Molecular Catalyst for H_2O oxidation / CO_2 reduction
~ model for oxidation (reduction) center for Artificial Photosynthesis

0. Introduction

@ **Photosynthesis** the process that converts solar energy to chemical energy which can be used by biological systems.

@ **Solar energy** abundant, totally huge --- but difficult to use whole energy
⇨ broad spectral

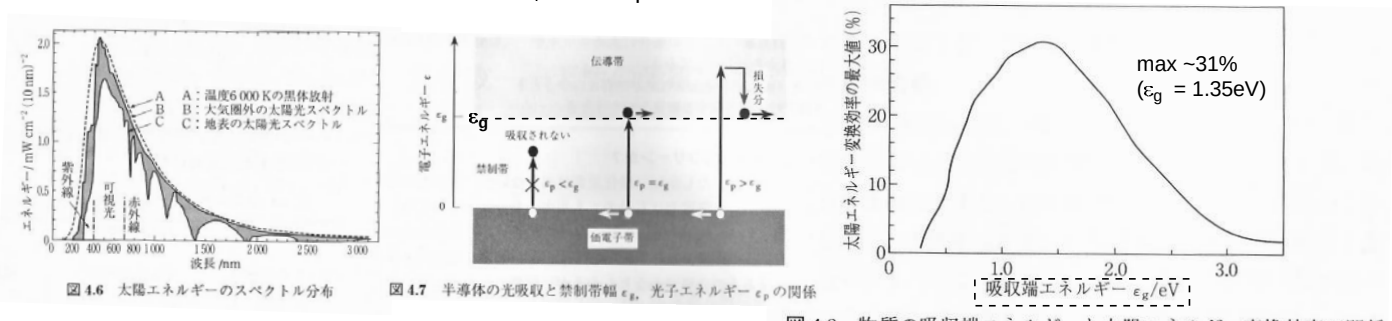

図 4.6 太陽エネルギーのスペクトル分布　図 4.7 半導体の光吸収と禁制帯幅 ε_g，光子エネルギー ε_p の関係

図 4.8 物質の吸収端エネルギーと太陽エネルギー変換効率の関係

< max conversion efficiency using solar light >

	(吸収端)	(光化学系)	
• solar cell	(silicon (ε_g = 1.1eV) <25%)		**<25%**
• photosynthesis	(anntena pigment (<690nm ; ε_g = 1.8eV) <24%) ×	(2hv / 1e⁻ ; 4e⁻ / 3ATP, 4e⁻ / 2NADPH <42%)	**<10%**
• water splitting $2H_2O \longrightarrow O_2 + 2H_2$	(<500nm) ×	(*hv* / 1e⁻ ; 4e⁻ / $2H_2$, 4e⁻ / O_2)	**<8%**

@ Solar Energy Conversion

semiconductor photocatalyst
エネルギー変換効率 <0.1% (Φ ~low)

photosynthesis
エネルギー変換効率 2% (Φ ~1.0)

possibility

chemical **(easy to store)** ⇐ ***hv***

electrolysis
変換効率 <100%

practicality

fuel cell
($2H_2 + O_2 \longrightarrow 2H_2O$)
高出力
on demand
エネルギー変換効率 35-60%
(熱を含めると80%)

E
(difficult to store)

solar cell
低出力
daytime only
エネルギー変換効率
10~20%

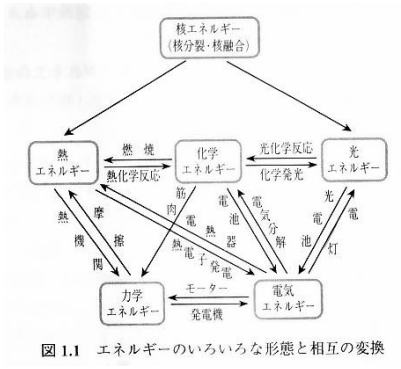

図 1.1 エネルギーのいろいろな形態と相互の変換

Photosynthesis is a good model for converting solar energy to chemical energy without producing CO_2.

< contents >

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1. About Photosynthesis

1-1. Green plants' photosynthesis

@ In chloroplast (葉緑体)

(チラコイド膜,明反応,光化学系) **photochemical**　(ストロマ,暗反応, カルビン回路) **biochemical**

hv → ATP + NADPH ⇄ ADP + $NADP^+$; $CO_2 + H_2O$ ⇄ $(CH_2O)_n + O_2$

hv → chemical → chemical

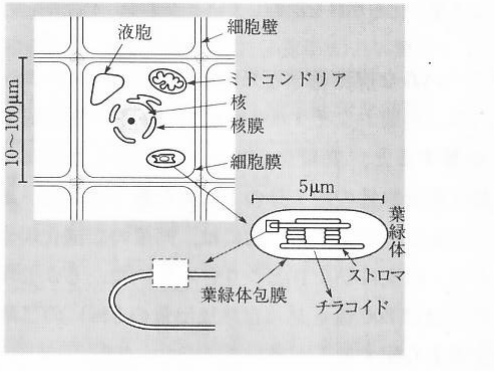
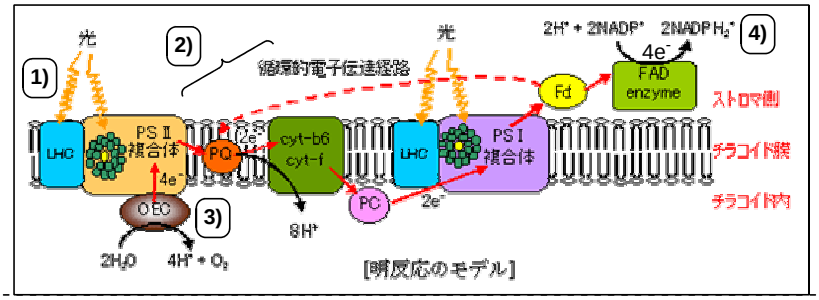


図 5.2 光合成の起こる場（細胞→葉緑体→チラコイド膜の拡大）

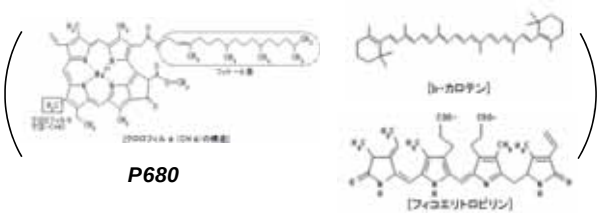
@ In thylakoid membrane (See Lit. Dr. Oisaki (M1)) 参考：光合成の科学（東京大学出版），電子移動の化学（日本化学会）

photoenergy transduction is realized by electron transfer (ET) system.

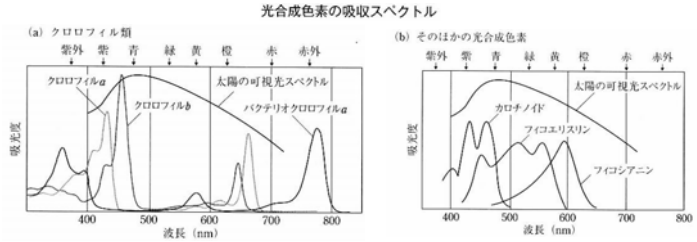


1) Light is gathred efficiently by LHC (Light Harvesting Complex)

• chlorophyll + • pheophytin • carotenoid • phycobilin etc.



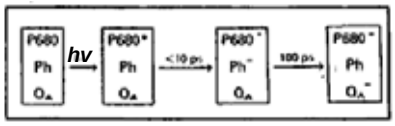
P680

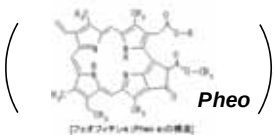


2) In reaction center, photoenergy is stored in a **charge-separation (CS)**

> to avoid **charge recombination (CR)** very fast electron transfer occurr.

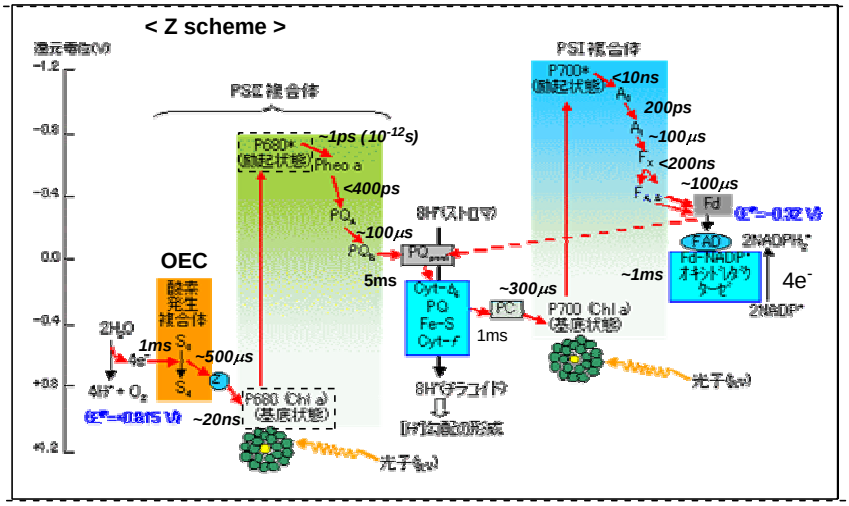
(PSII)





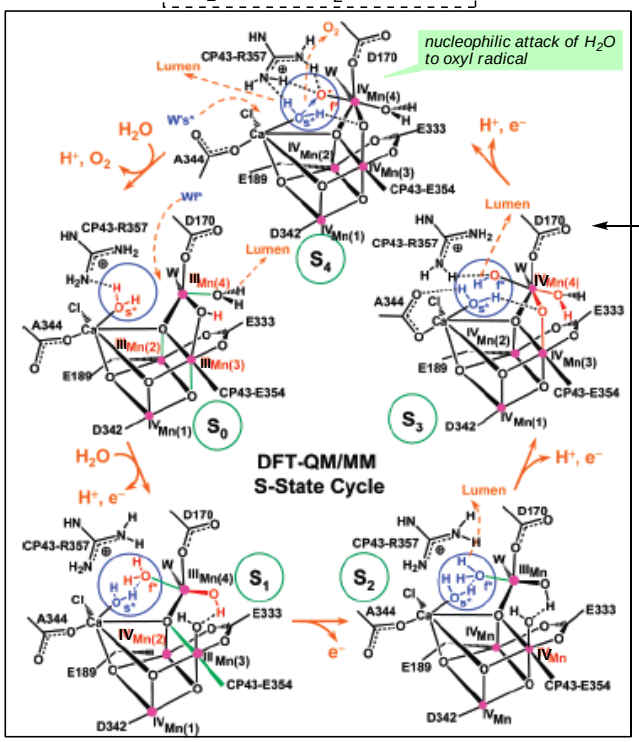
Pheo

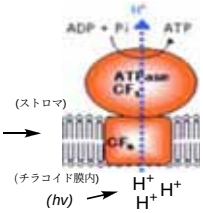
< Z scheme >



3) H_2O is 4 electron oxidized by **OEC** (Oxygen Evolving Complex , Mn-cluster) and O_2 is genarated

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (E^0 = + 0.815 V) (pH = 5, チラコイド膜内)





(H^+ gradient is generated and used for **ATP** synthesis)

< OEC in PSII >
- Mn_3CaO_4Mn complex
- *Rate 50 moleculeO_2 / s*

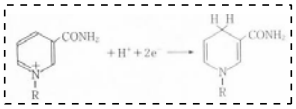
Catalytic cycle of water splitting suggested by DFT QM/MM models of the OEC of PSII.

V. S. Batista et al. (*J. Am. Chem. Soc.* **2008**, *130*, 3428.)

(Dashed arrows indicate transformations leading to the following S state in the cycle. The circles highlight substrate water molecules.)

cf) There are many possibilities.
(*Chem. Rev.* **2001**, *101*, 21) (*Chem. Rev.* **2006**, *106*, 4455)

4) $NADP^+$ is 2 electron reduced and **NADPH** is generated at the end (it is used for CO_2 reduction in some biochemical cycle...etc)

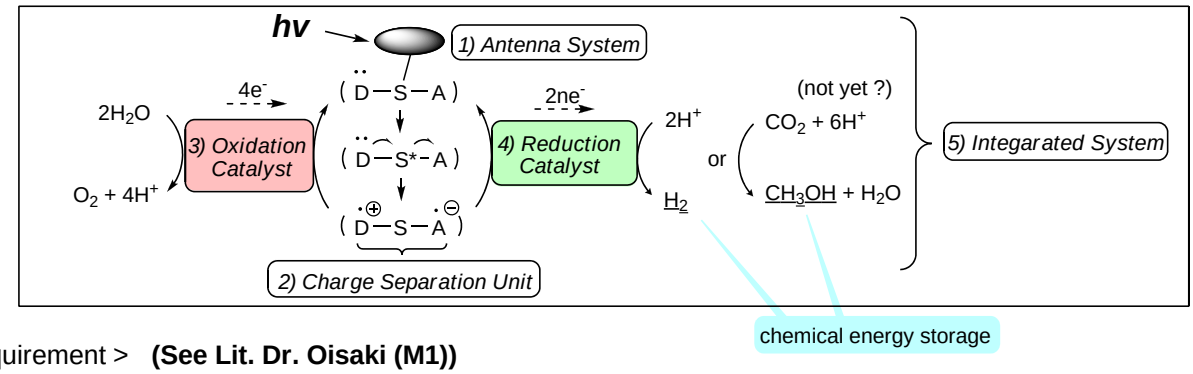


(E^0 = -0.32 V) (pH = 8, チラコイド膜外)

1-2. Toward artificial photosynthesis

> omitting further biochemical energy conversions (Of course, they are interesting research areas.)
> using H_2O as electron donor (H_2O oxidation) is reasonable.
> making useful chemical energy (for human) at the reduction center is desirable.

@ *simple molecular system for artificial photosynthesis*

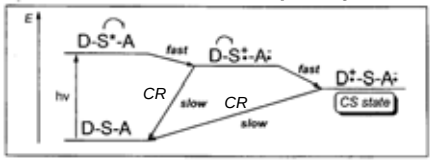


< requirement > **(See Lit. Dr. Oisaki (M1))**

1) ⇨ • possessing high absorption in visible light
• stable toward photo-decomposition
"Harvesting Device of Visible Light"

2) ⇨ • properly long lifetime (τ)
• sufficiently high energy content
• higher quantum yield (Φ), higher energy conversion efficiency
"Photoenergy Storage Device Posessing CS Ability"

concept) ***Donor - Sensitizer - Acceptor system***



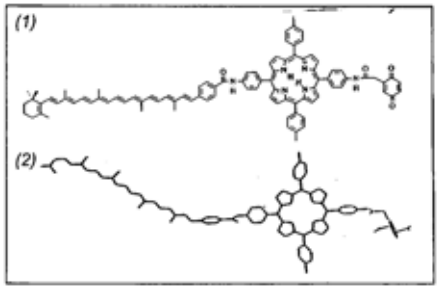
Donor : Ferrocene, Carotenoid etc.
Sensitizer : Porphyrin, $Ru(bpy)_3^{2+}$ etc.
Acceptor : Quinone, **Fullerene(C_{60})**
Dyad (2成分系) ~ Hexad (6成分系)

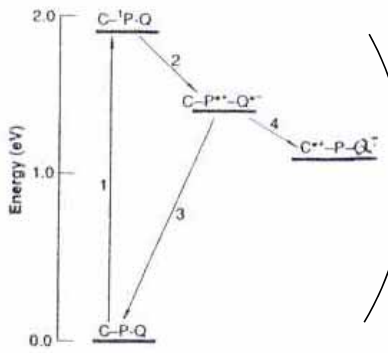
pioneering work
by T. A. Moore, D. Gust et al
(*Nature* **1984**, *307*, 630-632)

lifetime (τ) = 300ns (CH_2Cl_2) / 3μs (CH_3CN) / 2.5μs (CH_2Cl_2 sat. with nBu_4NBF_4)

quantum yield (Φ) = ~0.04 (CH_2Cl_2 or CH_3CN) / ~0.25 (CH_2Cl_2 sat. with nBu_4NBF_4)

" Cartenoid - Porphyrin - Quinone Triad"
(C-P-Q)





progressive work by S. Fukuzumi et al.

comparable in CS life time to photosynthesis center

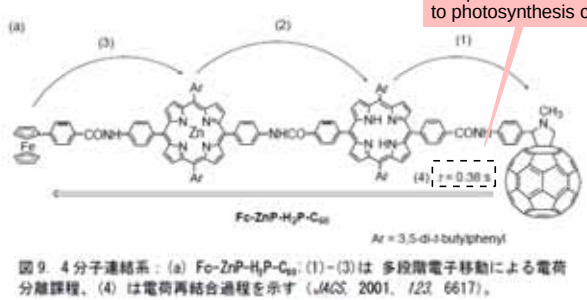
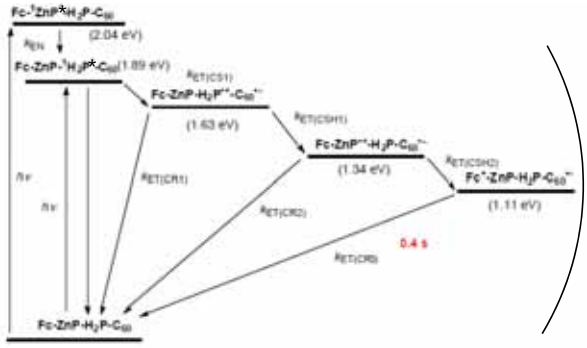


図 9. 4 分子連結系：(a) Fc-ZnP-H_2P-C_{60}; (1)–(3)は 多段階電子移動による電荷分離課程、(4) は電荷再結合過程を示す (*JACS*, 2001, *123*, 6617)。



3) ⇨ (section 2) $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

4) ⇨ (section 3) $2H^+ + 2e^- \longrightarrow H_2$
$CO_2 + 6e^- + 6H^+ \longrightarrow CH_3OH + H_2O$

(reaction itself difficult)
• multi-electrons donor (acceptor)
• stable under highly oxidizing (reducing) conditions

5) ⇨ (section 4)
• appropriate oxidation-reduction potential at both site
• minimun energy loss
• higher energy conversion efficiency / lower cost than bio-photosynthesis totally

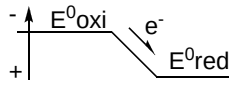
@ occuring reaction

<oxi.> ③ $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ ($E^0 = +1.23$ V) (pH = 0)

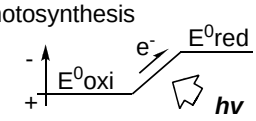
<red.> ④ $2H^+ + 2e^- \longrightarrow H_2$ ($E^0 = 0$ V)

$CO_2 + 6e^- + 6H^+ \longrightarrow CH_3OH + H_2O$ ($E^0 = -0.62$ V) (pH = 0)

> thermodynamically



> in photosynthesis

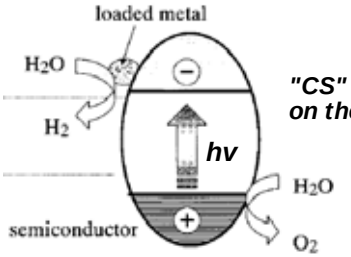


cf) semiconductor photocatalyst (section 4)

simple system for water splitting by hv

($2H_2O \longrightarrow O_2 + H_2$)

- bad responce for visible light ($\lambda > 500$ nm)
- low quantum yield (Φ) <10%
  (low energy conversion efficiency)



"CS" state on the surface

@ molecular catalyst

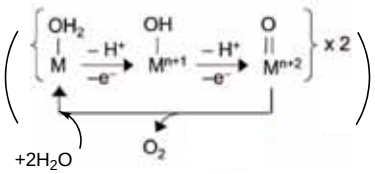
Homogeneous, simple catalyst is hardly applied.

a) **multi-electrons donor (acceptor) at one catalytic cycle**
b) **stable under highly oxidizing (reducing) conditions**
which causes most chemical functional groups to degrade
} are desirable
c) high efficincy
d) cheap, easily prepared

③ ($E^0 = +1.23$ V)

< H_2O oxi. > (section 2)

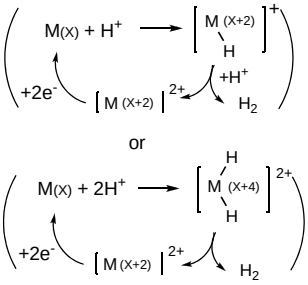
- 4e oxidation, difficult
- nature --- Mn_3CaO_4Mn cluster
- **M** --- Mn, Ru, Ir, Co
  mono or dinuclea, aqua (oxo) complex



($E^0 = 0$ V) ④

< H^+ red. >

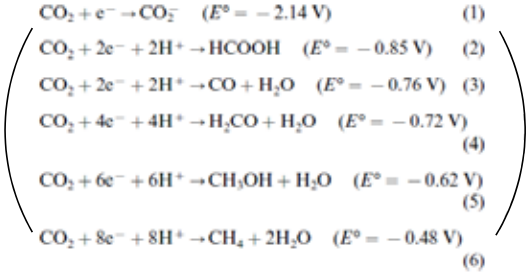
- 2e reduction
- nature --- Fe
- **M** --- Co, Ni, Rh



($E^0 = -0.62$ V)

< CO_2 red. > (section 3)

- 1-8e reduction, very difficult



- nature --- Fe-Ni sluster
- **M** --- Ru, Re, Cu

< combining oxi. and red. > (section 4)

- finding appropriate mediator

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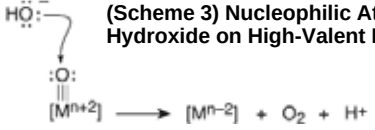
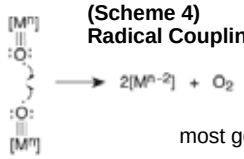
cf) mechanistic possibilities of O_2 evolving from metal oxos (*PNAS*, 2006, *103*, 15729.)



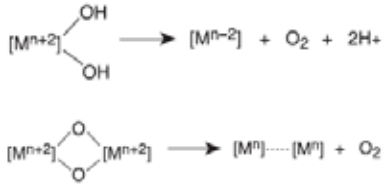
(Scheme 3) Nucleophilic Attack of Hydroxide on High-Valent Metal Oxos



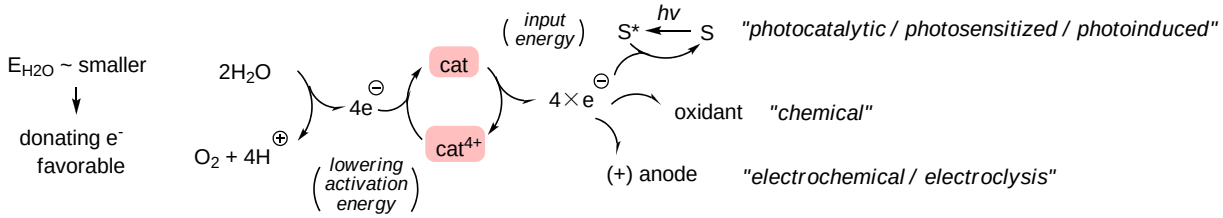
(Scheme 4)
Radical Coupling of Two Oxos

most general

(Scheme 5)
Reductive Elimination of bis Hydroxos or bis μ-Oxos unknown



2. Water Oxidation by Molecular Catalyst



2-1. Water Oxidation

•H	→ H$^+$ + e$^-$	(E^0 = - 2.2 V)
H$_2$	→ 2H$^+$ + 2e$^-$	(E^0 = ~ 0 V)
2H$_2$O	→ O$_2$ + 4H$^+$ + 4e$^-$	(E^0 = + 1.32 V)
2H$_2$O	→ H$_2$O$_2$ + 2H$^+$ + 2e$^-$	(E^0 = + 1.76 V)
H$_2$O	→ •OH + H$^+$ + e$^-$	(E^0 = + 2.72 V)

(at pH = 0, vs NHE)

> Water oxidation is inherently difficult.

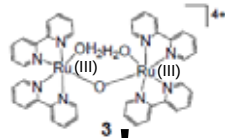
(a) **4-electron O$_2$-evolving water oxidation** requires least oxidation potential
(b) But it demands the loss of 4e$^-$ and 4H$^+$ from 2H$_2$O, all accompanied by the formation of an O-O bond

Even plants find this task difficult:
under ambient sunlight in the chloroplast, the **OEC** (oxygen-evolving complex) must be resynthesized every half an hour or so
owing to the oxidation damage it suffers from O$_2$ that it has produced.

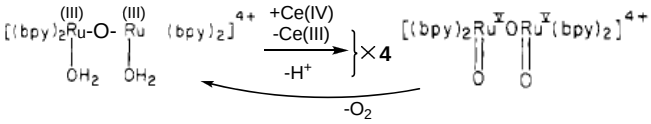
2-2. Pioneering work

oxo-bridged dinuclea Ru

T. J. Meyer et al. (*J. Am. Chem. Soc.* **1982**, *104*, 4029) (*J. Am. Chem. Soc.* **1985**, *107*, 3855)



(cat. cycle)



(a few eq.)

Ruthenium 'blue dimer'

c 4Ce(IV) + 2H$_2$O → 4Ce(III) + O$_2$ + 4H$^+$

(~25 eq) aq.HClO$_4$

TON$_{O2}$ 2~3 (loses its catalytic efficiency after just a few cycles.)
catalyst (0.1M)
pH ~0.7 (aq.H$_2$SO$_4$), CAN as oxidant (Y$_{Ce}$<30%)

cf) 2H$_2$O → O$_2$ + 4H$^+$ + 4e$^-$ (E^0 = + 1.23 V) (pH = 0, vs NHE)
Ce^{4+} + e$^-$ → Ce^{3+} (E^0 = + 1.72 V) - - → only capable of water oxidation very slowly

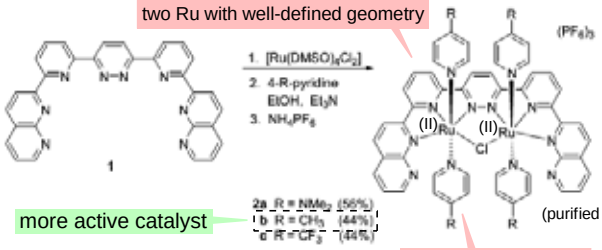
2-3. Recent work

Review (*Angew. Chem. Int. Ed.* **2008**, *47*, 5888)

oxo- or bridged, bi-, and multinuclear transition metal complex

> Ligand-Ru$_2$ R. P. Thummel et al. (*J. Am. Chem. Soc.* **2005**, *127*, 12802) (*Inorg. Chem.* **2008**, *47*, 1835)

two Ru with well-defined geometry



more active catalyst

electrochemical tuning

(purified by chromatography on alumina)

(for 2b)

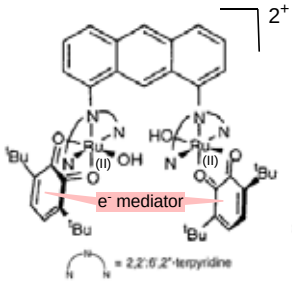
TON$_{O2}$ 572 (48h)
catalyst (6.6×10^{-5}M)
pH ~1 (aq. CF$_3$SO$_3$H)
with Ce(IV) (Y$_{Ce}$~46%)

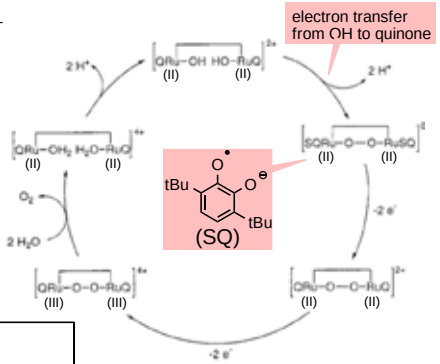
• The reaction is first order in catalyst
↓
cooperative interaction of the two Ru centers of a single catalyst molecule

> Ligand-Ru$_2$ + quinone-ligand (solid state)

catalyst is immobilized on ITO electrode

K. Tanaka et al. (*Inorg. Chem.* **2001**, *40*, 329)
(*Inorg. Chem.* **2008**, *47*, 1787)





TON$_{O2}$ 33500 (40h)
pH ~4 (aq. H$_3$PO$_4$ / KOH, 1.0 M)
E = + 1.70V (vs Ag/AgCl)

> Ru-containing polyoxometalate All-inorganic

$[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ **(1)**
(IV ?)

M. Bonchio et al. (*J. Am. Chem. Soc.* **2008**, *130*, 5006)

$Li_{10}[1]$

TON$_{O2}$ 500 (2h)
(Rate$_{O2}$ max 0.125 /s)
pH ~0.6
with Ce(IV) (Y$_{Ce}$ <90%)

futher Ce(IV) addition induced an quivalent O$_2$ evolution.

robust catalyst

B. Botar et al. (*Angew. Chem. Int. Ed.* **2008**, *47*, 3869)

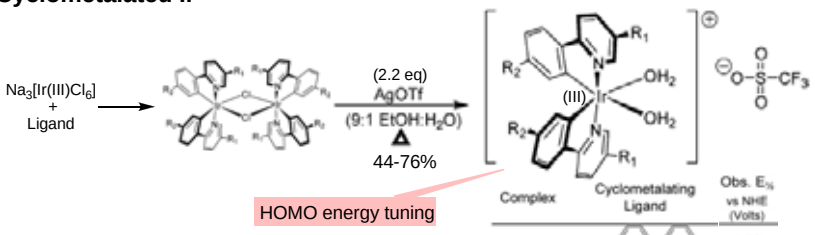
$Rb_8K_2[1]$ • 25H$_2$O

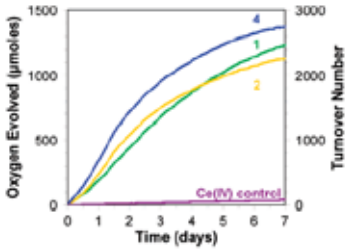
*TON$_{O2}$ 18 (**30~40s**)*
(Rate$_{O2}$ 0.6 /s)
pH 7 (phospate buffer)
with [Ru(III)(byp)$_3$]$^{3+}$

continuation ?

> Cyclometalated Ir

S. Bernhard et al. (*J. Am. Chem. Soc.* **2008**, *130*, 210) (*Nature (News and Views)* **2008**, *451*, 778)





- synthetically accessible, robust, efficient
- broad range of oxidation potential can be obtained by ligand tuning
- machanism is not clear (non-1st order dependence in catalyst conc.)

TON_{O2} 2760 (7d)
catalyst (3×10^{-4}M)
pH ~0.7
with CAN (Y_{Ce} ~37% (7d))
~100% (6h)

Next Challenge ~ without noble metal homogeneous photocatalytic water oxidation

---

2-4. New amorphous catalyst for water electrolysis

In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+}

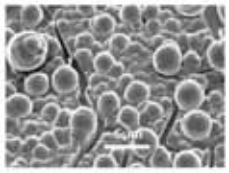
Matthew W. Kanan and Daniel G. Nocera*

(*Science* **2008**, *321*, 1072)
(*Science (News this week)* **2008**, *321*, 620)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E_{anodic} = 1.23\,V - 0.059\,(pH)\,V$ vs NHE
$4H^+ + 4e^- \rightleftharpoons 2H_2$ $E_{cathodic} = 0\,V - 0.059\,(pH)\,V$ vs NHE
$2H_2O \rightarrow 2H_2 + O_2$ $E_{rxn} = -1.23\,V$

$Co(II)(NO_3)_2$
pH 7 (potassium phosphate buffer)
E = +1.29V (@ITO)

continuous O_2 evolving from a dark coating on the ITO surface



(SEM image of coating)

utilize as electrochemical catalyst

> easily prepared, earth-abundant catalysts that oxidize water.

(i) forming from **earth-abundant metal ions in aqueous solution**
(ii) a plausible pathway for self-repair
(iii) a carrier for protons in neutral water
(iv) the generation of O_2 at low overpotential, **neutral pH, 1 atm, and room temperature**

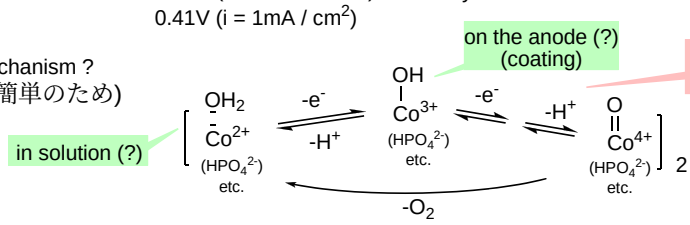
"elements of natural photosynthesis "

< other >

> O_2 (3.0mg, 95μmol) was produced by cat.(~0.2mg) in 10h ⇨ *TON_{O2} 143 (10h)* *($Rate_{O2}$ 4×10^{-3}/s)* (E = 1.29 V) (触媒を$Co_2H_2KO_7P$と仮定)

> overpotential (η) ~0.32V (i = 0.1mA / cm^2) relatively low
0.41V (i = 1mA / cm^2)

> mechanism ?
(簡単のため)



< Requirement for electrode in practical sense >

> low overpotential ⟶ 過電圧(η) : 電極電位とその反応の平衡電極電位との差（ある程度の反応を進行させるのに必要）
（反応物質の吸着・電子授受・結合の開裂・表面拡散・新たな結合の形成・生成物の脱着などを総合した活性化エネルギーを反映）
> neutral (pH ~7)
> without noble metal

表 7.1 水の電解に関係する過電圧の概略値 ($i = 0.1\,mA\,cm^{-2}$ のとき)

水素発生		酸素発生	
電極	過電圧の絶対値	電極	過電圧の絶対値
Pt	0.03 V	RuO_2	0.1 V
Fe	0.3	Fe	0.3
Cu	0.4	Ni	0.4
Zn	0.8	黒鉛	0.4
Hg	0.9	Ag	0.4
Pb	1.0	Pt	0.6

so far...

- first-row spinel and perovskite metal oxides
  moderate overpotentials (<0.4V)
  concentrated basic solutions (pH > 13)
- precious metals and precious metal oxides
  similar efficiencies
  acidic conditions (pH < 1)

< Co^{2+} >

Co^{2+} + $Ru(bpy)_3^{3+}$ in neutal phospate solutions can catalyze water oxidation. (E^0 = + 1.26V) ...but oxidized Co species were precipited gradually.

V. Y. Shafirovich et al. (*Nouv. J. Chim.* **1980**, *4*, 81)
C, Creutz, N. Sustin et al. (*J. Am. Chem. Soc.* **1983**, *105*, 4832)

⇩

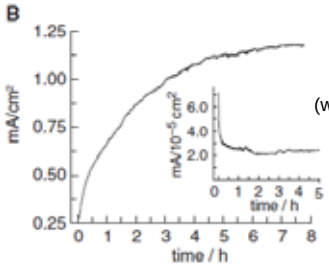
Can precipitation be exploited for electrolysis ?

< This paper >

> Indium tin oxide (ITO) (a minimal background activity for O_2 production)
+
E = + 1.29 V
+
$Co(NO_3)_2$ (0.5 mM)
potassium phosphate (0.1 M, pH 7.0; KPi electrolyte)

⇩

a dark coating on the ITO surface
effervescence becomes increasingly vigorous
（気泡） (same results with $CoSO_4$, $Co(NO_3)_2$, or $Co(OTf)_2$)
‖
O_2



(w/o Co^{2+})
⇩
almost no electrolysis

(B) Current density profile for bulk electrolysis at 1.29 V (versus NHE) in 0.1 M KPi electrolyte at pH 7.0 containing 0.5 mM Co^{2+}.

cf) >40 C are passed over 8 hours
(all the Co^{2+}---> Co^{3+} requires 1.9 C) ⇨ ***in situ formation of an oxygen evolving catalyst***

< What is this coating ? >

> morphology

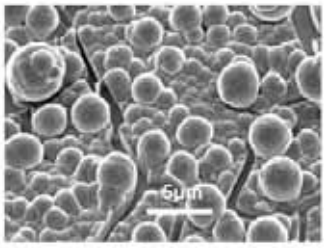


Fig. 2A. *SEM image (30° tilt) of the electrodeposited catalyst after 30 C/cm² were passed in KPi (0.1 M, pH 7.0) containing Co^{2+} (0.5 mM). The ITO substrate can be seen through cracks in the dried film.*

- The film thickness gradually increases.
  At maximum activity, the film is >2μm thick.
- The x-ray powder diffraction pattern shows broad amorphous features
  No peaks indicative of crystalline phases

> composition

- Energy-dispersive x-ray analysis (EDX) spectra
  Co, P, K, and O as the principal elemental
  (2~3 : 1 : 1)
- Microanalytical elemental analysis
  (Co:P:K) = (2.1 : 1.0 : 0.8)

> surface

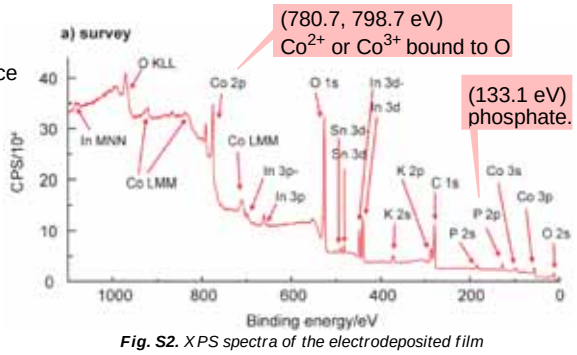
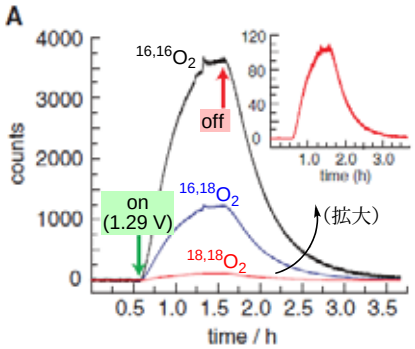


Fig. S2. *XPS spectra of the electrodeposited film*

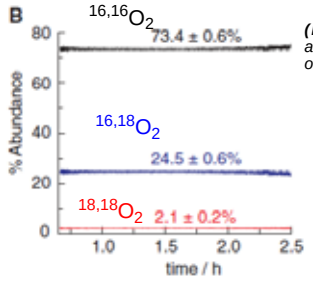
⇨ ***an amorphous Co oxide or hydroxide incorporating a substantial amount of phosphate anion at a stoichiometric ratio of (Co : P : K) = (~2 : 1 : 1)***

< Is O_2 really derived from water ? >

- prepared catalyst coatings (1.3 cm2, stored under ambient laboratory conditions) were used following experiments.

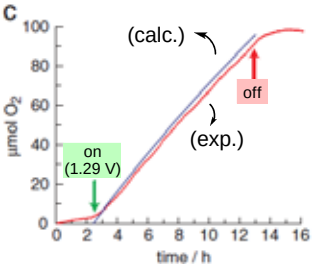


(Fig. 3A) *Mass spectrometric detection of isotopically labeled O_2 during electrolysis of a catalyst film on ITO in a KPi electrolyte containing* ***14.6% $^{18}OH_2$.***



(Fig. 3B)
abundance of each isotope over the course of the experiment.

same as statistical abundances (72.9, 24.9, and 2.1%)



(Fig. 3C)
O_2 production measured by fluorescent sensor (exp.) and by calculation (calc.)

Faradic efficiency ~ 100%.

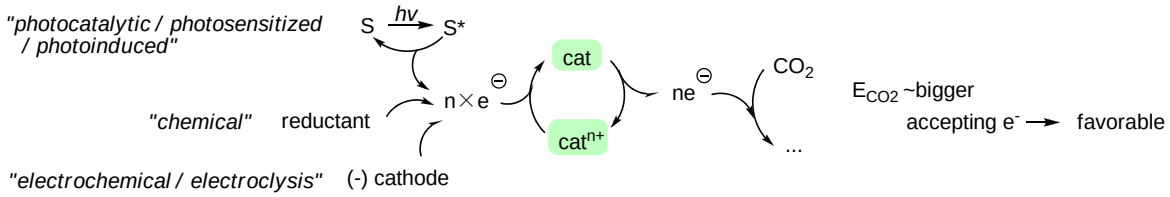
all of the current was caused by 4e⁻ oxidation of water to produce O_2

- phospate is stable
  (^{31}P NMR after stoichiometric(?) electrolysis).

⇨ ***electrodeposited catalyst cleanly oxidizes H_2O to O_2 in neutral KPi solutions.***

X線光電子分光(X-ray photoelectron spectroscopy: XPS)
試料にX線を照射した時に起こる光電効果により放出される電子の運動エネルギーを測定することにより内殻電子の結合エネルギーを測定する手法がX線光電子分光(X-ray photoelectron spectroscopy: XPS)である。表面に存在する原子種とその量、結合状態を知ることができる。具体的には、SAMなどの超薄膜の膜厚や分子の吸着形態などをＸＰＳを用いて調べている。

3. CO_2 Reduction by Molecular Catalyst



3-1. CO_2 Reduction

(*Coord. Chem. Rev.* **2002,** *226,* 211-218)

$CO_2 + e^- \rightarrow CO_2^-$ ($E^\circ = -2.14$ V) **(pH = 7)** (1)

$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$ ($E^\circ = -0.85$ V) (2)

$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$ ($E^\circ = -0.76$ V) (3)

$CO_2 + 4e^- + 4H^+ \rightarrow H_2CO + H_2O$ ($E^\circ = -0.72$ V) (4)

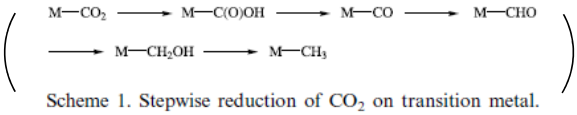
$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O$ ($E^\circ = -0.62$ V) (5)

$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$ ($E^\circ = -0.48$ V) (6)

$2H^+ + 2e^- \rightarrow H_2$ (E^0 = - 0.41 V)

(a) might be important for global warming
(b) very difficult (multielectron transfer)
> more electron reduction, more energetically-favored
But **controlling number of electrons is difficult.**
(c) **Reduction of protons to H_2 is competitive**
(more thermodynamically favored)

transition metal catalyst
selective coordination of CO_2 to metal before reduction



Scheme 1. Stepwise reduction of CO_2 on transition metal.

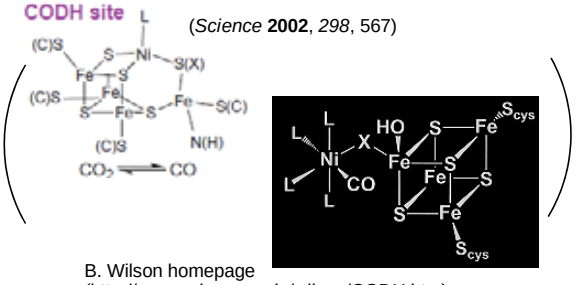
> d_6 metal (Ru(II), Re(I)) or Ni(II) is good for CO_2 to CO.
> Re(I) $(CO)_3$ is exceptionally good
(acts as reduction-catalyst and photosensitizer)

3-2. CO_2 to CO

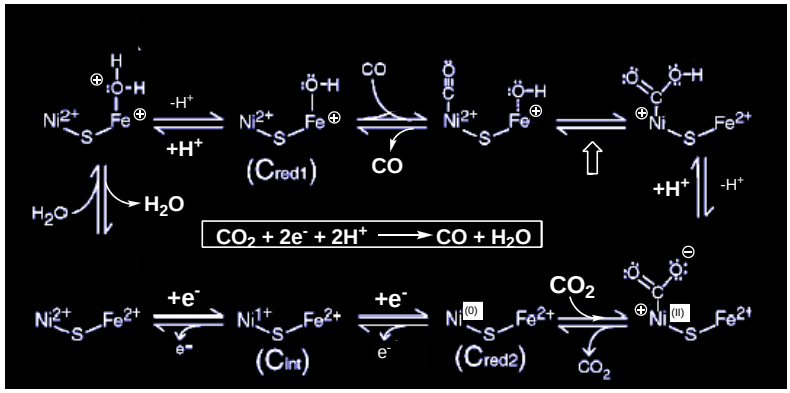
< In nature >

> In Moorella thermoacetica (酢酸生産菌)
[Ni-L-Fe_4S_4] cluster (in carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS))

bifunctional { reversible reduction of CO_2 to CO
synthesis of acetyl-CoA from CO & CoA



B. Wilson homepage
(http://research.uvsc.edu/wilson/CODH.htm)



" CODH remains notably the most efficient catalyst for this reduction " (*J. Am. Chem. Soc.* **2003**, *125*, 14688)

< Early example >

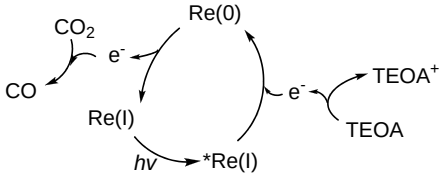
> $Re(I)(CO)_3$ acts both as photosensitizer and as reduction catalyst

$Re(I)(bpy)(CO)_3Cl$ (8.7×10^{-4} M)
1 atm CO_2, in DMF-TEOA($(HOCH_2CH_2)_3N$) (5:1)
250W halogen lamp, >400nm, 4h
TON_{CO} 30 quantum yield ?

J-M. Lehn et al. (*J. C. S. Chem. Commun.* **1983**, 536)

- efficient genaration of CO, no dectable amount of H_2 (H_2 was formed in the absence of CO_2)
- the activity of the system decreases slowly with time (due to labilization of ligand species)

(supposed cycle)



cf) TEOA → $TEOA^+ + e^-$ (E^0 =ca. +0.8V)
*$[Re(I)(bpy)(CO)_3X] + e^- \rightarrow [Re(0)(bpy)(CO)_3X]^-$ (E^0 = ca. +1.25V)

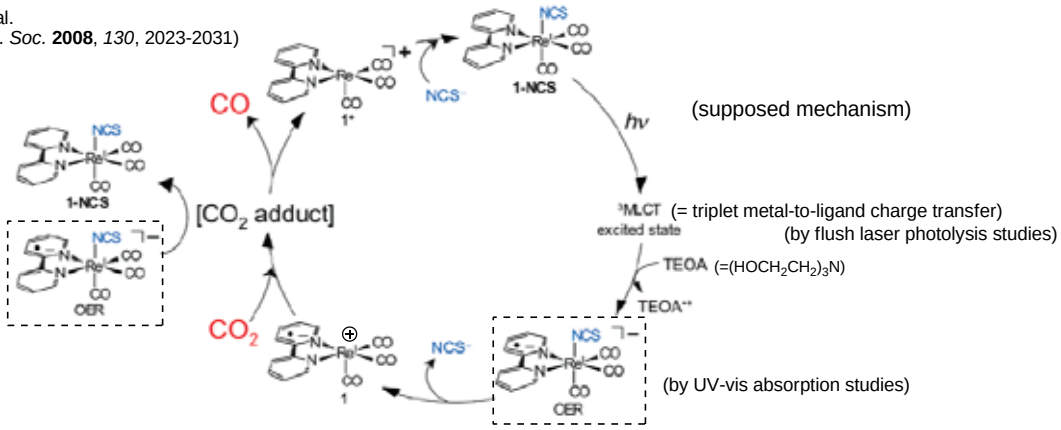
cf2) $[Re(0)(bpy)(CO)_3X]^- \rightarrow [Re(I)(bpy)(CO)_3X] + e^-$ (E^0 = ca. -1.05V)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ (E^0 = -0.76V)

< Recent study >

Re(0) ⇨ OER (one-electron-reduced species)

(a) capturing CO_2 after loss of the monodentate ligand (L)
(b) donation of the second electron to CO_2 by another OER without loss of L.

O. Ishitani et al.
(*J. Am. Chem. Soc.* **2008**, *130*, 2023-2031)



> So far, the most efficient homogeneous photocatalyst

$[Re(I)(bpy)(CO)_3(CH_3CN)]^+$ / $[Re(I)\{4,4'\text{-}(MeO)_2bpy\}(CO)_3\{P(OEt)_3\}]^+$ = (1 : 25)

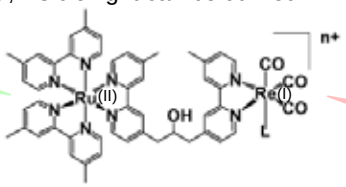
(as catalyst)
- easy L dissociation
- by itself
  low photocatalytic activity

(as photosensitizer)
- very high Φ for OER
- OER has enough reduction power for [Re(I)-CH3CN]+ (to make **1**)

Φ = 0.59 *at 365nm*
in DMF-TEOA (5:1)

> For CO_2 to CO, visible-light can be utilized

visible light active photosensitizer



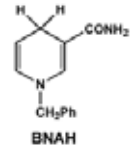
catalyst

O. Ishitani et al. (*Photochem. Photobiol. Sci.* **2007,** *6,* 454)

L = Cl⁻ [Ru-ReCl]2+
= P(OEt)3 [Ru-ReP(OEt)3]3+
= py [Ru-Repy]3+

Φ = 0.12, TN_{CO} = 160
Φ = 0.21, TN_{CO} = 232

catalyst (5 × 10⁻⁵ M)
Hg lamp ***(>500nm)***
DMF-TEOA (5:1)
BNAH (0.1M) as reducing reagent for Ru



< Other report for CO_2 to CO >

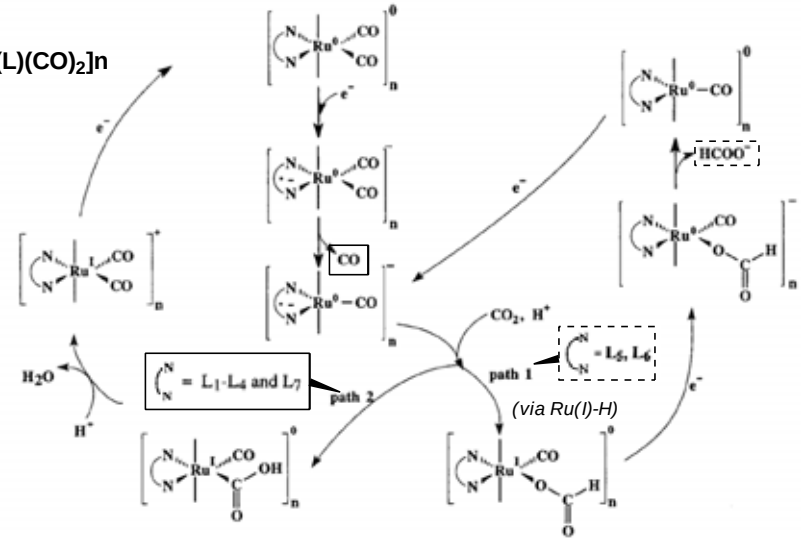
- stoichio --- Fe(I)
- electrochemical --- Ni, di-Pd, Ru, Re
- chemical --- (Cu(I)NHC + B-B), (Met + H_2) etc...

3-3. Other Reduction

> CO_2 to HCOOH ($2e^-$ reduction) selectively

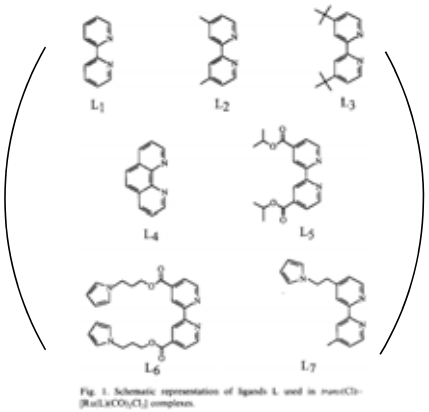
--- a few examples

Scheme 10. Ligand-Dependent Pathways for the Catalytic Reduction of CO_2



electrochemical reduction
at carbon electrodes modified by films of $[Ru(0)(L)(CO)_2]n$

A. Deronzier et al. (*J. Electroanal. Chem.* **1998,** *444,* 253)



> CO_2 to formaldehyde, methanol, methane selectively --- very rare ***next challenge***

4. Integrated System { energy uptake oxi./red. reaciton by hν / H_2O as electron source

4-1. semiconductor material

> originally repoted by Honda and Fujishima

TiO_2 (λ= 380~413 nm)

Nature (1972) 238, 37-38

Electrochemical Photolysis of Water at a Semiconductor Electrode

Akira Fujishima, Kenichi Honda

> many efforts toward improvemnts of semiconductor materials *"one step mechanism"*

> first example of water splitting under **visible light (λ> 420 nm)** *"two step mechanism"* *"artificial Z scheme"*

Stoichiometric water splitting into H_2 and O_2 using a mixture of two different photocatalysts and an IO_3^-/I^- shuttle redox mediator under visible light irradiation K. Sayama, H. Arakawa et al. (*Chem. Comm.* **2001**, 2416.)

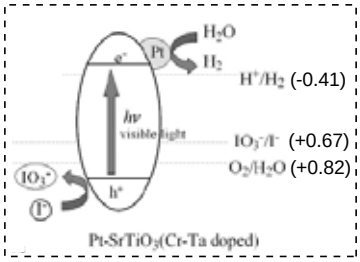
Review (*表面科学* **2003**, *24*, 19.)

@ finding appropriate reversible electron donor (I^-) is important

$6H^+ + 6e^- \rightarrow 3H_2$ (E^0 = - 0.41 V) (pH = 7)

$I^- + 6OH^- + 6h^+ \rightarrow IO_3^- + 3H_2O$ (E^0 = + 0.67 V) (pH = 7)

< red. >



- Pt-loaded $SrTiO_3$(Cr-Ta doped) is best.
  - Pt is co-catalyst
  - no oxidation of H_2O (only oxidation of I^-)
- The initial rate of H_2 evolution was 0.8 μmol h^{-1} but the evolution rate decreased gradually and stopped after 20 h ***(Fig. 1(a))***.
  - Activity was recovered by replacing rxn. solution with a new NaI
  - H_2 formation was significantly suppressed (< 0.1 μmol h^{-1}) when a small amount of $NaIO_3$ (0.1 mmol l^{-1}) was added

⇨ ***accumulation of IO_3^- inhibits H^+ reduction (due to competitive IO_3^- reduction on Pt (?))***

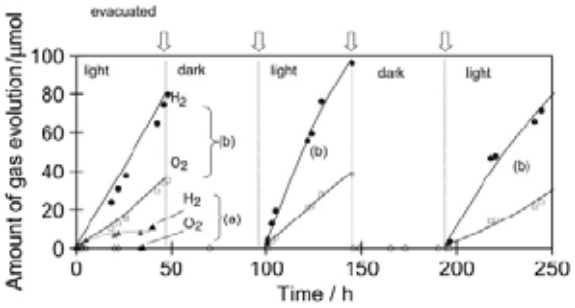
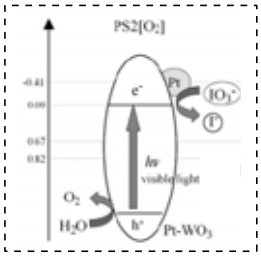


Fig. 1 Reaction time course of the photocatalytic splitting of water into H_2 and O_2 under visible light (λ > 420 nm, 3.1 W, window area: 16 cm^2). (a) 0.2 g of Pt(0.3 wt%)-$SrTiO_3$ doped with Cr and Ta (both 1 mol% of Ti) was suspended in the NaI aqueous reaction solution (100 mmol l^{-1}, 250 ml, pH = 7.0). (b) Both 0.2 g of Pt(0.3 wt%)-$SrTiO_3$ doped with Cr and Ta (both 1 mol% of Ti) and 0.2 g of Pt(1 wt%)-WO_3 were suspended in the NaI aqueous reaction solution (100 mmol l^{-1}, 250 ml, pH = 7.0). The magnetic stirring was continued during the light irradiation and in the dark.

< oxi. >



$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$ (E^0 = + 0.67 V) (pH = 7)

$6OH^- + 6h^+ \rightarrow {}^3/_2O_2 + 3H_2O$ (E^0 = + 0.82 V) (pH = 7)

- Pt loaded WO_3 is best.
  - no reduction of H_2O (only reduction of IO_3^-)
- I^- oxidation by h^+ in the valence band was very slow.

< mixing both catalyst >

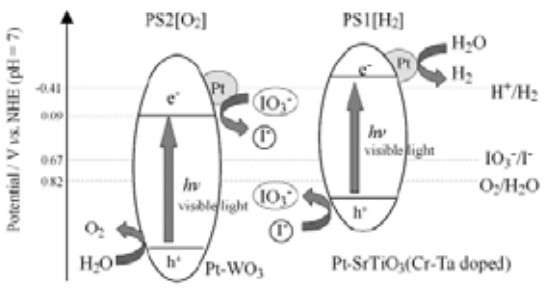


Fig. 2 Speculated reaction mechanism for the water splitting using a mixture of Pt-$SrTiO_3$, Pt-WO_3 and NaI aqueous solution.

- H_2 and O_2 gases evolved under visible light (>440nm) ***(Fig.1(B))***
- stoichiometric water splitting more than 250 h.
- added Pt-WO_3 effectively eliminated the IO_3- ion by reduction to I-
  - concentration of I^- (100 mmol l^{-1}) did not change
  - formation of the IO_3^- was negligible

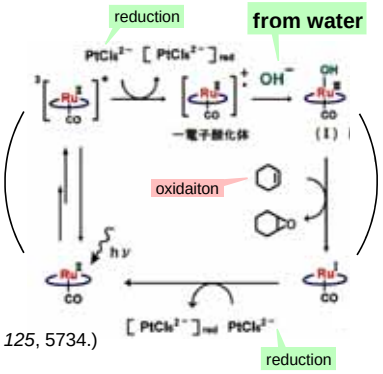
(merit)
- 2回に分けて励起 **(ΔGが少なくて済む)**
- 組み合わせが可能

(drawback)
- 4hv / 2e- / H_2
- low efficiency quantum efficiency ~0.1% (420.7 nm)

4-2. Homogeneous Catalyst System

水を電子源とする光による二酸化炭素還元系の構築をめざし金属ポルフィリンと二酸化炭素還元能を有するレニウム錯体の連結系分子を新たに合成しその光化学挙動について検討した。（図 １８）
金属ポルフィリンへのS2励起により、ポルフィリンからレニウム錯体への電子移動に続いて二酸化炭素還元による一酸化炭素の生成に成功した。

quantum yield ?
TON ?



H. Inoue et al.
(*J. Am. Chem. Soc.* **2003**, *125*, 5734.)

O. Ishitani et al. (CREST H17 report)

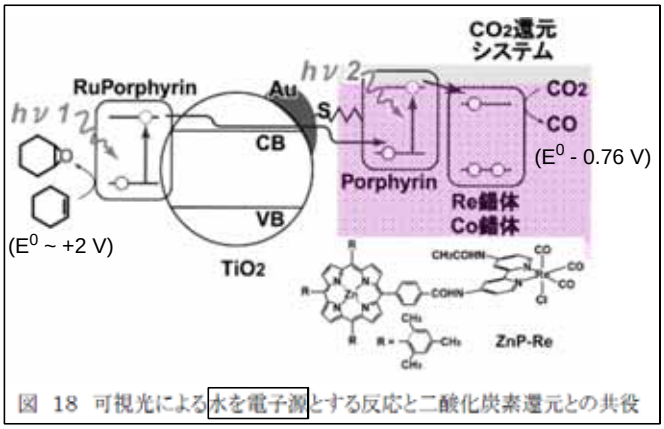


図 18 可視光による水を電子源とする反応と二酸化炭素還元との共役

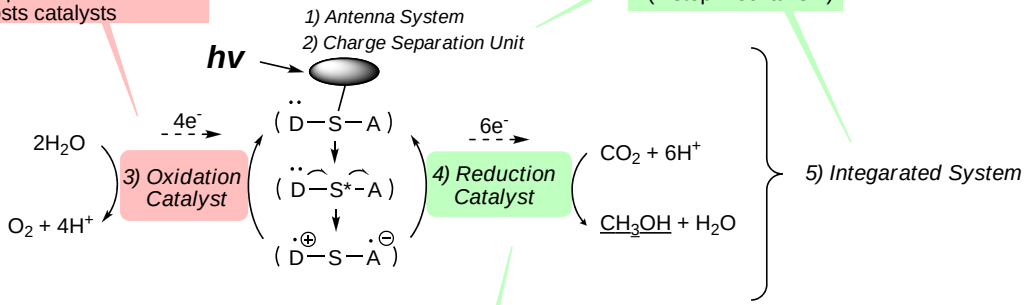
homogeneous, integrated system for H_2O oxidation / XXX reduction is very rare.
big challenge in future

@ Future Challenge ~ from molecular catalyst field

semiconductor is more practical (?)

* Photoinduced system
* New approaches
* Low costs catalysts

• arificial Z scheme
(2 step mechanism)



* reduce CO_2 by 4 or 6 or 8 electrons with high selectivity
* New approaches
* Low costs catalysts

semiconductor ?
heterogeneous catalyst ? } *in gas phase*