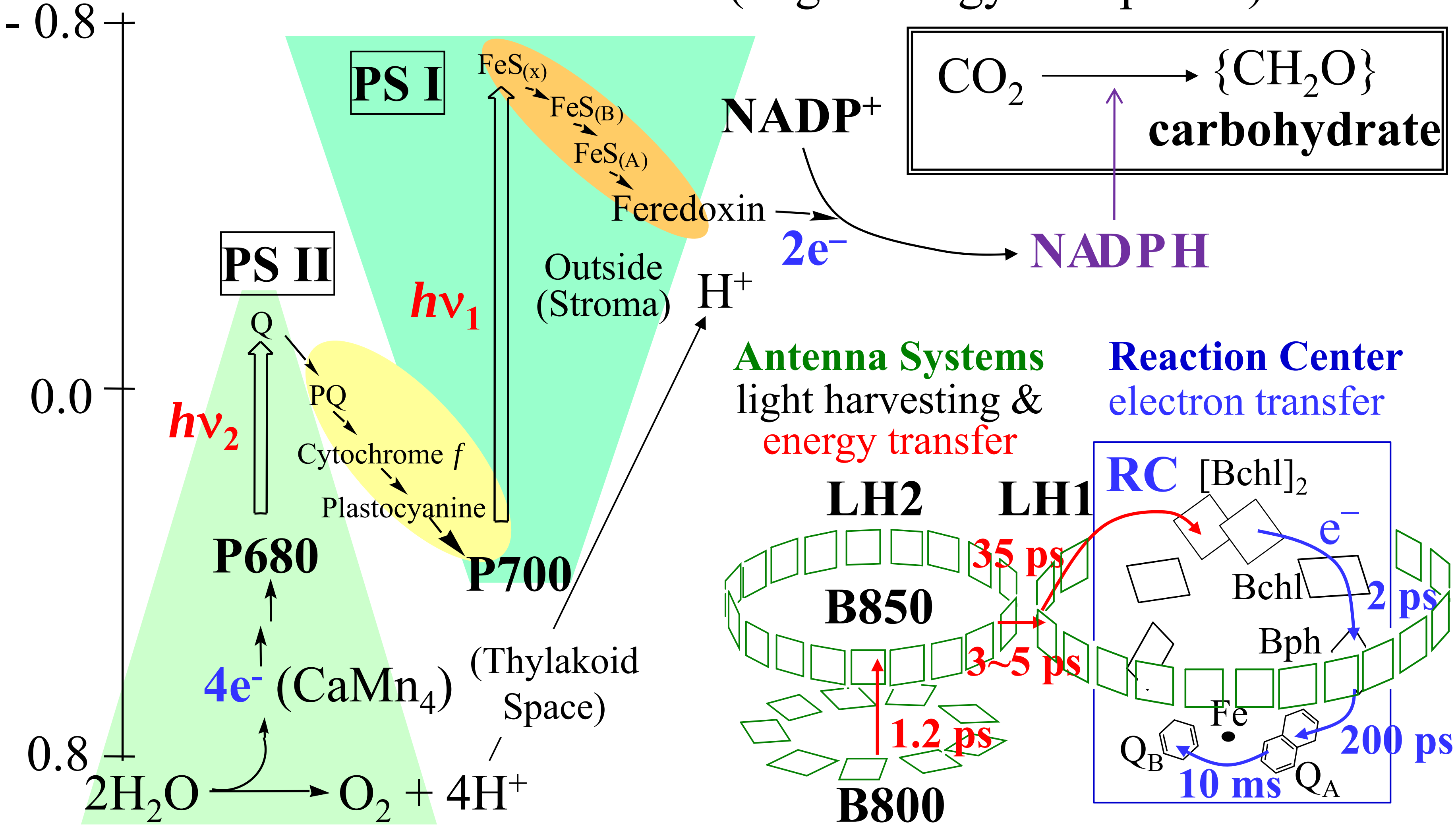


Chemical Conversion & Storage of Solar Energy

Chemical & Physical Processes in Photosynthesis

$H_2O + NADP^+ \longrightarrow 1/2O_2 +$ **NADPH** (Reductant) + H^+

ADP + Pi $\longrightarrow$ **ATP** (High-Energy Compound)



Basic Requirements for Artificial Photosynthesis

Antenna Function

Efficient Harvesting of Visible-to-Near IR Light Quanta

Fast & Efficient Energy Transfer to Reaction Center

Charge Separation

Fast and Efficient Charge Separation: $D + A + h\nu \rightarrow D^{\bullet+} + A^{\bullet-}$

Minimization of Charge Recombination: $D^{\bullet+} + A^{\bullet-}$ –//→ $D + A$

Catalysis Function

Catalysis of One-Electron-to-Multi-Electron Conversion Chemistry

- $2H^+ + 2e^- \rightarrow H_2$; $4H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ or $HCOOH$

Energetic Requirements for 1e⁻-to-2e⁻ Conversion

V *vs.* NHE at *p*H = 7

$H^+ + e^- \rightarrow H\bullet$ (–2.61 V)

$CO_2 + e^- \rightarrow CO_2^{\bullet-}$ (–1.90 V)

Proton-Coupled Multi-Electron Processes

$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$ (–0.61 V)

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ (–0.53 V)

$CO_2 + 4H^+ + 4e^- \rightarrow H_2C{=}O$ (–0.48 V)

$2H^+ + 2e^- \rightarrow H_2$ (–0.41 V)

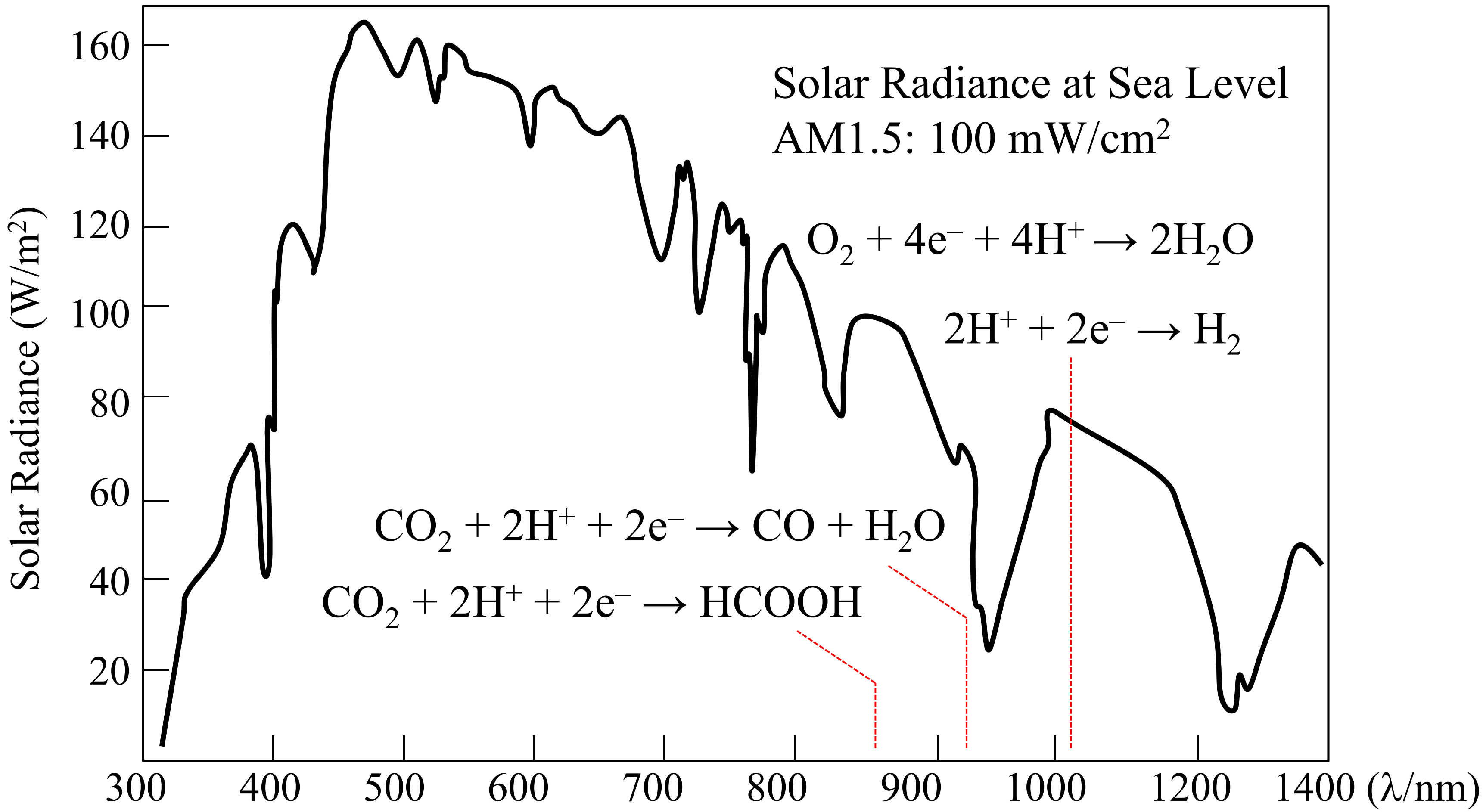
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (0.82 V)

0.0

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (1.35 V)

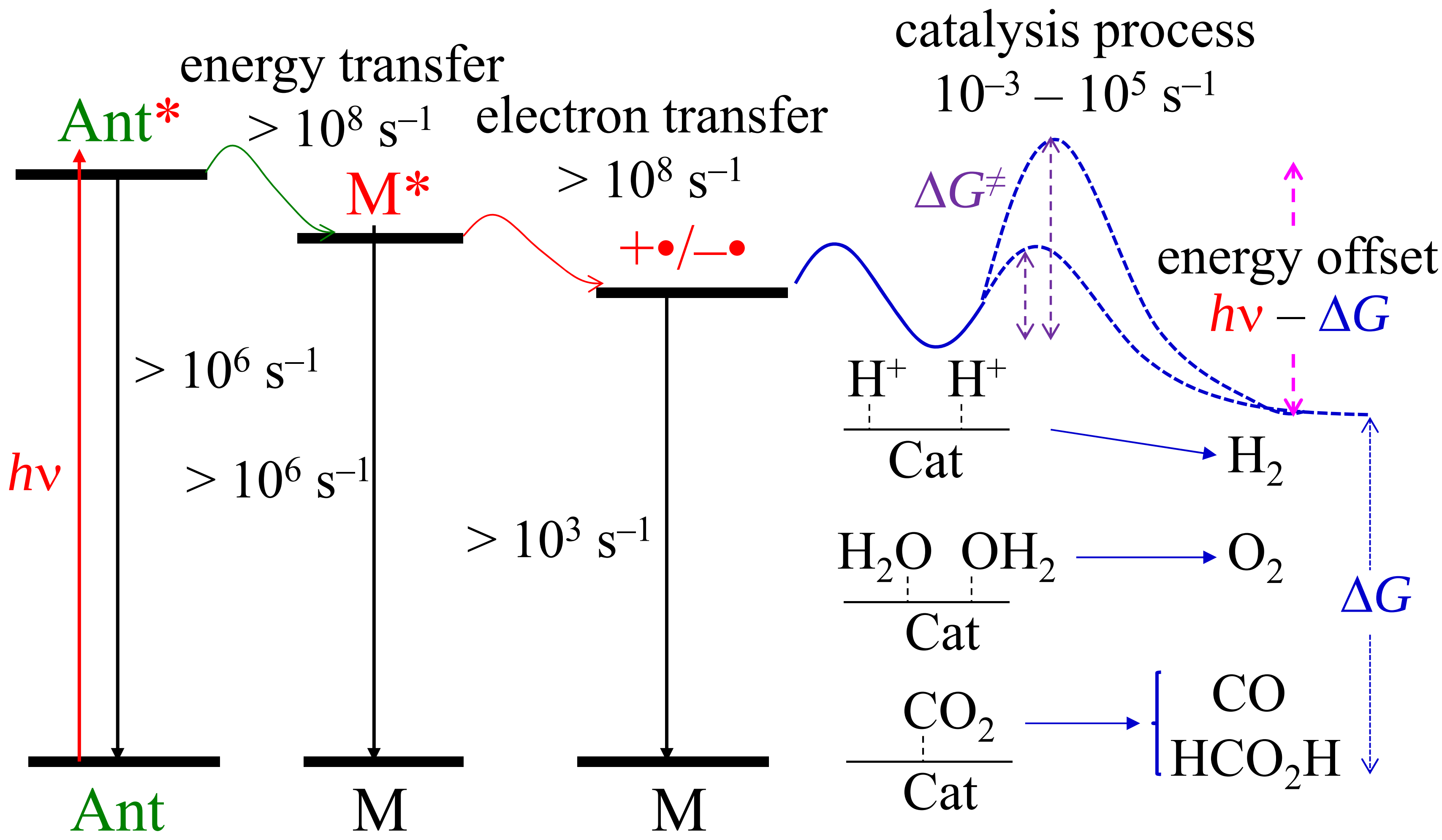
$2OH\bullet + 2H^+ + 2e^- \rightarrow 2H_2O$ (2.31 V)

Solar-Radiance Spectrum & Energy



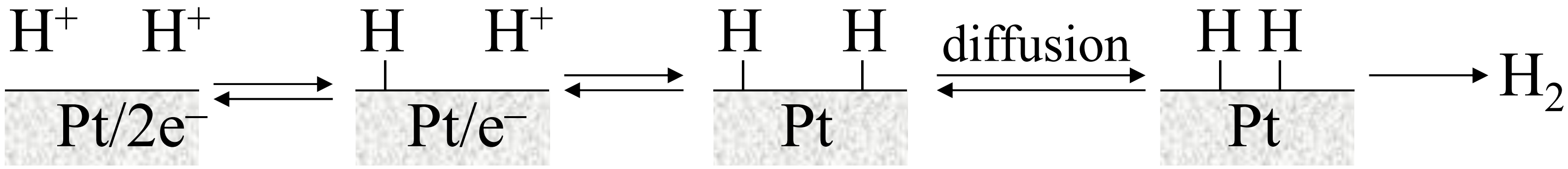
Energy/299	239	199	171	150	133	120	100	(kJ/mol)
71.5	57	47.6	41	36	32	28.7	24	(kcal/mol)
3.1	2.48	2.07	1.77	1.55	1.38	1.24	1.03	(eV)

Time Scales of Essential Processes

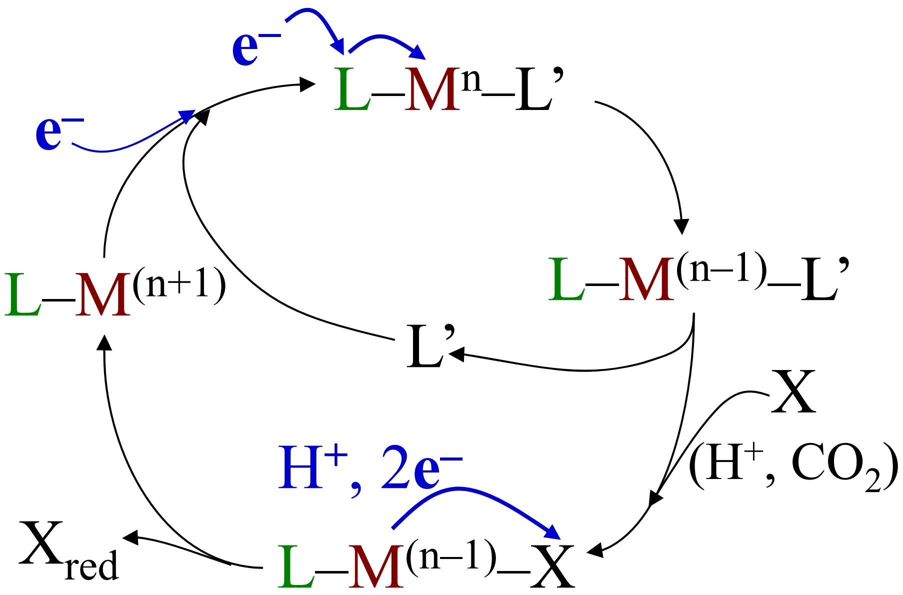


How About Details of Catalysis Process?

Pt is a metal with a very small overvoltage for H_2 evolution ($\Delta G^{\neq}$).



What happens for molecular catalyst? How much is the overvoltage?



Transition-Metal Complex:

π-Ligand – Electron Pool

Metal – Valence Jump

$L^{\bullet-}\text{–}M^{n}\text{–}CO_2 \xrightarrow{H^+} L\text{–}M^{n}\text{–}CO_2H$

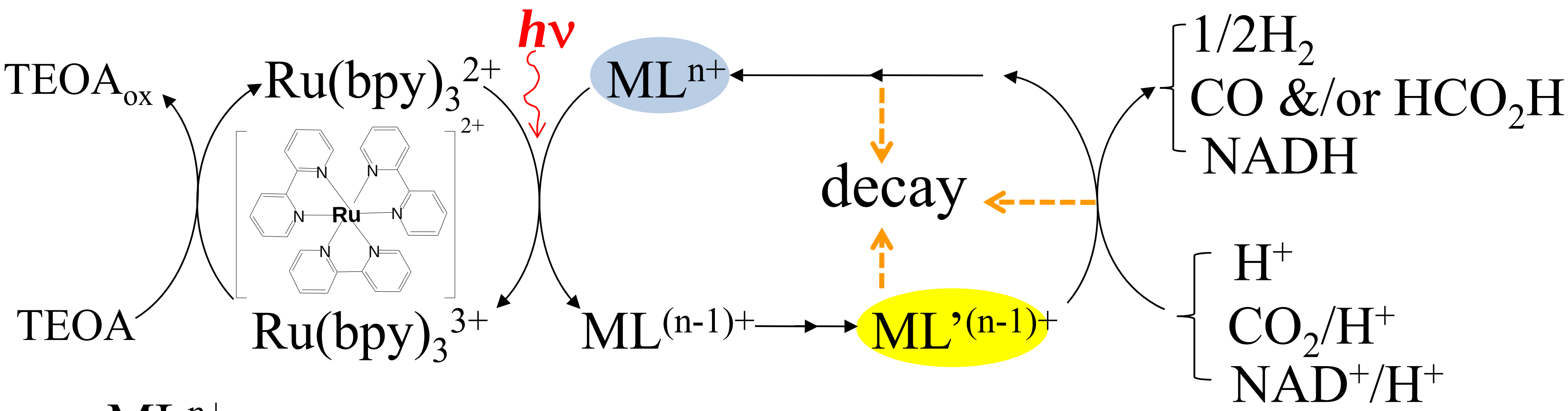
(M^n = Re^{I}, Ru^{II})

$L\text{–}Ru^{II}\text{–}OH_2 \xrightarrow[H_2O]{-m(e^-,\ H^+)} L\text{–}Ru^{V}\text{–}O_2$

$L\text{–}Ru^{II}\text{–}OH_2 \xrightarrow{-m(e^-,\ H^+)} L\text{–}Ru^{IV}\text{=O}$

Classical Examples of Molecular Catalysis

Typical 1e$^-$-to-2e$^-$-Conversion Molecular Catalysts



ML^{n+}

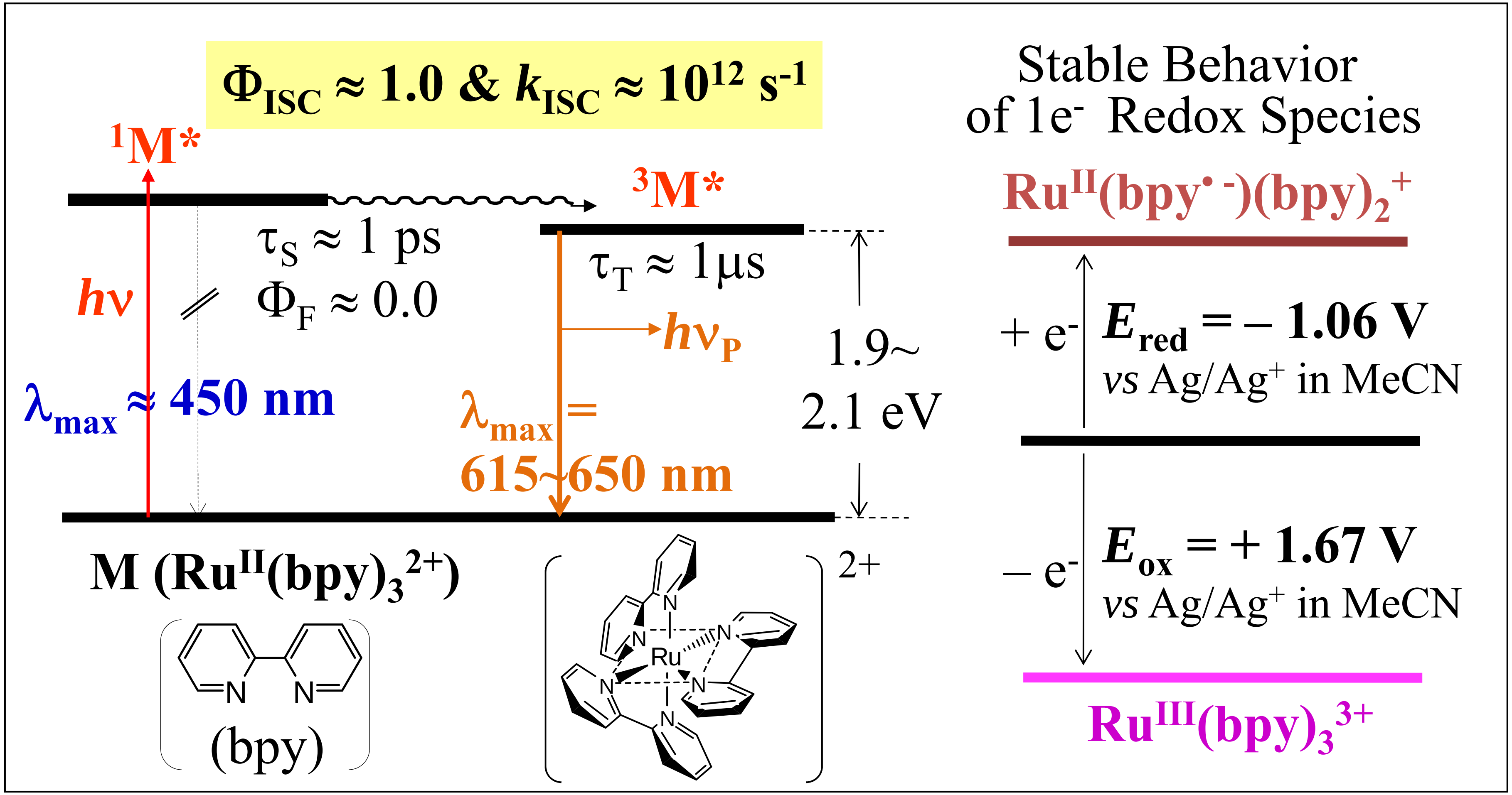
$$Co(bpy)_3^{3+} \xrightarrow{e^-} \xrightarrow{-\,bpy + H^+} Co(bpy)_n(H^-)^{2+}\ (n \le 2) \dashrightarrow H_2$$

$$Ru(bpy)_2(CO)_2^{2+} \xrightarrow[-\,CO]{e^-} \xrightarrow{CO_2 + H^+} \begin{cases} Ru(bpy)_2(CO)(CO_2H)^{2+} \dashrightarrow CO \\ Ru(bpy)_2(CO)(O_2CH)^{2+} \dashrightarrow HCO_2H \end{cases}$$

$$Rh(bpy)_3^{3+} \xrightarrow{e^-} Rh(bpy)_3^{2+} \longrightarrow 1/2\ Rh(bpy)_2^{+} \dashrightarrow \begin{cases} H_2 \\ NADH \end{cases}$$

$$-1/2(bpy + Rh(bpy)_3^{3+})$$

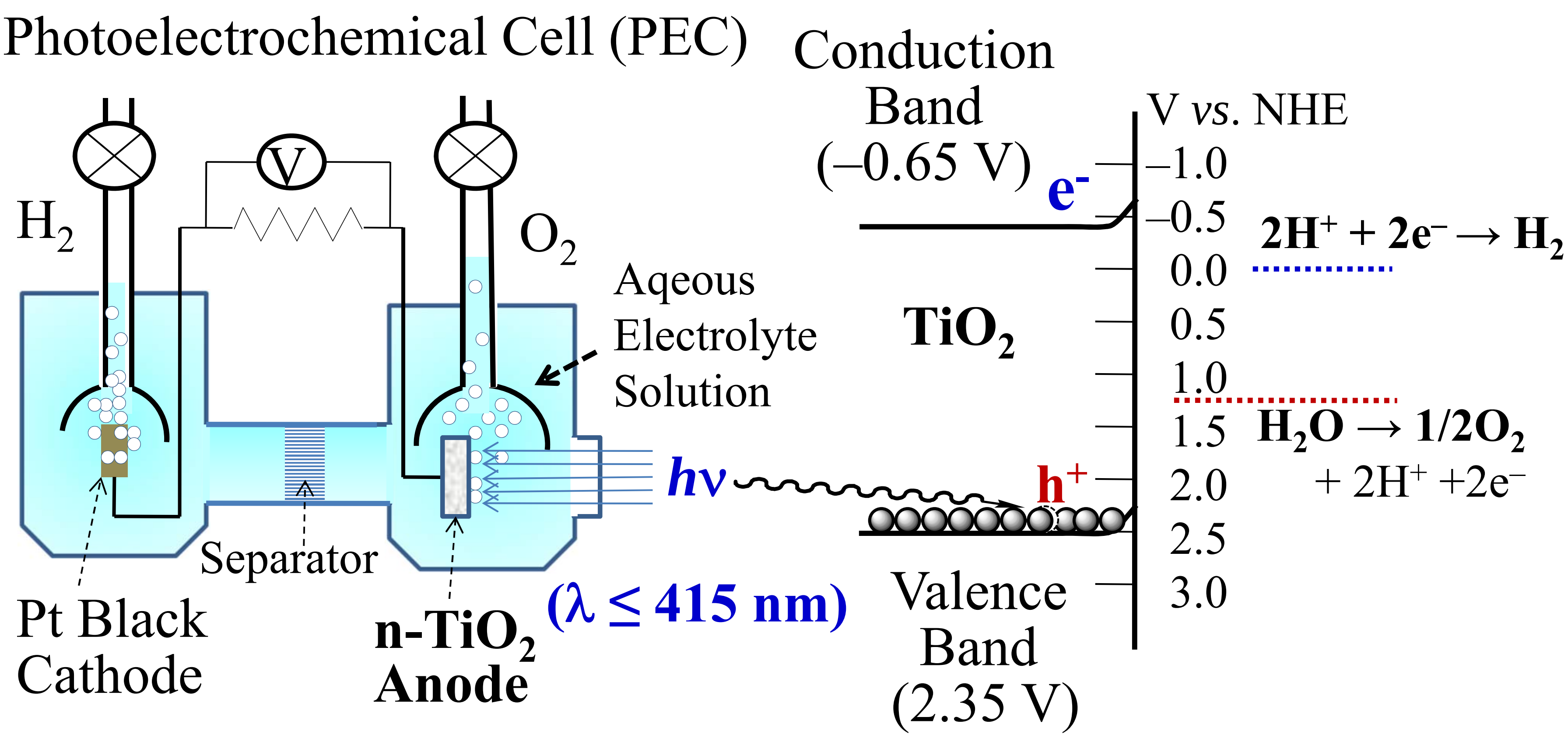
A Typical Visible-Light Absorbing Photosensitizer



Many photosensitizers developed so far do not exceed $Ru(bpy)_3^{2+}$.

Can we develop new robust light-harvesting photosensitizers?

The Beginning of Artificial Photosynthesis



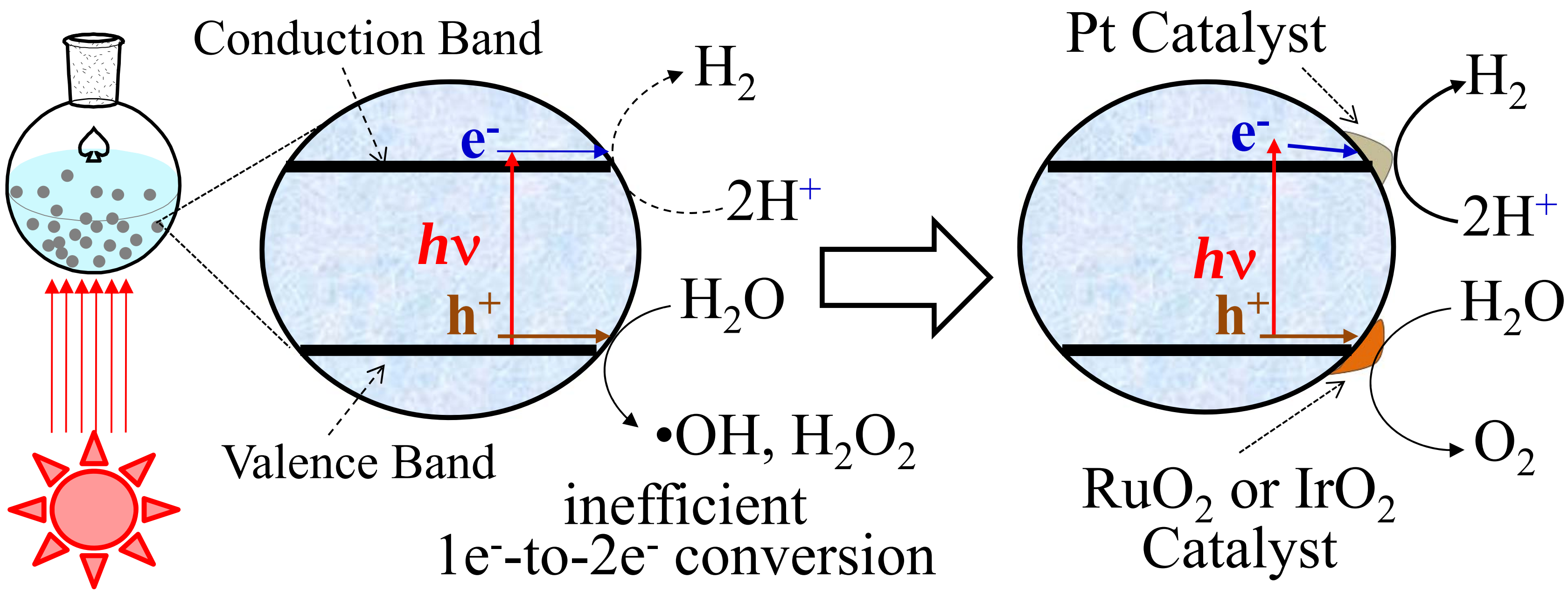
$$H_2O + h\nu\ (TiO_2) \longrightarrow H_2 + 1/2O_2$$

A. Fujishima and K. Honda, *Nature*, **1972**, *238*, 37.

First-Generation Artificial Photosynthesis by TiO_2

TiO_2 : Chemically Stable Charge Reservoir and Transporter

TiO_2 Particulate Dispersion ⇨ Loading of Co-catalysts



($\lambda \leq$ 415 nm)

Requiring Antenna Function for Visible-Light Utilization

Potential Materials for Artificial Photosynthesis

Molecular Materials:

Organic Dyes as Antenna & as Electron-Transfer Component

Transition-Metal Complexes as Antenna & as Catalyst

* Availability of Versatile Functional Molecules

* Easy Tuning of Electronic States, *e.g.*, HOMO-LUMO Levels

Semiconductor Materials:

Chemically Stable Charge Transporter and Charge Reservoir

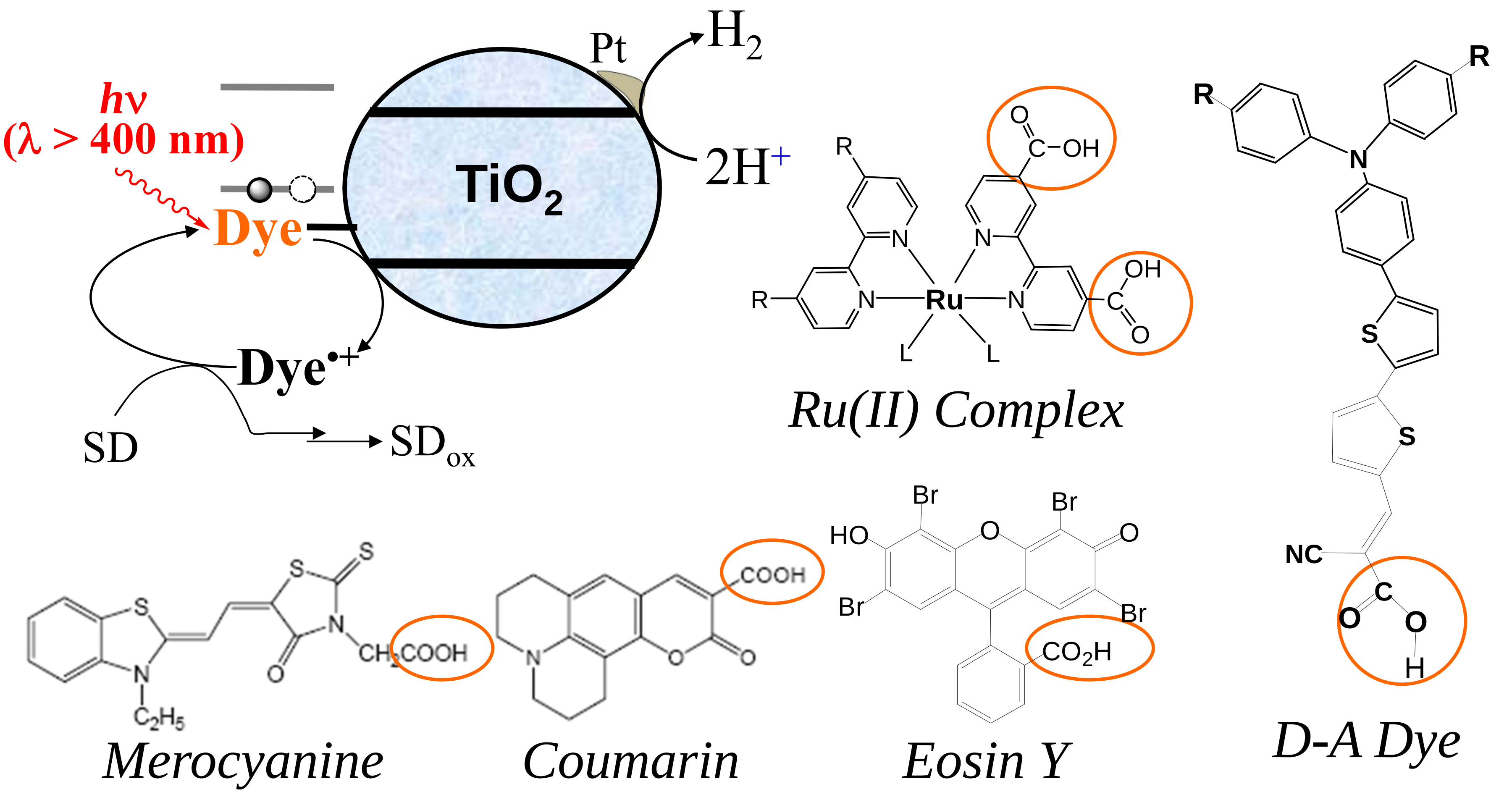
One-Electron-to-Multi-Electron Conversion Function

Molecule-Semiconductor-Catalyst Hybrids:

Excellent Antenna Function + Efficient Electron Transfer +

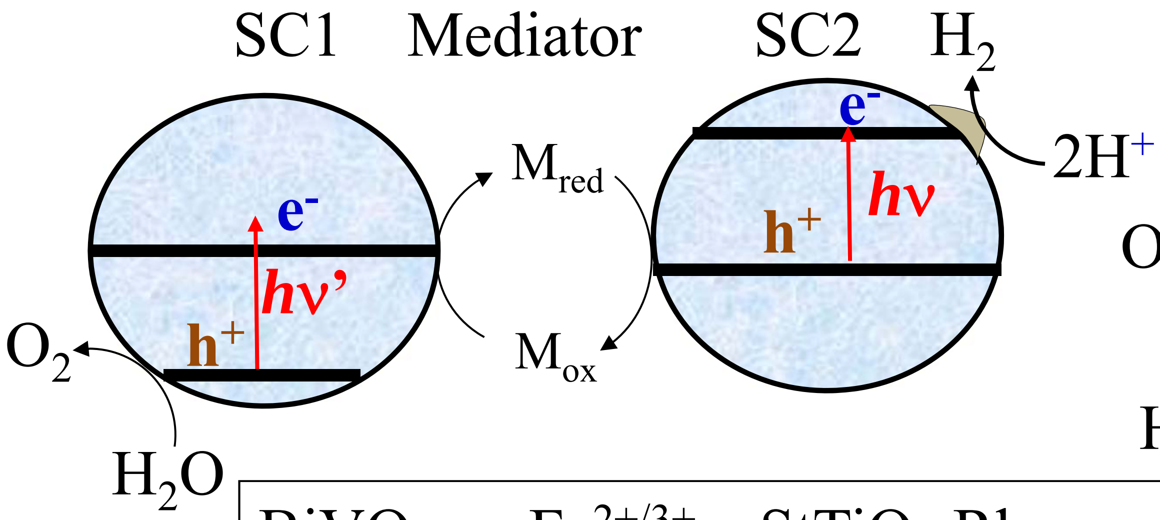
Charge Transport & Accumulation for $1e^{-}$-to-$2ne^{-}$ Conversion

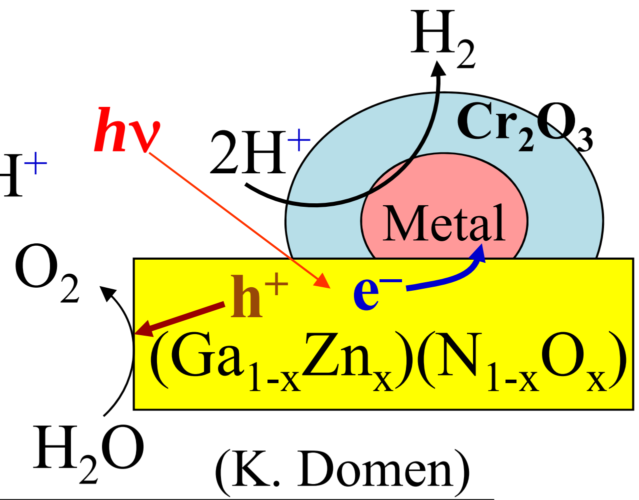
Typical Hybrid Systems for H_2 Generation Based on TiO_2



little information on stability and structure-activity relationships

Visible-Light Water Splitting into H_2 & O_2 Using Inorganic Semiconductors



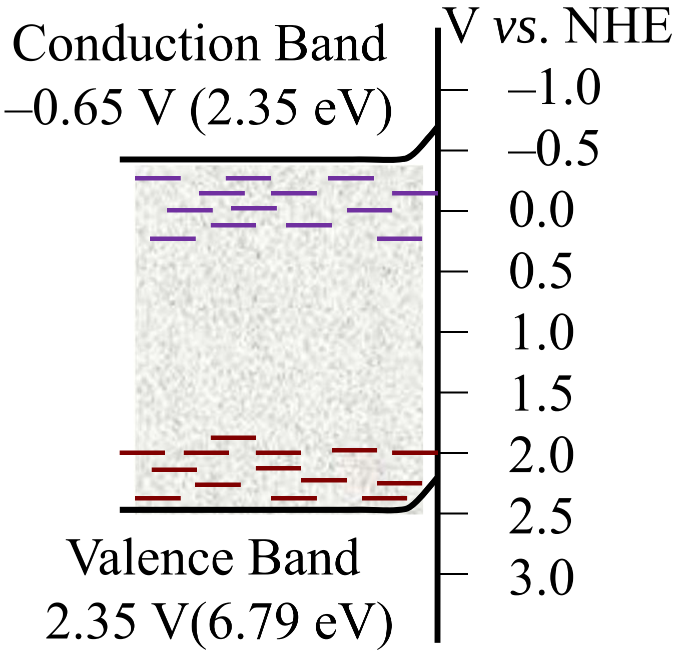


$BiVO_3$	$Fe^{2+/3+}$	$StTiO_3$:Rh	(A. Kudo)
Pt/WO_3	I^-/IO_3^-	$TaON/ZrO_2/Pt$	(K. Domen)
WO_3	I^-/IO_3^-	$Dye/K_4Nb_6O_{17}/Pt$	(R. Abe)

Little information on kinetics of essential processes & on possible participation of electron transfer between M_{ox} & e^- in SC2, between M_{red} & h^+ in SC1 etc.

Which Dominates the Electronics of Semiconductor Particles, Bands or Trap States?

Pure Single-Crystal TiO_2 ⇨ TiO_2 Nanoparticles



Trap States & Surface Defects are dominant and broadly distributed below conduction band & above valence bands.
In DSSC, 90% injected e^{-}'s reside in traps.

⇩

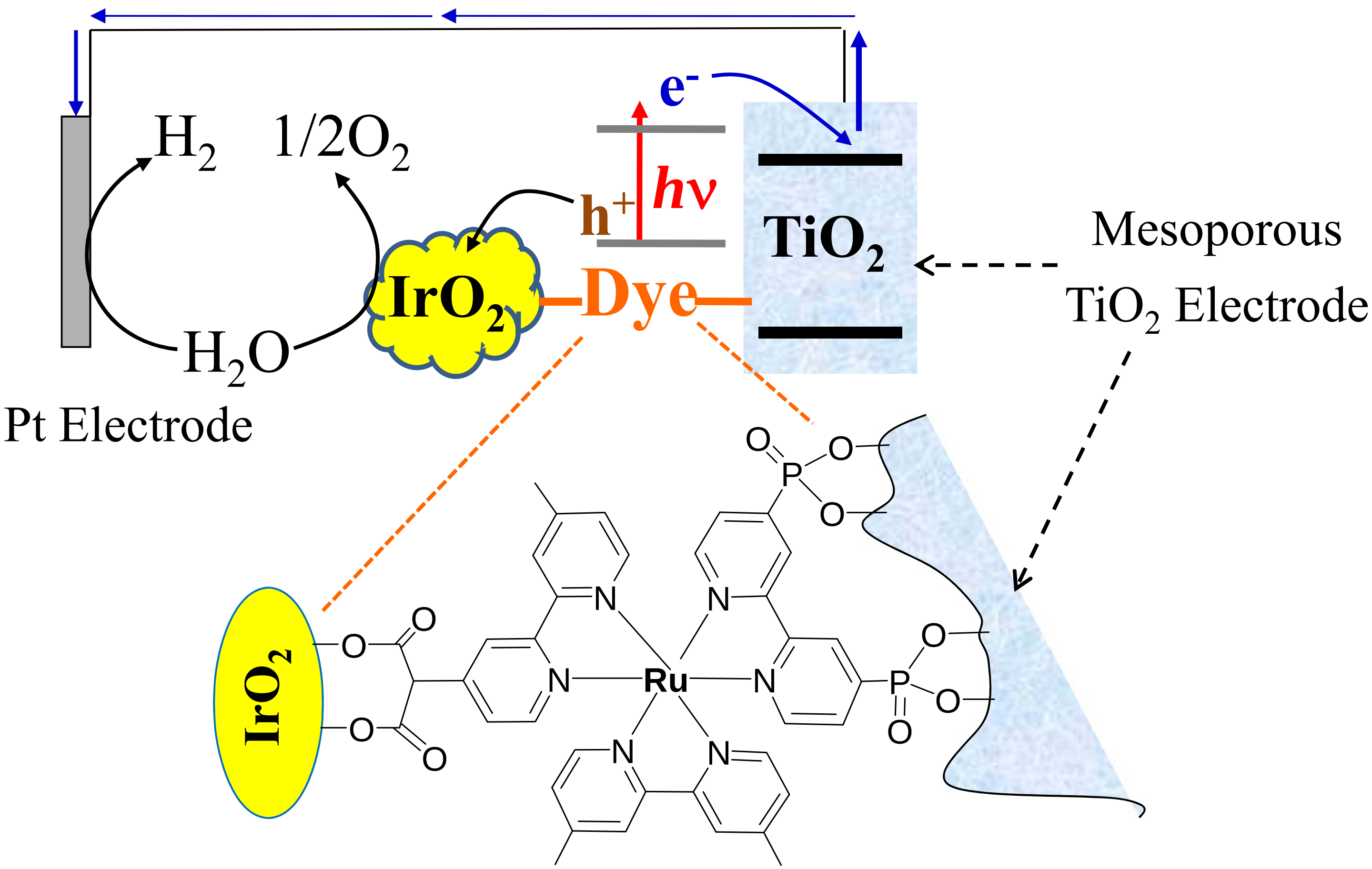
Low Charge Mobility
due to hopping from trap to trap &
due to the presence of grain boundaries

⇩

Significant Participation of
Charge Recombination

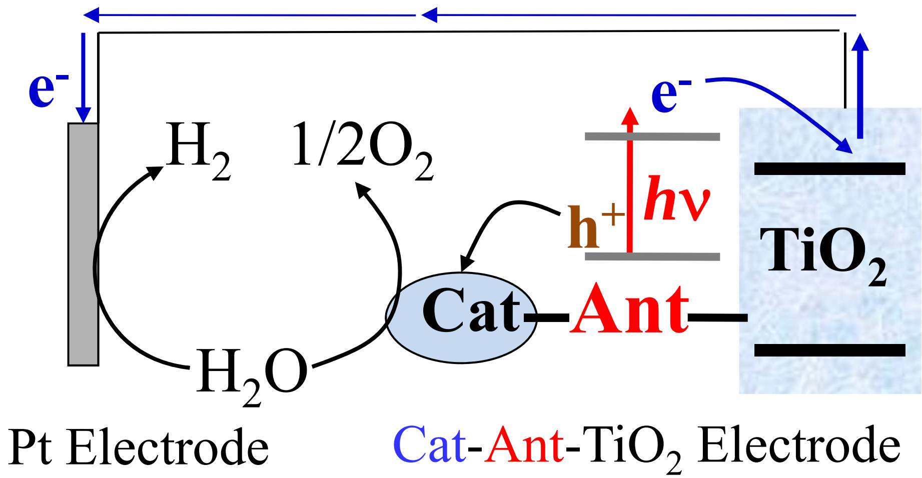
What about other semiconductor particles?
Details of kinetics and energetics of semiconductor particles are not known.

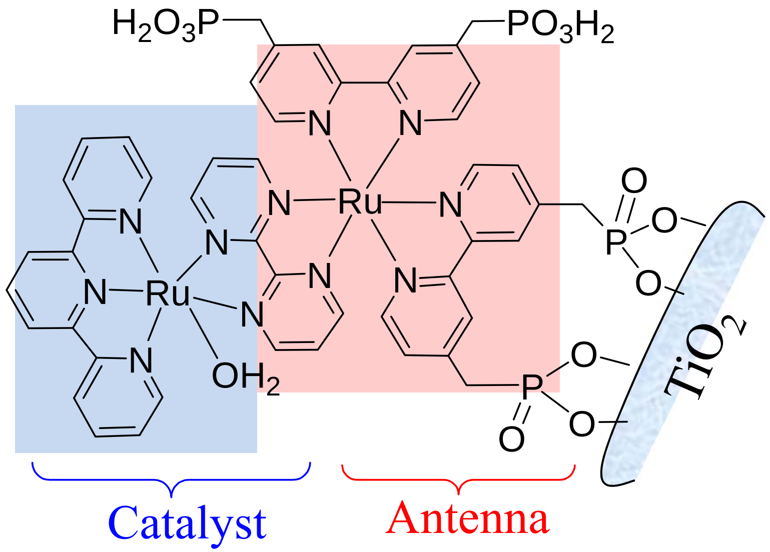
Visible-Light Water Splitting into H_2 & O_2 Using Dye-Semiconductor Hybrid PEC

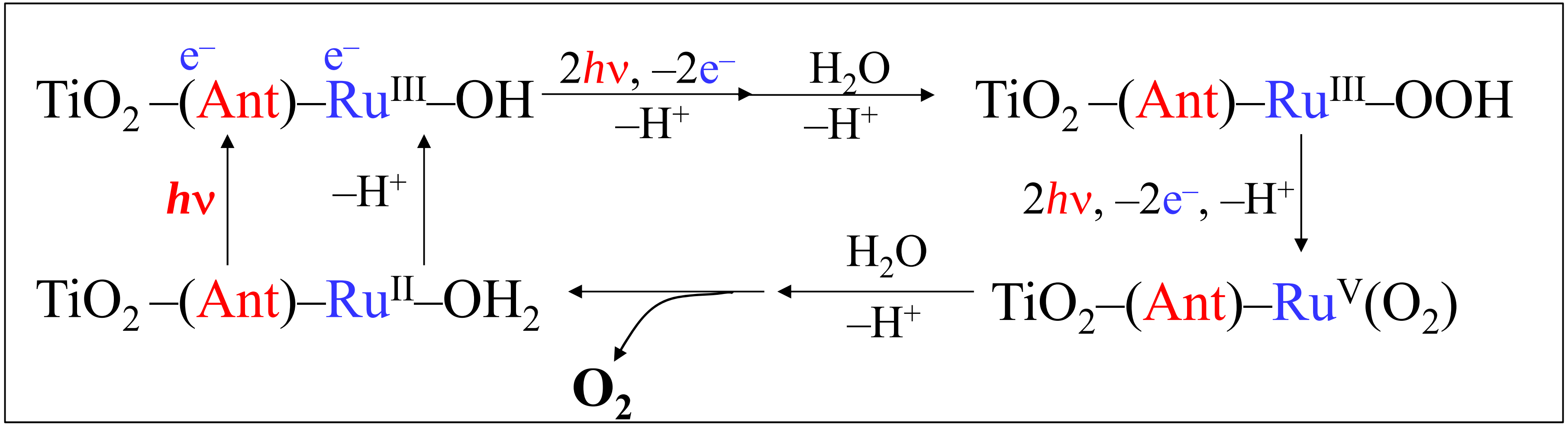


(T. E. Mallouk, 2009)

Visible-Light Water Splitting into H_2 & O_2 Using Dye-Semiconductor Hybrid PEC



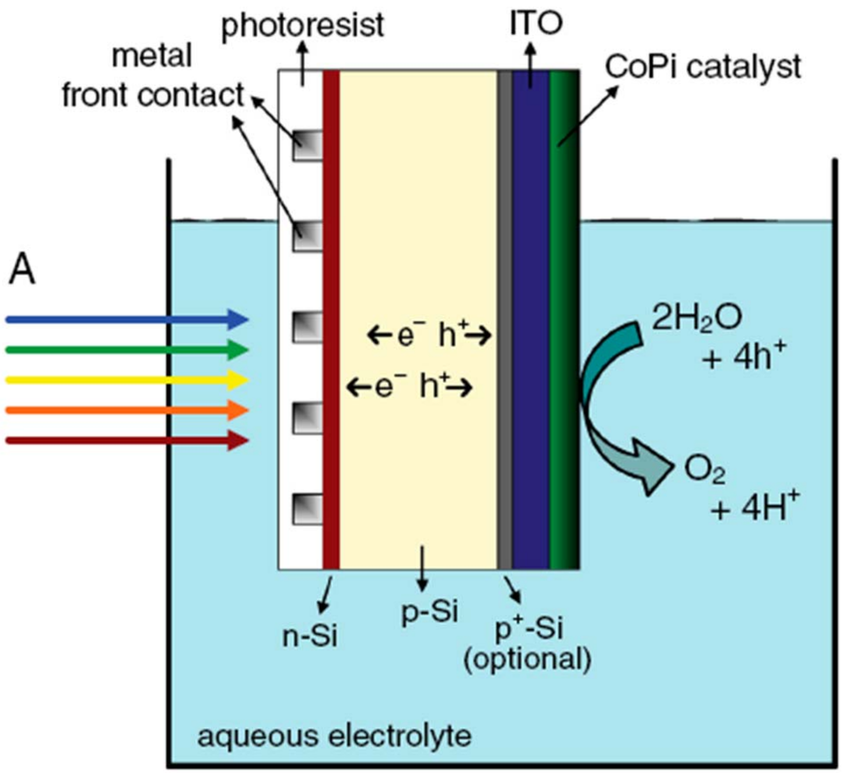




(T. J. Meyer, 2010)

Visible-Light O_2-Evolving Systems Using Cobalt Catalysts

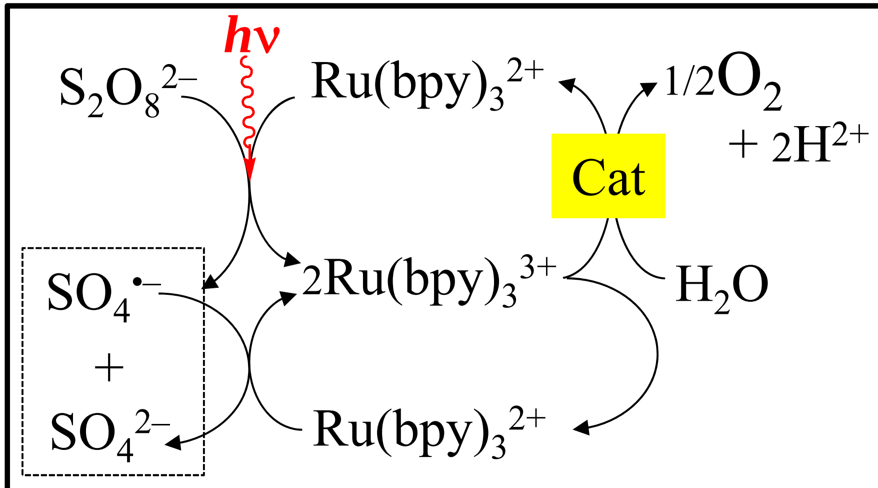
Electrode-Type
O_2-Evolving System Using CoPi



(D. G. Nocera, 2011)

Water-Soluble
O_2-Evolving Catalyst

$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$



O_2 Yield/$S_2O_8^{2-}$ = 45%, $\Phi(O_2)$ = 0.3
TON = 224

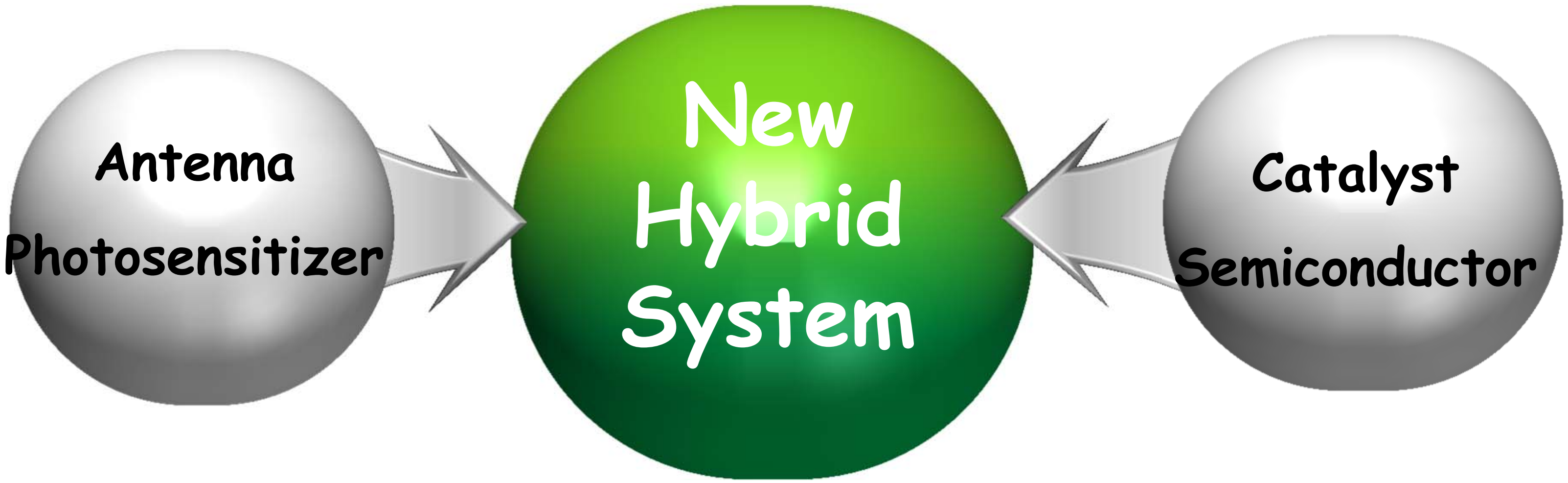
(C. L. Hill, 2011)

What New Materials and Systems Are Available for Artificial Photosynthesis?

1. Persistent Antenna/Photosensitizer: (a) $\lambda_{abs} \leq 700$ nm & $\varepsilon_{max} > 10^4$,
   (b) HOMO/LUMO levels relevant to fast charge generation, & (c) stability
   ⇨ **Organic Dyes *vs.* Transition-Metal Complexes or Others?**
2. Robust Catalysts Working with High TON/TOF at *p*H 7:
   (a) H_2 generation with minimum overvoltage, (b) selective CO_2 reduction with low overvoltage *vs*. no H_2 formation by high overvoltage,
   (c) efficient water oxidation based on mechanistic verification.
   (d) no degradation of components involving antenna and catalyst
   ⇨ **Molecular *vs.* Inorganic Catalysts or Homogeneous *vs.* Solid States?**
3. Construction of Suitable Reaction Systems:
   (a) homogeneous system; incapable of controlling the movement of charges
   (b) semiconductor system; difficult in preparing high quality of nanoparticles with red-light absorption dispersible in water without agglomeration,
   (c) dye-semiconductor hybrid; difficult in persistent anchoring of dye
   ⇨ **Homogeneous or Dispersion System *vs.* Electrochemical Cell System?**

What and How Shall We Do for Artificial Photosynthesis?

We have still no exact answer but many things to do.
The target is clear: Development of New Systems for Artificial Photosynthetic Fuel Generation



$$H_2O + 2e^- + h\nu \rightarrow H_2$$
$$H_2O + 2e^- + h\nu + CO_2 \rightarrow CO$$

→ CH_3OH, C_mH_n etc