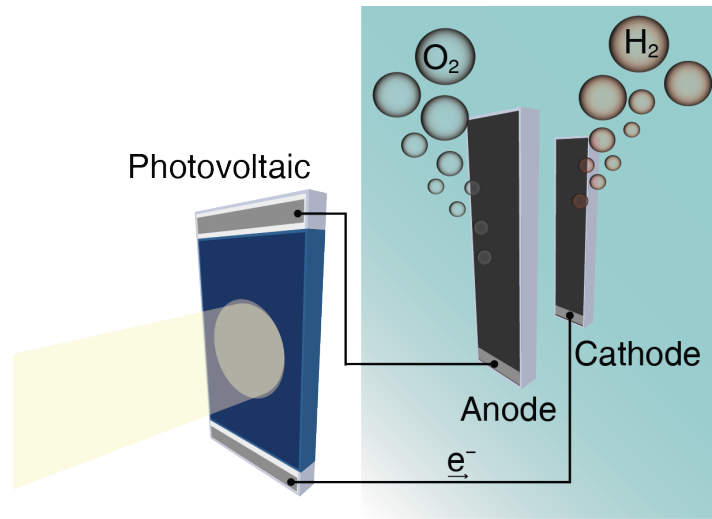


Energy Conversion by Semiconductor Devices

Jun-Ho YUM

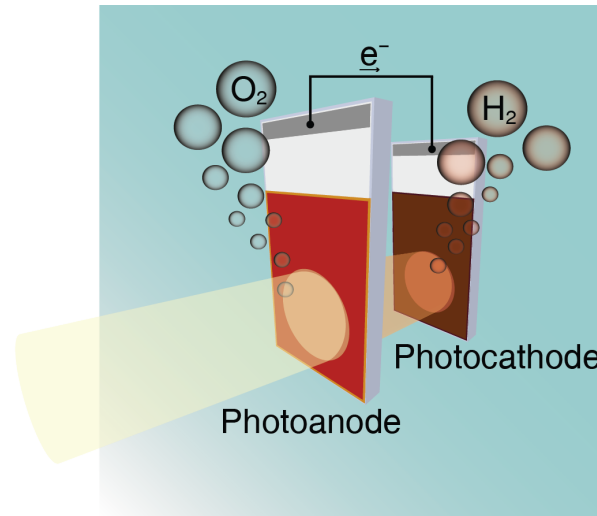
junho.yum@epfl.ch

PV-EC



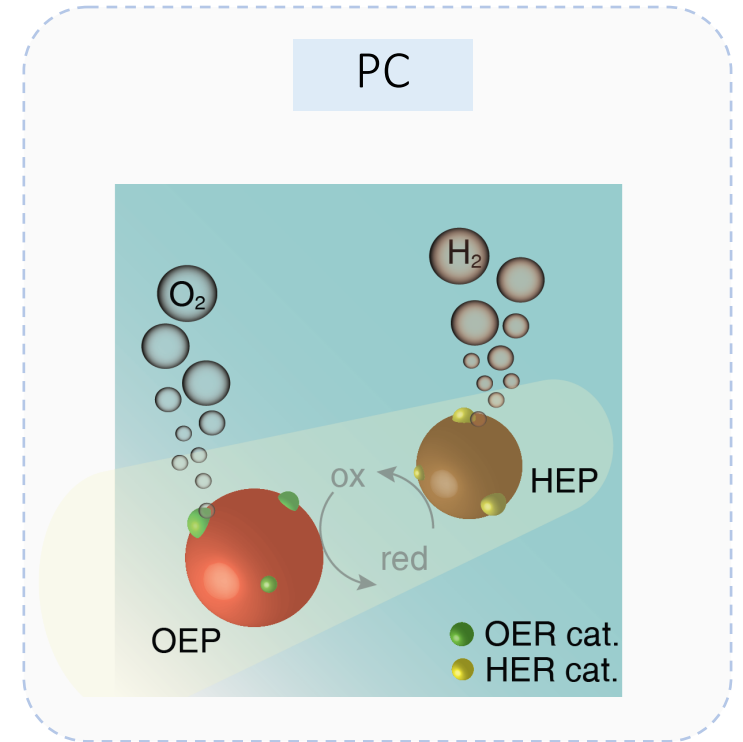
5 – 12 \$/Kg H₂ ⁽¹⁾

PEC



3 – 18 \$/Kg H₂ ⁽²⁾

PC



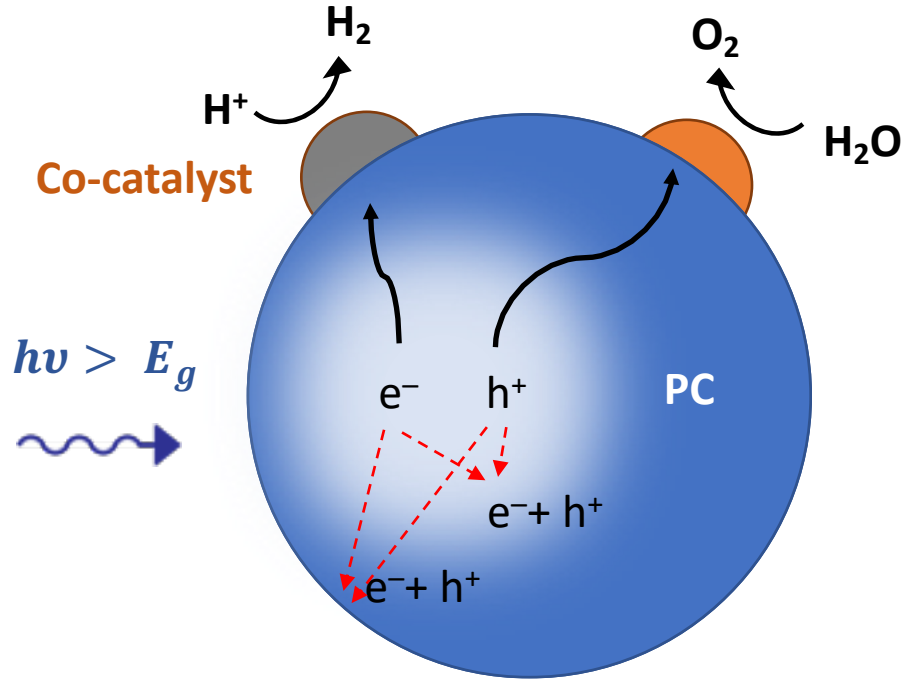
1 – 3 \$/Kg H₂ ⁽²⁾



- 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)



Photoexcitation \rightarrow Exciton \rightarrow 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)

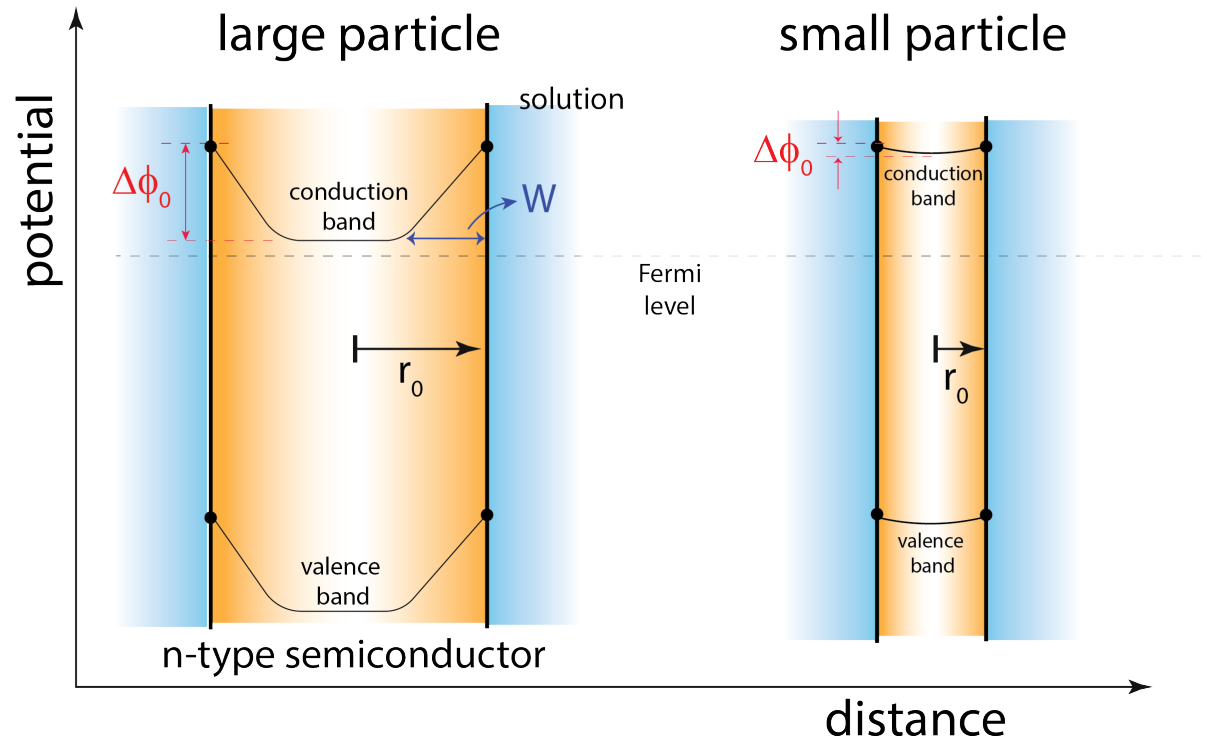
Typically diffusion can occur more rapidly than recombination

The efficiency of photoreaction is expressed by the quantum yield (Φ)

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

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

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}).



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

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

$$\text{Debye Length } L_D = \left(\frac{\epsilon_r \epsilon_0 k_B T}{e^2 N_D} \right)^{1/2}$$

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

Large particles
 $(r_0 \gg W)$

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

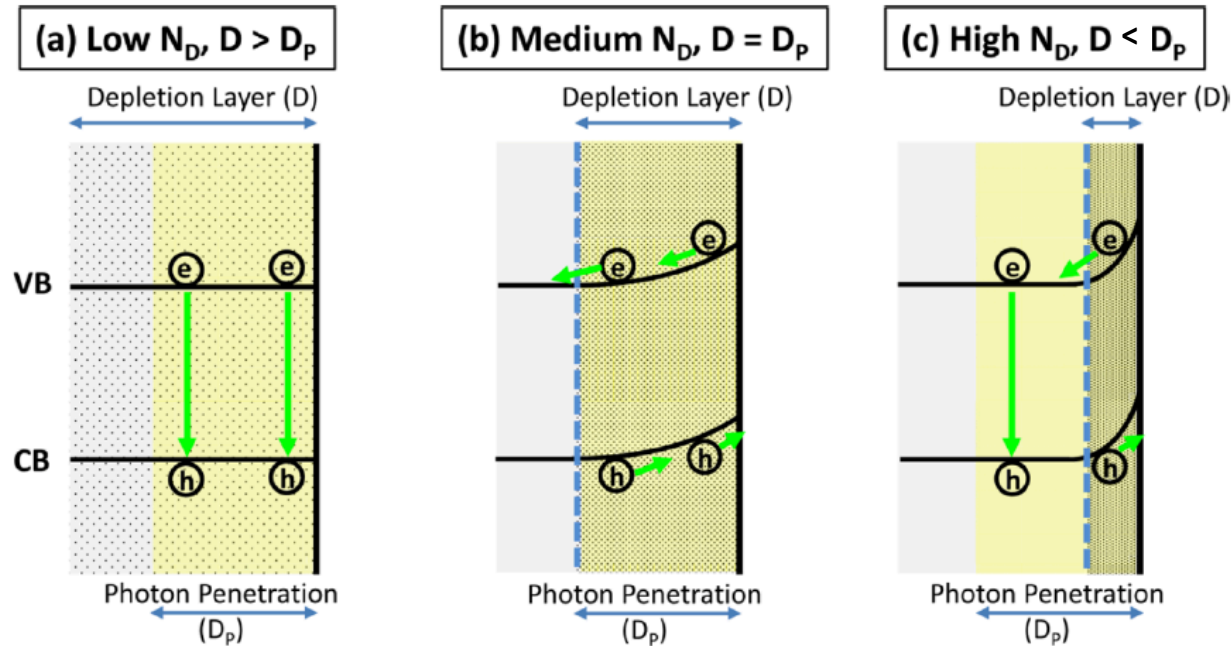
Small particles
 $(r_0 < \sqrt{3}W)$

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

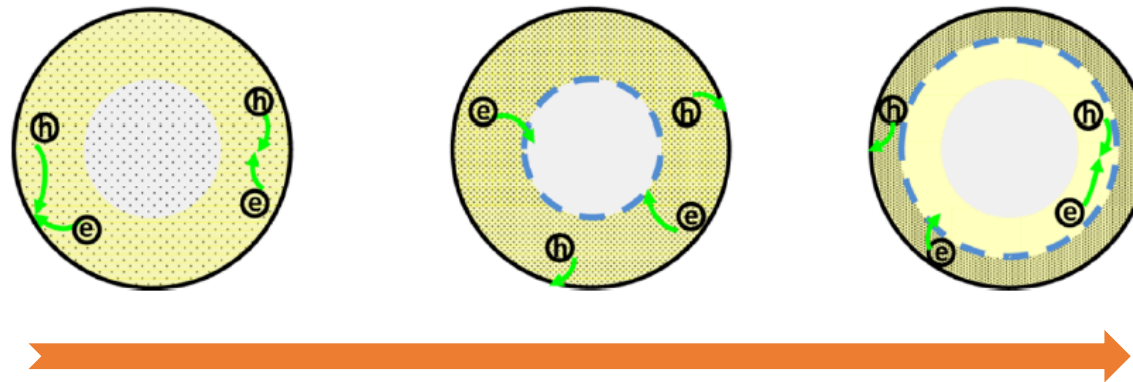
For TiO_2 , $L_D = 3.8 \sim 12 \text{ nm}$, $\epsilon_r \approx 100$,

$N_D \approx 10^{18} \sim 10^{19} \text{ cm}^{-3}$, $\Delta\phi_0 = \sim 0.004 \text{ V}$

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!

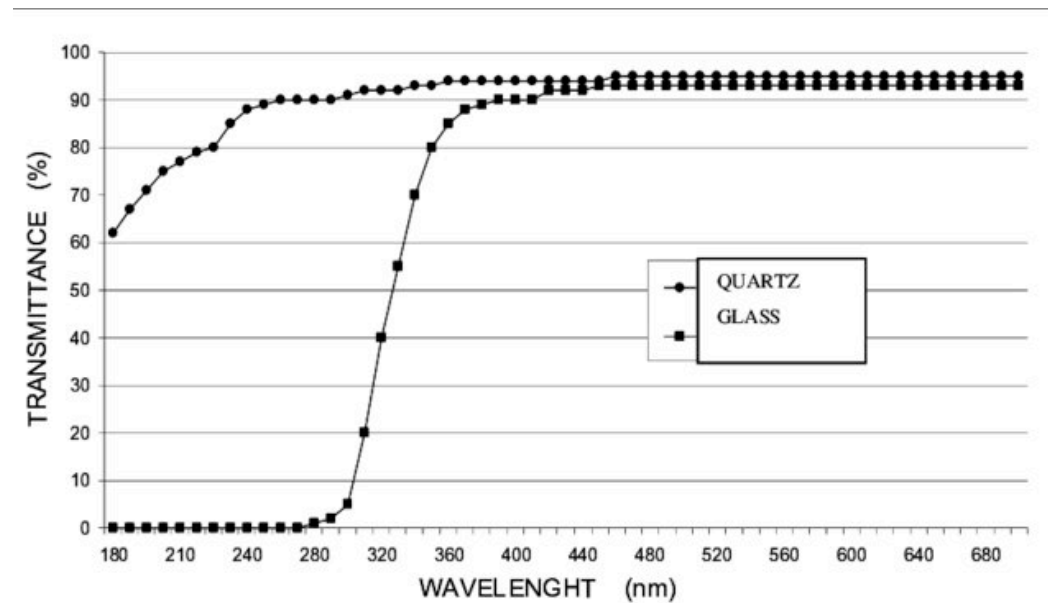
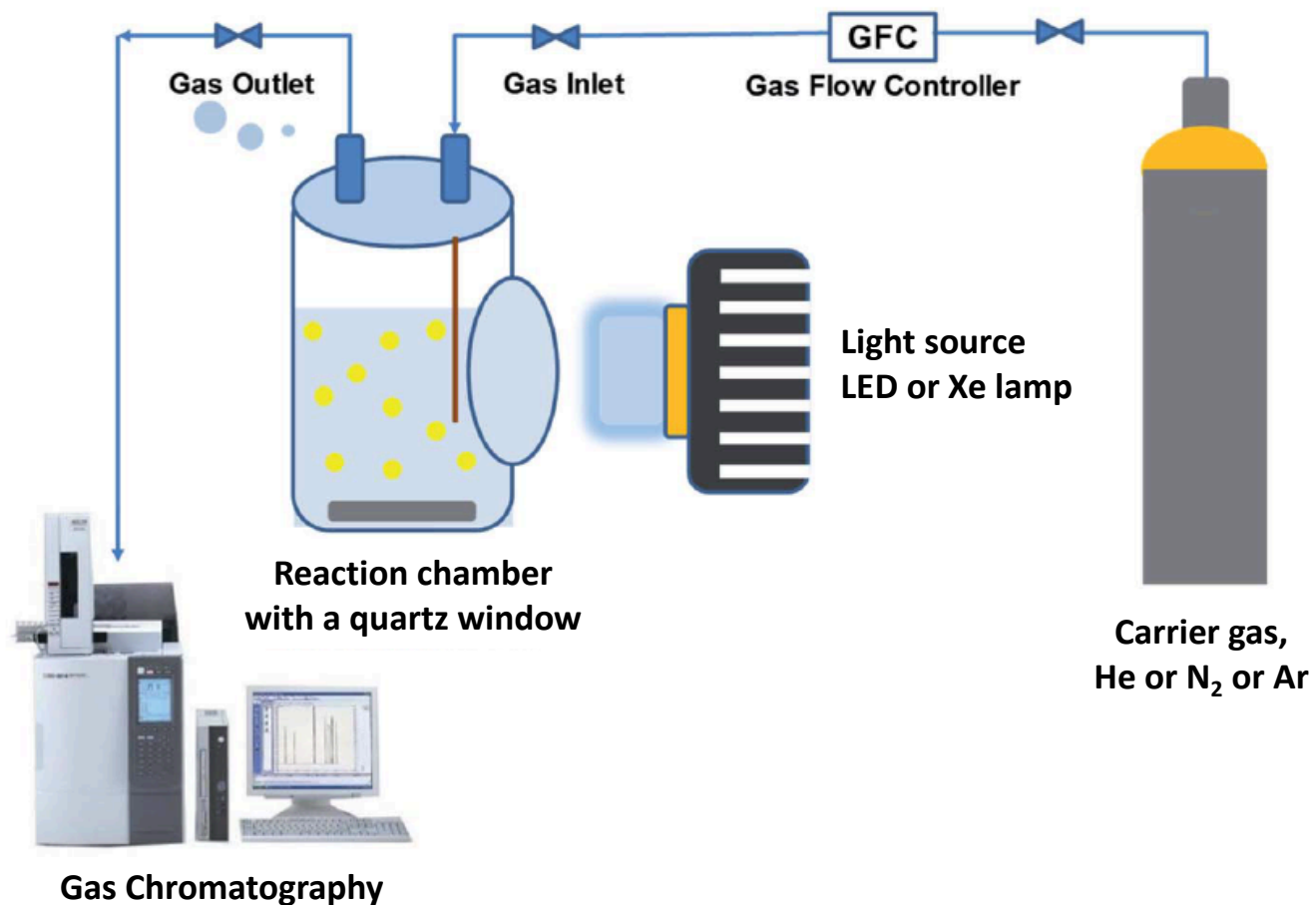
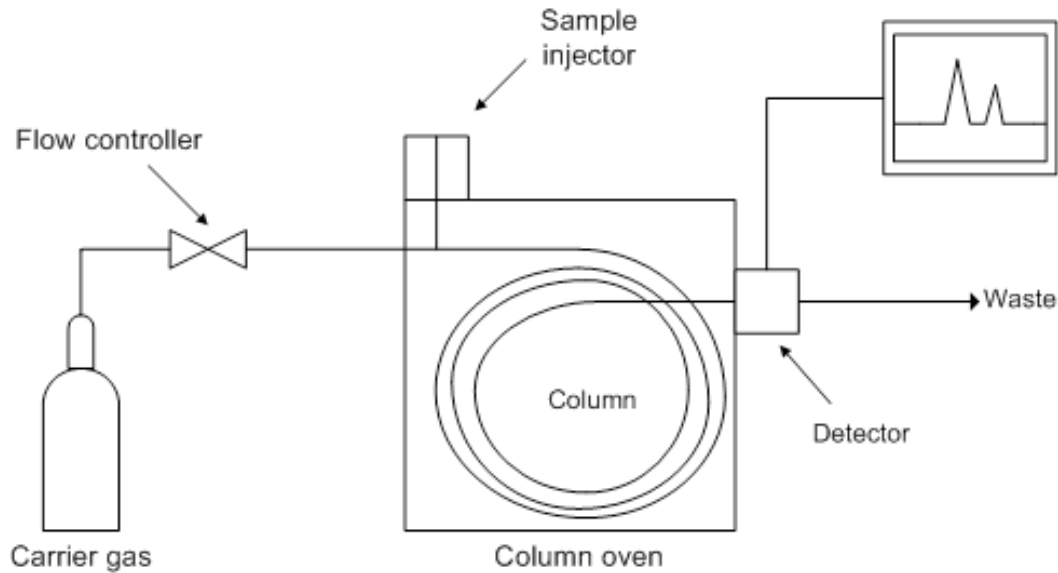
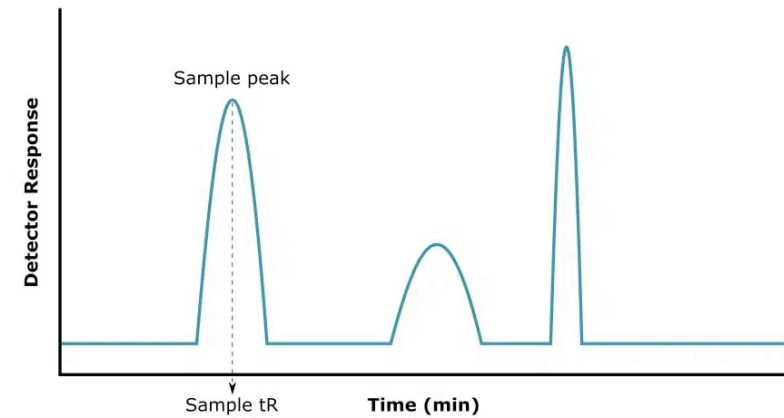
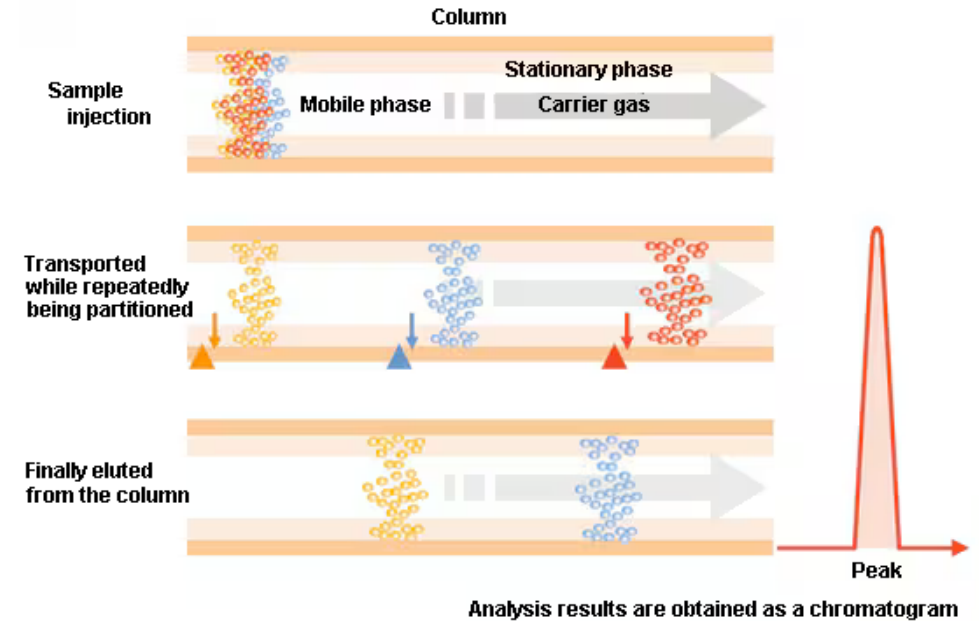


Image inspired from H. El-Bery et al., *RSC Adv.*, **11**, 13229 (2021)



Low-boiling-point or non-polar compounds interact less strongly with the stationary phase and are carried along more quickly by the mobile phase.



EPFL Metrics in PC Water Splitting

AQY: the number of reacted electrons relative to the total number of photons incident in the reaction system for a particular wavelength of light.

Apparent Quantum Yield (AQY)

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

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

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

$$= \frac{(1.2 \times 10^8) \times 2 \times \text{reaction rate} \left(\frac{\text{mol } H_2}{s} \right)}{P_{in} \left(\frac{W}{m^2} \right) \times A(m^2) \times \lambda_{in}(nm)} \times 100\%$$

STH: the overall efficiency of a complete system in converting solar energy into the chemical energy of hydrogen gas.

$$STH = \left[\frac{(\text{mmol } H_2/s) \times (237,200 \text{ J/mol})}{P_{total} \left(\frac{mW}{cm^2} \right) \times \text{Area} (cm^2)} \right]_{AM1.5G}$$

EPFL Metrics in PC Water Splitting

AQY: the number of reacted electrons relative to the total number of photons incident in the reaction system for a particular wavelength of light.

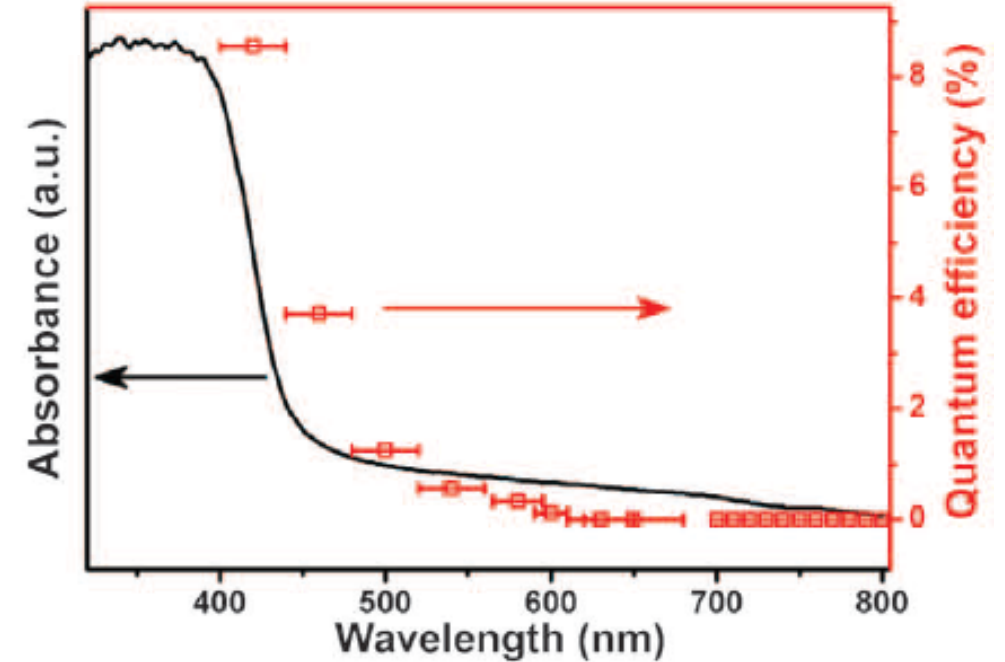
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$$= \frac{(1.2 \times 10^8) \times 2 \times \text{reaction rate} \left(\frac{\text{mol } H_2}{s} \right)}{P_{in} \left(\frac{W}{m^2} \right) \times A(m^2) \times \lambda_{in}(nm)} \times 100\%$$



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

EPFL Metrics in PC Water Splitting

AQY: the number of reacted electrons relative to the total number of photons incident in the reaction system for a particular wavelength of light.

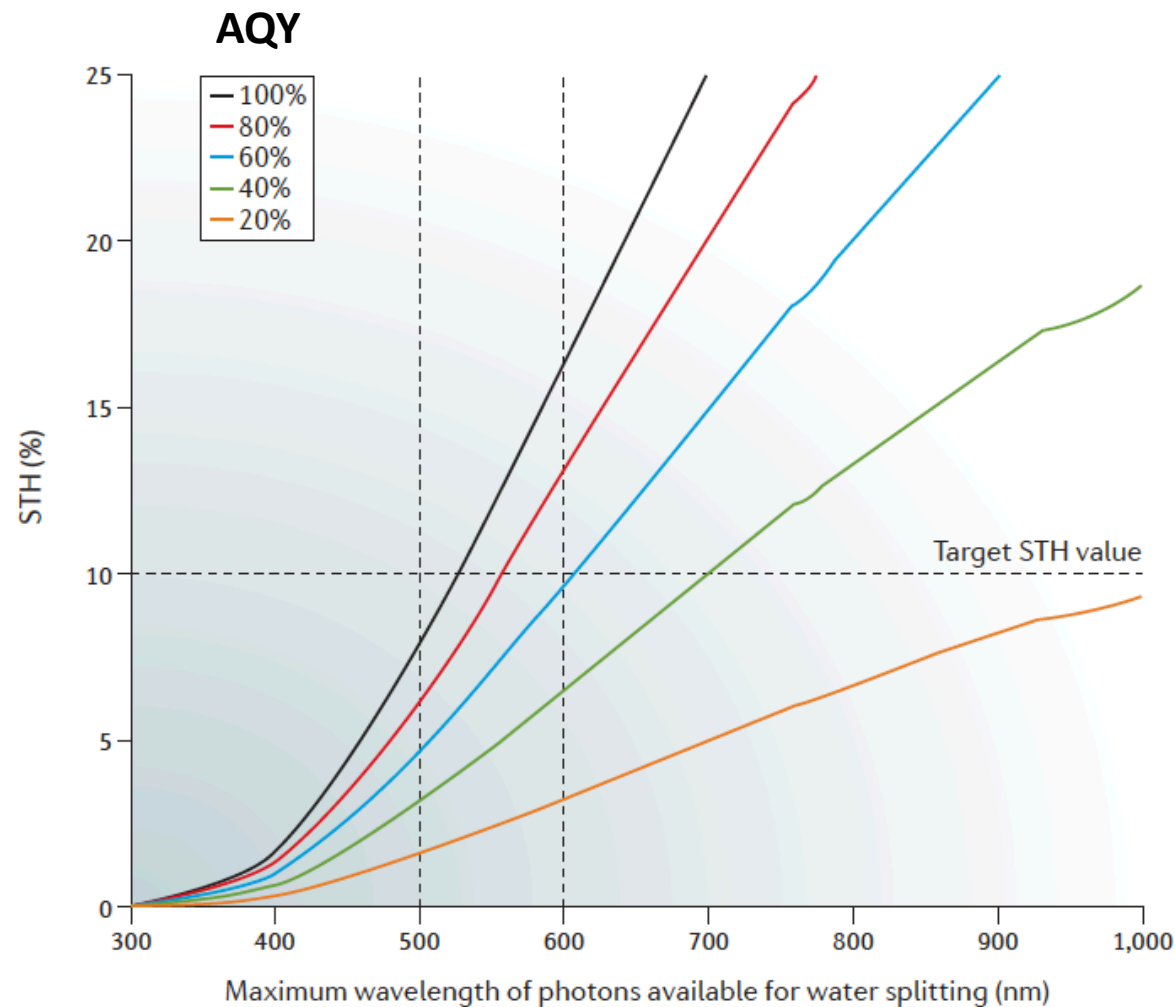
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$$= \frac{4 \times \text{number of evolved } O_2 \text{ molecules}}{\text{number of incidents photons}} \times 100\%$$

$$= \frac{(1.2 \times 10^8) \times 2 \times \text{reaction rate} \left(\frac{\text{mol } H_2}{s} \right)}{P_{in} \left(\frac{W}{m^2} \right) \times A(m^2) \times \lambda_{in}(nm)} \times 100\%$$



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

Single Component Photocatalyst

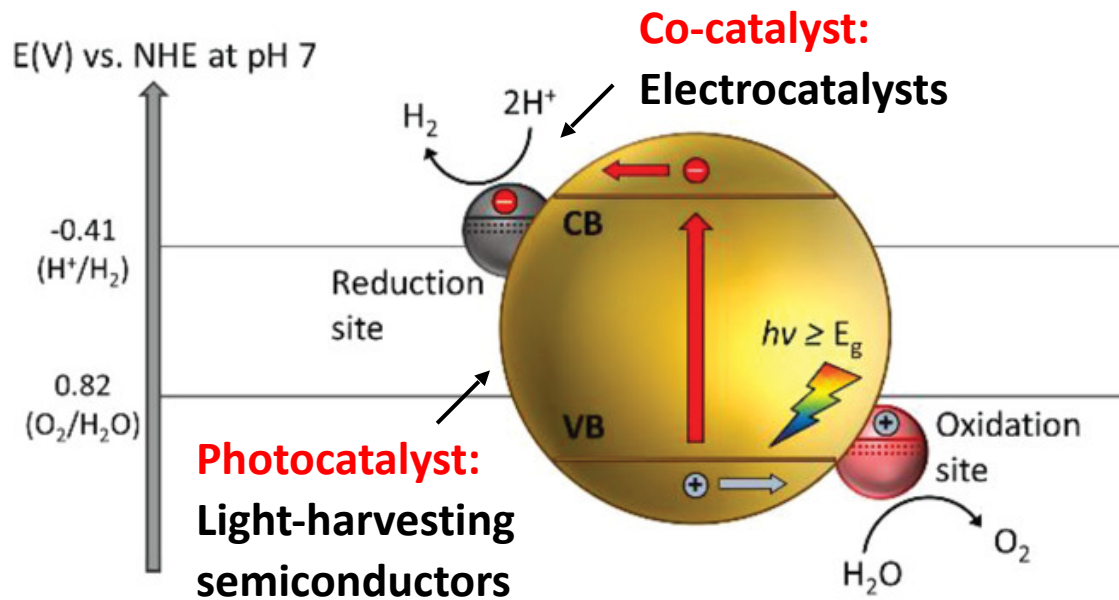
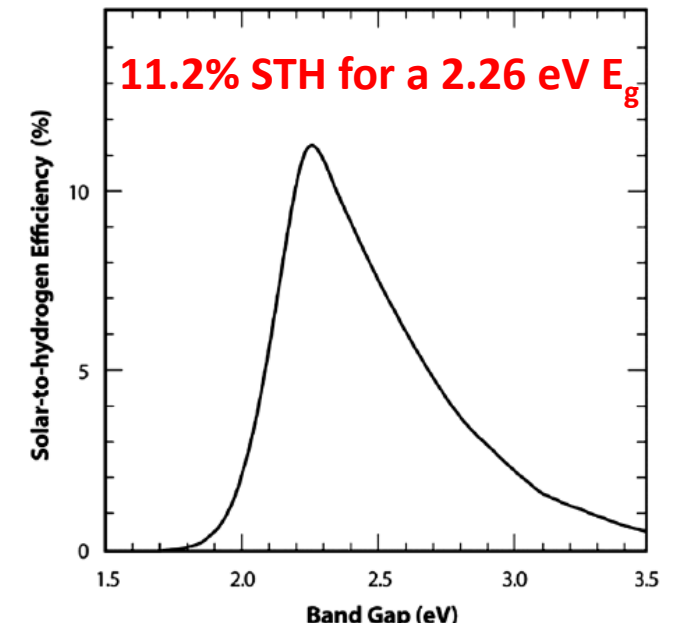
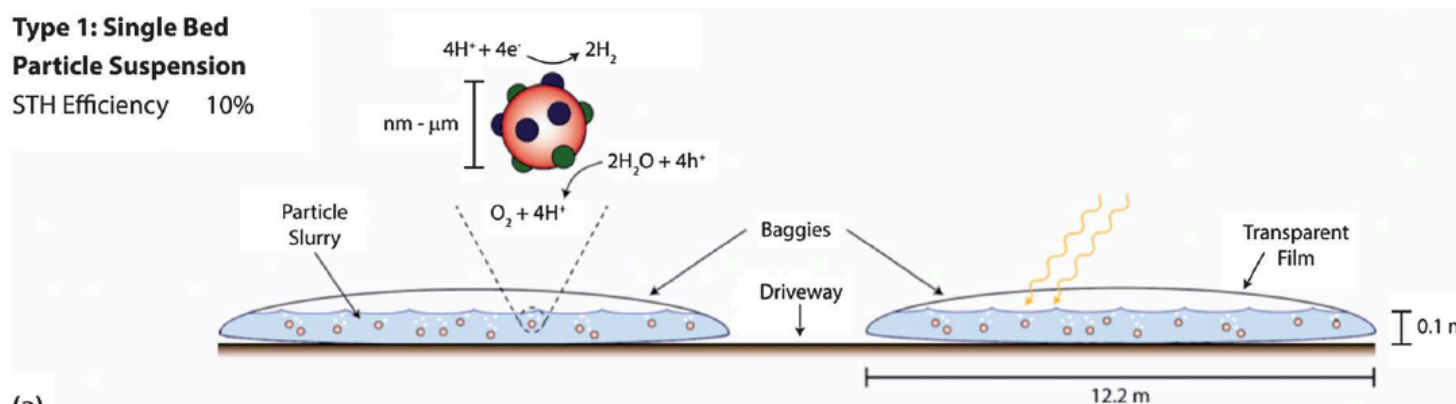


Image taken from B.-J. Ng et al., *Adv. Sci.*, **7**, 1903171 (2020)

- **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
- **Mixed O₂ and H₂**

Type 1: Single Bed Particle Suspension
STH Efficiency 10%



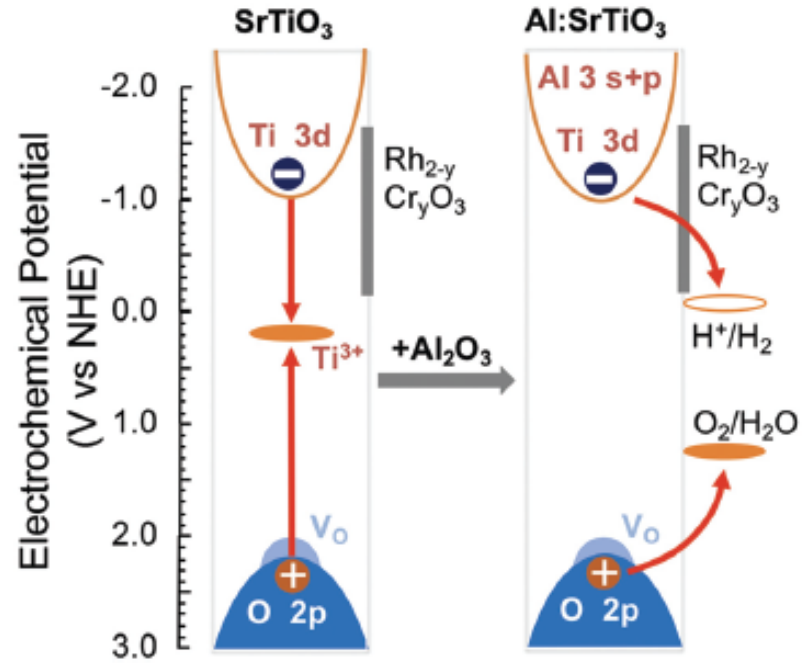
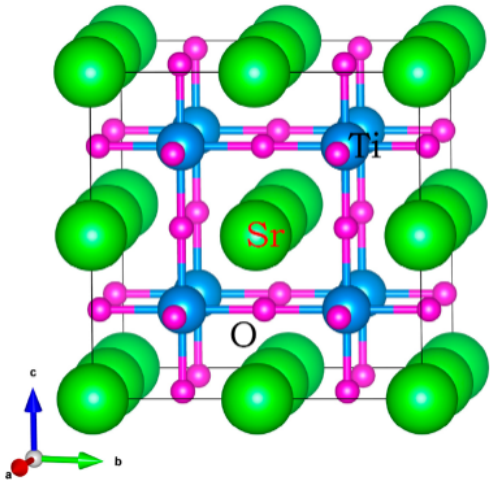
Photocatalyst	Co-catalyst (HER, OER)	Bandgap, Absorption edge (nm)	Reactant solution	Efficiency	Durability (retention, %)
Al-doped SrTiO ₃	Rh/Cr ₂ O ₃ , CoOOH (photodeposition)	3.2 eV, 390	H ₂ O	AQE = 96% at 350 – 360 nm STH = 0.51%	12.5 h (94)
C ₃ N ₄	Carbon dots	2.8 eV, 450	H ₂ O	AQE = 16% at 420 nm STH = 2%	4800 h (98)
CoO	-	2.4 eV, 515	H ₂ O	STH = 5%	-
Y ₂ Ti ₂ O ₅ S ₂	Ru/Cr ₂ O ₃ , IrO ₂	1.9 eV, 650	H ₂ O	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>

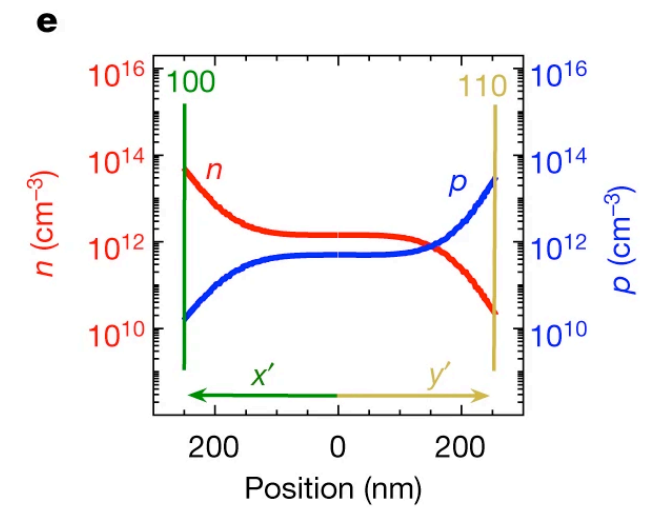
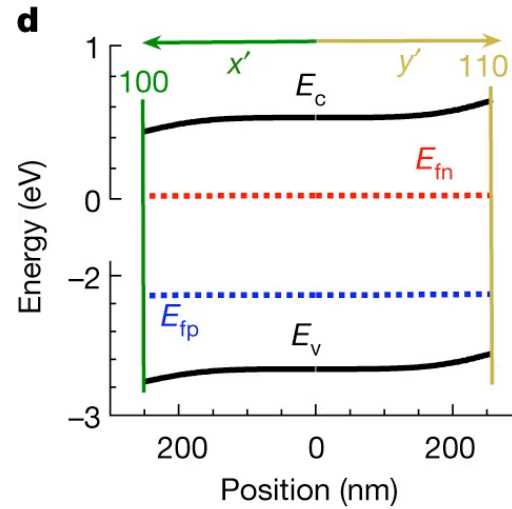
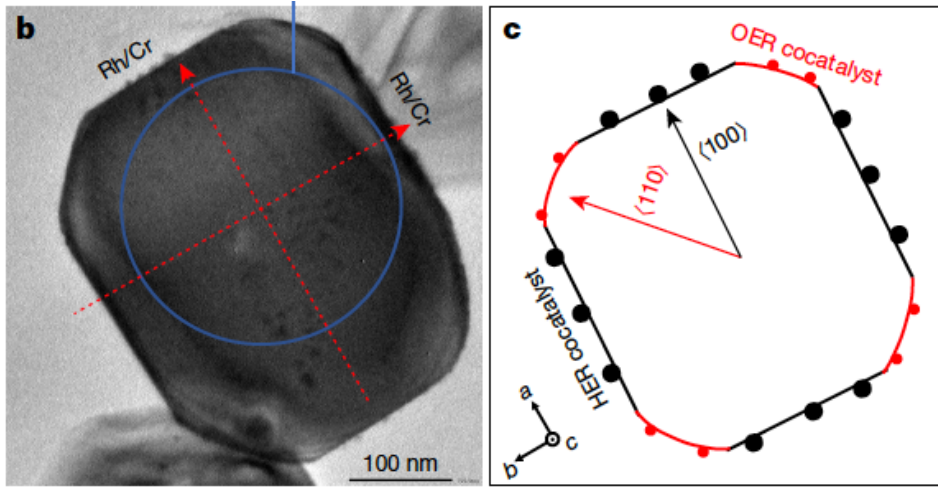
<https://www.nature.com/articles/nnano.2013.272>

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

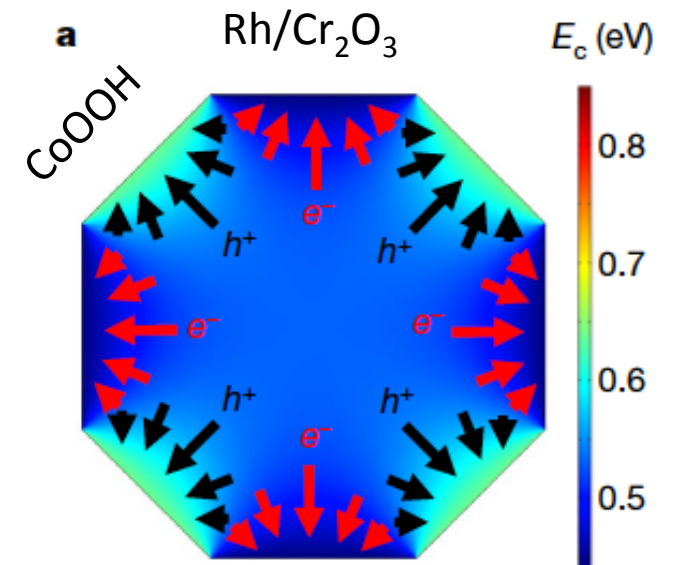


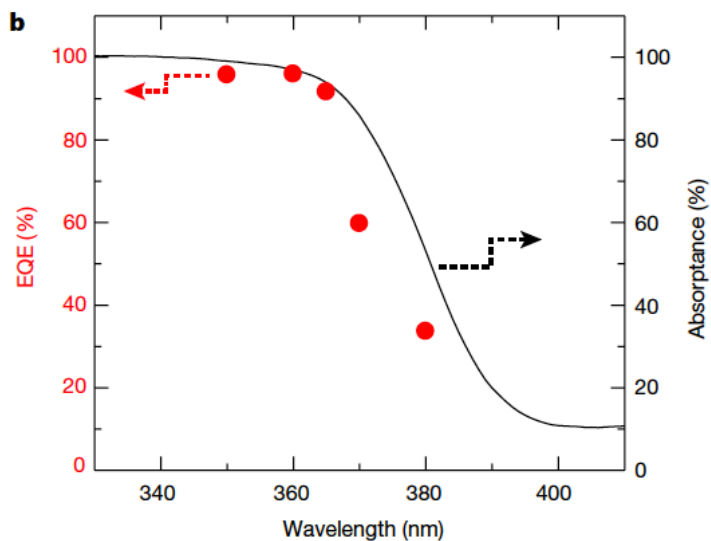
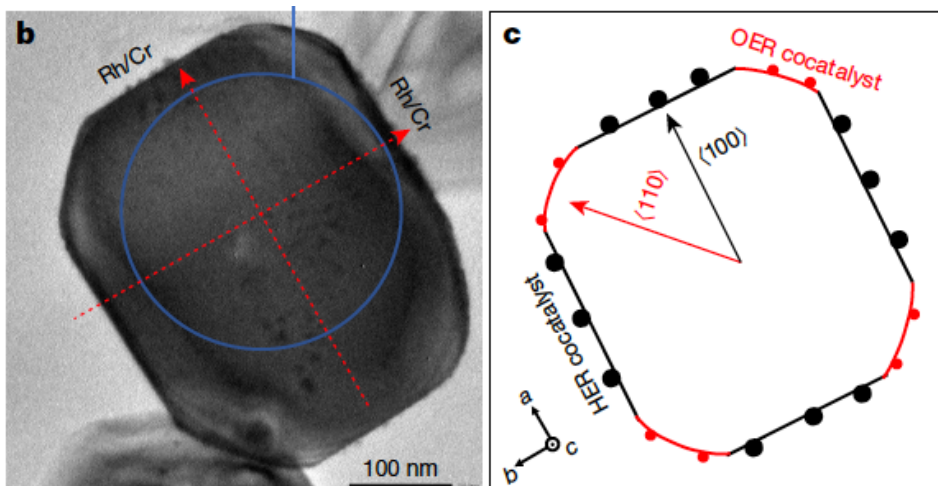
Z. Zhao et al., *Energy Environ. Sci.*, **12**, 1385 (2019)

- Non-doped SrTiO₃:
 - Oxygen vacancy is associated with two Ti³⁺.
 - Deep electron traps to promote SRH recombination.
- Al-doped SrTiO₃:
 - Reduced Ti³⁺ recombination sites to enables prolonged carrier lifetime.



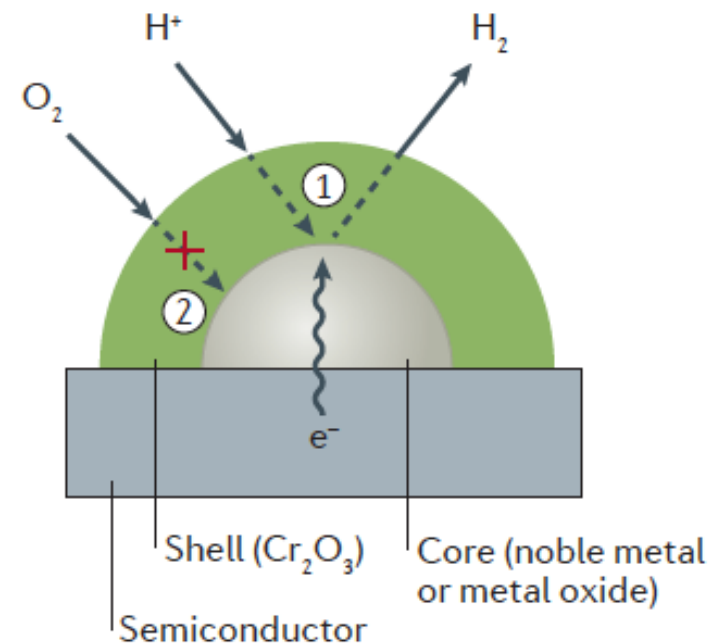
- A W_F difference of 0.2 eV between the {110} and {100} surfaces induce anisotropic charge separation.
- HER Rh/Cr₂O₃ cocatalyst photodeposited (reduction from Rh³⁺) on electron-attracting {100} facets.
- OER CoOOH photodeposition (oxidation from Co²⁺) on {110} facets.





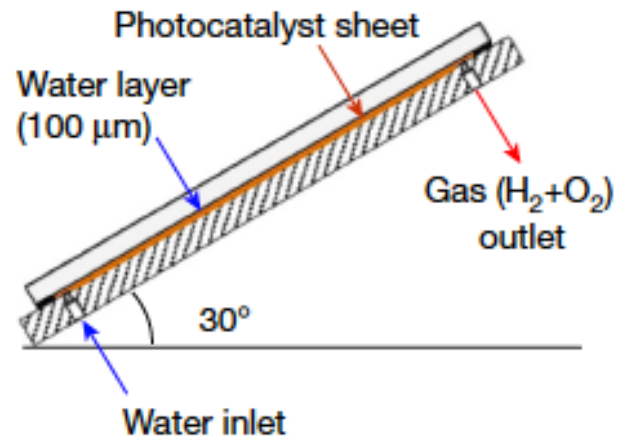
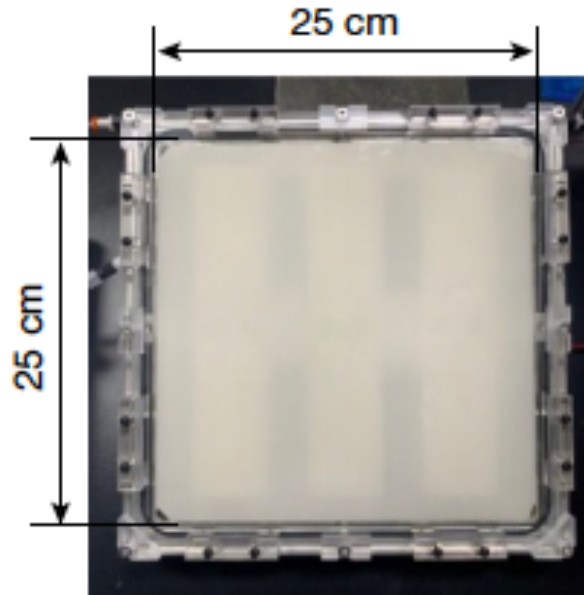
T. Takata et al., *Nature*, **581**, 411 (2020)

Forward reaction: ① HER
Inhibited reaction: ② ORR



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

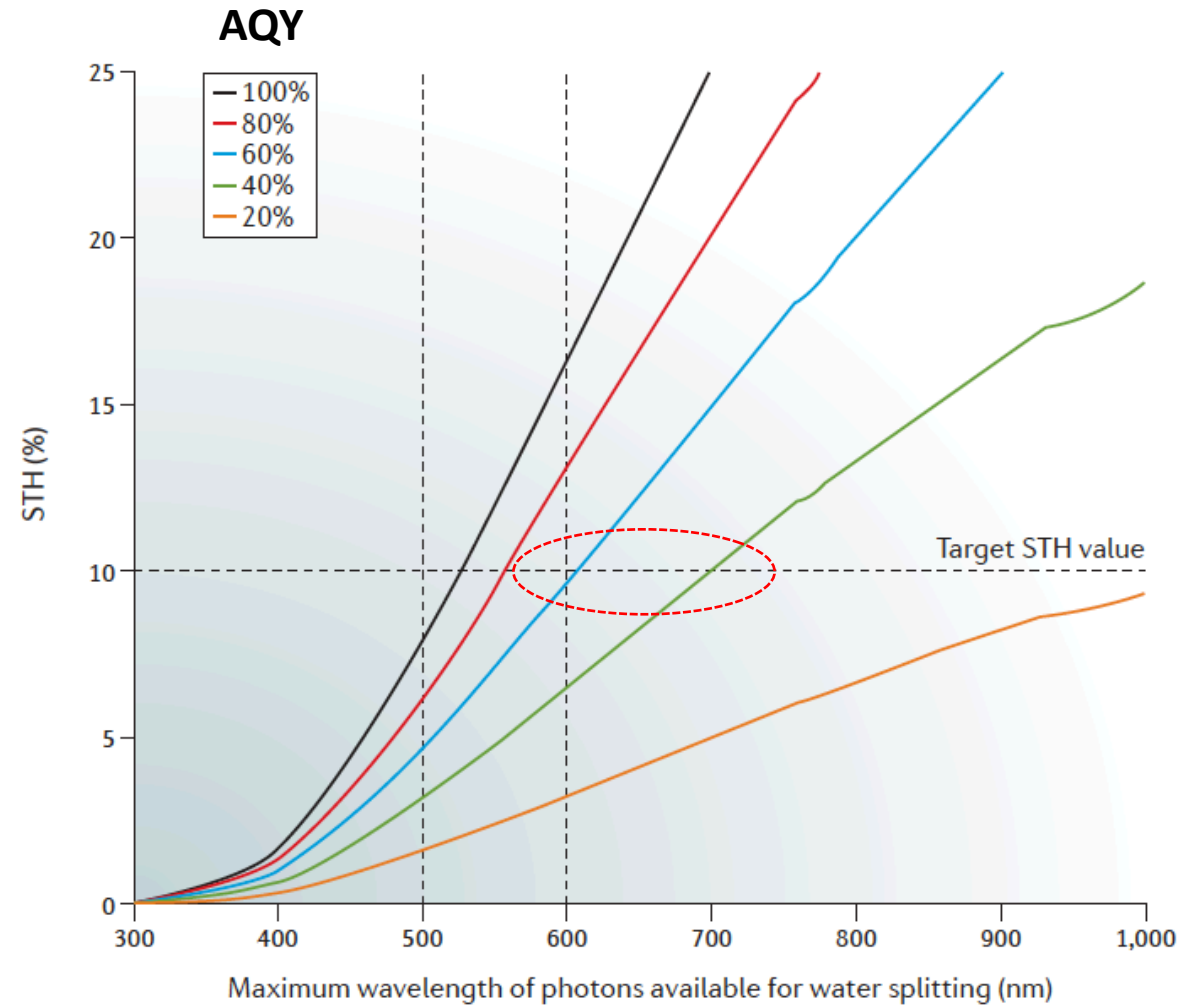
- The Rh promotes both the HER and the oxygen reduction reaction (ORR; a major backward electron transfer process).
- The Cr₂O₃ shell inhibits only the ORR by blocking the access of evolved O₂ to the surface of the Rh core.

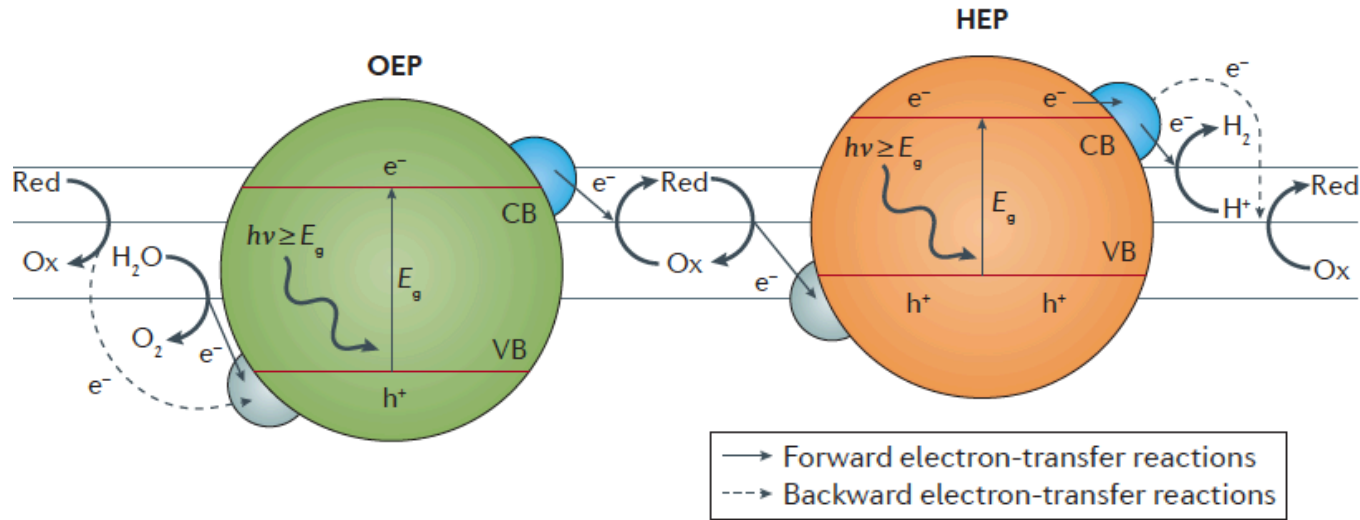


- A 100-m² array of panel reactors over several months
- **STH of 0.76 %**

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

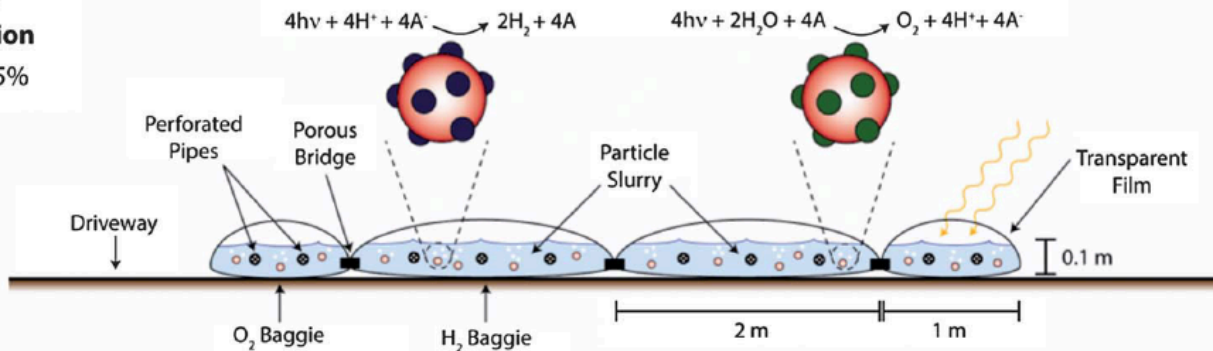
- Operable wavelength range up to 600 – 700 nm with an AQY 40 – 60 % should be developed.
- Co-catalyst/semiconductor, co-catalyst/solution, semiconductor/solution interfaces to maximize forward charge transfer.
- The use of rare and expensive elements should be eliminated.
- More advanced material designs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





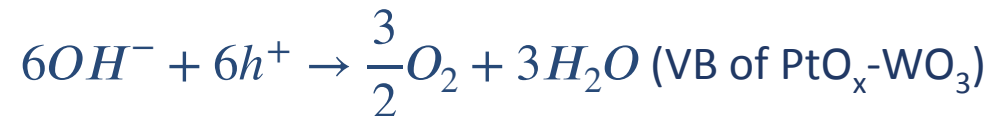
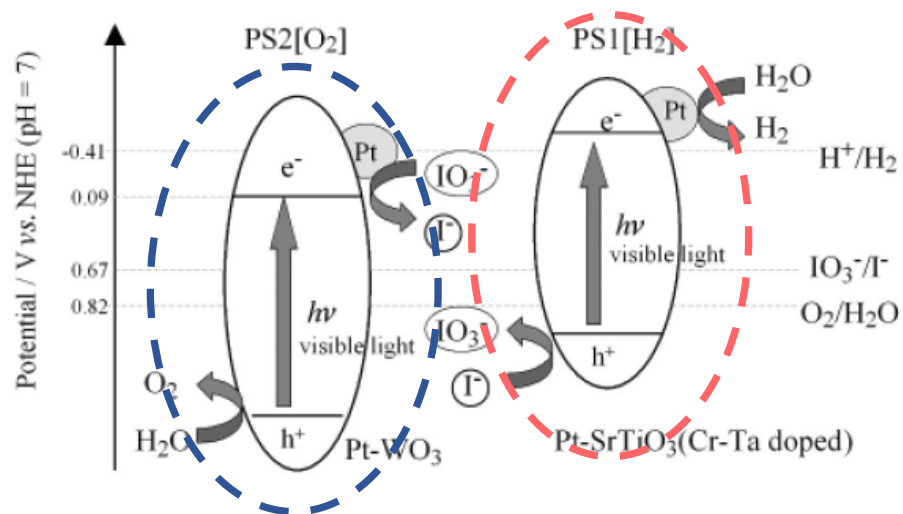
- The number of photons needed in a two-step PC is eight vs four in a one-step PC: A half amount of products
- Relaxation of the thermodynamic requirements: small bandgap
- Separation of O₂ and H₂
- Theoretical STH efficiency of 36% with 1.01 eV for HEP and 1.46 eV for OEP
- Needs an electron mediator
- Essential to suppress charge recombination and backward reaction (dashed line)

Type 2: Dual Bed Particle Suspension
STH Efficiency 5%

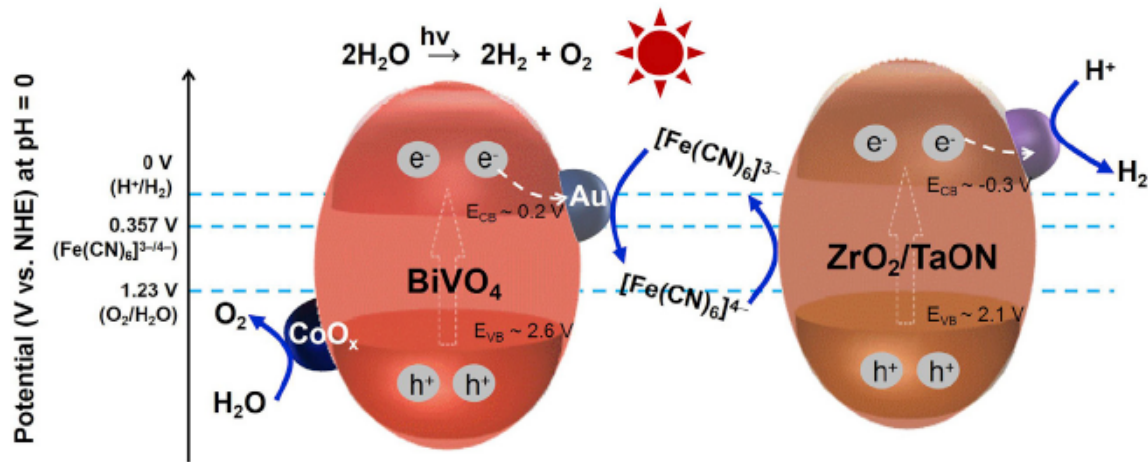


B. A. Pinaud et al., *Energy Environ. Sci.*, **6**, 1983 (2013)

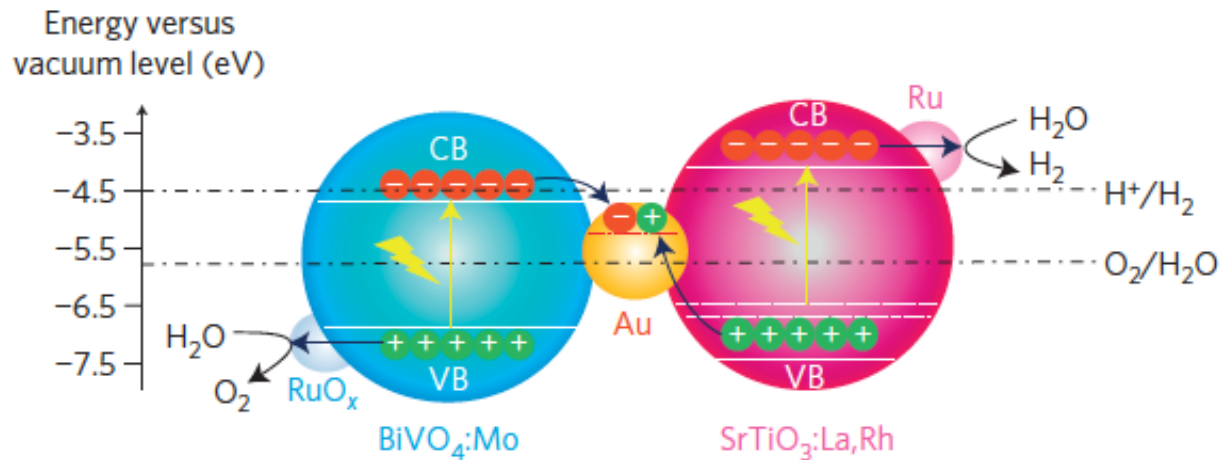
HEP	OEP	Electron mediator	Reactant solution	Efficiency
0.5 wt% Pt/ZrO ₂ /TaON (< 500 nm)	0.5 wt% PtO _x /WO ₃ (< 450nm)	IO ₃ ⁻ /I ⁻ (1.085 – 0.059 pH)	H ₂ O	AQY: 6.3% at 420 nm
1 wt% Ru/SrTiO ₃ :Rh (<520 nm)	BiVO ₄ (<520 nm)	Fe ³⁺ /Fe ²⁺ (0.771 V vs NHE)	H ₂ O (pH = 2.4, H ₂ SO ₄ mediated)	AQY: 4.2% at 420 nm, STH: 0.1%
Rh _y Cr _{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 ₂ O (pH = 2.4, H ₂ SO ₄ mediated)	AQY: 10.3% at 420 nm, STH: 0.5%
Ru/Cr ₂ O ₃ /SrTiO ₃ :La,Rh (<520 nm)	BiVO ₄ (<520 nm)	Au, Rh or Ni (solid mediator)	H ₂ O	STH = 1.1%



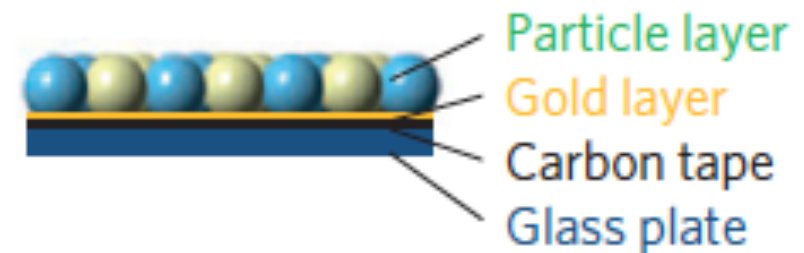
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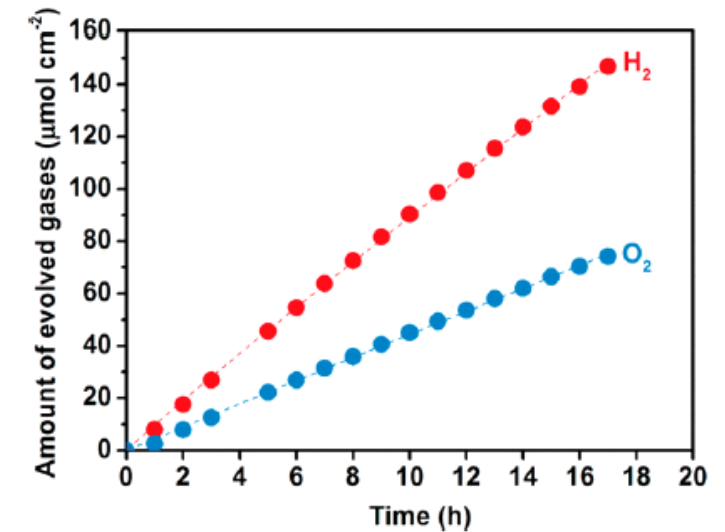
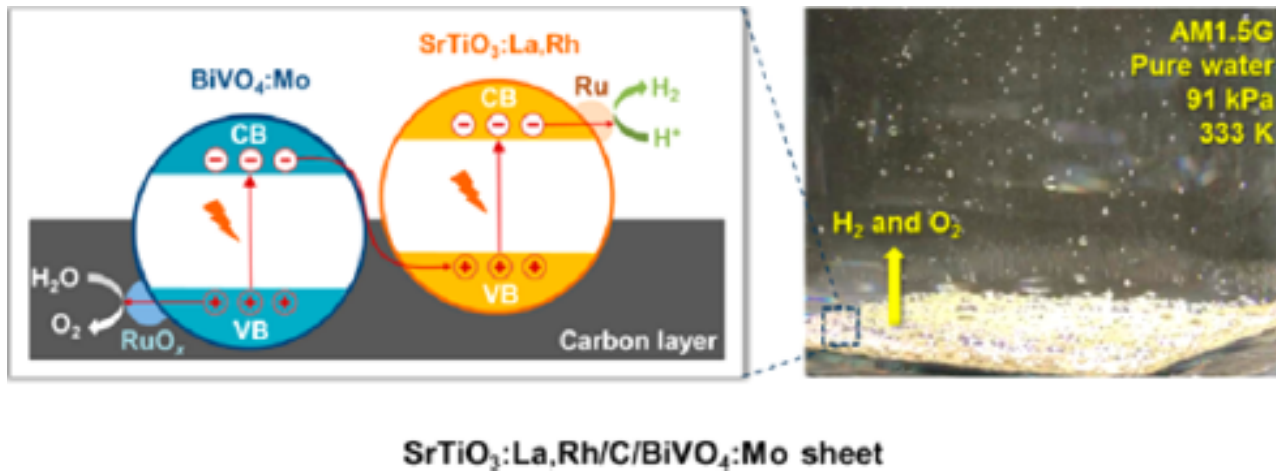


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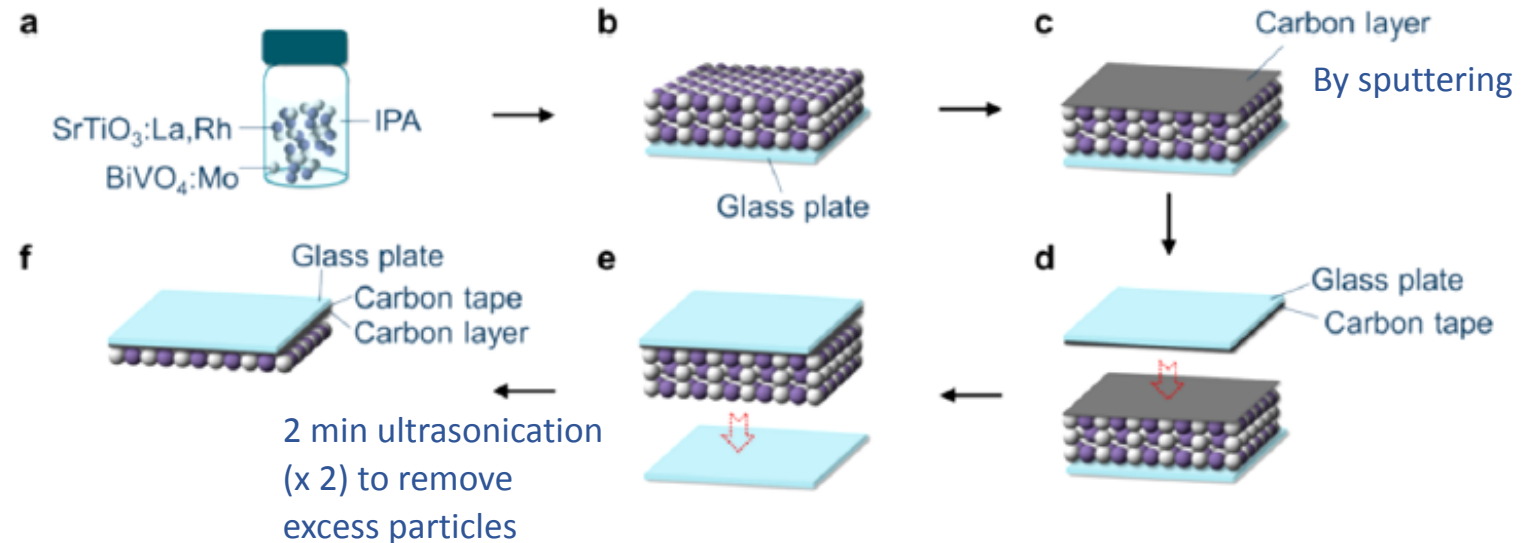
Photocatalyst sheet

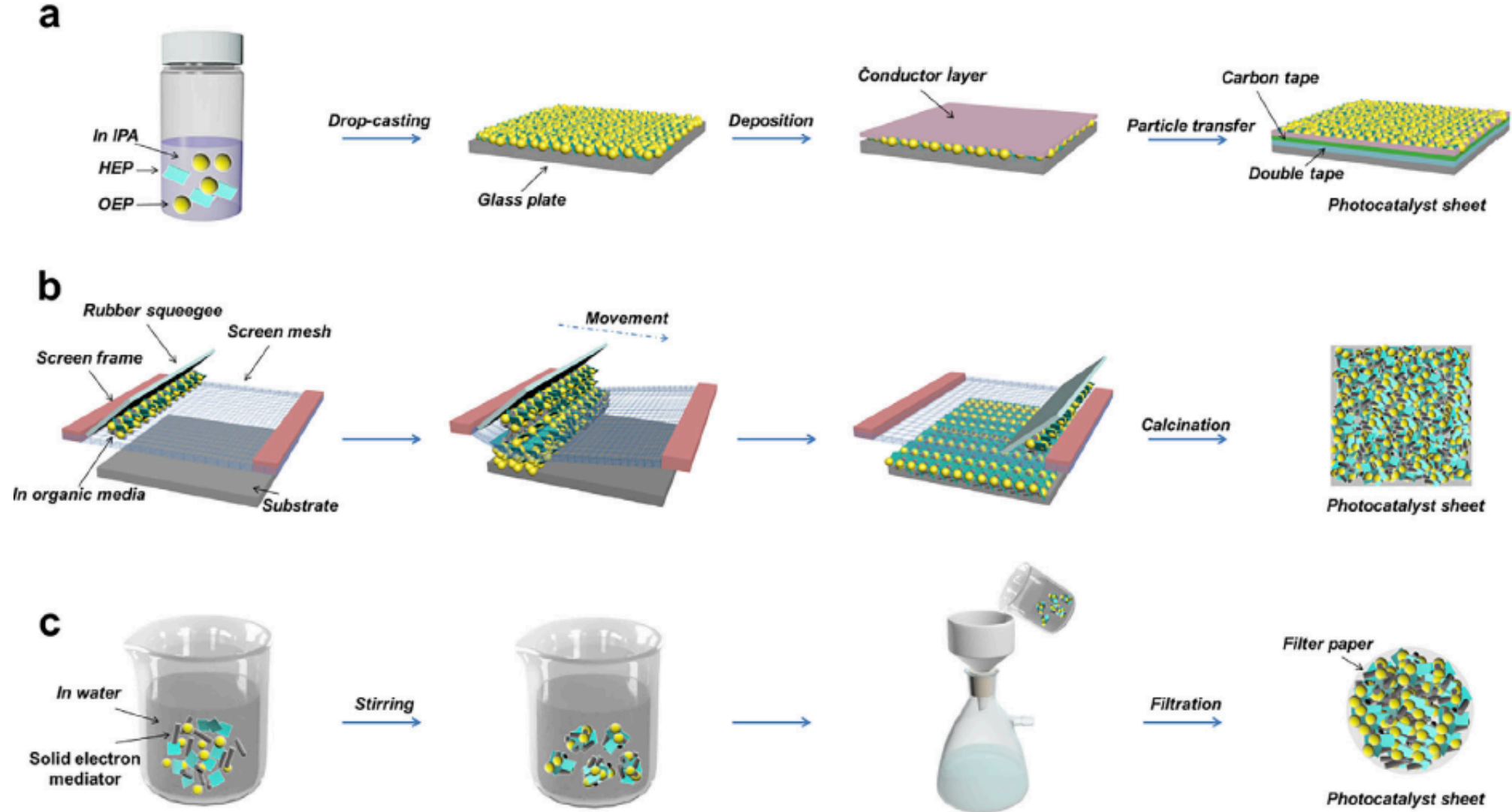




Carbon is less active than gold for oxygen reduction reaction (ORR)

STH efficiency = 1 %





Gu et al., *Adv. Funct. Materials*, 2506171 (2025)

HEP	OEP	Electron mediator	Reactant solution	Efficiency
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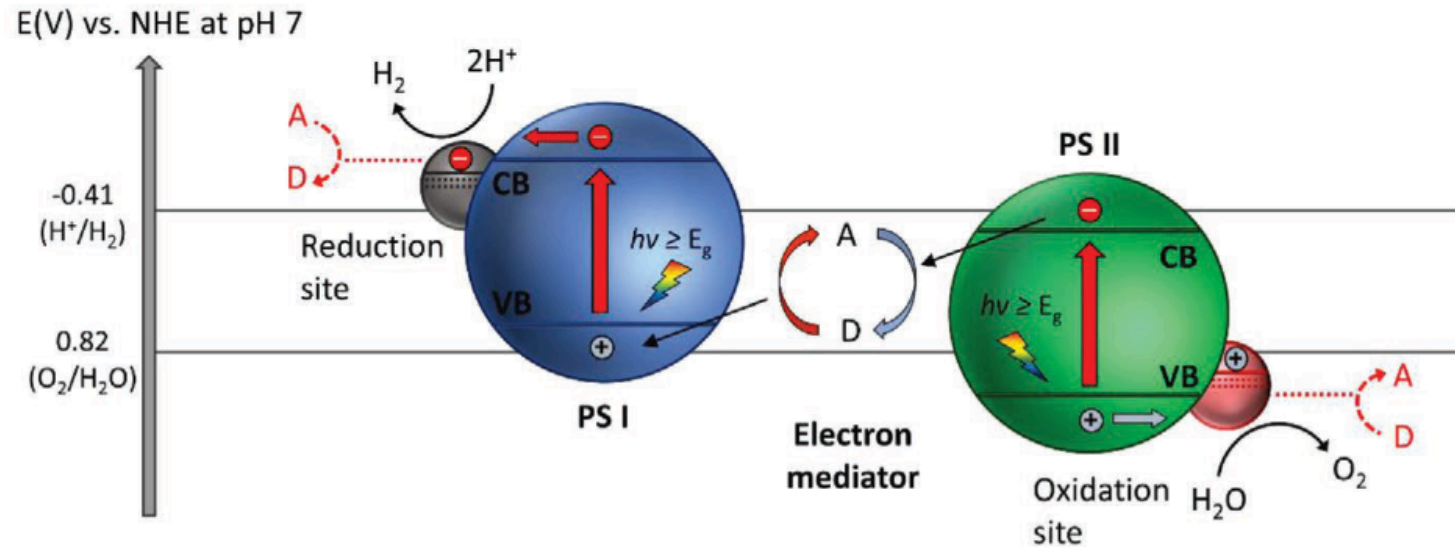
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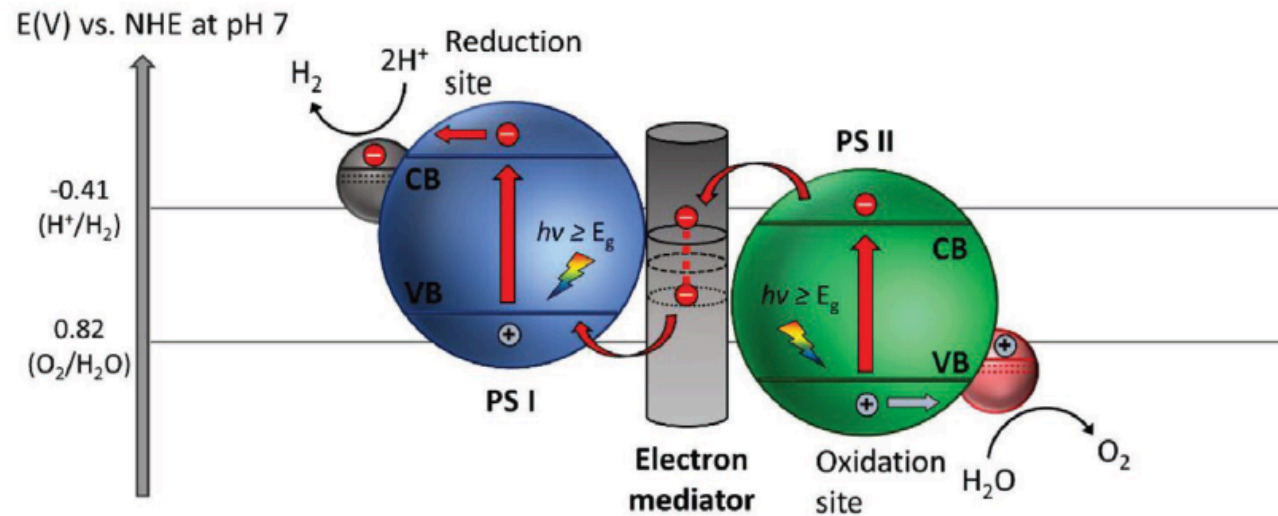
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<https://www.nature.com/articles/nmat4589>

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

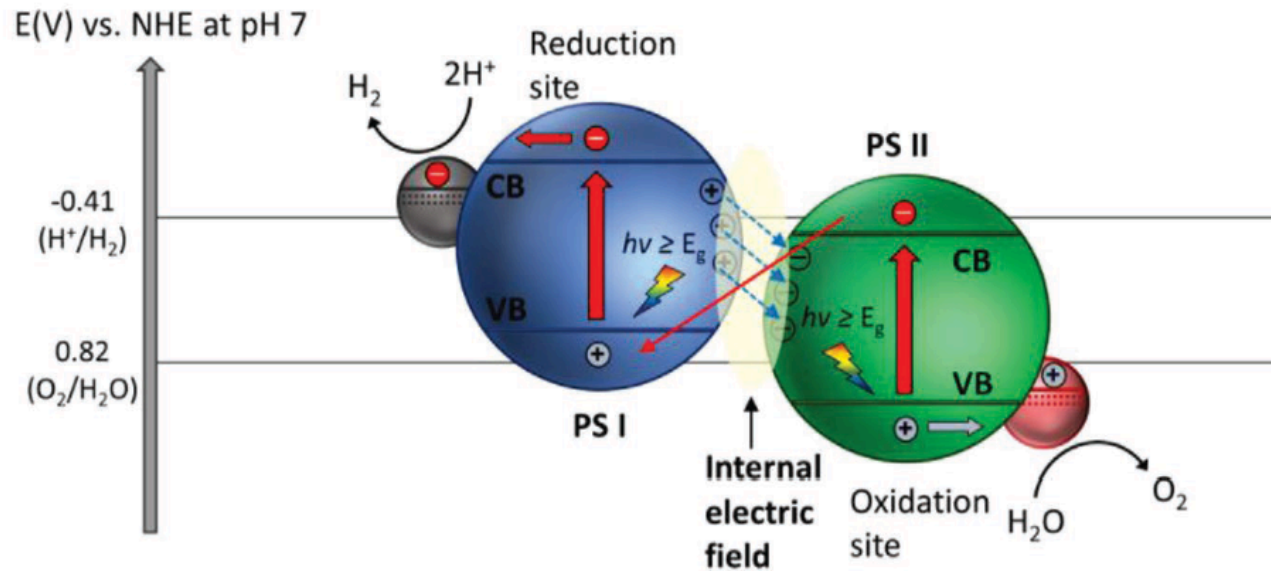


- Strong pH dependency:
 - IO_3^-/I^- can only function at pH more than 9 due to the formation of inactive I_3^- at lower pH value.
 - Fe^{3+}/Fe^{2+} is only stable at pH lower than 2.5 due to the precipitation of $Fe(OH)_3$ at higher pH value.
- Parasitic light absorption by redox mediator, i.e., strong absorption up to 450 nm by aqueous Fe^{3+} .
- Backward reaction due to back donation of charge carriers (red dotted lines), e.g. $6e^-$ in IO_3^-/I^- redox reaction.
- 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.

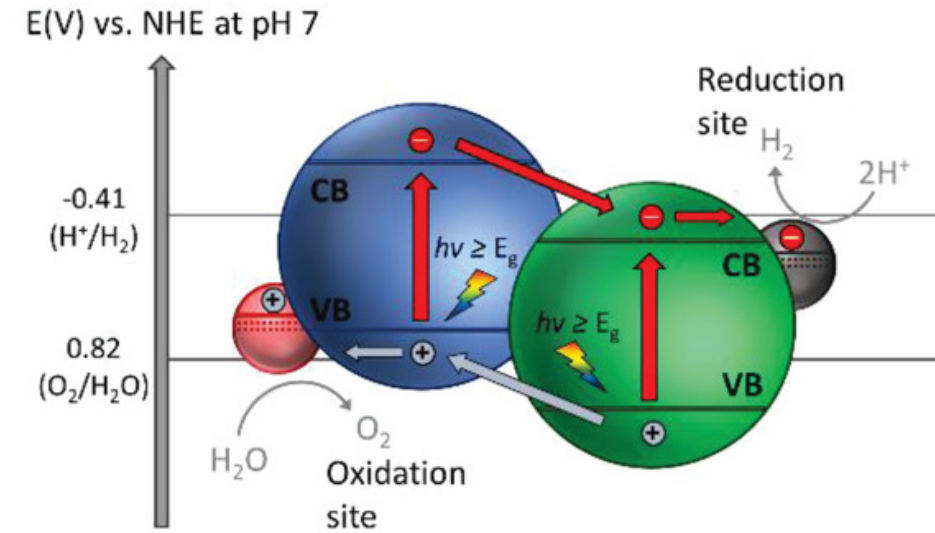


- Constraints in the development of PS-C-PS: The PS and electron mediator have to be assembled in a single unit.
- Suitable fabrication methods are essential for the development of these systems to ensure intimate contact interface between PS and electron mediator.
- Costly electron mediator: metals (Ag, Au, Ir etc) or nanocarbons (CNT, reduced graphite oxide, graphite etc).

Z-scheme with direct contact

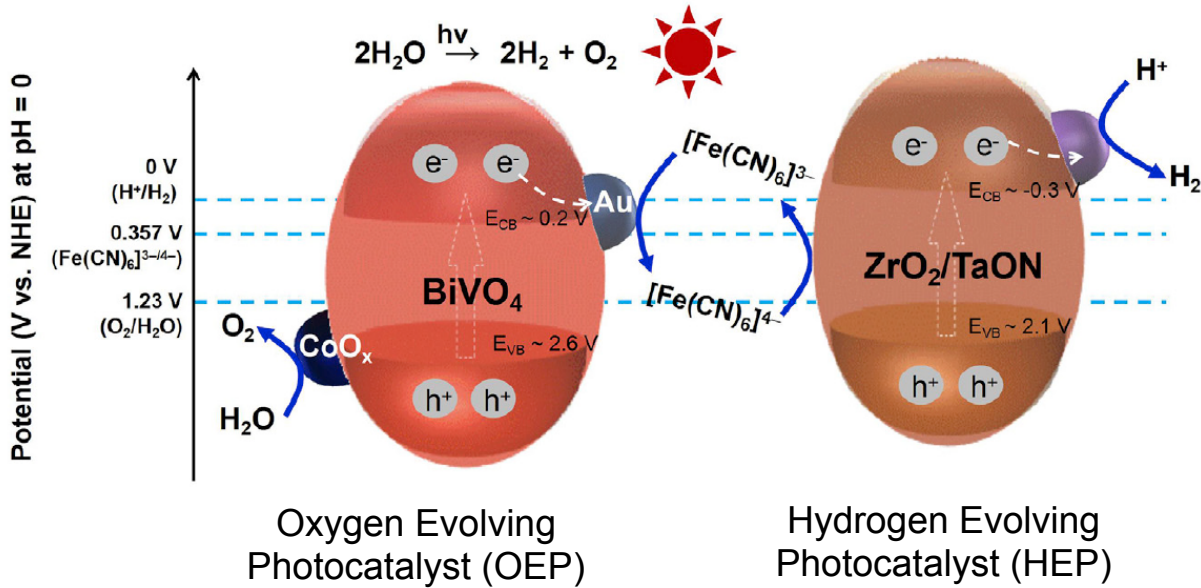


Type-II Heterojunction PC



- 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.

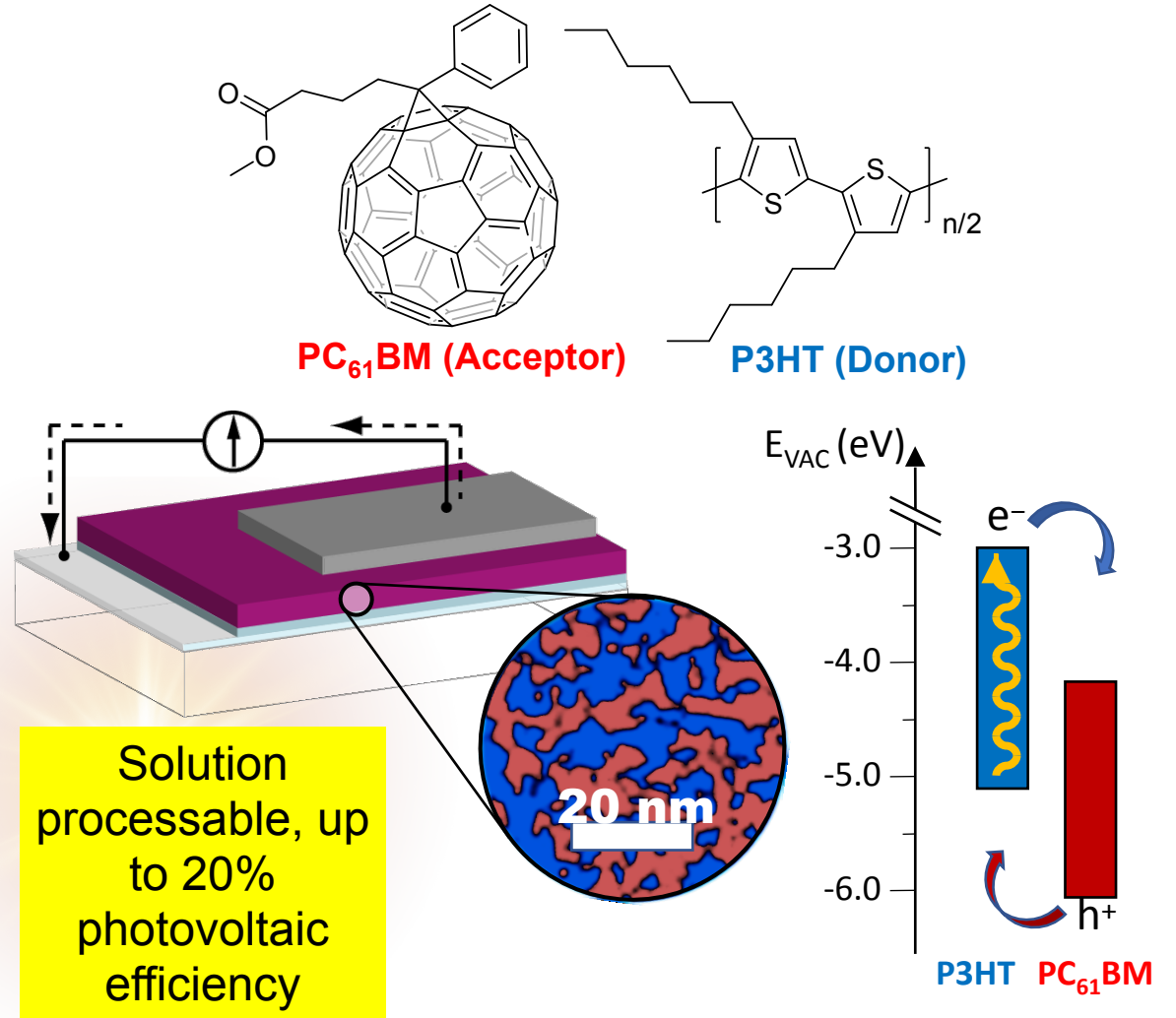
Performance is limited with inorganic photocatalysts



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)



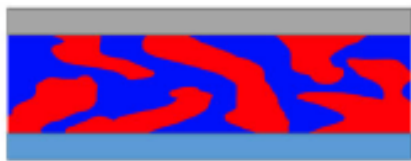
Organic photovoltaic cells



Single layer OPV



Planar heterojunction OPV



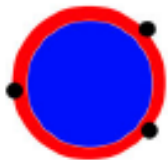
Bulk heterojunction OPV



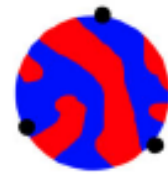
Organic photocatalysts



Single component photocatalyst



Core-shell morphology photocatalyst

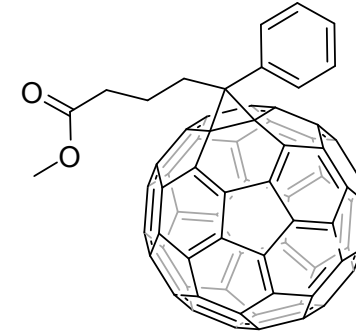


Heterojunction photocatalyst

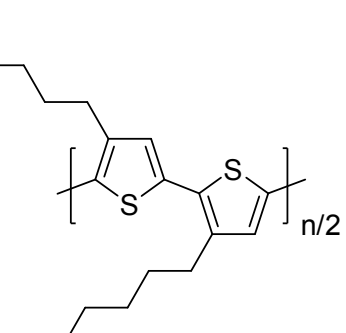
● Metal co-catalyst, *i.e.* Pt, Pd

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

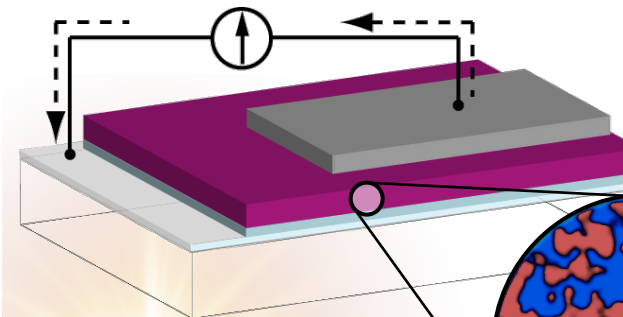
Organic semiconductor bulk heterojunction (BHJ)



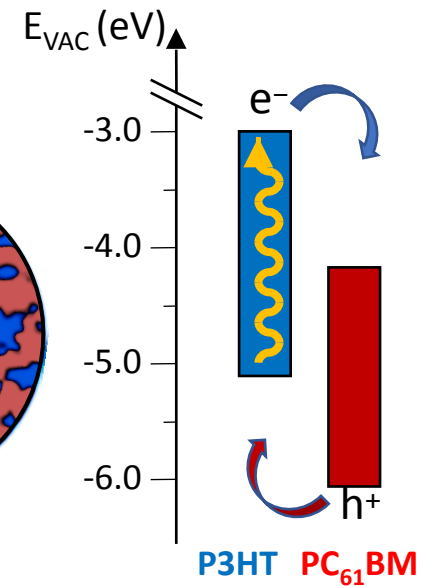
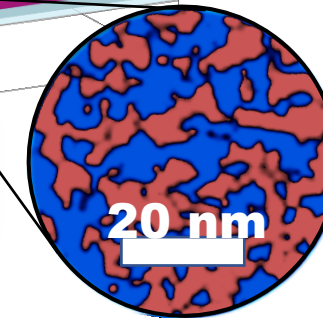
PC₆₁BM (Acceptor)

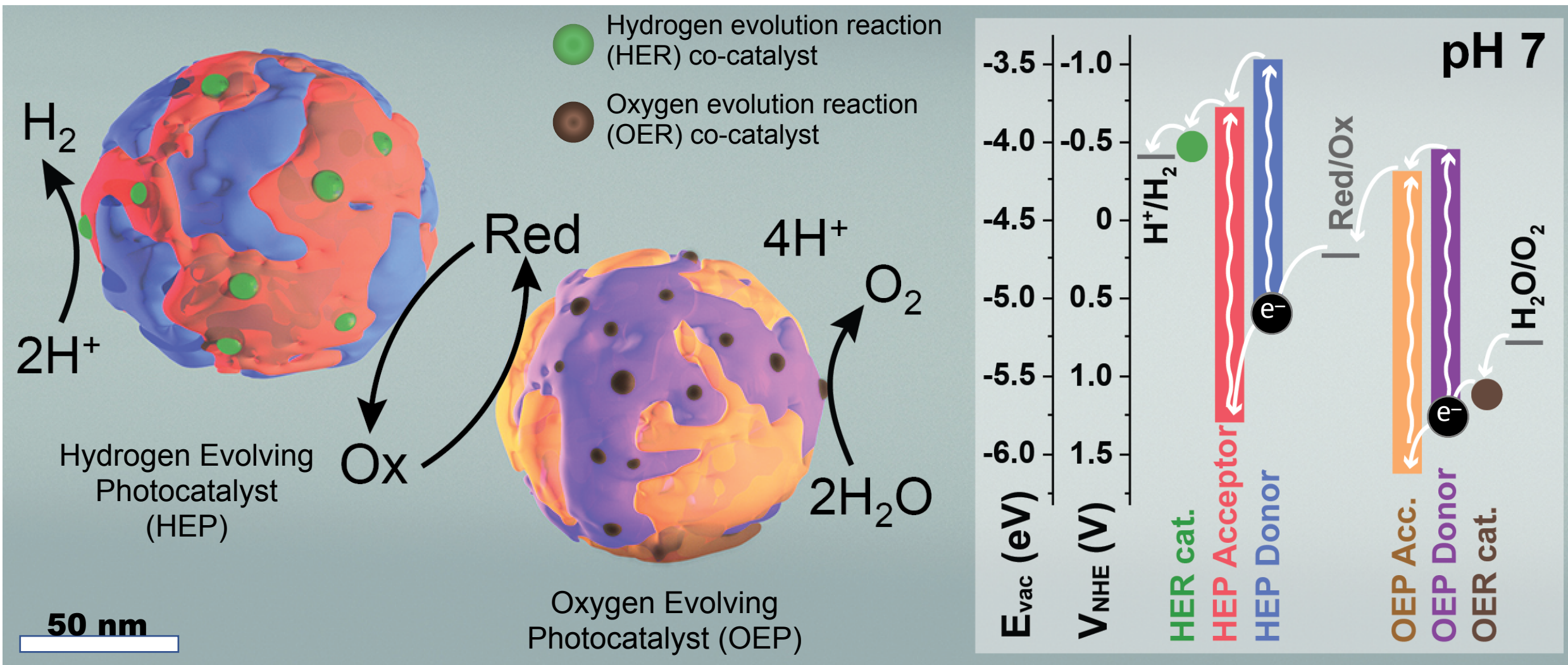


P3HT (Donor)

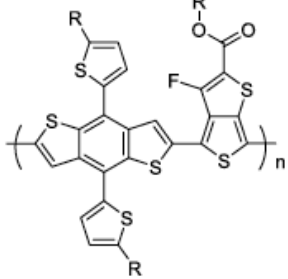


Solution processable, up to 20% photovoltaic efficiency

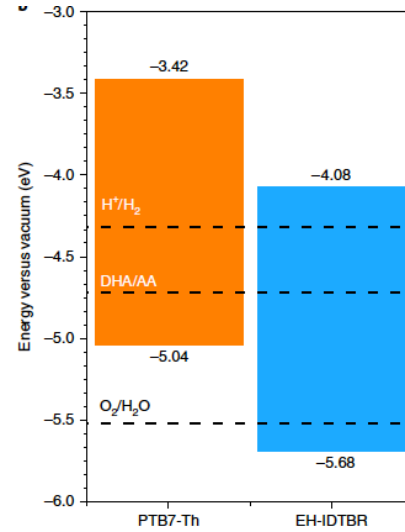
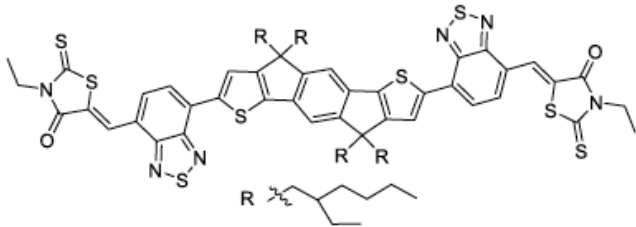




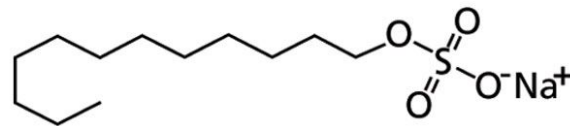
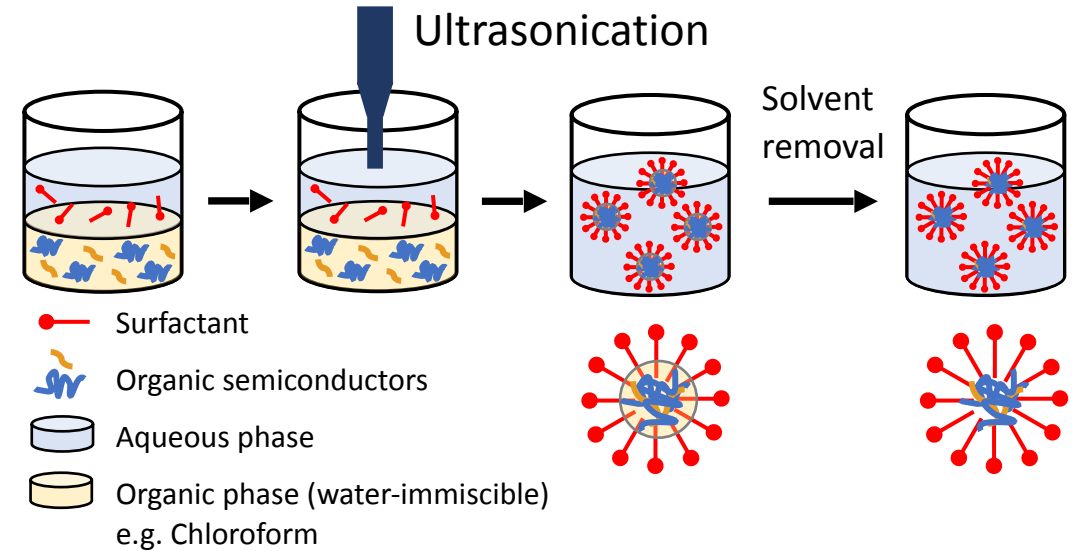
PTB7-Th



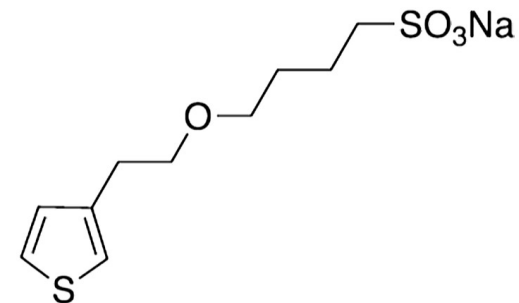
EH-IDTBR



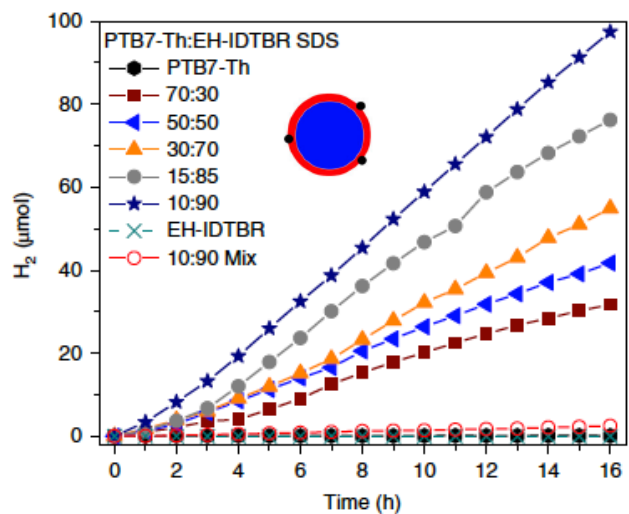
Miniemulsion method



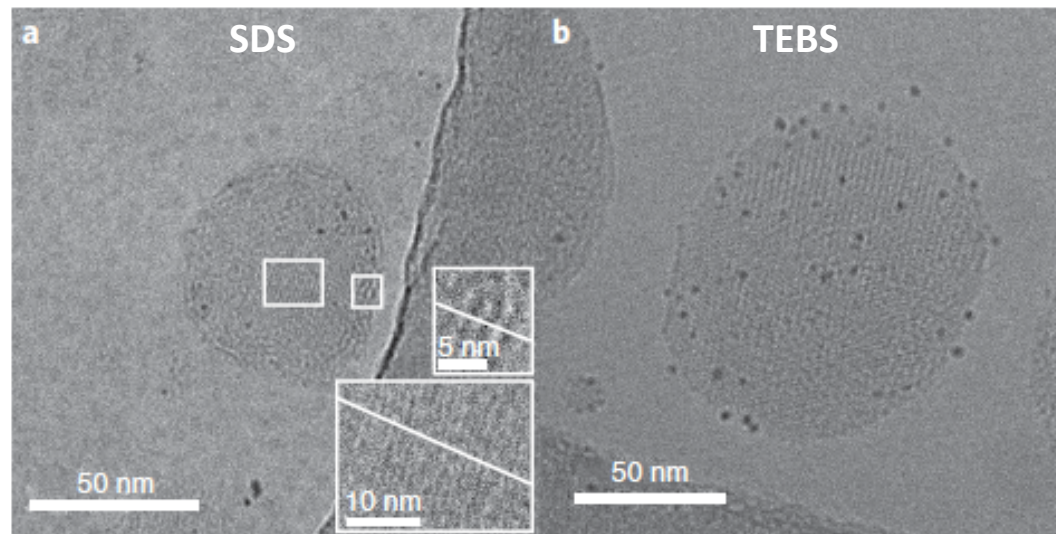
SDS: sodium dodecyl sulfate



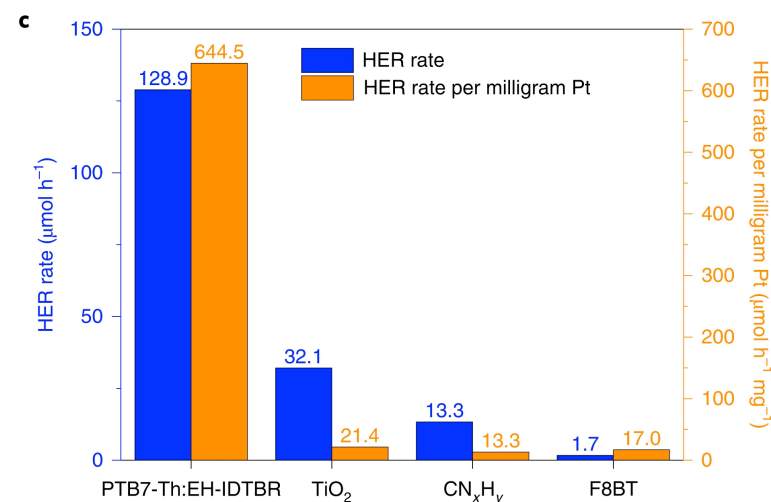
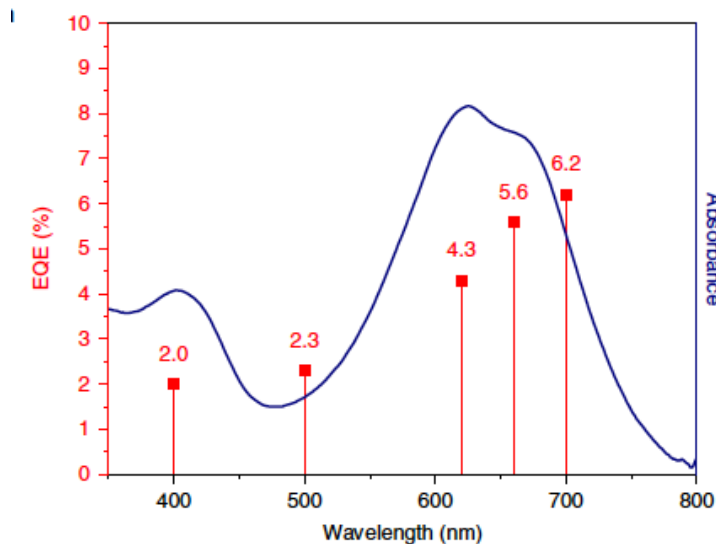
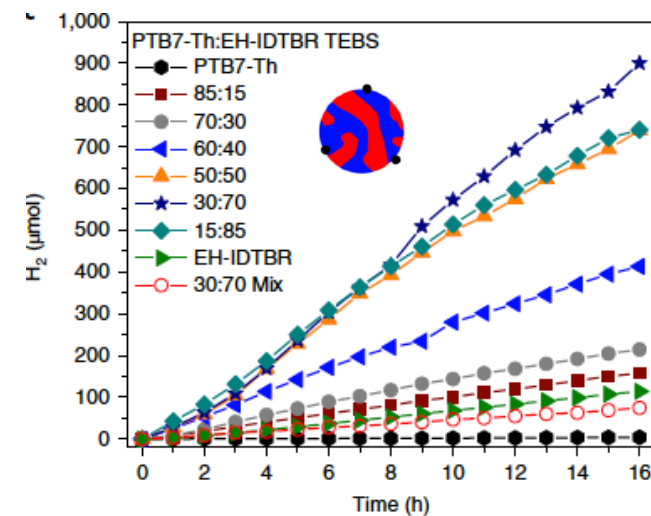
TEBS: 2-(3-thienyl)ethoxybutylsulfonate sodium salt

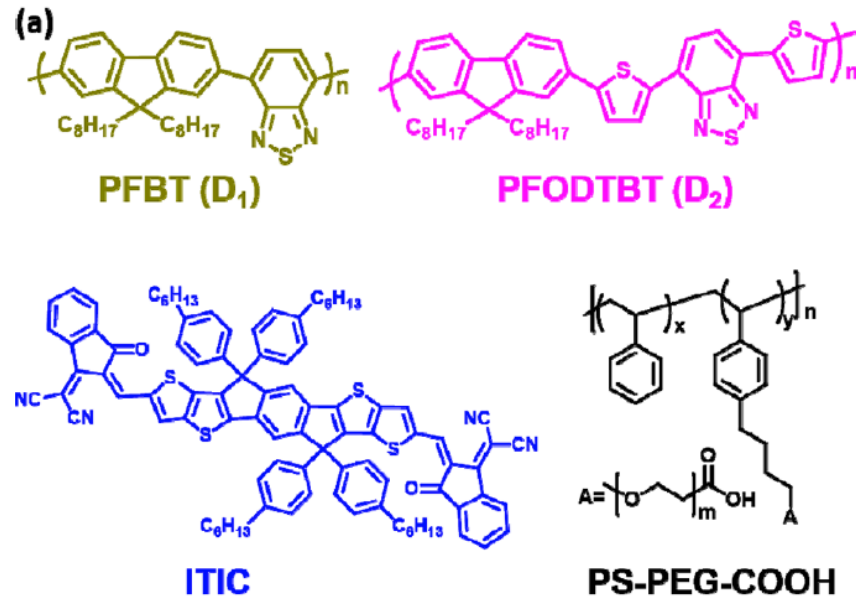


a PTB7-Th-rich shell and an EH-IDTBR-rich core



Transmission Electron Microscopy (TEM)





Nanoprecipitation method

