



COLLÈGE
DE FRANCE
—1530—

Des catalyseurs moléculaires à des matériaux d'électrodes

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Water electrolysis and photoelectrolysis on electrodes engineered using
Biological and bio-inspired molecular systems
PD Tran, V Artero, M. Fontecave
Energy and Environmental Science 2010 (sous presse)

→ Pt, Ru, Ir (+ alliages) coût élevé et disponibilité limitée

→ Oxydes métalliques AB_2O_4 spinelles ex: Co_3O_4 (H Frei)
Nanoparticules Co:P:O électrodéposées (D Nocera)

Matériaux solides pour électrodes

Oxydes métalliques TiO_2 , $NaTaO_3$, $SrTiO_3$ absorbent UV
Oxydes WO_3 , Fe_2O_3 ont une BC insuffisamment énergétique

CdS, CdSe ont des BV et BC adaptées mais sont instables

→ Couplage avec un élément photovoltaïque pour apporter un complément de potentiel (rendt 3% en H_2)

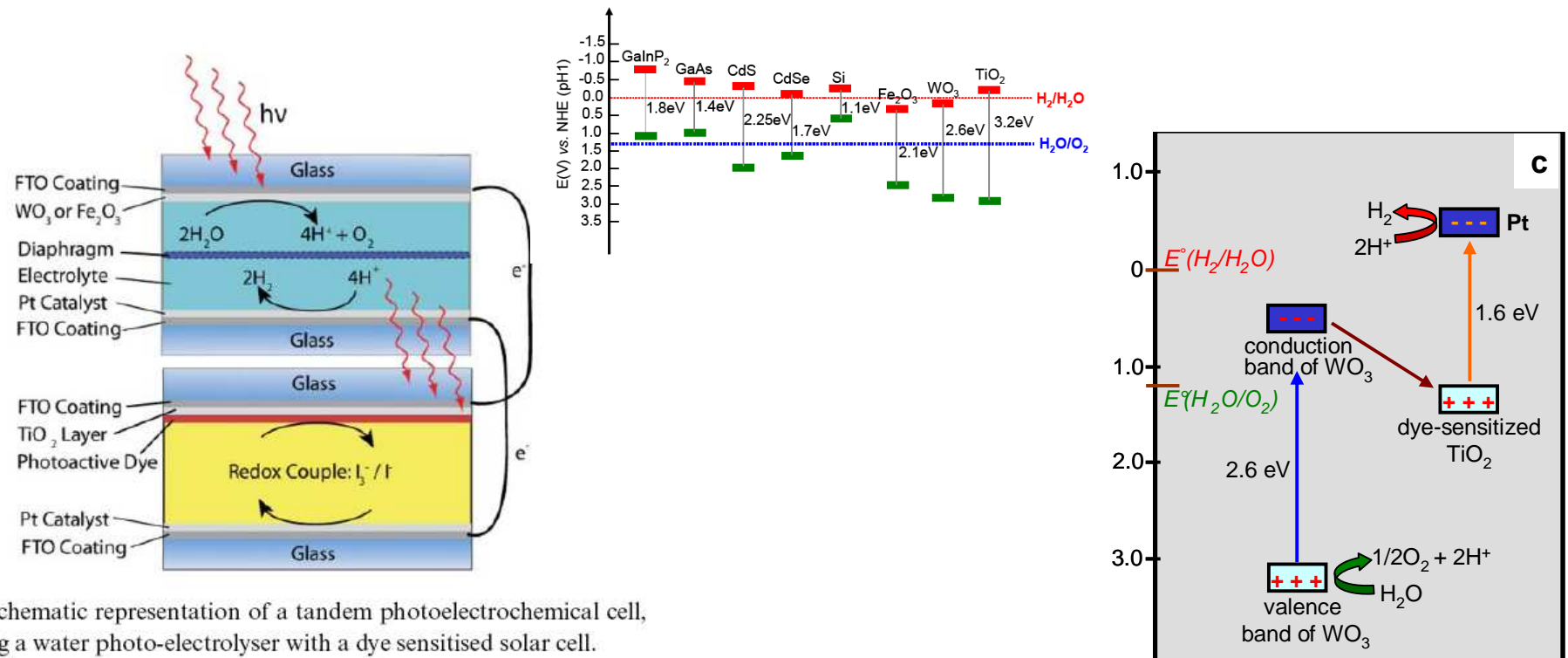


Fig. 1 Schematic representation of a tandem photoelectrochemical cell, combining a water photo-electrolyser with a dye sensitised solar cell.

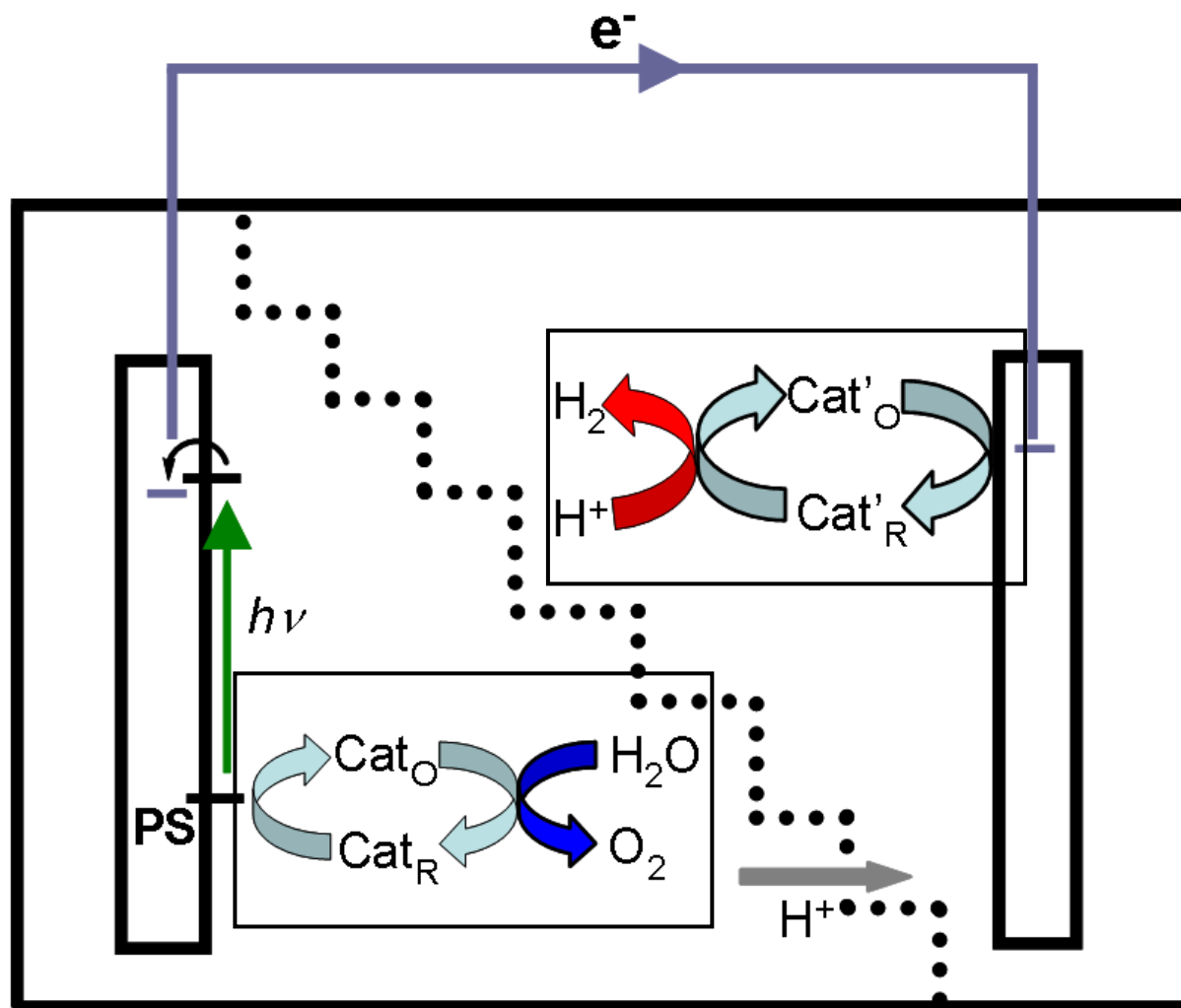
Des électrodes « moléculaires » pour une cellule photoélectrochimique (PEC)

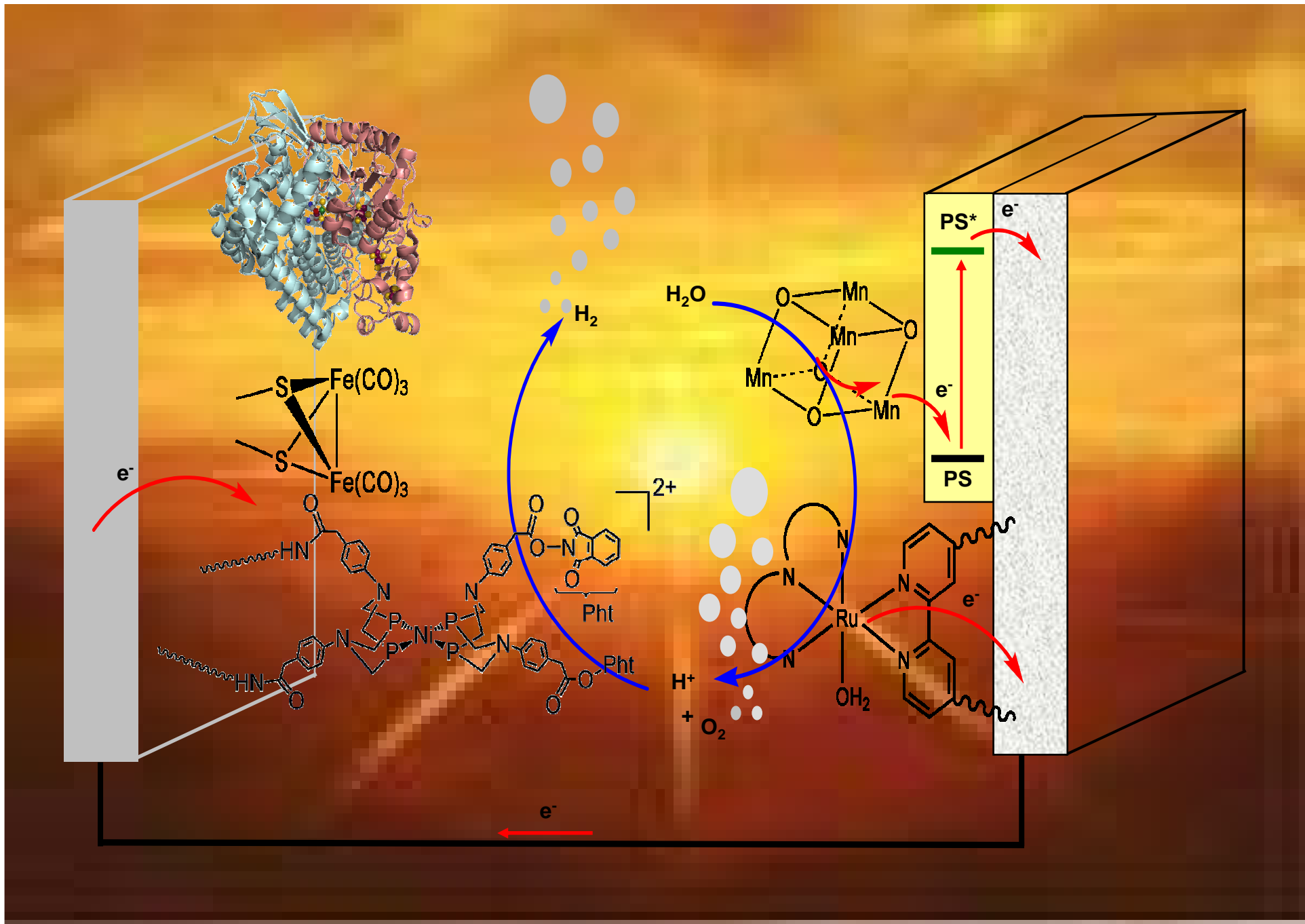


Des méthodes de **greffage**
non destructives de:
-catalyseurs
-photosensibilisateurs

Sur des surfaces
peu coûteuses:
-carbone
-oxydes transparents

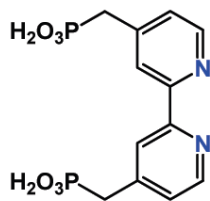
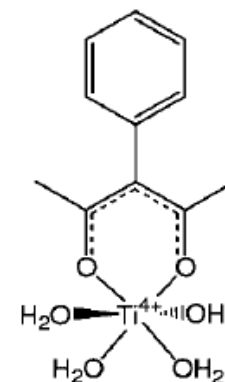
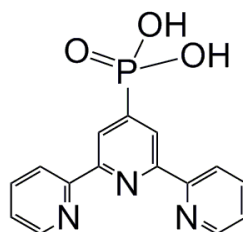
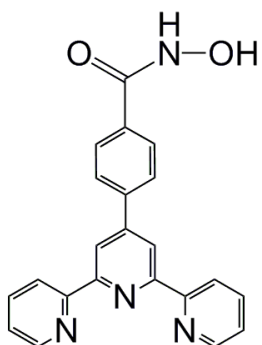
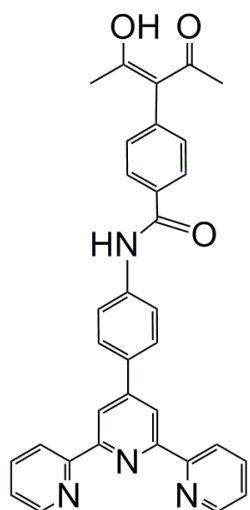
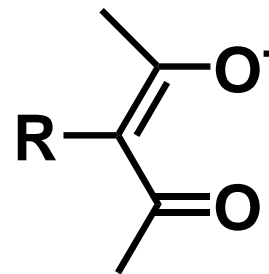
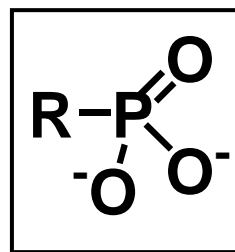
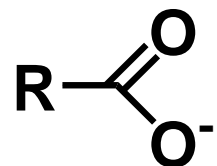
ITO oxyde d'indium (dopé Sn^{4+})
FTO oxyde d'étain (dopé F)



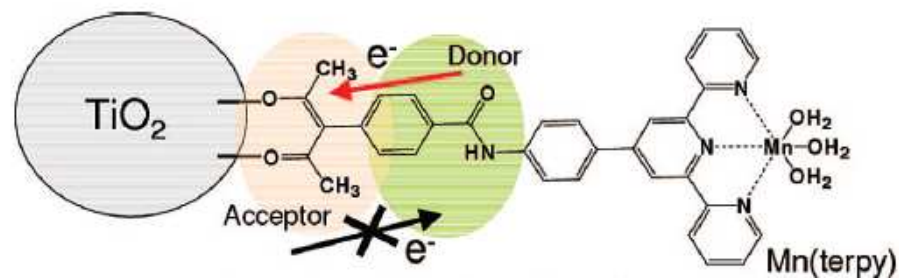
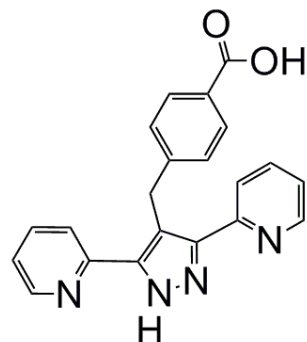


Fixation « covalente » de petites molécules sur des surfaces d'oxydes métalliques:

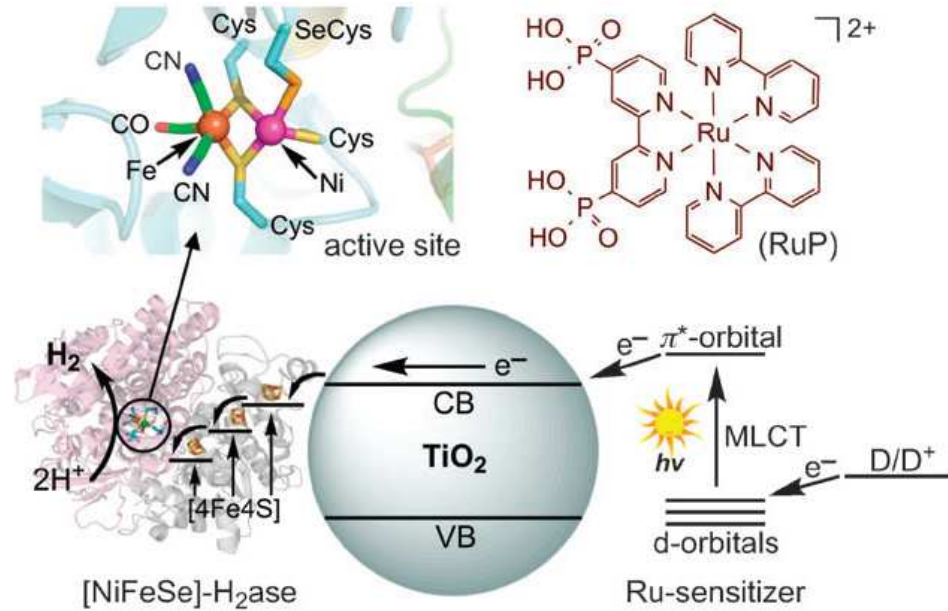
1. carboxylates, phosphonates, acetylacetonates,...



4,4'-((HO)₂(O)PCH₂)₂bpy

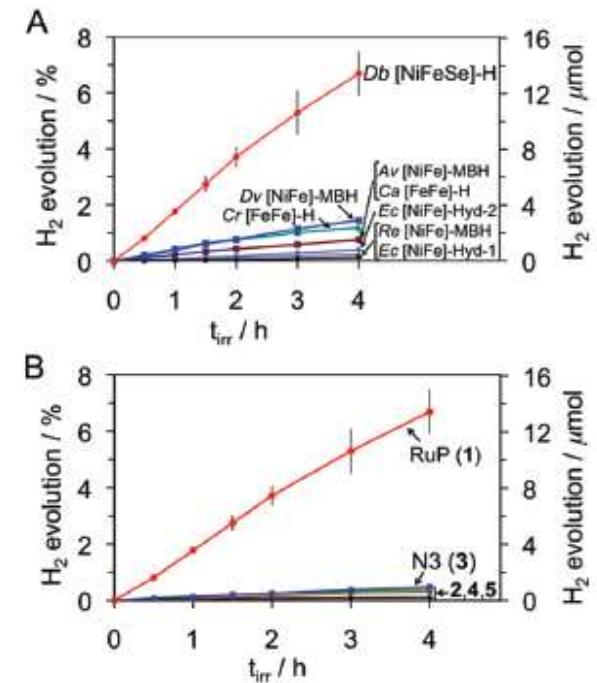
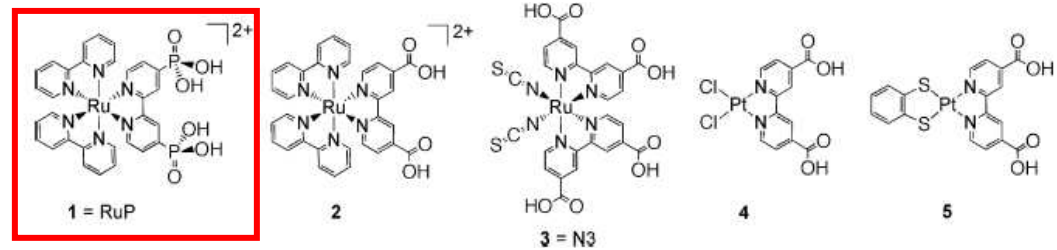


Une photocathode H₂ase/TiO₂/PS ?



Desulfomicrobium baculatum

- ★ forte activité de production H₂
- ★ stable (O₂)
- ★ fixation sur TiO₂/ITO (électrode)-électroactif

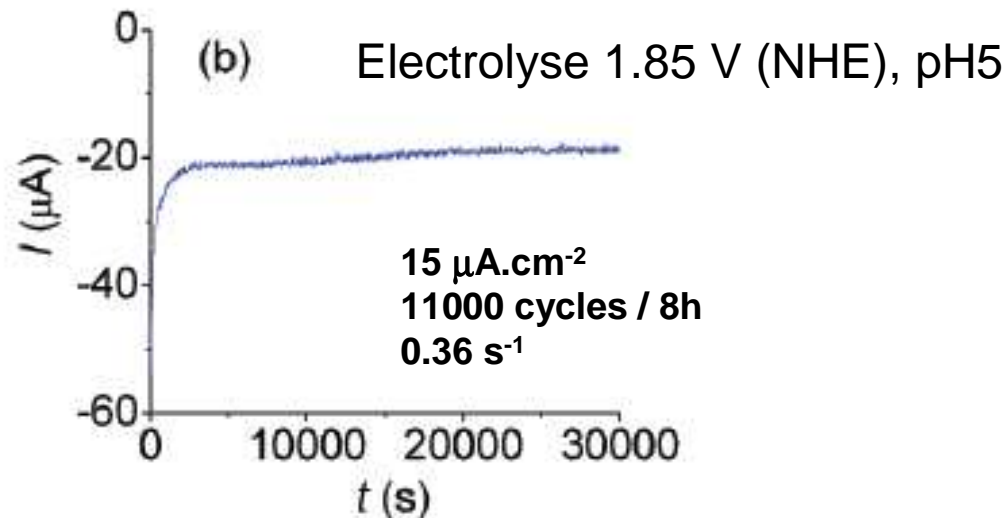
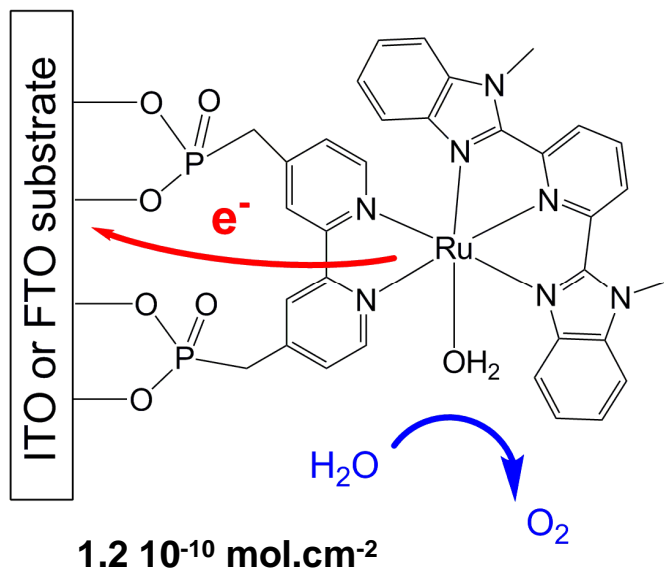


H₂O (pH 7), TEOA
 $\lambda > 420\text{nm}$
 Suspension TiO₂-PS-H₂ase

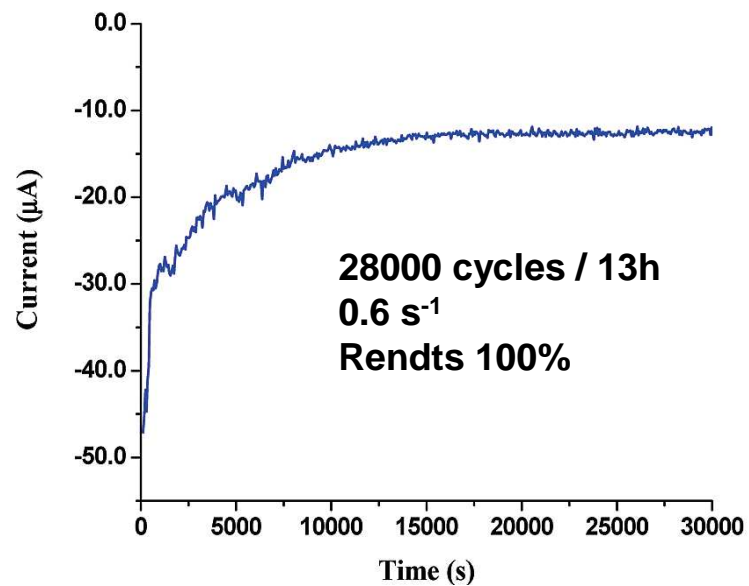
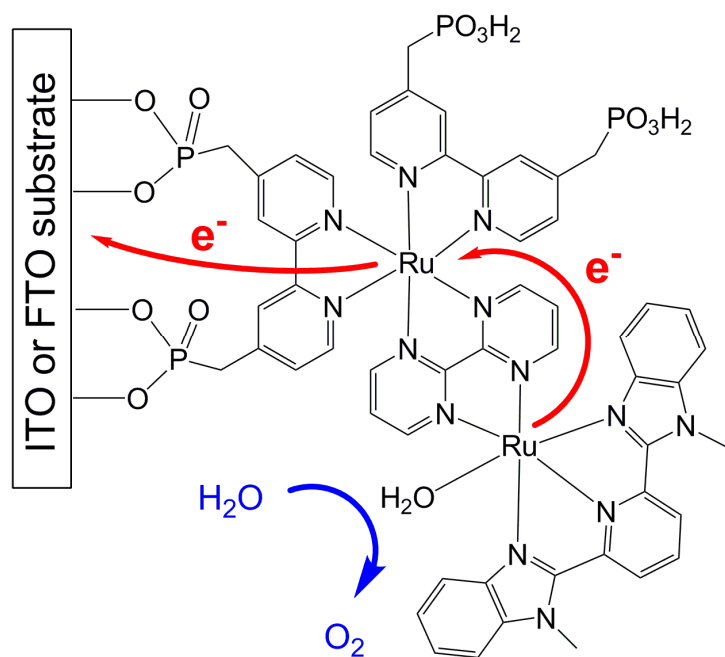


TOF_i = 50 s⁻¹ (cobaloxime: 0.06 s⁻¹; Pt: 0.04 s⁻¹)
stabilité

Catalyseurs d'oxydation de l'eau: Ru

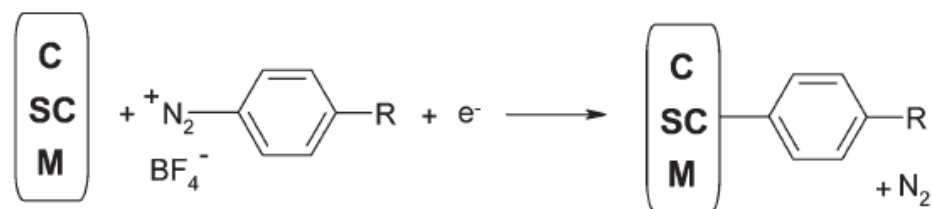


TJ Meyer J Am Chem Soc 2009 131 15581



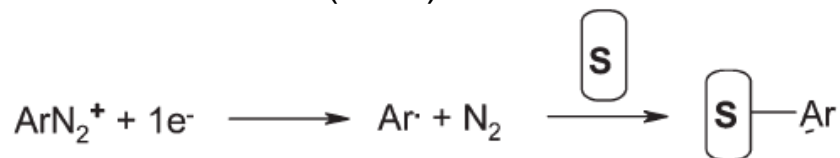
TJ Meyer Angew Chem 2009 48 9473
 Acc Chem Res 2009 42 15580

Fixation « covalente » de petites molécules sur des surfaces d'oxydes métalliques: 2. Réduction électrochimique de sels de diazonium

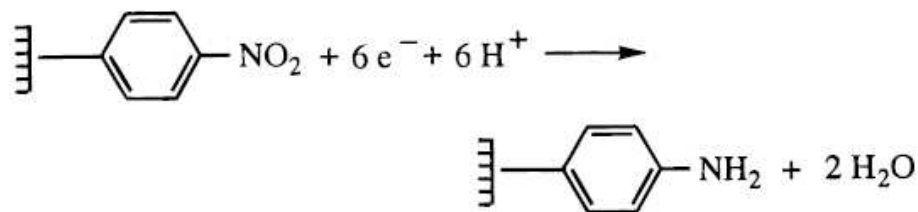


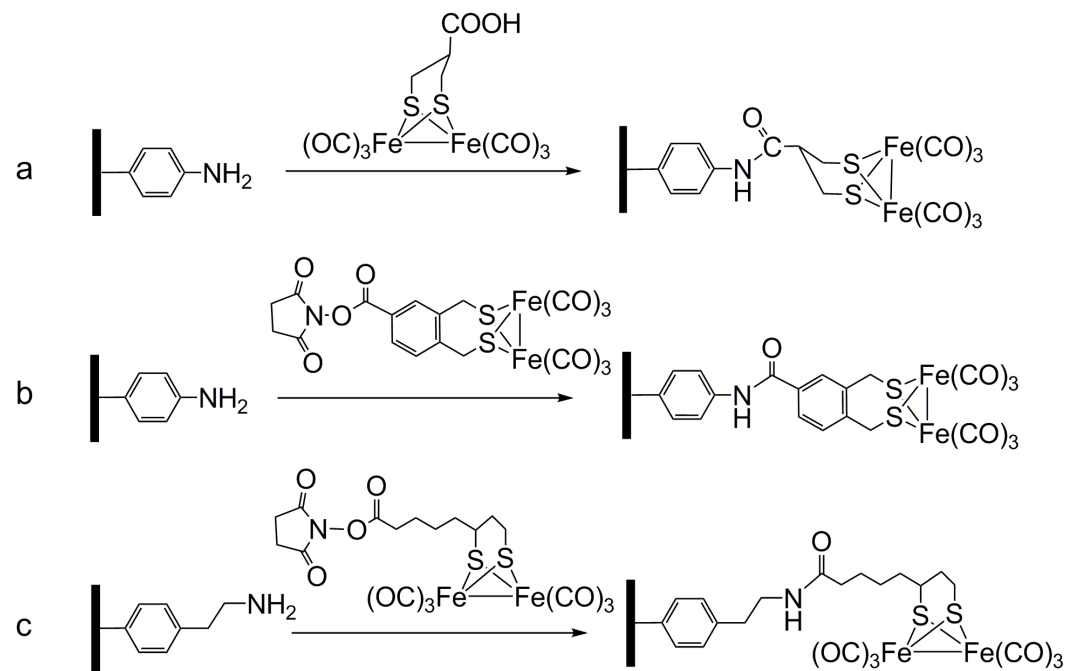
C: carbon, SC: semiconductor, M: metal

$$E \sim -0.1 \pm 0.2 \text{ V (SCE)}$$



S = substrate: carbon, semiconductor or metal



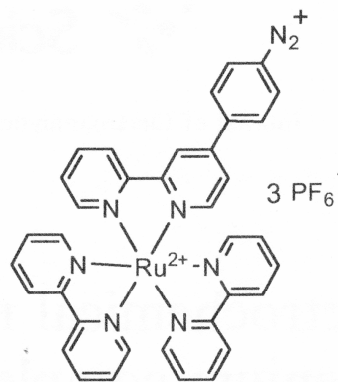


Très faible activité
Instabilité (perte CO)

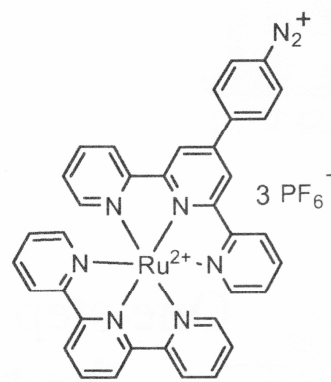
F Gloaguen Electrochem Commun 2005 7 427

MY Darensbourg 2007 26 3976

M Fontecave, V Artero Int J Hydr En. 2010 sous presse



[Ru(bpy)₂(bpy-ph-N₂⁺)](PF₆)₃ (1)

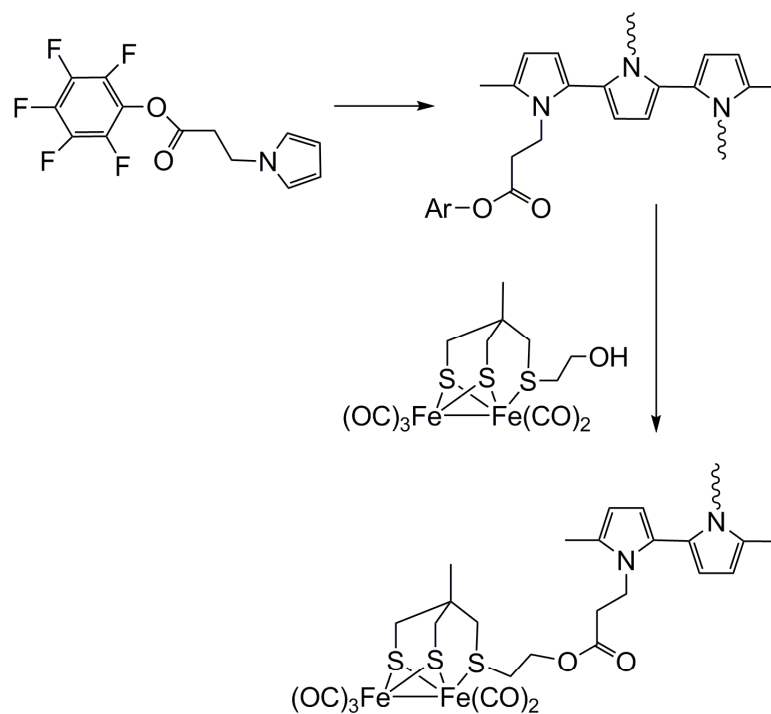


[Ru(tpy)(tpy-ph-N₂⁺)](PF₆)₃ (2)

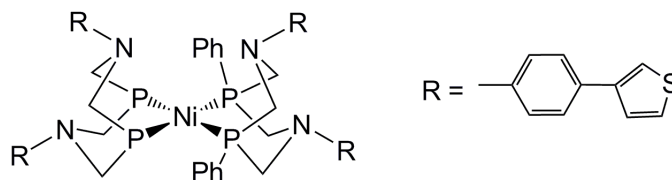
B Jusselme J Electroanal Chem 2008 621

Polymères

CJ Pickett Chem Commun 2007 1535



Très forte surtension

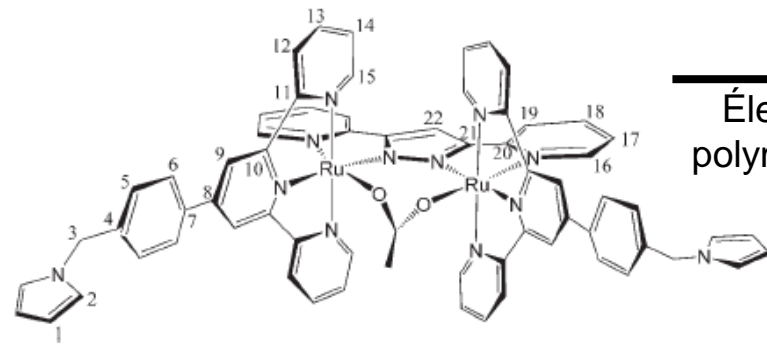


inactif

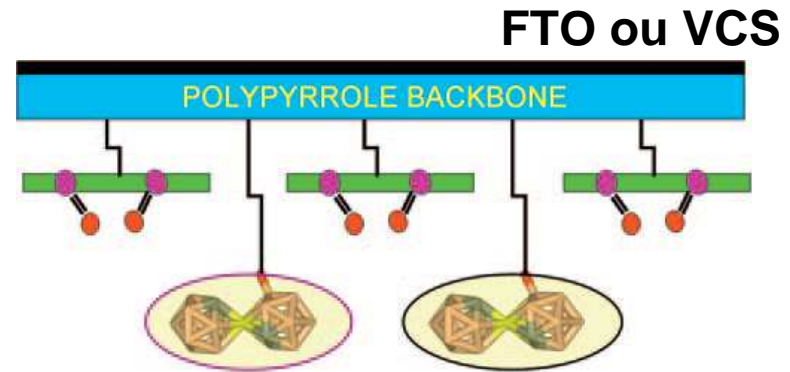
D Dubois J Organomet Chem 2009 694 2858

Catalyseurs hétérogénéisés

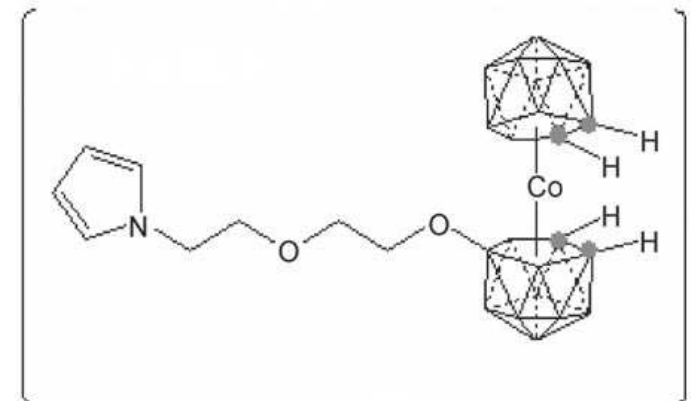
Llobet Angew Chem 2008 47 5830



Électro-co-polymérisation



Ce⁴⁺: 250 cycles catalytiques
1,17 V (ECS): 120 cycles



Nanotubes de Carbone

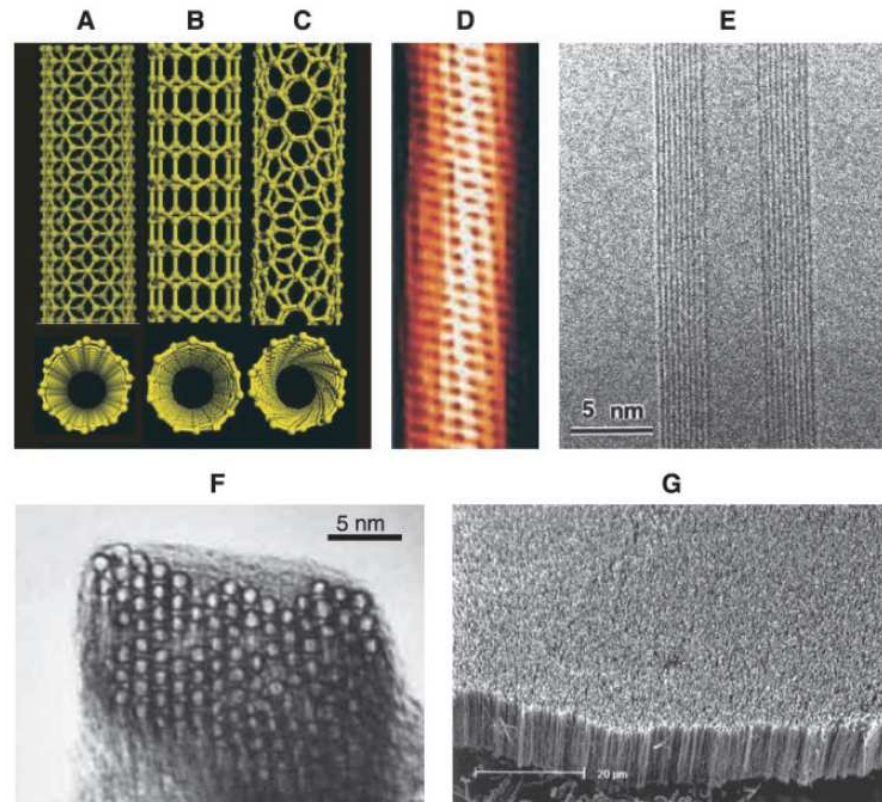
→ Grande conductivité électrique

→ Grande surface spécifique

→ Bonnes propriétés mécaniques

SWNT

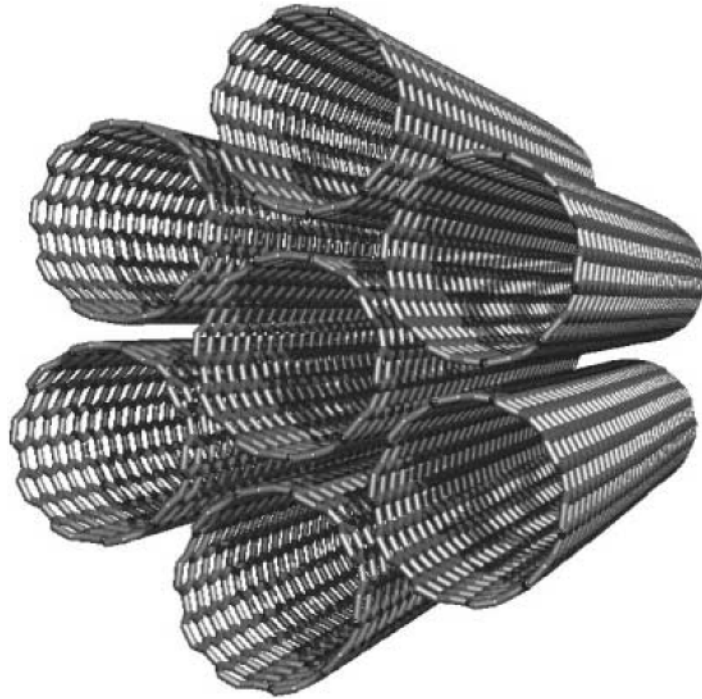
A, B = métallique
C = semiconducteur



MWNT

Fig. 1. Schematic illustrations of the structures of (A) armchair, (B) zigzag, and (C) chiral SWNTs. Projections normal to the tube axis and perspective views along the tube axis are on the top and bottom, respectively. (D) Tunneling electron microscope image (72) showing the helical structure of a 1.3-nm-diameter chiral SWNT. (E) Transmission electron microscope (TEM) image of a MWNT containing a concentrically nested array of nine SWNTs. (F) TEM micrograph (18) showing the lateral packing of 1.4-nm-diameter SWNTs in a bundle. (G) Scanning electron microscope (SEM) image of an array of MWNTs grown as a nanotube forest (micrograph courtesy of L. Dai).

Single-Walled NanoTubes (SWNTs)



Agrégation: fagot de NT

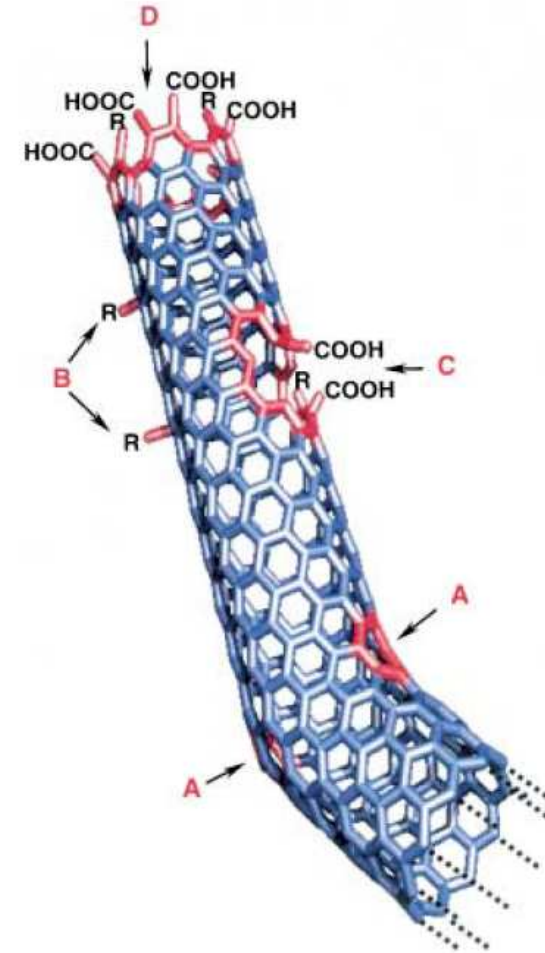


Figure 3. Typical defects in a SWNT: A) five- or seven-membered rings in the C framework, instead of the normal six-membered ring, leads to a bend in the tube, B) sp³-hybridized defects (R = H and OH), C) C framework damaged by oxidative conditions, which leaves a hole lined with -COOH groups, and D) open end of the SWNT, terminated with -COOH groups. Besides carboxy termini, the existence of which has been unambiguously demonstrated, other terminal groups such as -NO₂, OH, H, and =O are possible.

Fonctionnalisation des NanoTubes de Carbone

Angew Chem 2002 41 1853

Chem Rev 2006 106 1105

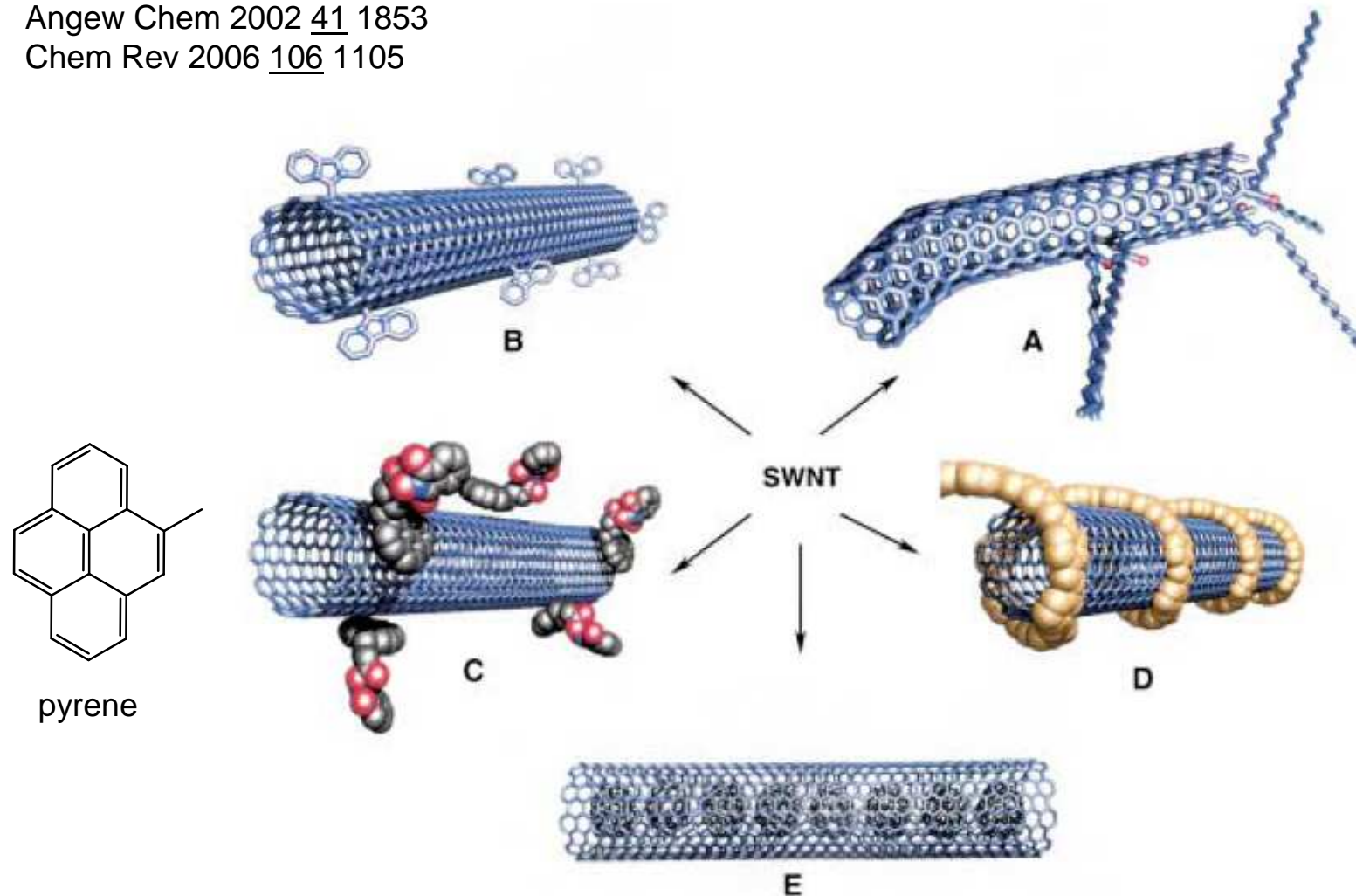
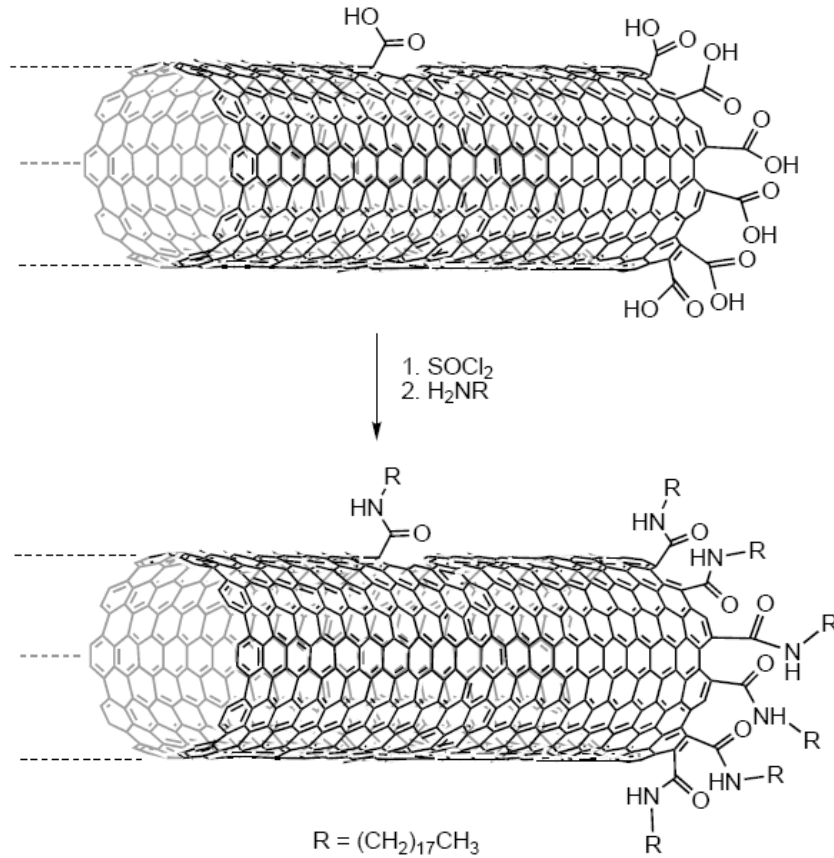


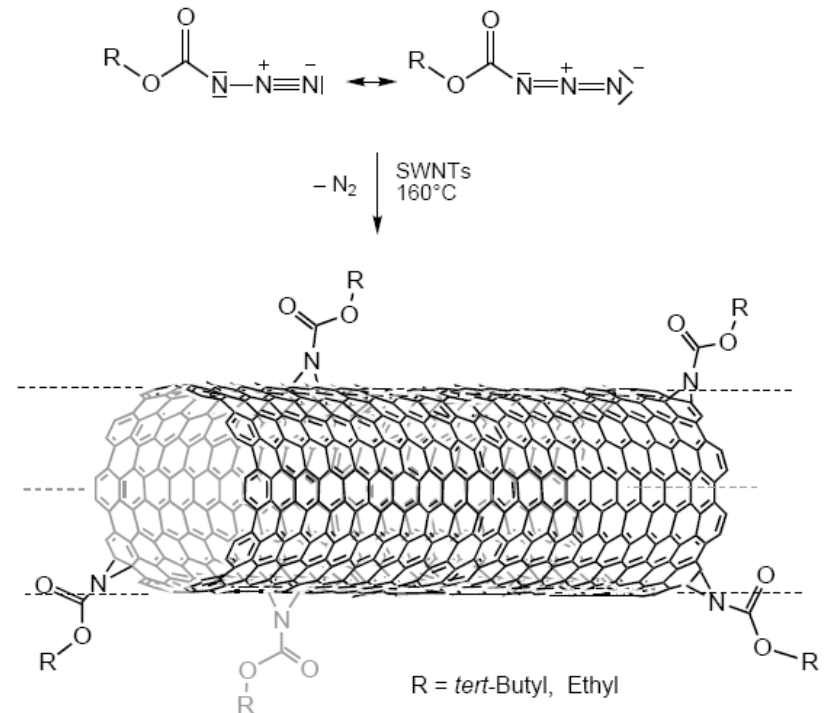
Figure 5. Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C_{60} . For methods B–E, the tubes are drawn in idealized fashion, but defects are found in real situations.

Fonctionnalisation covalente des NanoTubes de Carbone

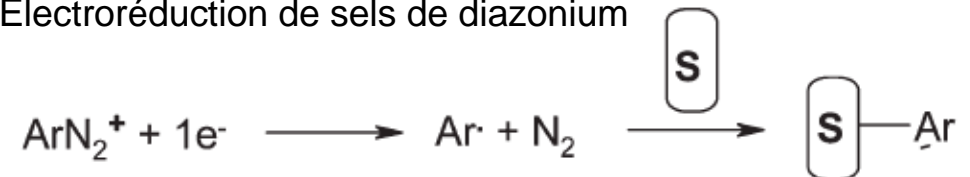
Exploitation des carboxylates

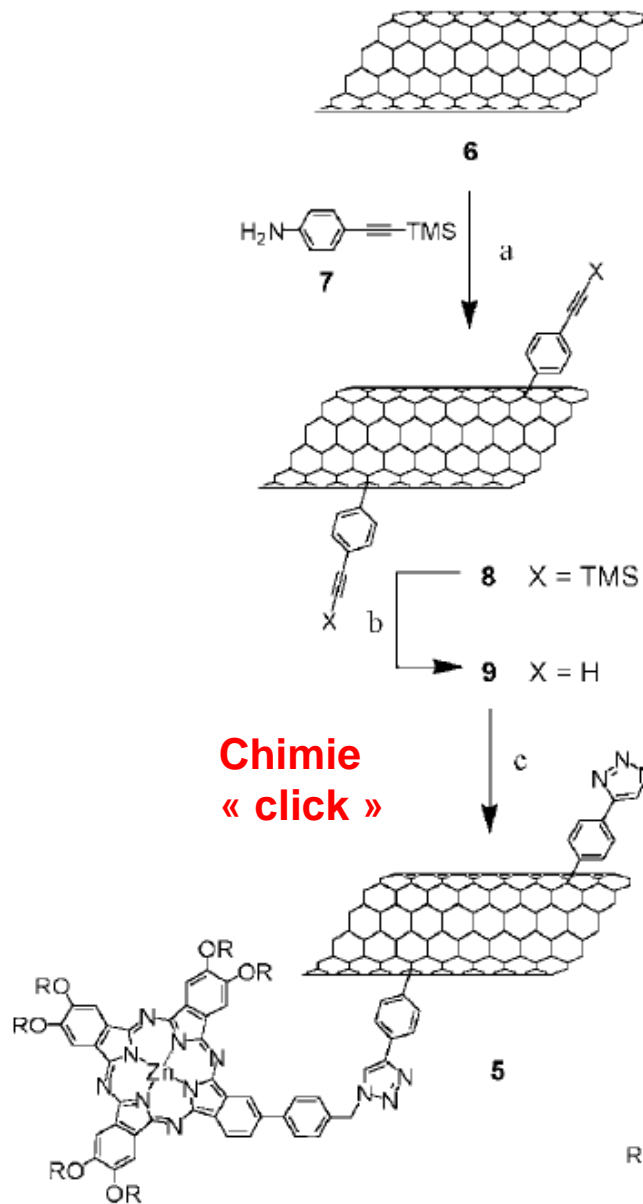


Réaction avec des espèces réactives
(nitrènes, radicaux, carbènes)

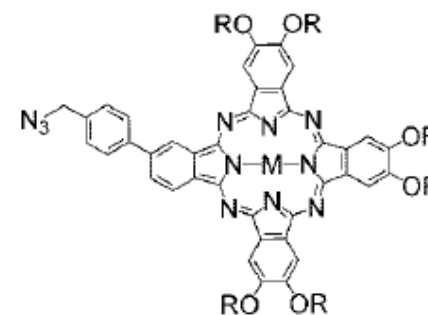
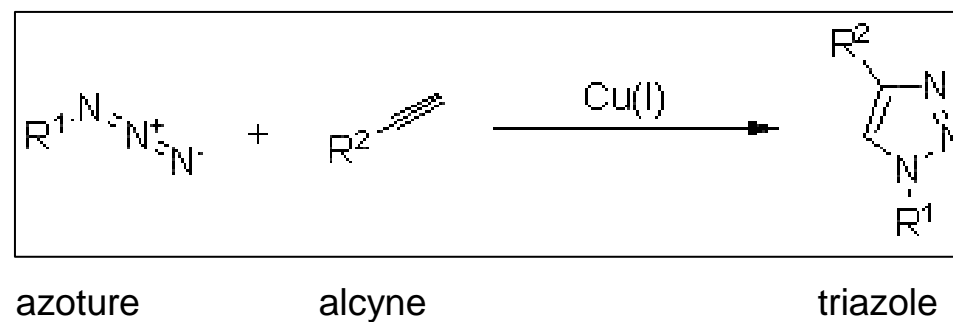


Électroréduction de sels de diazonium





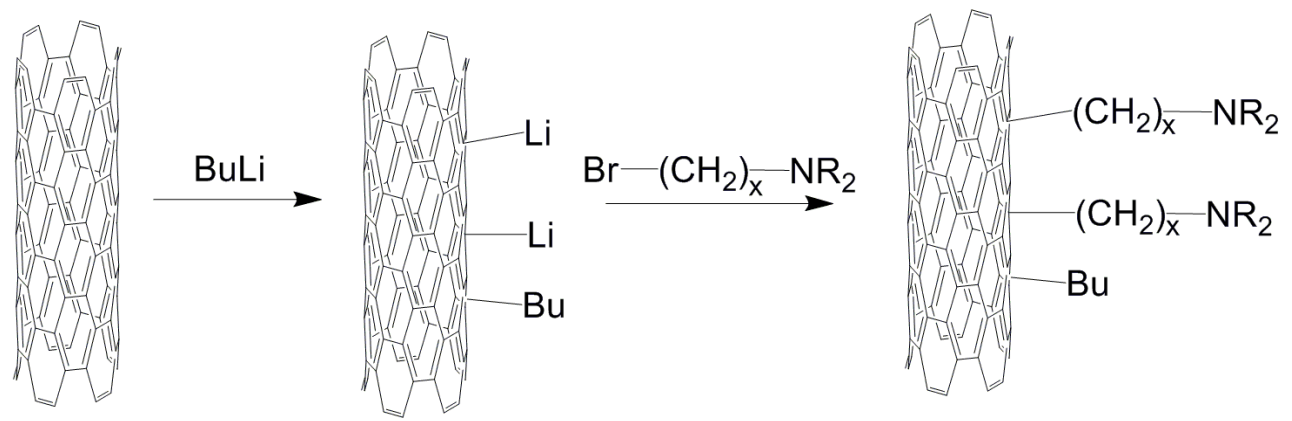
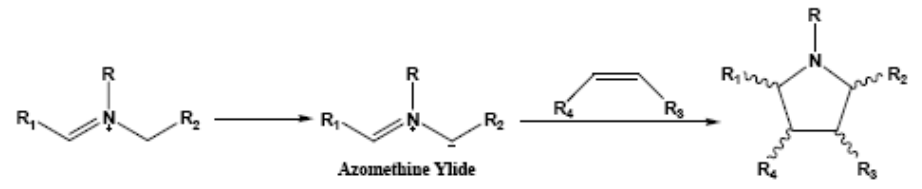
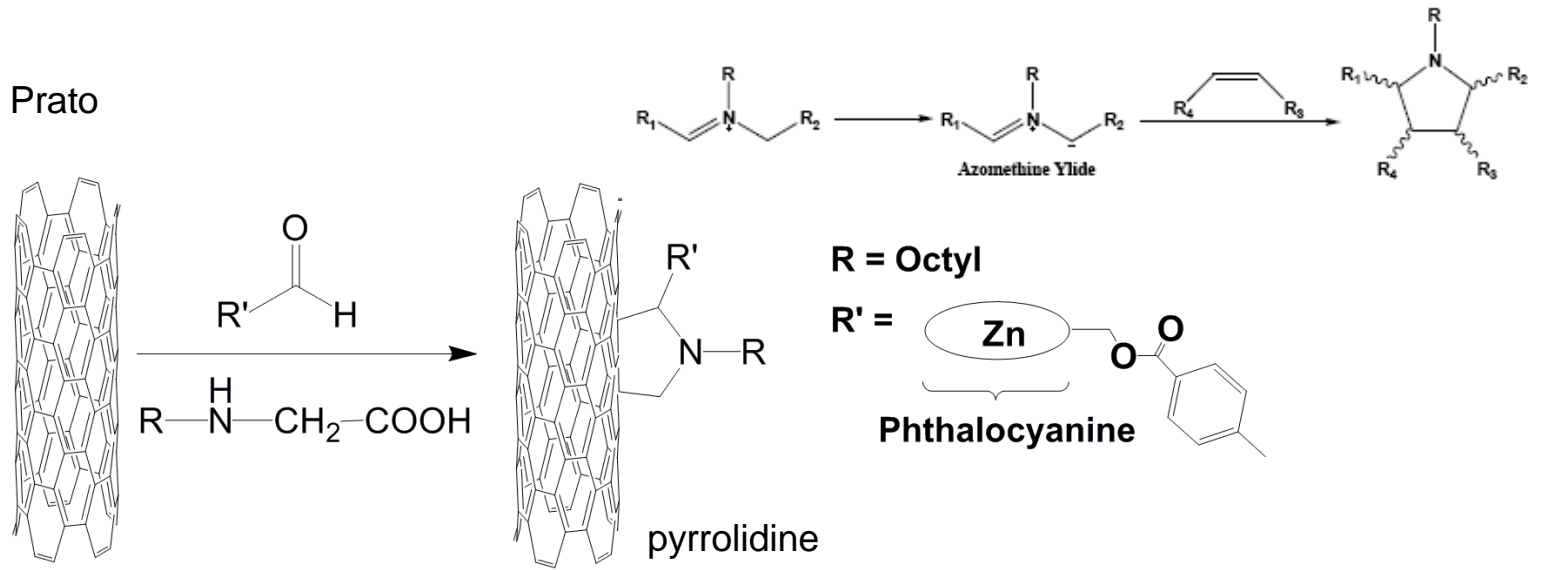
Chimie
« click »



Chem Mater 2001 13 3823
JACS 2008 130 11503

^a (a) Isoamyl nitrite, NMP, 60 °C, 48 h; (b) NBu₄F, THF/NMP, rt, 1 h;
(c) 1, CuSO₄·5H₂O, sodium ascorbate, NMP, 70 °C, 48 h.

Réaction de Prato



« sp³ Defect-mediated functionalization »

Angew Chem 2009 48 6543

**Un exemple de catalyseur moléculaire
gréffé sur des NTCs
pour la production et l'oxydation d'H₂**

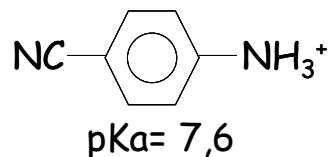
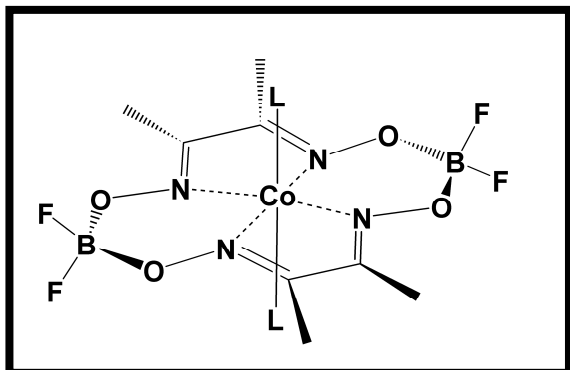
Vers une électrode pour PEMFC

**From Hydrogenases to Noble
Metal-Free Catalytic Nanomaterials
for H₂ Production and Uptake**

Alan Le Goff,¹ Vincent Artero,^{2*} Bruno Jusselme,¹ Phong Dinh Tran,² Nicolas Guillet,³
Romain Métayé,¹ Aziz Fihri,² Serge Palacin,^{1*} Marc Fontecave^{2,4}

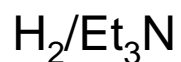
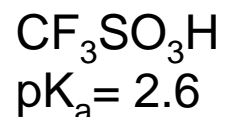
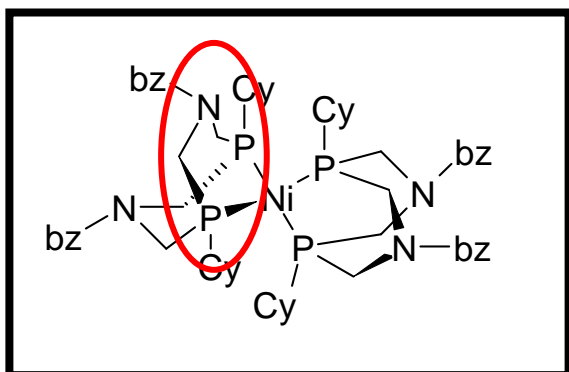
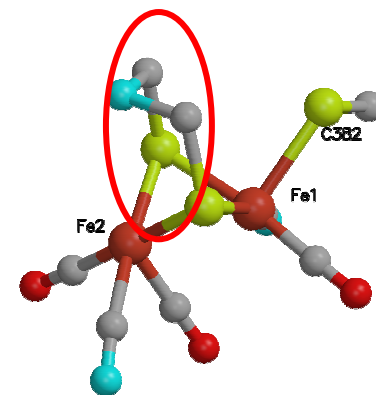
4 DECEMBER 2009 VOL 326 SCIENCE

Les meilleurs catalyseurs de réduction de H⁺ surtensions, TOF,..



$E_{\text{her}} = -0.4 \text{ V vs Ag/AgCl in CH}_3\text{CN}$
92 TON.h⁻¹ (- 0.5 V)

Cobaloximes as functional models for hydrogenases. 2. Proton electroreduction catalyzed by difluoroboryl-bis(dimethylglyoximate)-cobalt(II) complexes in organic media
C. Baffert, V. Artero, M. Fontecave
Inorg. Chem., 2007, **46**, 1817-1824

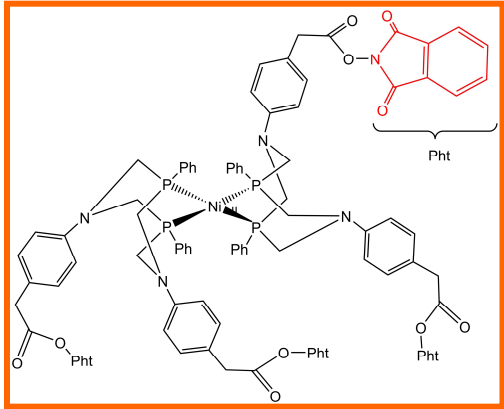
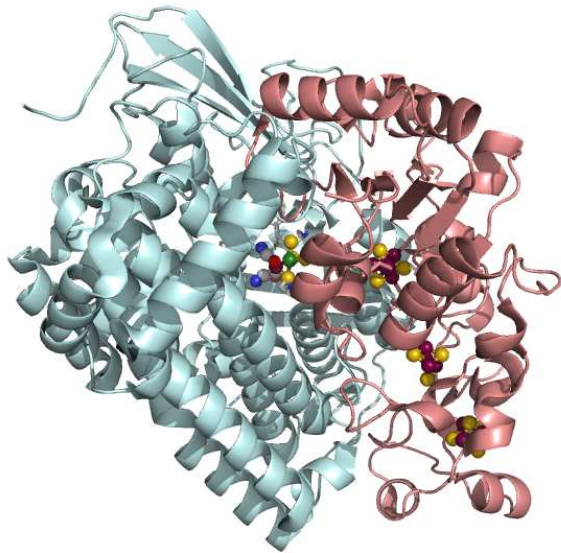


$E_{\text{her}} = -0.4 \text{ V vs Ag/AgCl}$

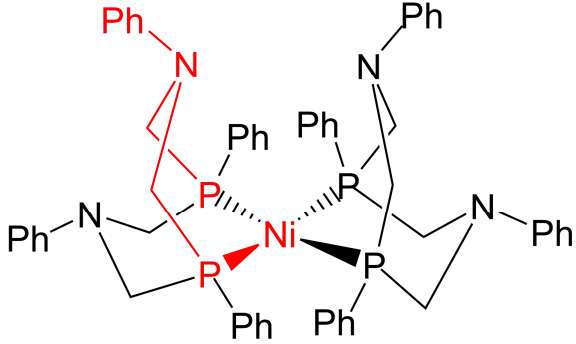
un des rares catalyseurs
pour l'oxydation de H₂
 $E = -0.27 \text{ vs Ag/AgCl}$

Dubois et al. *J. Am. Chem. Soc.*, 2006 and 2007.

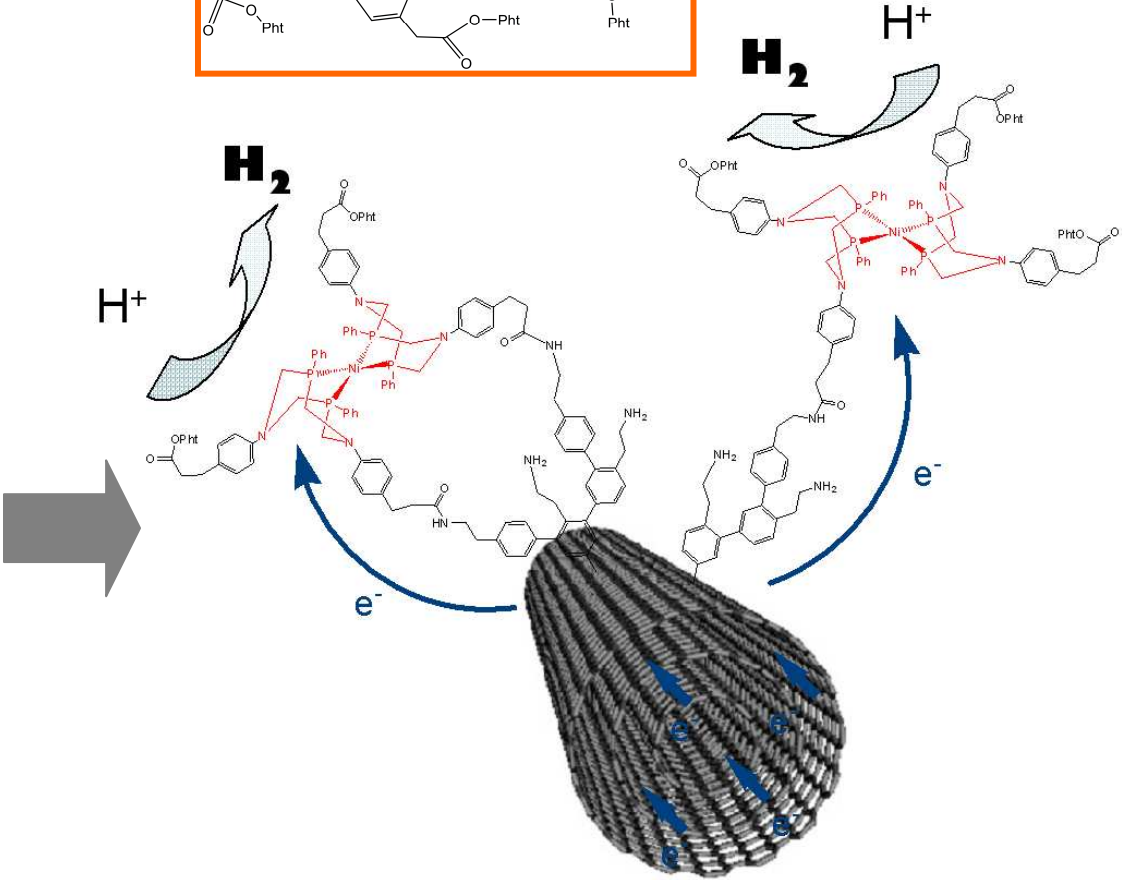
Nanomatériaux bio-inspirés



Hydrogénases

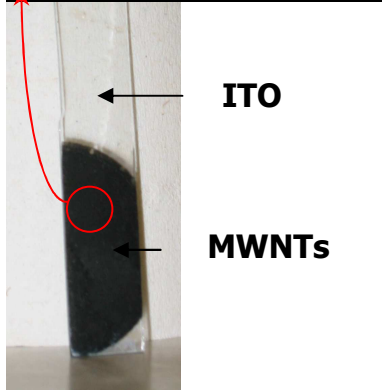
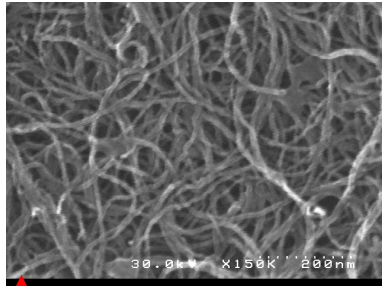
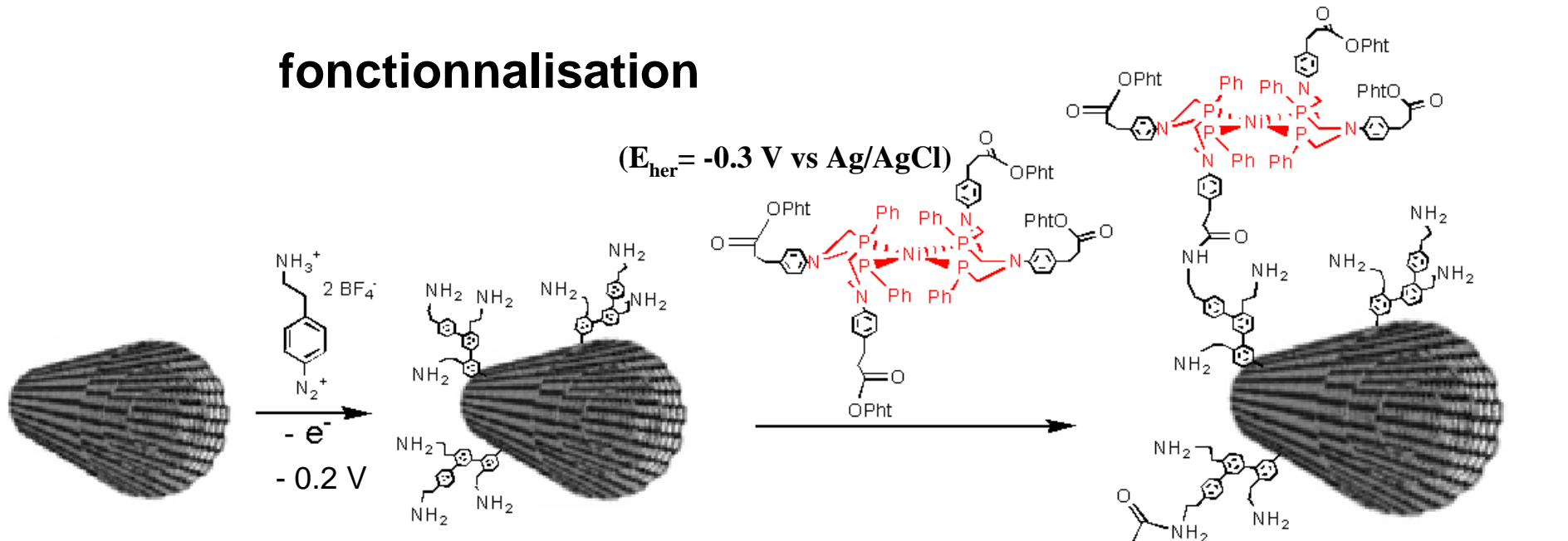


Catalyseurs bioinspirés

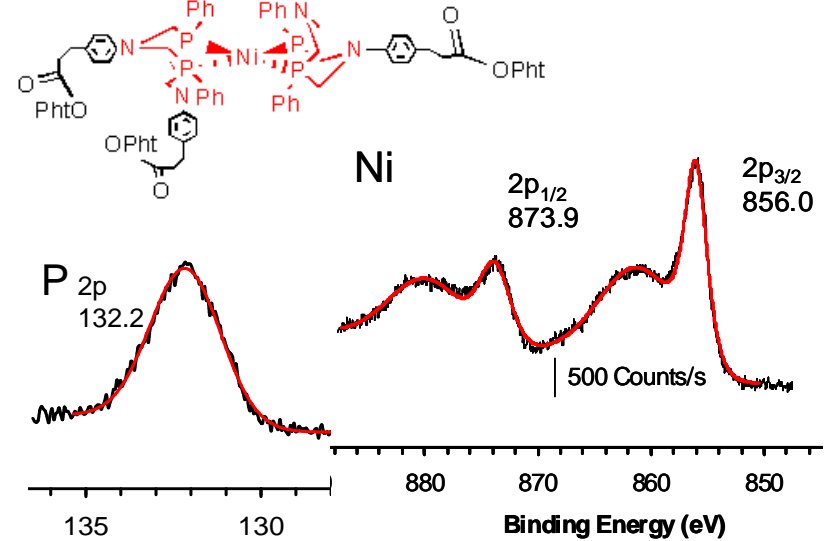
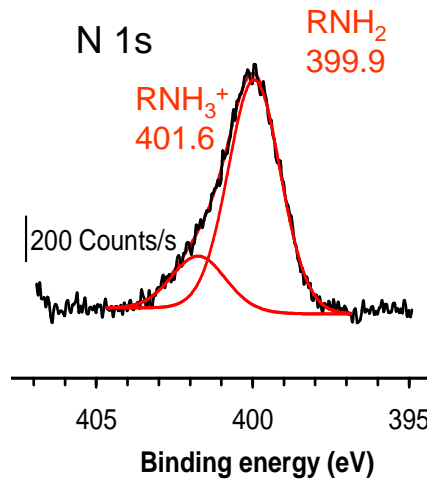


Quelle activité après fixation sur des NTCs ???

fonctionnalisation



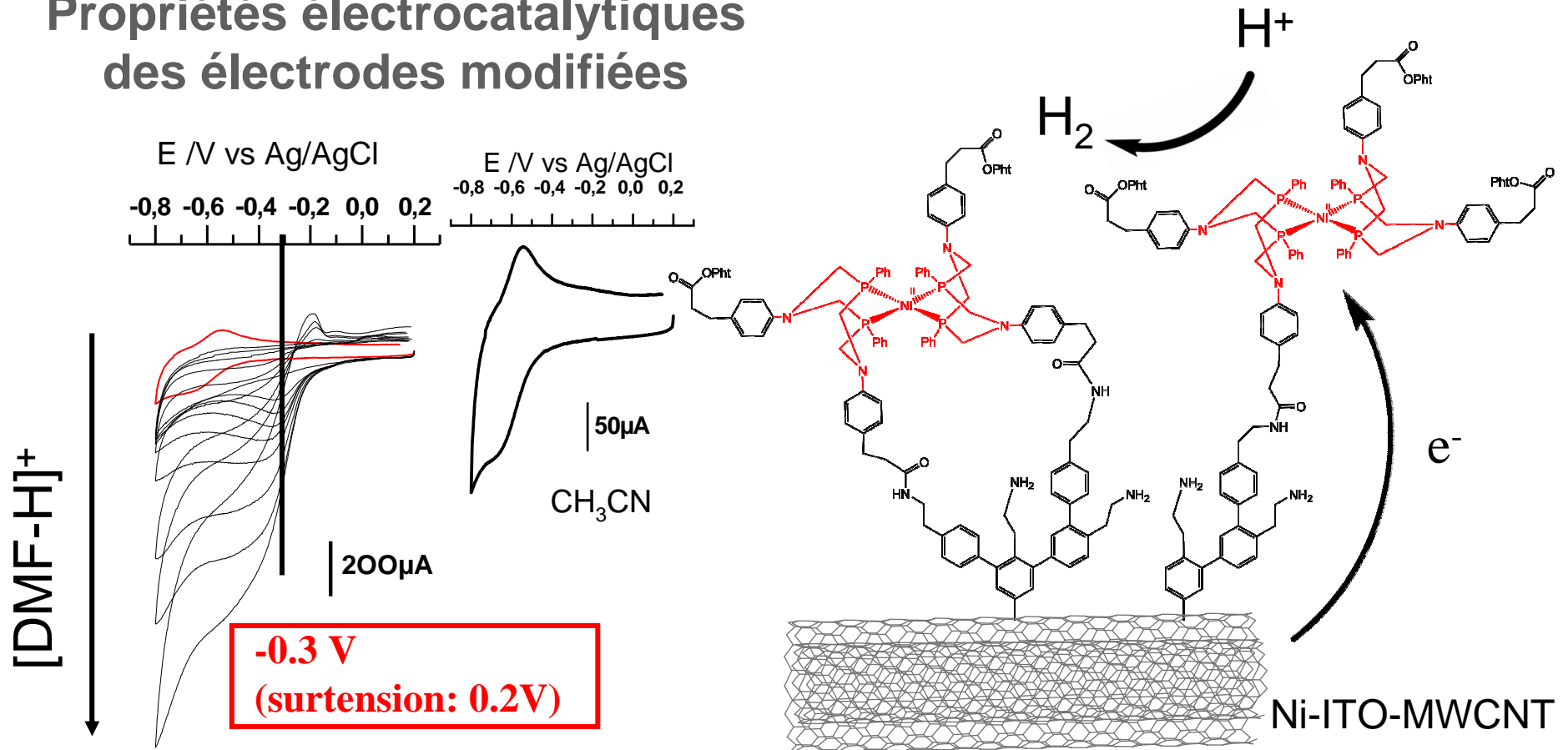
$n = 1.5 \cdot 10^{-9} \text{ mol.cm}^{-2}$



X-ray Photoelectron Spectroscopy (XPS)

Scanning Electron Microscopy (SEM)

Propriétés électrocatalytiques des électrodes modifiées



DMFH^+ : $\text{pK}_a=6.1$ in CH_3CN
 $E^\circ = -0.1 \text{ V vs Ag/AgCl}$

Coulométrie à potentiel contrôlé
 (-0.5 V vs Ag/AgCl)
 $\text{CH}_3\text{CN} / [\text{DMFH}](\text{OTf})$ 60 mM
 GC analyse de H_2



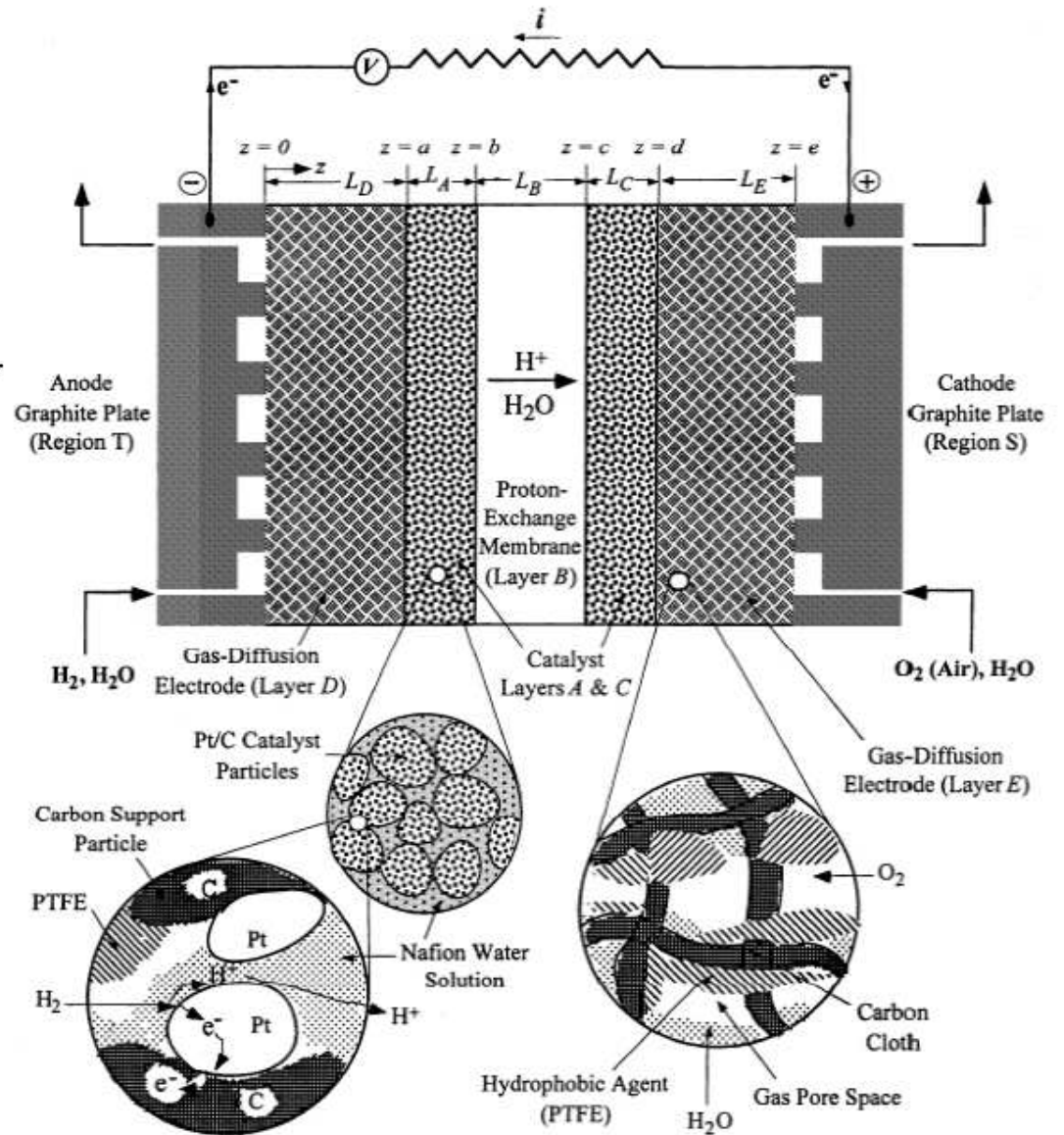
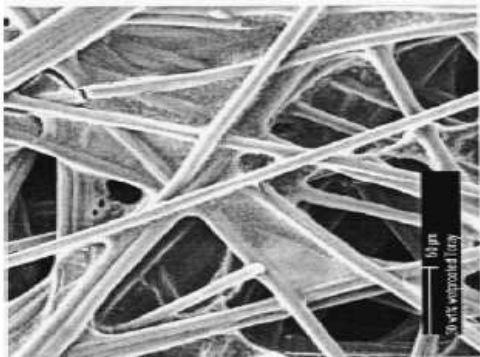
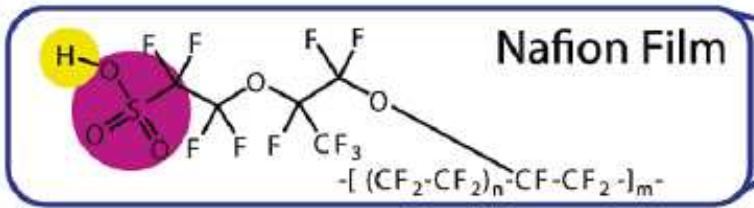
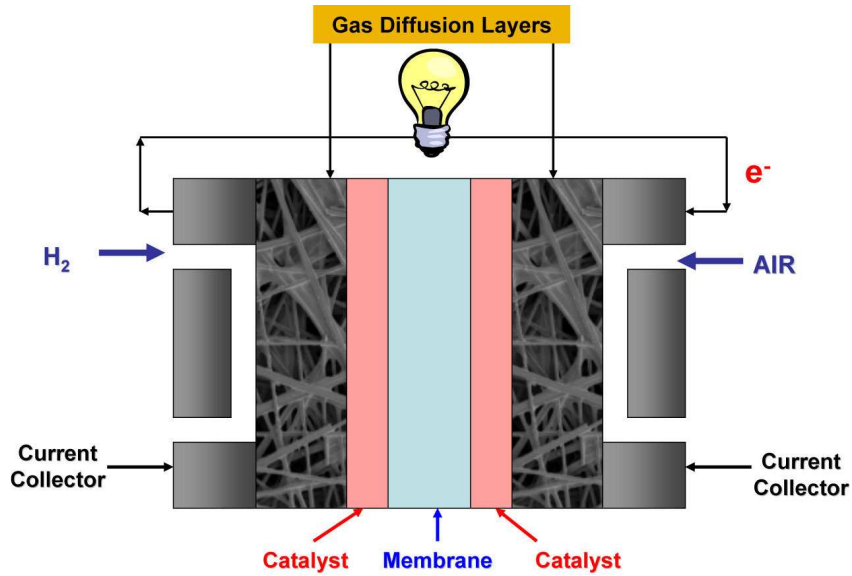
>20.000 turnovers en 1h !! (6 s^{-1})

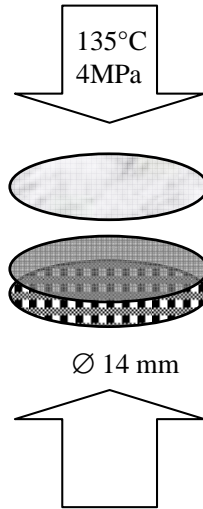
94% rendt faradique

Pas de perte d'activité

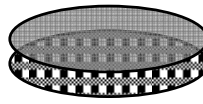
Pas d'inhibition par CO , O_2

PEMFC

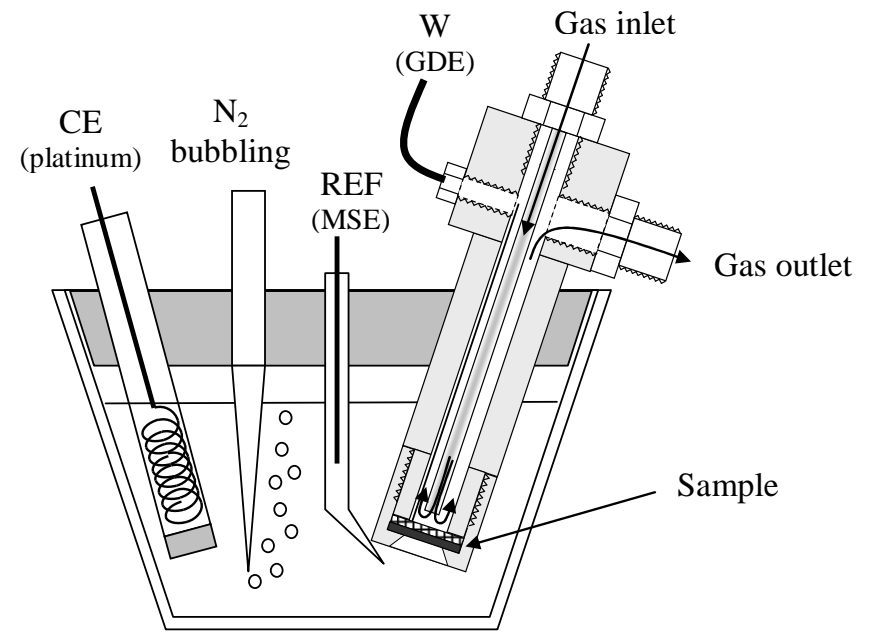
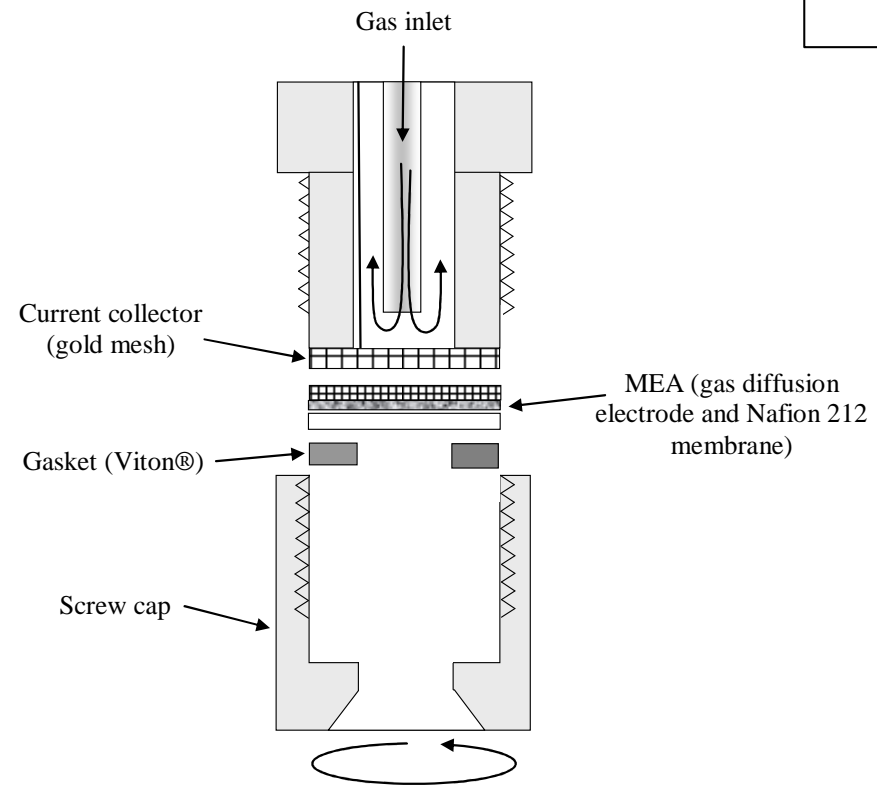




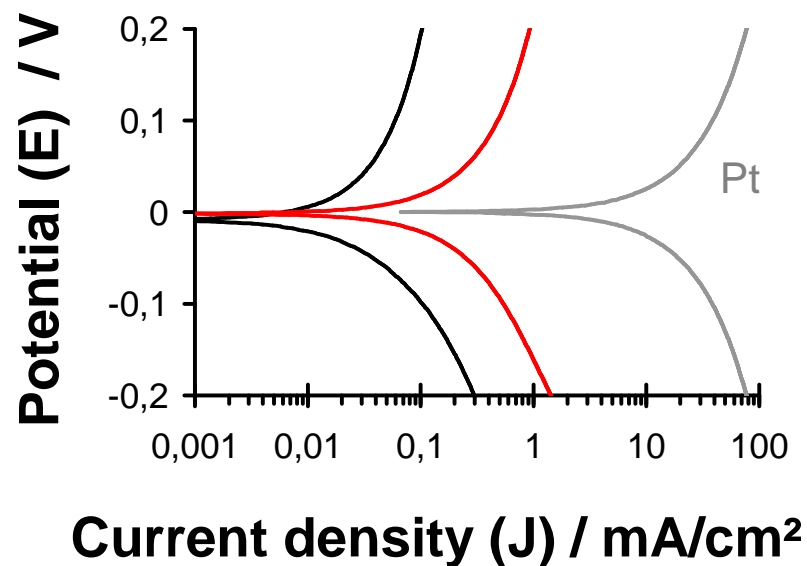
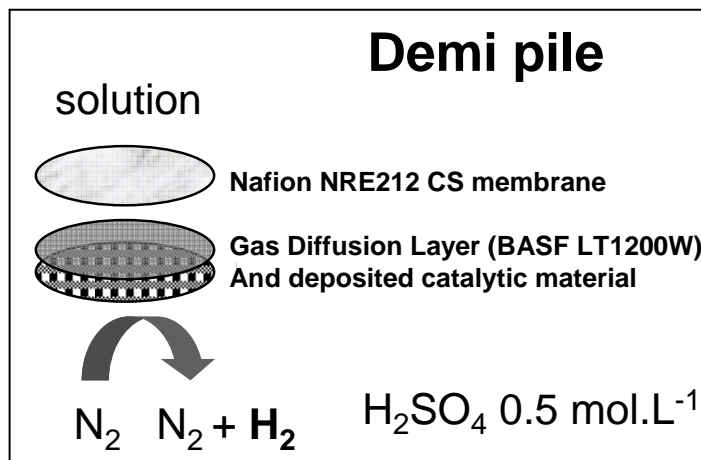
Nafion NRE 212 CS membrane



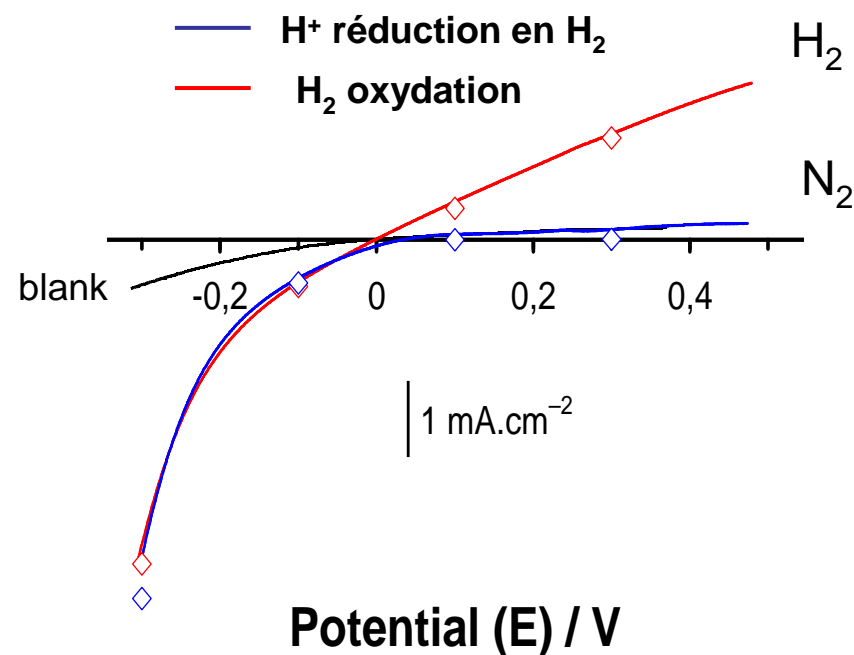
Gas diffusion layer (BASF LT 1200W) and deposited catalyst



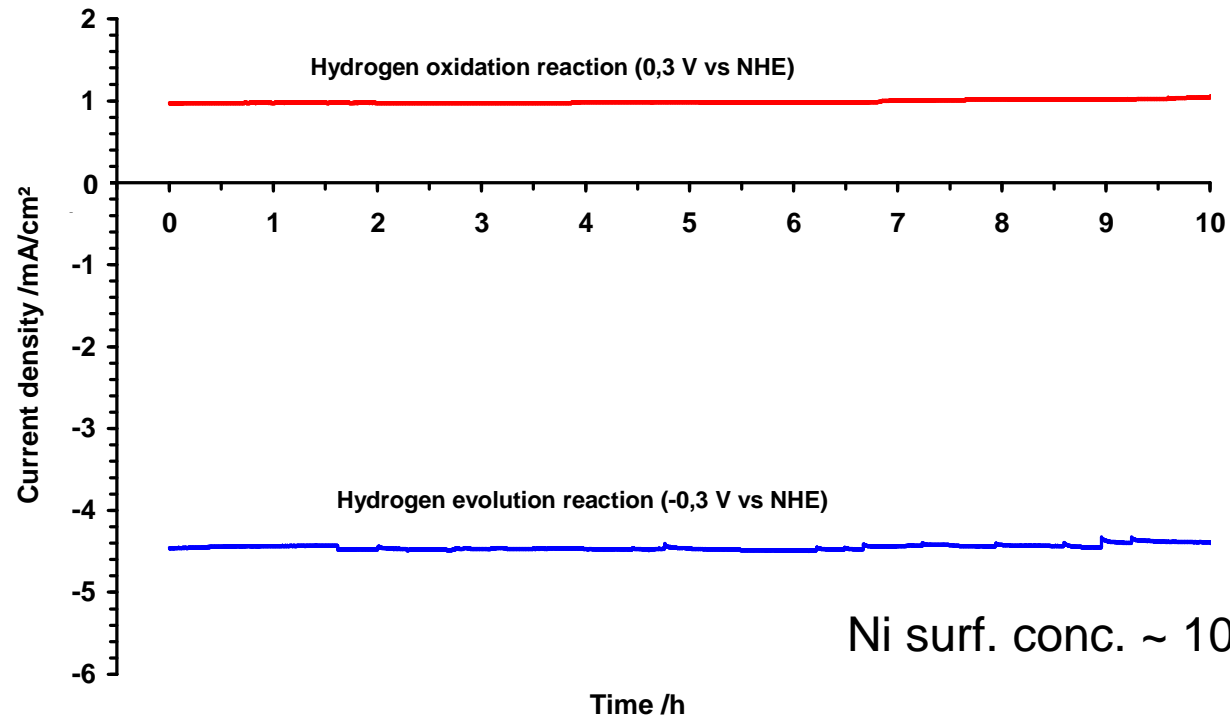
-Un matériau catalytique à la fois pour la production et l'oxydation de H_2
 -Compatible avec la Technologie PEM (membrane Nafion, Conditions acides)



Ni 0.06 mg cm⁻² Pt 0.5 mg cm⁻²



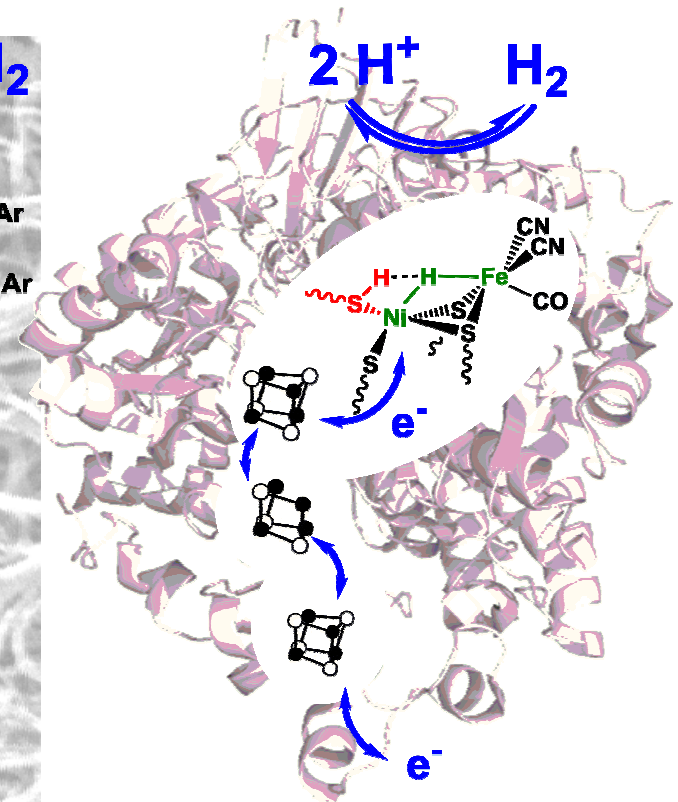
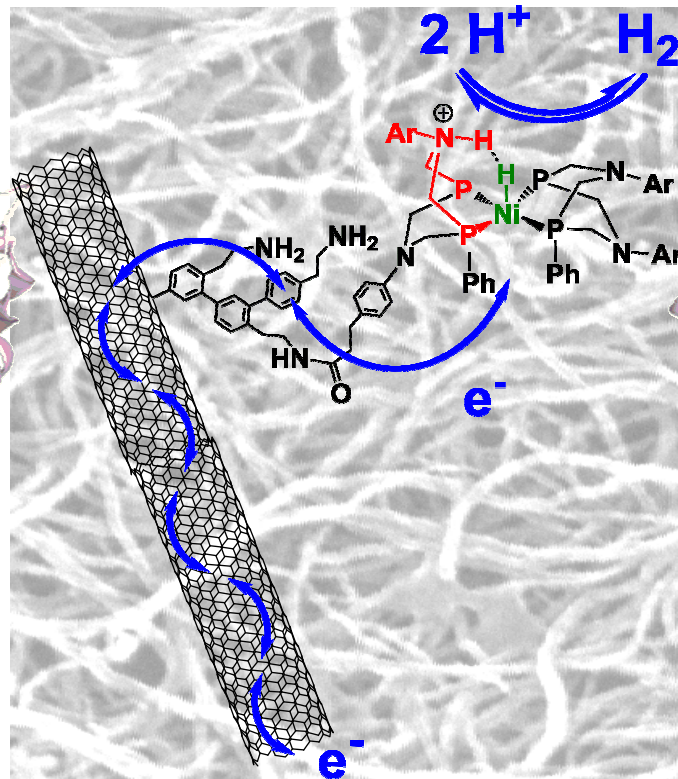
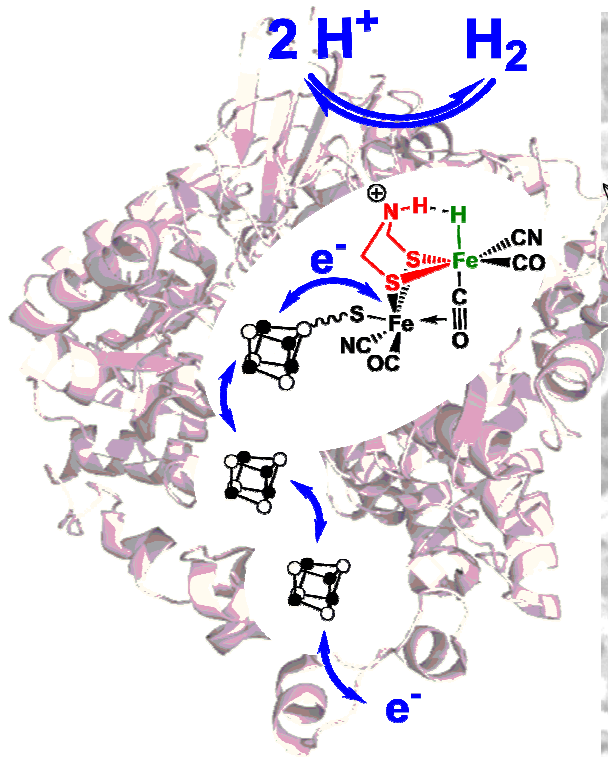
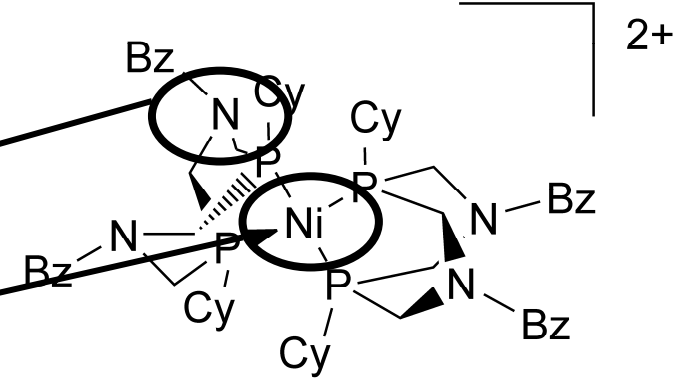
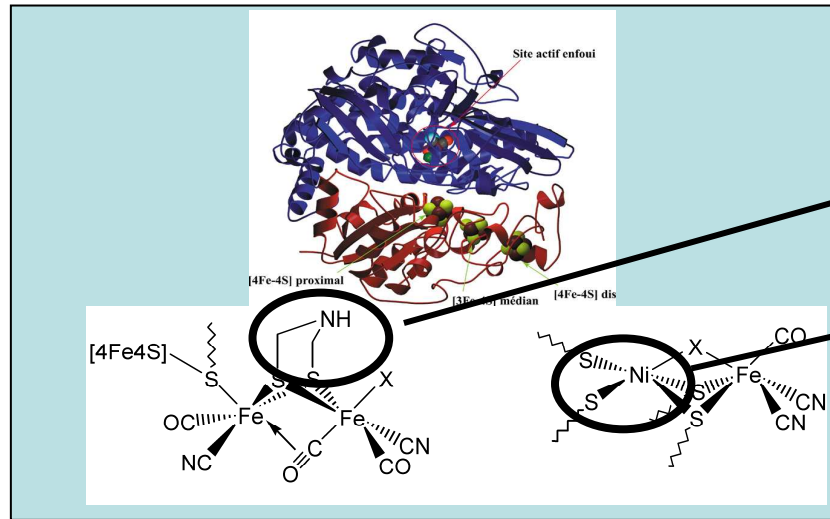
Coulométrie à pot contrôlé
H₂SO₄ 0.5 M



Ni surf. conc. $\sim 10^{-9}$ mol.cm⁻²

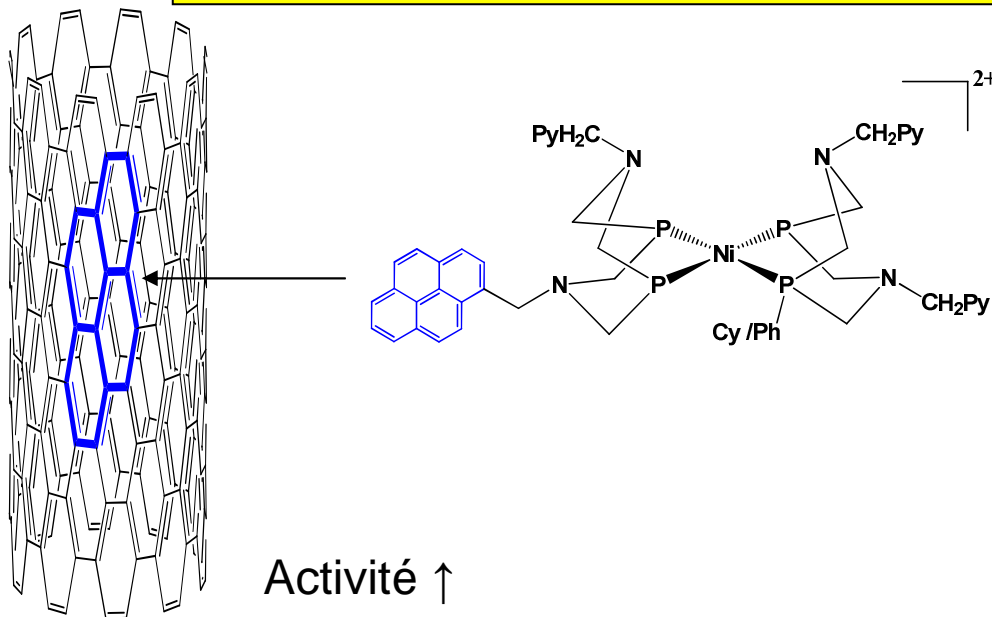
>100.000 cycles catalytiques
Pas de perte d'activité

Des enzymes aux nanocatalyseurs bio-inspirés



Optimisation: nouvelles stratégies d'immobilisation

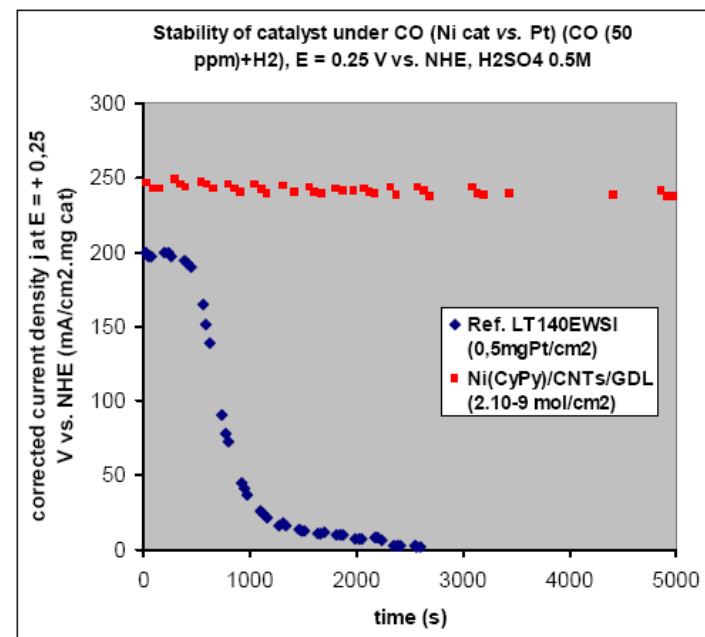
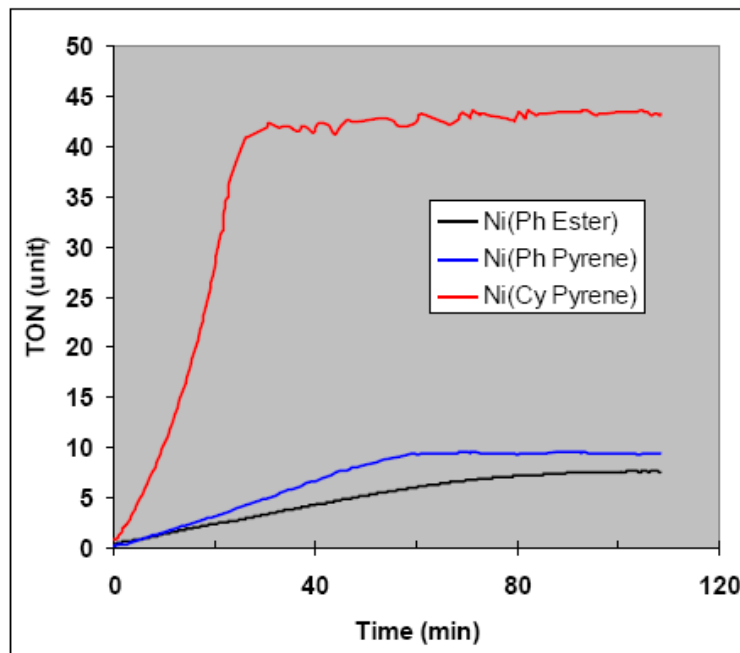
(soumis)



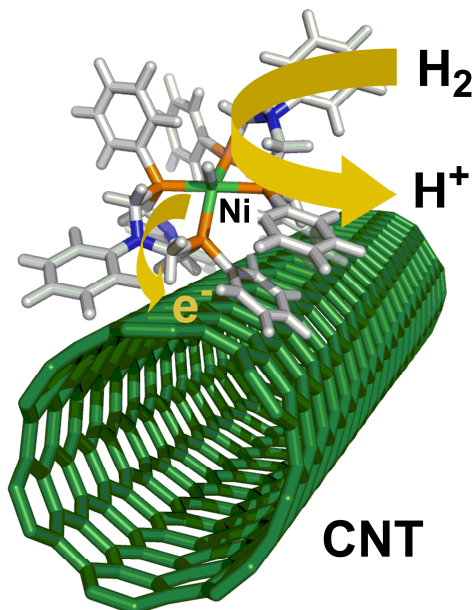
- ➔ Préparation simplifiée
- ➔ Charge en catalyseur ↑
- ➔ Densités de courant ↑

Activité ↑

Résistance à CO



CONCLUSION



Un complexe bioinspiré
de Ni
gréffé sur des NTCs
déposés sur électrode



V. Artero (CEA-DSV)
+DSM + LITEN

From Hydrogenases to Noble Metal-Free Catalytic Nanomaterials for H₂ Production and Uptake

Alan Le Goff,¹ Vincent Artero,^{2*} Bruno Jusselme,¹ Phong Dinh Tran,² Nicolas Guillet,³
Romain Métayé,¹ Aziz Fihri,² Serge Palacin,^{1*} Marc Fontecave^{2,4}

4 DECEMBER 2009 VOL 326 SCIENCE

European patent application EP-08 290 988.8

+++

Un catalyseur pour l'oxydation et la production d'H₂
>100.000 cycles !!

Grande stabilité du matériau

Compatible avec la technologie PEM
surtension= 20 mV !!

Résistance à CO

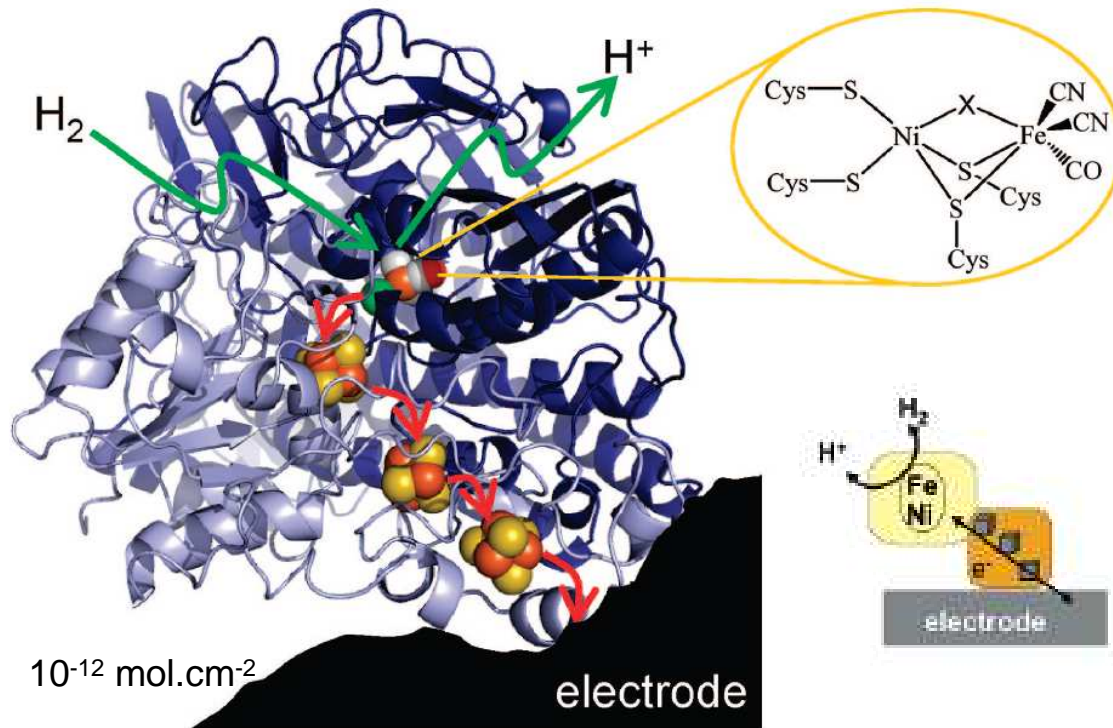
Coût: 20 euros/kg (Pt: 20000 euros/kg)

Faibles densités de courant
(1/10 vs Pt)

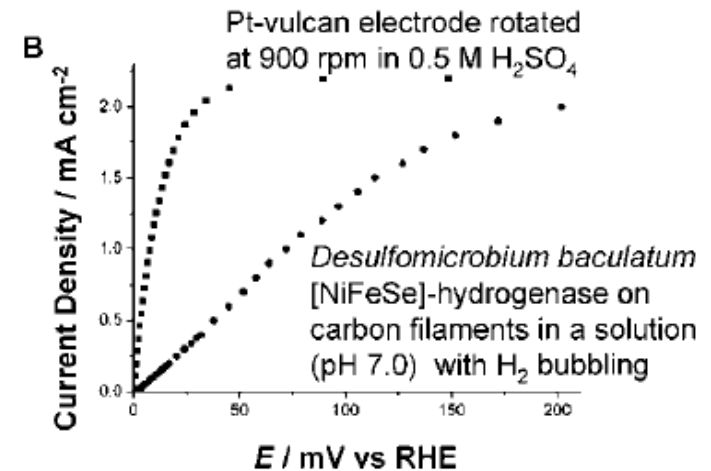
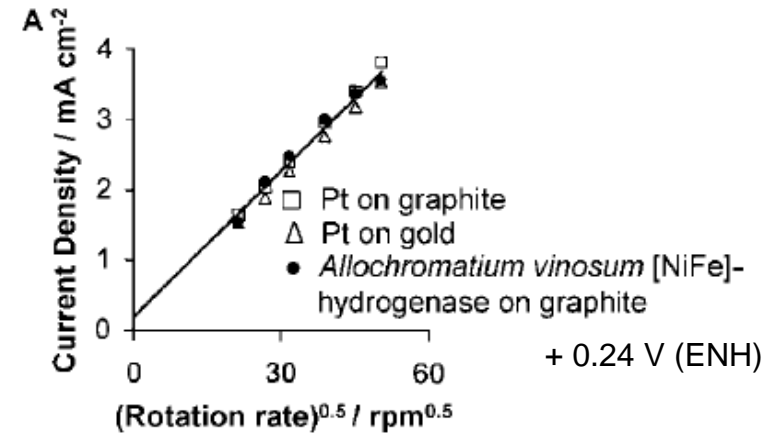
Des électrodes à « hydrogénases »

→ Simple adsorption

FA Armstrong Chem Rev 2008 108 2439

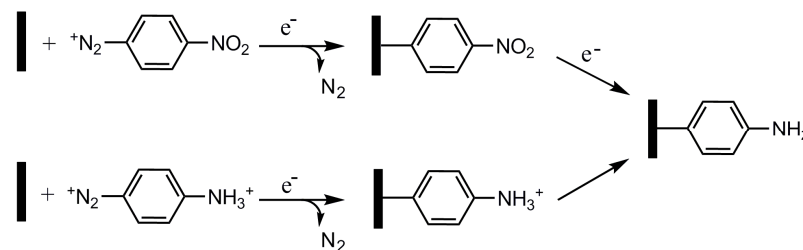
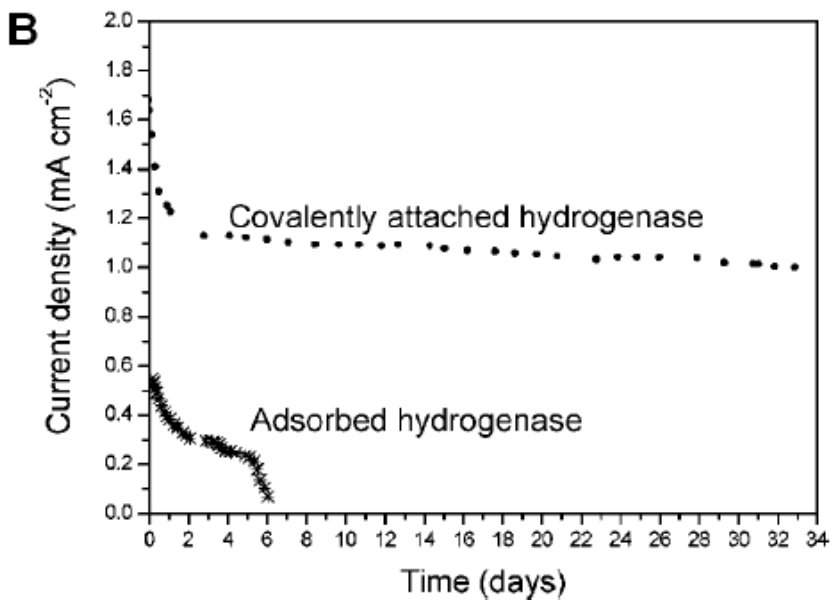
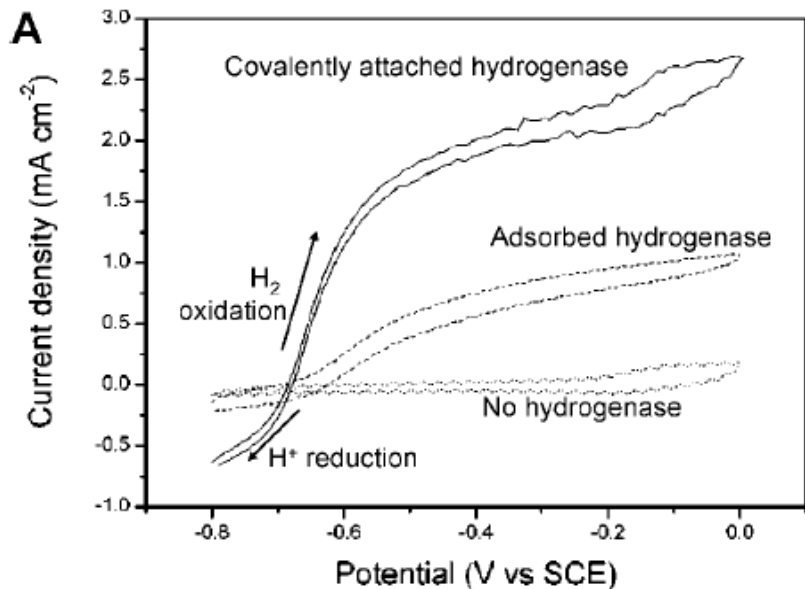


→ Stabilisation par
-polyamines(polylysine)
-polymères (polypyrrole)

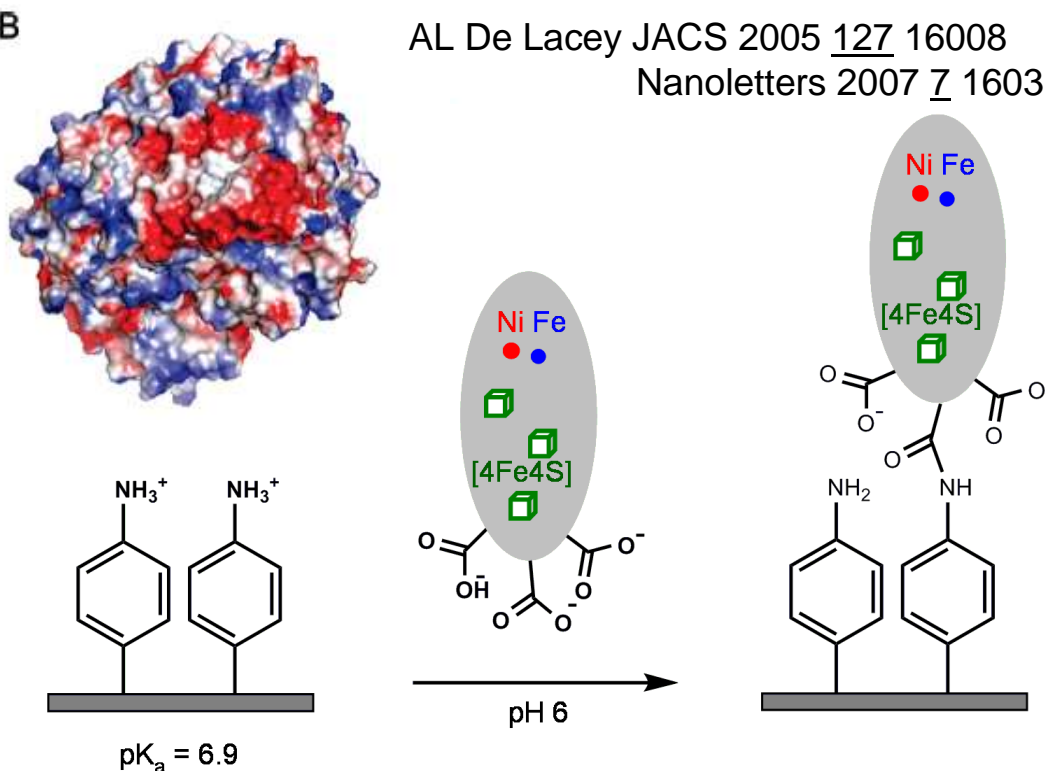


Des électrodes à « hydrogénases »

→ **Fixation covalente**
(graphite – nanotubes de carbone)



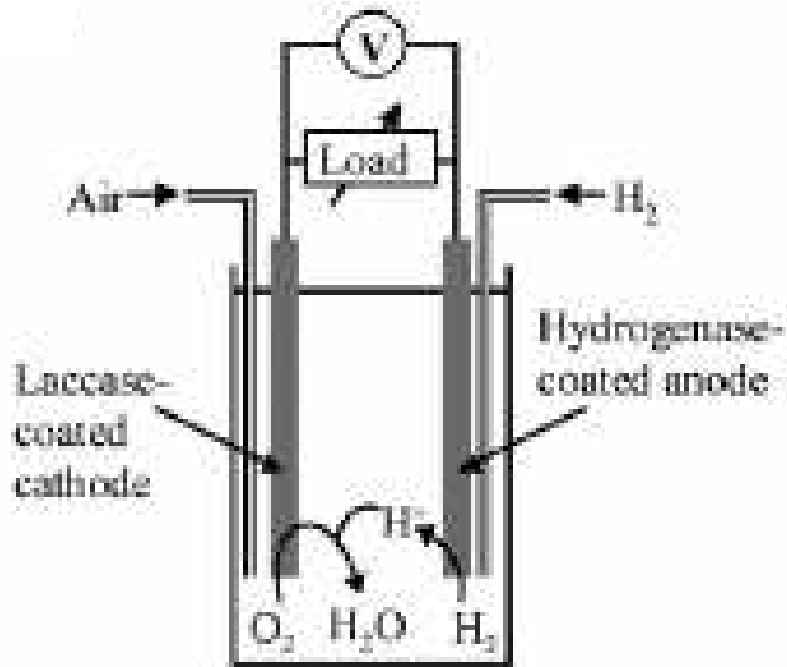
AL De Lacey JACS 2005 127 16008
Nanoletters 2007 7 1603



pH 6: interactions électrostatiques
contrôle de l'orientation (surface chargée +)
pH 7.6: pas de contrôle (surface neutre)

Applications technologiques

Vers des biopiles à hydrogène



Vincent *et al.* (2005) PNAS 102:16951-4

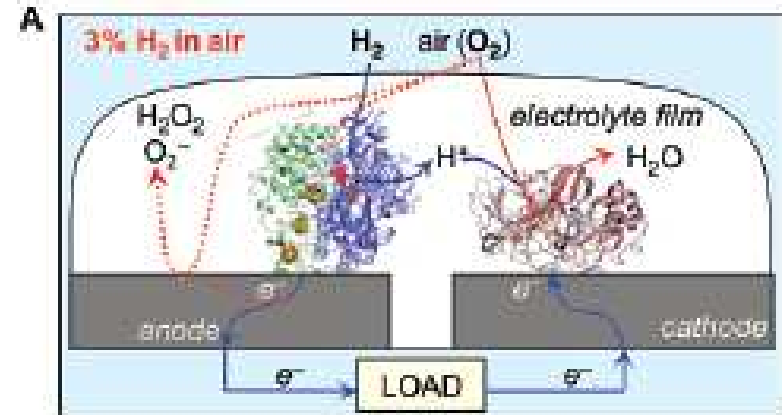
980 mV en circuit ouvert; 7 $\mu\text{W}\cdot\text{cm}^{-2}$; CO n'inhibe pas

Vincent *et al.* (2006) Chem. Commun. (Camb). 48:5033-5.

Ralstonia metallidurans, *R. eutropha*

950 mV en circuit ouvert; 5 $\mu\text{W}\cdot\text{cm}^{-2}$ tension 500mV

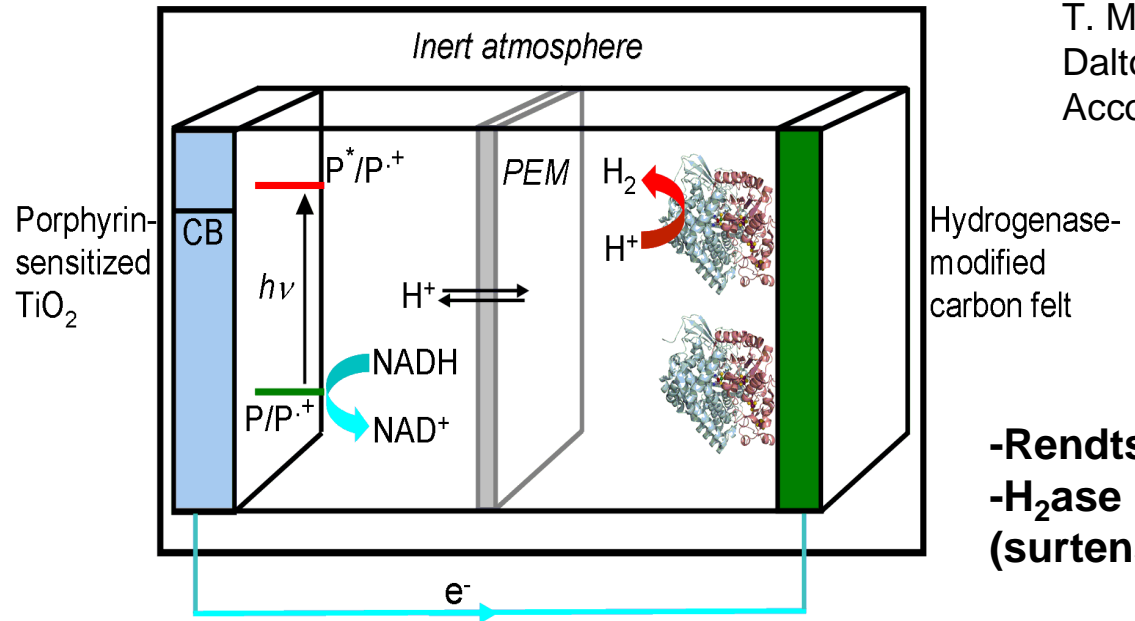
- ➔ Instabilité
- ➔ Puissances faibles
- ➔ Pas d'inhibition par CO



880 mV en circuit ouvert

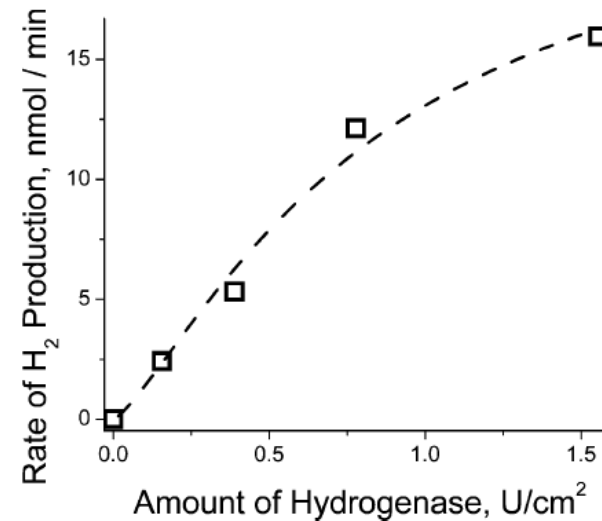
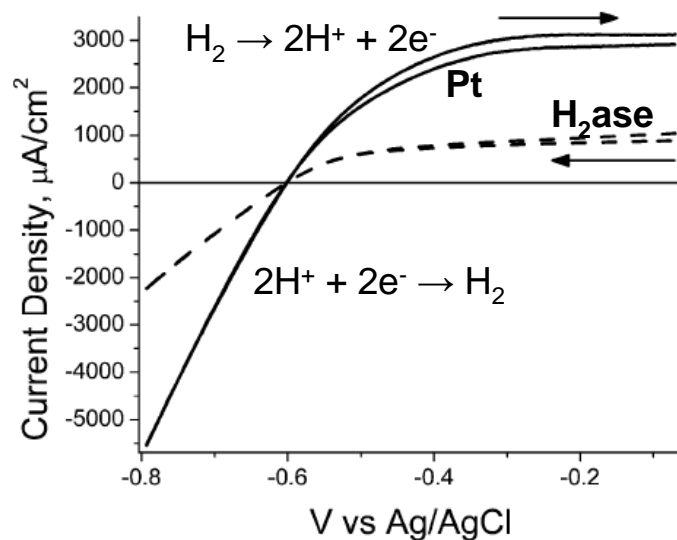
5 $\mu\text{W}\cdot\text{cm}^{-2}$

La première bio-cellule photoélectrochimique

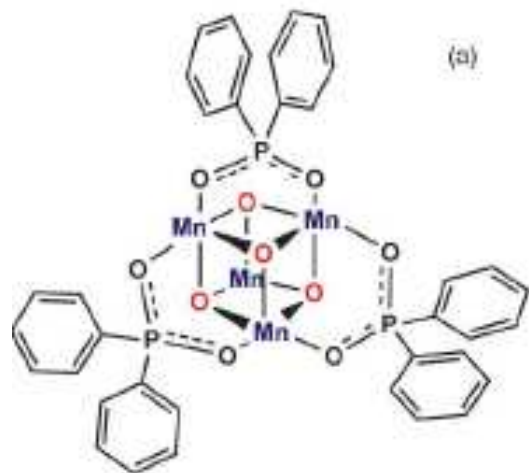


T. Moore JACS 2008 130 2015
 Dalton trans 2009 9979
 Accounts Chem Res 2009 42 1890

-Rendts quantiques: 5%
-H₂ase ~ Pt
(surtension, densité de courant)



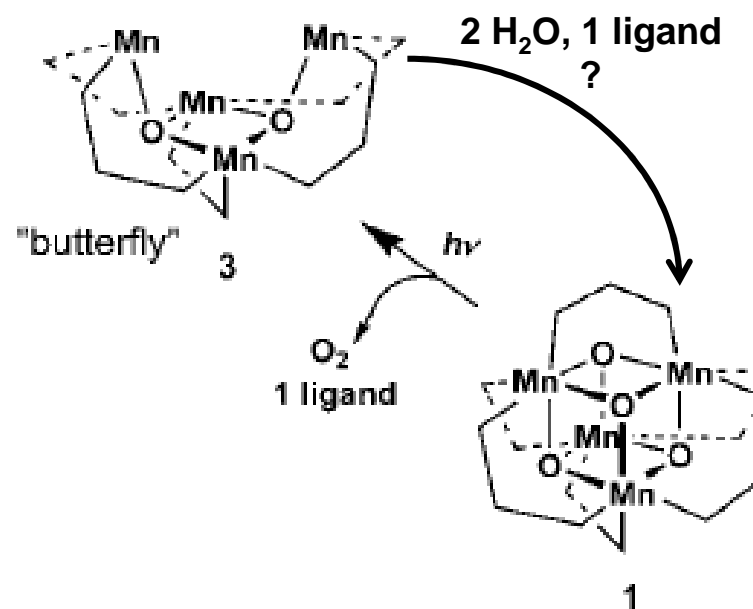
Catalyseur de Dismukes (Dismukes; Angew Chem 2008)



Ligand: $(Ar)_2PO_2^-$
diarylphosphinate

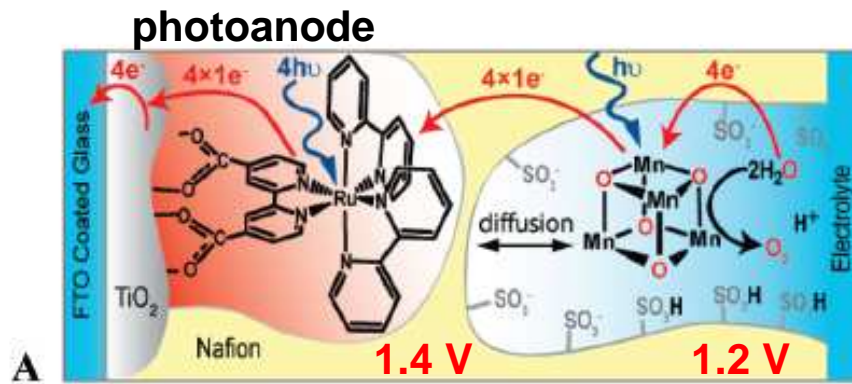
Incorporé dans une membrane de Nafion
Sur électrode potentiel **1 Volt**
Irradiation lumière blanche (Xe)

O_2 : 1000 mol/mol (65 h)



Une cellule photoélectrochimique (Mn)

GC Dismukes JACS 2010 132 2892



pH 6.5 Na₂SO₄
hv >290 (395)nm

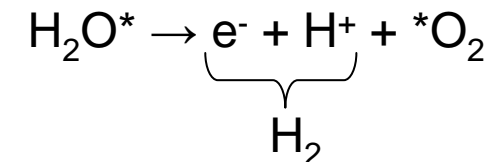
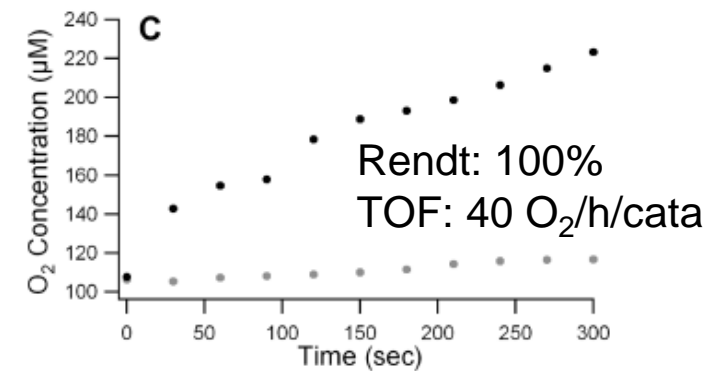
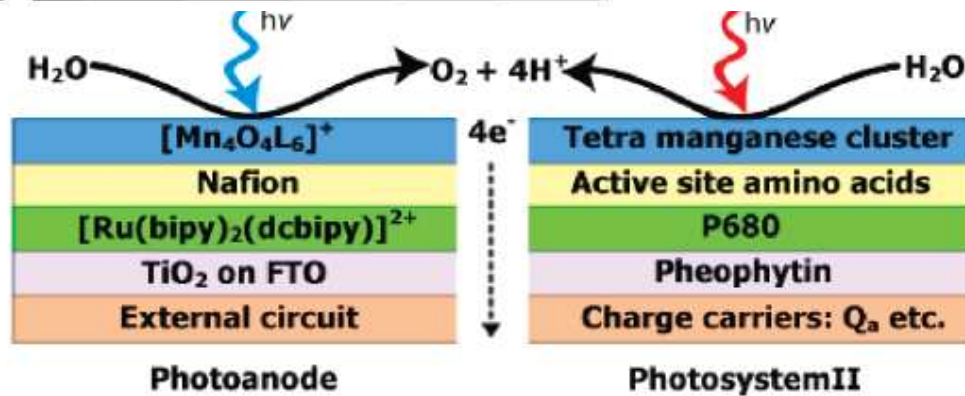
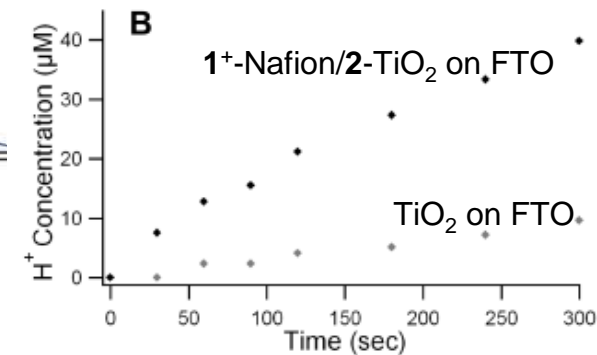
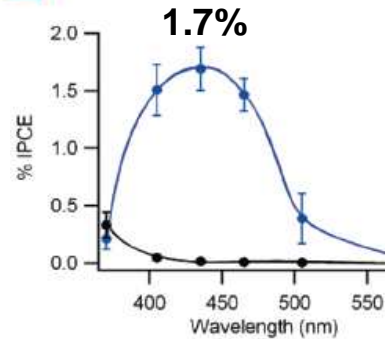
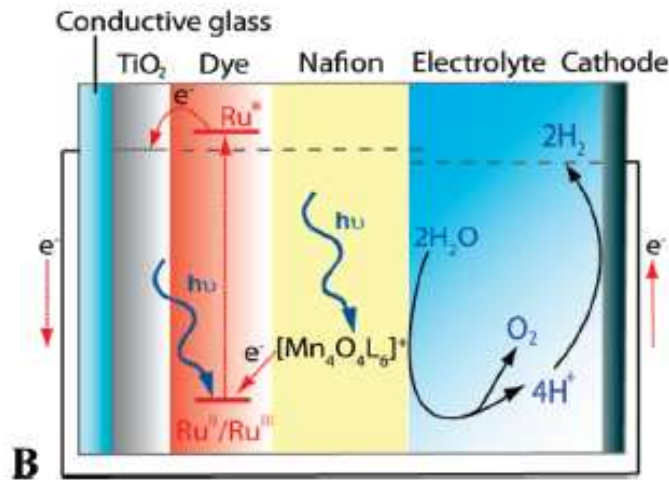
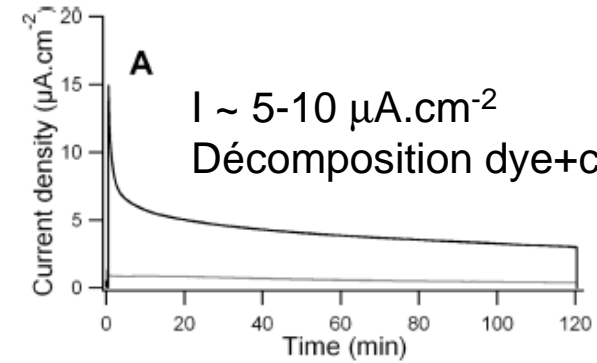


FIGURE 5. Schematic showing the conceptual similarity of the photoanode **1b**⁺-Nafion/Ru(4)-TiO₂, with the PSII-WOC.



COLLÈGE
DE FRANCE
—1530—

Des catalyseurs moléculaires à des matériaux d'électrodes

Marc Fontecave

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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

Water electrolysis and photoelectrolysis on electrodes engineered using
Biological and bio-inspired molecular systems
PD Tran, V Artero, M. Fontecave
Energy and Environmental Science 2010 (sous presse)

