



COLLÈGE
DE FRANCE
—1530—

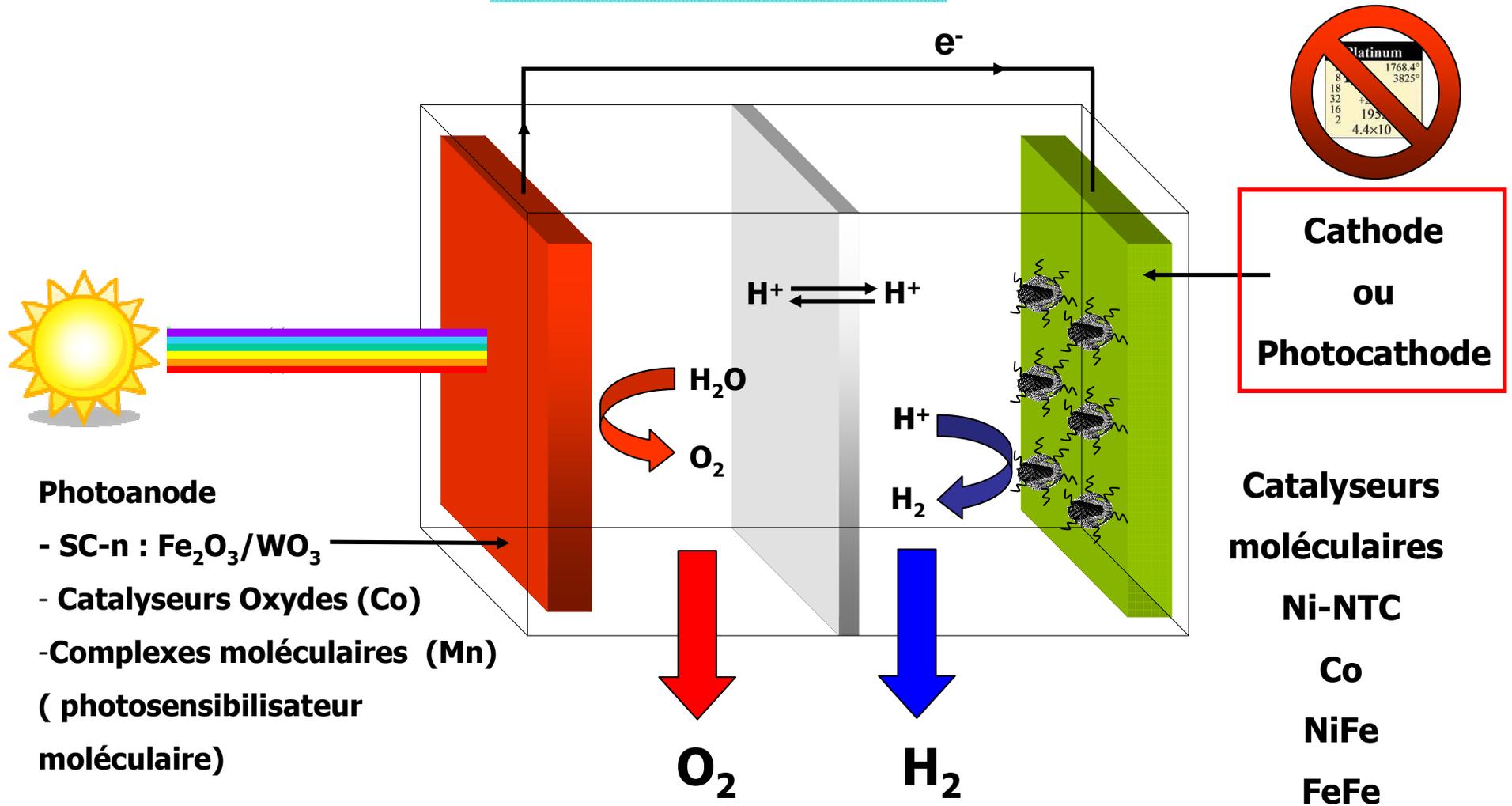
Nouveaux développements vers la photo-oxydation de l'eau en oxygène

Marc Fontecave

*Laboratoire de Chimie et Biologie des Métaux, Université Joseph Fourier, CNRS, CEA/DSV/iRTSV
CEA-Grenoble 17 rue des martyrs 38054 Grenoble cedex 9, France
mfontecave@cea.fr; Phone: (0033)438789103 ; Fax: (0033)438789124*

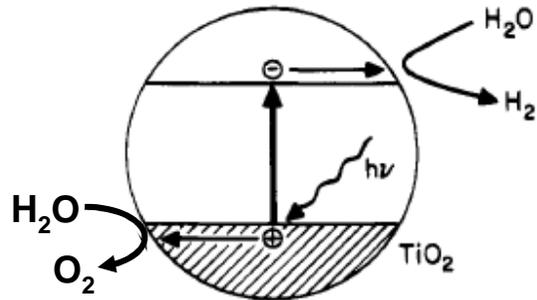
Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05

Photolyse de l'eau: Vers une nouvelle classe de photolyseurs



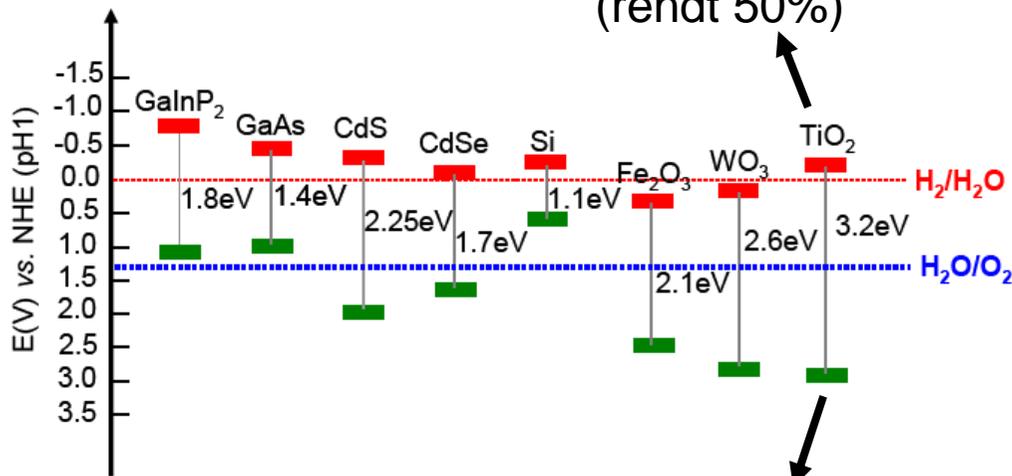
1972: Fujishima A. and Honda K. *Nature* 238 37
 Photolyse de l'eau via le SC TiO₂ (rendt <3%)

VERROUS:

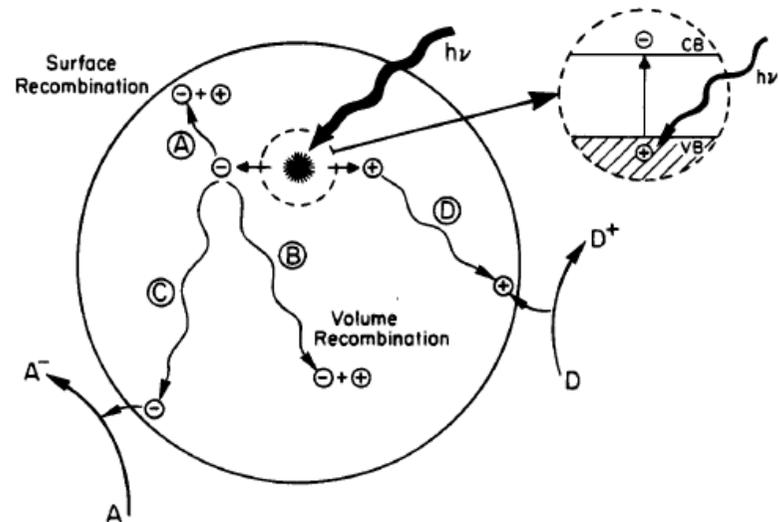


1. Il faut des matériaux absorbant la lumière visible
2. Dans ce cas, ils ne peuvent pas à la fois réduire et oxyder H₂O
3. Il faut des catalyseurs (sans métaux nobles)
4. Pour optimiser les rendements limiter les recombinaisons de charge

Pb 1
 Irradiation UV uniquement
 (rendt 50%)



Pb 2
 Cinétique/catalyse



Former un « trou » pour oxyder l'eau → Oxydes métalliques semiconducteurs (TiO₂, WO₃, Fe₂O₃)

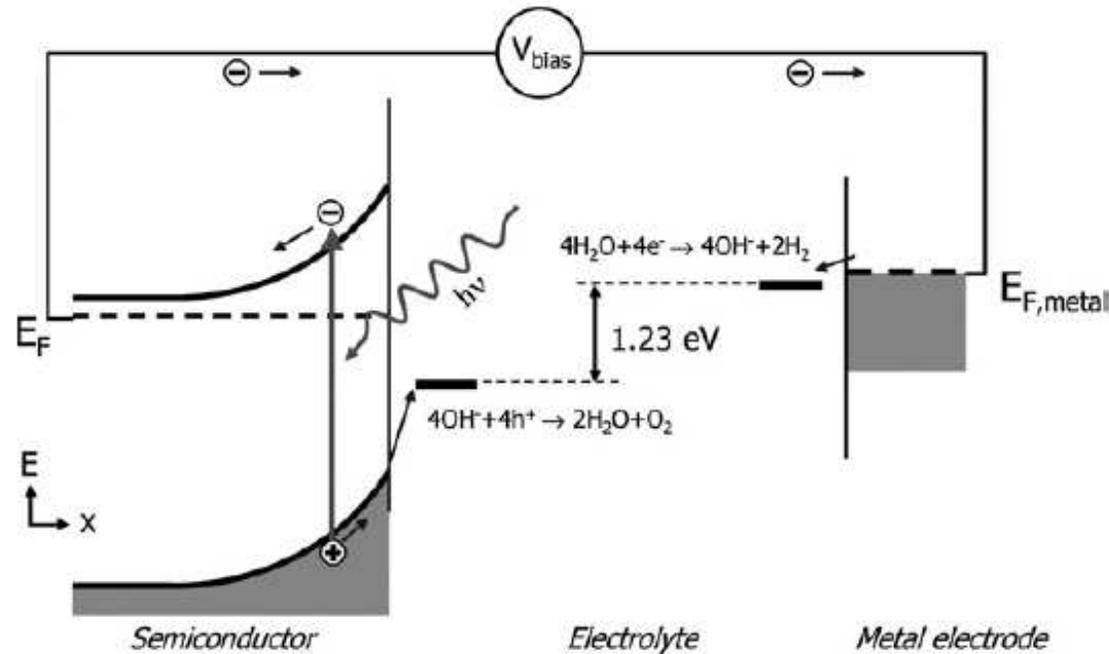


Fig. 1 Energy diagram of a PEC cell for the photo-electrolysis of water. The cell is based on an n-type semiconducting photo-anode.

Cahier des charges pour les matériaux de photoélectrodes:

- Absorption dans le visible
- Stabilité à la lumière
- Énergies des bandes de valence et de conduction adaptées
- Transport des charges dans le semiconducteur efficace
- Faibles surtensions
- Faibles coûts

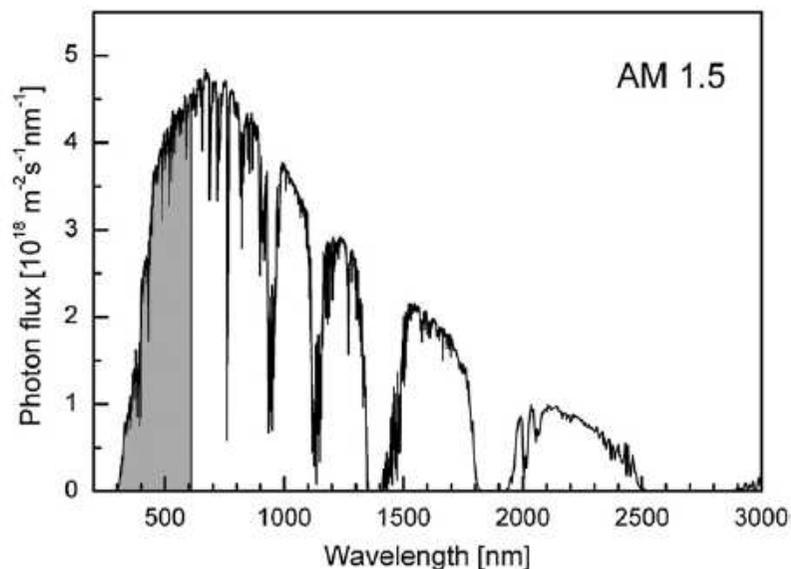


Fig. 2 Intensity of sunlight *versus* wavelength for AM1.5 conditions. The grey area represents the part of the spectrum that can be absorbed by a hypothetically ideal bandgap of 2.03 eV.⁷

➔ **3.1 eV > SC « gap » > 1.9 eV** (0.3 eV pertes thermodynamiques + 0.4 eV surtensions cinétiques) = 1.23 + 0.3 + 0.4
 3.1 eV = 400 nm; 1.9 eV = 650 nm

➔ Efficacité de conversion (énergie H₂/énergie solaire)

$$\eta_{\text{STH}} = \frac{j(V_{\text{redox}} - V_{\text{B}})}{P_{\text{light}}}$$

- j densité de photocourant (Am⁻²)
- P_{light} intensité de lumière incidente (Wm⁻²)
- $V_{\text{redox}} = 1,23\text{V}$
- V_{B} potentiel supplémentaire nécessaire (bias)

$\eta_{\text{STH}}^{\text{max}} = 16.8 \%$ (gap=2.03 eV) *Int. J. Hydr. En. 2006* 31 1999

TiO₂

Avantages:

- Ti 3^{ème} élément le + abondant
- Très utilisé en photocatalyse (synthèse, désinfection,....)
- Production: 5,5 millions de tonnes
- Toxicité limitée
- peu de photocorrosion (peu de réaction h⁺/O²⁻ de la matrice solide)

Inconvénients:

- Cinétiques de réaction faibles (cata)
- Absorption UV (6% spectre solaire)
- faibles rendements (< qq %)

Table 1 Overview of particle-based photo-catalyst systems reported in the literature that are able to split water in stoichiometric ratios

Photo-catalyst	Co-catalyst	Lamp, electrolyte ^a	Efficiency (solar-to-hydrogen)	Stability	Absorption
<i>Single particle systems:</i>					
M ₂ Sb ₂ O ₇ M=Ca, Sr	RuO ₂	L1	—	>4 h	UV
NaTaO ₃	NiO	L2, 10 ⁻³ M NaOH	20% @ 270 nm	>14 h	UV
BaIn _{0.5} Nb _{0.5} O ₃	NiO _x	L3	—	>40 h	UV/VIS
In _{0.9} Ni _{0.1} TaO ₄	NiO _x	L3	0.66% @ >420 nm	>120 h	UV/VIS
(Ga _{1-x} Zn _x)(N _{1-x} O _x)	Cr-Rh oxide	L2/L3, pH 4.5 (H ₂ SO ₄)	2.5% @ 420 nm	>35 h	UV/VIS
TiSi ₂	TiO ₂ /SiO ₂	350 or 540 nm lamps, spectral width ±60 nm	3.9% @ 540 nm	>1000 h	UV/VIS
<i>Layered materials:</i>					
Ba:La ₂ TiO ₇	NiO	L2, >12 mM NaOH	50% in UV	—	UV
Sr ₂ Ta ₂ O ₇	NiO	L3	12% @ 270 nm	>20 h	UV
<i>Composite particles:</i>					
Zn:Lu ₂ O ₃ /Ga ₂ O ₃	NiO	L2	—	>220 h	UV
Cr:Ba ₂ In ₂ O ₅ :In ₂ O ₃	NiO _x	L2	4.2% @320 nm	>400 h	UV
<i>Particle mixtures, Z-scheme:</i>					
WO ₃ /(Ca,Ta):SrTiO ₃	Pt/Pt	L3, 100 mM NaI	0.1% @ 420 nm	>250 h	UV/VIS
an-TiO ₂ /ru-TiO ₂	Pt/Pt	L2, 0.1 M NaI, pH 11	—	>100 h	UV

H₂O

^a L1 = 200 W Hg-Xe; L2 = 400–500 W high pressure Hg; L3 = 300 W Xe.

Fe₂O₃ matériau « idéal » pour une photoanode

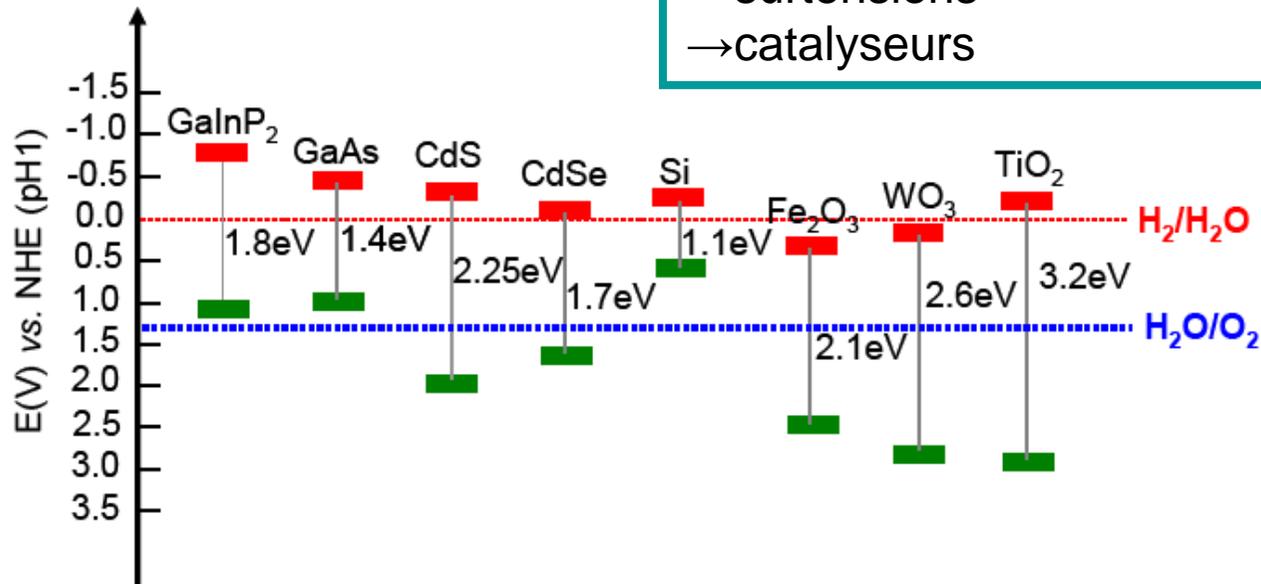
Avantages:

- Fe 2^{ème} élément le + abondant
- Absorption visible (2,1 eV=539 nm)
- Stabilité

Inconvénients:

- Énergie de la BC trop faible
- Faible efficacité (<5-20%)
- ×faible réactivité des « trous » en surface
- ×diffusion des « trous » lente (qq nm; 10⁻¹cm²V⁻¹s⁻¹)

- surtensions
- catalyseurs

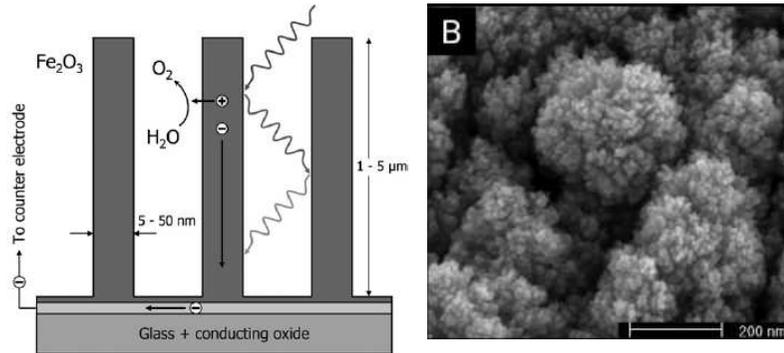


Fe₂O₃ photoanode

➔ Dopage (Nb, SiO₂, ...); rendt: 35-40%

➔ Nanostructuration des électrodes (Grätzel)

JACS 2006 128 15714



- Nanostructure dendritique
- Dopage SiO₂
- Dépôt de Co(II)

2,7 mA.cm⁻² à 1,23 V(ENH)
Rendt: **42%** (370 nm; 1,23V)

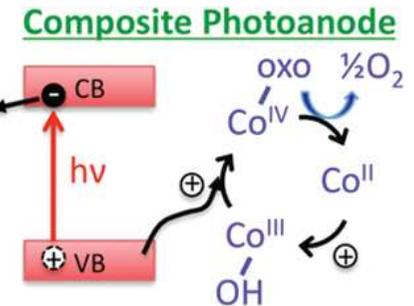
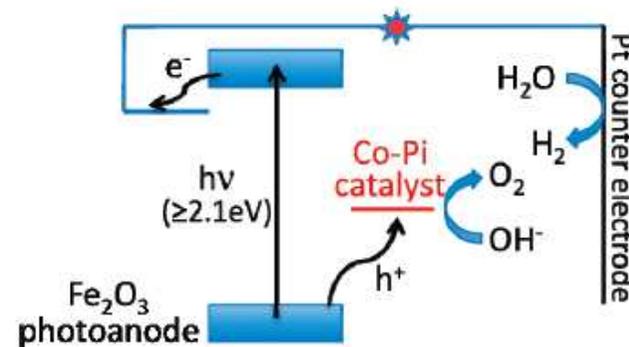
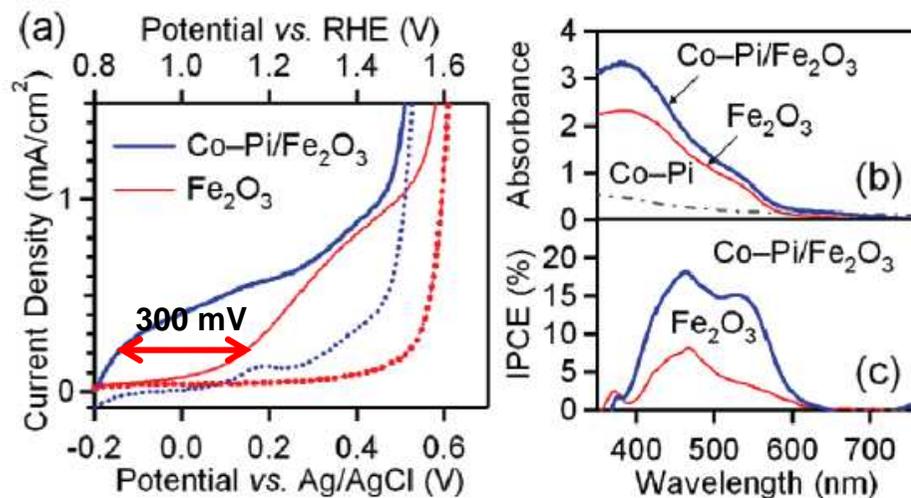


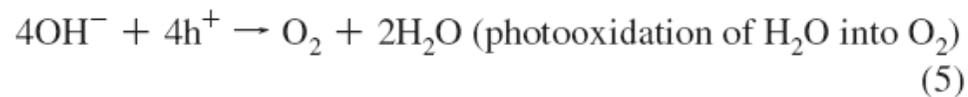
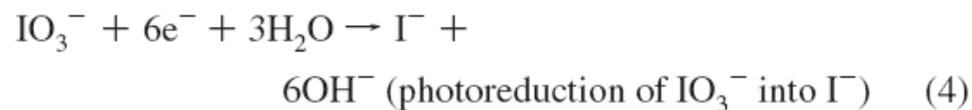
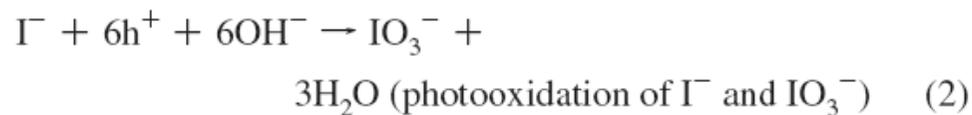
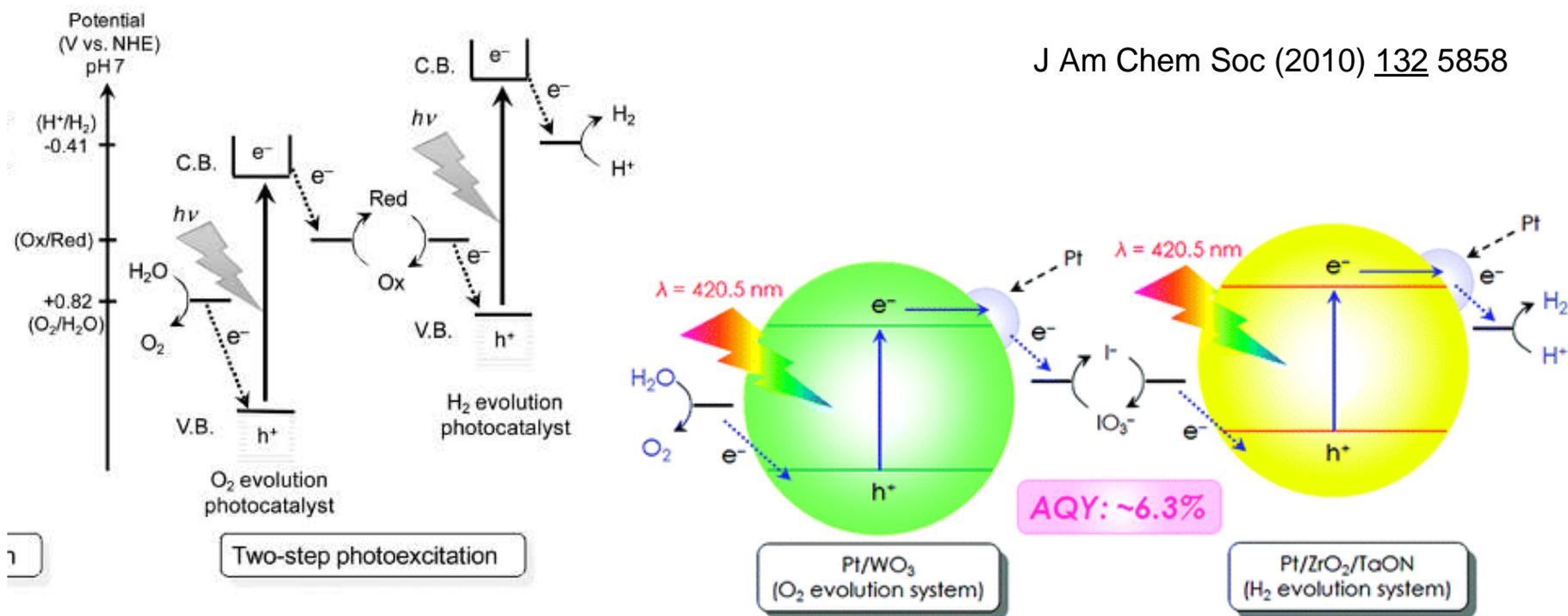
Fig. 7 Optimized morphology for an α -Fe₂O₃ photo-anode for water splitting. The small diameter of the nanowires ensures short hole diffusion path lengths.

➔ Catalyseurs (Co...) JACS 2009 131 6086



Photoanode WO₃

J Am Chem Soc (2010) 132 5858



entry	cocatalyst (loading/wt %)	loading method	activity ^b /μmol h ⁻¹		
			H ₂	O ₂	H ₂ /O ₂ ratio
1	none		<0.2	0	
2	Ru (1.0)	impregnation	9.8	4.2	2.33
3	Rh (1.0)	impregnation	8.5	2.6	3.27
4	Pd (1.0)	impregnation	3.3	1.0	3.30
5	Ir (1.0)	impregnation	28.4	12.1	2.35
6	Pt (1.0)	impregnation	52.1	26.7	1.95
7	Au (1.0)	impregnation	2.3	trace	
8	Pt (1.0)	photodeposition	6.0	2.0	3.00
9	Pt (0.1)	impregnation	6.1	2.3	2.62
10	Pt (0.5)	impregnation	41.3	21.4	1.93
11	Pt (2.0)	impregnation	25.2	12.1	2.09
12	Pt (3.0)	impregnation	25.1	12.4	2.03

^a Reaction conditions: catalyst, 100 mg of Pt/WO₃ and 50 mg of Pt/ZrO₂/TaON; aqueous NaI solution, 100 mL (1.0 mM); light source, xenon lamp (300 W) fitted with a cold mirror (CM-1); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, 350 < λ < 800 nm.

^b Average rates of gas evolution in 5 h.

entry	catalyst	reactant soln	activity ^b /μmol	
			H ₂	O ₂
1	Pt/ZrO ₂ /TaON + Pt/WO ₃	NaI	260	133
2	Pt/ZrO ₂ /TaON + Pt/WO ₃	FeCl ₂	0.9	0
3	Pt/ZrO ₂ /TaON + BiVO ₄	FeCl ₂	1.0	0
4	Pt/ZrO ₂ /TaON + BiVO ₄	FeCl ₃	0.7	42.4
5	Pt/ZrO ₂ /TaON + TiO ₂ rutile	NaI	59.5	28.9
6 ^c	Pt/ZrO ₂ /TaON + RuO ₂ /TaON	NaI	22.0	8.8
7	Pt/ZrO ₂ /TaON + BiVO ₄	NaI	10.9	1.6
8	Pt/ZrO ₂ /TaON	NaI	7.4	0
9	Pt/ZrO ₂ /TaON	FeCl ₂	0.4	0

^a Reaction conditions: catalyst, 50 mg of Pt/ZrO₂/TaON or 100 mg of an O₂ evolution photocatalyst; aqueous solution, 100 mL (1.0 mM); light source, xenon lamp (300 W) fitted with a cold mirror (CM-1); reaction vessel, Pyrex top-irradiation type; irradiation wavelength, 350 < λ < 800 nm. ^b Total amount of gas evolution after 5 h. ^c RuO₂/TaON 50

Pt/WO₃ (O₂)
Pt/ZrO₂/TaON (H₂)
420 nm

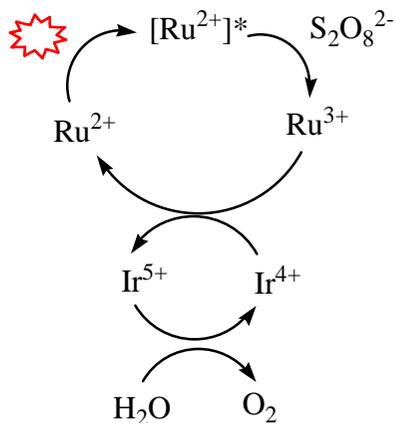
rendt quantique: 6,3 %

Catalyseurs

1. Les catalyseurs doivent opérer le plus près possible du **potentiel de la réaction d'oxydation de l'eau** (rendt énergétique maximal)
2. Les catalyseurs doivent être **stables** (corrosion limitée)



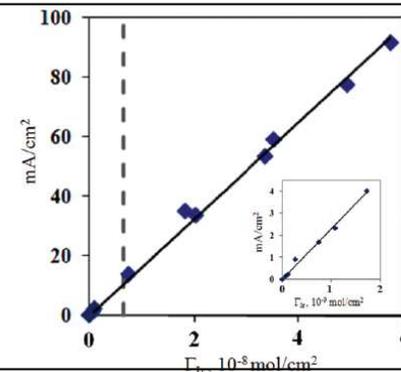
J. Phys Chem C 2004 108 9115



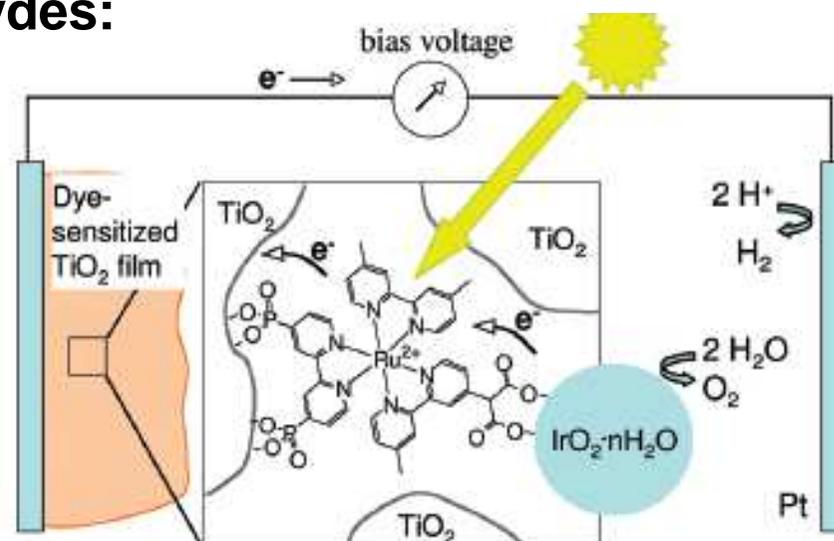
TOF=40 s⁻¹, OV=370mV

J. Phys Chem C 2009 113 12958

Film de nanoparticules IrO₂ sur électrode de C
 TOF= 5-6 s⁻¹, OV=0.25 V pour I = 0.5 mA.cm⁻²
 Rendt:100%; 0.1 A.cm⁻² (1.35 V vs Ag/AgCl)



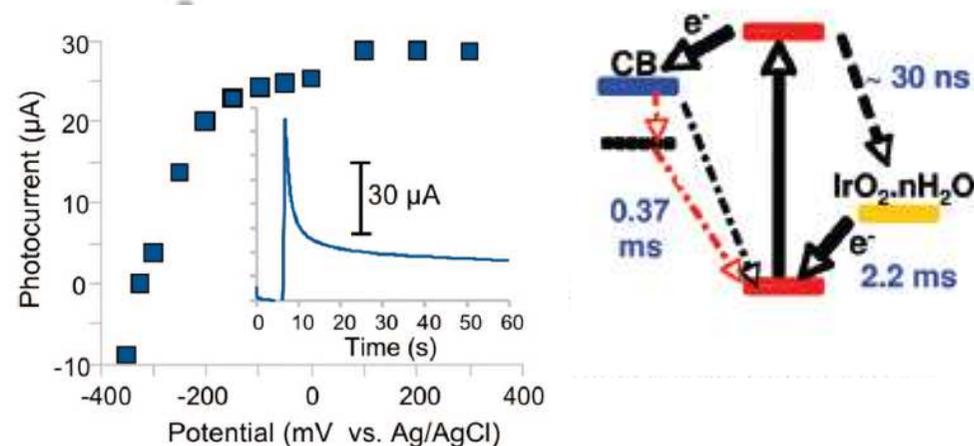
Catalyseurs oxydes: IrO₂



CELLULE PHOTOELECTROCHIMIQUE

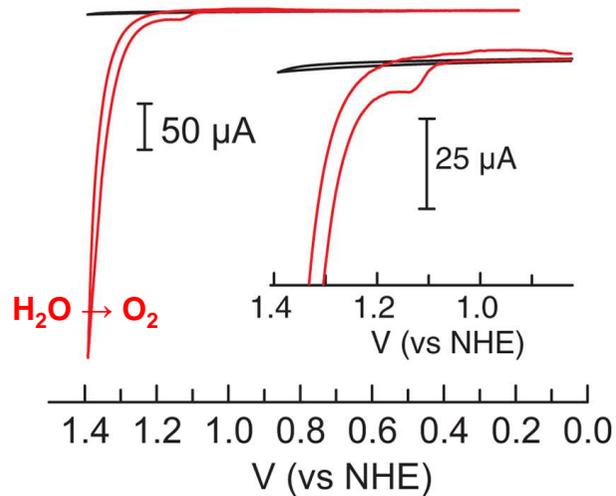
- Photocourant : 10-30 μA (>410 nm, bias > -325 mV vs Ag/AgCl)
- Instabilité du système
- Rendt < 1%

J. Am. Chem. Soc. 2009 131 926



Catalyseurs oxydes: cobalt

D. Nocera, Science 2008 321 1072



Voltammétrie cyclique sels de Co^{2+}
Tampon phosphate, pH 7



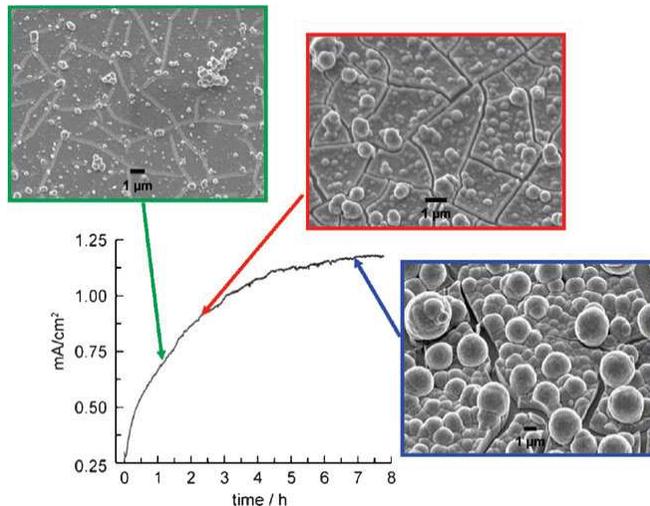
Oxydation de Co^{2+} à 1,13V
Vague catalytique à 1,23 V

Électrolyse (ITO) de sels de Co^{2+}
Tampon phosphate, pH 7, 1,3V



Dépôt de nanoparticules
 $\text{Co}^{3+}(\text{O})(\text{OH})(\text{Pi})$
sur électrode

Dégagement O_2 (marquage isotopique)
Rendt: 100%
Surtensions: 400 mV



Catalyseurs oxydes: cobalt



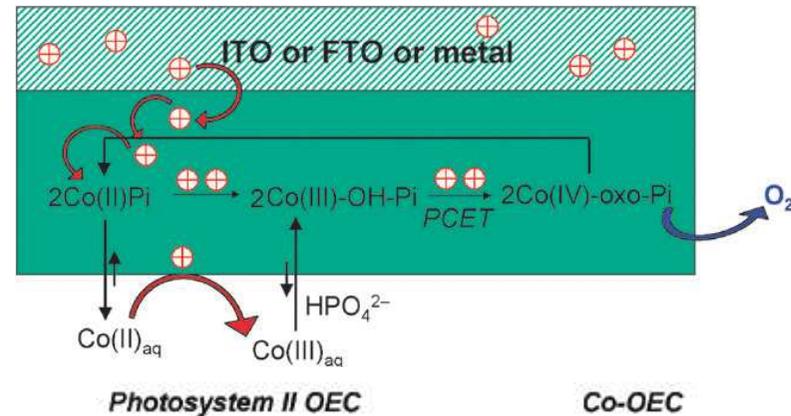
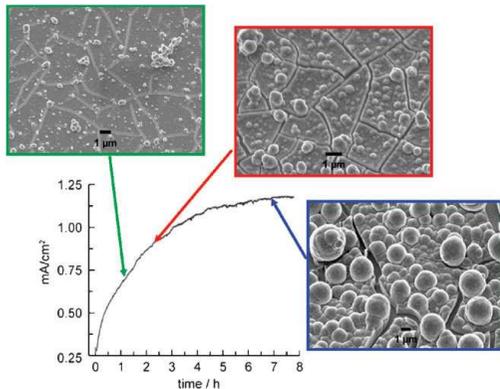
In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺

Matthew W. Kanan, *et al.*
Science 321, 1072 (2008);

D. Nocera (MIT)

D. Nocera *Chem Soc Rev* 2009 38 109

D. Nocera *J. Am. Chem. Soc* 2009 131 3838

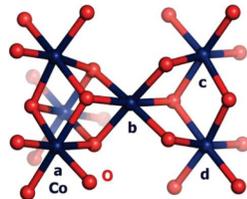


	Photosystem II OEC	Co-OEC
Self-Assembly	earth-abundant metal (Mn) all oxo core self-assembled from water by oxidation of Mn ²⁺ to Mn ³⁺	earth-abundant metal (Co) all oxo framework self-assembled from water by oxidation of Co ²⁺ to Co ³⁺
Repair	D1 protein	HPO ₄ ²⁻ /Co ³⁺ equilibrium
O₂ Generation	from neutral water at 1 atm and RT at low overpotential proton carrier (amino acids)	from neutral water at 1 atm and RT at low overpotential (250 mV) proton carrier (HPO ₄ ²⁻)
Structure	a Mn-oxo cubane d(Mn-Mn) = 2.8 Å d(Mn-O) = 1.9 Å	a Co-oxo cubane d(Co-Co) = 2.8 Å d(Co-O) = 1.9 Å

Électrolyse (ITO) de sels de Co²⁺
Tampon phosphate, pH 7, 1,3V



Dépôt de nanoparticules
Co³⁺(O)(OH)(Pi)
sur électrode



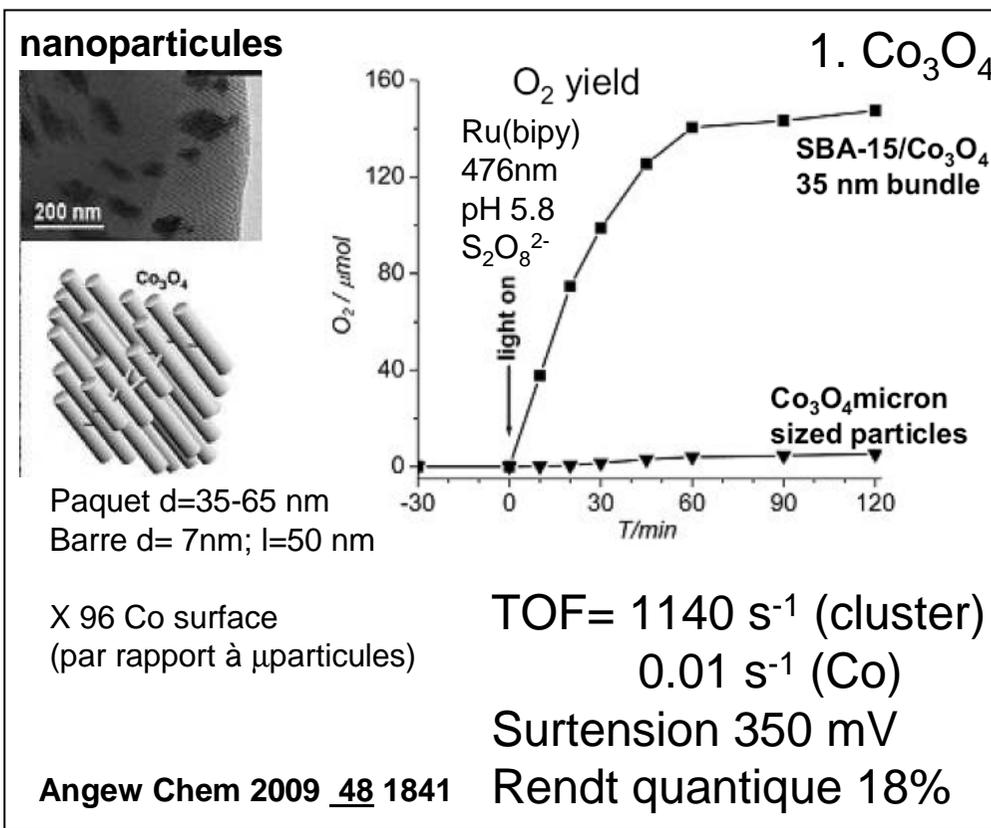
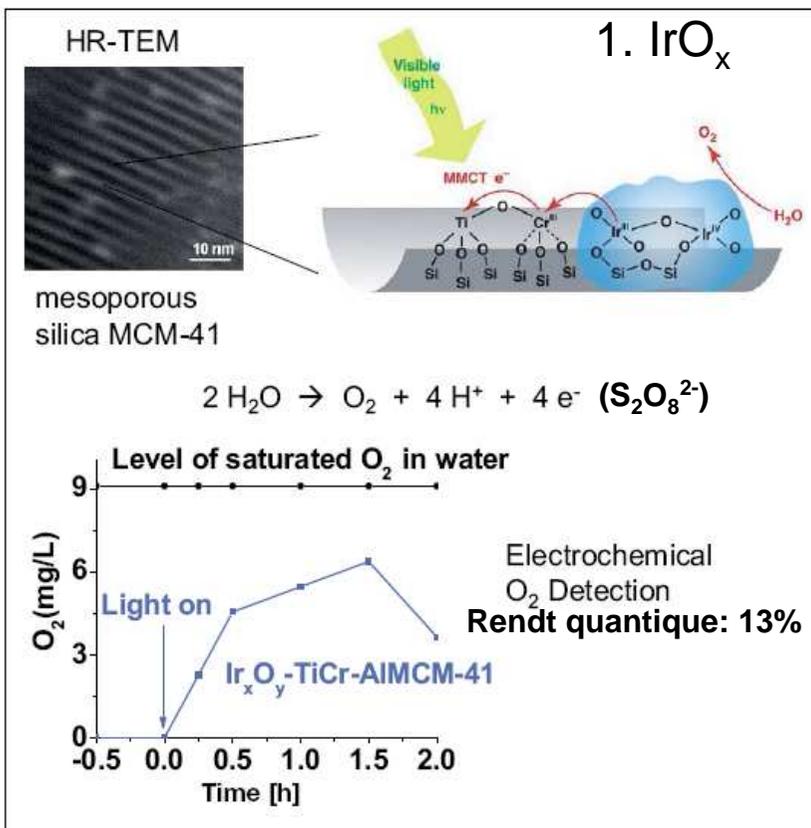
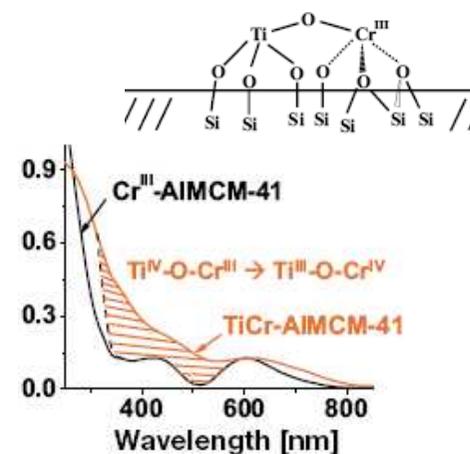
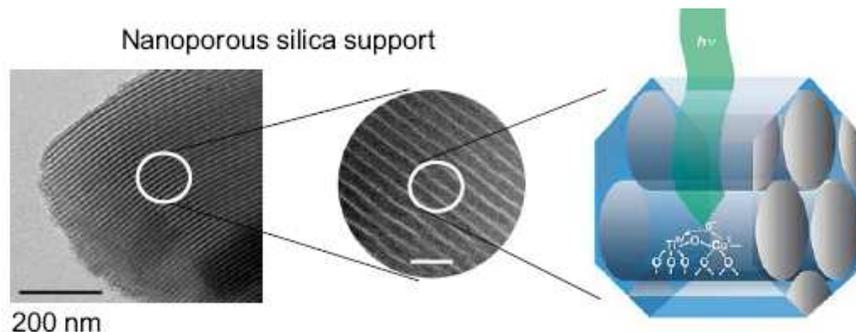
Dau, H *J. Am. Chem. Soc* 2009



H. Frei, LBNL

JACS 2009 131 16589

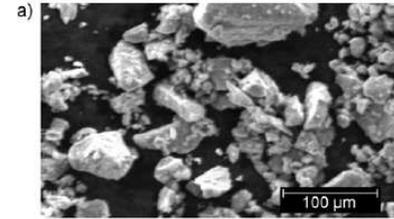
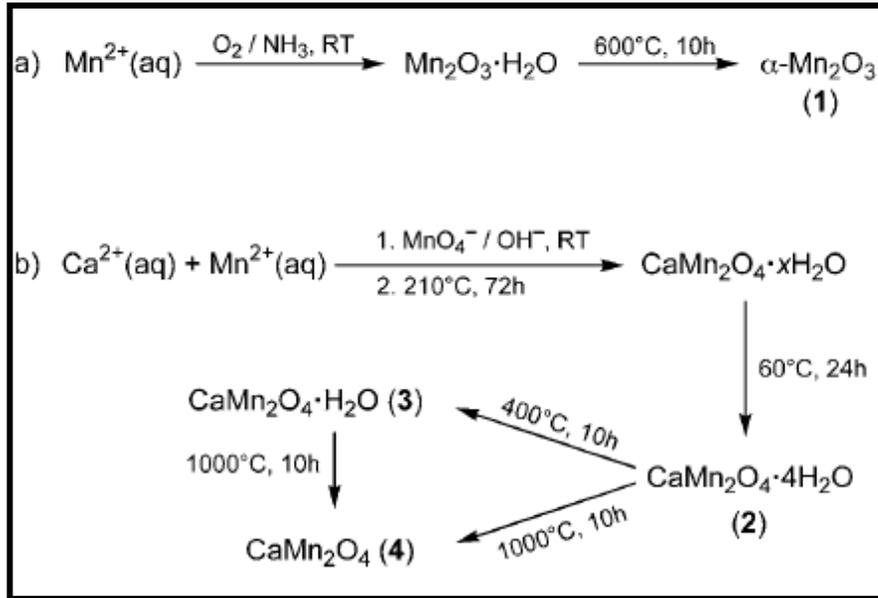
Catalyseurs oxydes: cobalt



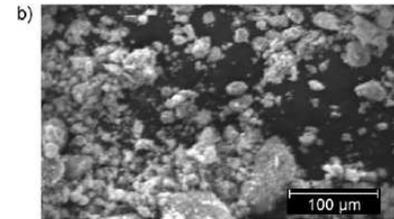
Oxide	TOF (sec ⁻¹) ^a	Overvoltage, ? (mV)	pH	T (°C)	Quantum yield	Ref.	
Co ₃ O ₄	0.035	325	5	RT	58%	[1]	Ru(bipy) + hv + persulfate
Co ₃ O ₄	≥ 0.0025	350	14	30	--	[2]	
Co ₃ O ₄	≥ 0.020	295	14	120	--	[3]	
Co ₃ O ₄	≥ 0.0008	414	14.7	25	--	[4]	
Co ₃ O ₄	≥ 0.006	235	14	25	--	[5]	
Co,P film	≥ 0.0007 ^b	410	7	25	--	[6]	
MnO ₂	≥ 0.013	440	7	30	--	[7]	
Mn ₂ O ₃	0.055	325	5	RT	35%	[1]	Ru(bipy) + hv + persulfate

Catalyseurs oxydes: manganese-Ca

Angew Chem 2010 49 2233

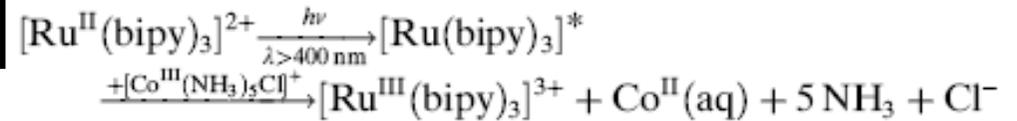


Mn_2O_3

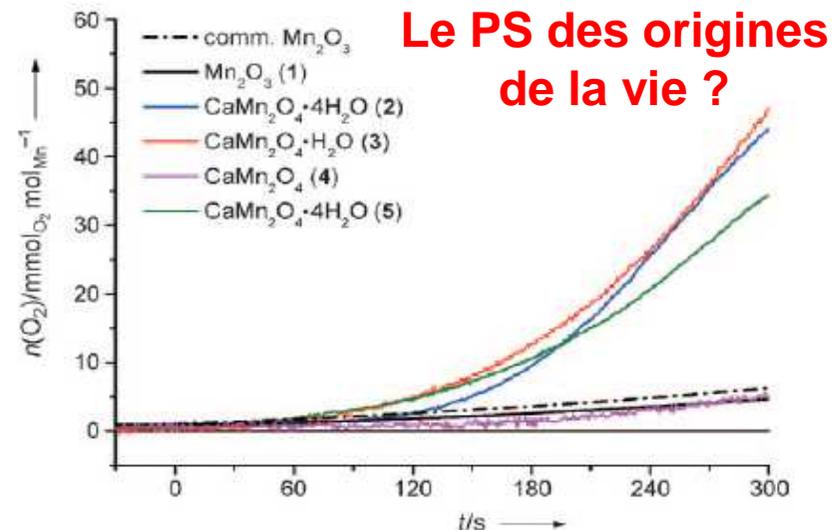
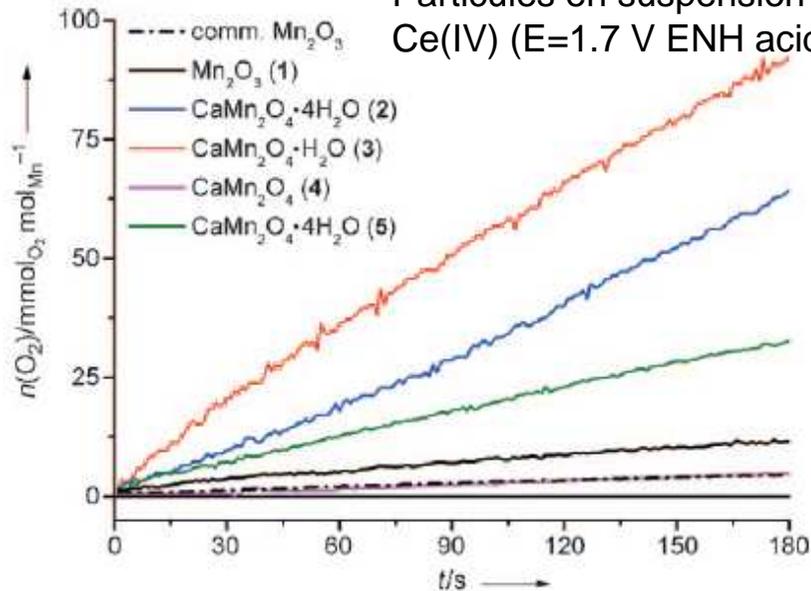


CaMn_2O_4

Photooxydation (Ru + Co + $\lambda > 400\text{nm}$)



Particules en suspension
Ce(IV) ($E = 1.7 \text{ V ENH acide}$)

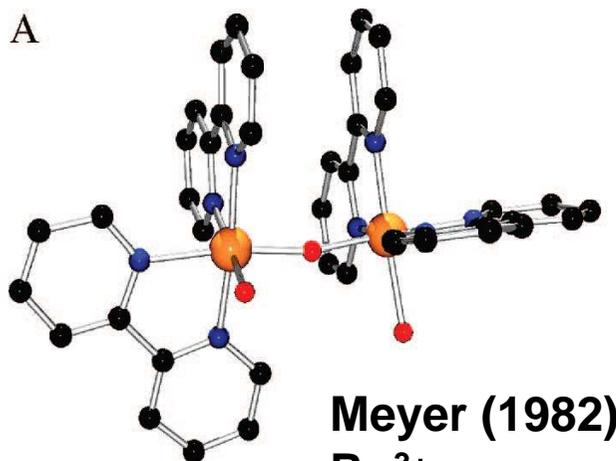


Catalyseurs moléculaires

Complexes binucléaires Ru-X-Ru

Ce⁴⁺: 1,53V (NHE) pH1

A

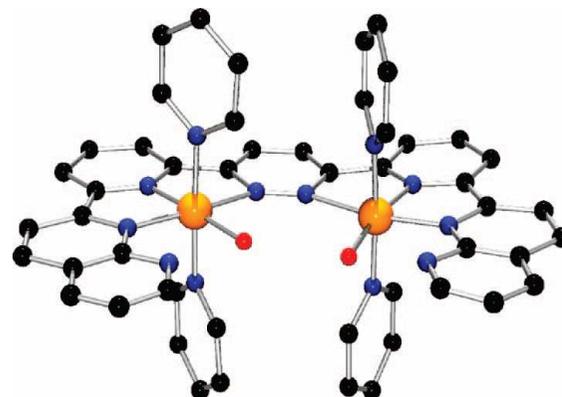


Meyer (1982)

Ru³⁺

X = O

Ce⁴⁺ : 13-70

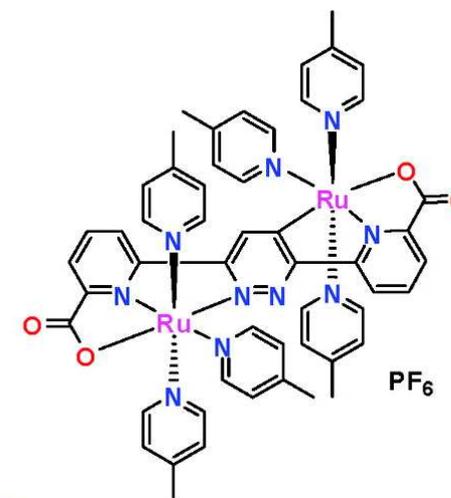


Thummel (2005)

Ru²⁺

X = pyrazole

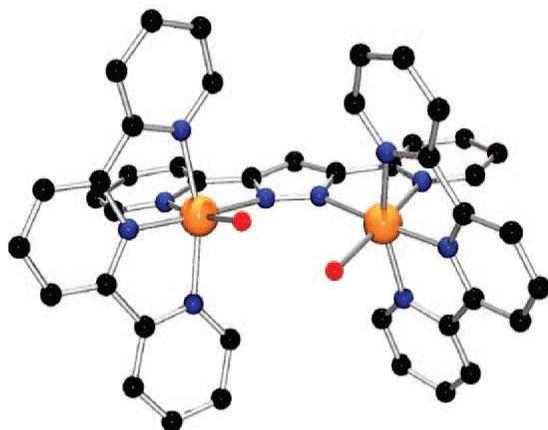
Ce⁴⁺ : 100-500



Sun (2009)

Ru²⁺

Ce⁴⁺ : 1700



Llobet (2004)

Ru²⁺

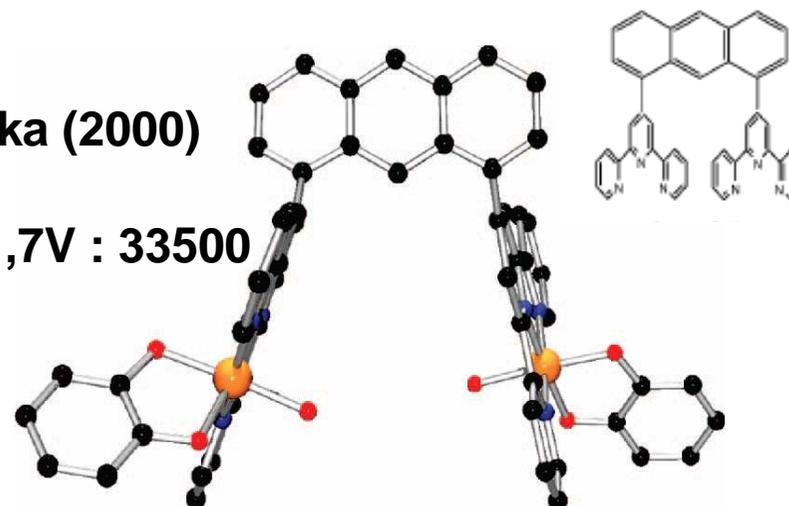
X = pyrazole

Ce⁴⁺ : 18-200

Tanaka (2000)

Ru²⁺

ITO/1,7V : 33500



Divers

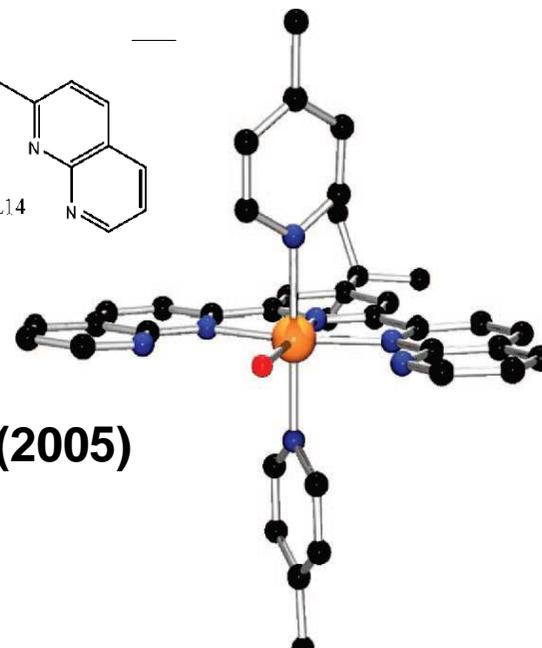
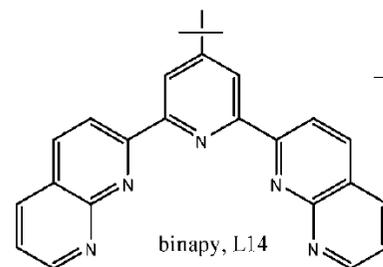
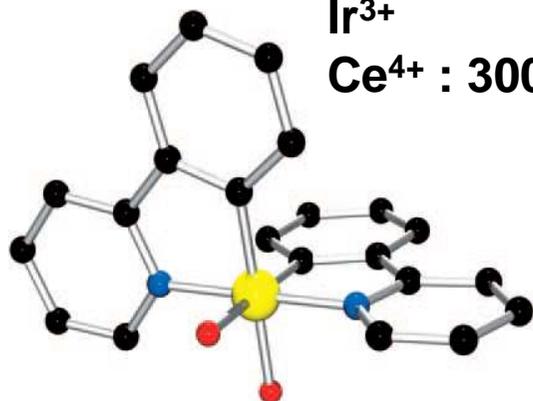
Ru: mononucléaire

Ir: mononucléaire

Bernhard (2007)

Ir³⁺

Ce⁴⁺ : 3000 (jours)

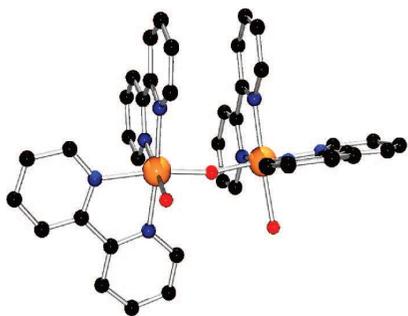


Thummel (2005)

Ru²⁺

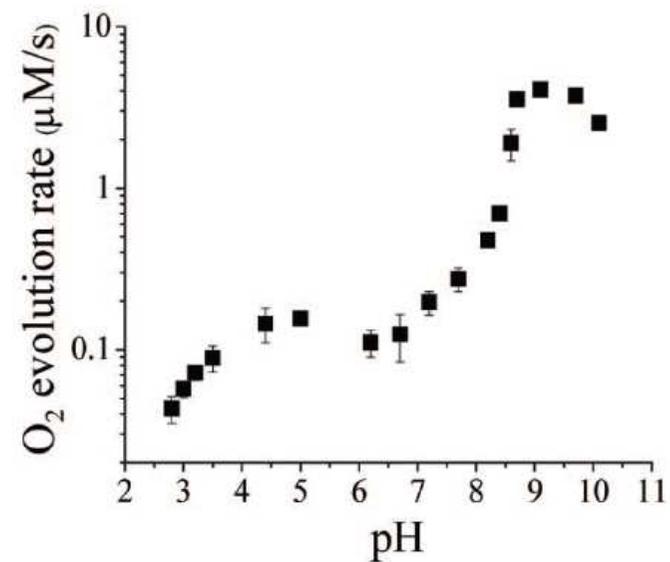
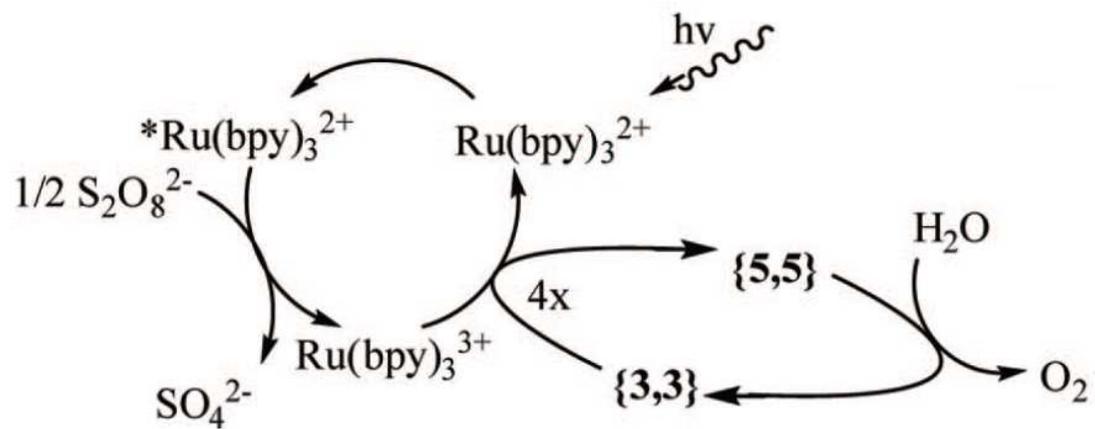
Ce⁴⁺ : 260

Complexe
de Meyer



Photooxydation de l'eau

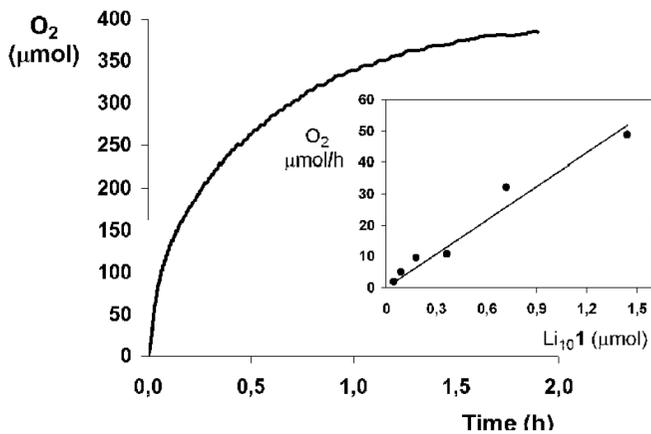
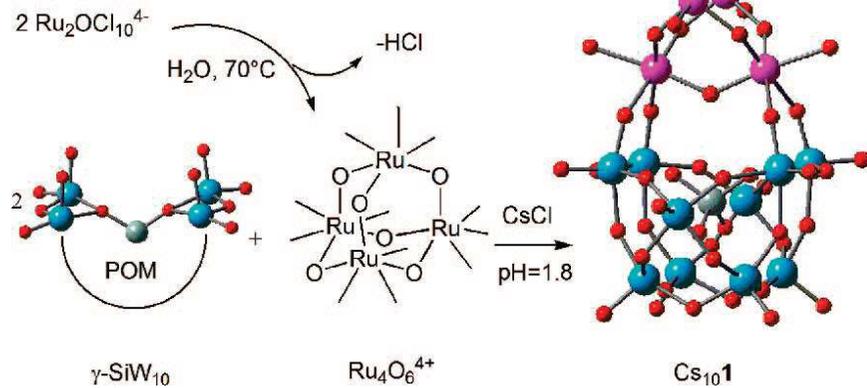
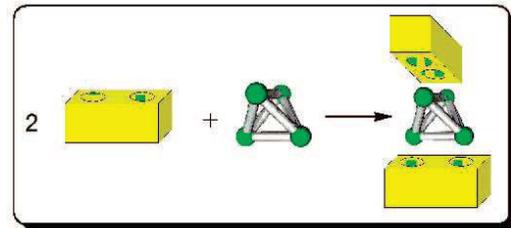
(Hurst, Inorg Chem 2008 47 1753)



Divers

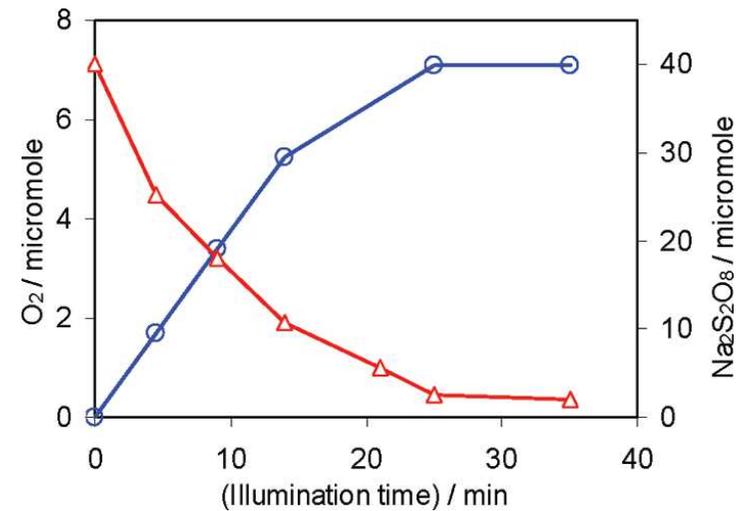
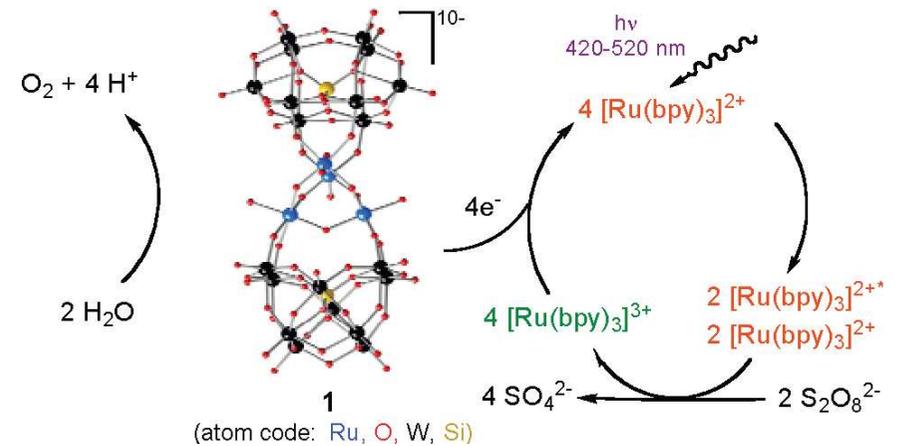
Ru: polyoxométallate

Bonchio, Hill (2008)
 Ce⁴⁺ : 385/90% (2h)



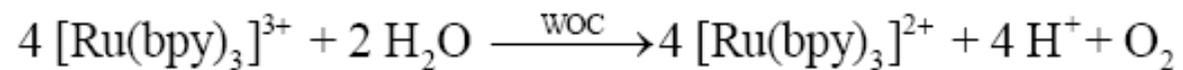
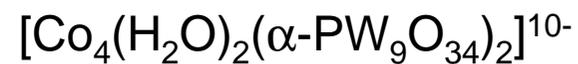
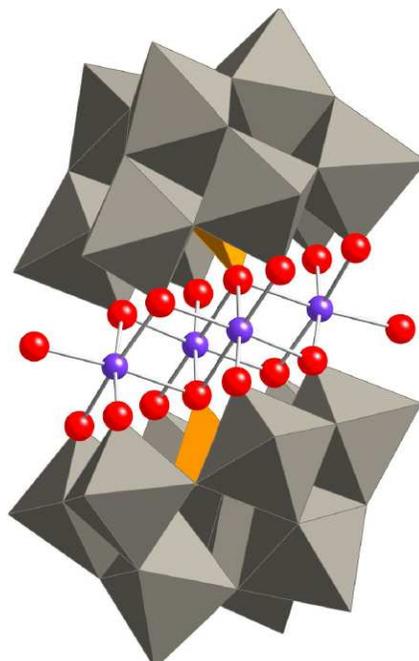
Photooxydation de l'eau

(CL Hill J Am Chem Soc 2009)



Un « oxyde de cobalt » moléculaire

CL Hill, Science 2010



Rendt = 65%

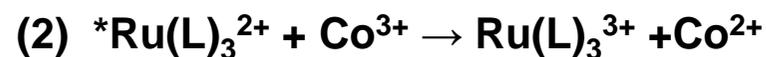
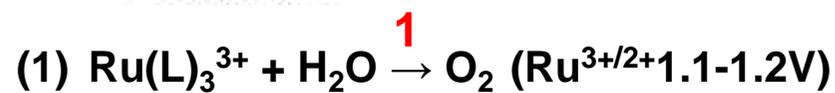
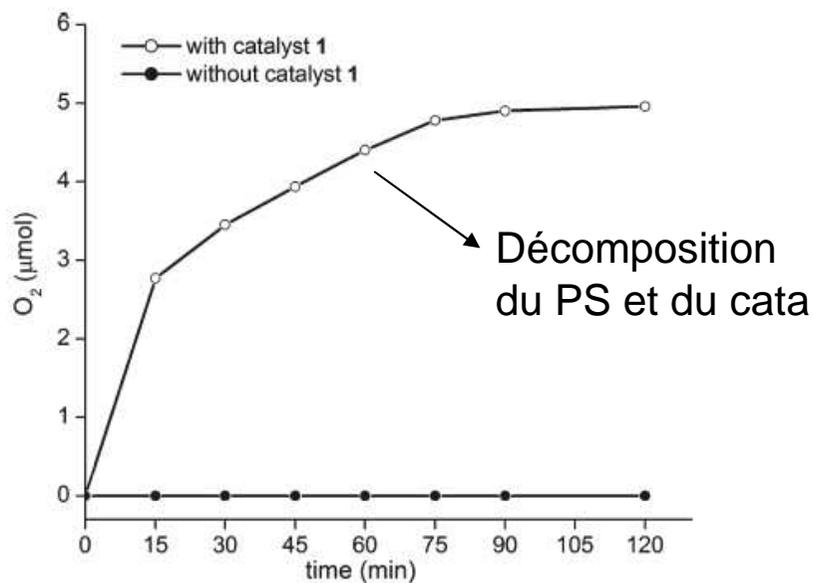
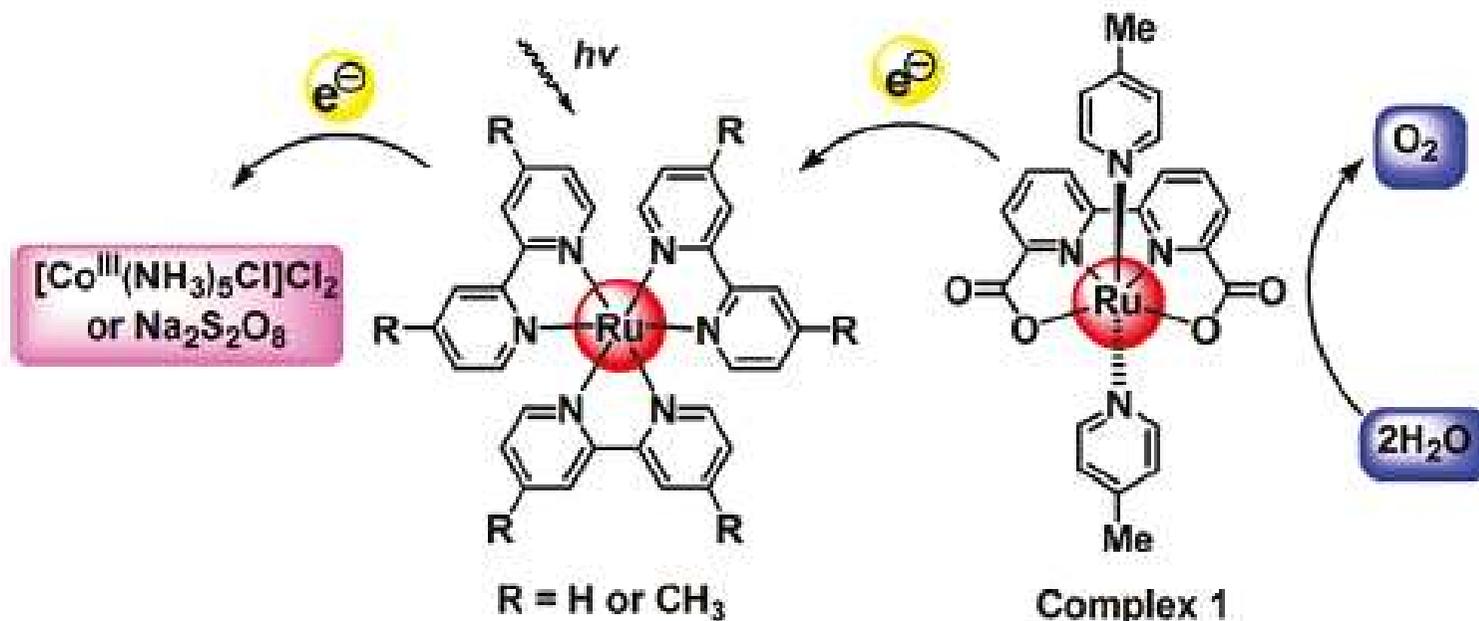
TOF = 5 s⁻¹

TON = 1000

(dégradation du PS)

Photocatalyseurs moléculaires (Ru)

Inorg Chem 2010 49 209

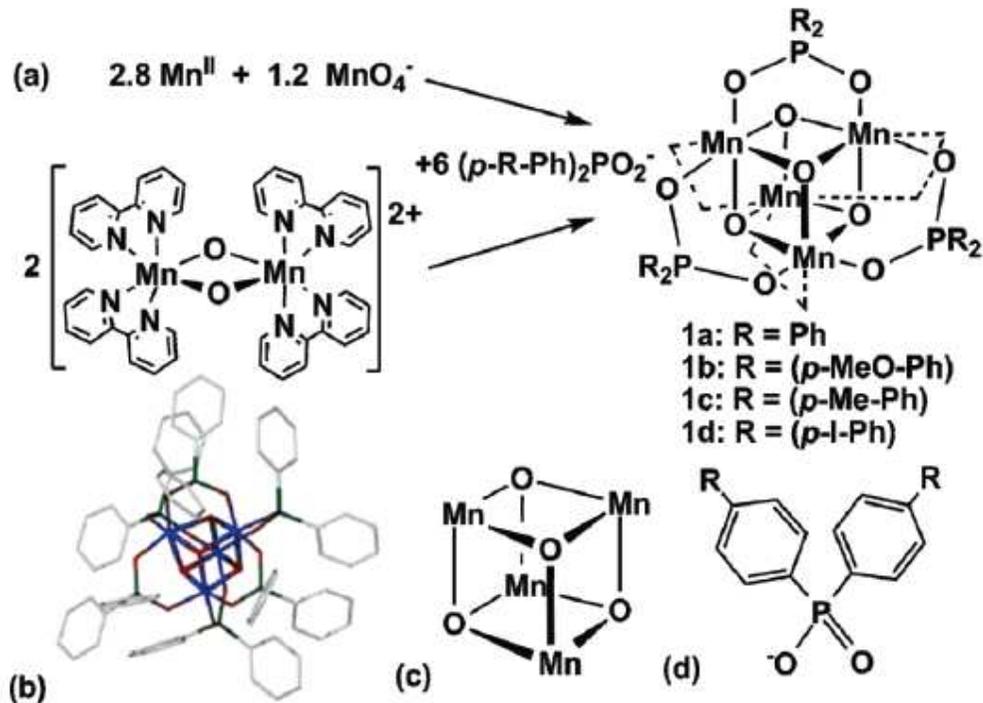


TOF = 550/h

TON = 100 (2h)



C. Dismukes
(Princeton)



Un tétranucléaire de Mn Modèle du site actif de PSII

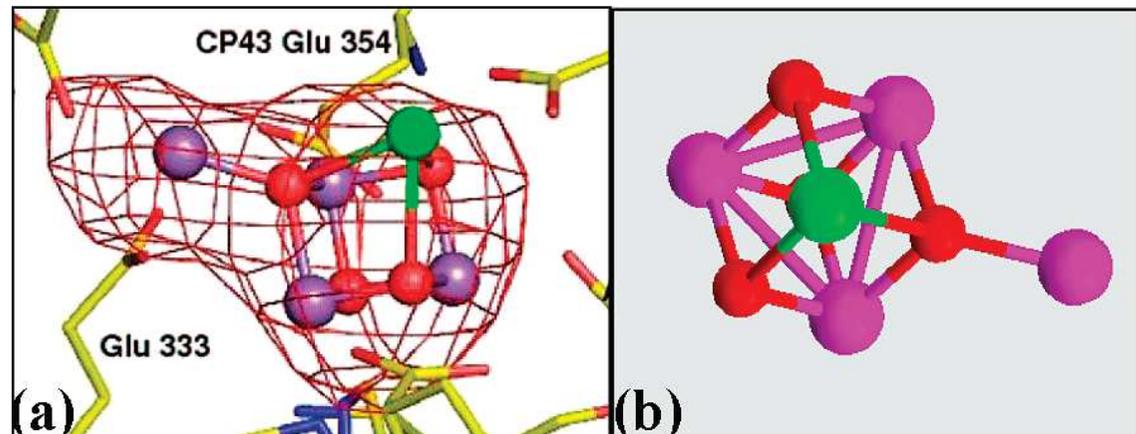
Angew. Chem 2008 47 1-5

Acc. Chem Res. 2009 42 1935

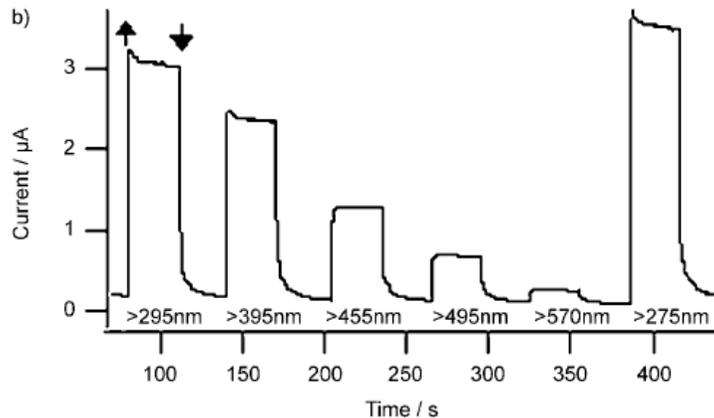
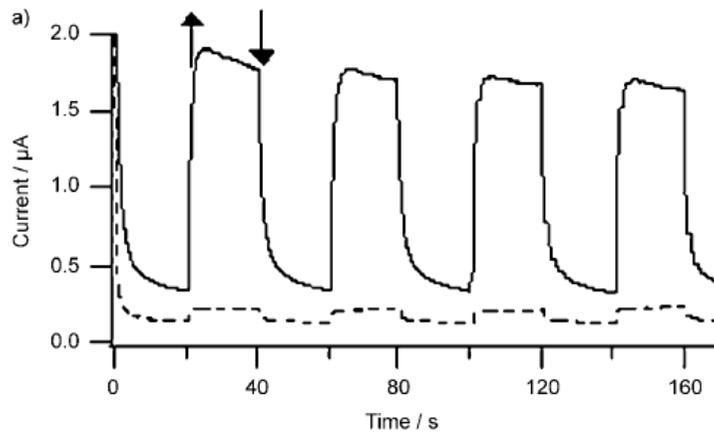
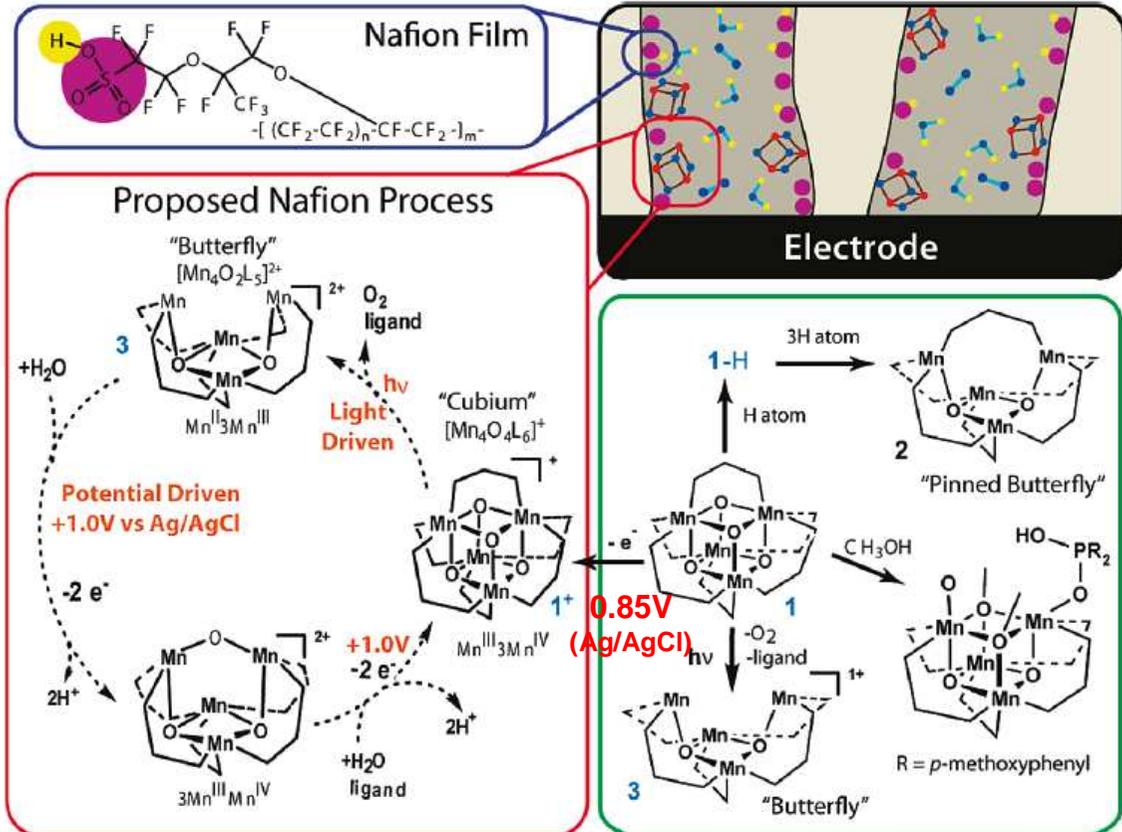
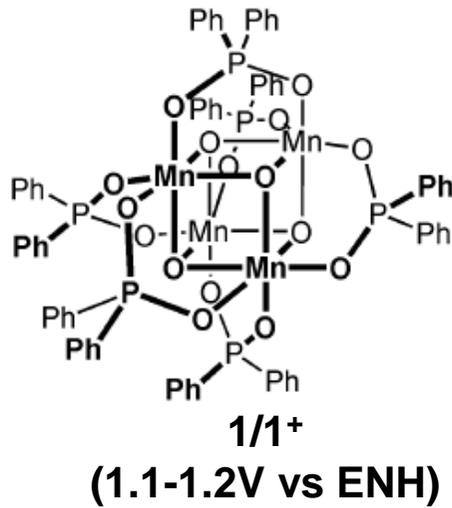
JACS 2010 132 2892

FIGURE 2. (a) Synthetic routes to Mn₄O₄L₆ by self-assembly of preformed dimers (**1a–d**) or from Mn^{II} and MnO₄⁻ ions (**1a**),^{18,19} (b) X-ray crystal structure of **1a** (L₆Mn₄O₄, L = Ph₂PO₂⁻),¹⁹ (c) [Mn₄O₄] cubane core, and (d) phosphinate ligand.

2 Mn(III) 2 Mn(IV)



Le premier catalyseur à manganèse pour la photo-oxydation de l'eau



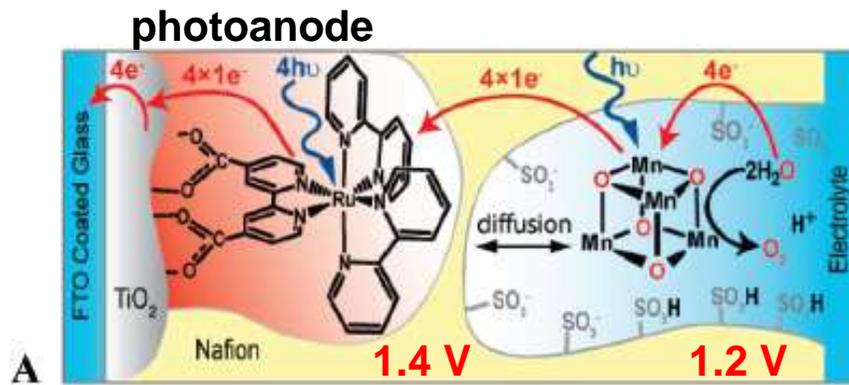
+ 1 V (Ag/AgCl), Na₂SO_{4(aq)}, hv (275-750 nm)

$H_2O^* \rightarrow e^- + H^+ + ^*O_2 \rightarrow$ Rendt: 100%
(pas d'oxydant sacrificiel
oxydant= électrode)

TON: 1000
TOF: 20-270 O₂/h/cata
vitesse $\sim 10^{-4}$ v_{PSII}

Une cellule photoélectrochimique (Mn)

JACS 2010 132 2892



pH 6.5 Na₂SO₄
hv >290 (395)nm

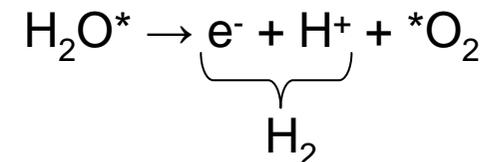
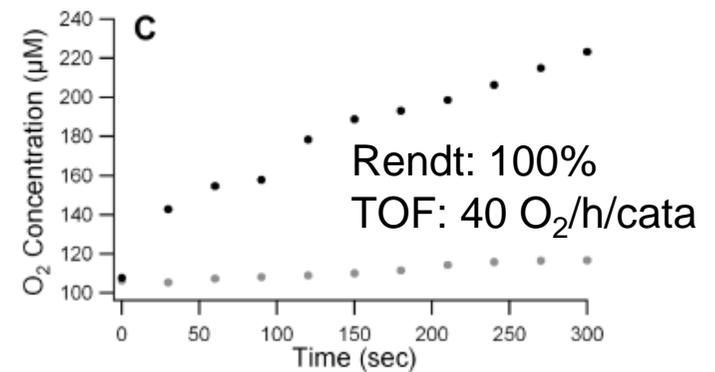
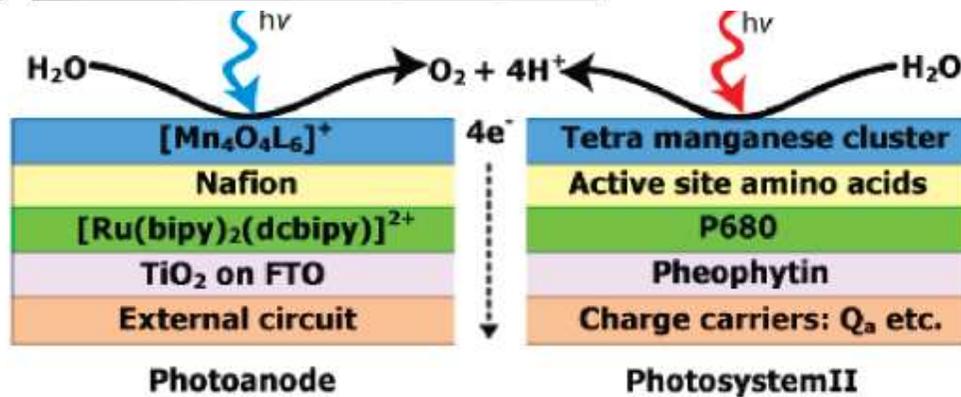
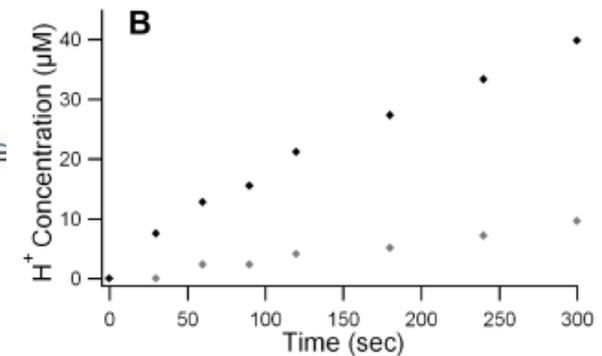
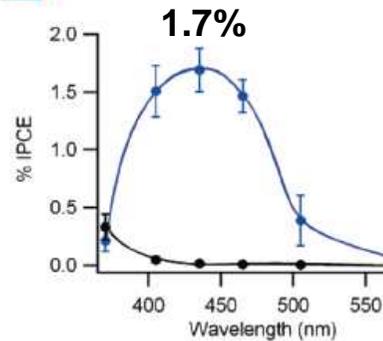
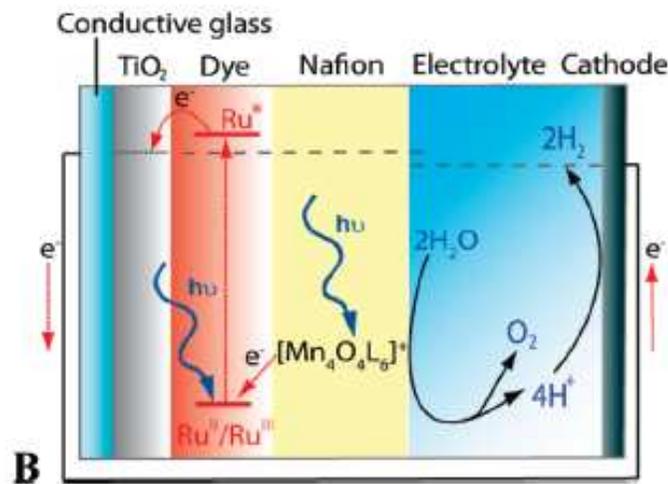
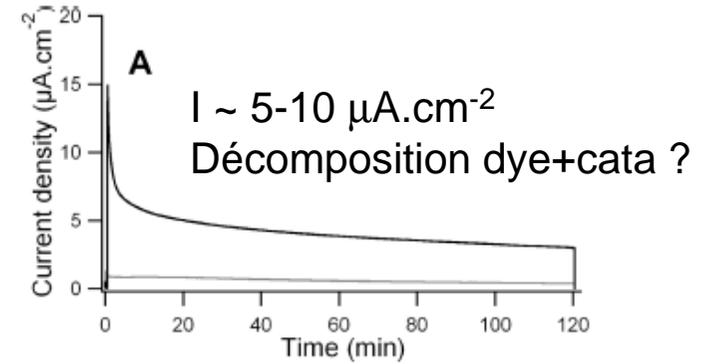


FIGURE 5. Schematic showing the conceptual similarity of the photoanode **1b**⁺-Nafion/Ru(4)-TiO₂, with the PSII-WOC.



COLLÈGE
DE FRANCE
—1530—

Nouveaux développements vers la photo-oxydation de l'eau en oxygène

Marc Fontecave

*Laboratoire de Chimie et Biologie des Métaux, Université Joseph Fourier, CNRS, CEA/DSV/iRTSV
CEA-Grenoble 17 rue des martyrs 38054 Grenoble cedex 9, France
mfontecave@cea.fr; Phone: (0033)438789103 ; Fax: (0033)438789124*

Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05