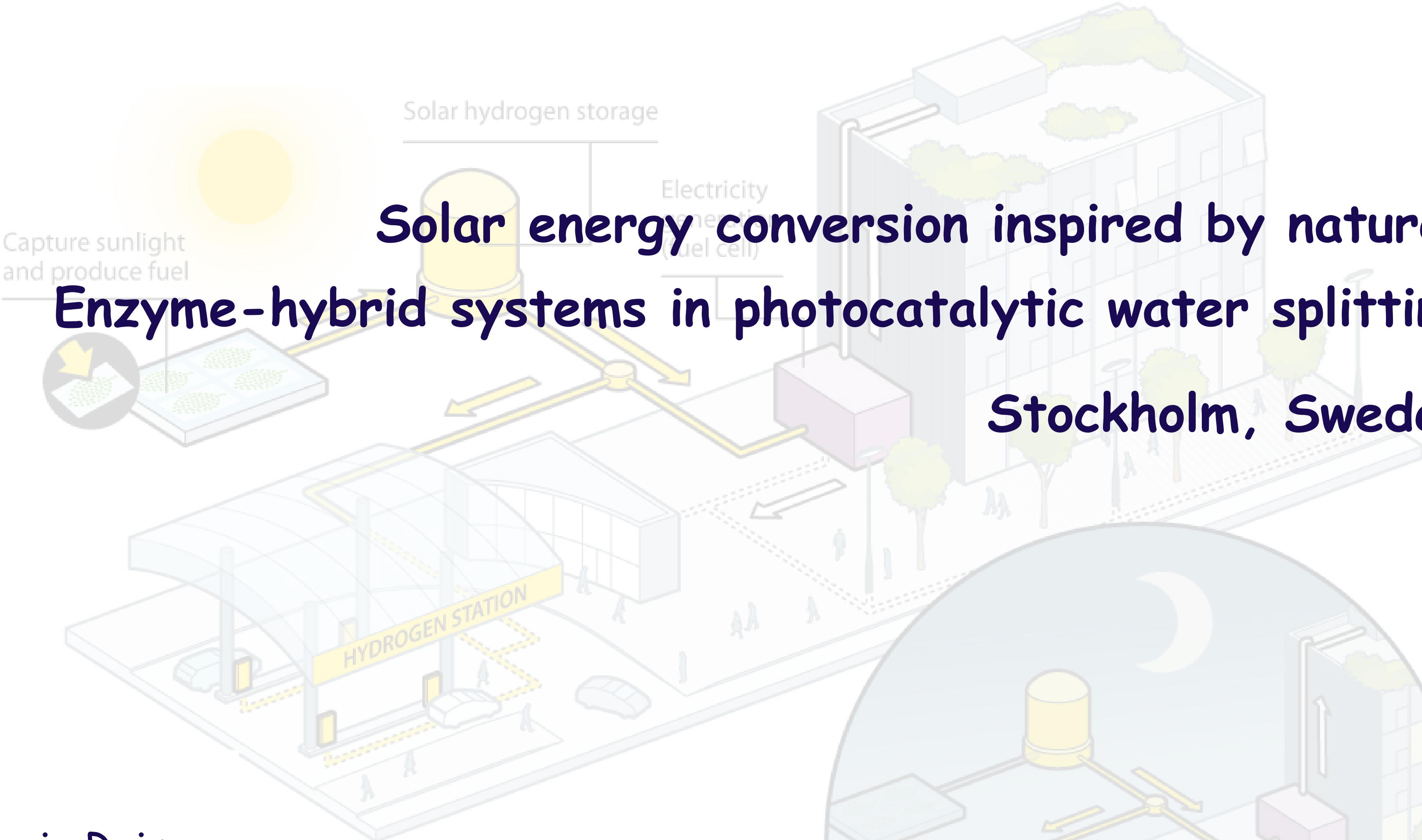



# Solar energy conversion inspired by nature: Enzyme-hybrid systems in photocatalytic water splitting

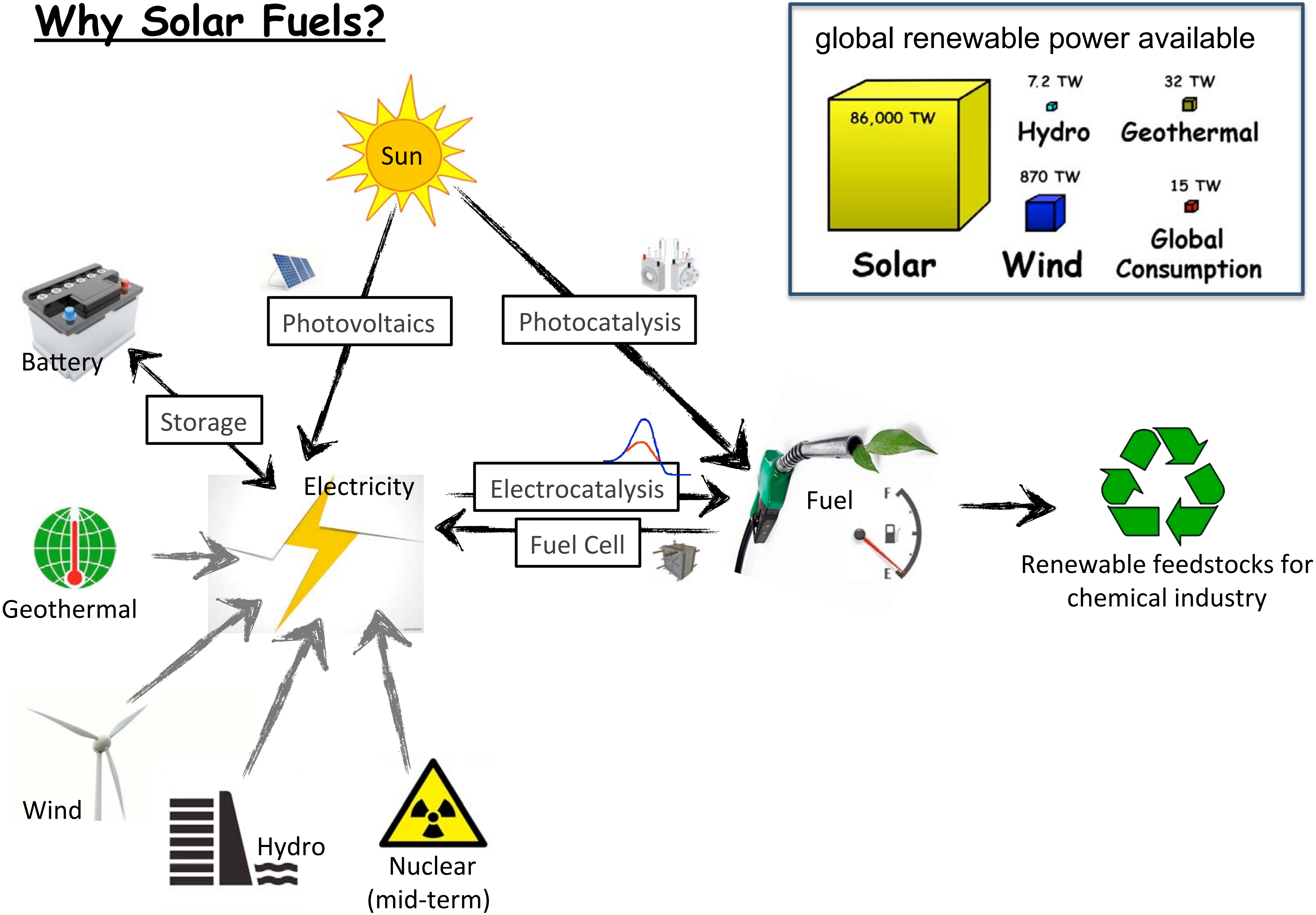
Stockholm, Sweden

Erwin Reisner
Department of Chemistry
University of Cambridge
Lensfield Road, Cambridge CB2 1EW, UK
e-mail: reisner@ch.cam.ac.uk
web: http://www-reisner.ch.cam.ac.uk/

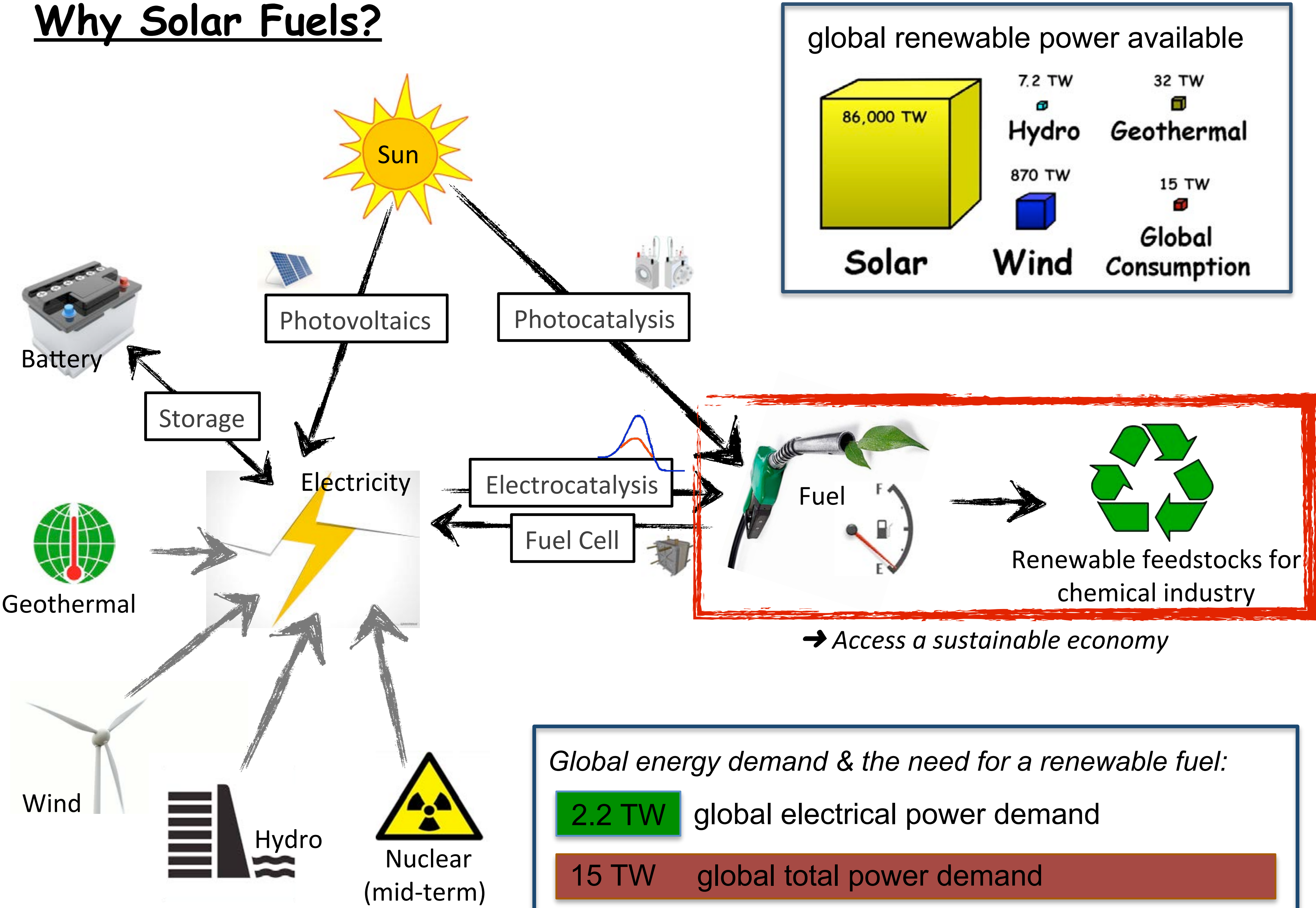



www.rsc.org/solar-fuels

# Why Solar Fuels?



# Why Solar Fuels?




➜ *Access a sustainable economy*

*Global energy demand & the need for a renewable fuel:*

| | |
|---|---|
| 2.2 TW | global electrical power demand |
| 15 TW | global total power demand |

# Which fuel (energy storage)?

hydrocarbons


hydrogen


electricity

# Which fuel (energy storage)?

Present: dirty
Future: sustainable?


Present: dirty
Future: sustainable?


Present: dirty
Future: sustainable?

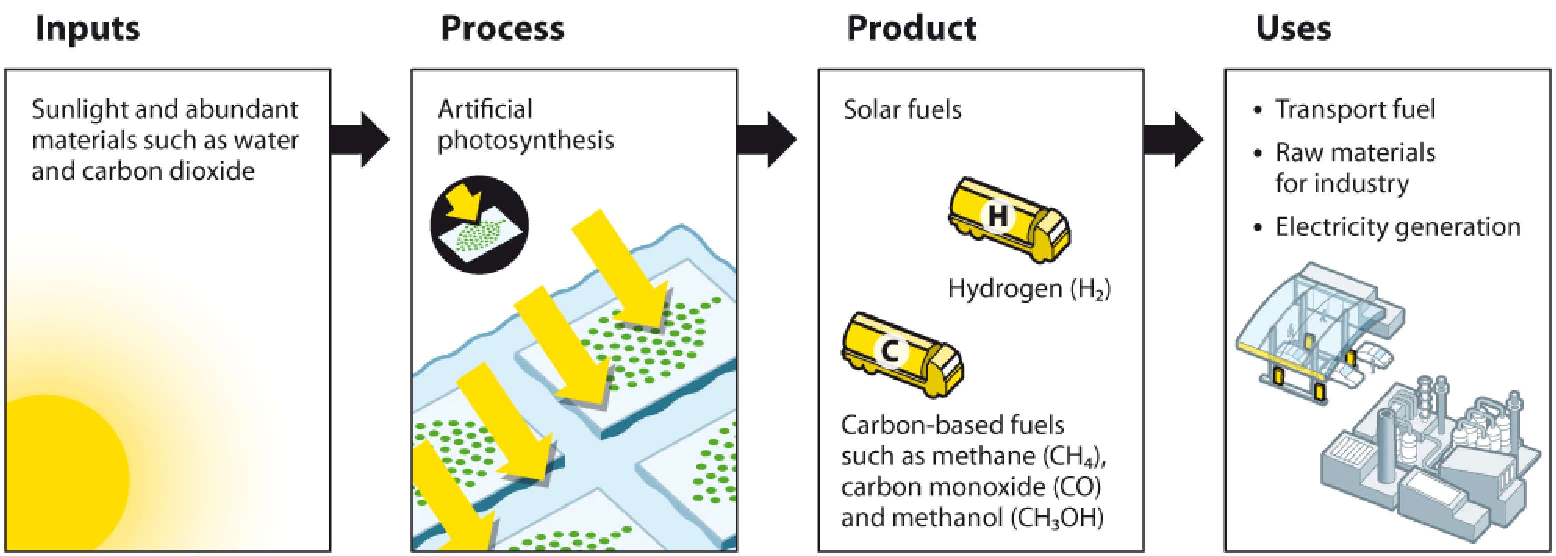
# Which fuel (energy storage)?

Present: dirty
Future: sustainable?


Present: dirty
Future: sustainable?


Present: dirty
Future: sustainable?

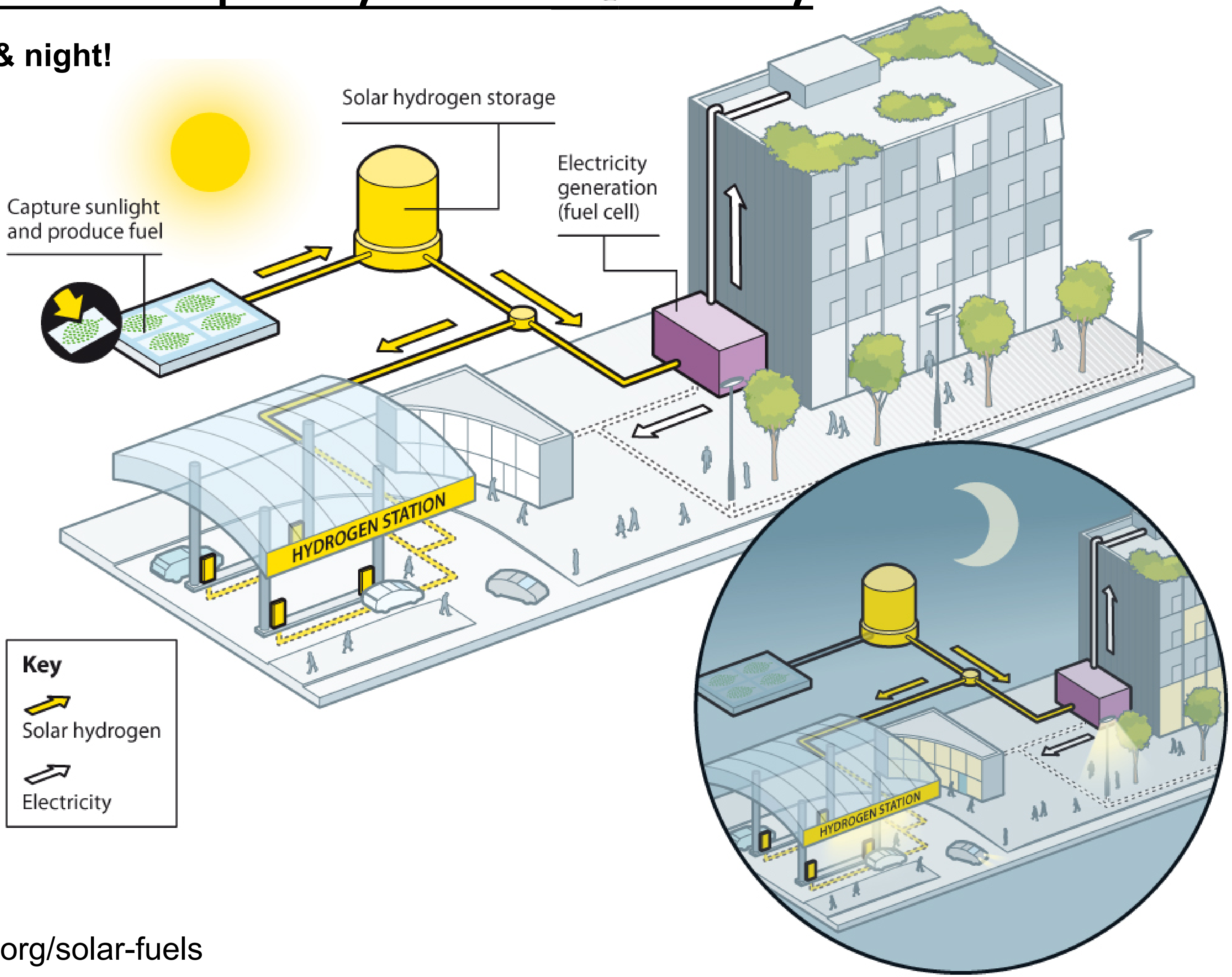
# The generation of solar fuels: artificial photosynthesis




www.rsc.org/solar-fuels

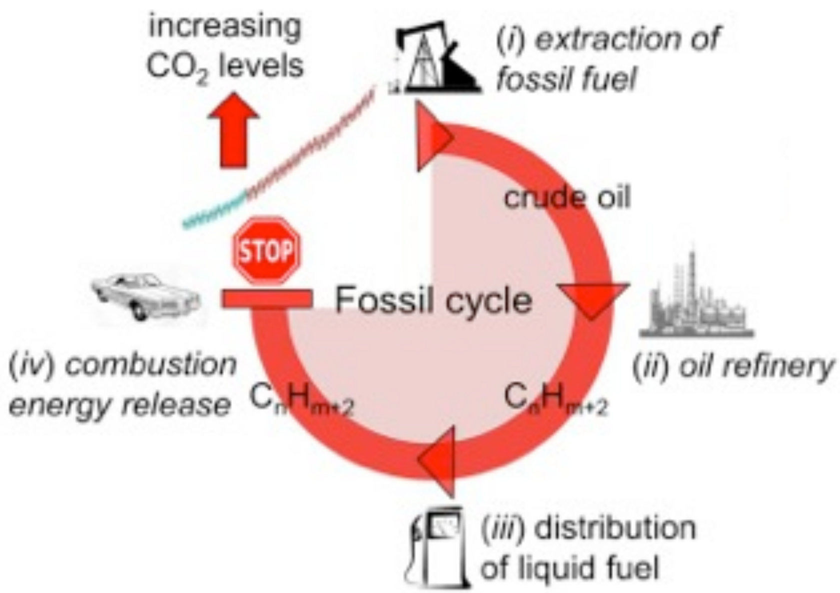
# About artificial photosynthesis: $H_2$ economy

**By day & night!**

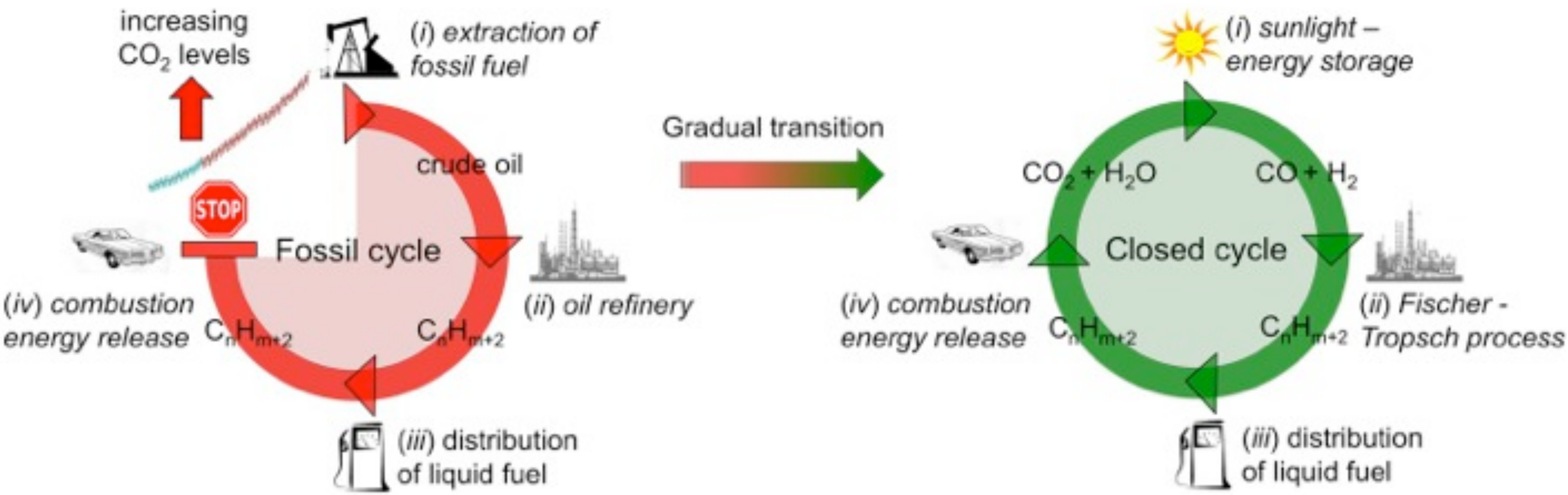



www.rsc.org/solar-fuels

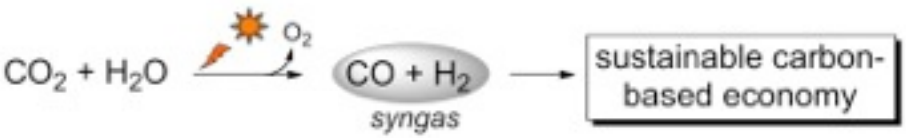
# About an Unsustainable Carbon-Cycle

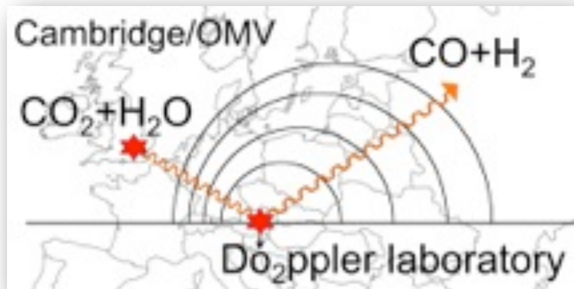


# About a Sustainable Carbon-Cycle: a Syngas Economy




**Or simplified:**

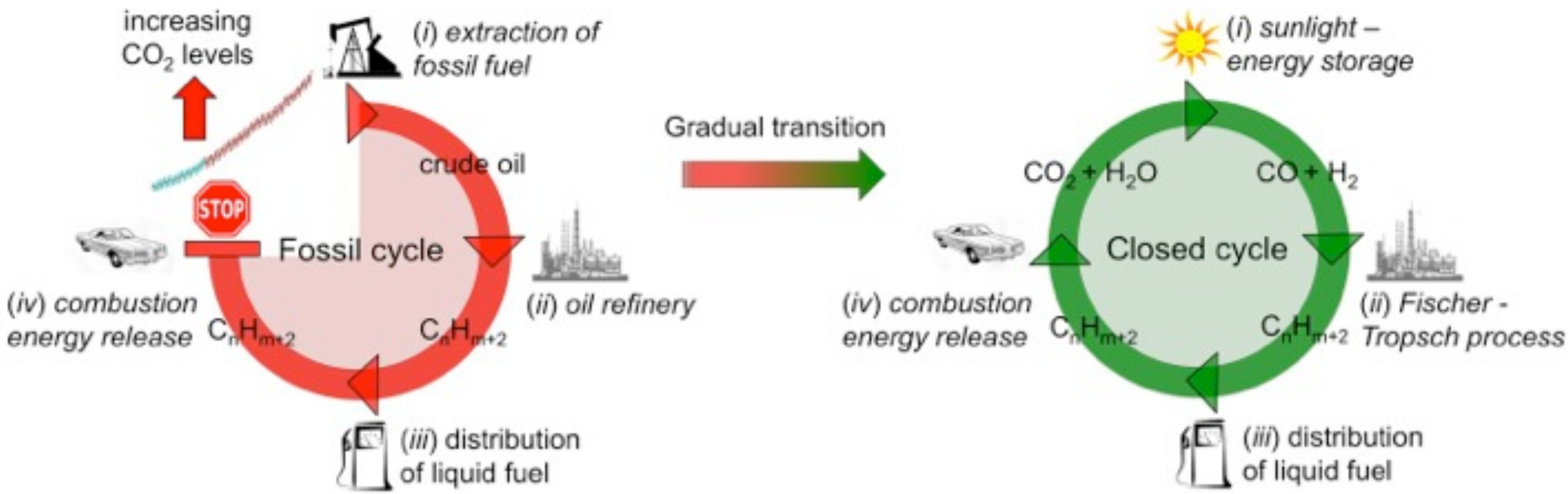


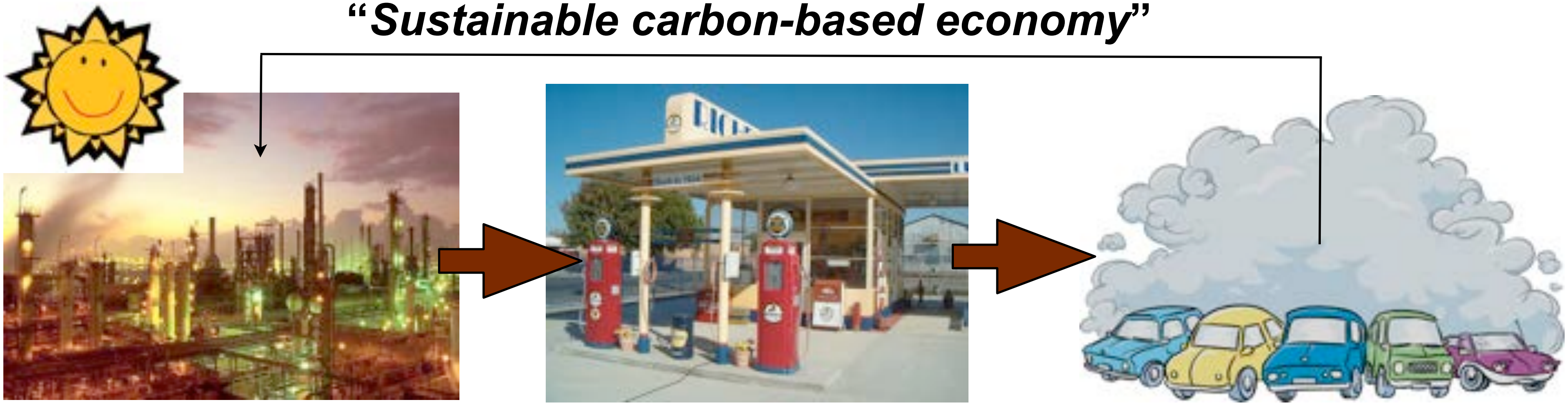

Syngas is invaluable chemical feedstock for the petrochemical industry.

- Intermediary building block to liquid fuels, *e.g*. hydrocarbons (CD-Lab).
- Synthesis of fertilizers, plastics, pharmaceuticals, etc.

# About a Sustainable Carbon-Cycle: a Syngas Economy




***"Sustainable carbon-based economy"***



# Overview: Inspired by Nature's High Performance Enzymes

**The quest for inexpensive, efficient, durable and scalable catalysts!**

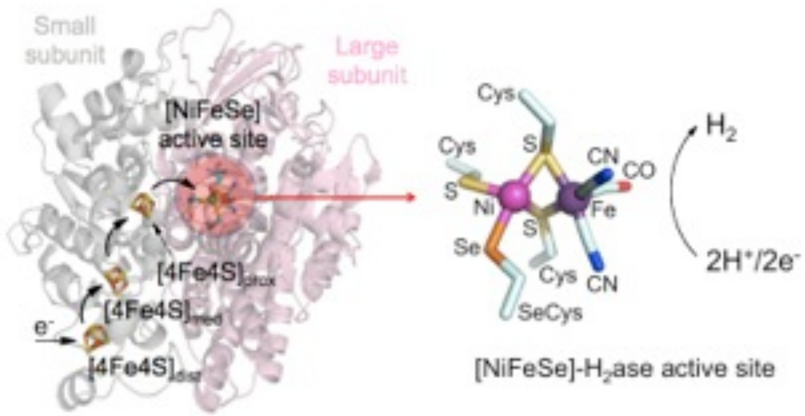
**State-of-the-art: Noble metals; *e.g.* Pt:**

(*i*) expensive/limited resources
(*ii*) non-selective (at low potentials it is an excellent $O_2$ reduction catalyst)
(*iii*) poisoned by several inhibitors (*e.g.* CO, $H_2S$)

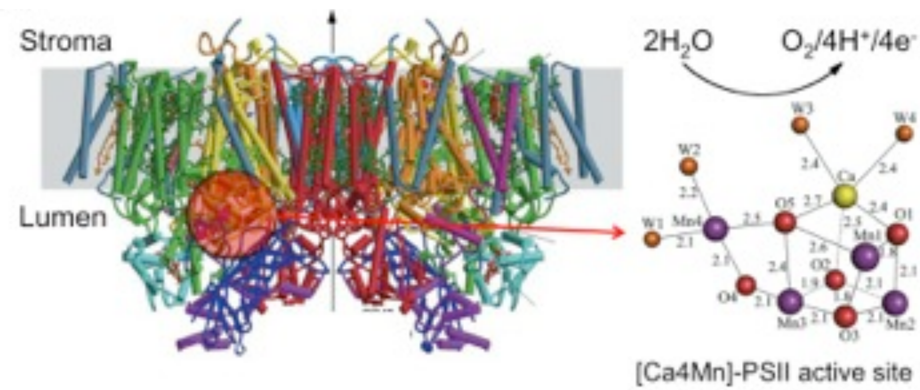
**Nature's choice - enzymes**

(*i*) can be 'grown' and non-toxic
(*ii*) certain enzymes operate in the presence of inhibitors as $O_2$, $H_2$ and CO
(*iii*) often no or negligible over-potentials - highly efficient catalysts

**BUT:** large foot-print per catalytic entity & fragile (*e.g.*, $O_2$-sensitive)

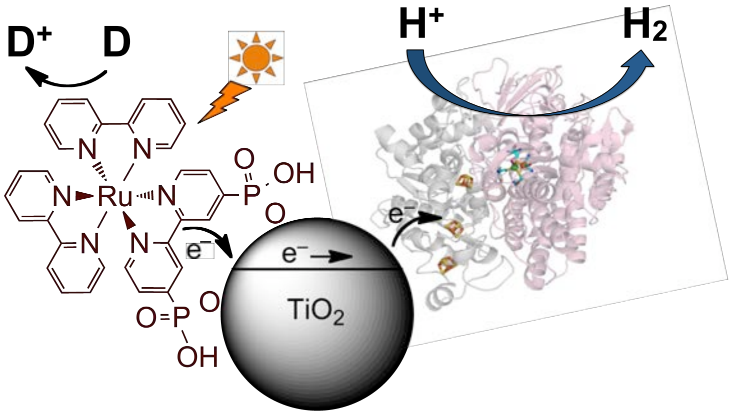



Hydrogenase ($H_2$ase)

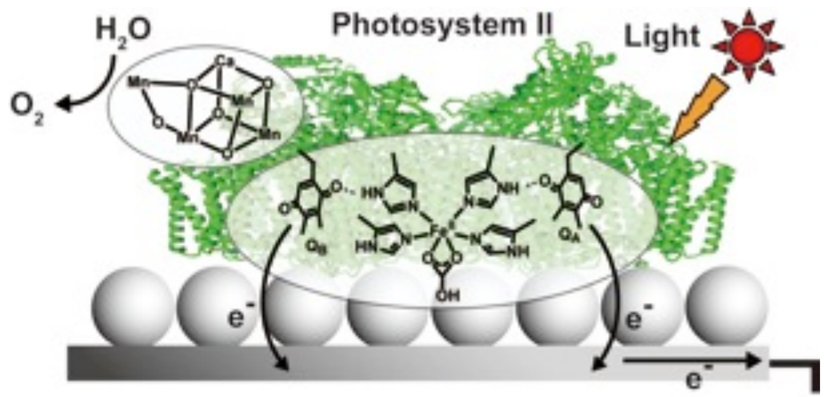



Photosystem II (PSII)

# Overview Photocatalysis: Enzyme Hybrid Systems

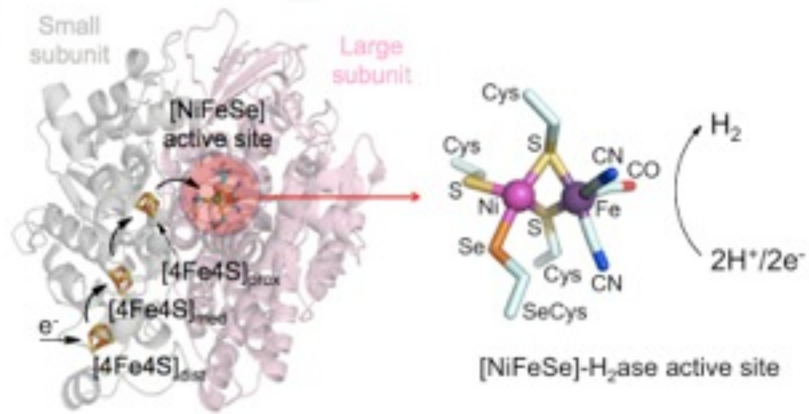



*Chem. Commun.* **2009**, 550–552.
*J. Am. Chem. Soc.* **2009**, *131*, 18457–18466.
*Angew. Chem. Int. Ed.*, **2013**, *in press*.

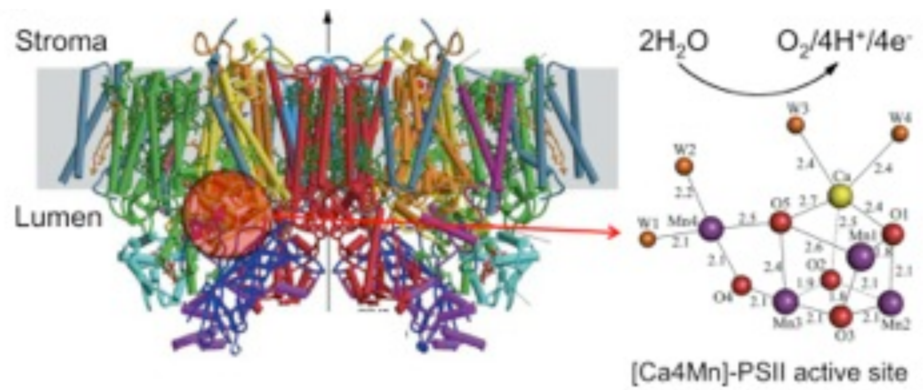



*J. Am. Chem. Soc.*, **2012**, *134,* 8332–8335.
*J. Am. Chem. Soc.*, **2013**, *135*, 10610–10613.

*'Artificial photosynthesis through hybridisation'*

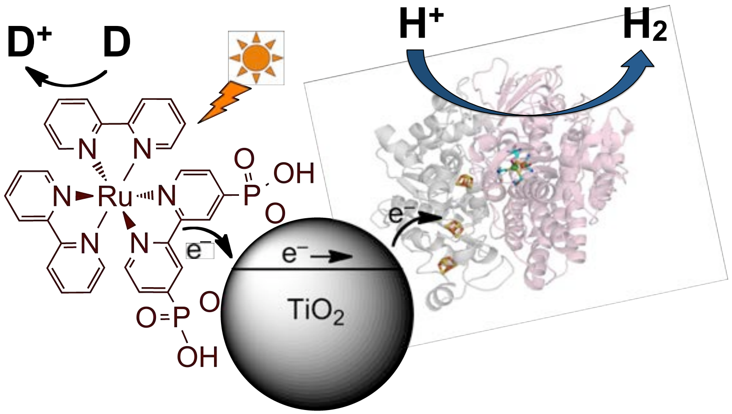



Hydrogenase ($H_2$ase)

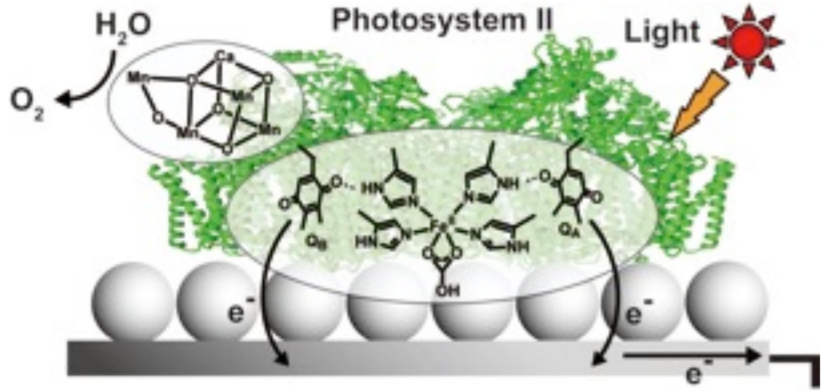



Photosystem II (PSII)

# Overview Photocatalysis: Synthetic Hybrid Systems

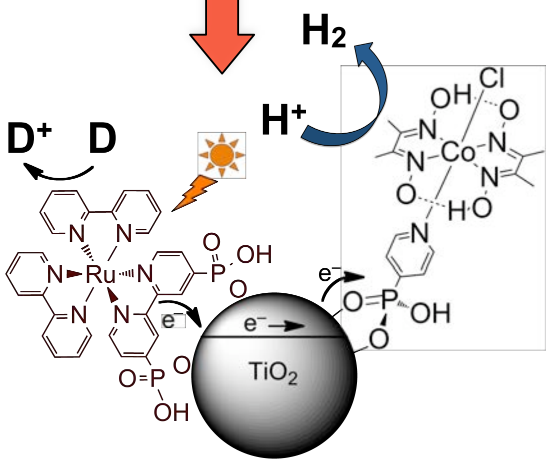



*Chem. Commun.* **2009**, 550–552.
*J. Am. Chem. Soc.* **2009**, *131*, 18457–18466.
*Angew. Chem. Int. Ed.*, **2013**, *in press*.

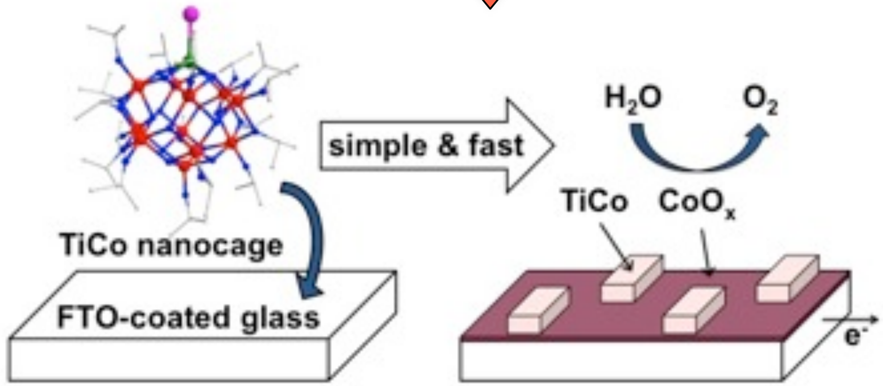



*J. Am. Chem. Soc.*, **2012**, *134*, 8332–8335.
*J. Am. Chem. Soc.*, **2013**, *135*, 10610–10613.

*'From enzymes to synthetic systems'*

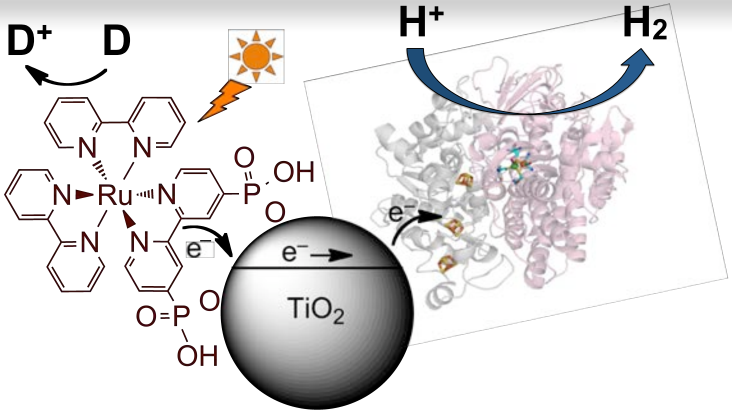



*Chem. Commun.*, **2011**, *47*, 1695–1697.
*Angew. Chem. Int. Ed.*, **2012**, *51*, 9381–9384.
*Angew. Chem. Int. Ed.*, **2012**, *51*, 12749–12753.
*Chem. Commun.*, **2013**, *in press*.

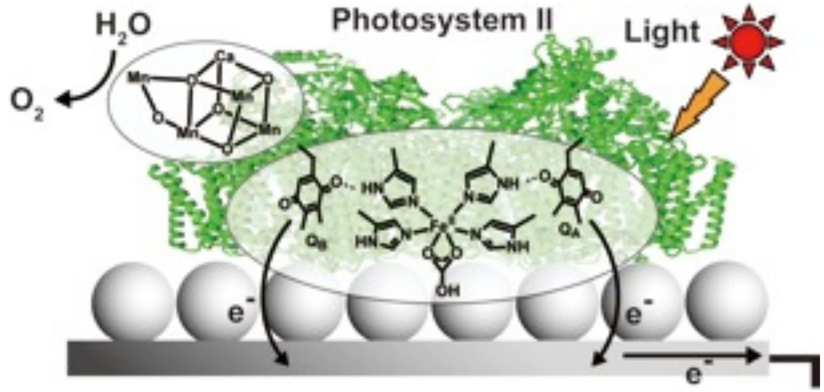



*Chem. Sci.*, **2012**, *3*, 3482–3487.
*Chem. Commun.*, **2013**, *49*, 4331–4333.
*Chem. Eur. J.* **2013**, *in press*.

# Overview Photocatalysis: Synthetic Hybrid Systems

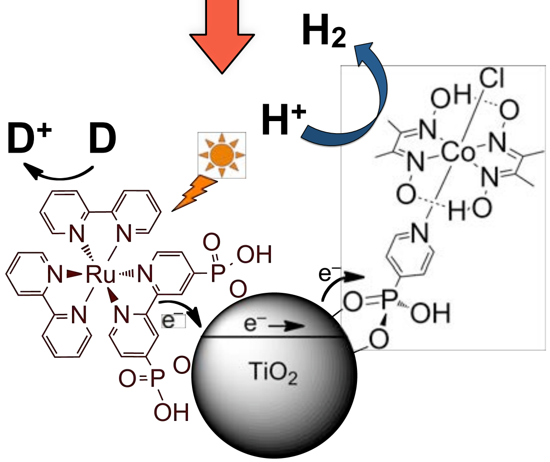



*Chem. Commun.* **2009**, 550–552.
*J. Am. Chem. Soc.* **2009**, *131*, 18457–18466.
*Angew. Chem. Int. Ed.*, **2013**, *in press*.

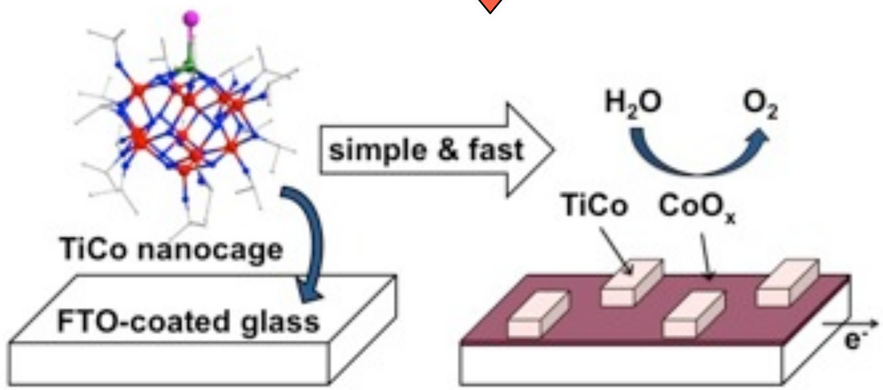



*J. Am. Chem. Soc.*, **2012**, *134,* 8332–8335.
*J. Am. Chem. Soc.*, **2013**, *135*, 10610–10613.

‘*From enzymes to synthetic systems*’



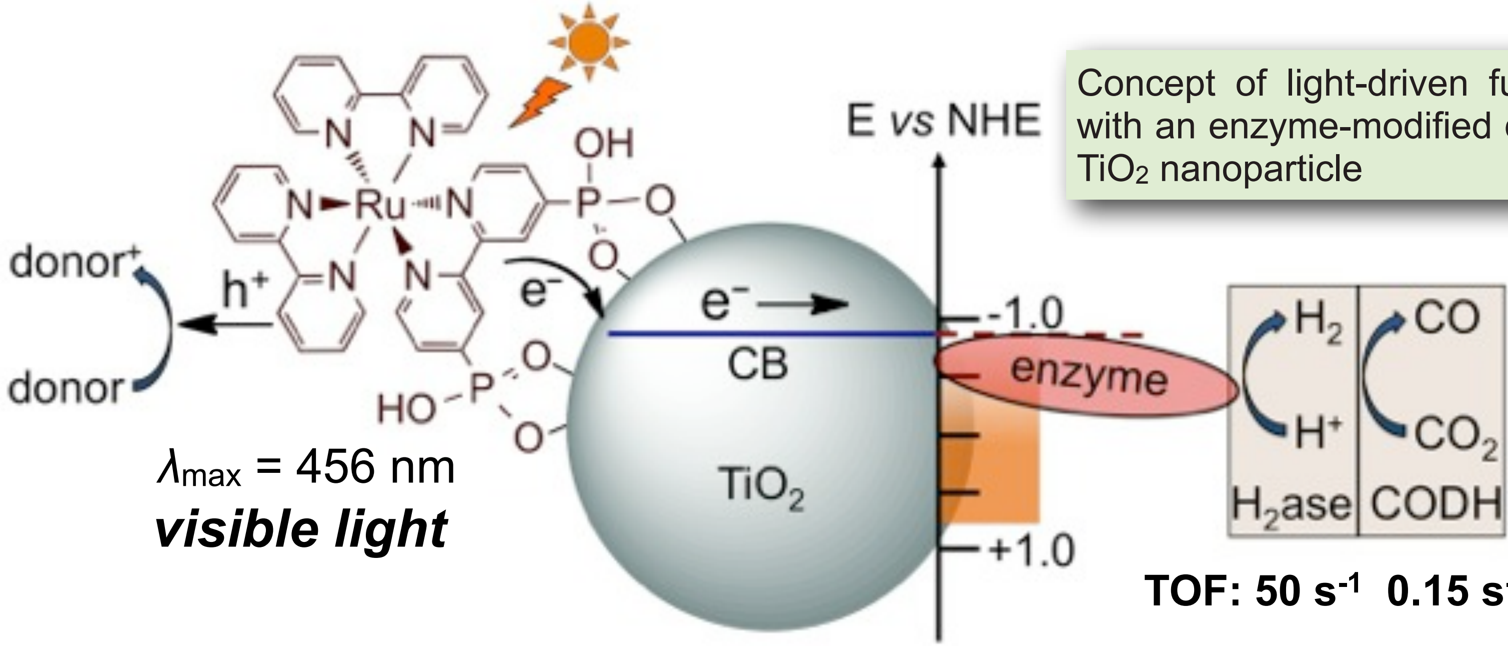

*Chem. Commun.*, **2011,** *47*, 1695–1697.
*Angew. Chem. Int. Ed.*, **2012**, *51*, 9381–9384.
*Angew. Chem. Int. Ed.*, **2012**, *51*, 12749–12753.
*Chem. Commun.*, **2013,** *in press*.




*Chem. Sci.*, **2012**, *3*, 3482–3487.
*Chem. Commun.*, **2013**, *49*, 4331–4333.
*Chem. Eur. J.* **2013**, *in press*.

# About Photocatalysis with Enzyme-modified $TiO_2$ Nanoparticles

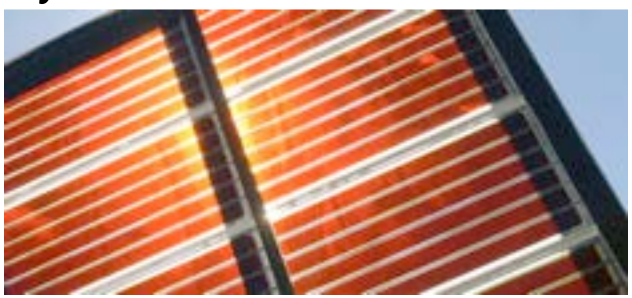
→ *from 'light to electricity' (PV) to 'light to fuel' (solar fuel) conversion*

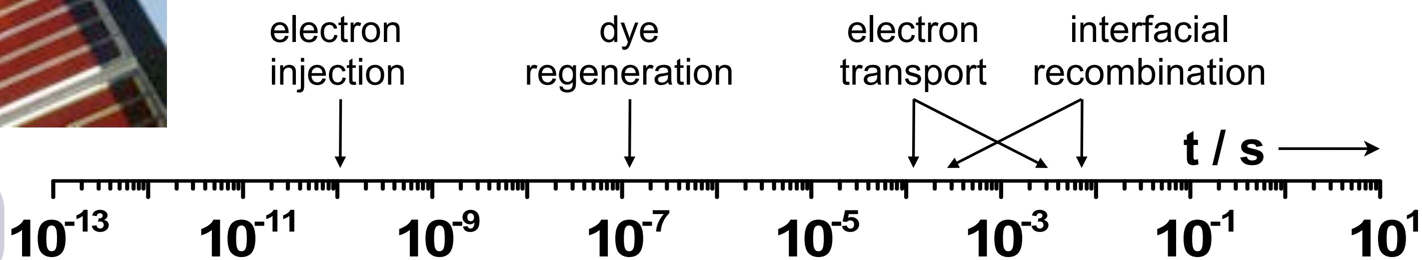



Concept of light-driven fuel production with an enzyme-modified dye-sensitized $TiO_2$ nanoparticle

**TOF: 50 $s^{-1}$ 0.15 $s^{-1}$** (pH 6-7; r.t.)

*Dye-sensitized Solar Cell*

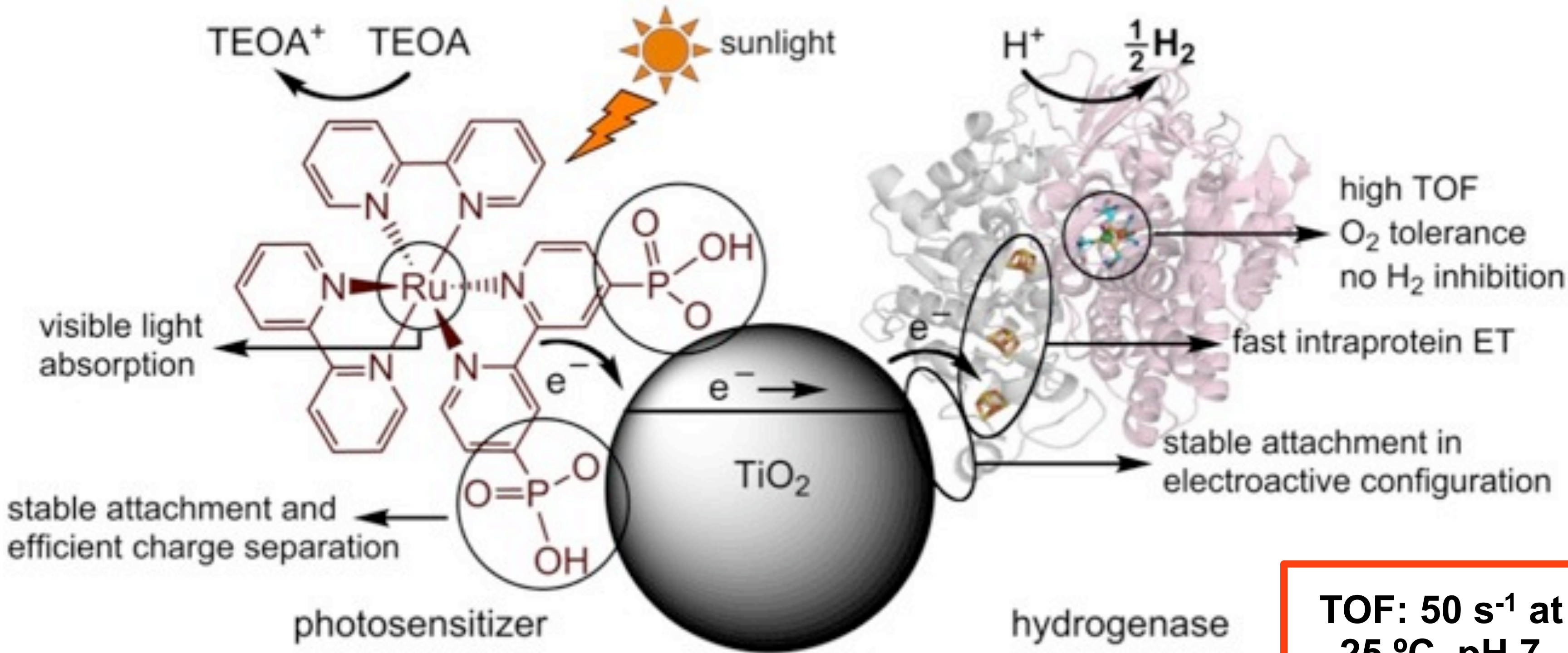





Grätzel, *Inorg. Chem.* **2005**, *44*, 6841-6851.

# Photocatalytic $H_2$ production with hydrogenases

$H_2$ production with *Desulfomicrobium baculatum* (*Db*) [NiFeSe]-H on dye-sensitised $TiO_2$

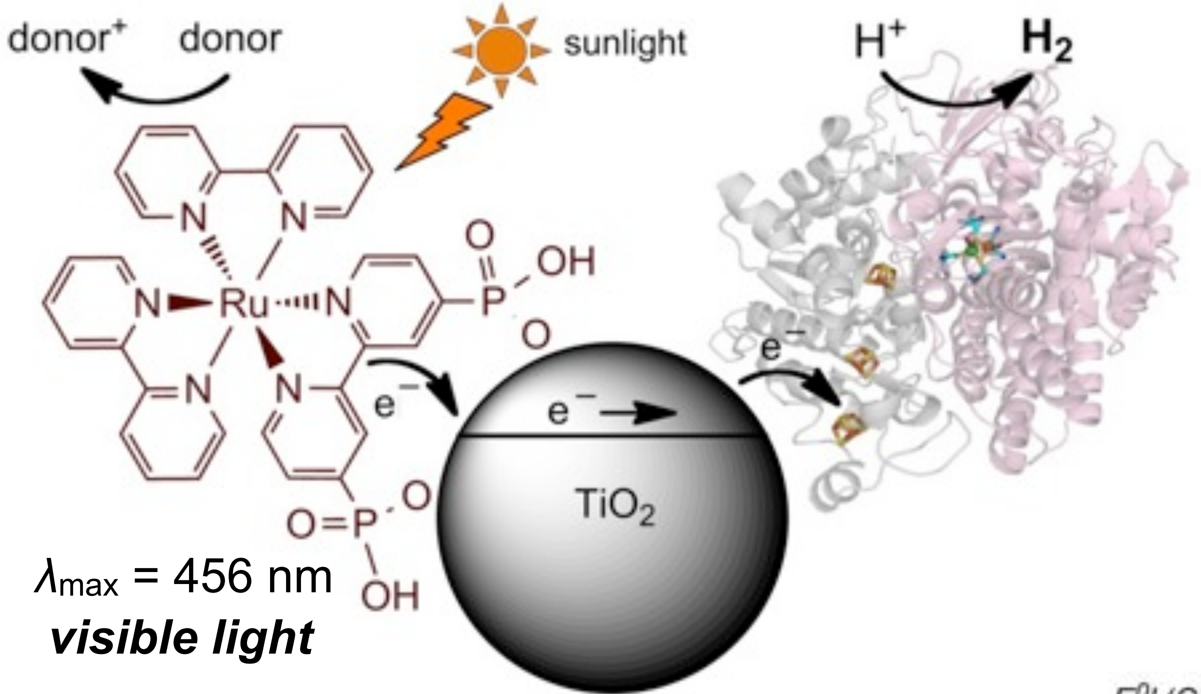



**TOF: 50 $s^{-1}$ at 25 ºC, pH 7**

TEOA = triethanolamine

Cartoon representation of a hybrid (enzyme-$TiO_2$) nanoparticle system showing aspects that are desirable for efficient and practical $H_2$ production from sunlight.

# Photocatalytic $H_2$ production with hydrogenases

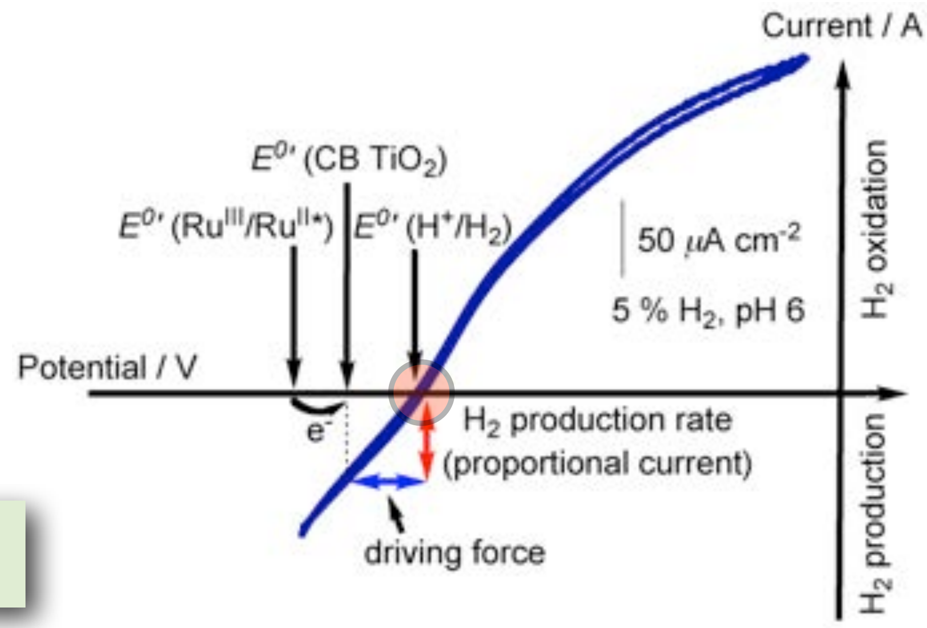



$\lambda_{max}$ = 456 nm
***visible light***

Concept of light-driven fuel production with an enzyme-modified dye-sensitized $TiO_2$ nanoparticle

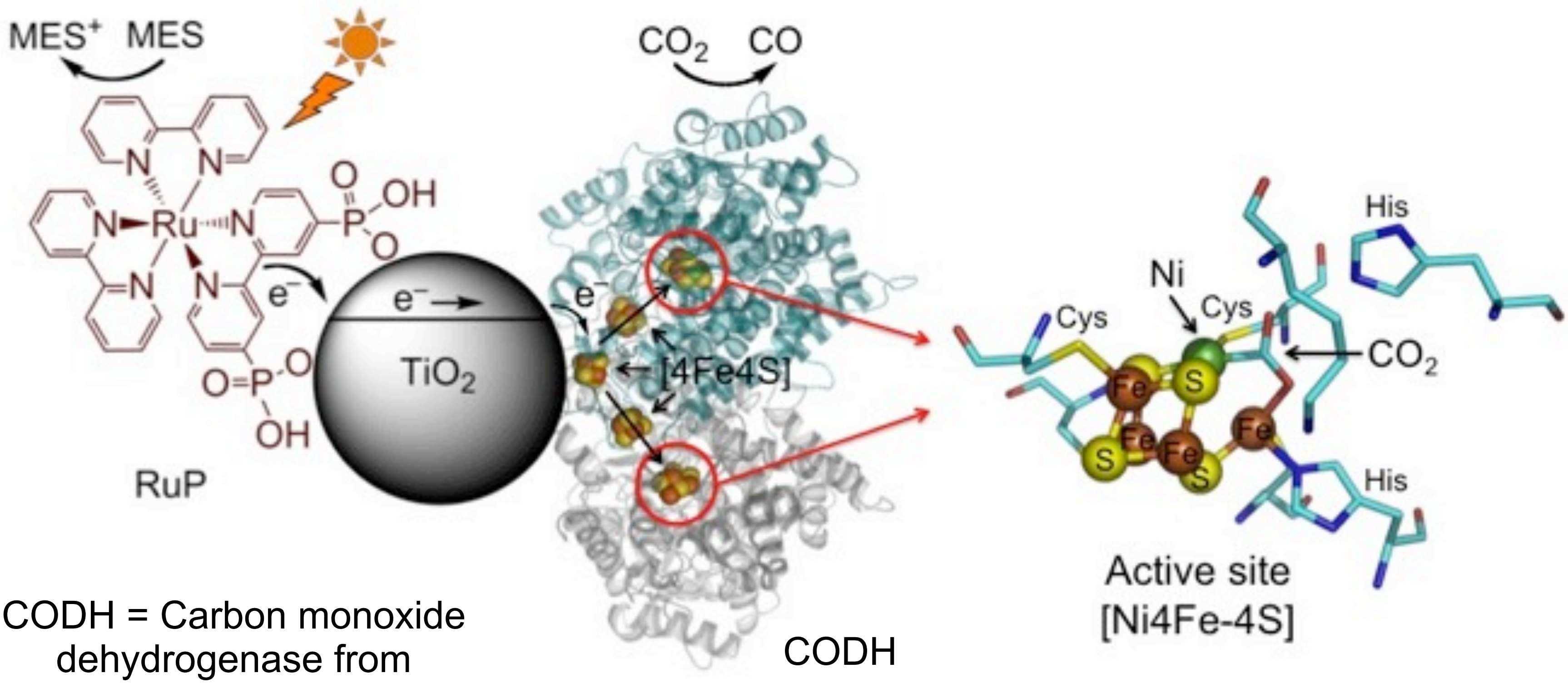
**TOF: 50 $s^{-1}$ at 25 ºC, pH 7**

Enzyme operates at thermodynamic potential →




Protein film voltammogram of *Db* [NiFeSe]-hydrogenase at pH 6 at 25 ºC (10 mV $s^{-1}$ and 2500 rpm).

# Visible light driven $CO_2$ to CO conversion with CODH.

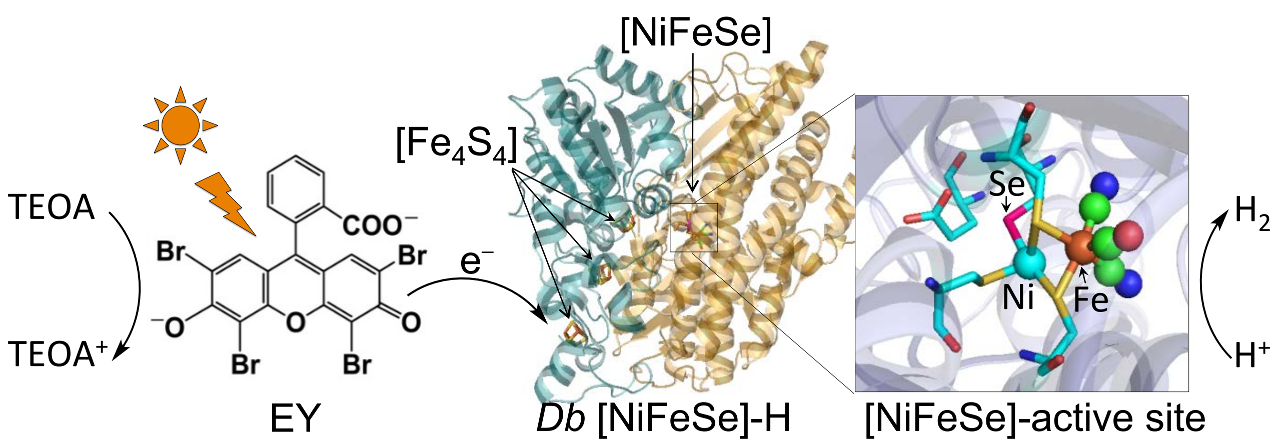


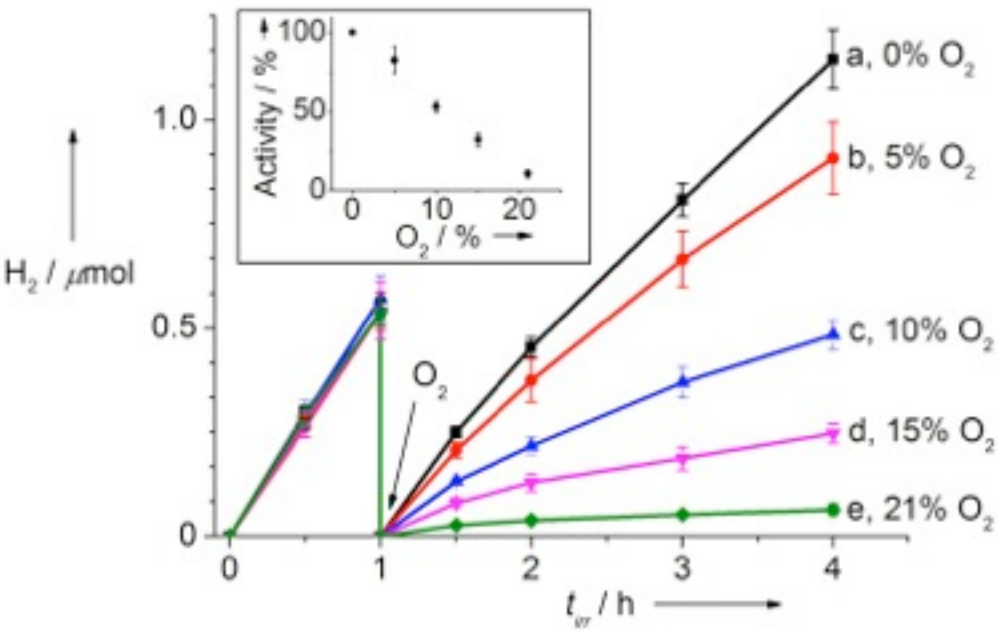

CODH = Carbon monoxide dehydrogenase from *Carboxydothermus hydrogenoformans*

**TOF: 0.15 $s^{-1}$, 20 ºC, pH 6, 98% $CO_2$**

**100% selectivity!**

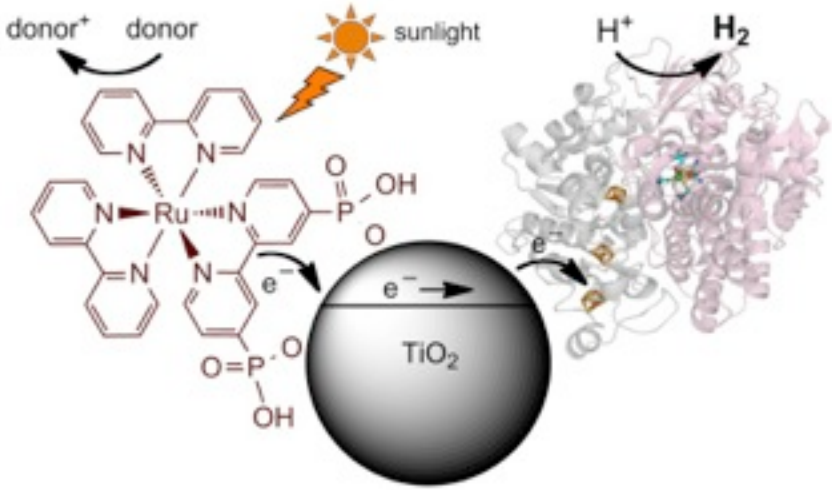
# About Photoactivity under High $O_2$ Levels with a Hydrogenase

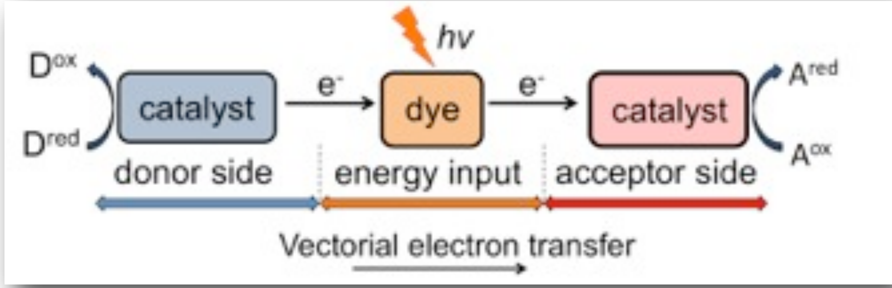


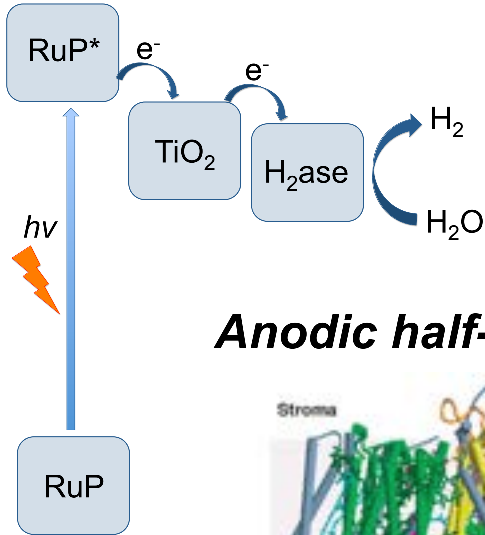




Amount of $H_2$ generated with the EY-$H_2$ase system in an aqueous TEOA solution (150 mM, pH 7.0) during visible light irradiation ($t_{irr}$, 100 mW cm$^{-2}$, AM 1.5G, $\lambda$ > 420 nm) at 25 ℃. The EY-$H_2$ase system was exposed to different $O_2$ headspace concentrations after one h irradiation.

# About a Photo-Tandem Cell

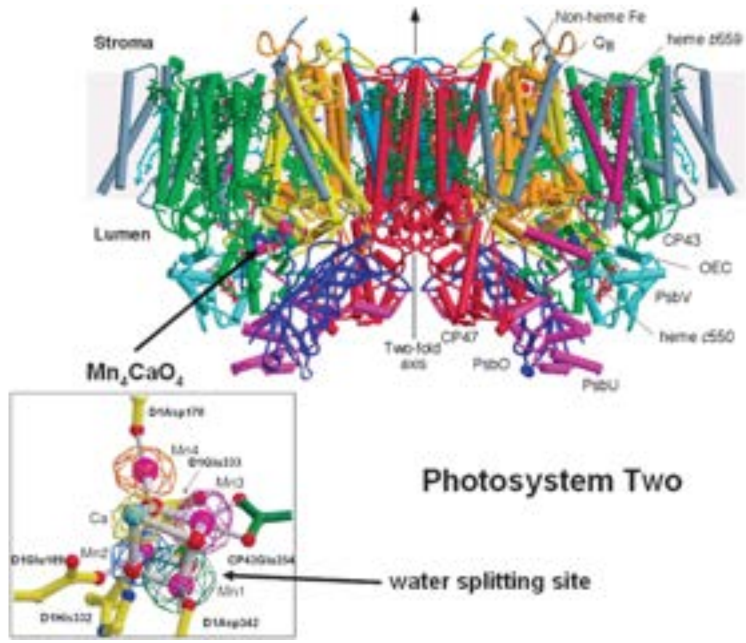


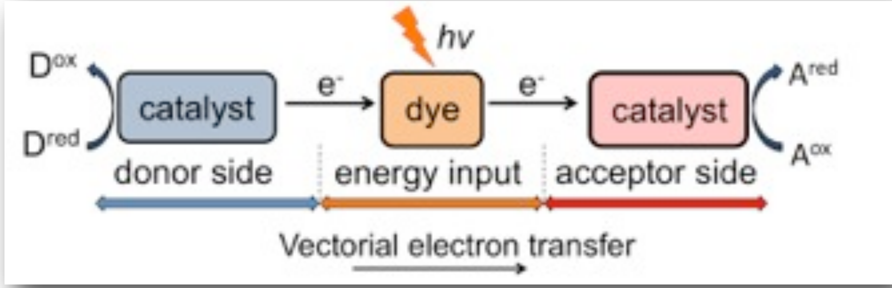

***We need to close the redox cycle***

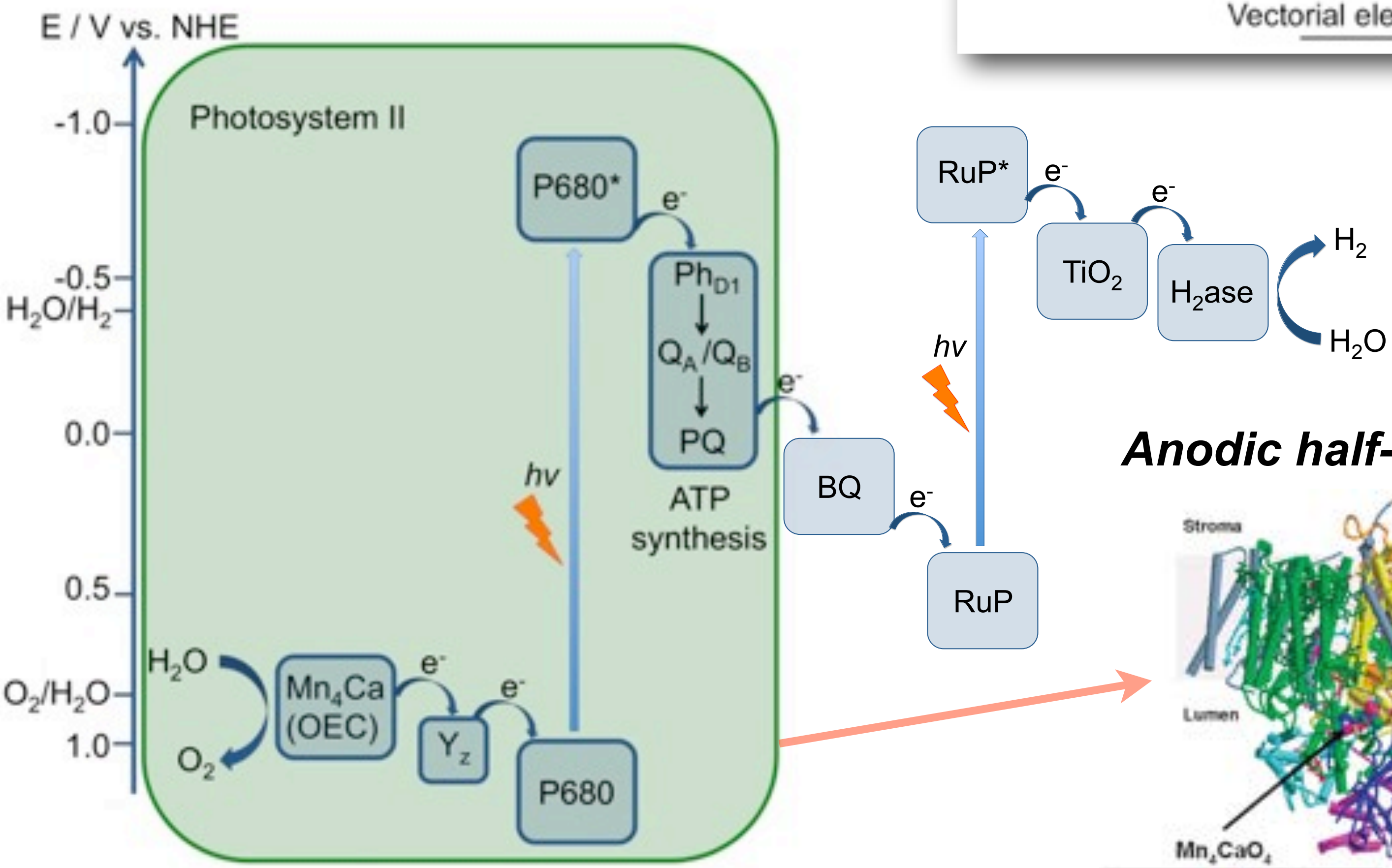
***Anodic half-reaction: PSII***



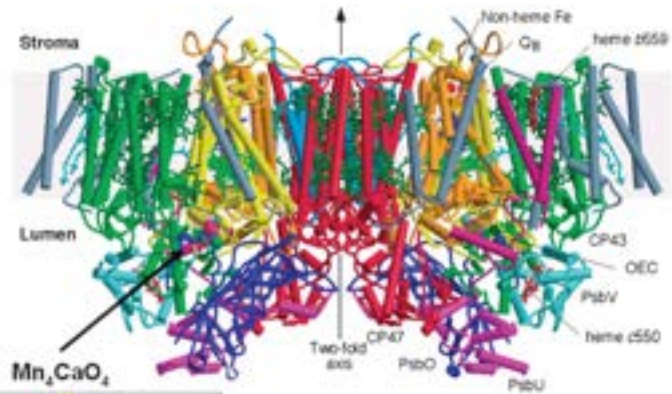

***To do: Coupling of cathodic with anodic half-reaction***

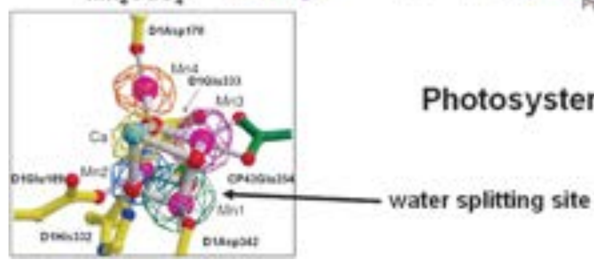
# About a Photo-Tandem Cell




## *Anodic half-reaction: PSII*

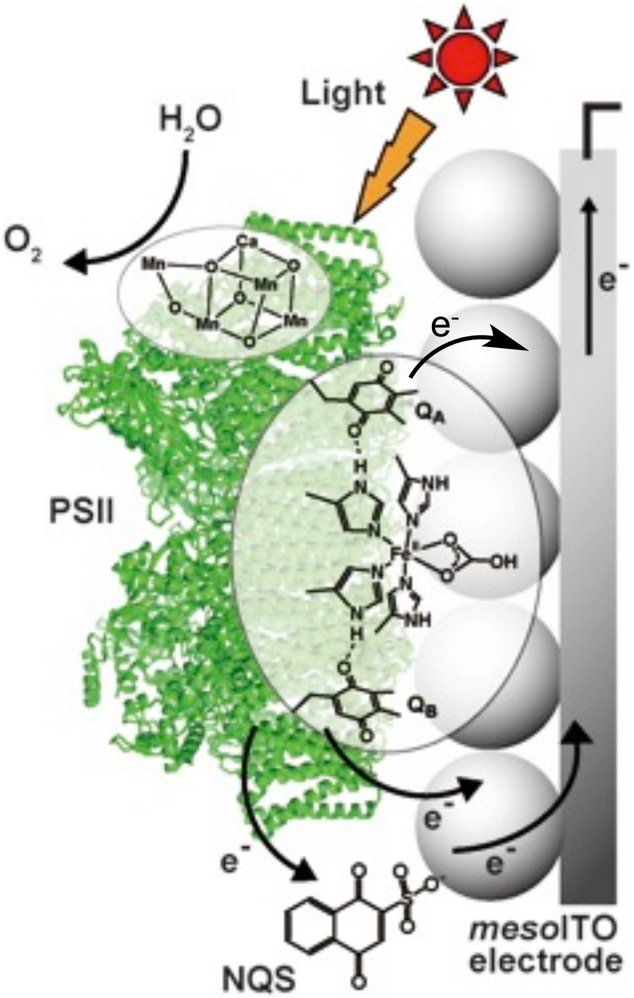


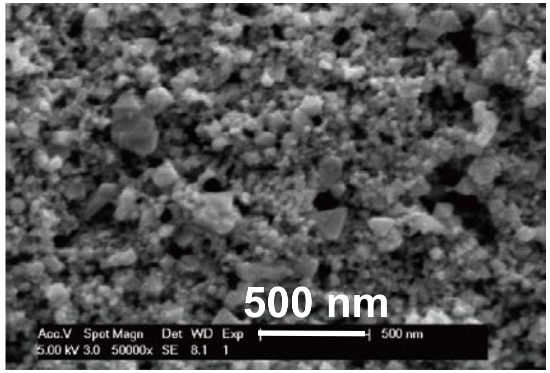

Photosystem Two

**Hybrid system for solar water splitting**

# About Water Oxidation with Photosystem II



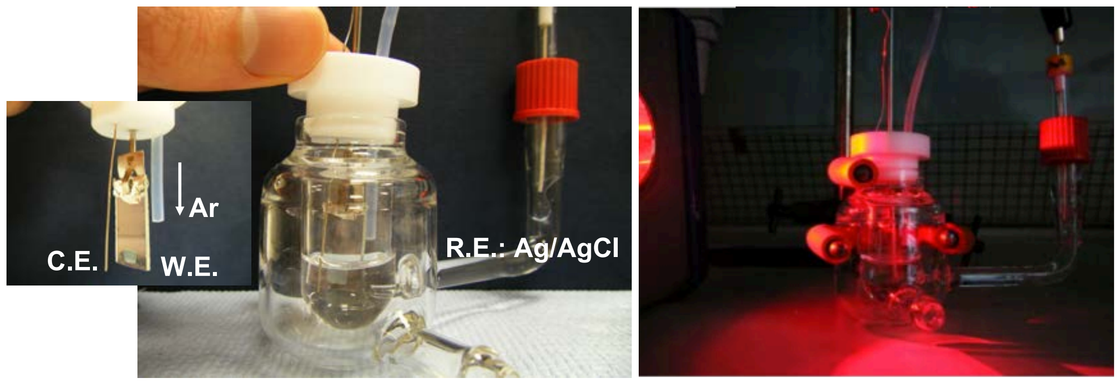

PSII from *Thermosynechococcus elongatus*




PSII dimer:
$11 \times 21 \times 11$ nm$^3$

<u>*meso*ITO as substrate:</u>

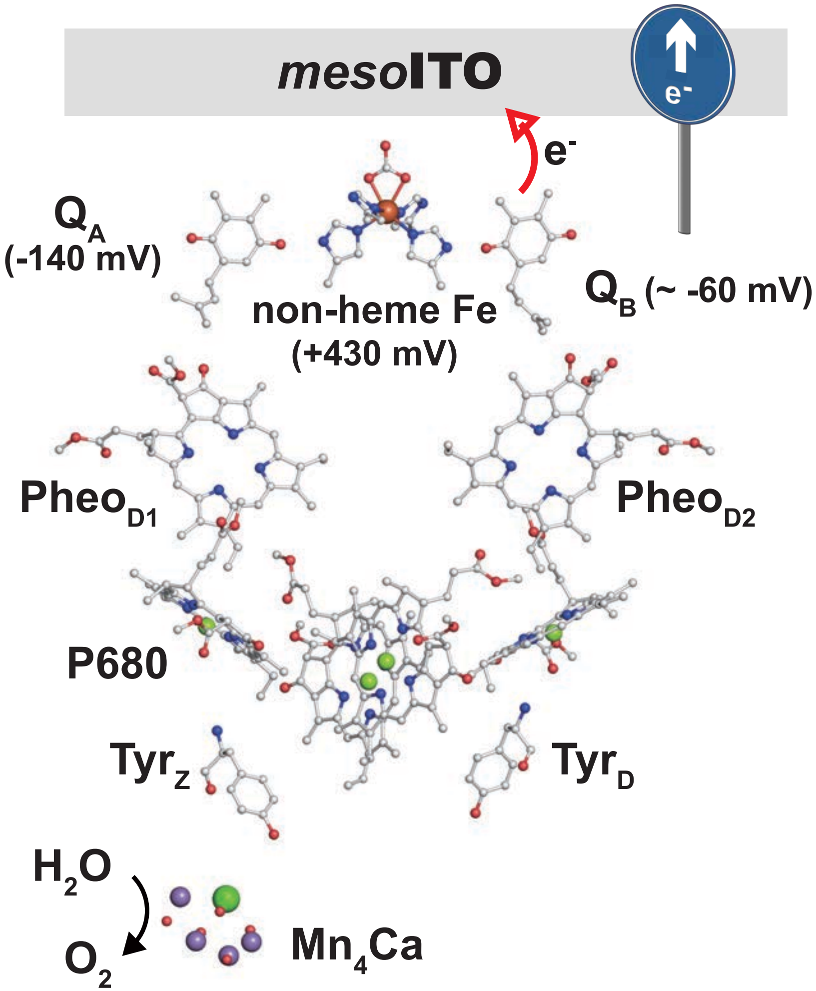
- Transparent
- 3D structure
- Hydrophilic

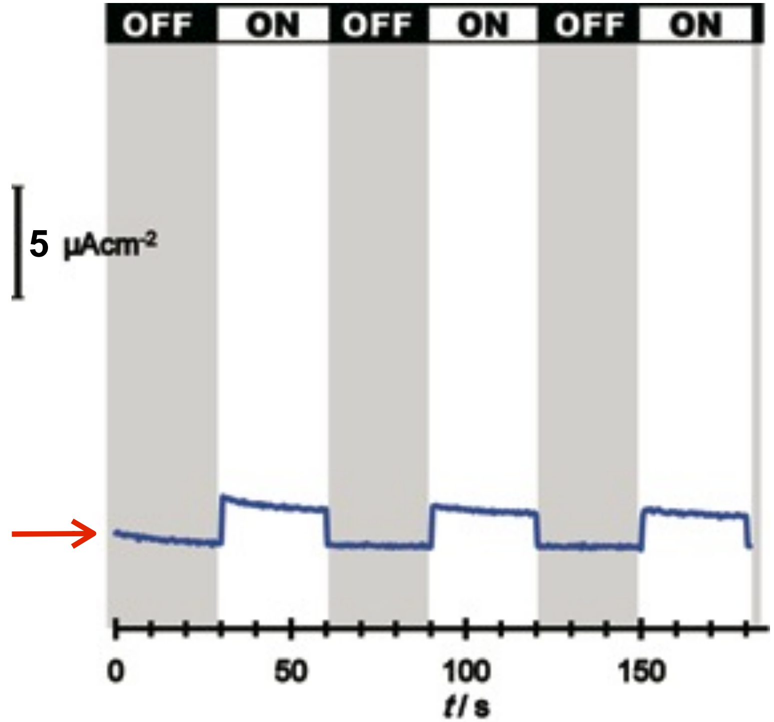



Electrochemical cell before and during irradiation.

# About Water Oxidation with PSII on mesoporous ITO

***PSII-mesoITO (blue trace): direct ET from PSII to ITO!***



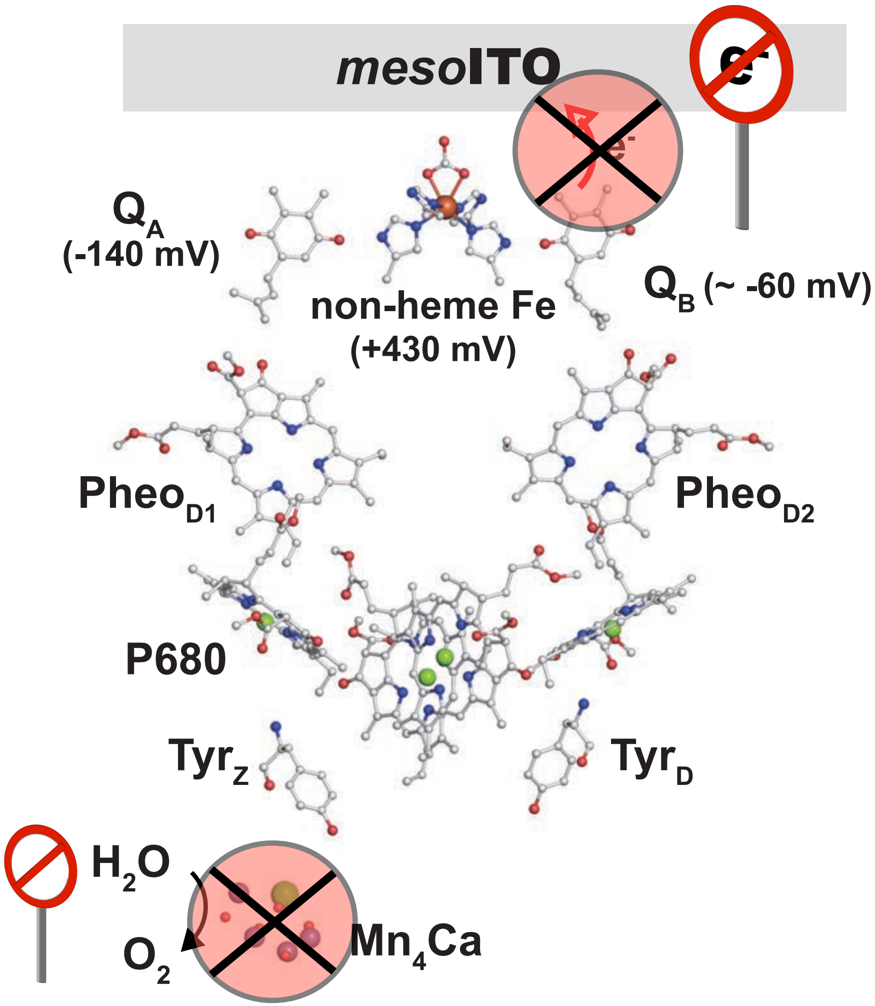

Photocurrent responses (red light) with +0.5 V *vs.* NHE in aqueous pH 6.5 buffer solution at 25ºC:

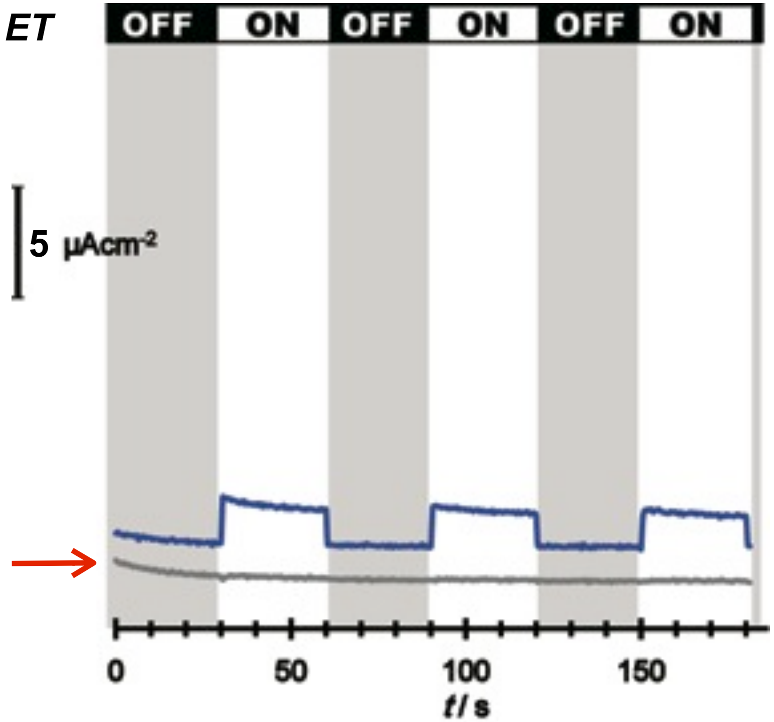
*PSII-mesoITO:*

$i = 1.6 \pm 0.3\ \mu A\ cm^{-2}$
TOF = 0.18 ± 0.04 (mol $O_2$) (mol PSII)$^{-1}$ $s^{-1}$

# About Water Oxidation with PSII on mesoporous ITO

*[Mn-depleted PSII]-mesoITO (grey trace): no interfacial ET*




Photocurrent responses (red light) with +0.5 V *vs.* NHE in aqueous pH 6.5 buffer solution at 25ºC:

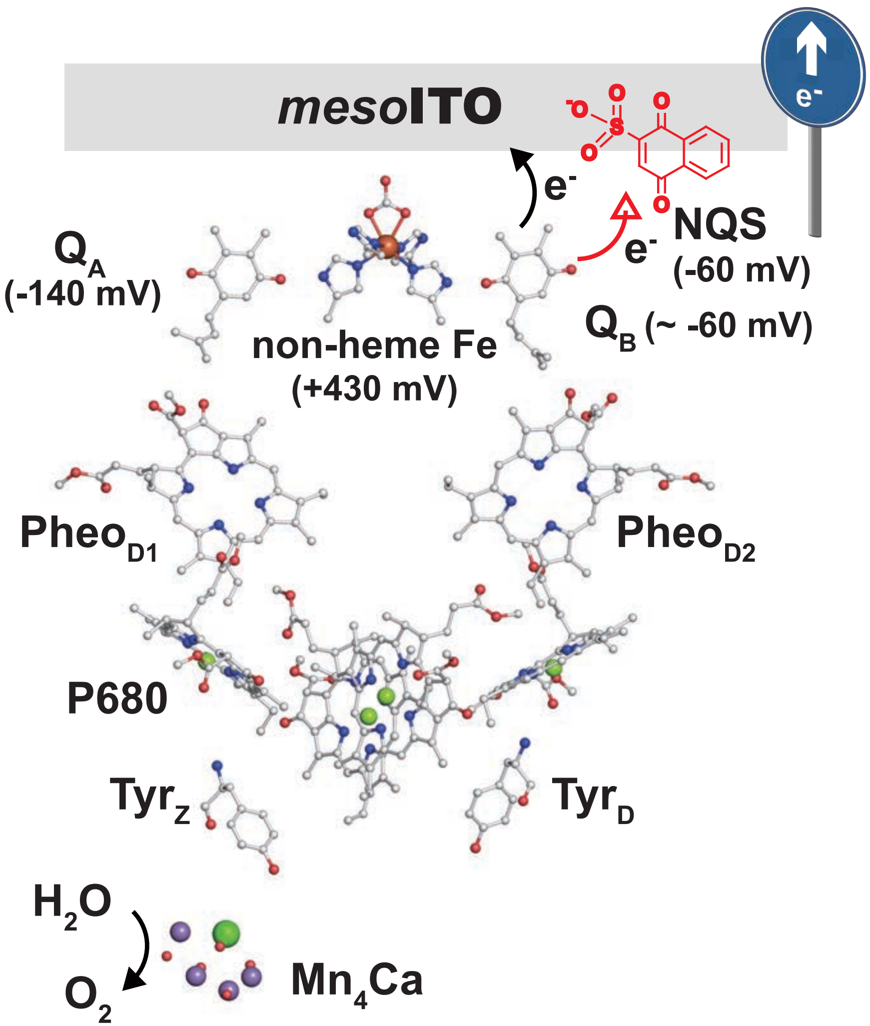
*[Mn-depleted PSII]-mesoITO:*

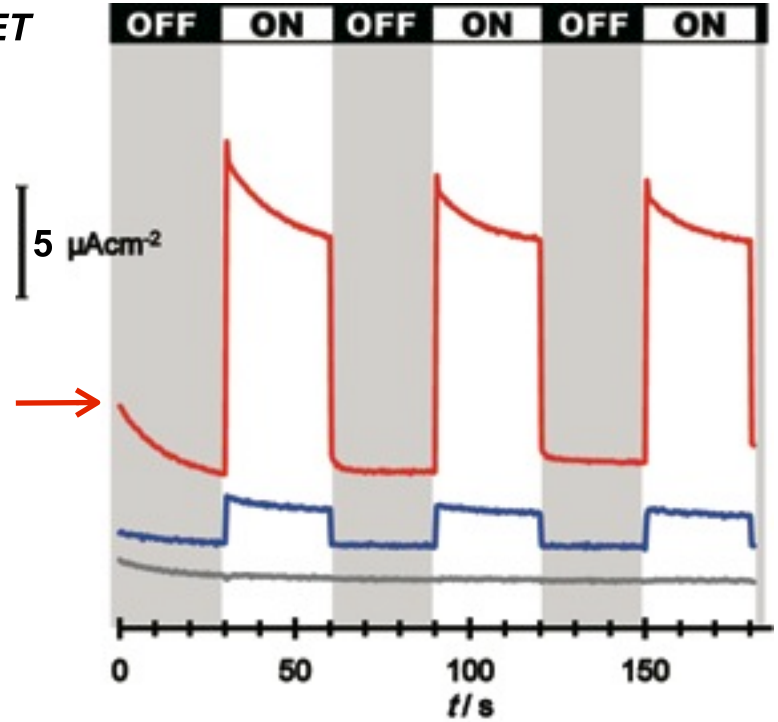
*i* = *n.d.*
TOF = *n.d.*

*n.b.*: no photocurrent with intact PSII on $TiO_2$

# About Water Oxidation with PSII on mesoporous ITO

***PSII-mesoITO + NQS (red trace): enhanced, mediated ET***



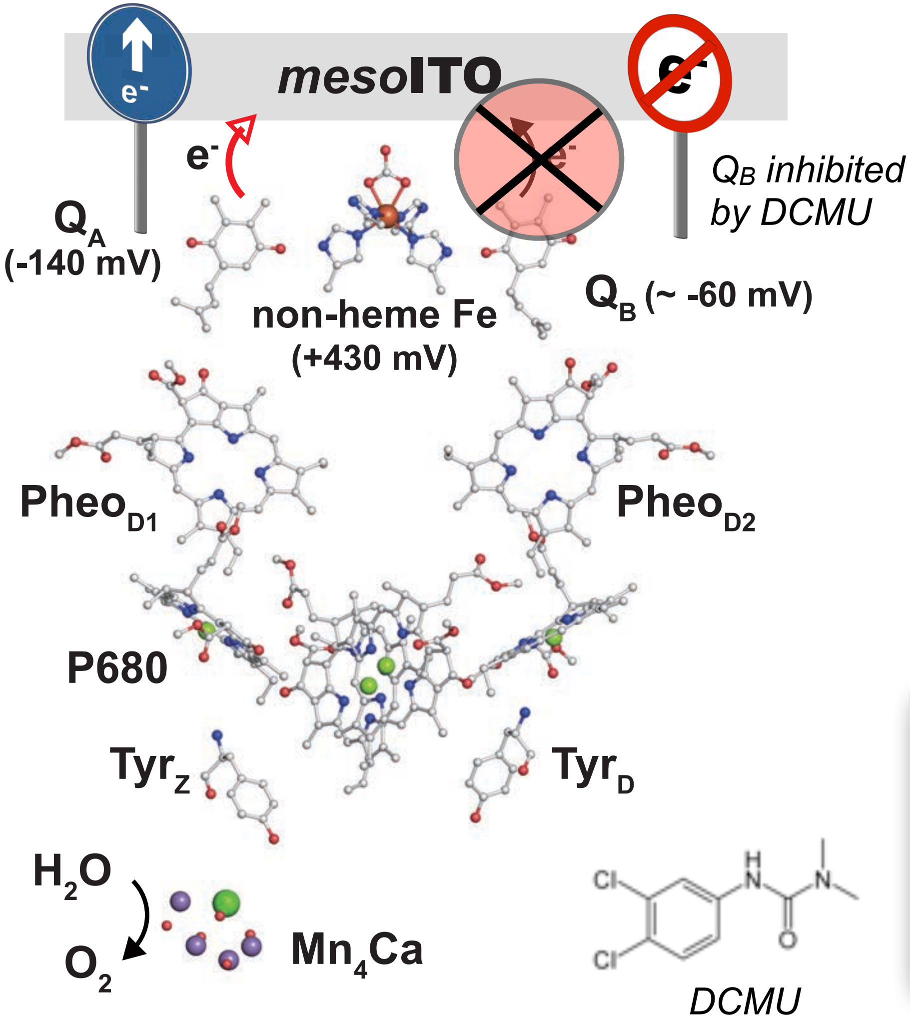

Photocurrent responses (red light) with +0.5 V *vs.* NHE in aqueous pH 6.5 buffer solution at 25ºC:

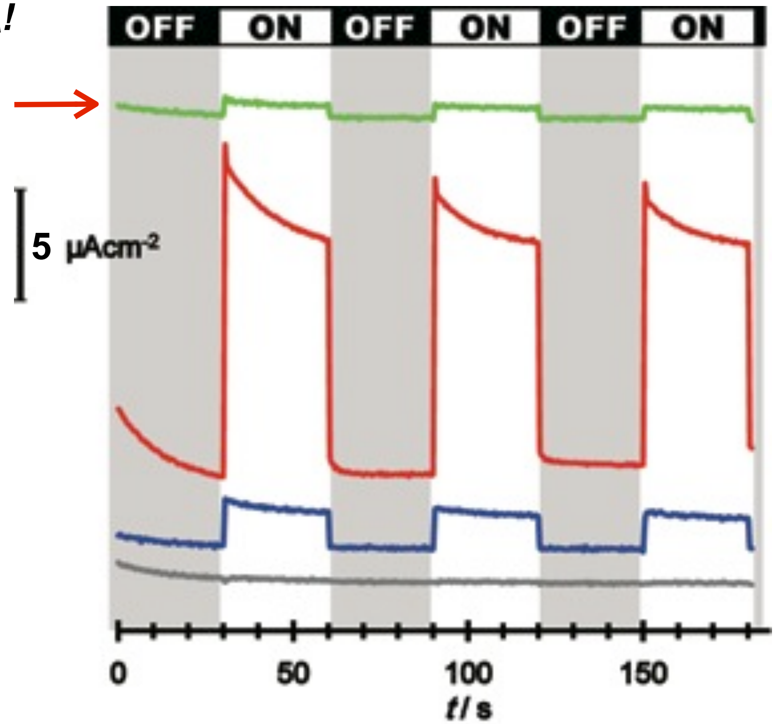
*PSII-mesoITO + NQS:*

$i$ = 12 ± 1 $\mu$A cm$^{-2}$.
TOF = 1.4 ± 0.1 (mol $O_2$) (mol PSII)$^{-1}$ s$^{-1}$

# About Water Oxidation with PSII on mesoporous ITO

***PSII-mesoITO + DCMU (green trace): direct ET from $Q_A$!***




Photocurrent responses (red light) with +0.5 V *vs.* NHE in aqueous pH 6.5 buffer solution at 25ºC:

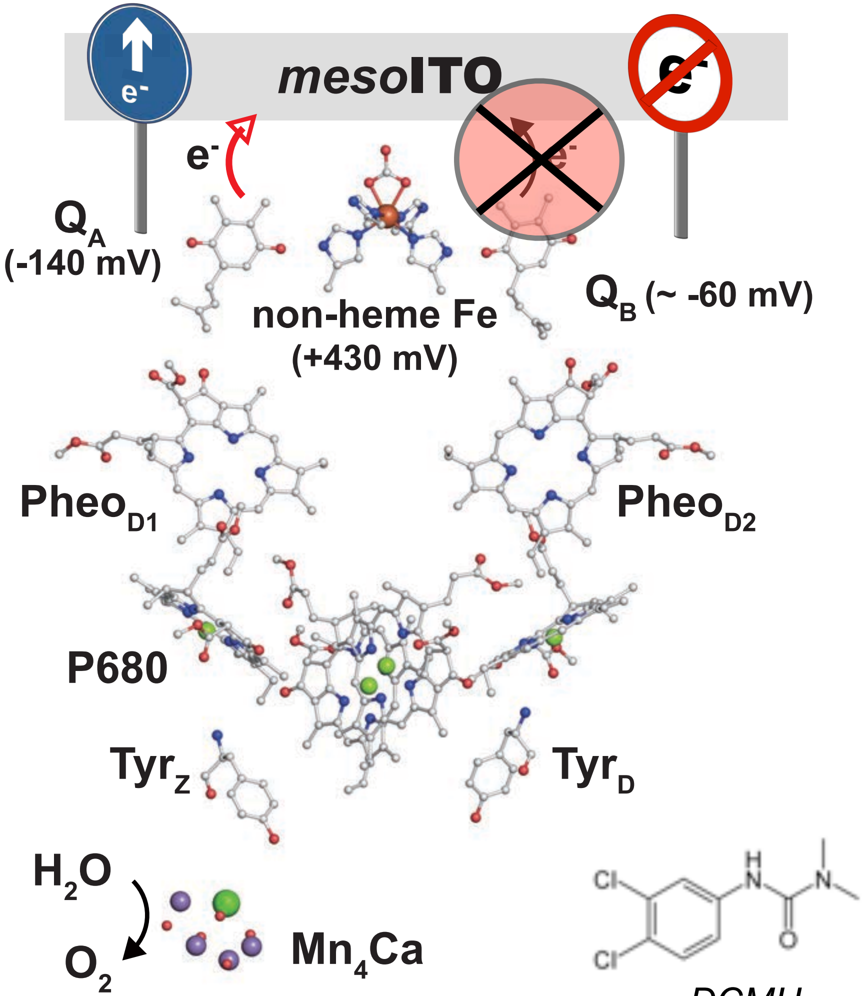
*PSII-mesoITO + DCMU:*

$i$ = 0.5 ± 0.1 $\mu$A cm$^{-2}$.

TOF = 0.05 ± 0.02 (mol $O_2$) (mol PSII)$^{-1}$ s$^{-1}$

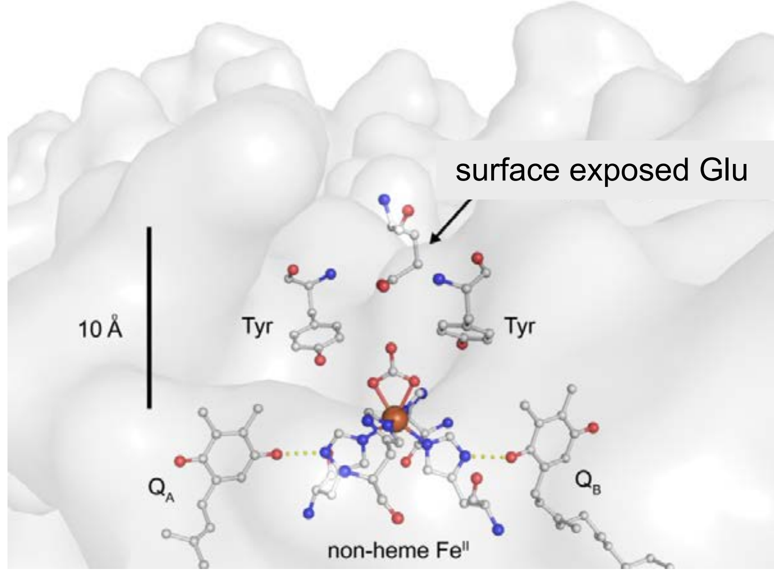
# About Water Oxidation with PSII on mesoporous ITO

***Direct ET from $Q_A$ to mesoITO!***




*DCMU*

*$Q_A$ approximately 9Å from stromal protein surface*

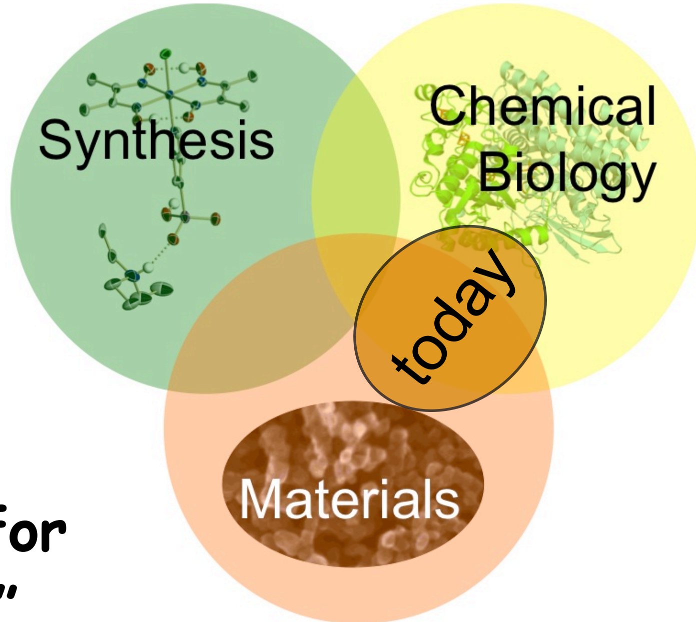



***Acceleration of PSII TOF by direct ET from $Q_A$?***

Diffusion of quinone $Q_B$ from protein pocket to electron acceptor rate limiting in PSII and 10-fold slower than the slowest catalytic step.

Can we accelerate water oxidation in PSII in an artificial environment by hijacking electrons upstream at $Q_A$ level?

# Conclusion

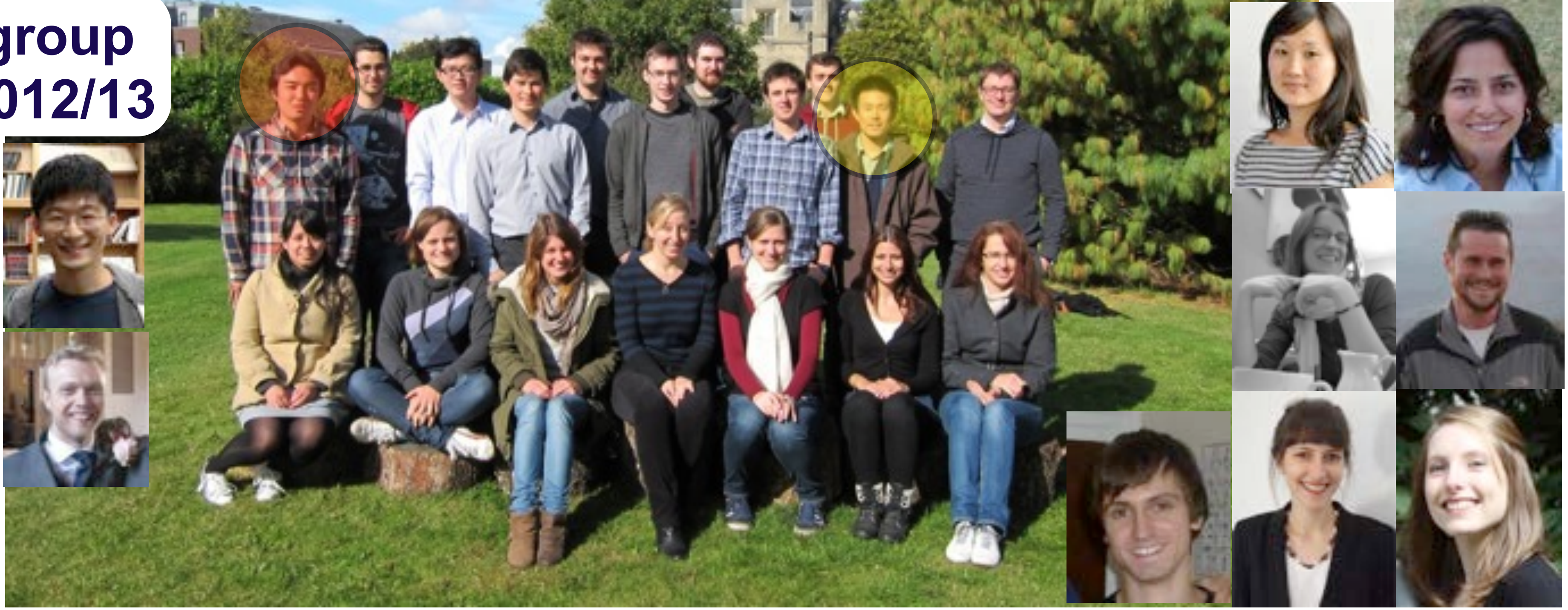



**"Developing the chemical toolbox for advanced photochemical systems"**

**Fuel generation: from enzymes to bio-inspired catalysis.**

- Solar $H_2$ production and with enzyme-nanoparticle system
- Solar water oxidation with enzyme-modified metal oxide electrodes
- Solar $H_2$ production with Co catalyst-nanoparticle system
- Solar water oxidation hybrid materials from molecular precursors

group 2012/13

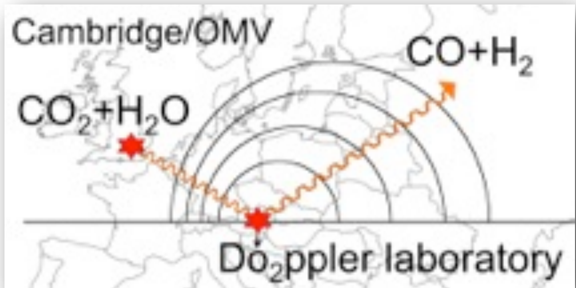


## Funding

EPSRC

BBSRC
bioscience for the future

**Doppler laboratory.**




OMV

bmwfi

UNIVERSITY OF CAMBRIDGE

Cambridge Overseas Trust

MARSHALL SCHOLARSHIP

wpi

DFG

行政院國家科學委員會
National Science Council

Schlumberger Foundation Faculty for the Future

SUNTORY

THE ROYAL SOCIETY