"Solar Energy" WS 2014/2015

Lecture 20: Solar Fuels
(Basic Photocatalysis and Photoelectrochemical Applications)

Prof. Dr. Bryce S. Richards / Dr. Engelbert Redel
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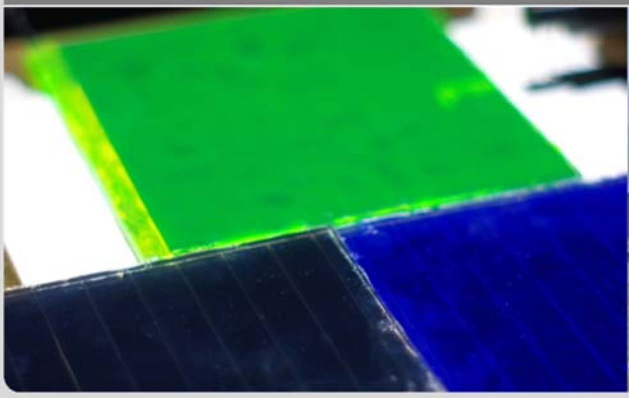
Light Technology Institute (LTI), Engesserstrasse 13, Building 30.34, 76131 Karlsruhe
Institute of Functional Interfaces (IFG), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

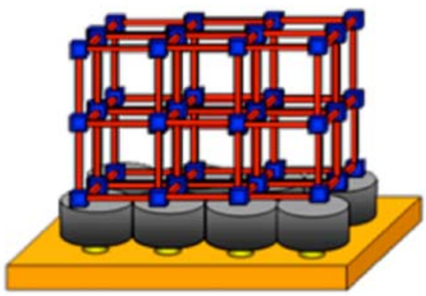
KIT Focus Optics & Photonics



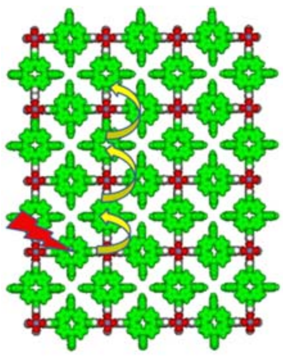
"Solar Energy" WS 2014/2015

- **Dr. Engelbert Redel**
  (Group Leader)

  Institute of Functional Interfaces (IFG),
  Hermann-von-Helmholtz-Platz 1,
  76344 Eggenstein-Leopoldshafen



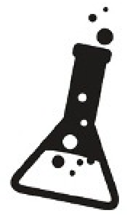
- **Research Interest:**
  - *Nanomaterials and Optical/Photonic Assemblies*
  - *Supramolecular Coordination Networks (CNCs)*
  - *Watersplitting and Photo(electro)catalysis*
  - *Devices and Energy Applications*



Overview & Introduction

•**Part I (45 min)**

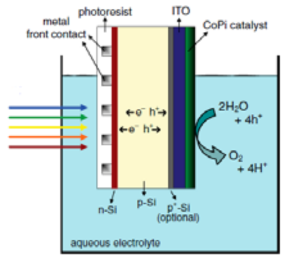
- Introduction (Photosynthesis)
- Basic SC Photochemistry
- Basic Photo-oxidation & Photo-reduction
- SC Tandem Systems



The Chemistry of e^- & h^+

•**Part II (45 min)**

- Photoelectrochemical (PEC) Applications
- Photovoltaic coupled Photoectrochemistry
- Dual energy systems, Solar Refinery & GAP



Devices/Applications

Introduction (Photosynthesis)

®***Sunlight energy*** is abundant, renewable and well distributed throughout the globe.

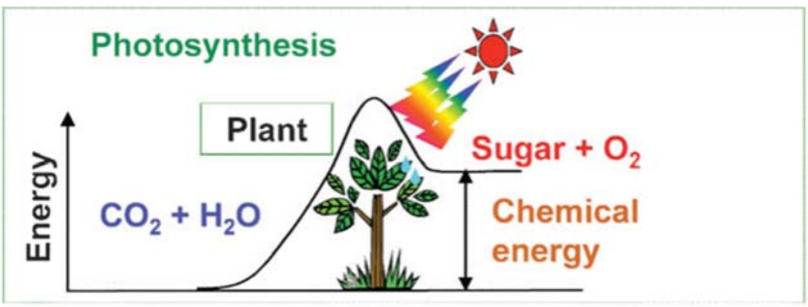
®Photosynthesis transform “photon-energy” into <u>high energy density organic-fuel products which are storable!</u>

Photosynthesis is the ultimate source of our:

► Oxygen

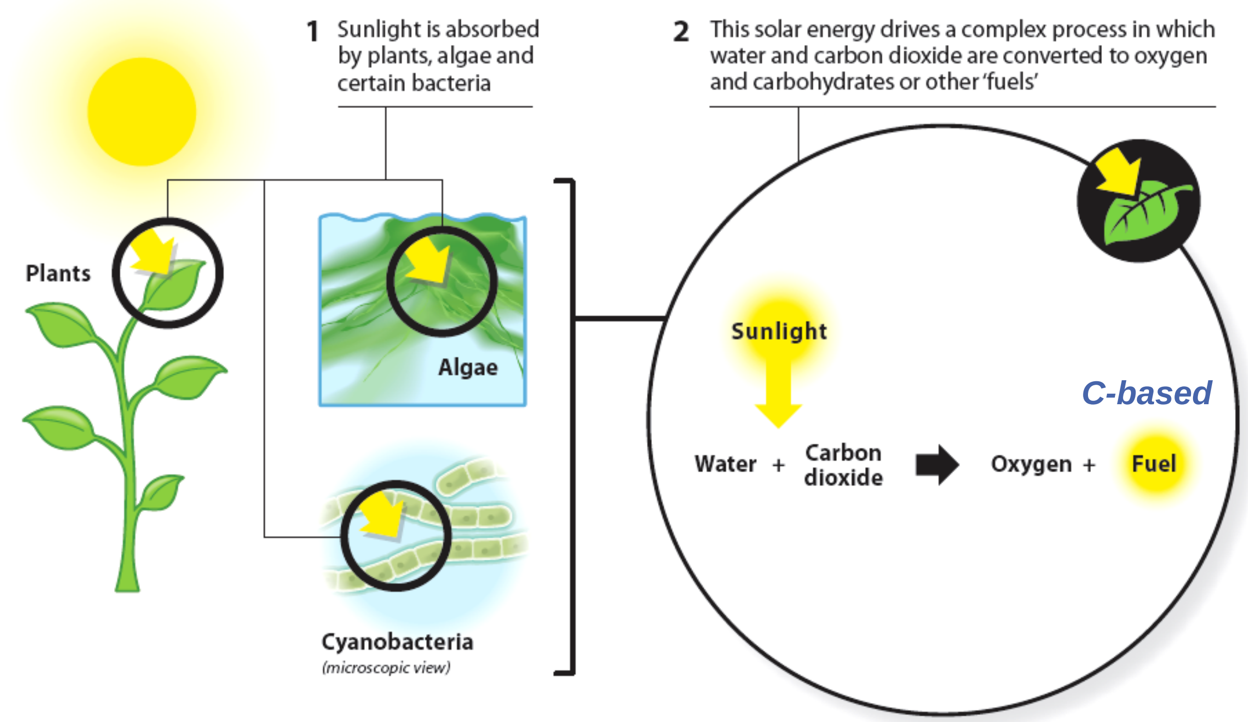
► Organic Food

► Fossil Fuels



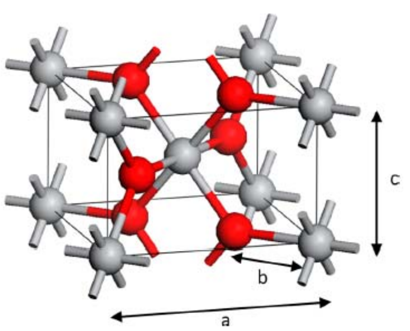
A. Kudo, Y. Miseki Chem. Soc. Rev., 2009, 38, 253–278.

Photosynthesis: Nature's way of making "solar fuels"



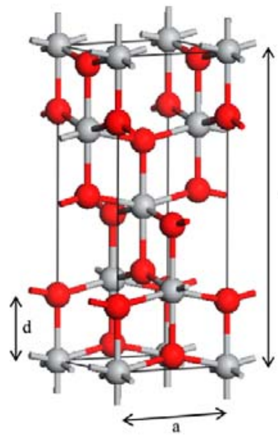
Source/picture from: Solar Fuels and Artificial Photosynthesis (Science and innovation to change our future energy options) January 2012, RSC Advancing the Chemcial Sciences, on p. 6 Figure 2; www.rsc.org/solar-fuels

Photocatalyst e.g. TiO_2 pigment



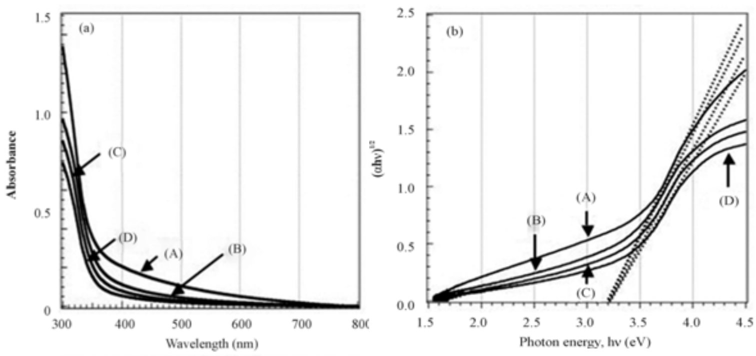
► Tetragonal structure of rutile

Materials Sciences and Applications, **2014**, *5*, 112-123



► Tetragonal structure of anatase.

TiO_2 White Powder Pigment

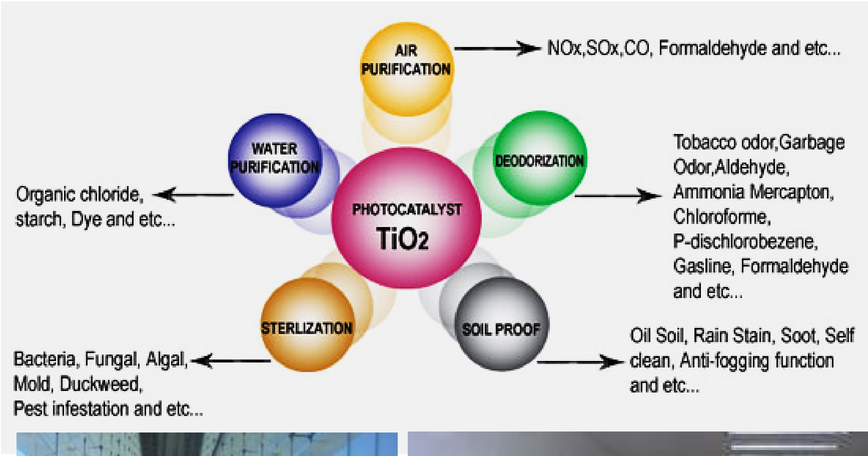


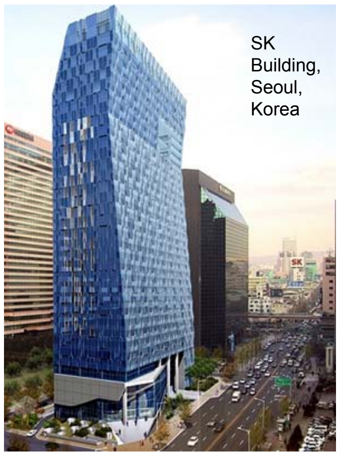
TiO_2 (rutile/anatase) indirect semiconductor

Eg from $(\alpha h\nu)^{1/2}$ versus photon energy *hv* ("Tauc Plot")

(A) TiO_2 film which was made from the sol solution (a); (B) TiO_2 film which was made from the sol solution (b); (C)TiO_2 film which was made from the sol solution (c); (D) TiO_2 film which was made from the sol solution (d).

Photocatalyst TiO_2 Applications



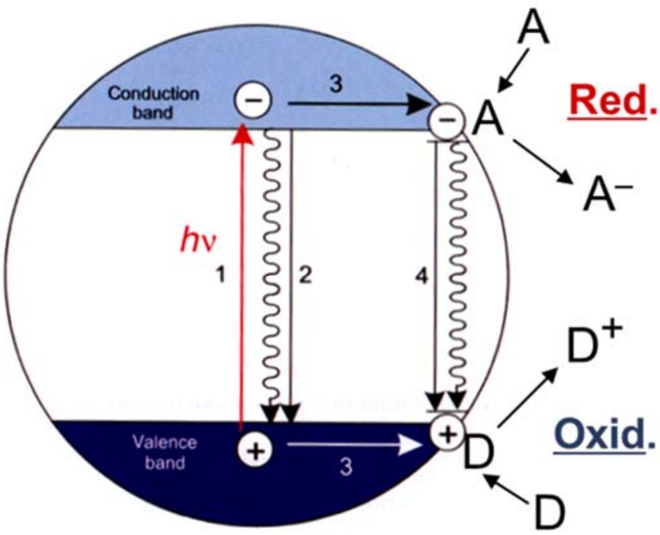


SK Building, Seoul, Korea

7 http://haximpower.com/

Basic Photochemistry SC

► Primary physical processes taking place after excitation of a SC particle:



(1)excitation

(2)radiative or non-radiative recombination

(3)charge trapping

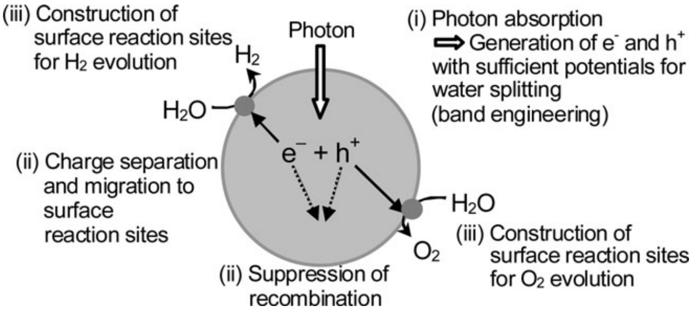
(4)recombination of trapped states

G. Stochel, M. Brindell, W. Macyk, Z. Stasicka, K. Szacilowski, *Bioinorganic Photochemistry,* Wiley-VCH, **2009**, p.88.

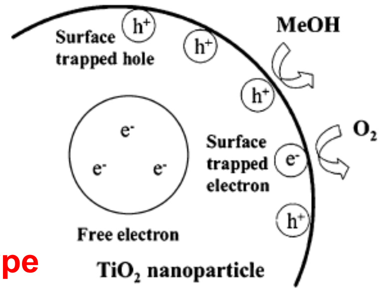
Basic Photochemistry (SC)

$TiO_2 + h\nu \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$

► e^- / h^+ generation process

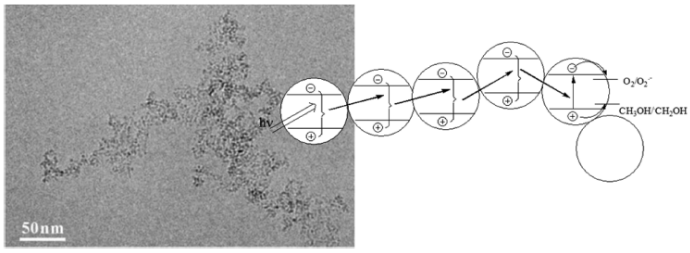


► Spatial resolution of photo-generated charge carriers in TiO_2 (***n*-type**) SC.

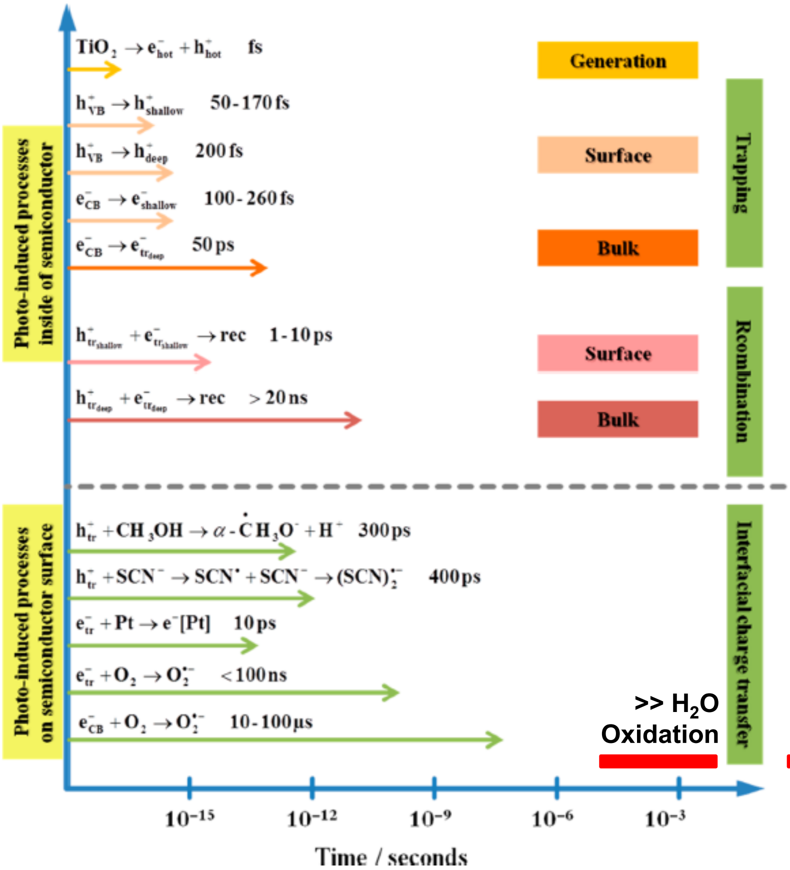


***n*-type**

► "Antenna effects" of charge carrier transfer in self-assembled decorated TiO_2 aggregates/nanoparticles.



D. W. Bahnemann, *et. al J. Mater. Chem.*, **2009**, *19*, 5089–5121. D. W. Bahnemann, *et. al Chem. Rev.* **2014**, *114*, 9919–9986.



$TiO_2 + h\nu \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$

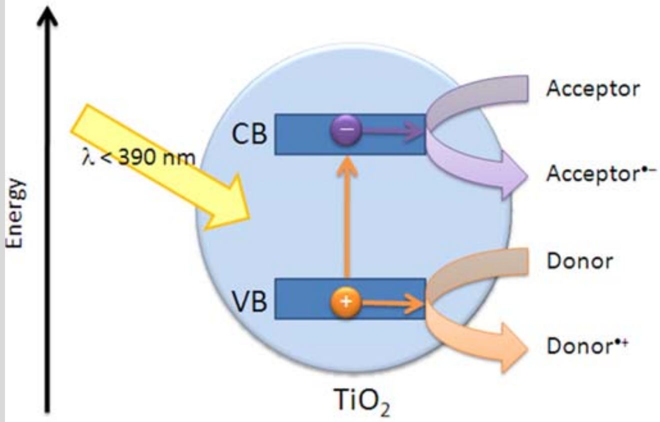
► Time scales of "*elemental steps*" occurring in a prototypical photocatalytic processes.

>> CO_2 Reduction

(≈ sec)

D. W. Bahnemann, *et. al Chem. Rev.* **2014**, *114*, 9919–9986.

Basic Photochemistry (SC)



$SC + h\nu(\geq E_g) \rightarrow h_{VB}^+ + e_{CB}^-$ (charge carrier generation)

$h_{VB}^+ + e_{CB}^- \rightarrow SC$ + heat (bulk recombination)

$h_{VB}^+ + \equiv SC\text{–}OH \rightarrow \equiv SC\text{–}OH^{\bullet+}$ (hole trapping)

$e_{CB}^- + \equiv SC\text{–}OH \rightarrow \equiv SC\text{–}OH/e_{tr}^-$ (electron trapping)

$\equiv SC\text{–}OH^{\bullet+} + Red \rightarrow \equiv SC\text{–}OH + Red^{\bullet+}$ (hole transfer)

$\equiv SC\text{–}OH/e_{tr}^- + Ox \rightarrow \equiv SC\text{–}OH + Ox^{\bullet-}$ (electron transfer)

Oxidation

$Ti^{IV}|H_2O + h^+_{vb} \leftrightarrow Ti^{IV}|{\bullet}OH + H^+$

$Ti^{IV}|OH^- + h^+_{vb} \leftrightarrow Ti^{IV}|{\bullet}OH$

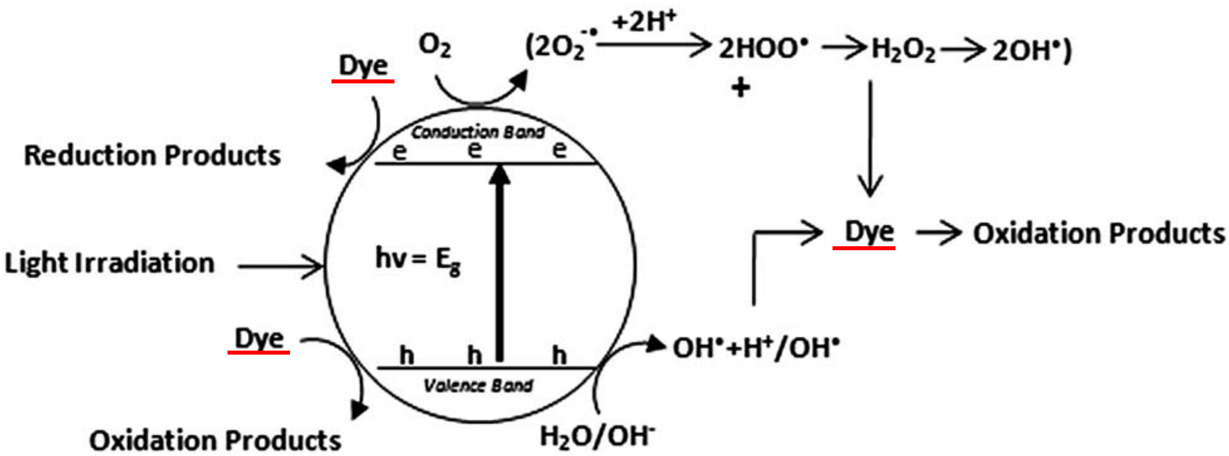
Reduction

$[Ti^{IV}] + e^-_{cb} \leftrightarrow [Ti^{III}] + O_2$ (abs) → **ROS**

ROS (Reduced Oxgen Species)
$\bullet O^-_2$; HO^-_2; $\bullet O^-$; Ti^{IV}-OOH

https://photochemistry.wordpress.com/page/2/
J. Mater. Chem., **2009**, *19*, 5089–5121.

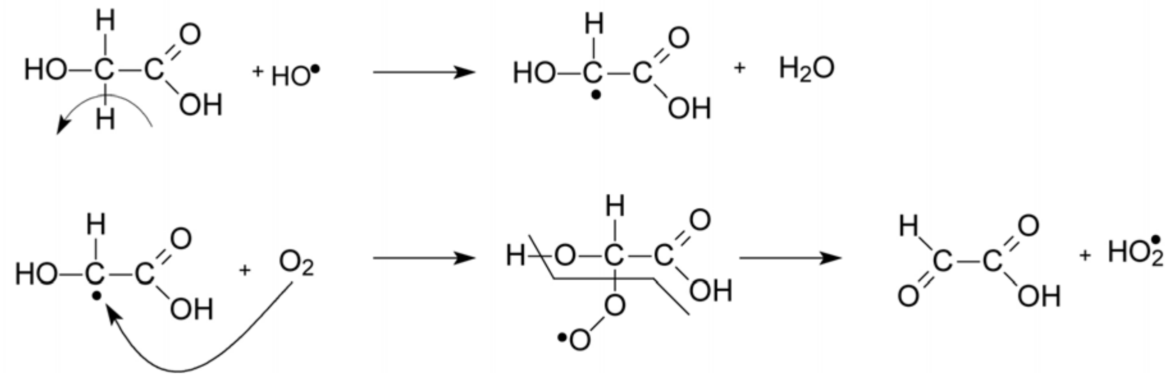
Basic Photo-oxidation & Photo-reduction



Source: A. Ajmal, I. Majeed, R. N. Malik, H. Idriss, M. A. Nadeem *RSC Adv.*, **2014**, *4*, 37003–37026.

Basic Photo-oxidation & Photo-reduction

- Photodegradation with •OH Radicals

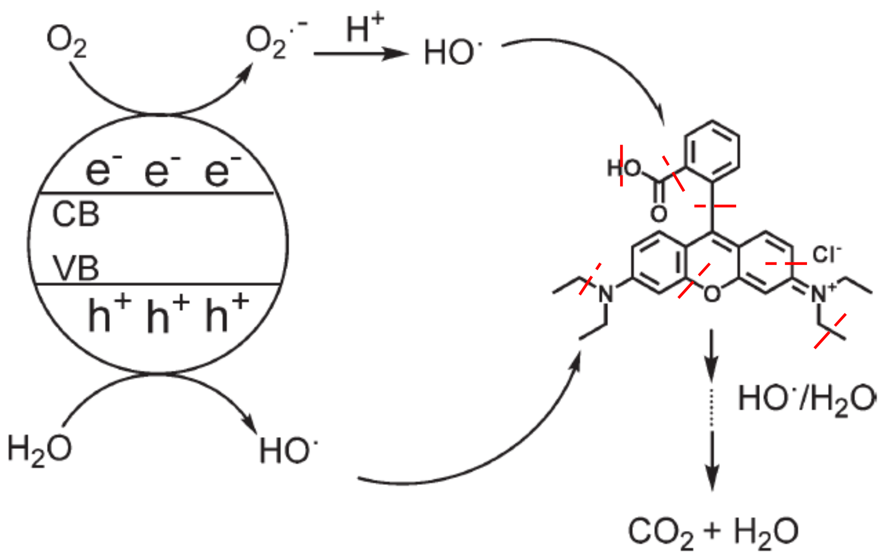


► Example: Photooxidation of carboxylic acids.

J. Braz. Chem. Soc., **2009**, *20*, 1467-1472.

Basic Photo-oxidation & Photo-reduction

- Photodegradation from reduced ⁻•O_2H / •OH species

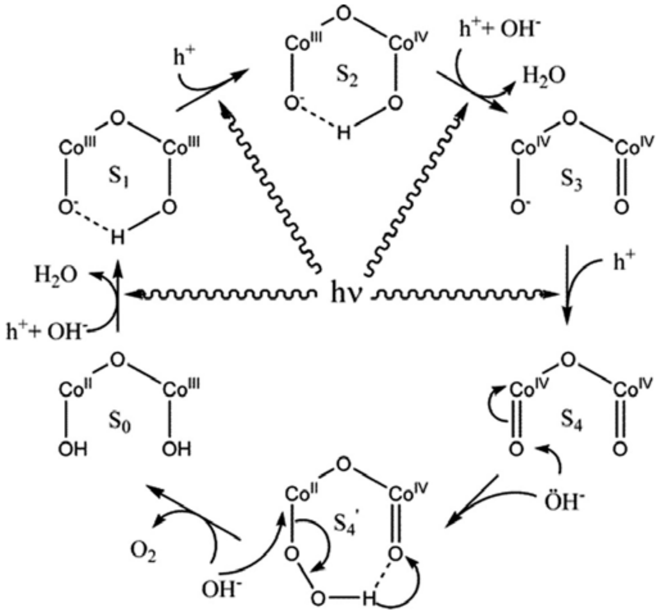


► Example: Photodegradation of an organic dye.

CrystEngComm, **2015**, **DOI:** 10.1039/C4CE02074J

Basic Photo-oxidation & Photo-reduction

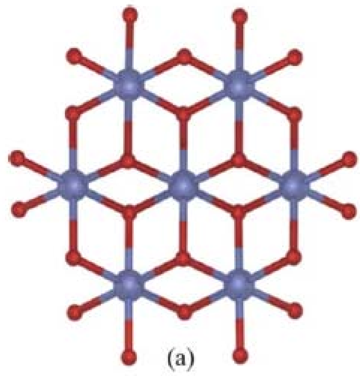
- Photo-oxidation with h^+ (holes)



► Example: Oxidation of Water (H_2O).

Catal. Sci. Technol., **2013**, ***3***, 1660-1671.

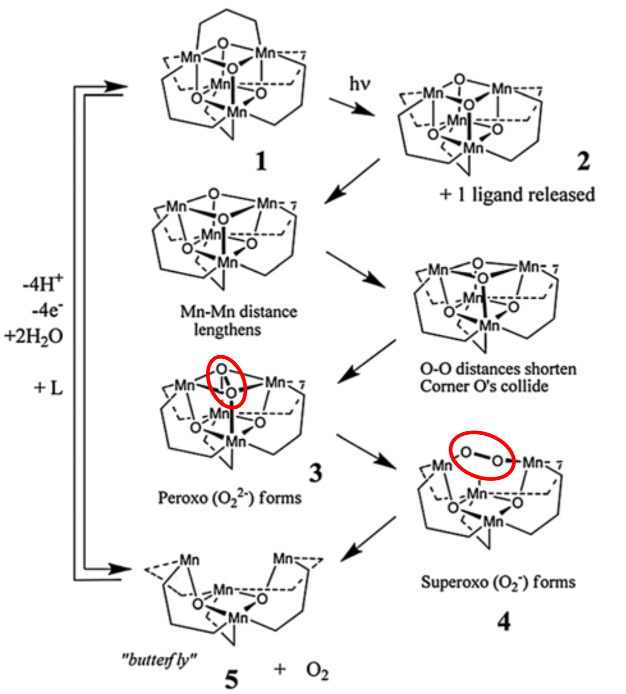
Co-OEC



Nocera *et al.*, *Science*, **2011**, *334,* 645.

Basic Photo-oxidation & Photo-reduction

- gas phase photochemical oxygen evolution from **$Mn_4O_4(PPh_2)_6$**
- proposed mechanism for **PSII (Mn_4O_5Ca)**



Chem. Soc. Rev., 2013, **42**, 2357-2387

1 "cubane" $Mn_4O_4(PPh_2)_6$

2 cationic species $[Mn_4O_4(PPh_2)_5]^+$ after hν illumination

3 Peroxo (O_2^{2-}) species formation

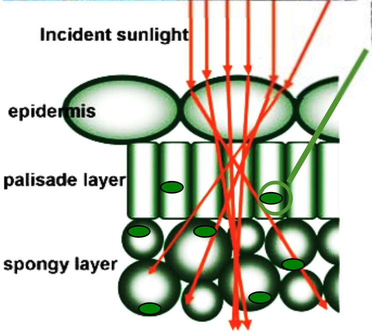
4 Superoxo species (O_2^{2-})

5 "Butterfly" and O_2 release

>> recycling and self-reparing **PSII (Mn_4O_5Ca)**

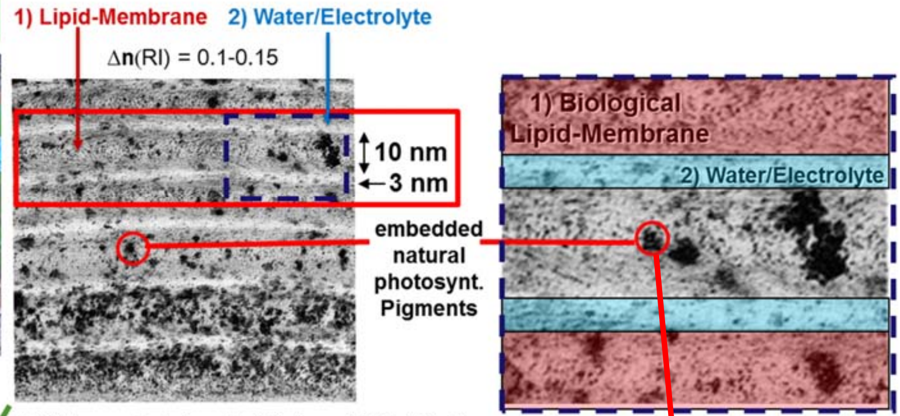
Nature's way of making "Solar Fuels"

"*Natural Leaf*"
1D Thylakoid Stacks; PSI; PSII (photochemical reaction)



D.Zhang, *et al*. *Adv. Mater.* **2010**, *22*, 951.

Site of "Photosynthesis" Thylakoid-Membrane/Stacks

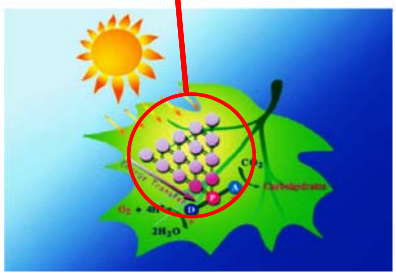


D.W. Lee, *et al. Am. J. of Botany* **1996**, *83*, 45.

>> Structural Hierarchy

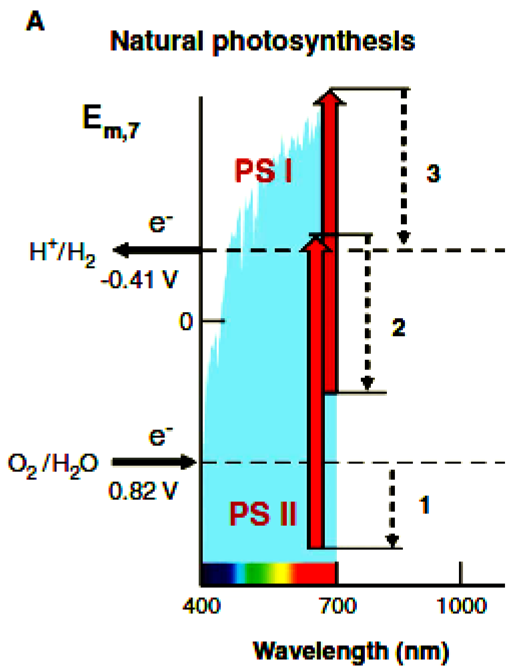
>> Photonic Multilayer Design

>> Supramolecular Light Harnessing Funnel Arrays

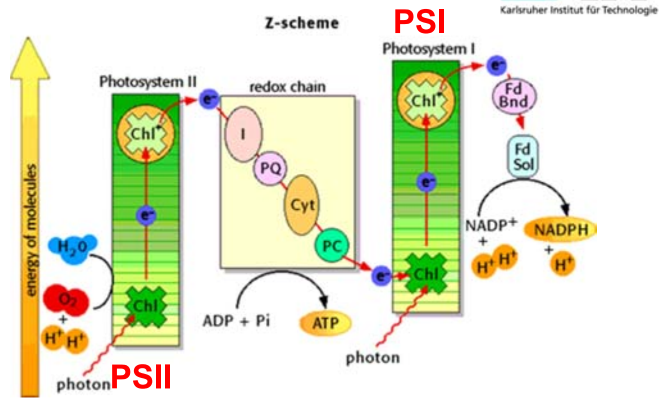


Natural Tandem Systems

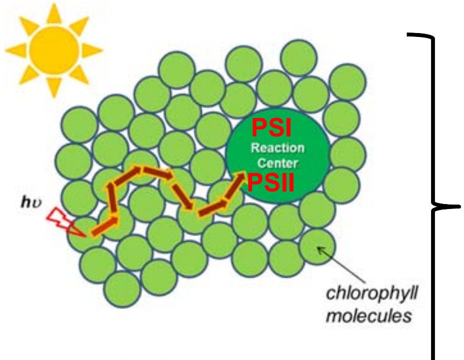
(PSI/PSII in Natural Photosynthesis)



R. E. Blankenship, *et al. Science* **2011**, *332*, 805-807.



http://www.biology.arizona.edu/biochemistry/problem_sets/photosynthesis_1/graphics/z-scheme.GIF



Pathways of "electron transfer" in the time range from ~ ps to μs.

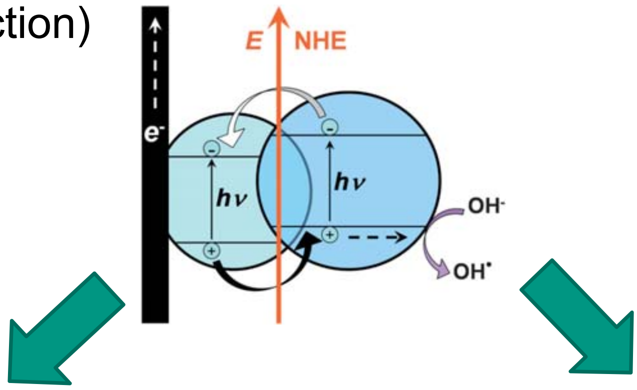
► PSII $[CaMn_4O_5]$

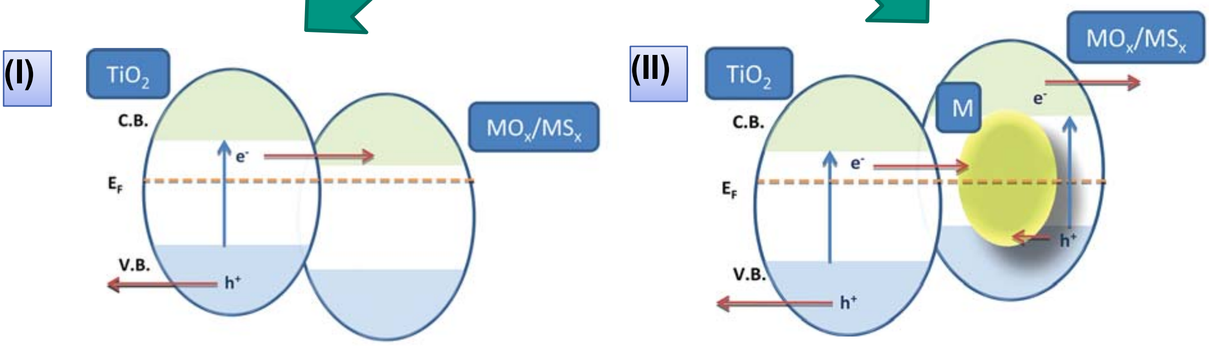
► PSI $[Fe_4S_4]$

source: www.photobiology.info

SC Tandem Systems

(SC Heterojunction)



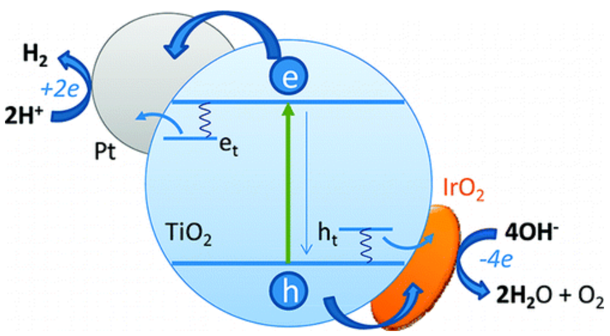


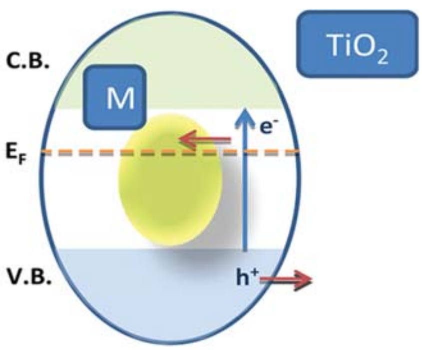
(I) $MO_x(MS_x)/TiO_2$ coupled or coreshell and **(II)** ternary$MO_x(MS_x)$/metal/TiO_2 systems

 J. Mater. Chem., **2009**, *19*, 5089–5121; and *Chem. Rev.* **2012**, *112*, 1555–1614 .

SC Tandem Systems

(charge separation systems)





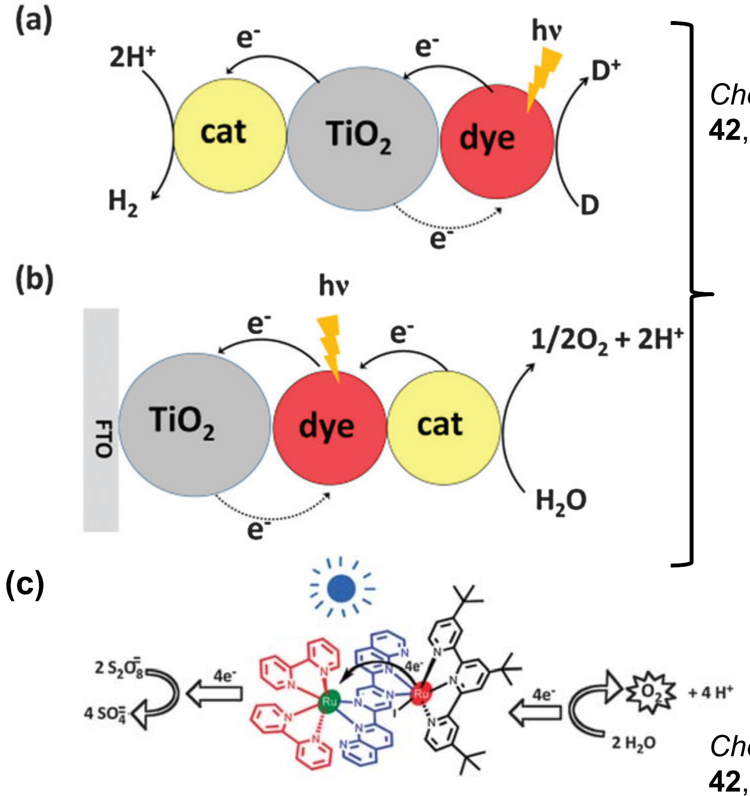
- **Charge separation**
  ® electron and hole trapping!

Kamat, P. V. *J. Phys. Chem. Lett.* **2012**, *3*, 663–672. (Perspective article)

- **Charge separation**
  ® electron trapping on nobel Metals (Ag, Pt or Cu)!

A. Kubacka, M. Fernandez-Garcia, G. Colon *Chem. Rev.* **2012**, *112*, 1555–1614.

Dye Sensitized (SC) Systems



Chem. Soc. Rev., 2013, **42**, 2281-2293

Chem. Soc. Rev., 2013, **42**, 2357-2387

Summary (Part I)

e^- and h^+ are doing <u>Redox-Reactions</u> (Oxidations or Reductions) on SC-surfaces

<u>Oxidation</u>

$Ti^{IV}|H_2O + h^+_{vb} \leftrightarrow Ti^{IV}|{\bullet}OH + H^+$

$Ti^{IV}|OH^- + h^+_{vb} \leftrightarrow Ti^{IV}|{\bullet}OH$

<u>Reduction</u>

$[Ti^{IV}] + e^-_{cb} \leftrightarrow [Ti^{III}] + O_2$ (abs) → **ROS**

ROS (Reduced Oxgen Species)
$\bullet O^-_2$; HO^-_2; $\bullet O^-$; Ti^{IV}-OOH

>> TiO_2 as example of a Photoactive Material

>> Timescales from fs to ms

>> Surface/Bulk & Interface

>> Different SC Heterojunction (charge separation)

>> Dye Sensitized Systems (charge separation)

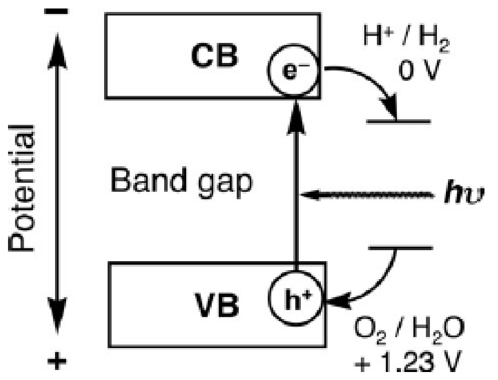
Part II

http://www.kth.se/ Prof. Licheng Sun

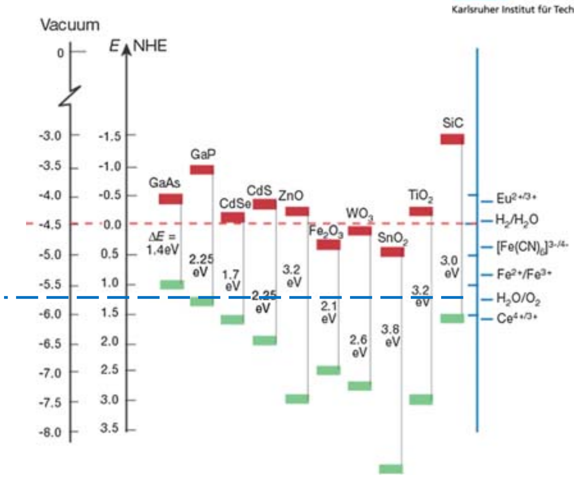
- Basic Photoelectrochemical PEC Applications
- Different PEC Devices/Designs
- Photovoltaic coupled (Photo)electrochemistry PECs
- Dual energy systems, Scale up, Solar Refinery and GAP

Principle of Water Splitting

Band Gap (eV) = **1240/wavelength** (nm)



Chem. Soc. Rev., **2009**, *38*, 253–278.



Electrochemical decomposition of water a potential difference of more than 1.23 V is necessary! This potential different is equivalent to the Energy Radiation with a wavelength of ≈ 1100 nm.

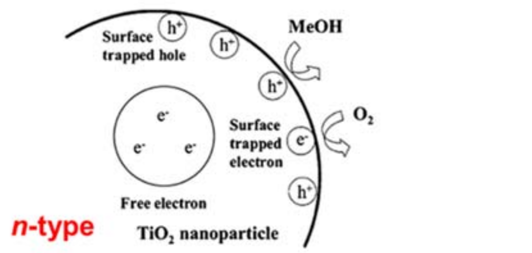
>> SC E_g choice with absorption properties of VB and CB levels

more negation than the Redox-Potential of H_2/H_2O

more positiv than the Redox Potential of H_2O/O_2

Over potential and Light Irradiation

▸ Spatial resolution of photo-generated charge carriers in TiO_2 (***n*-type**) SC.

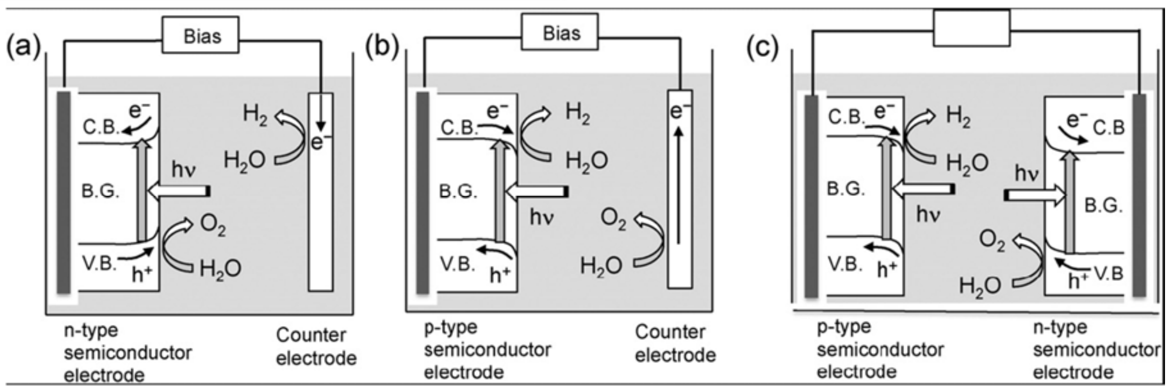


D. W. Bahnemann, *et. al J. Mater. Chem.*, **2009**, *19*, 5089–5121.

>> ***n*-type SC** (h^+) on their surface Water-Oxidation H_2O/O_2

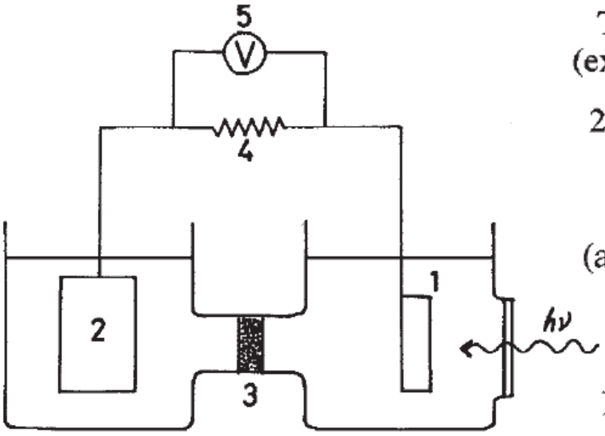
>> ***p*-type SC** (e^-) on their surface Water-Reduction H_2/H_2O

>> Coupled Systems *n*/*p*-type PECs



http://solar.iphy.ac.cn

Historic H_2O Splitting on TiO_2
(Honda-Fujishima Effect 1972)



$$TiO_2 + 2\,h\nu \rightarrow 2\,e^- + 2\,p^+ \qquad (1)$$
(excitation of TiO_2 by light)

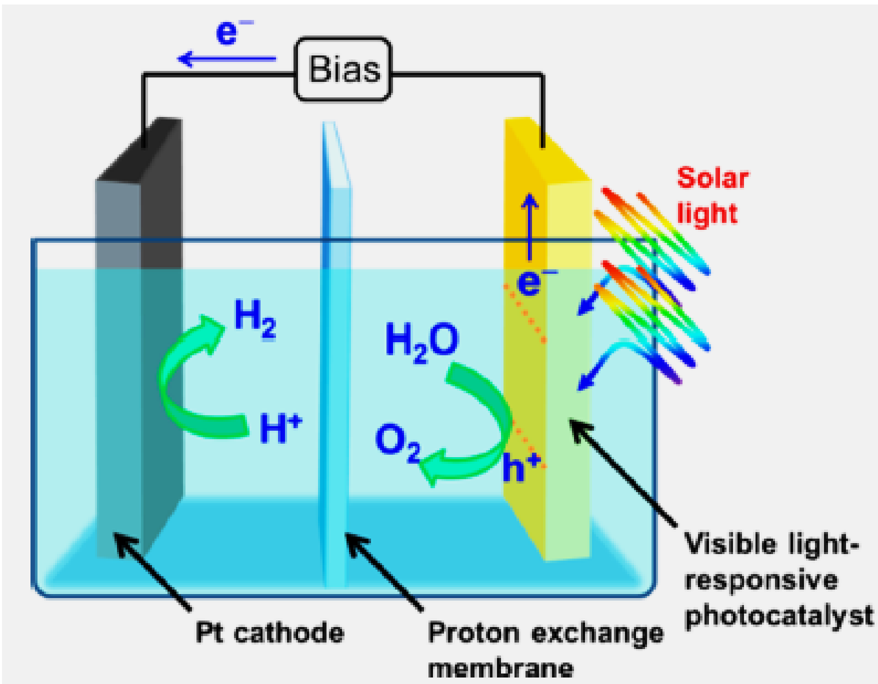
$$2\,p^+ + H_2O \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ \qquad (2)$$
(at the TiO_2 electrode)

$$2\,e^- + 2\,H^+ \rightarrow H_2 \qquad (3)$$
(at the platinum electrode)

$$H_2O + 2\,h\nu \rightarrow \tfrac{1}{2}\,O_2 + H_2 \qquad (4)$$

A. Fujishima, K. Honda, *Nature,* **1972**, *238*, 37-38.

Photoelectro-chemical cell

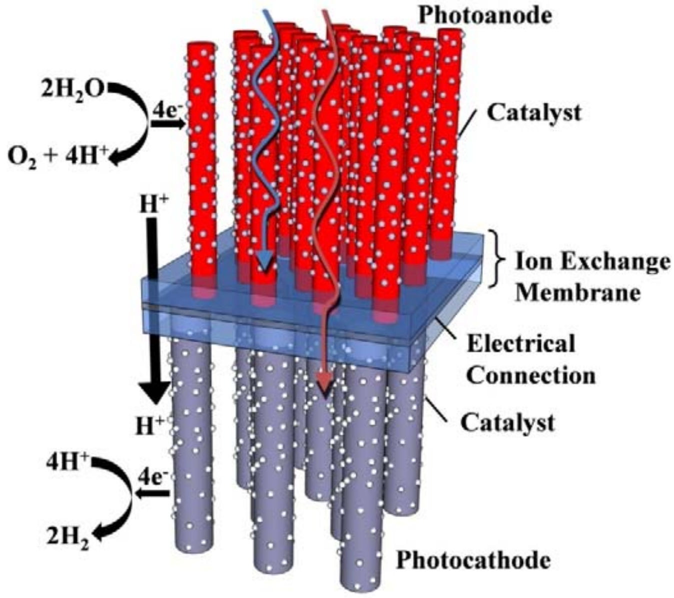


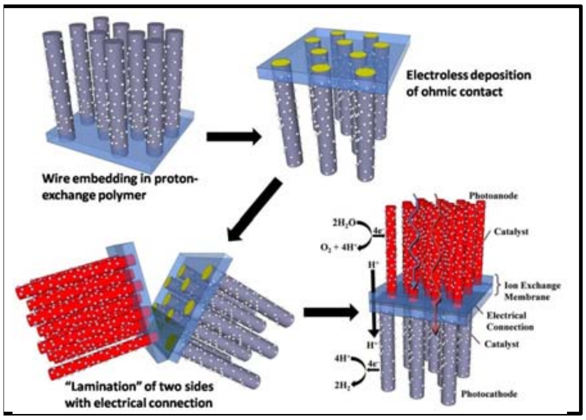
>> SC Photoanodes:

- TiO_2
- WO_3
- ZnO
- RuC
- SiC
- $SrTiO_3$
- $KTaO_3$
- Fe_2O_3
- $BiVO_4$
- (ZnS)
- (CdS)

D. W. Bahnemann, *et. al Chem. Rev.* **2014**, *114*, 9919–9986.

Photoelectro-chemical Membrane

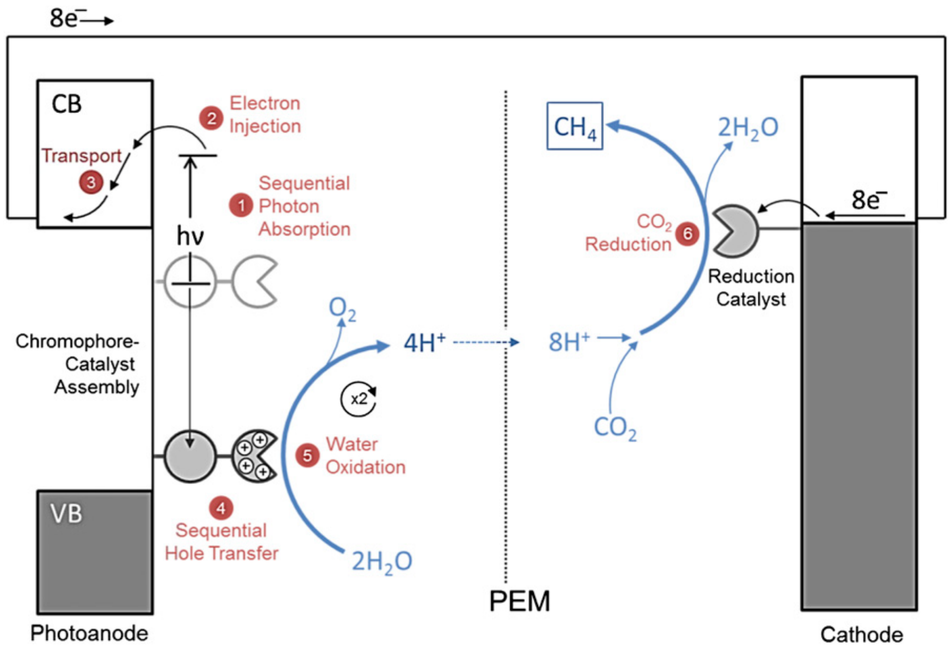




JCAP JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

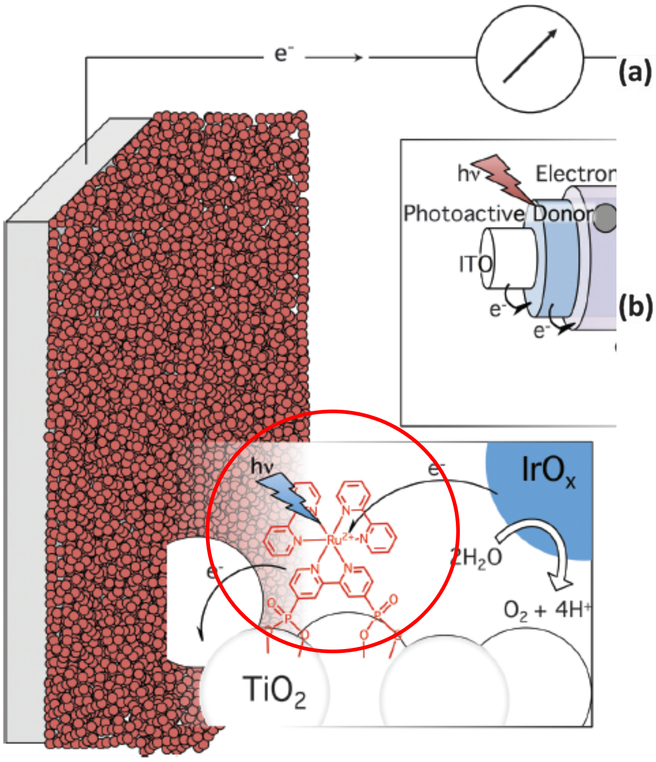
http://www.its.caltech.edu/~spurgeon/Water%20Splitting.html

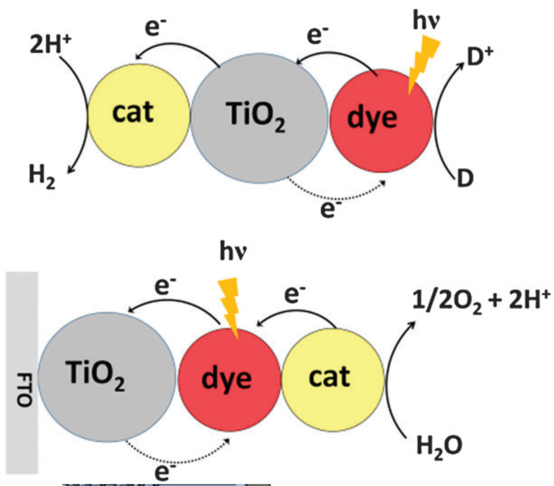
Dye sensitized photoelectrosynthesis cell (DSPEC)

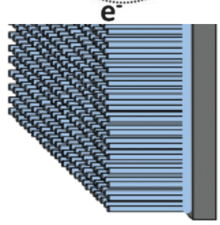


PNAS | September 25, 2012 | vol. 109 | no. 39 | 15563

Dye-based Photoelectrochemical Cell (PEC)





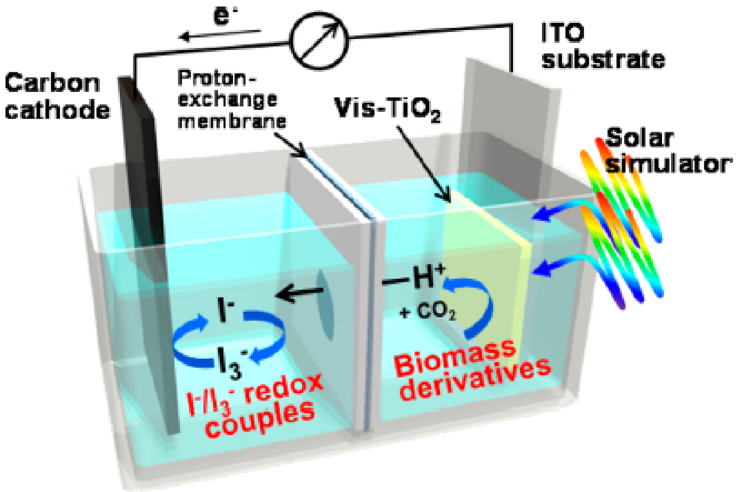


Chem. Soc. Rev., 2013, **42**, 2281.

Thomas E. Mallouk, *et. al Chem. Soc. Rev.*, 2013, **42**, 2357

SPFC Photochemical cell

SPFC = Separator-type photofuel cell



biomass derivatives	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
none	0.42	0.10	0.22	0.009
methanol (10 vol %)	0.66	0.39	0.24	0.062
ethanol (10 vol %)	0.65	0.33	0.20	0.043
ethylene glycol (10 vol %)	0.68	0.52	0.28	0.099
glycerin (10 vol %)	0.72	0.57	0.27	0.111
glucose (9 wt %)	0.68	0.41	0.26	0.073

Photovoltaic performances is based on various SPFCs based on Vis-TiO_2

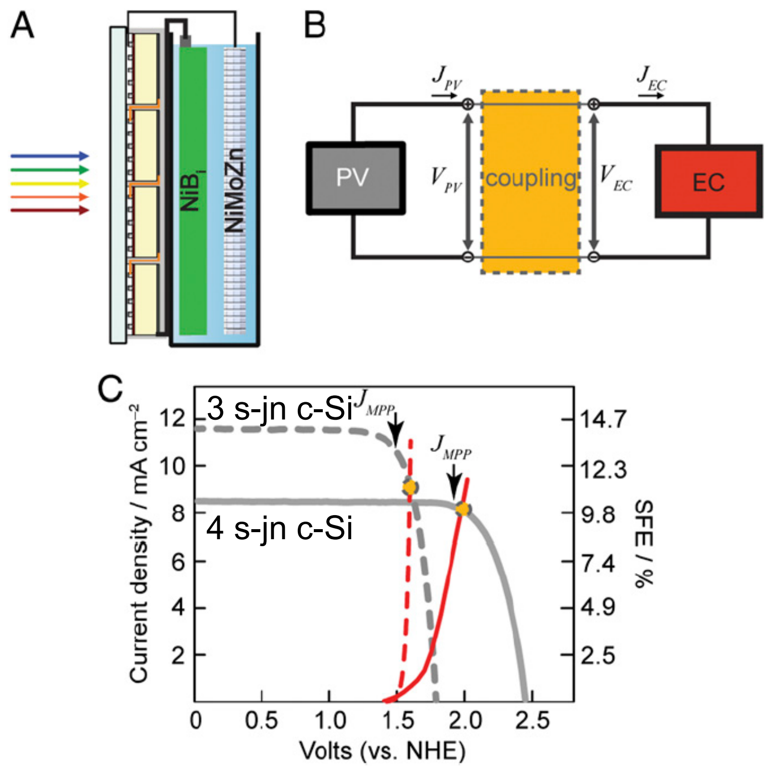
$$I_3^- + 2e^- \rightarrow 3I^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The reduction reaction of I_3^- ions to I^- ions is rather preferred than the oxygen reduction reaction takes place at the carbon cathode.

D. W. Bahnemann, *et. al Chem. Rev.* **2014**, *114*, 9919–9986.

PV-EC Cell coupled Devices



PNAS | September 30, 2014 | vol. 111 | no. 39 | 14057–14061

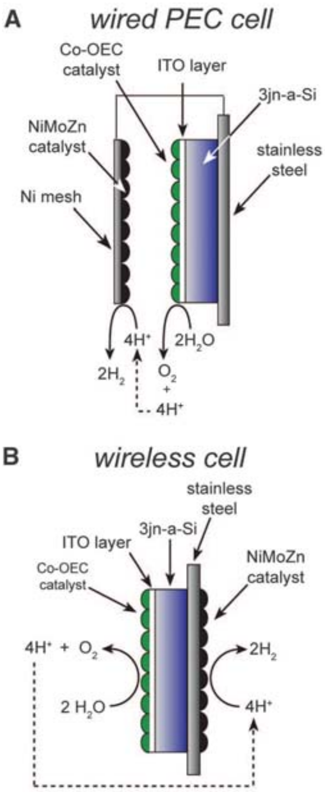
>> Coupled PV/EC-Cell

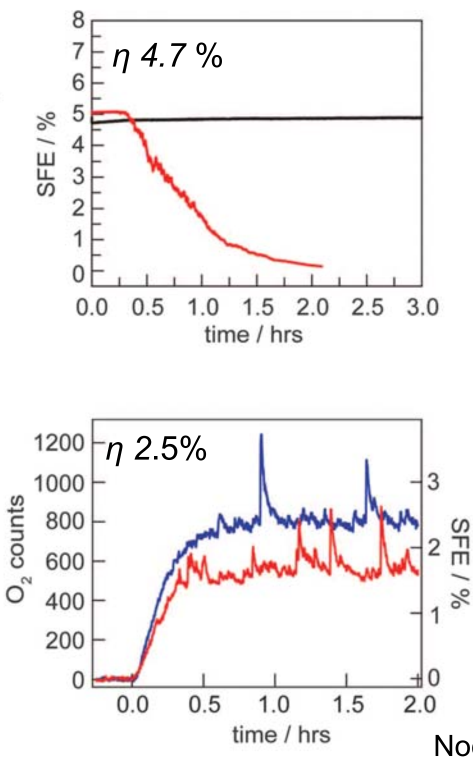
>> 10% SFE (Solar to Fuel Efficiency)

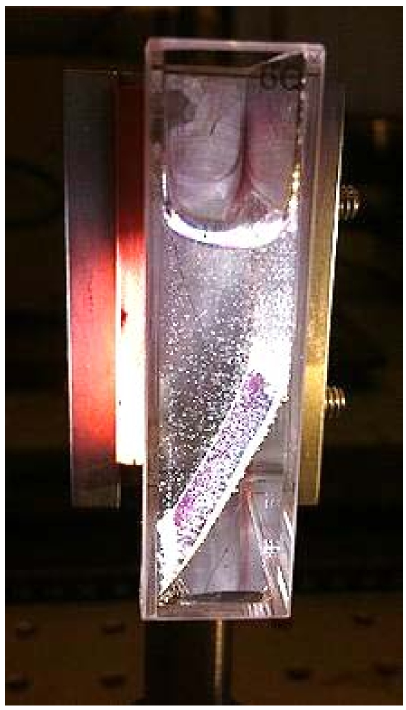
>> usage of nonprecious materials

>> monolithic approach
NiB (OEC) - p-type (PV)
NiMoZn (HEC) - n-type (PV)

Nocera's Photoelectro-chemical Cell



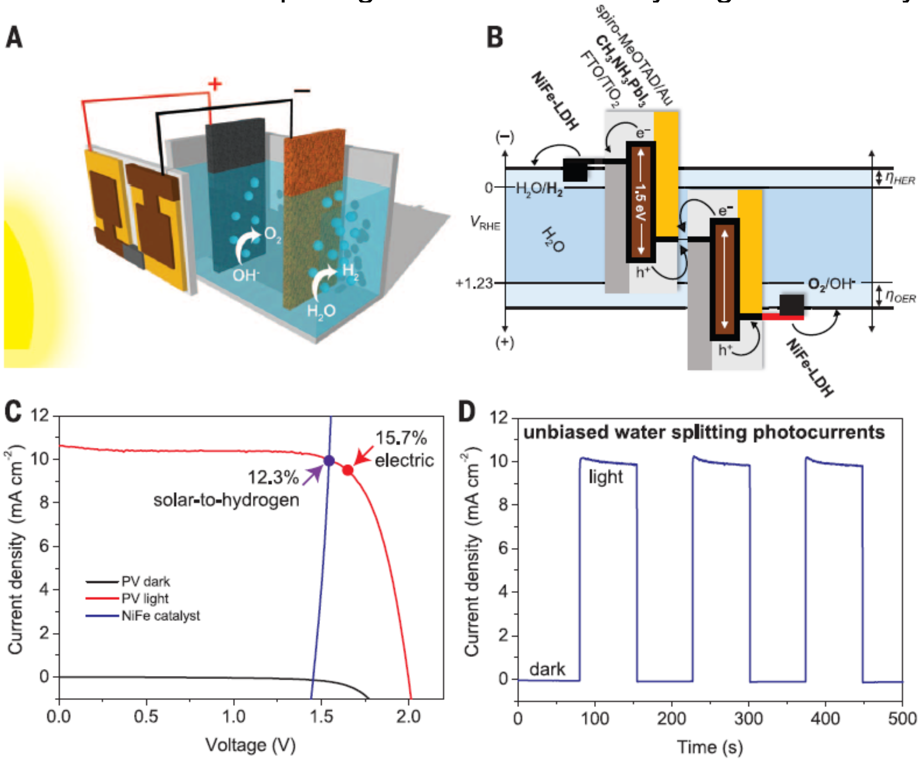


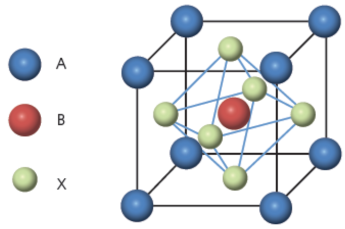


Nocera *et al.*, *Science*, **2011**, *334,* 645.

EPFL Perovskite PV-EC Cell

► low-cost water splitting cell with solar-to-hydrogen efficiency of η 12.3%



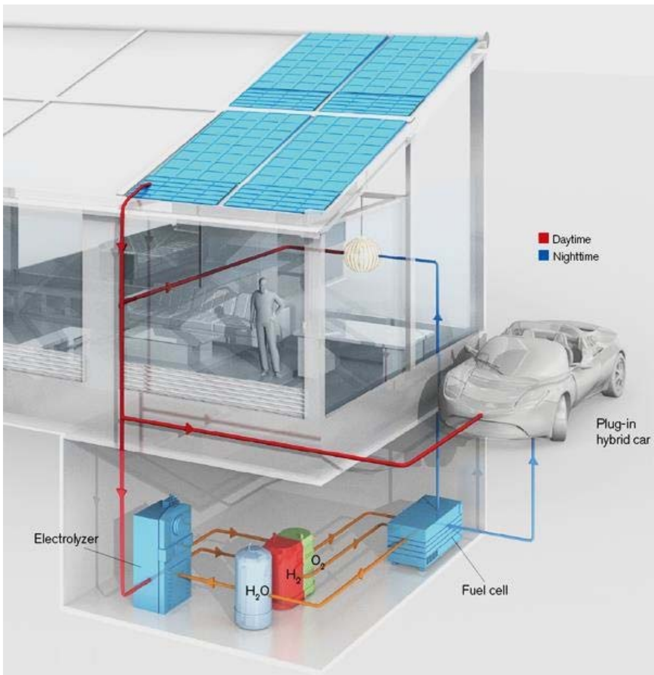


► $CH_3NH_3PbI_3$

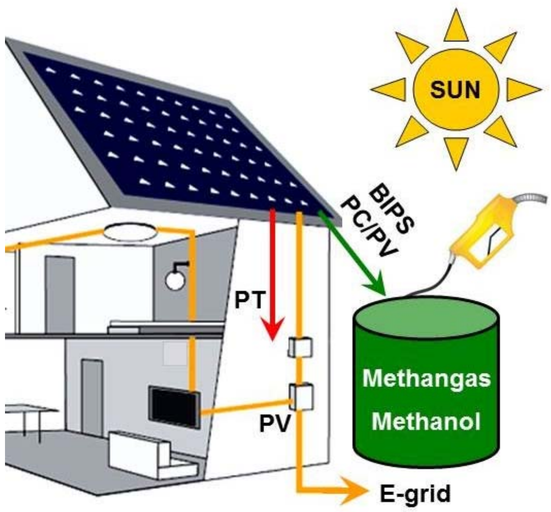
► ABX_3

Science **2014**, *345*,1593-1596.

Up Scale (SF) House Facilities



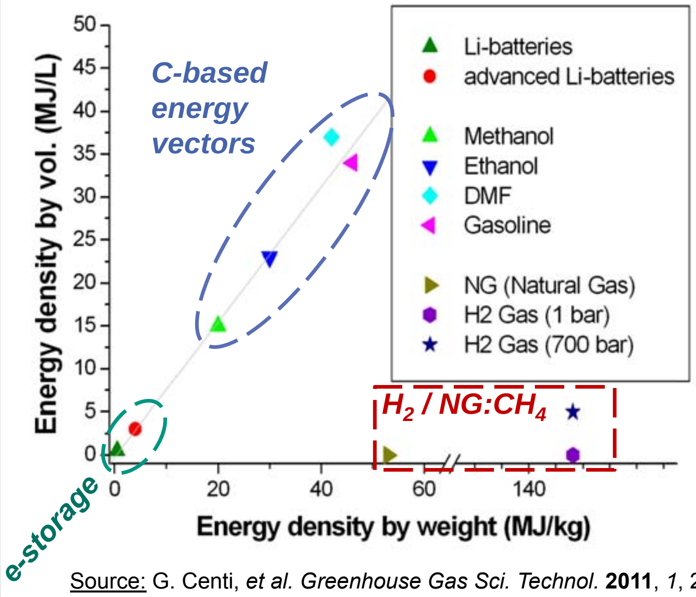
http://www.technologyreview.com/



KIT INNOVATION gemeinnützige GmbH

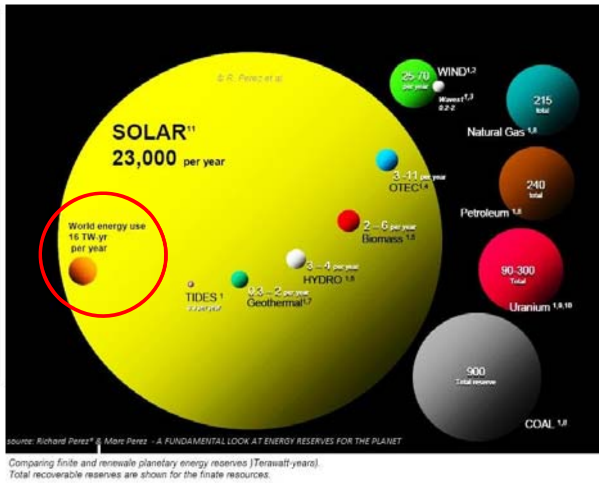
Up Scale (SF) Energy Densities

► **Energy Vector Plot**: **Fuel Sources**



Source: G. Centi, *et al. Greenhouse Gas Sci. Technol.* **2011**, *1*, 21-35.

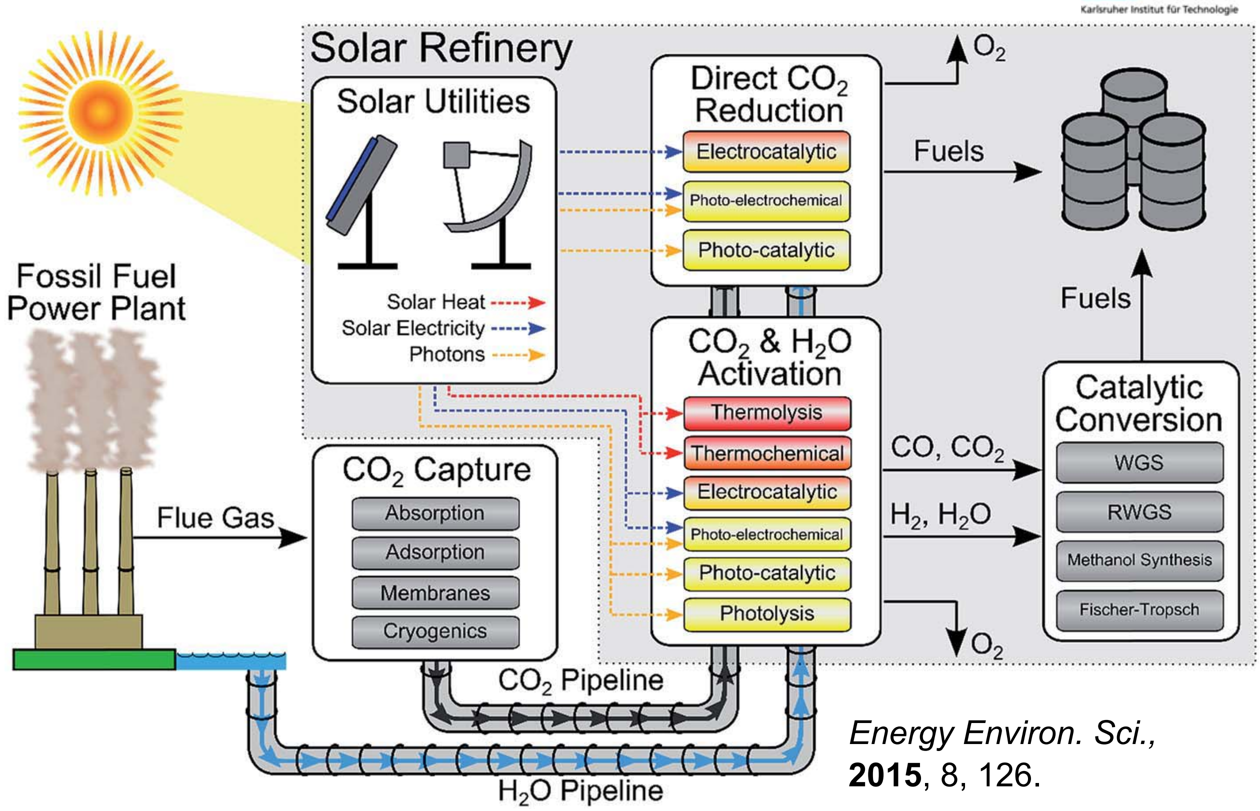
http://www.asrc.albany.edu/people/faculty/perez/Kit/pdf/a-fundamental-look-at%20the-planetary-energy-reserves.pdf



► **Solar Energy** *vs* Planetary Energy Resources

Worlds Energy Needs !! ∑ ≈ 16 TW/year

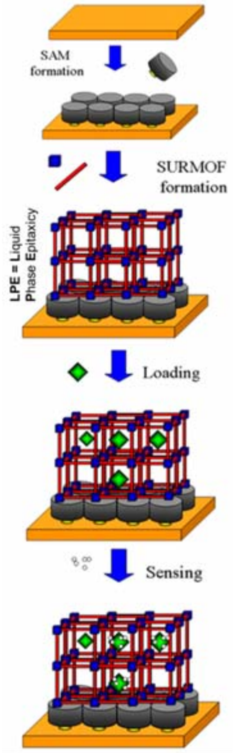
Solar Refinery / Production Facilities

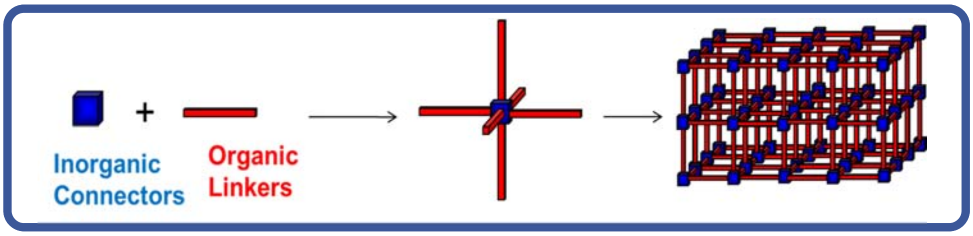


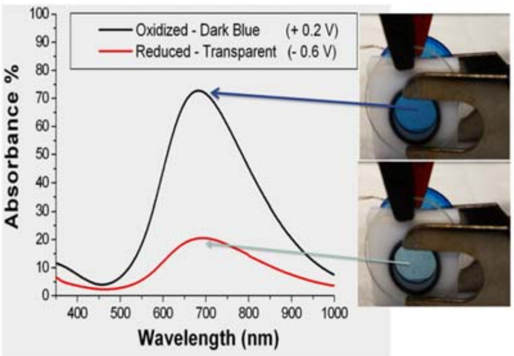
Energy Environ. Sci., **2015**, 8, 126.

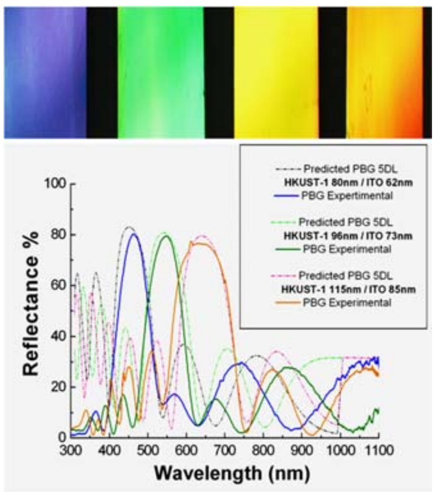
Own Research Approach at IFG/IMT

► SURMOFs and CNCs for Solar Energy/Solar Fuels Applications



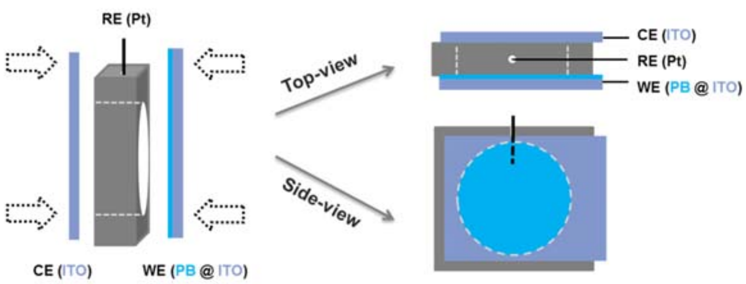


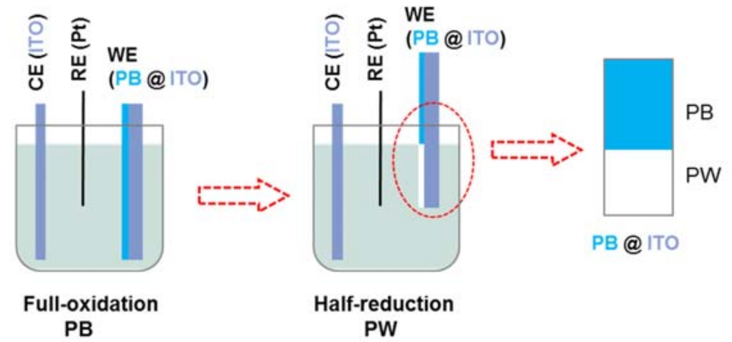




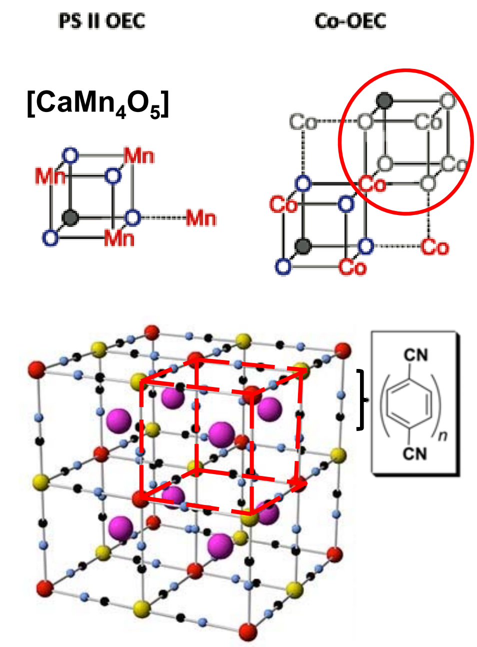
>> Optoelectronic Devices
>> Photonic Applications
>> Optical Sensing

Own Research Approach at IFG/IMT



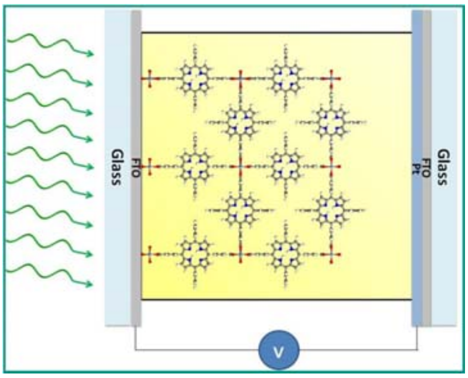


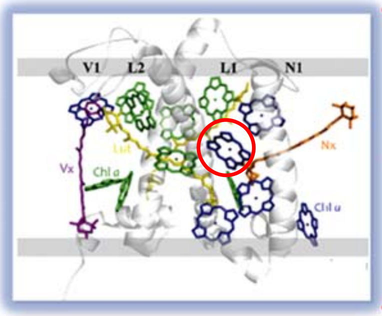
E. Redel *et. al*, Optics Express submitted 2015

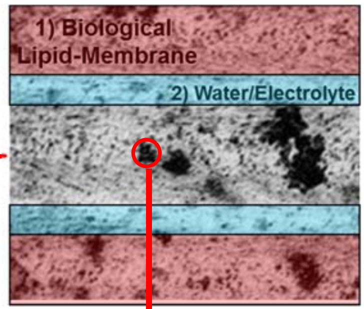


Nocera *et al.*, *Accounts of Chemical Research*, **2012**, *45*, 767-776.
S. Pintado *et al. J. Am. Chem. Soc.*, **2013**, *135*, 13270-13273.

Own Research Approach at IFG/IMT

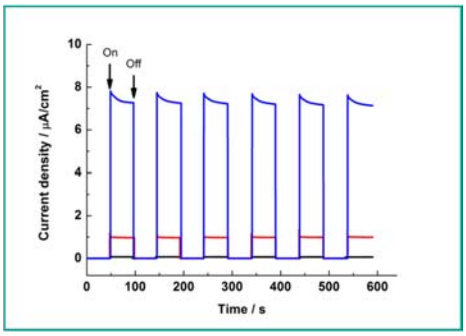




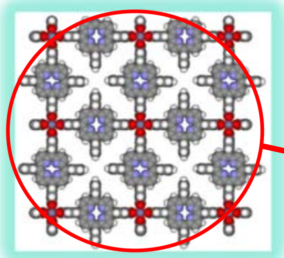


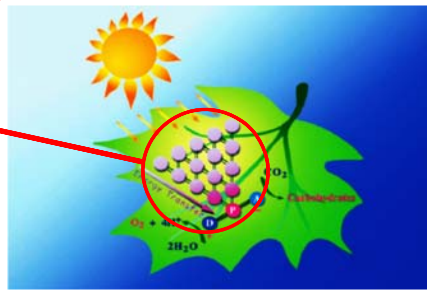
Z. Liu *et al*., Nature **2004**, 428, 287.

Embedded natural Photosynthetic Pigments



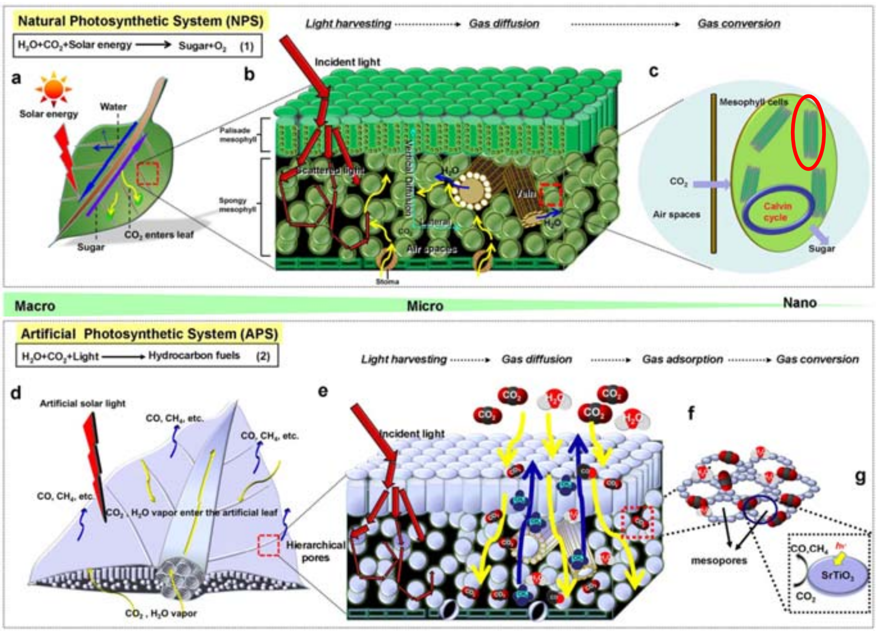
J. Liu, J. Liu, I. Howard, E. Redel, T. Heine and Ch. Wöll *in review* Nature Materials **2015**





Supramolecular Artificial LHC
e.g. as Porphyrin-SURMOFs
in collaboration with Prof. Ruben, Prof. Liu and Prof. Wöll.

Global Artificial Photosynthesis (GAP)

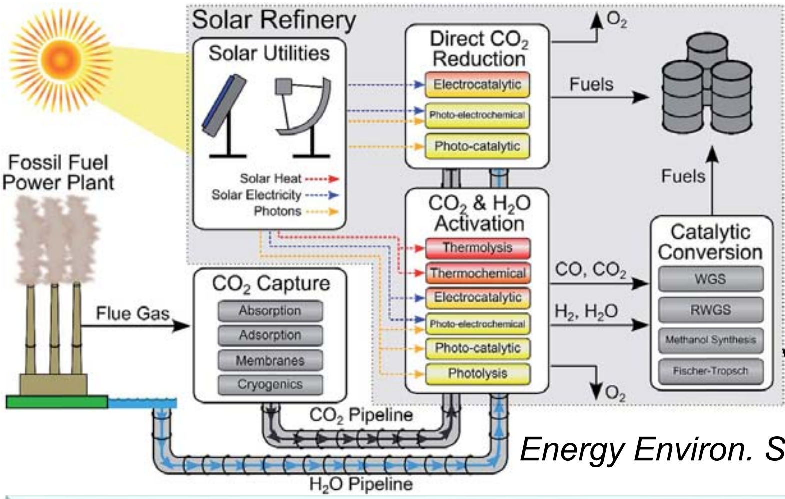


SCIENTIFIC REPORTS **2013** | 3 : 1667 | DOI: 10.1038/srep01667

>> Mimic Photosynthesis on a global Scale!!

www.business2community.com

Summary (Part II)



www.inhabitat.com/

Energy Environ. Sci., **2015**, 8, 126.

- Basic Photoelectrochemical PEC Applications
- Different PEC Devices/Designs
- Photovoltaic coupled (Photo)electrochemistry PECs
- Dual Energy Systems, Scale up, Solar Refinery & GAP