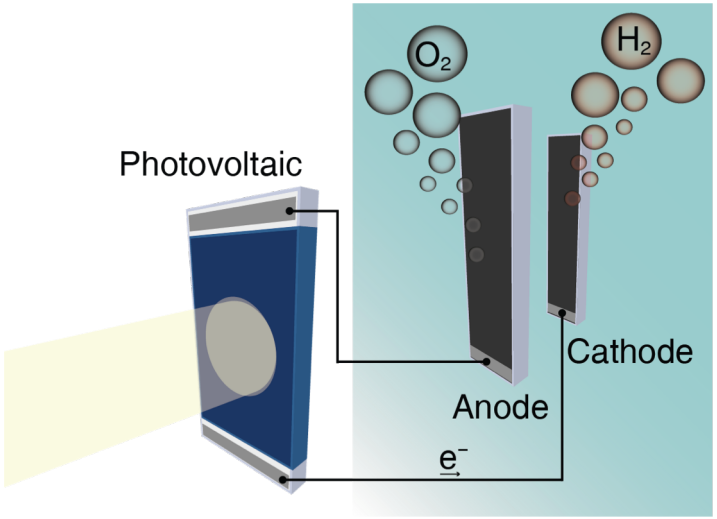
Energy Conversion by Semiconductor Devices

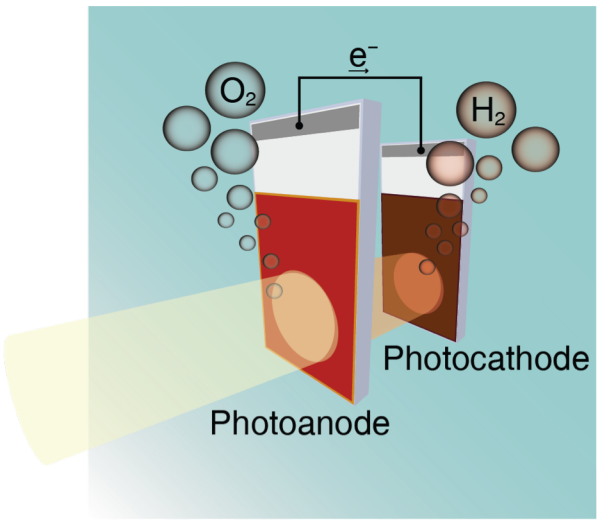
Jun-Ho YUM
junho.yum@epfl.ch

Solar Hydrogen Production

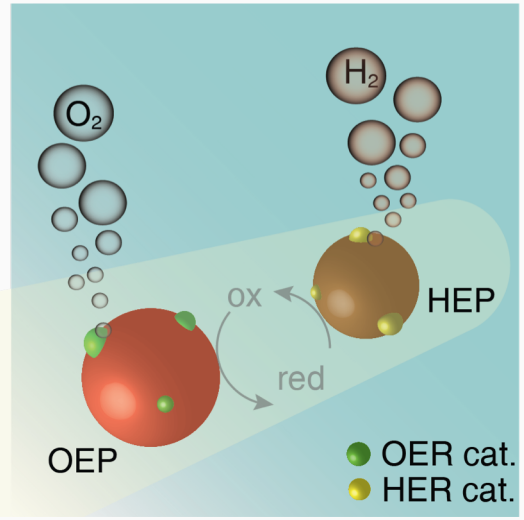
PV-EC



PEC



PC



5 – 12 $/Kg H_2 (1)

3 – 18 $/Kg H_2 (2)

1 – 3 $/Kg H_2 (2)

- Higher efficiency
- Complexity of the system and higher cost

(1) "DOE Technical Targets for Hydrogen Production from Electrolysis" http://www.energy.gov

(2) B.A. Pinaud, et al. *Energy Environ. Sci.*, **6**, 1983 (2013)

- Jun-Ho YUM, junho.yum@epfl.ch

Solar Water Splitting using a Particulate Photocatalyst

Single Component Photocatalyst

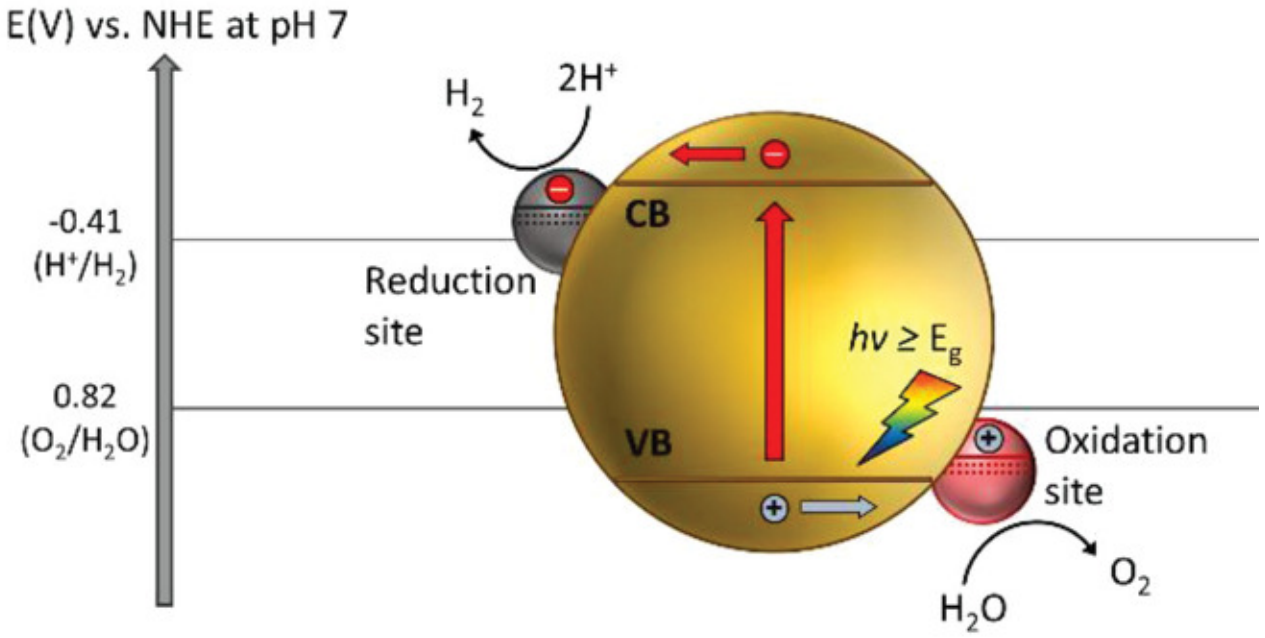


Image taken from B.-J. Ng et al., *Adv. Sci.*, **7**, 1903171 (2020)

- Difficult to simultaneously fulfill two important aspects:
  - Suitable energy levels for both water oxidation and reduction
  - Small bandgap for broad range of light absorption
- Rapid recombination of photogenerated electron-hole pairs

Solar Water Splitting using a Particulate Photocatalyst

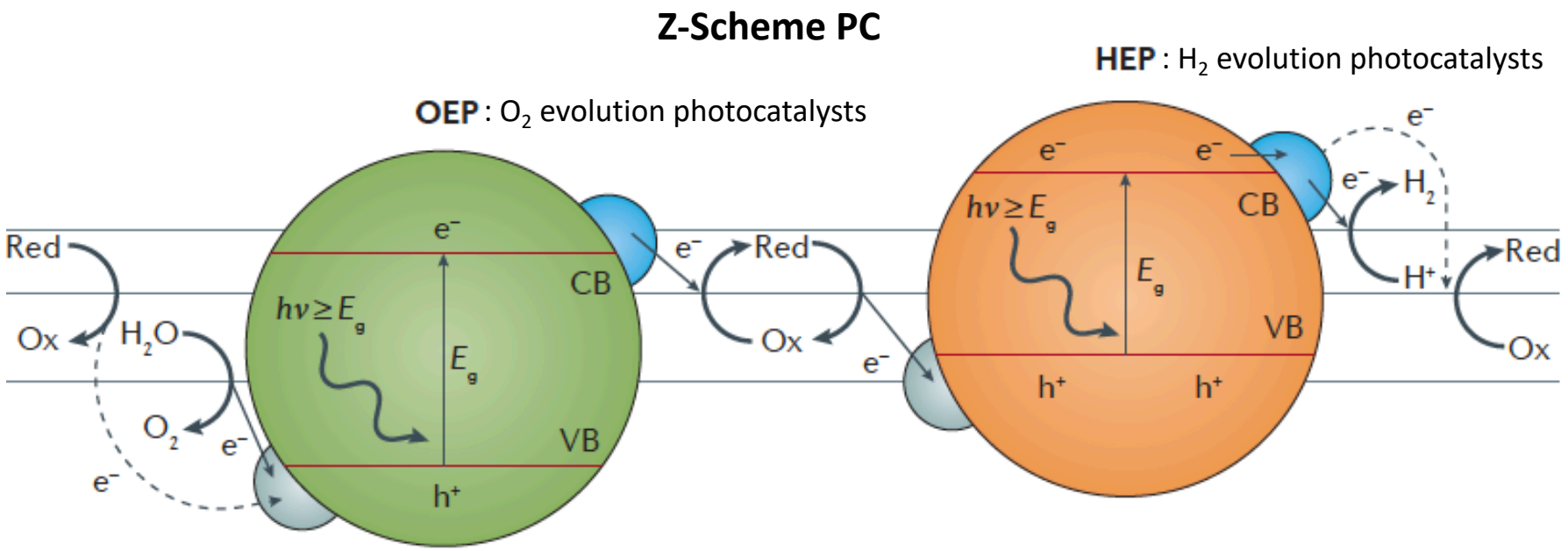
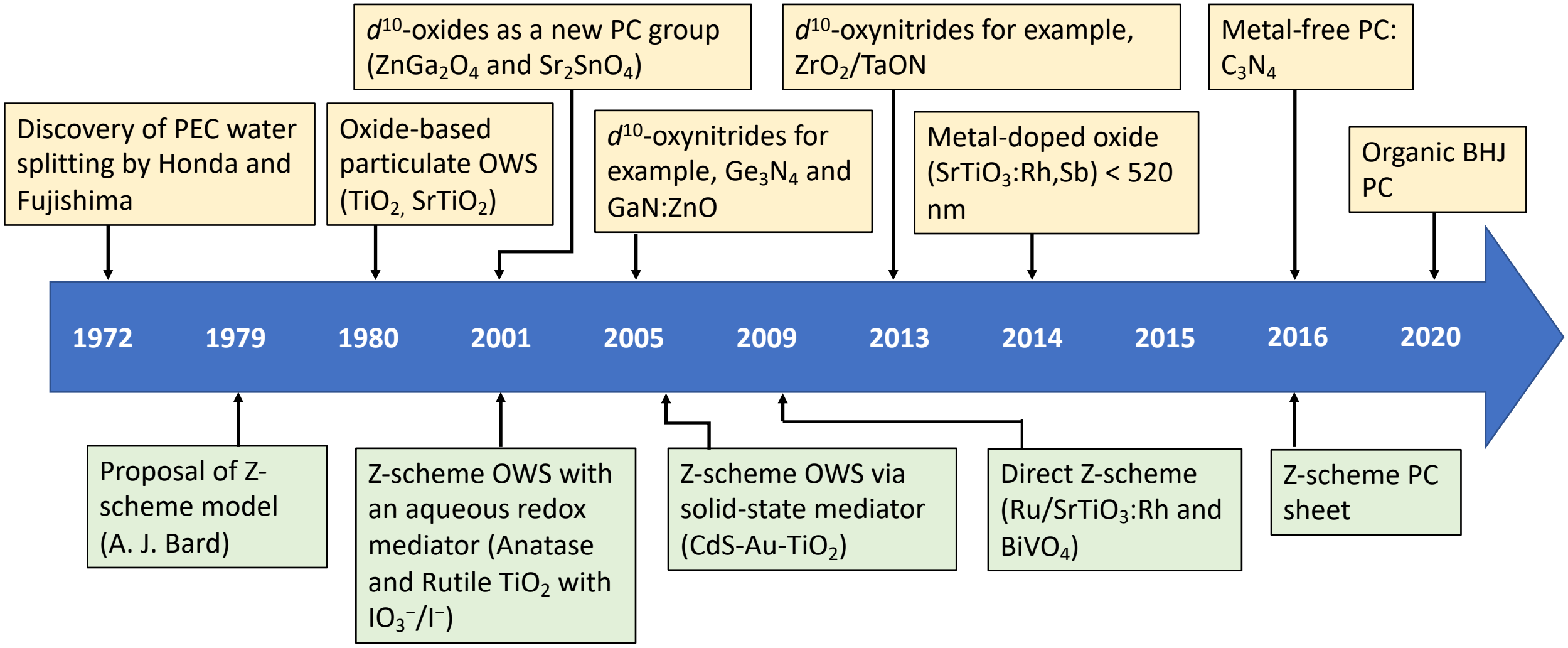


Image taken from S. Chen et al., *Nat. Rev. Maters.*, **2**, 17050 (2017)

- Inspired by natural photosynthesis
- Relaxation of the thermodynamic requirements: small bandgap → wider range of light
- Needs an electron mediator
- Required suppression of charge carrier recombination and backward reaction (dashed lines)

Timeline of the Key Development in PC-based Water Splitting

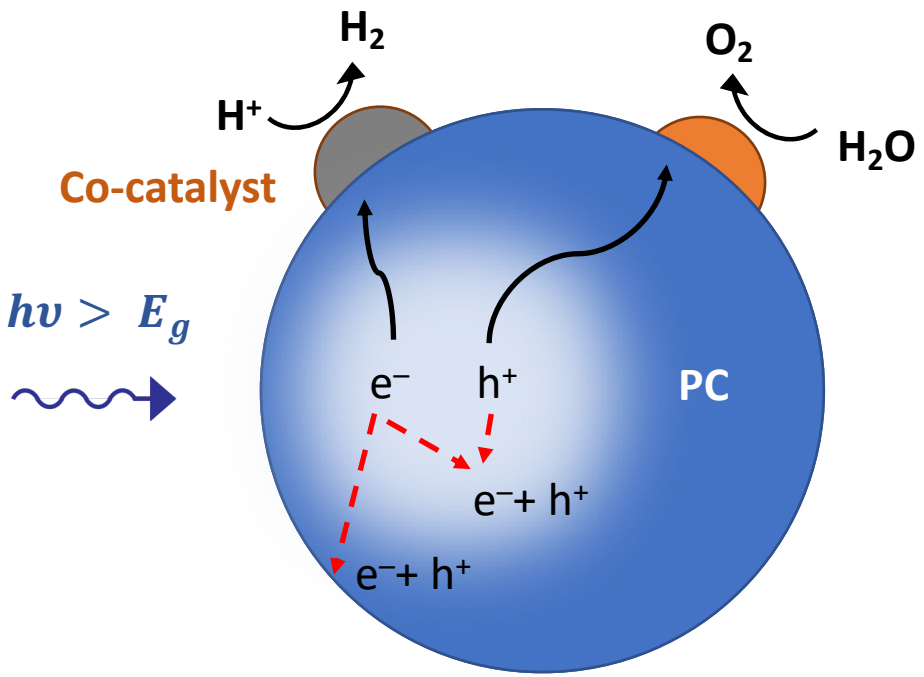


OWS: Overall Water Splitting

B.-J. Ng et al., *Adv. Sci.*, **7**, 1903171 (2020)
S. Chen et al., *Nat. Rev. Maters.*, **2**, 17050 (2017)

- Jun-Ho YUM, junho.yum@epfl.ch

Operation Principle in PC Water Splitting



Photoexcitation → Exciton → Separated e^- and h^+ pair

e^- and h^+ diffuse to the surface and induce photocatalytic reactions

e^- and h^+ recombine in the bulk or at the surface (trap)

Typically diffusion can occur more rapidly than recombination

The efficiency of photoreaction is expressed by the quantum yield ($\boldsymbol{\Phi}$)

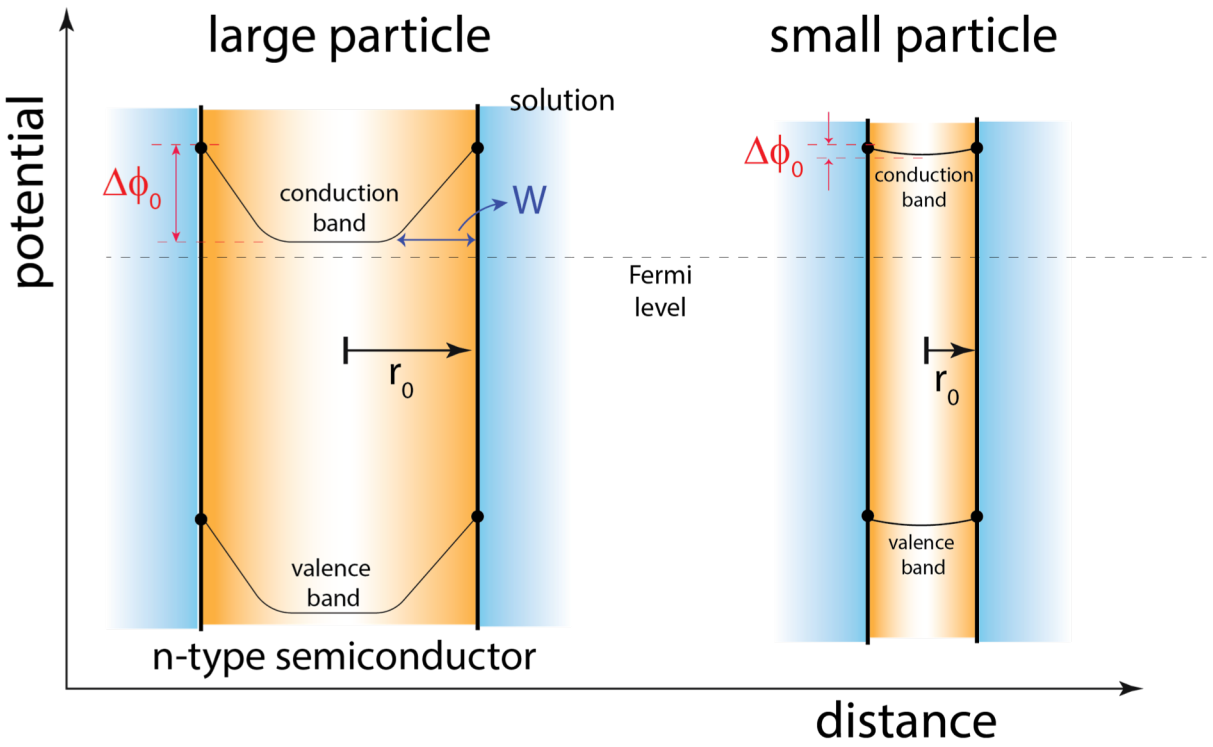
$$\boldsymbol{\Phi} = \frac{rate\ of\ reactant\ consumption\ or\ product\ formation}{rate\ of\ photon\ absorption}$$

$$\boldsymbol{\Phi} \propto \frac{\boldsymbol{k_{CT}}}{\boldsymbol{k_{CT} + k_{Rec}}}$$

The rate of reactant consumption or product formation is proportional to the rate of charge (electron/hole) transfer (k_{CT}) from the semiconductor to the reactant molecules, and the rate of photon absorption is proportional to the sum of the rates of the charge transfer (k_{CT}) and electron–hole recombination (k_{Rec}).

- Jun-Ho YUM, junho.yum@epfl.ch

Operation Principle in PC Water Splitting



Smaller particles have a higher surface area and more reaction sites at constant mass.

The band bending will decrease with the size of the SC particle.

Electric field is very small and **optimized doping density** to develop potential difference between surface and center is required.

The potential drop ($\Delta\phi_0$) in a spherical SC particle

$$\Delta\phi_0(r) = \frac{k_B T}{6e}\left(\frac{r-(r_0-W)}{L_D}\right)^2\left(1+\frac{2(r_0-W)}{r}\right)$$

$$Debye\ Length\ \ L_D = \left(\frac{\varepsilon_r \varepsilon_0 k_B T}{e^2 N_D}\right)^{1/2}$$

r is the distance to the surface,
r_0 is radius of SC particle,
N_D is the donor concentration,

Large particles ($r_0 \gg W$)

$$\Delta\phi_0 = \frac{k_B T}{6e}\left(\frac{r_0}{L_D}\right)^2$$

Small particles ($r_0 < \sqrt{3}W$)

$$\Delta\phi_0 = \frac{k_B T}{2e}\left(\frac{W}{L_D}\right)^2$$

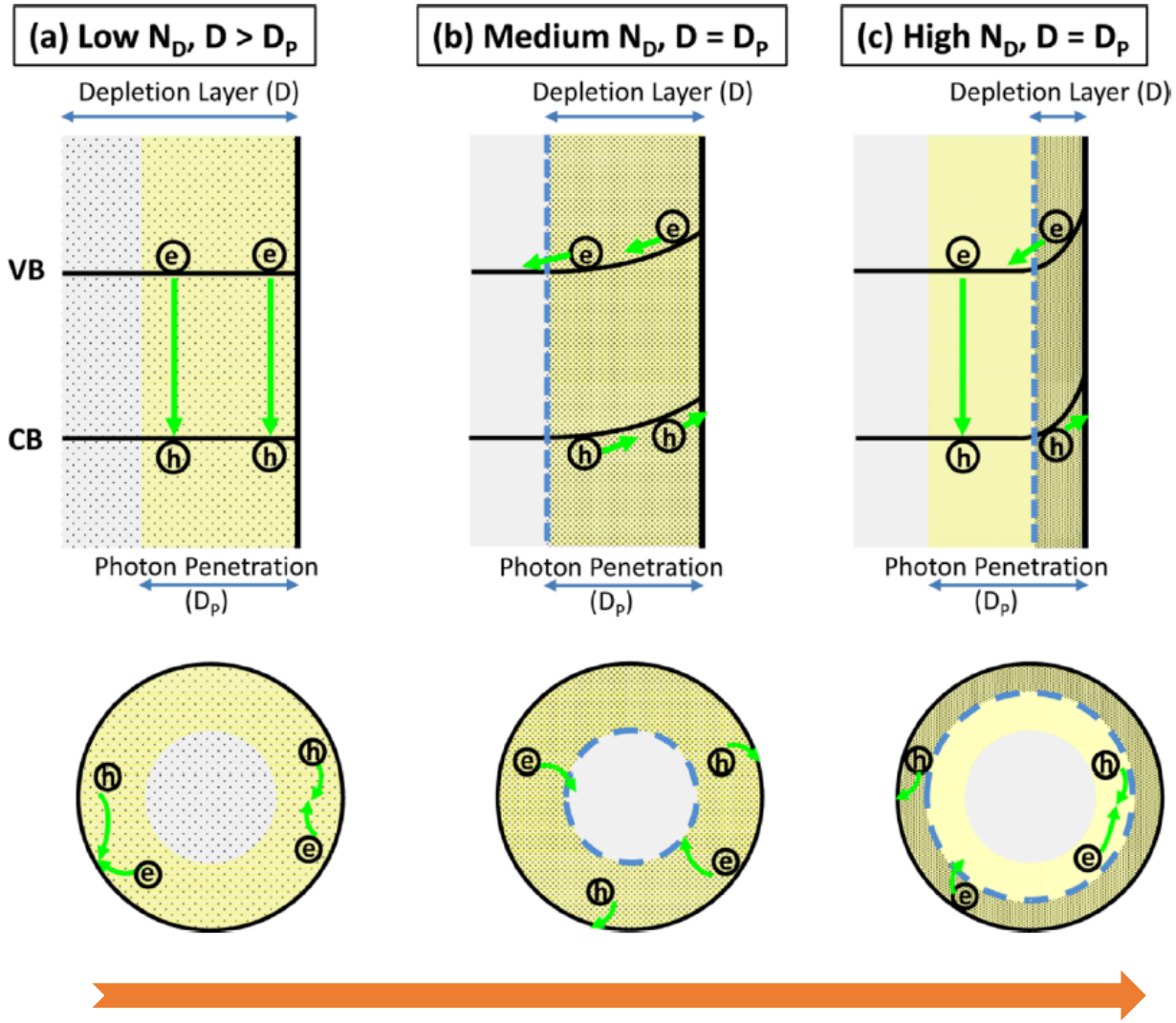
For TiO_2, $L_D = 3.8 \sim 12$ nm, $\varepsilon_r \approx 100$,

$N_D \approx 10^{18}\sim10^{19} cm^{-3}$, $\boldsymbol{\Delta\phi_0}$ **= ~0.004 V**

- Jun-Ho YUM, junho.yum@epfl.ch

Hagfeldt *et al.*, *Chem. Rev.* **95**, 49 (1995)

Operation Principle in PC Water Splitting



Most of the excited e^- and h^+ will recombine in the bulk or in the surface region.

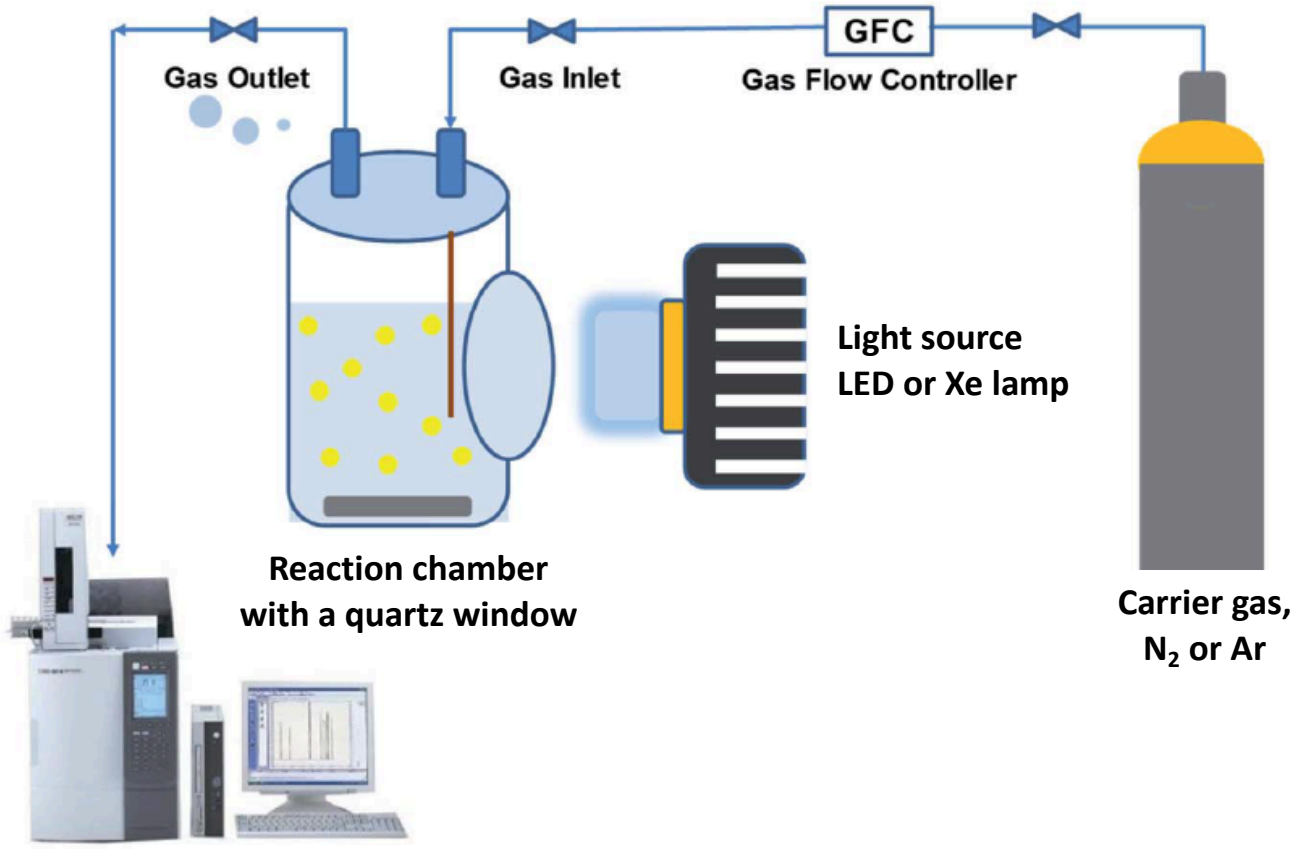
The depletion region decreases in depth to become less than the photon penetration region. Only the photogenerated e^--h^+ pair in the depletion region can be separated effectively.

The band bending increases and the depletion layer decreases in depth!

Z. Zhang et al., *Chem. Rev.*, **112**, 5520–5551 (2012)

Metrics in PC Water Splitting

Gas production over time and STH conversion efficiency



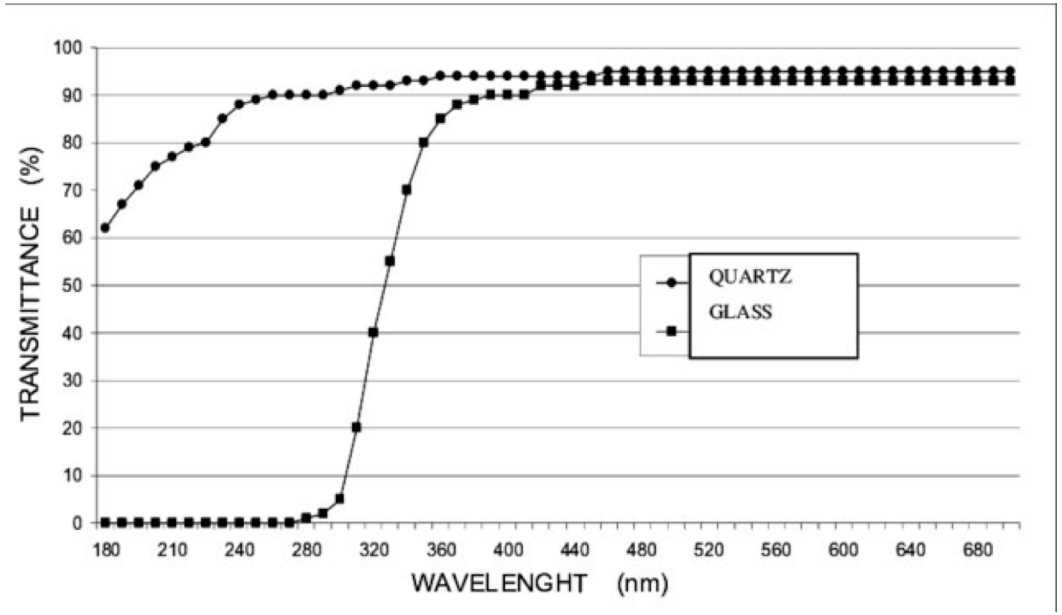


Image inspired from H. El-Bery et al., *RSC Adv.*, **11**, 13229 (2021)

Metrics in PC Water Splitting

Gas production over time and STH conversion efficiency

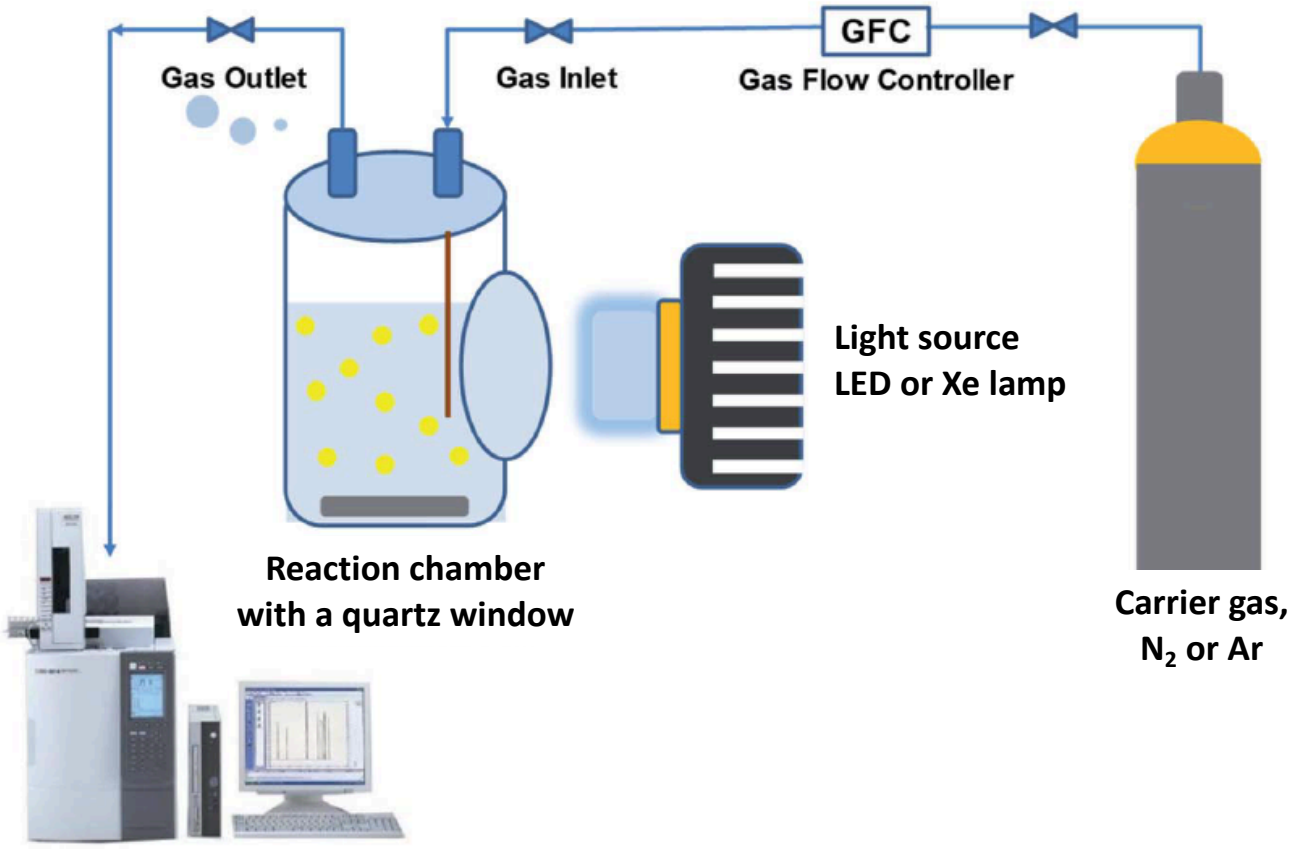
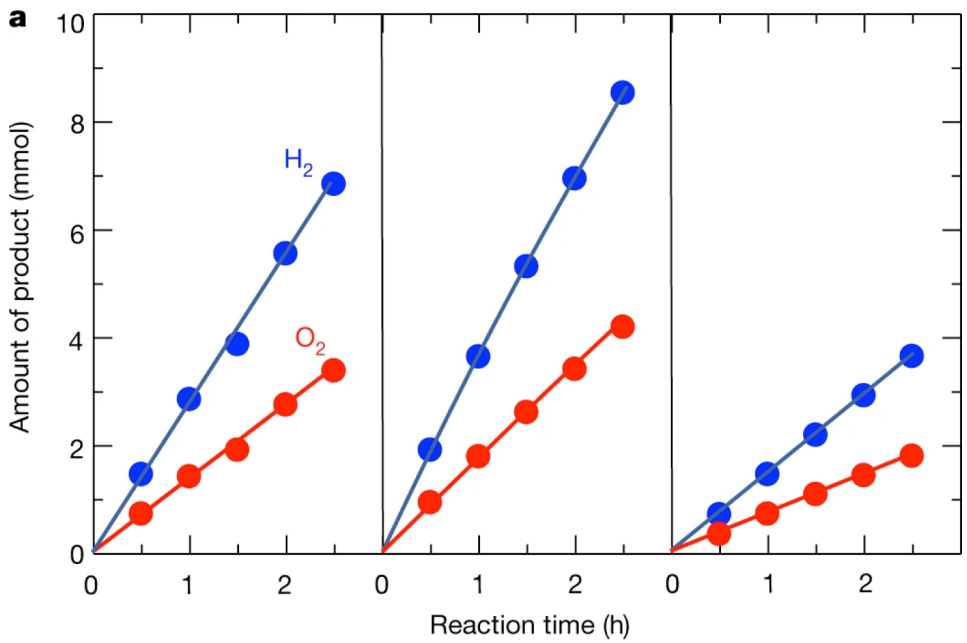


Image inspired from H. El-Bery et al., *RSC Adv.*, **11**, 13229 (2021)

$SrTiO_3$:Al loaded with various co-catalysts



T. Takata et al., *Nature*, **581**, 411 (2020)

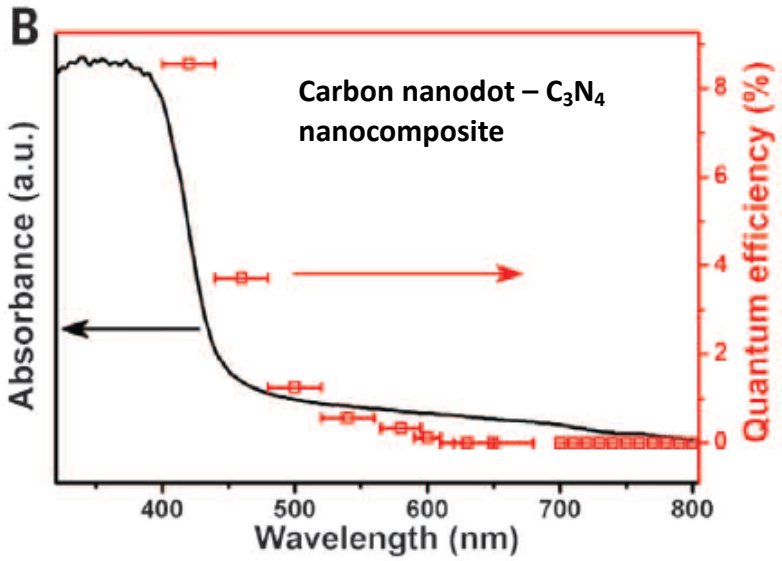
Metrics in PC Water Splitting

$$\textit{Apparent Quantum Yield (AQY)}$$

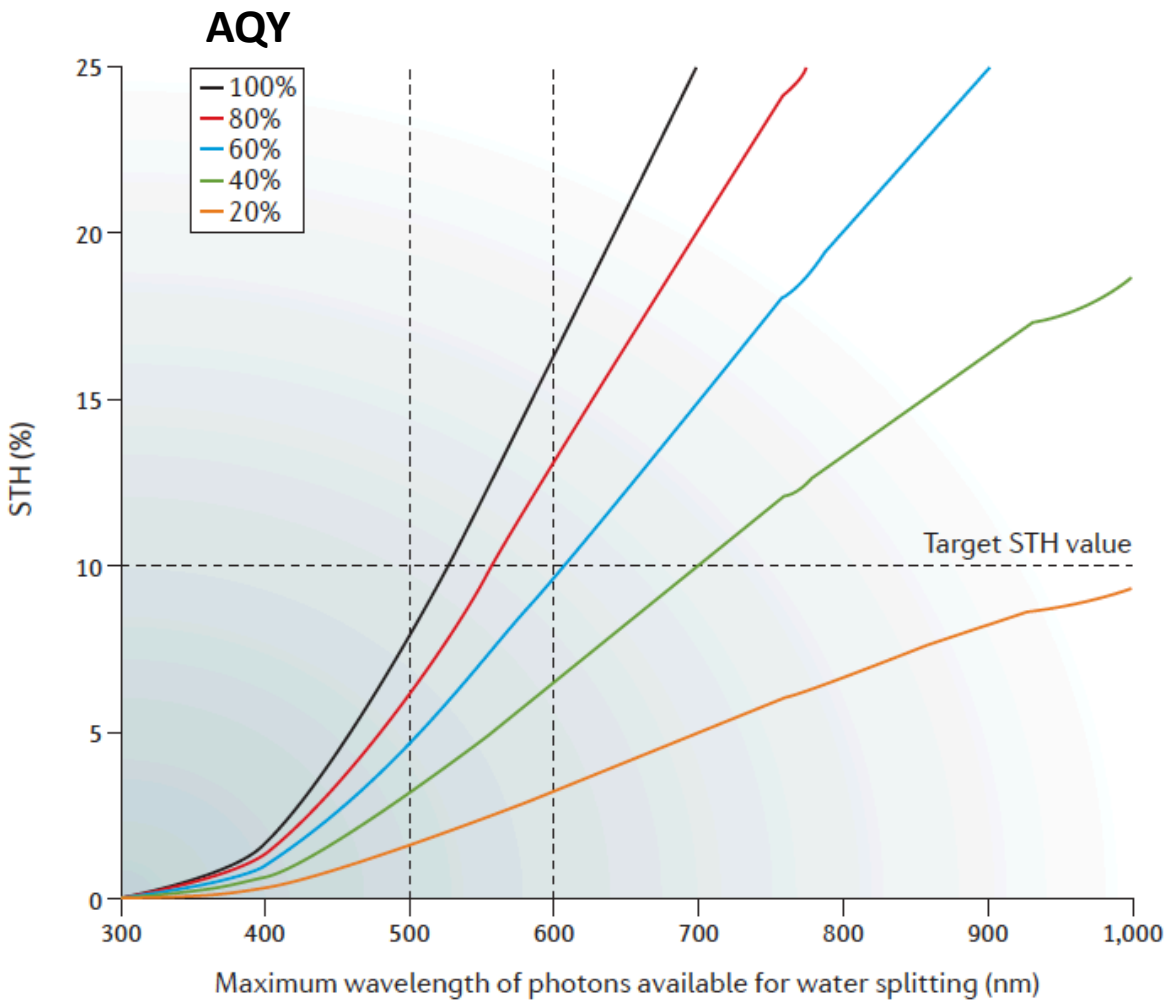
$$= \frac{\textit{number of reacted electrons}}{\textit{number of incidents photons}} \times 100\%$$

$$= \frac{2 \times \textit{number of evoluted } H_2 \textit{ molecules}}{\textit{number of incidents photons}} \times 100\%$$

$$= \frac{4 \times \textit{number of evoluted } O_2 \textit{ molecules}}{\textit{number of incidents photons}} \times 100\%$$

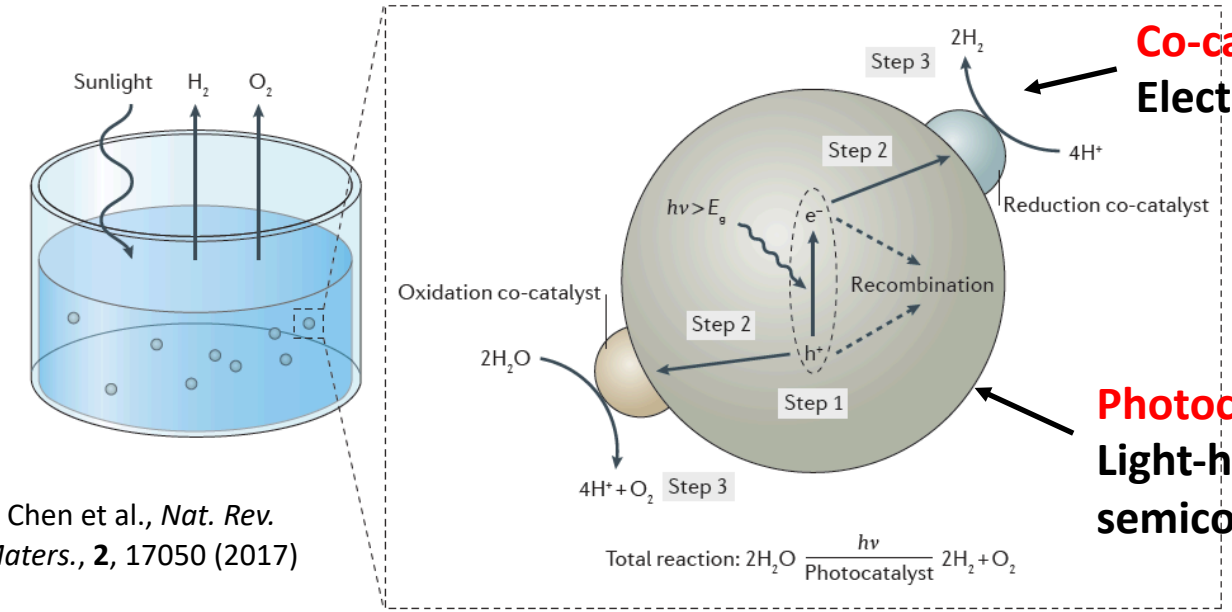


J. Liu et al., *Science*, **347**, 970 (2015)



S. Chen et al., *Nat. Rev. Maters.*, **2**, 17050 (2017)

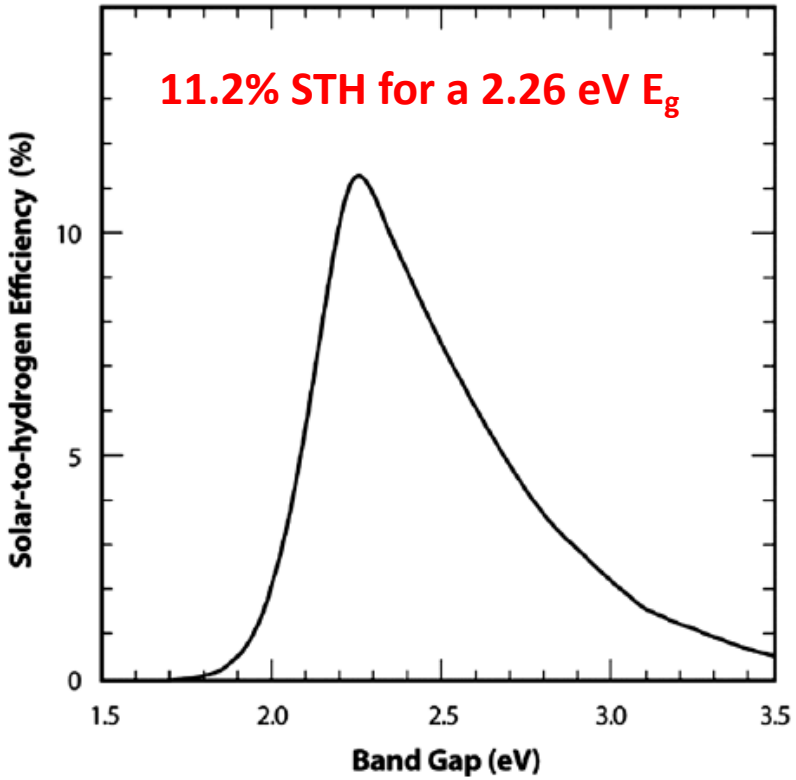
Single Absorber



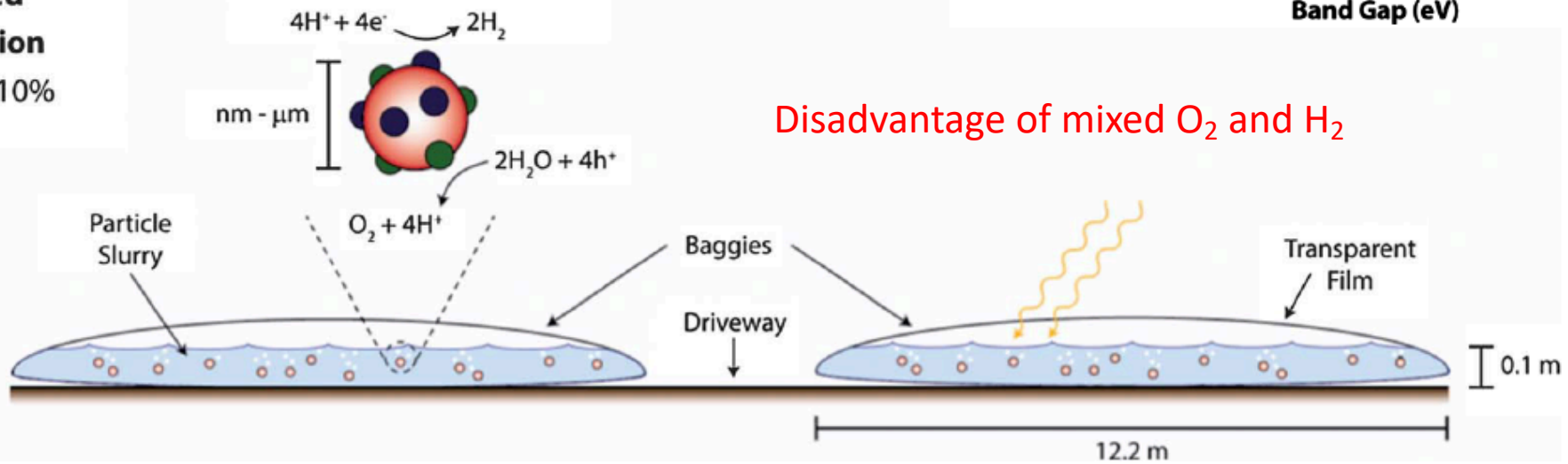
S. Chen et al., *Nat. Rev. Maters.*, **2**, 17050 (2017)

Co-catalyst:
Electrocatalysts

Photocatalyst:
Light-harvesting semiconductors



Type 1: Single Bed
Particle Suspension
STH Efficiency 10%



Disadvantage of mixed O_2 and H_2

B. A. Pinaud et al., *Energy Environ. Sci.*, **6**, 1983 (2013)

Examples of Single Absorber

Photocatalyst	Co-catalyst (HER, OER)	Bandgap, Absorption edge (nm)	Reactant solution	Efficiency	Durability (retention, %)
Al-doped $SrTiO_3$	Rh/Cr_2O_3, CoOOH (photodeposition)	3.2 eV, 390	H_2O	AQE = 96% at 350 – 360 nm STH = 0.51%	12.5 h (94)
C_3N_4	Carbon dots	2.8 eV, 450	H_2O	AQE = 16% at 420 nm STH = 2%	4800 h (98)
CoO	-	2.4 eV, 515	H_2O	**STH = 5%**	-
$Y_2Ti_2O_5S_2$	Ru/Cr_2O_3, IrO_2	1.9 eV, 650	H_2O	AQE = 0.36% at 420 nm AQE = 0.05% at 600 nm STH = 0.007%	20 h (81)

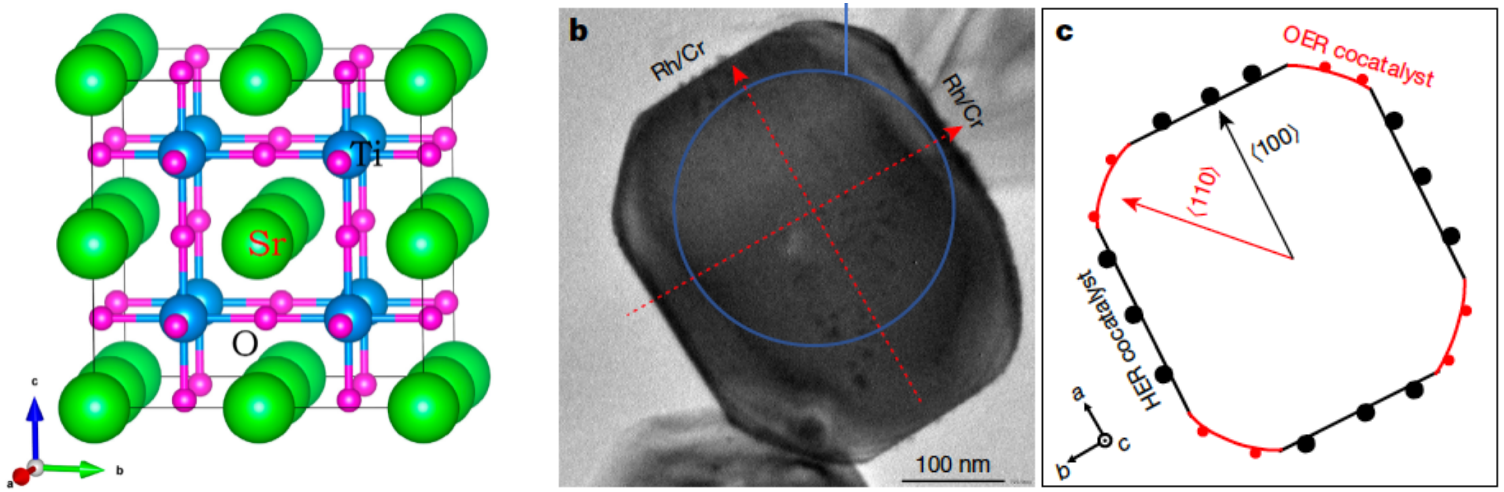
https://www.nature.com/articles/s41586-020-2278-9

https://www.science.org/doi/10.1126/science.aaa3145

https://www.nature.com/articles/nnano.2013.272

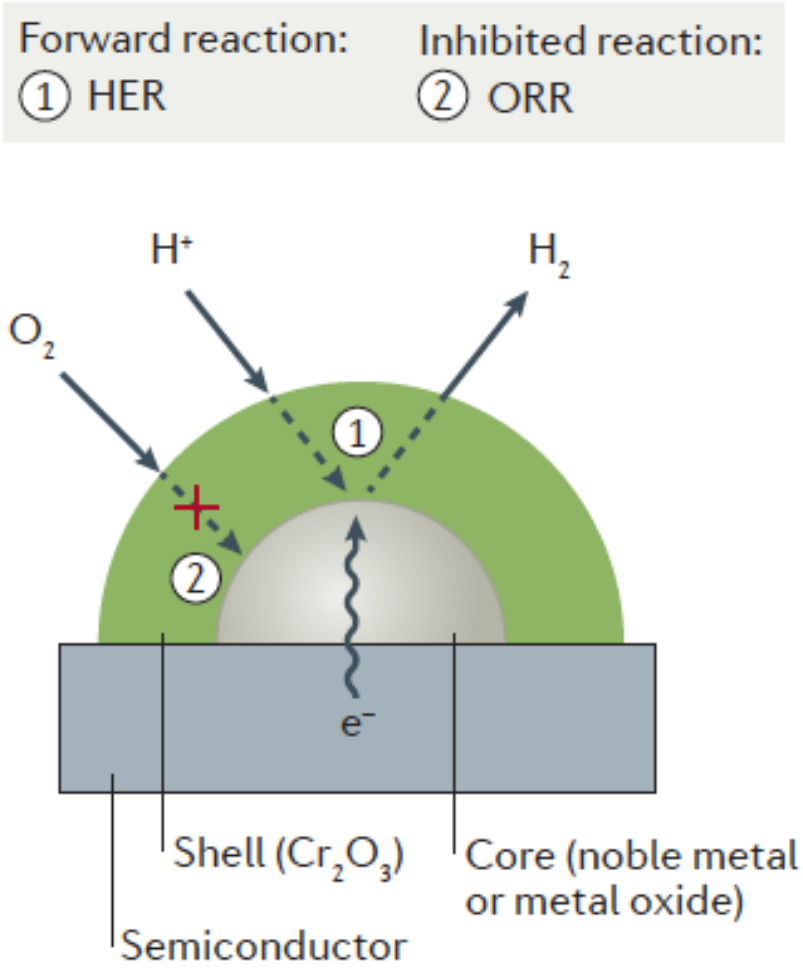
https://www.nature.com/articles/s41563-019-0399-z

Al doped $SrTiO_3$



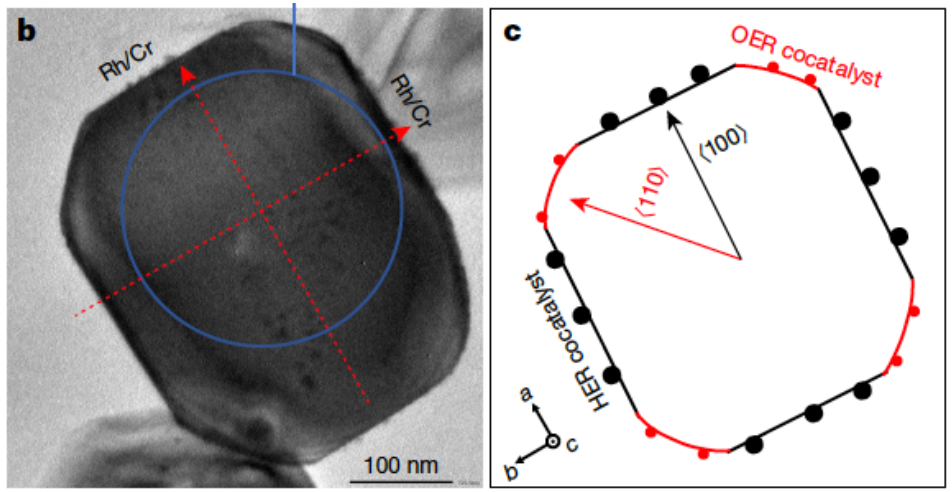
T. Takata et al., *Nature*, **581**, 411 (2020)

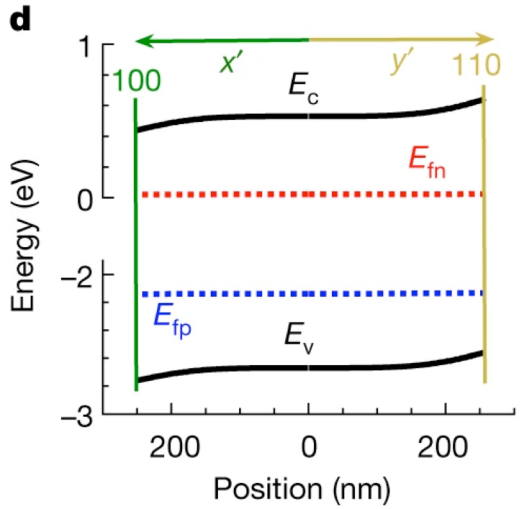
- The Rh promotes both the HER and the oxygen reduction reaction (ORR; a major backward electron transfer process).
- The Cr_2O_3 shell inhibits only the ORR by blocking the access of evolved O_2 to the surface of the Rh core.

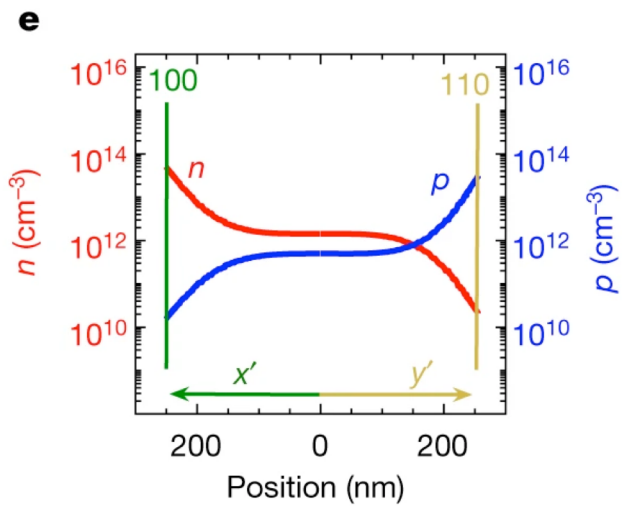


L. Maeda et al., *J. Phys. Chem. Lett.* **1**, 2655–2661 (2010)

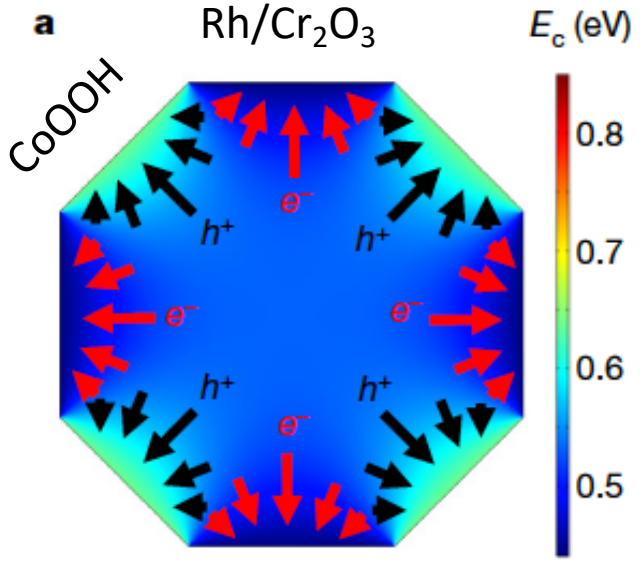
Al doped $SrTiO_3$





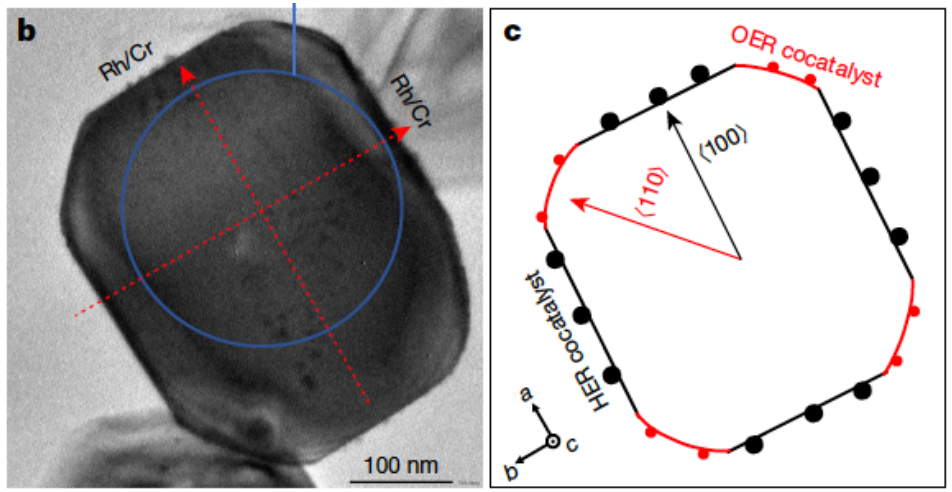


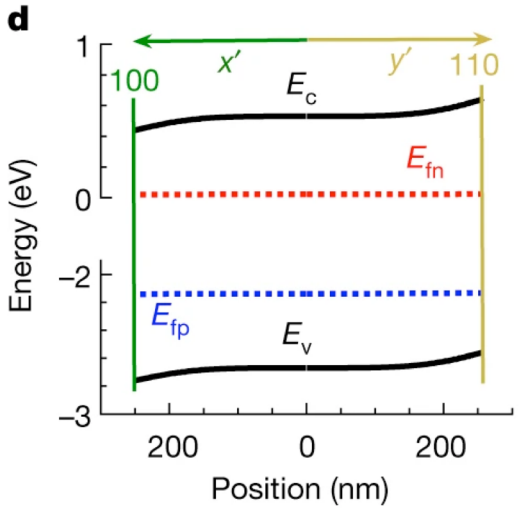
- A W_F difference of 0.2 eV between the {110} and {100} surfaces induce anisotropic charge separation, leading to HER Rh/Cr_2O_3 cocatalyst photodeposited on electron-attracting {100} facets and OER CoOOH photodeposition on {110} facets.

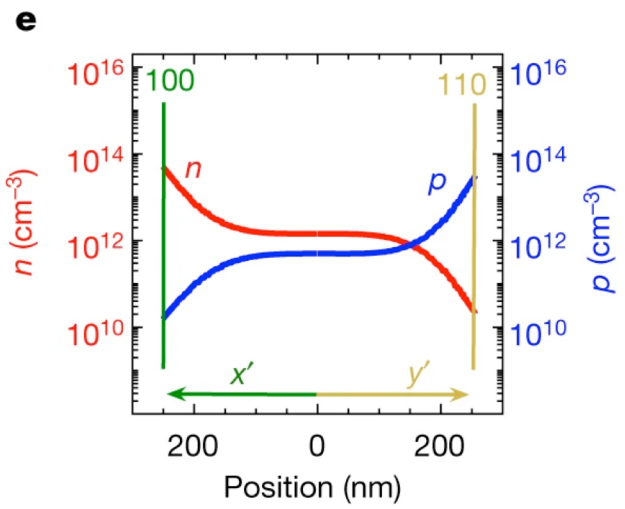


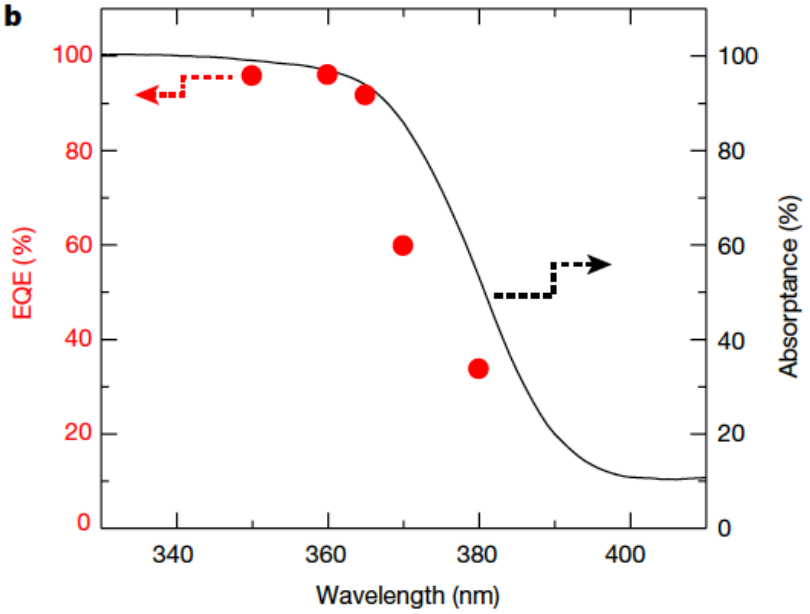
T. Takata et al., *Nature*, **581**, 411 (2020)

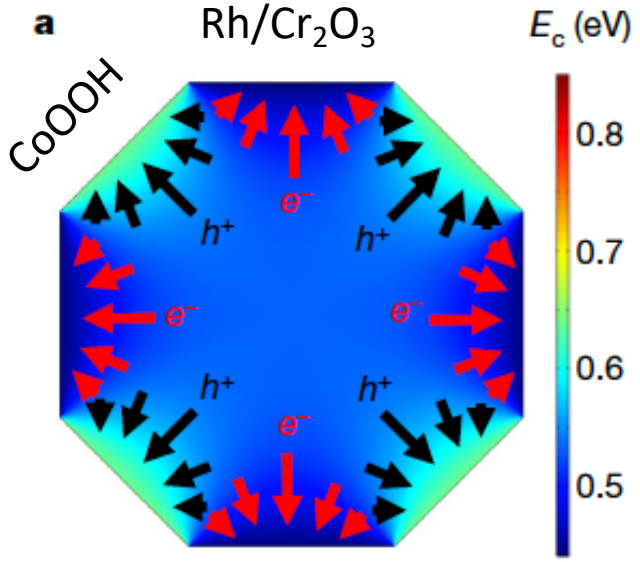
Al doped $SrTiO_3$



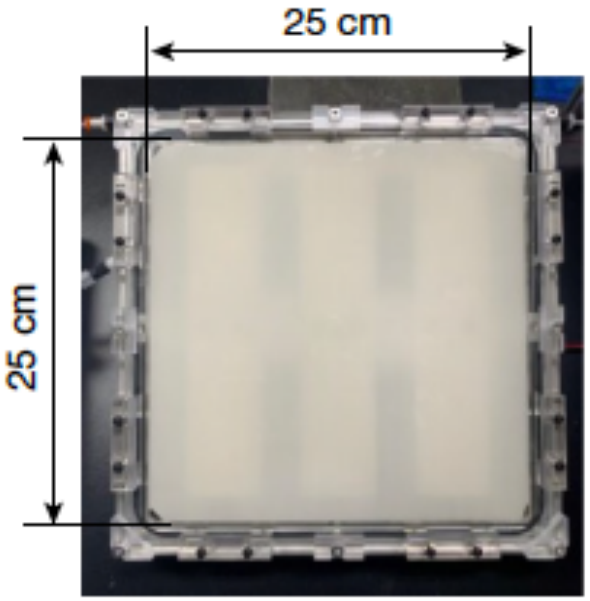


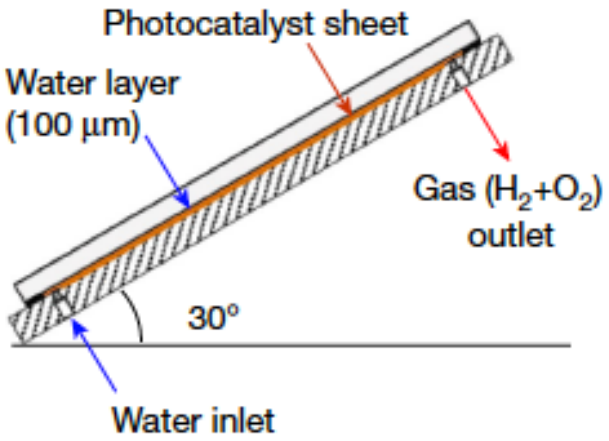






Al doped $SrTiO_3$



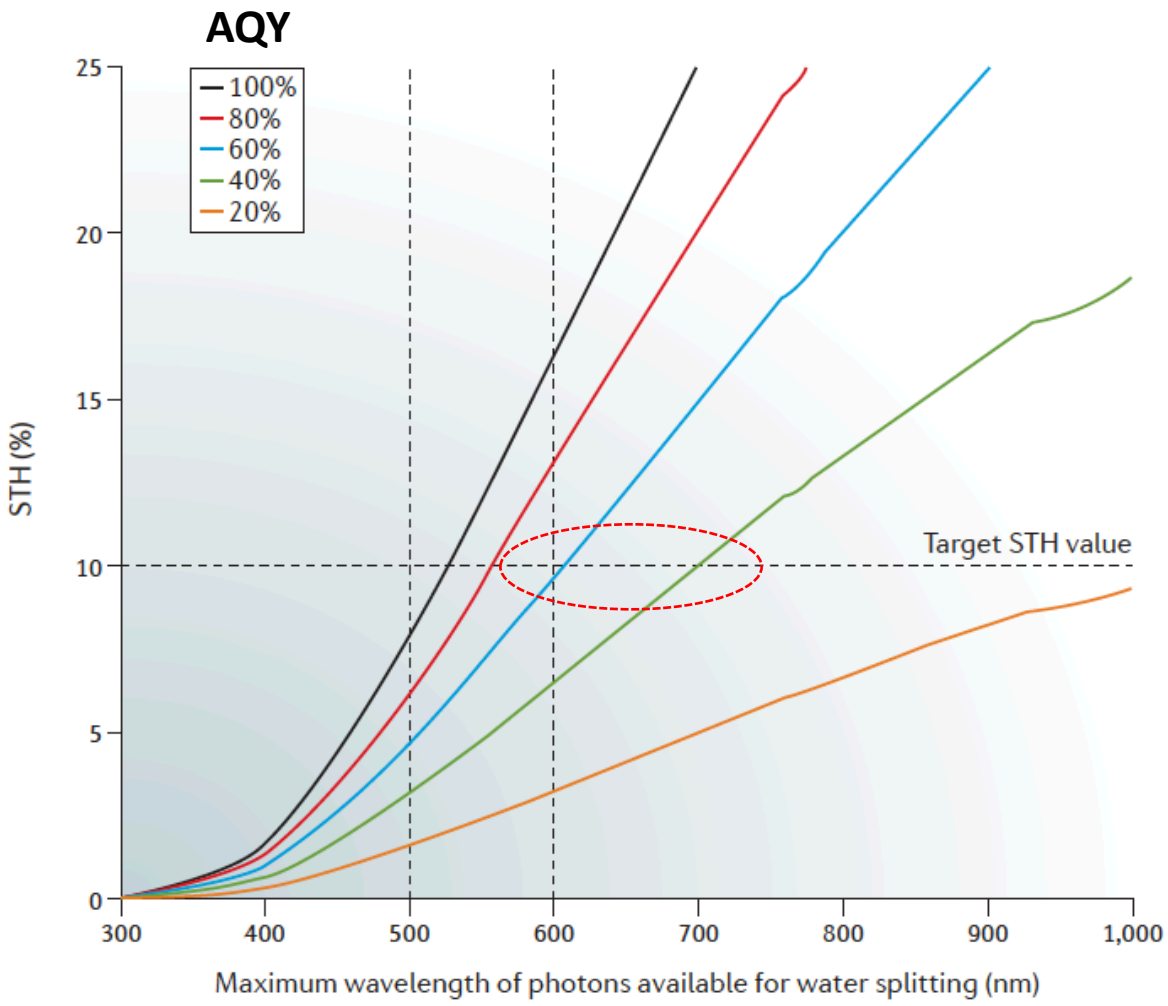


- **A 100-m^2 array of panel reactors over several months**
- **STH of 0.76 %**

Nishiyama, H., *et. al*. *Nature 598*, 304–307 (2021)

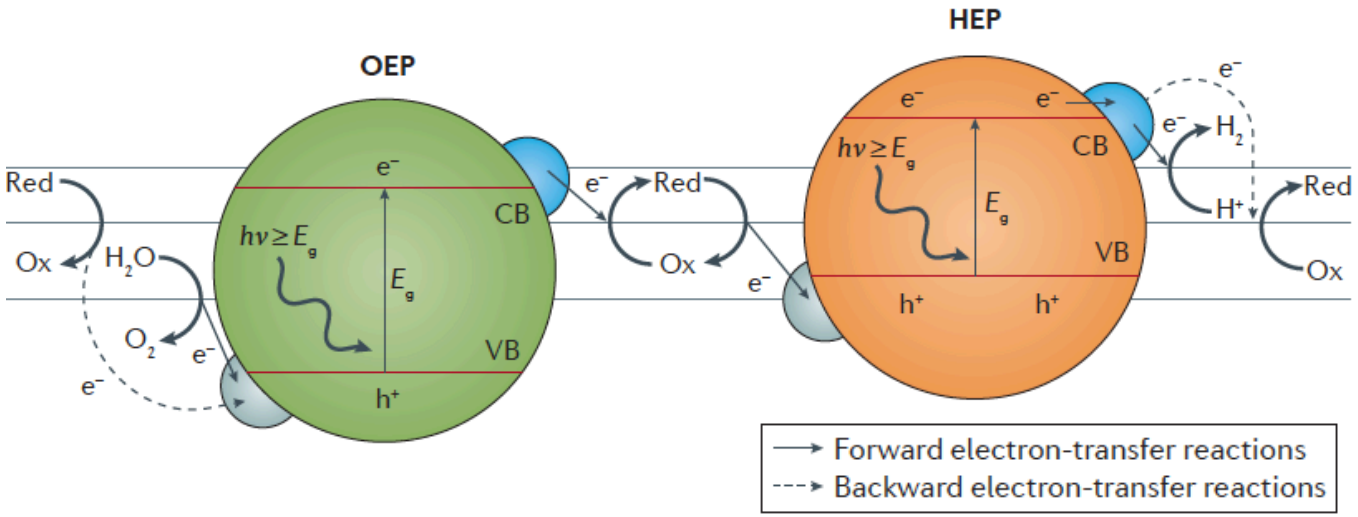
Perspectives

- Operable wavelength range up to 600 – 700 nm with an AQY 40 – 60 % should be developed.
- Co-catalyst/semiconductor, co-catalyst/solution, semiconductor/solution interfaces to maximize forward charge transfer.
- The use of rare and expensive elements should be eliminated.
- More advanced material designs are needed.

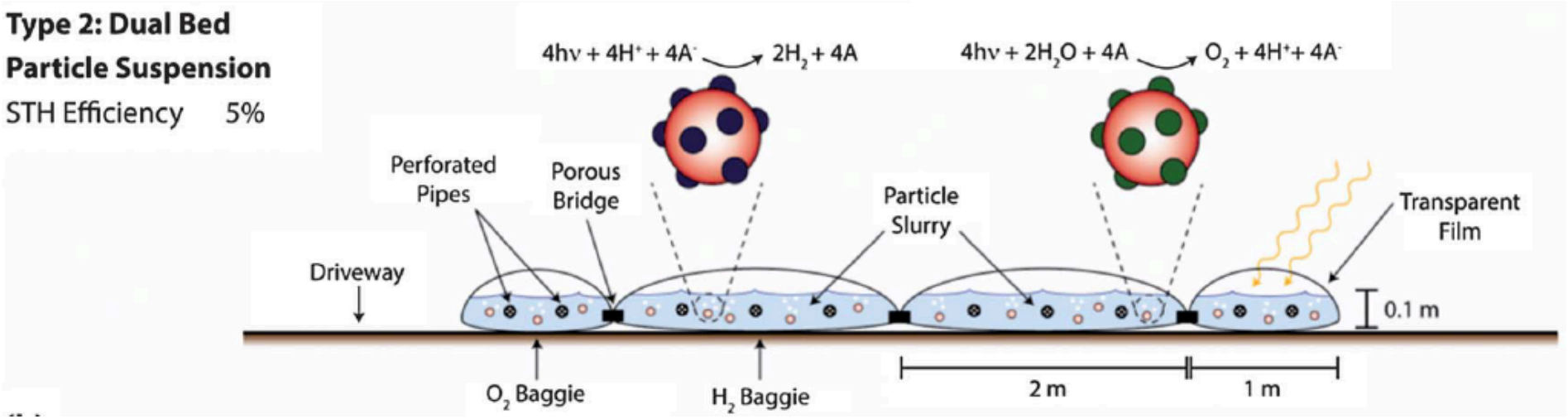


Jun-Ho YUM, junho.yum@epfl.ch

Dual Absorber for Z-scheme



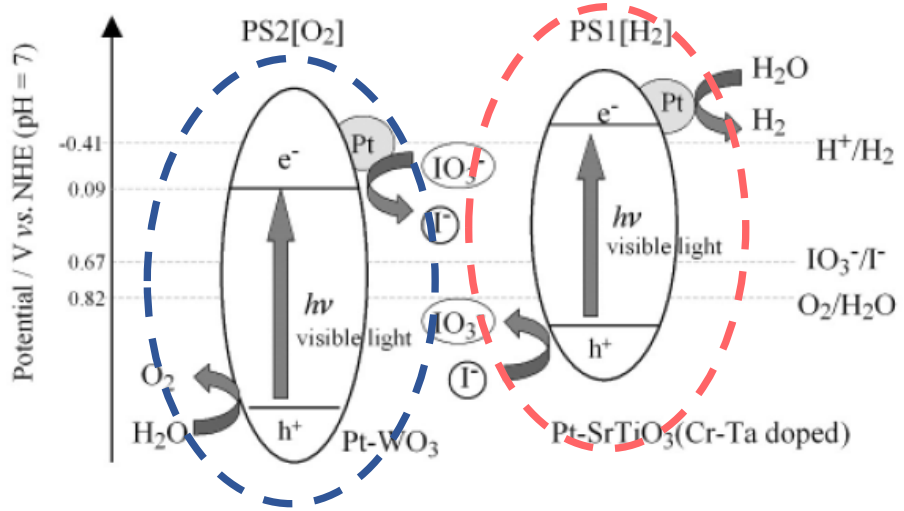
- The number of photons needed in a two-step PC is eight *vs* four in a one-step PC: A half amount of products
- Relaxation of the thermodynamic requirements: small bandgap
- Separation of O_2 and H_2
- Essential to suppress charge recombination and backward reaction



B. A. Pinaud et al., *Energy Environ. Sci.*, **6**, 1983 (2013)

Examples of Z-scheme

HEP	OEP	Electron mediator	Reactant solution	Efficiency
0.5 wt% $Pt/ZrO_2/TaON$ (< 500 nm)	0.5 wt% PtO_x/WO_3 (< 450nm)	IO_3^-/I^- (1.085 – 0.059 pH)	H_2O	AQY: 6.3% at 420 nm
1 wt% $Ru/SrTiO_3$:Rh (<520 nm)	$BiVO_4$ (<520 nm)	Fe^{3+}/Fe^{2+} (0.771 V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 4.2% at 420 nm, STH: 0.1%
$Rh_yCr_{2-y}O_3/ZrO_2/TaON$ (< 500 nm)	0.8 wt% Au/0.1 wt% $CoO_x/BiVO_4$ (<520 nm)	$Fe(CN)_6^{3-/4-}$ (0.358V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 10.3% at 420 nm, STH: 0.5%
$Ru/Cr_2O_3/SrTiO_3$:La,Rh (<520 nm)	$BiVO_4$ (<520 nm)	Au, Rh or Ni (solid mediator)	H_2O	**STH = 1.1%**



$6H^+ + 6e^- \rightarrow 3H_2$ (CB of Pt-$SrTiO_3$)

$I^- + 6h^+ + 6OH^- \rightarrow IO_3^- + 3H_2O$ (VB of Pt-$SrTiO_3$)

$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$ (CB of PtO_x-WO_3)

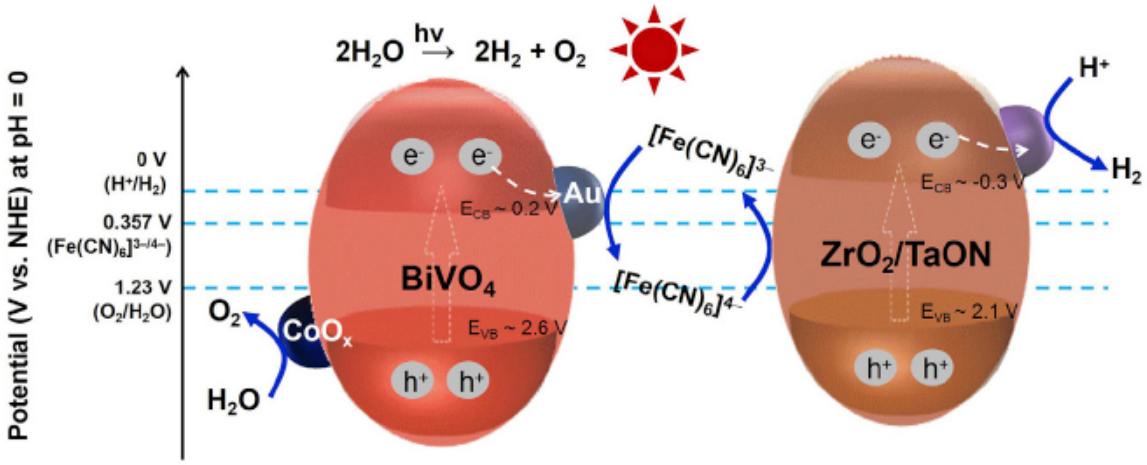
$6OH^- + 6h^+ \rightarrow {}^3/_2\, O_2 + 3H_2O$ (VB of PtO_x-WO_3)

- Jun-Ho YUM, junho.yum@epfl.ch

https://pubs.rsc.org/en/content/articlelanding/2001/cc/b107673f

Examples of Z-scheme

HEP	OEP	Electron mediator	Reactant solution	Efficiency
0.5 wt% $Pt/ZrO_2/TaON$ (< 500 nm)	0.5 wt% PtO_x/WO_3 (< 450nm)	IO_3^-/I^- (1.085 – 0.059 pH)	H_2O	AQY: 6.3% at 420 nm
1 wt% $Ru/SrTiO_3$:Rh (<520 nm)	$BiVO_4$ (<520 nm)	Fe^{3+}/Fe^{2+} (0.771 V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 4.2% at 420 nm, STH: 0.1%
$Rh_yCr_{2-y}O_3/ZrO_2/TaON$ (< 500 nm)	0.8 wt% Au/0.1 wt% $CoO_x/BiVO_4$ (<520 nm)	$Fe(CN)_6^{3-/4-}$ (0.358V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 10.3% at 420 nm, STH: 0.5%
$Ru/Cr_2O_3/SrTiO_3$:La,Rh (<520 nm)	$BiVO_4$ (<520 nm)	Au, Rh or Ni (solid mediator)	H_2O	**STH = 1.1%**



$4H^+ + 4e^- \rightarrow 2H_2$ (CB of ZrO_2/TaON)

$4[Fe(CN)_6]^{4-} + 4h^+ \rightarrow 4[Fe(CN)_6]^{3-}$ (VB of ZrO_2/TaON)

$4[Fe(CN)_6]^{3-} + 4e^- \rightarrow 4[Fe(CN)_6]^{4-}$(CB of $BiVO_4$)

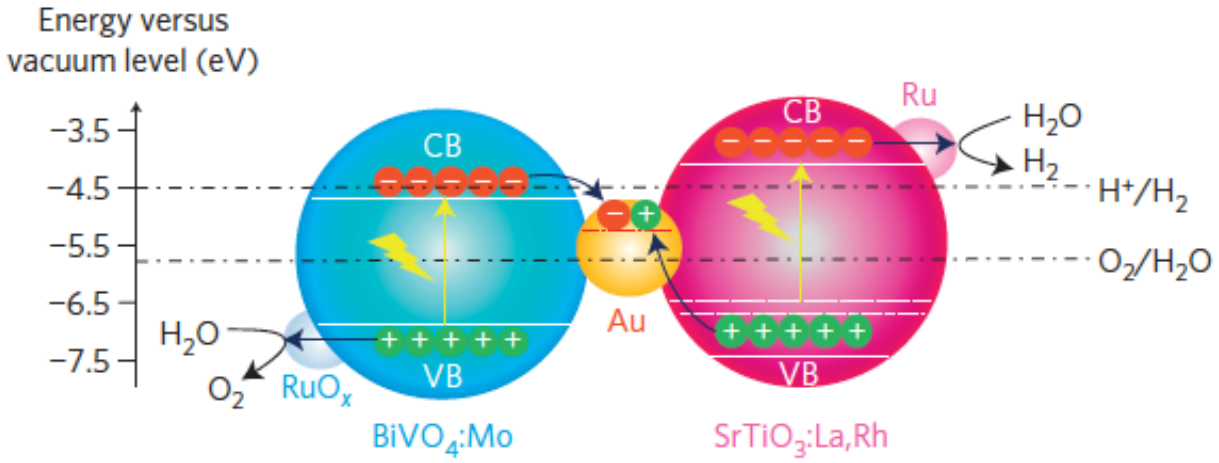
$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$(VB of $BiVO_4$)

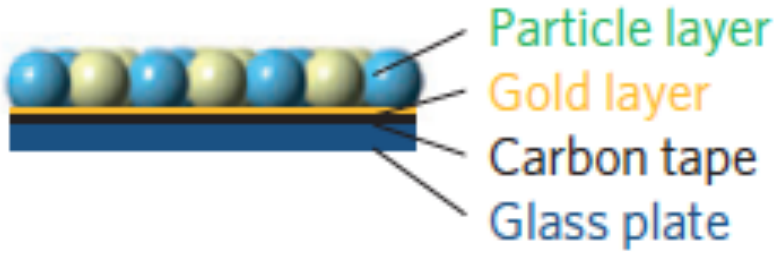
- Jun-Ho YUM, junho.yum@epfl.ch

https://www.sciencedirect.com/science/article/pii/S2542435118303404?via%3Dihub

Examples of Z-scheme

HEP	OEP	Electron mediator	Reactant solution	Efficiency
0.5 wt% $Pt/ZrO_2/TaON$ (< 500 nm)	0.5 wt% PtO_x/WO_3 (< 450nm)	IO_3^-/I^- (1.085 – 0.059 pH)	H_2O	AQY: 6.3% at 420 nm
1 wt% $Ru/SrTiO_3$:Rh (<520 nm)	$BiVO_4$ (<520 nm)	Fe^{3+}/Fe^{2+} (0.771 V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 4.2% at 420 nm, STH: 0.1%
$Rh_yCr_{2-y}O_3/ZrO_2/TaON$ (< 500 nm)	0.8 wt% Au/0.1 wt% $CoO_x/BiVO_4$ (<520 nm)	$Fe(CN)_6^{3-/4-}$ (0.358V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 10.3% at 420 nm, STH: 0.5%
$Ru/Cr_2O_3/SrTiO_3$:La,Rh (<520 nm)	$BiVO_4$ (<520 nm)	Au, Rh or Ni (solid mediator)	H_2O	**STH = 1.1%**





https://www.nature.com/articles/nmat4589

Examples of Z-scheme

HEP	OEP	Electron mediator	Reactant solution	Efficiency
0.5 wt% $Pt/ZrO_2/TaON$ (< 500 nm)	0.5 wt% PtO_x/WO_3 (< 450nm)	IO_3^-/I^- (1.085 – 0.059 pH)	H_2O	AQY: 6.3% at 420 nm
1 wt% $Ru/SrTiO_3$:Rh (<520 nm)	$BiVO_4$ (<520 nm)	Fe^{3+}/Fe^{2+} (0.771 V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 4.2% at 420 nm, STH: 0.1%
$Rh_yCr_{2-y}O_3/ZrO_2/TaON$ (< 500 nm)	0.8 wt% Au/0.1 wt% $CoO_x/BiVO_4$ (<520 nm)	$Fe(CN)_6^{3-/4-}$ (0.358V *vs* NHE)	H_2O (pH = 2.4, H_2SO_4 mediated)	AQY: 10.3% at 420 nm, STH: 0.5%
$Ru/Cr_2O_3/SrTiO_3$:La,Rh (<520 nm)	$BiVO_4$ (<520 nm)	Au, Rh or Ni (solid mediator)	H_2O	**STH = 1.1%**

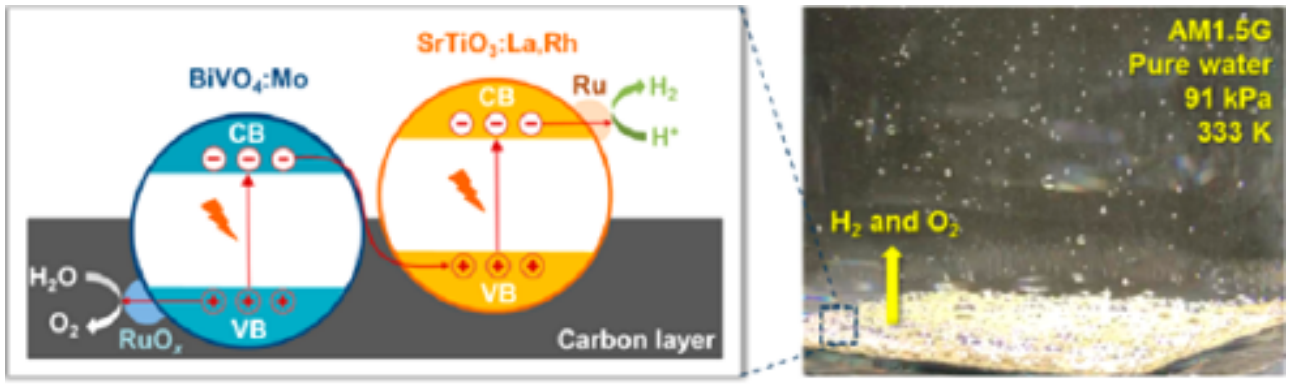
https://pubs.rsc.org/en/content/articlelanding/2001/cc/b107673f

https://pubs.rsc.org/en/content/articlelanding/2013/ta/c3ta12803b

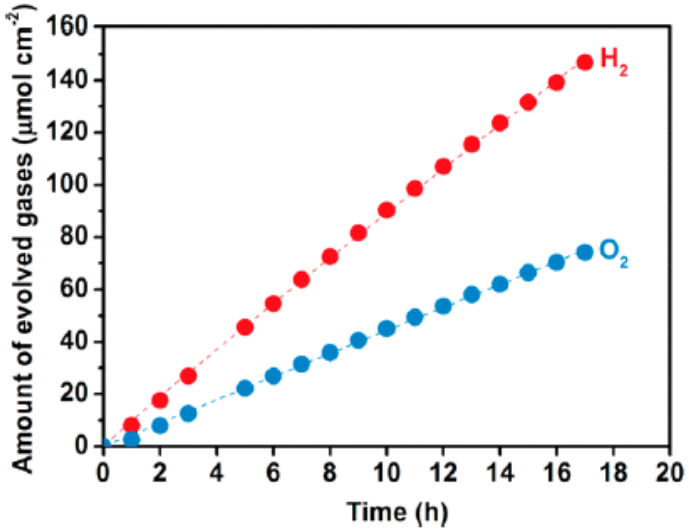
https://www.sciencedirect.com/science/article/pii/S2542435118303404?via%3Dihub

https://www.nature.com/articles/nmat4589

Z-scheme Particulate PC Sheets on Carbon Conductive Layer

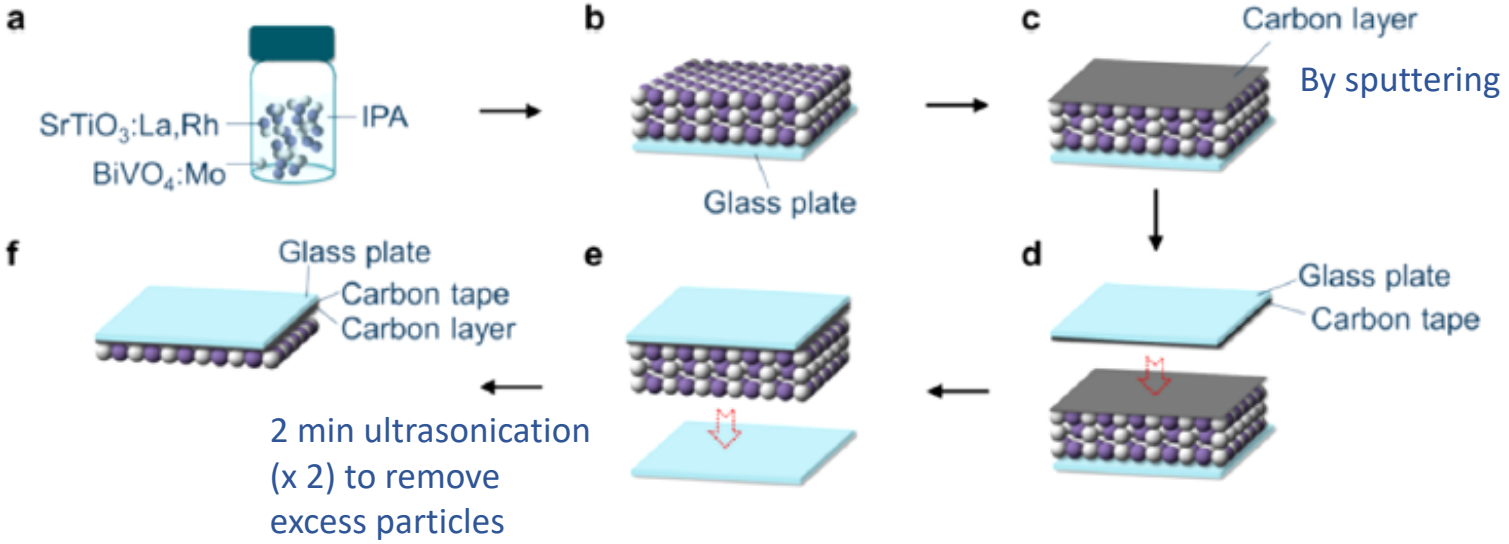


$SrTiO_3$:La,Rh/C/$BiVO_4$:Mo sheet



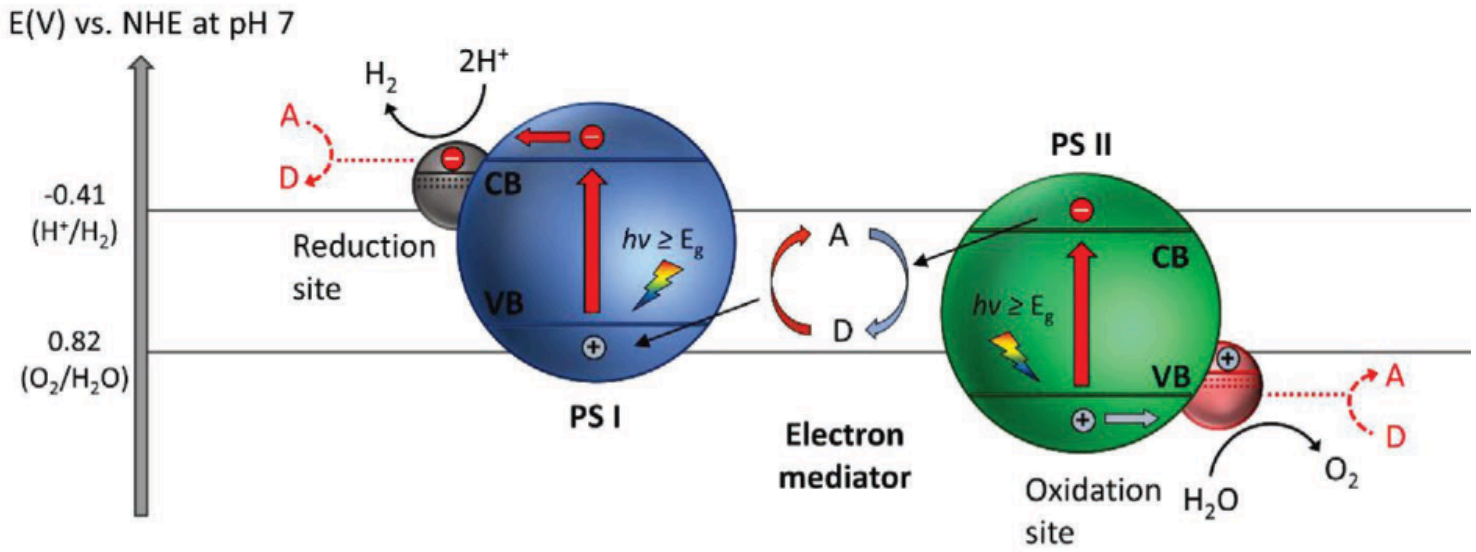
Carbon is less active than gold for oxygen reduction reaction (ORR)

STH efficiency = 1 %



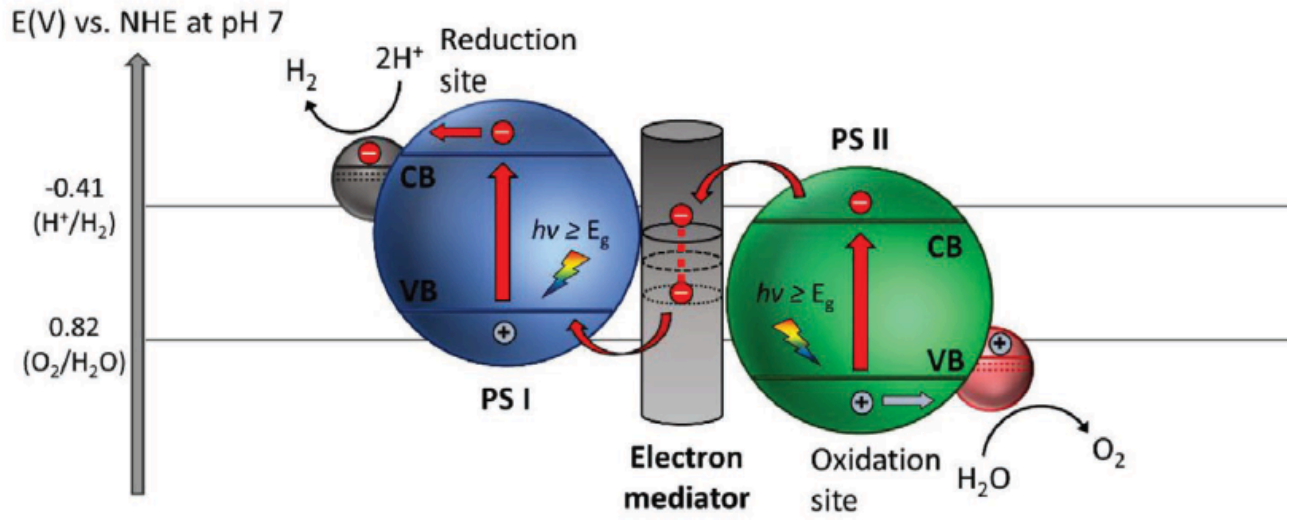
Q. Wang et al., *J. Am. Chem. Soc.* **139**, 1675−1683 (2017)

Key Issues of Different Dual Z-scheme Modes (with Redox Mediator)



- Strong pH dependency:
  – IO_3^-/I^- can only function at pH more than 9 due to the formation of inactive I_3^- at lower pH value.
  – Fe^{3+}/Fe^{2+} is only stable at pH lower than 2.5 due to the precipitation of $Fe(OH)_3$ at higher pH value.
- Light shielding effect by redox mediator, i.e., strong absorption up to 450 nm by aqueous Fe^{3+}.
- Backward reaction due to back donation of charge carriers (red dotted lines).
- PS I (HEP) and II (OEP) with suitable reduction and oxidation abilities are required to drive redox reaction of redox pairs.
- Question about scalability because only applicable in liquid form due to the ionic nature of redox pairs.

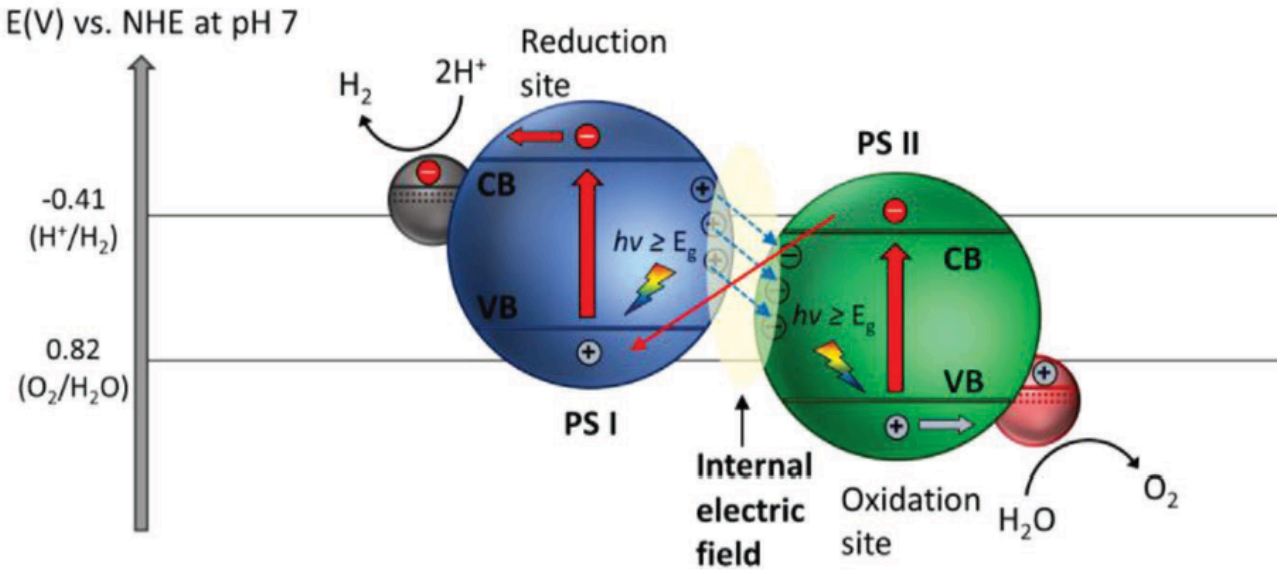
Key Issues of Different Dual Z-scheme Modes (with Solid State Mediator)



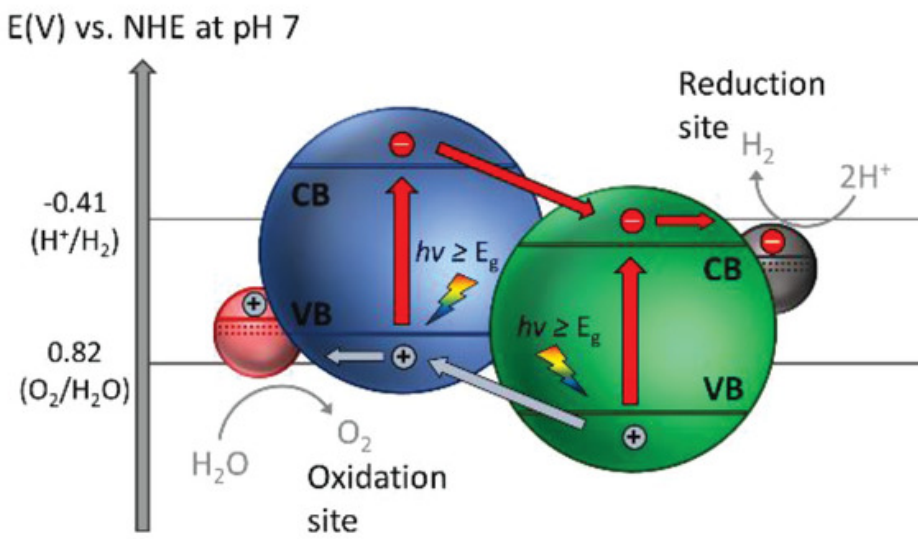
- Constraints in the development of PS-C-PS: The PS and electron mediator have to be assembled in a single unit.
- Suitable fabrication methods are essential for the development of these systems to ensure intimate contact interface between PS and electron mediator.
- Costly electron mediator: metals or nanocarbons.

Key Issues of Different Dual Z-scheme Modes (Direct Contact)

Z-scheme with direct contact



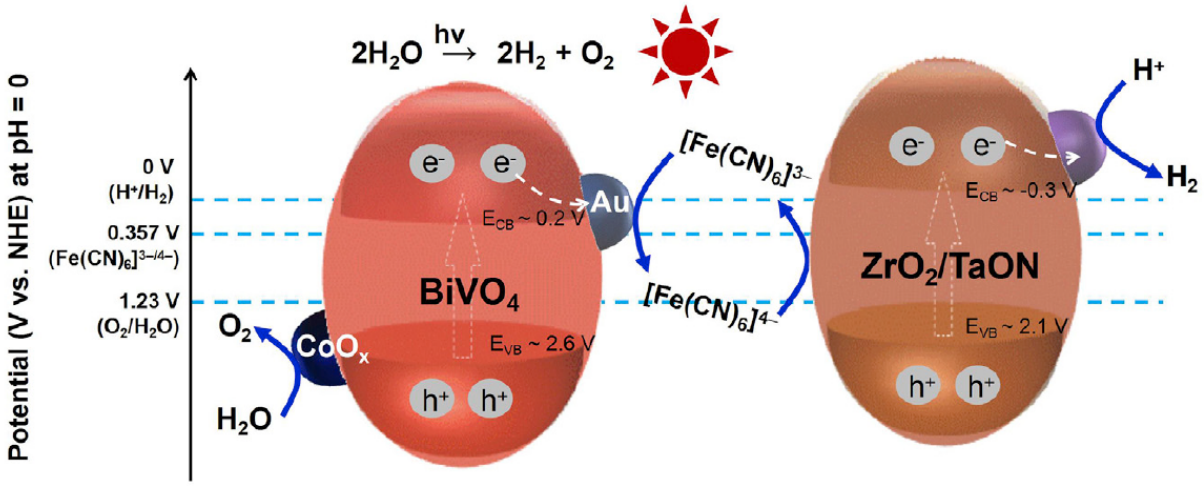
Type-II Heterojunction PC



- Electron transfer from PS I to PS II will be negligible due to electric field formed by accumulated charges at the interface (not to form the Type II heterojunction).
- Formation of internal electric field (blue dashed line) is highly dependent on the nature of PS I and PS II, i.e., PS I with higher Fermi level than PS II.
- Less efficient electron transfer than PS-C-PS system due to the absence of conductor as electron mediator.
- Formation of low resistance interface is critical.

State-of-the-Art PC Materials

Performance is limited with inorganic photocatalysts



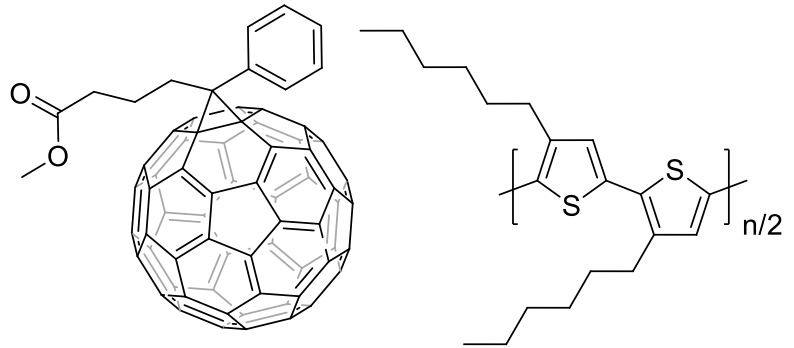
Oxygen Evolving Photocatalyst (OEP)

Hydrogen Evolving Photocatalyst (HEP)

Insufficient STH conversion efficiency < 1%
Due to poor photogenerated charge separation
Hard to tune optoelectronic properties

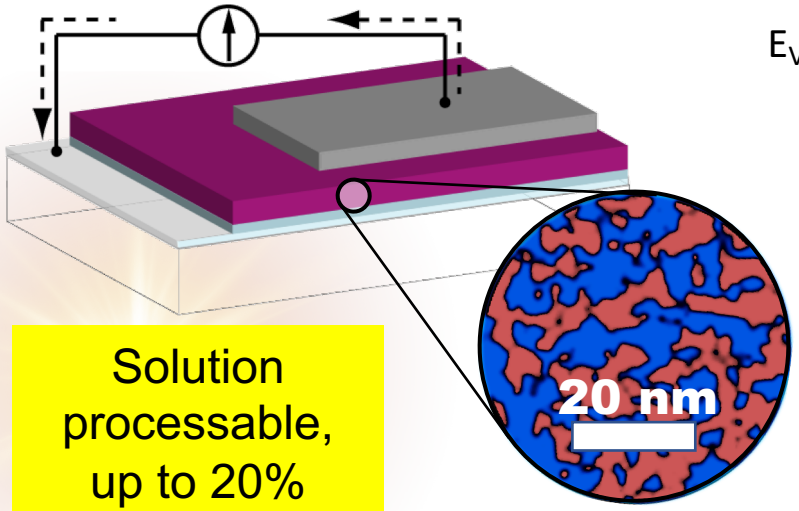
Y. Qi et al., *Joule,* 2, 2393 (2018)

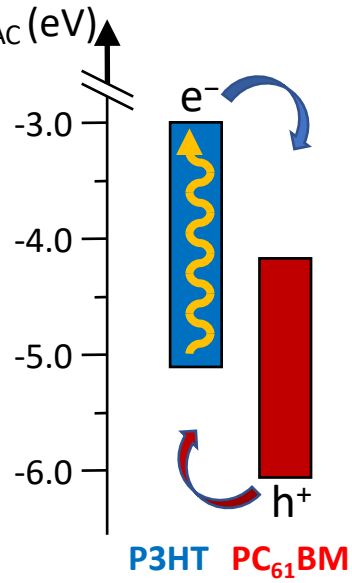
Organic semiconductor bulk heterojunction (BHJ)



$PC_{61}BM$ (Acceptor)

P3HT (Donor)





Solution processable, up to 20% photovoltaic efficiency

Bulk-Heterojunction (BHJ) Organic Photocatalysts

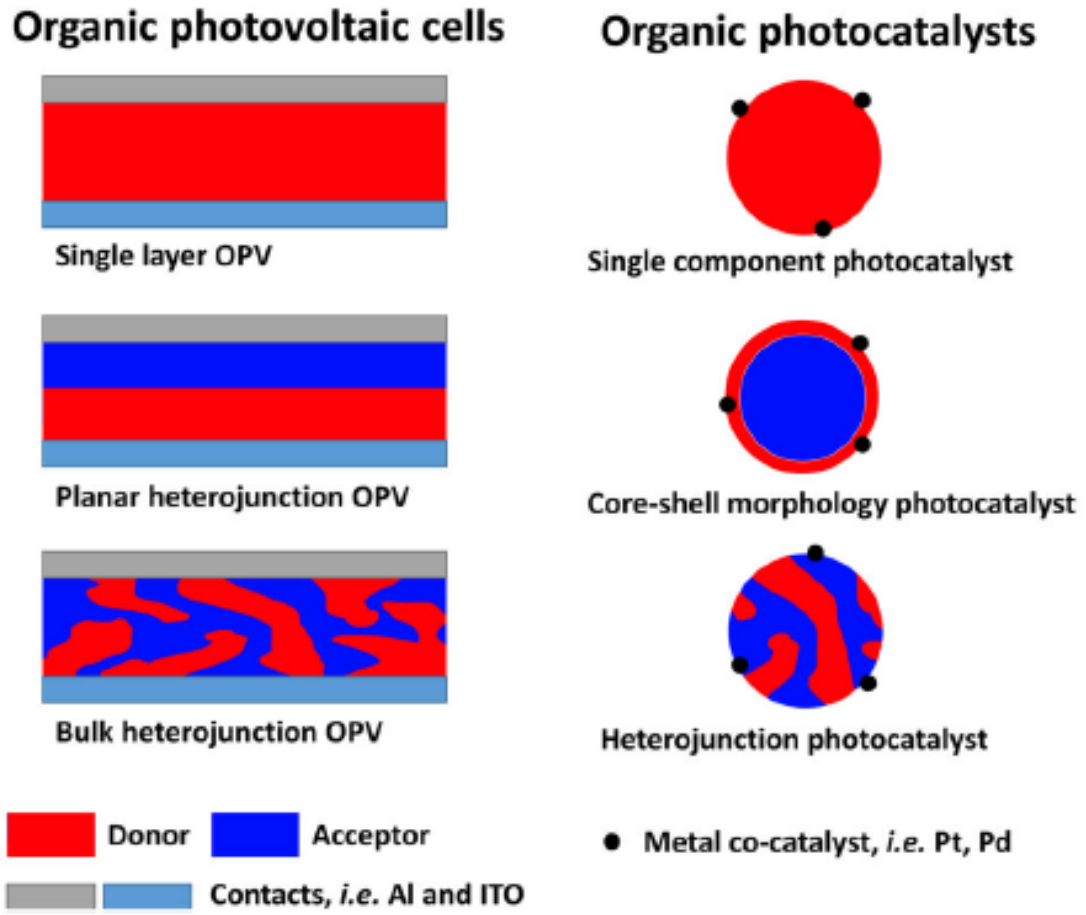
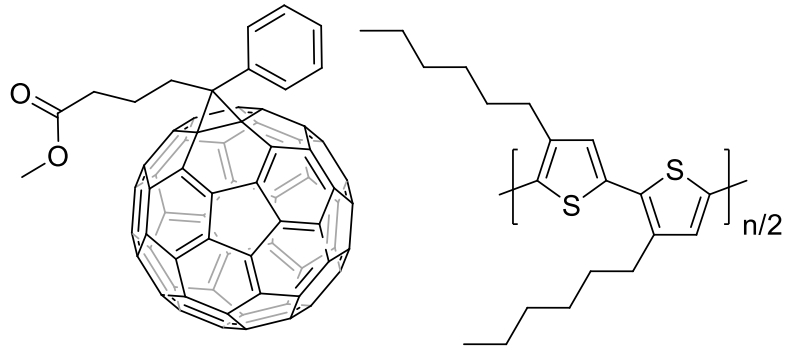
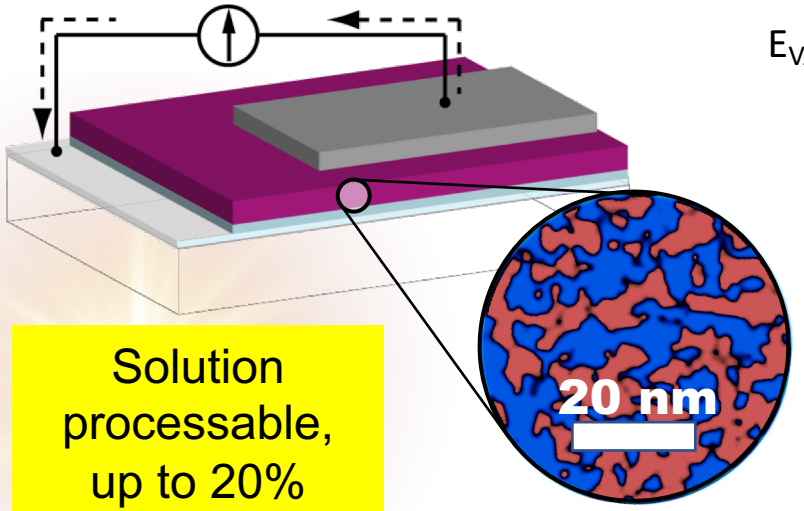


Image taken from R.S. Sprick et al., Commun Chem 3, 40 (2020)

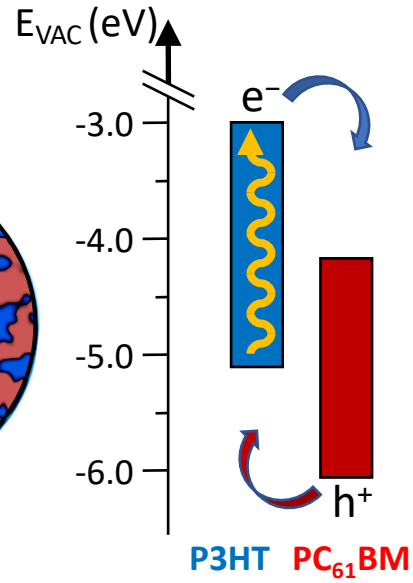
Organic semiconductor bulk heterojunction (BHJ)



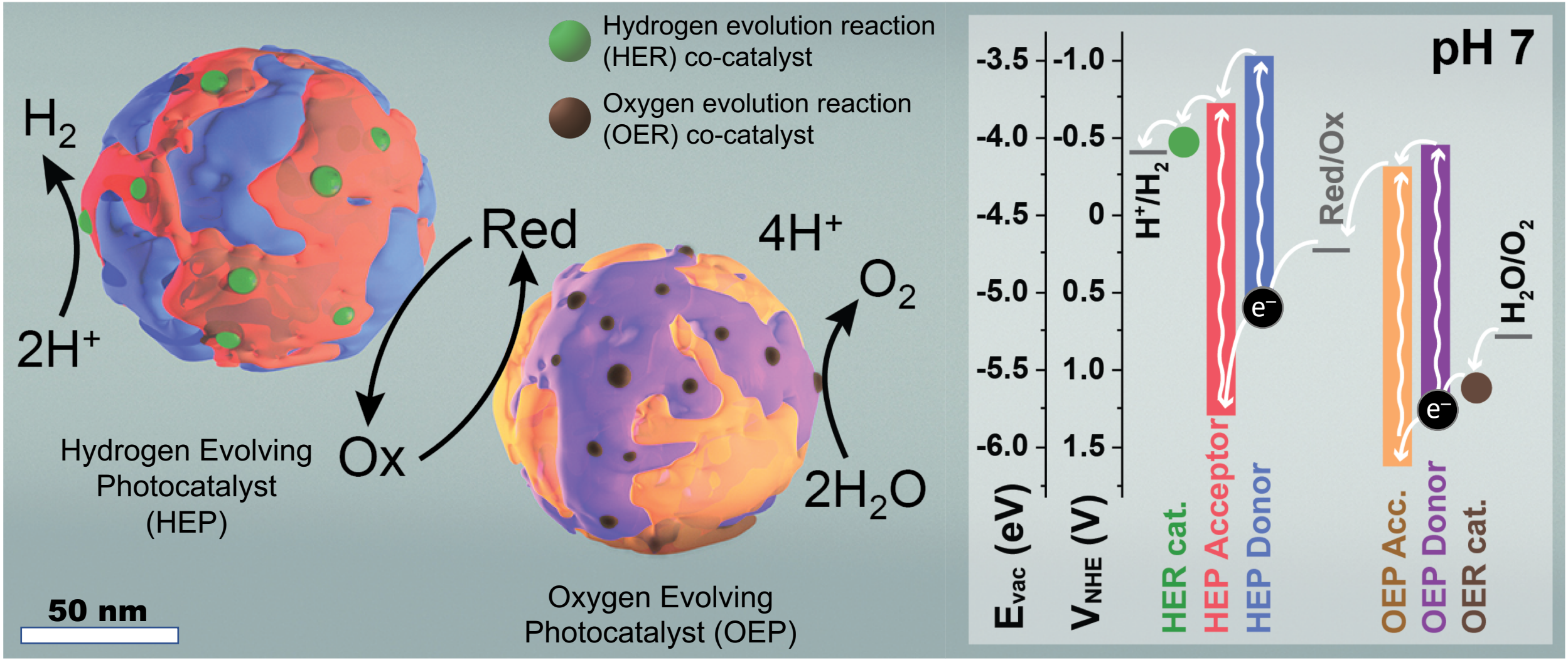
$PC_{61}BM$ (Acceptor) P3HT (Donor)



Solution processable, up to 20% photovoltaic efficiency

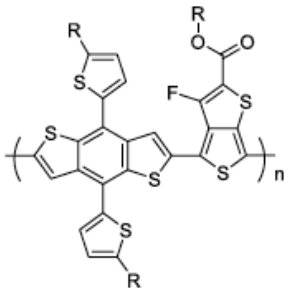


Bulk-Heterojunction (BHJ) Organic Photocatalysts

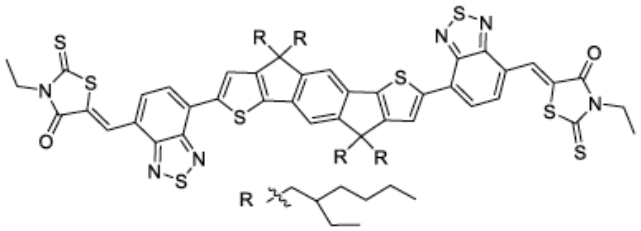


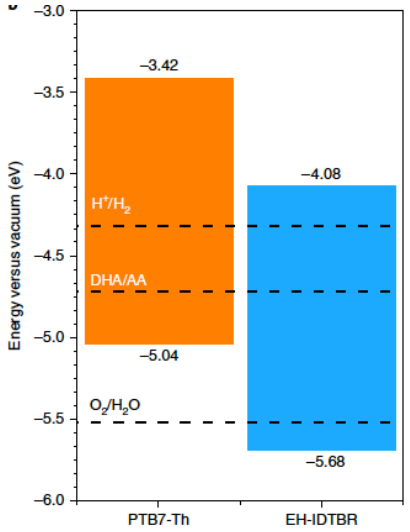
Bulk-Heterojunction (BHJ) HER Organic Photocatalysts

PTB7-Th

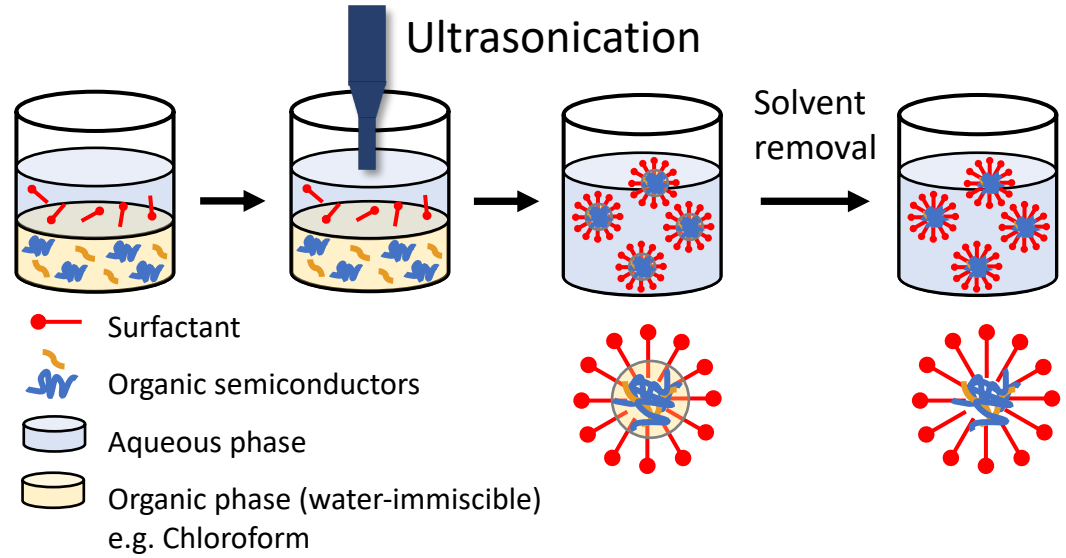


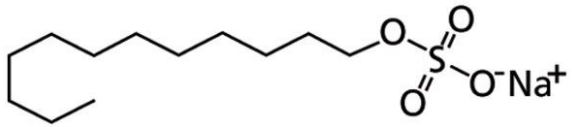
EH-IDTBR



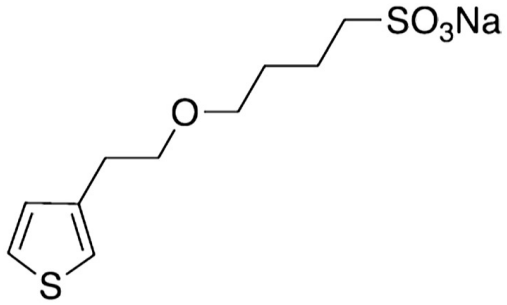


Miniemulsion method





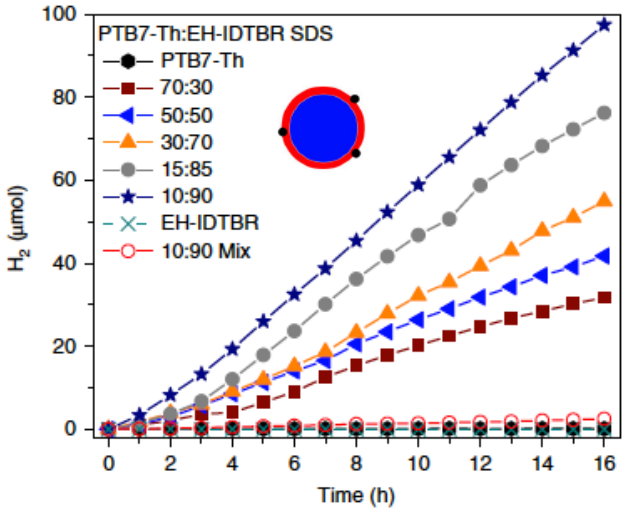
SDS: sodium dodecyl sulfate

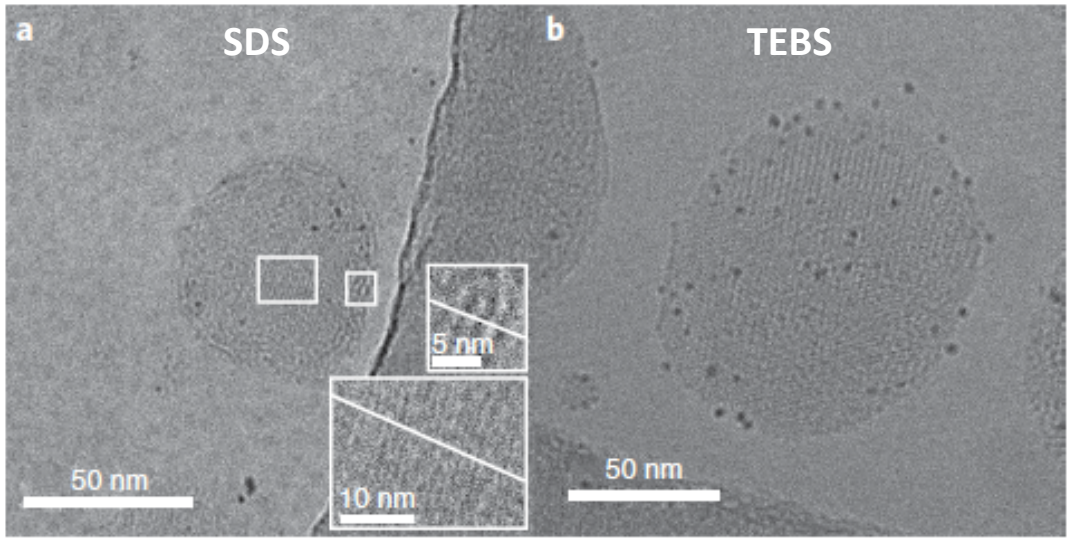


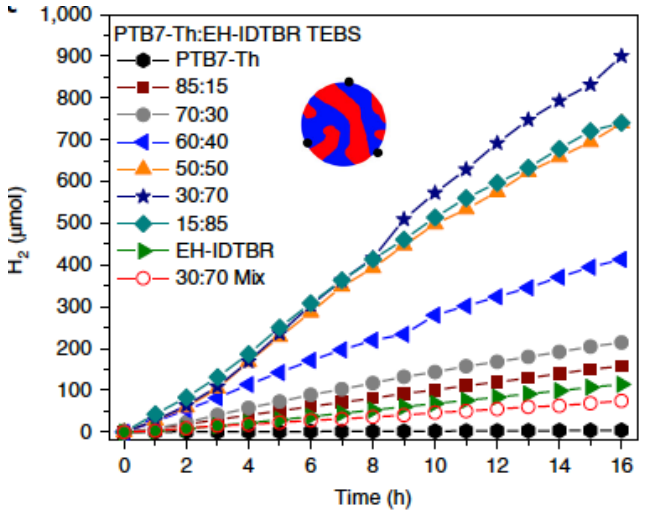
TEBS: 2-(3-thienyl)ethyloxybutylsulfonate sodium salt

J. Kosco et al., *Nat. Mater.* **19**, 559–565 (2020)

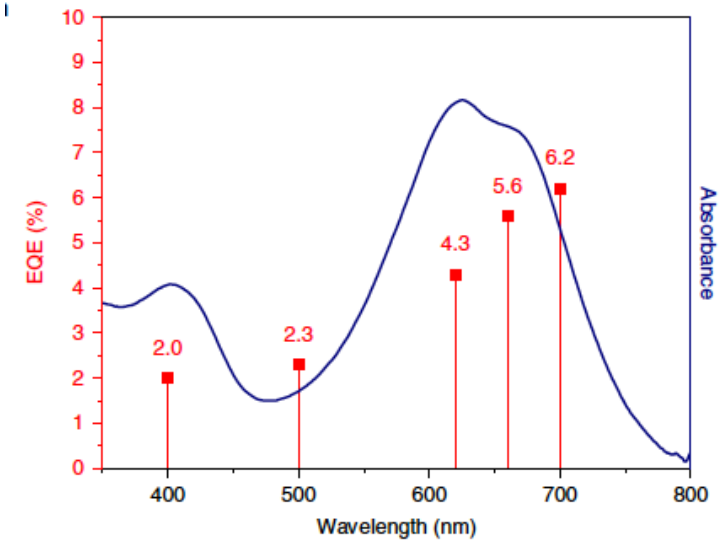
Bulk-Heterojunction (BHJ) HER Organic Photocatalysts

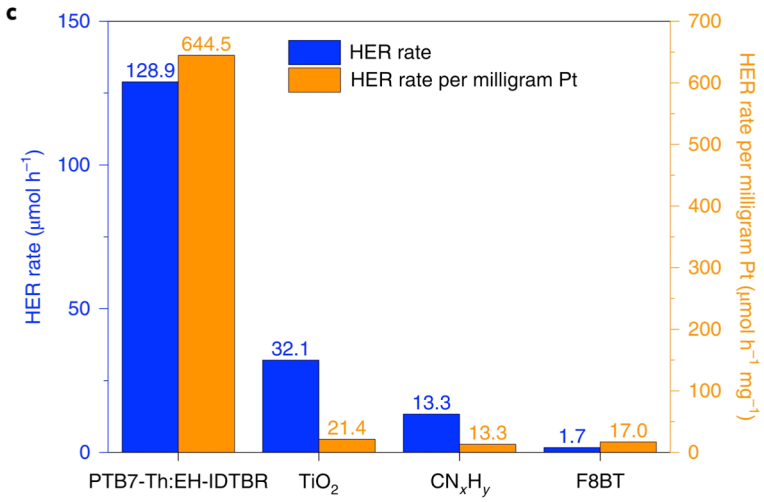






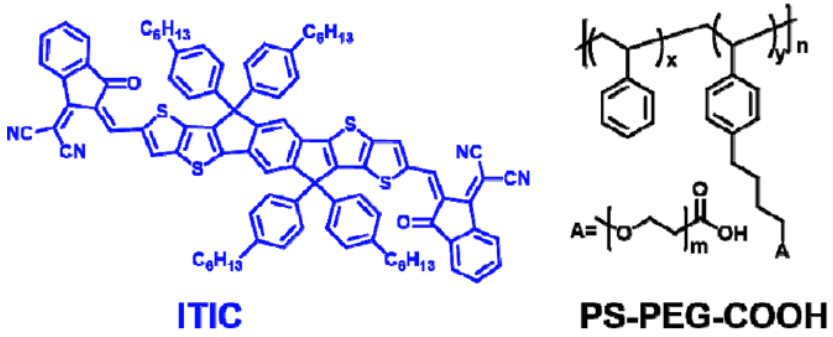
a PTB7-Th-rich shell and an EH-IDTBR-rich core



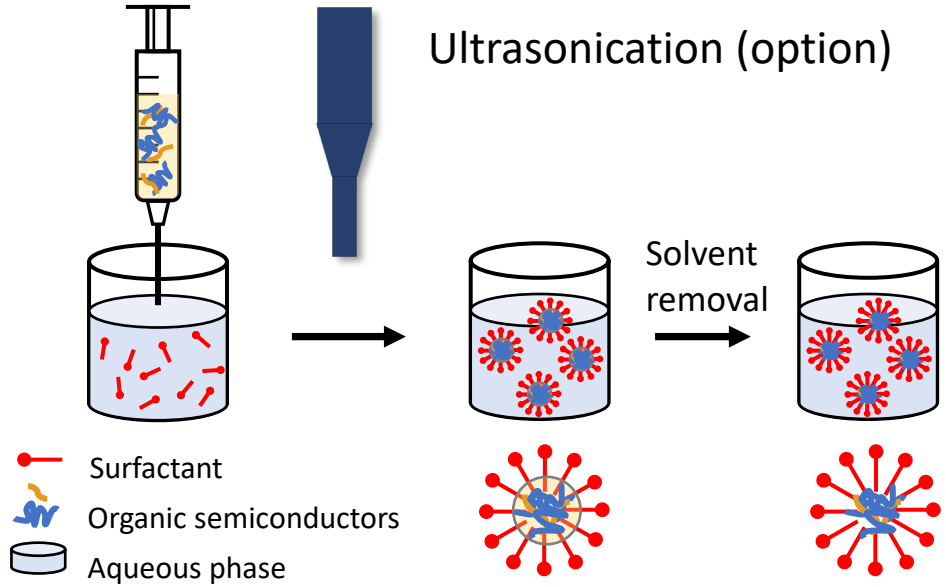


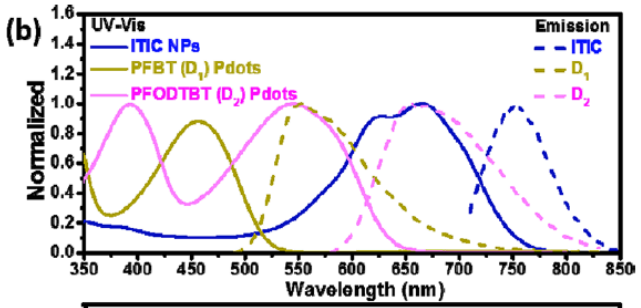
J. Kosco et al., *Nat. Mater.* **19**, 559–565 (2020)

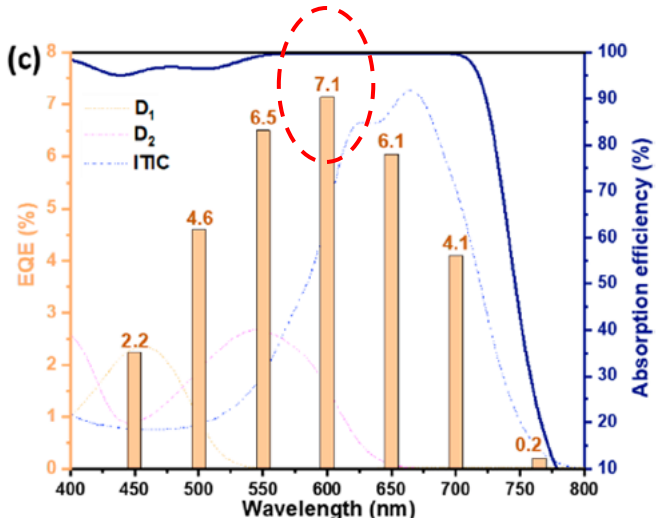
Bulk-Heterojunction (BHJ) HER Organic Photocatalysts

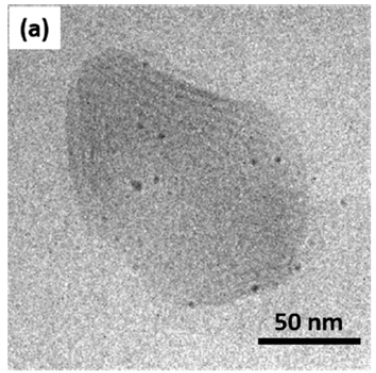


Nanoprecipitation method





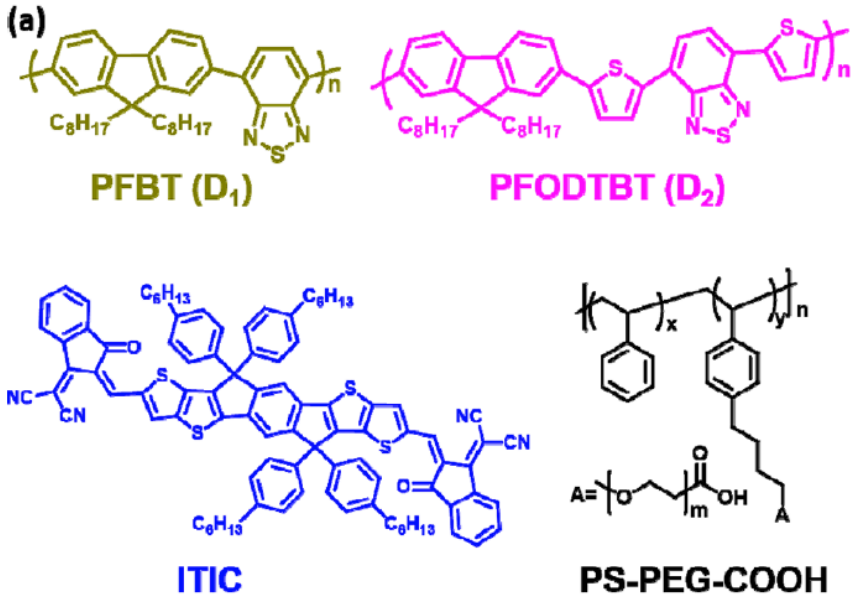


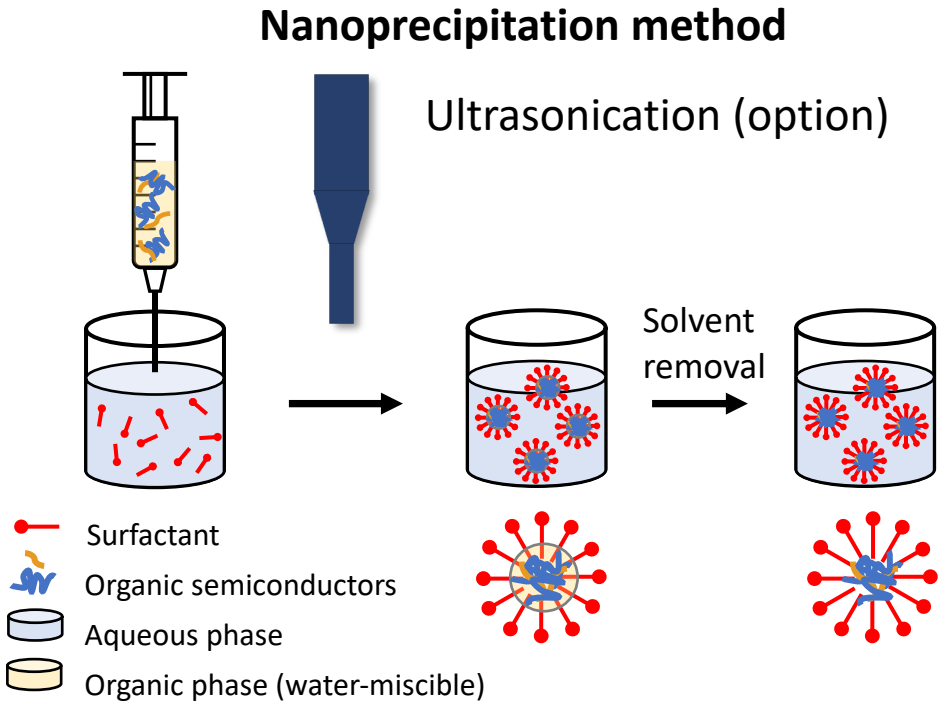


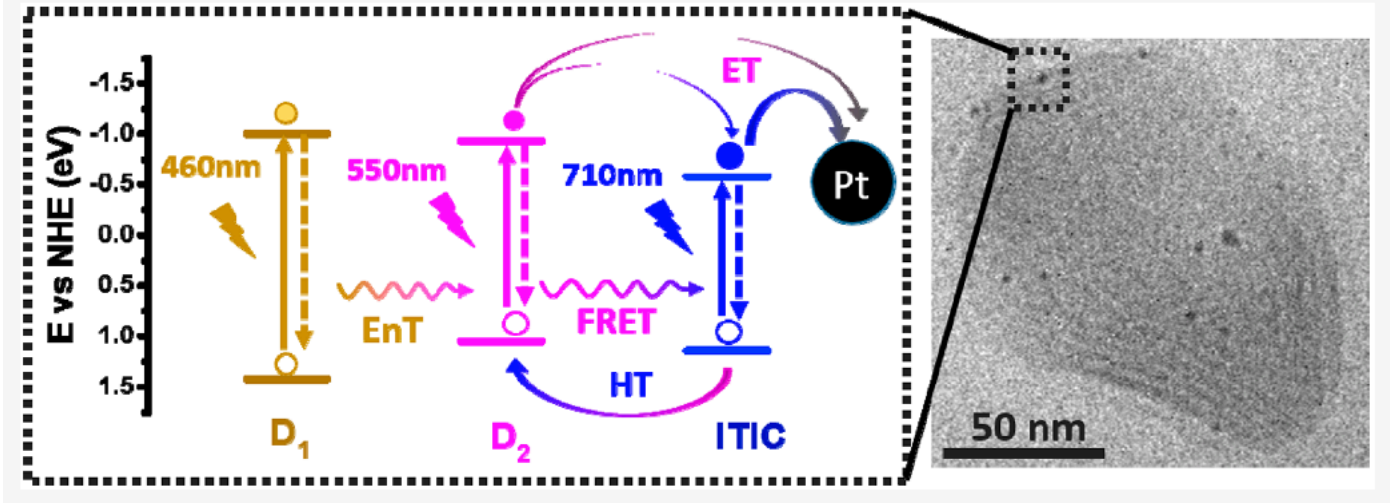
- Jun-Ho YUM, junho.yum@epfl.ch

A. Liu et al., *J. Am. Chem. Soc.*, **143**, 2875–2885 (2021)

Bulk-Heterojunction (BHJ) HER Organic Photocatalysts







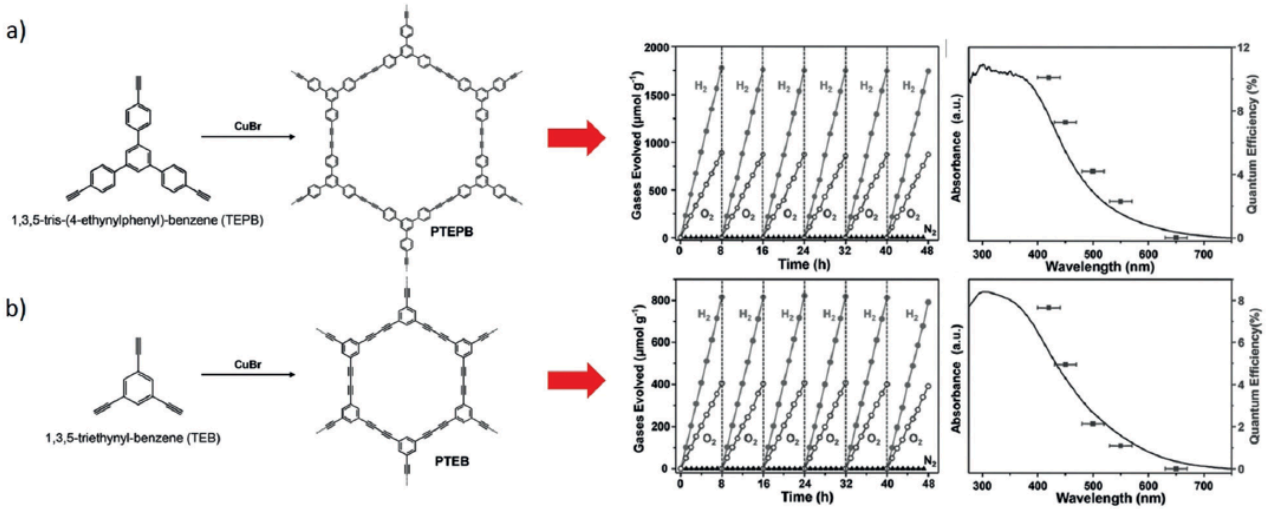
Energy transfer occurred from excited PFBT to PFODTBT and ITIC within 600 fs.

Charge transfer (electron et hole transfer) between PFODTBT and ITIC happened within 200 fs.

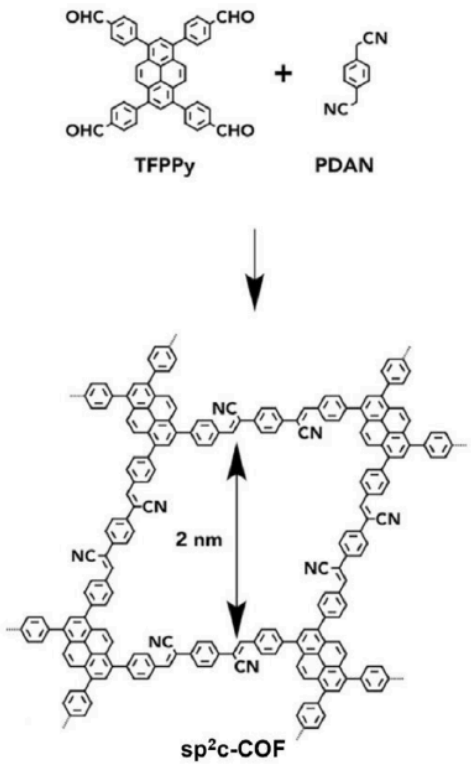
A. Liu et al., *J. Am. Chem. Soc.*, **143**, 2875–2885 (2021)

Other Organic Photocatalysts

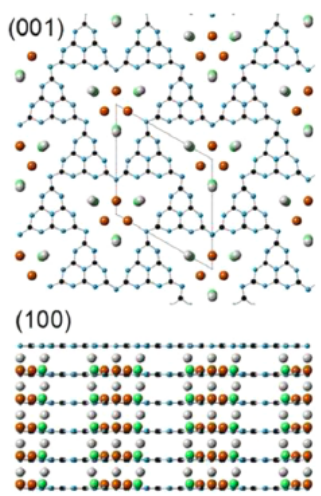
conjugated microporous polymers



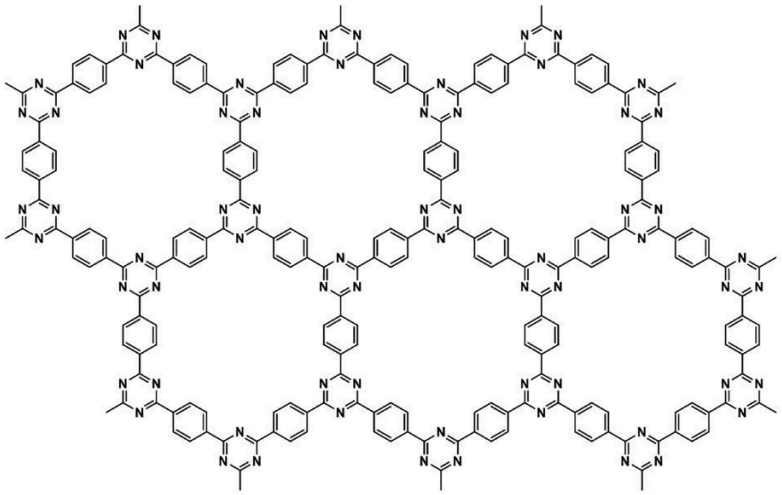
covalent organic frameworks



polymeric carbon nitrides



covalent triazine-based framework



M. Rahman et al., *Angew. Chem. Int. Ed.* 59, 16278 – 16293 (2020)
Y. Fang et al., *Chem. Rev.*, 122 (3), 4204-4256 (2022)