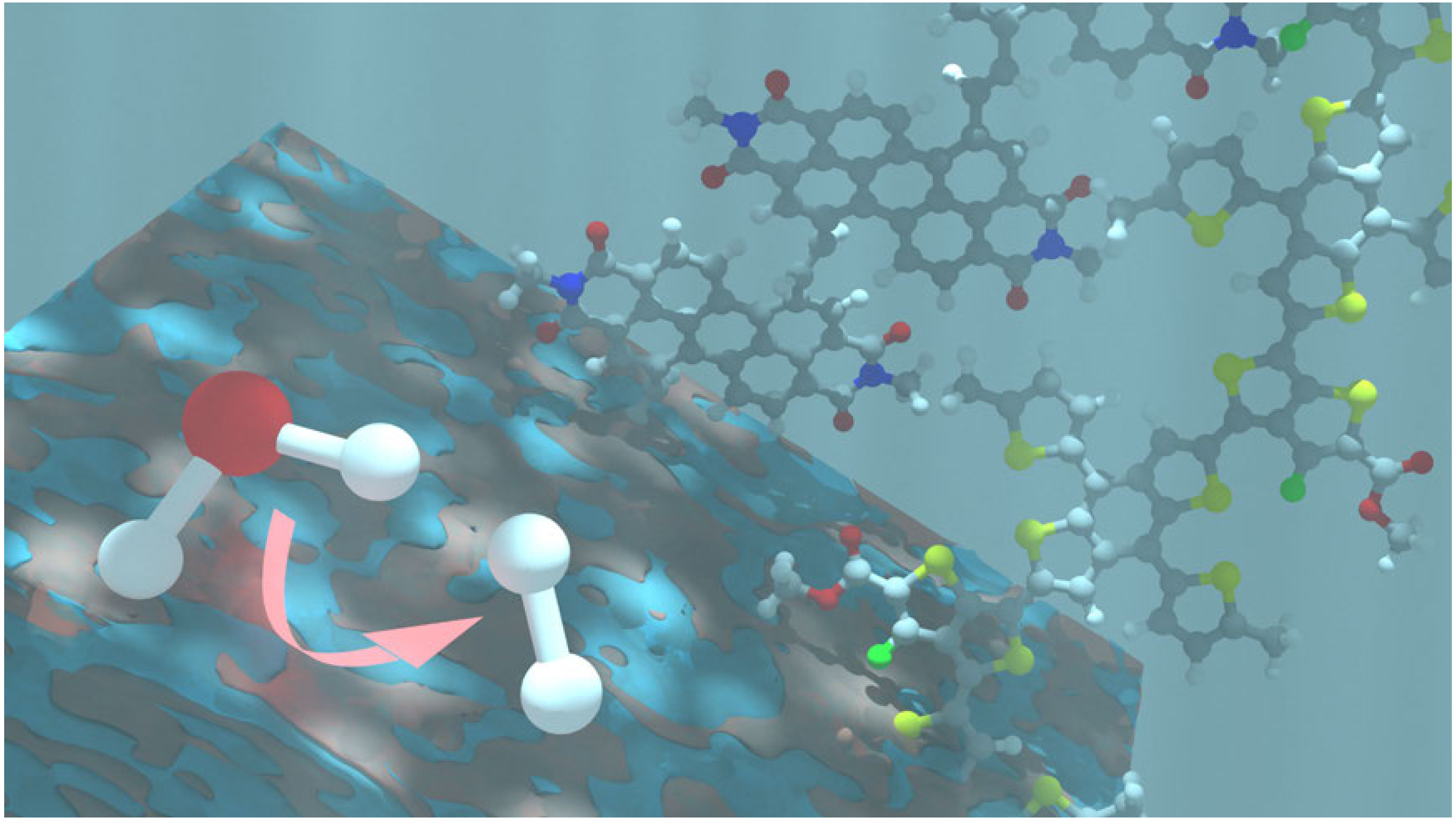


Solar-driven fuel production using semiconductor photocatalysts

Kevin Sivula

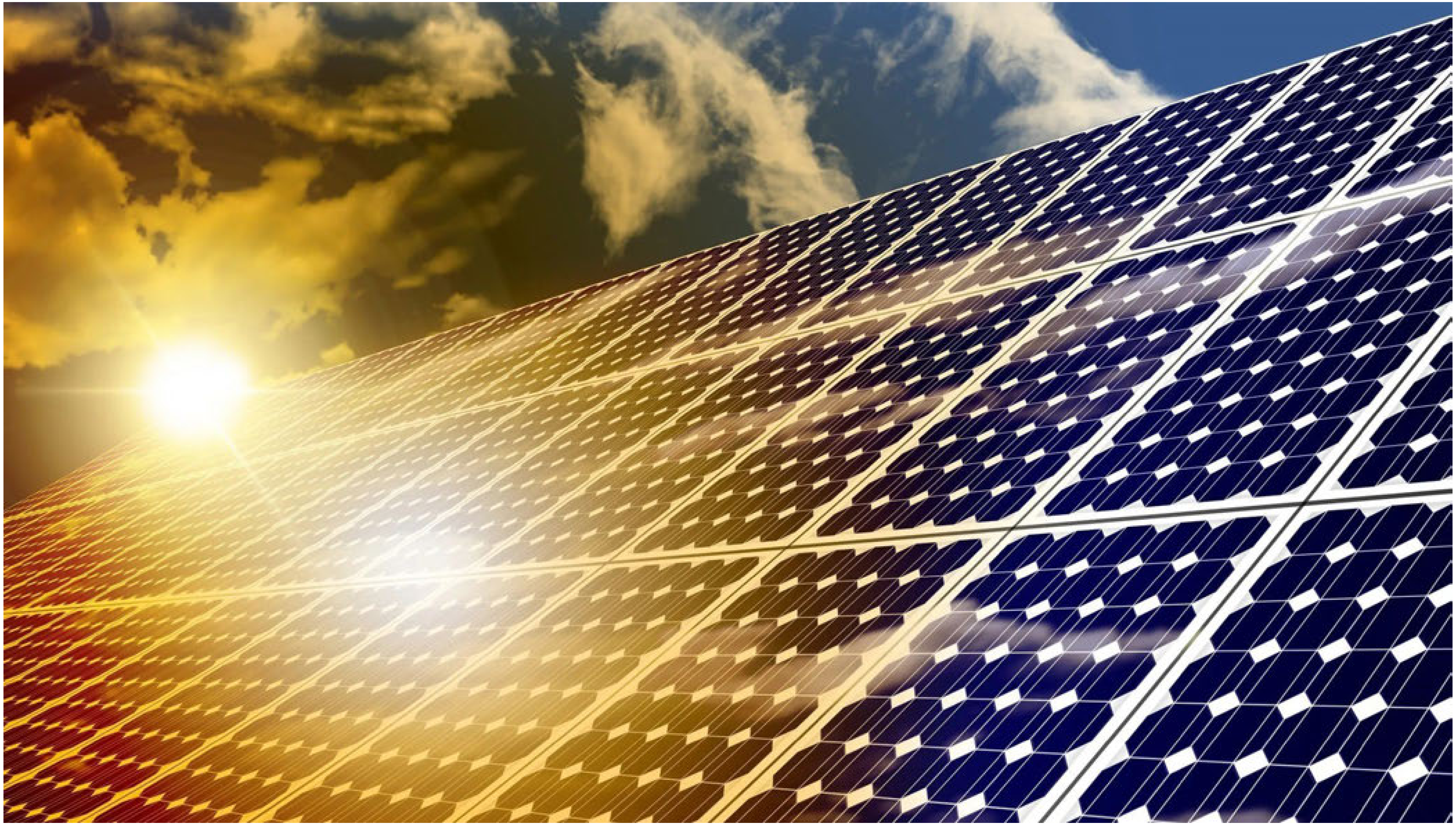
Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO)

EPFL

kevin.sivula@epfl.ch

- Optoelectronic materials detect, convert, and control light

Conversion and storage of solar energy



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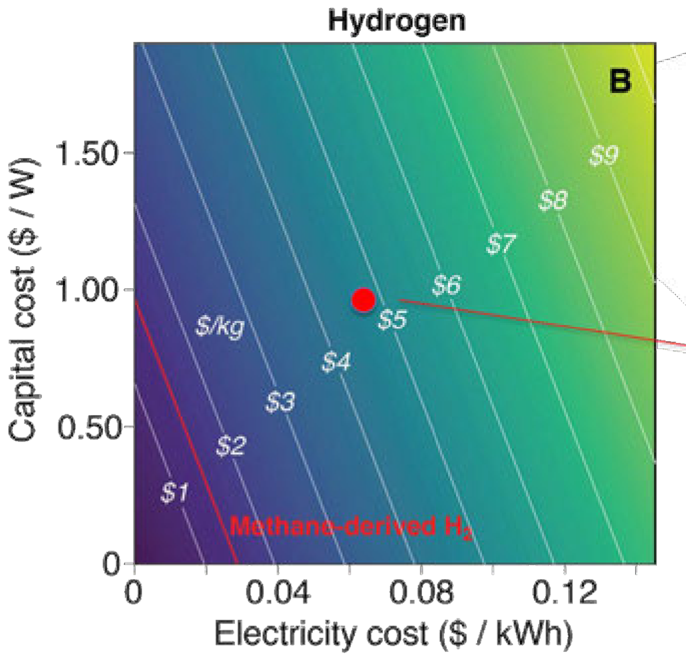
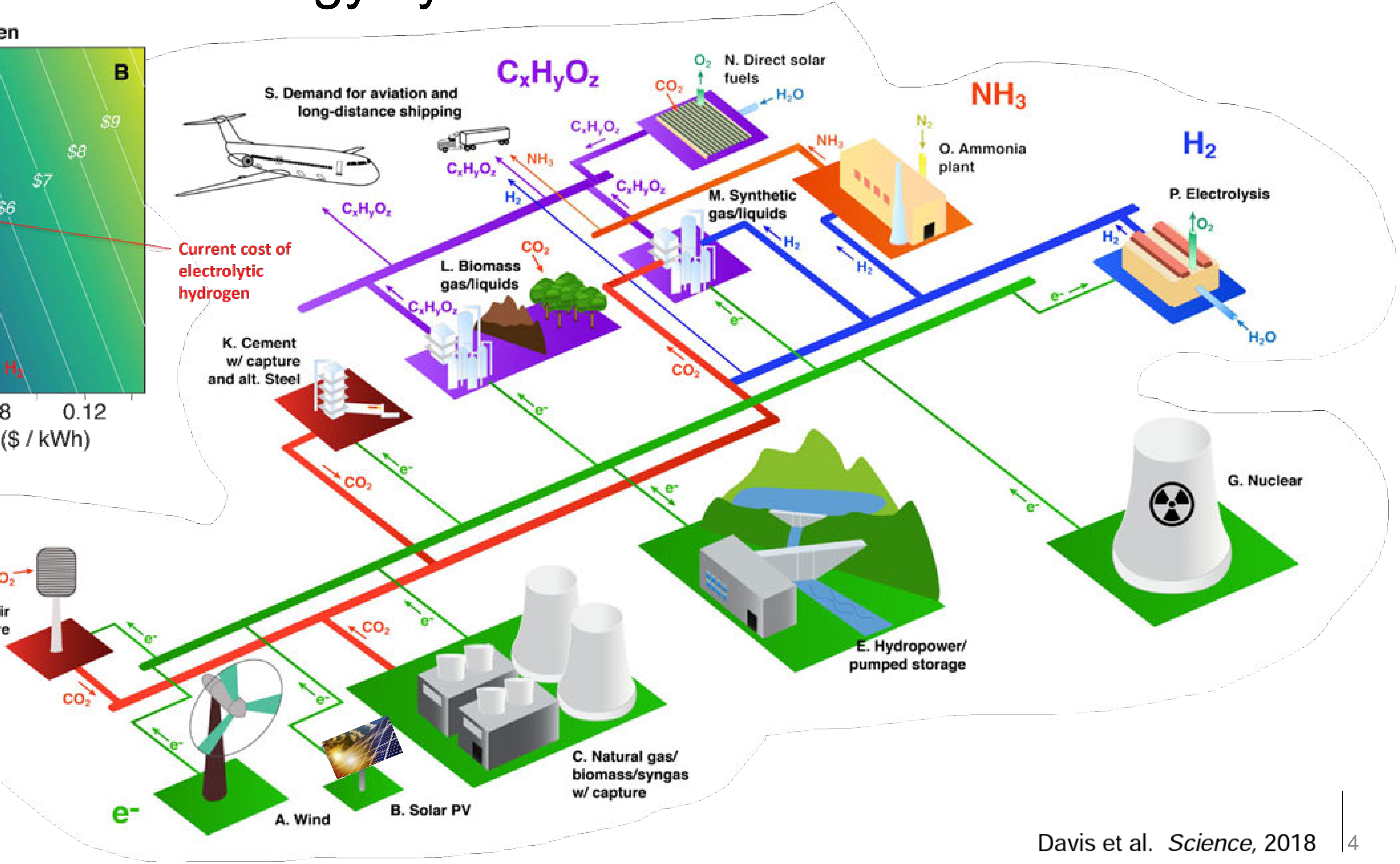
Carbon-neutral energy systems for fuels and chemicals

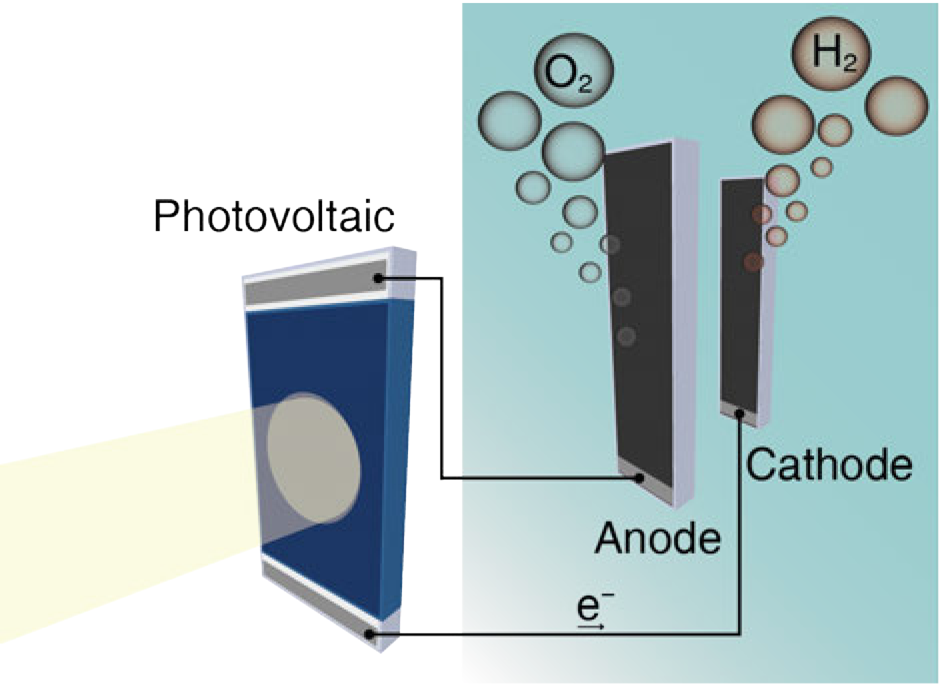




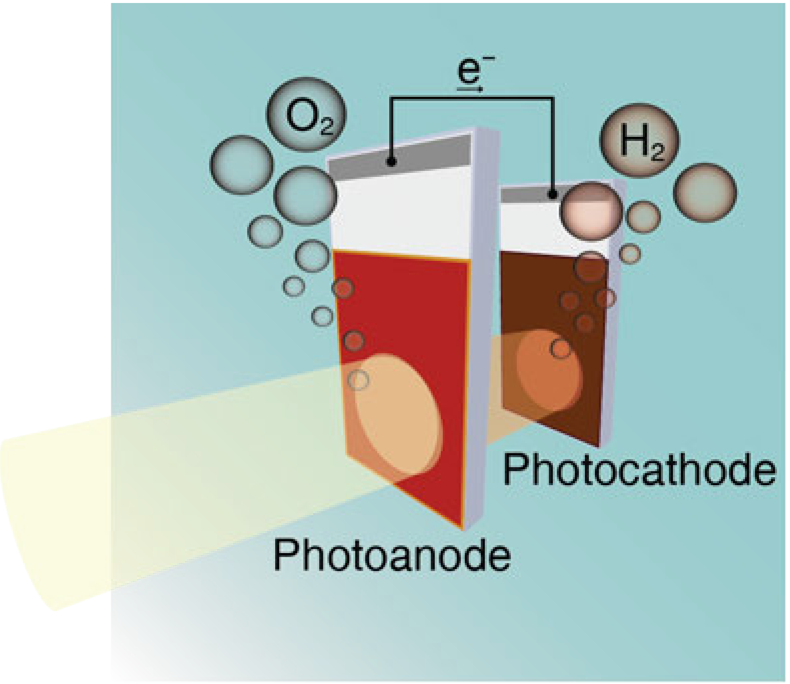
Davis et al. *Science*, 2018

Routes for Solar-to-Hydrogen Conversion

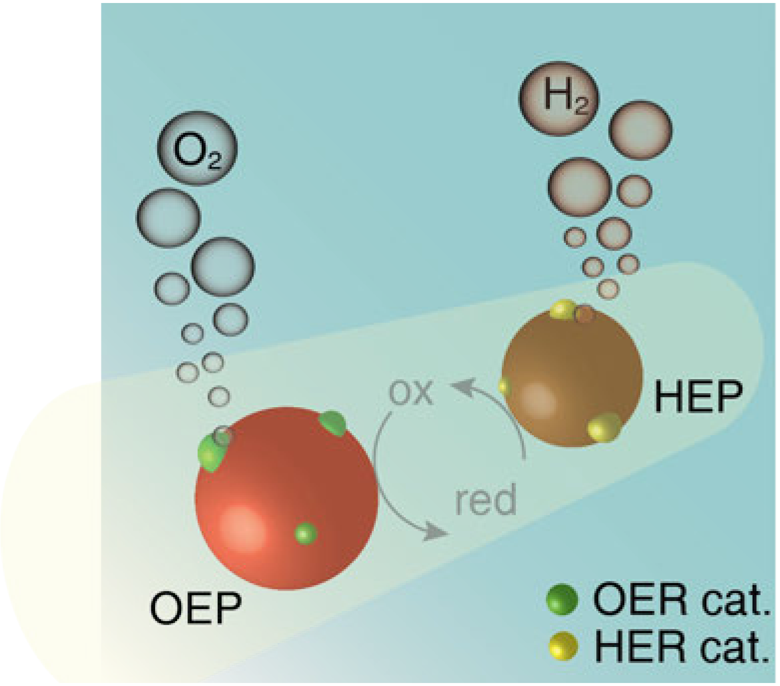
PV + Electrolysis



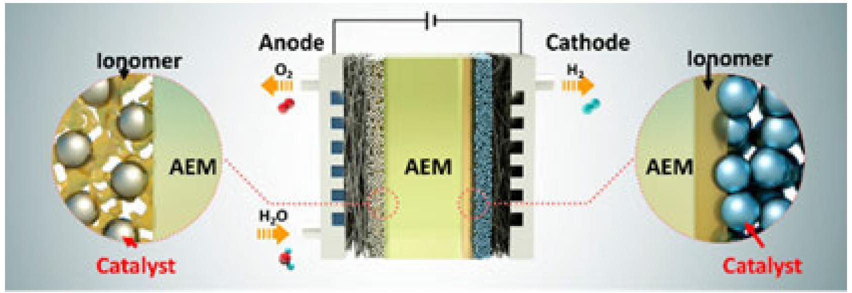
Photoelectrochemical (PEC)



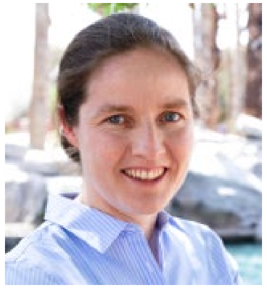
Photocatalytic (PC)



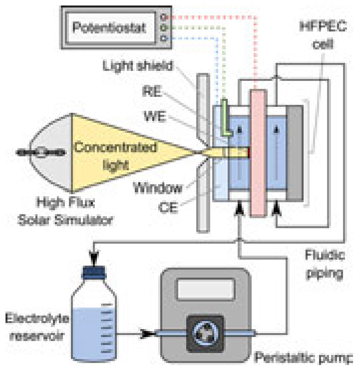
Prof. Xile Hu

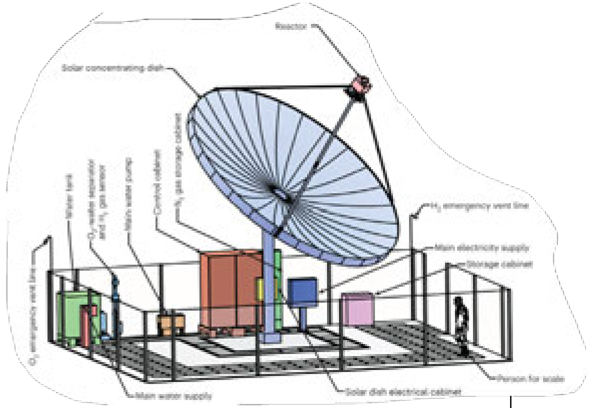


Anion exchange membrane water electrolyzer (AEMWE)



Prof. Sophia Haussener





kW-scale pilot plant capable of co-generation of hydrogen and heat

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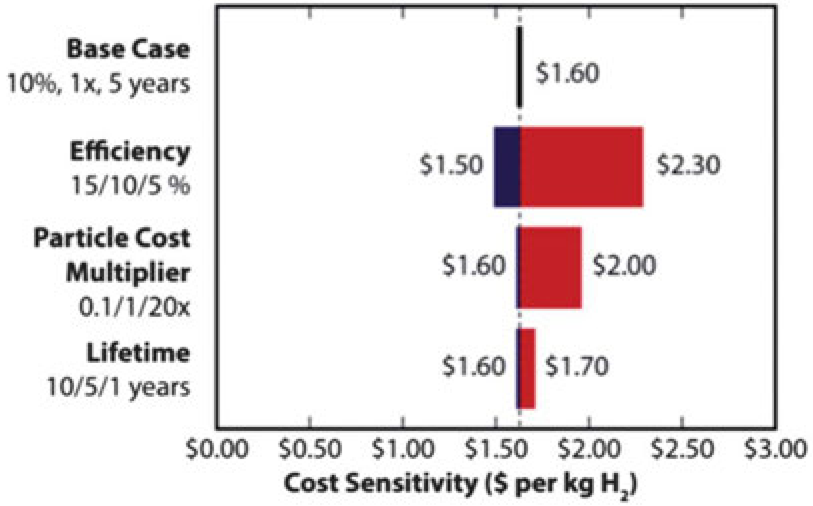
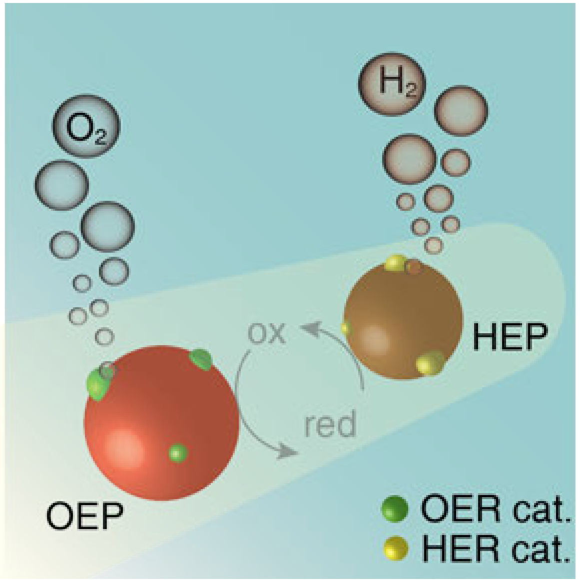
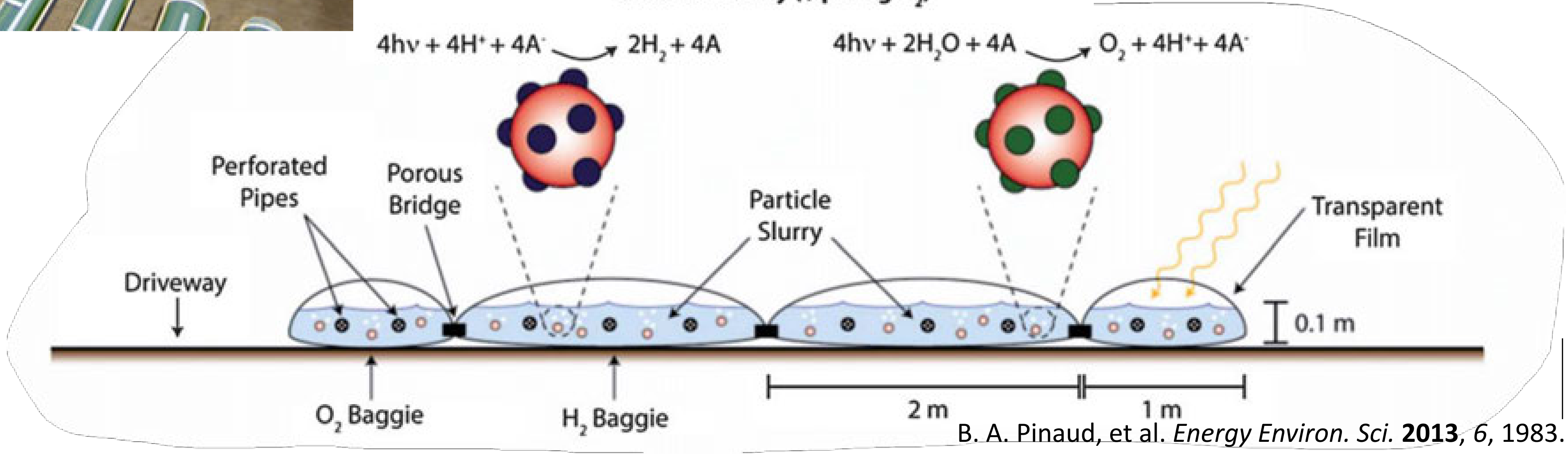
Photocatalytic Solar H_2 production: a scalable approach

HyperSolar

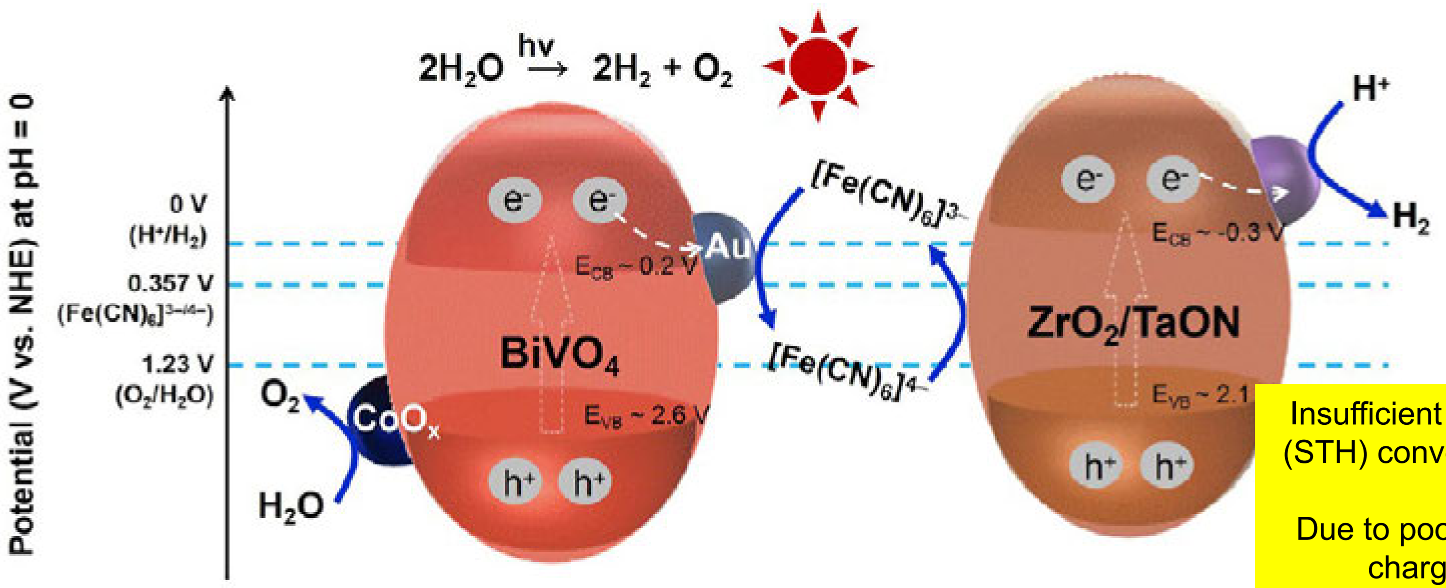






B. A. Pinaud, et al. *Energy Environ. Sci.* **2013**, *6*, 1983.

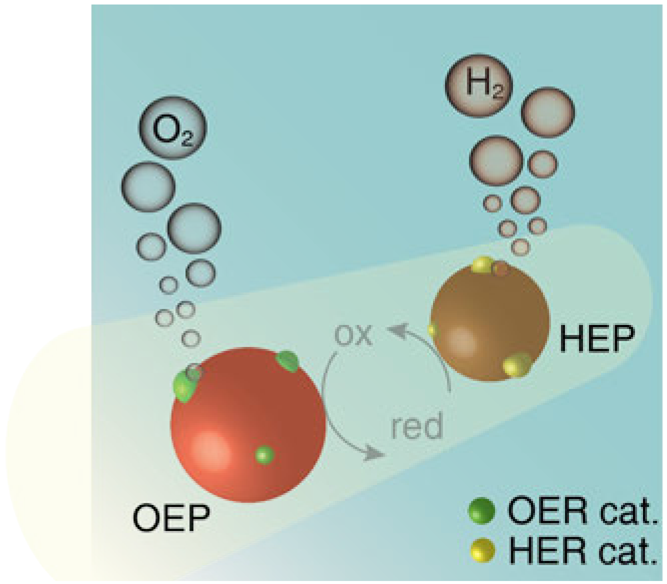
Inherent problem with photocatalysis



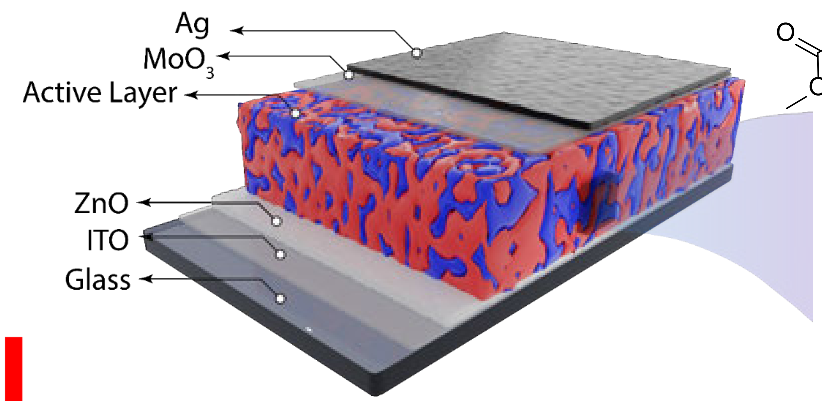
Oxygen Evolving Photocatalyst (OEP)

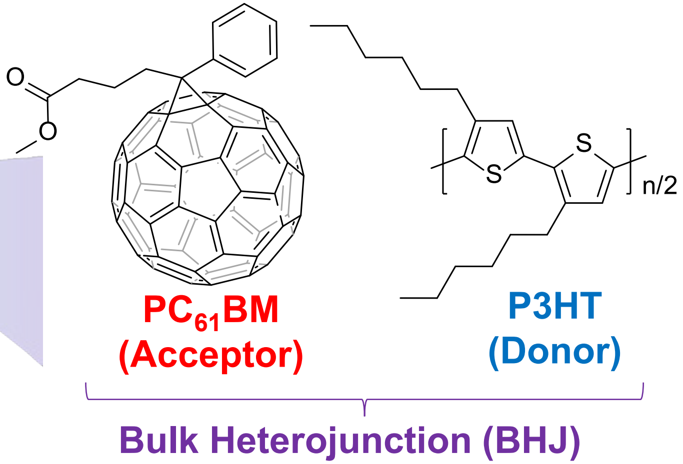
Hydrogen Evolving Photocatalyst (HEP)

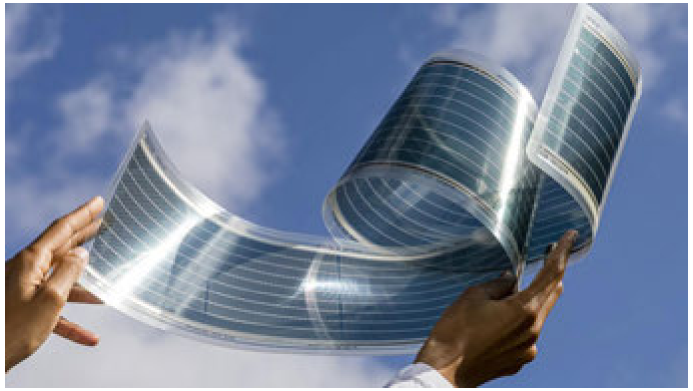
Insufficient solar-to-hydrogen (STH) conversion efficiency of ~ 1%
Due to poor photogenerated charge separation



Y. Qi, Y. Zhao, Y. Gao, D. Li, Z. Li, F. Zhang, C. Li, *Joule* **2018**, 2, 2393

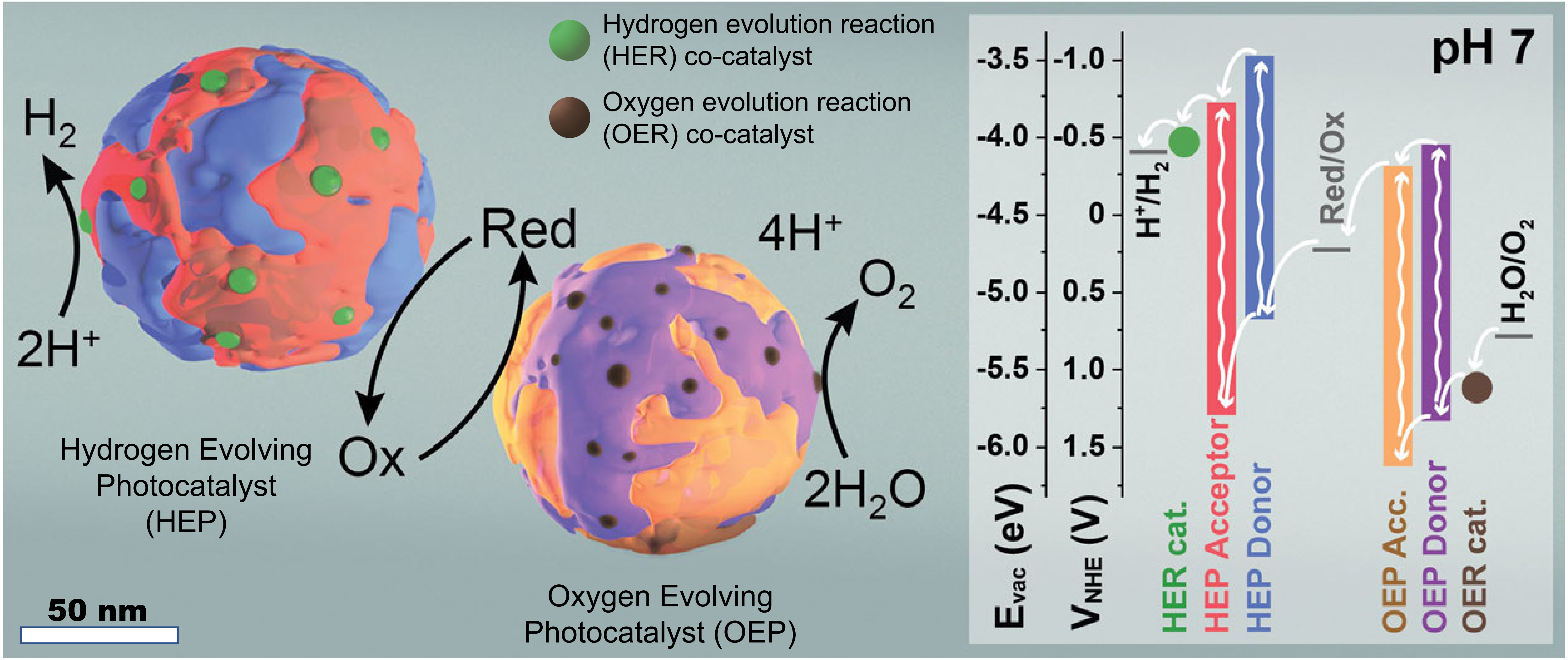






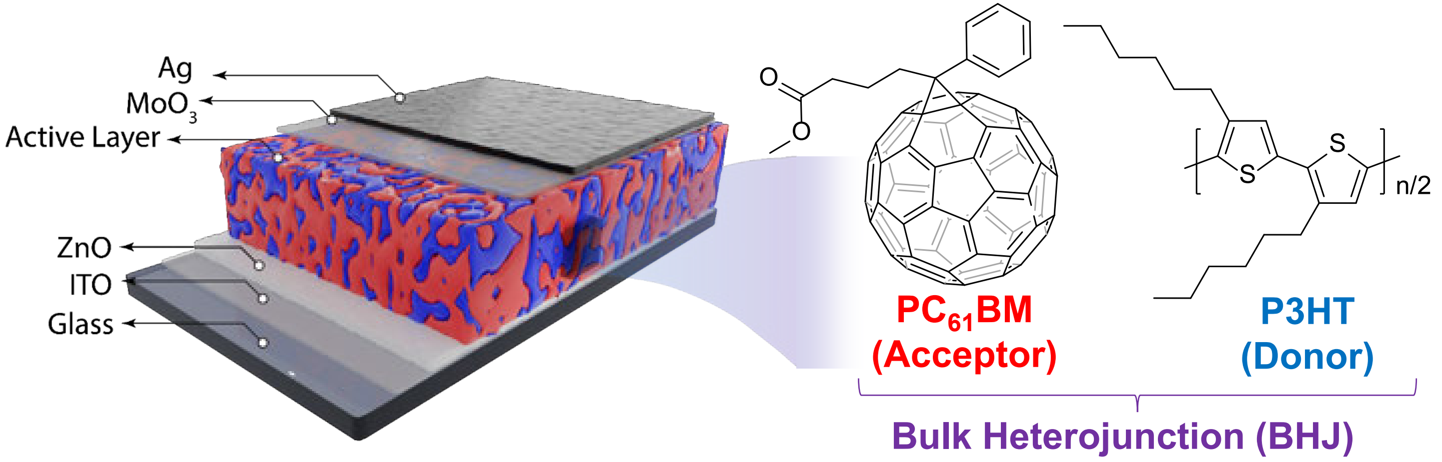
Bulk heterojunction organic semiconductor blends include a way to develop charge separation on a nanometer length scale !

Bulk-heterojunction (BHJ) organic photocatalysts

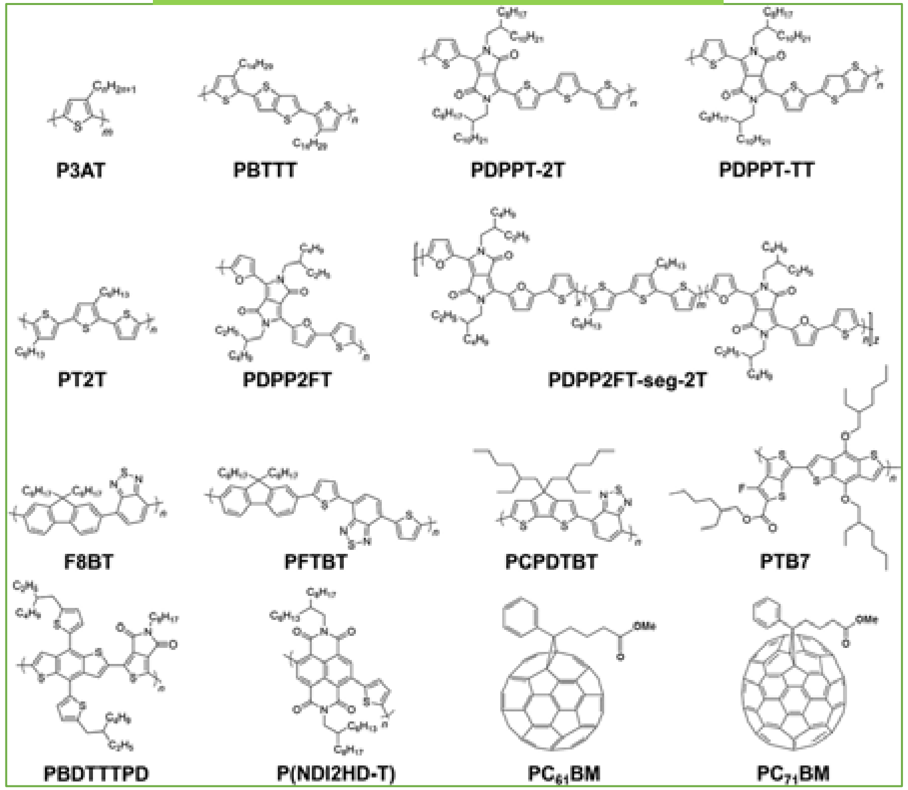


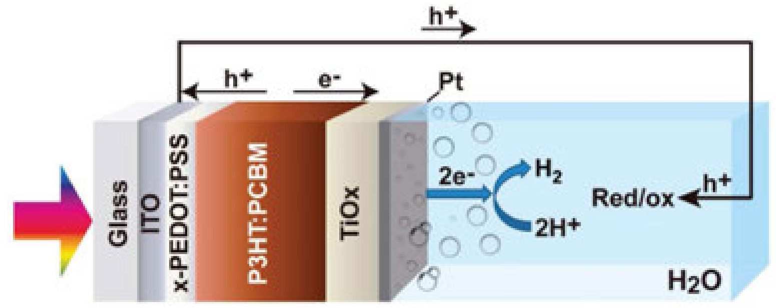
See recent demonstrations of this concept: *Nature Materials* **2020**, *19*, 559–565
Nature Energy **2022**, *7*, 340–351

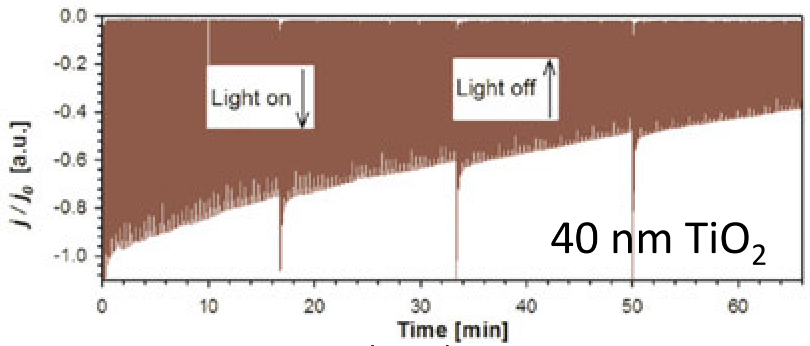
Towards organic semiconductors for solar H_2 production



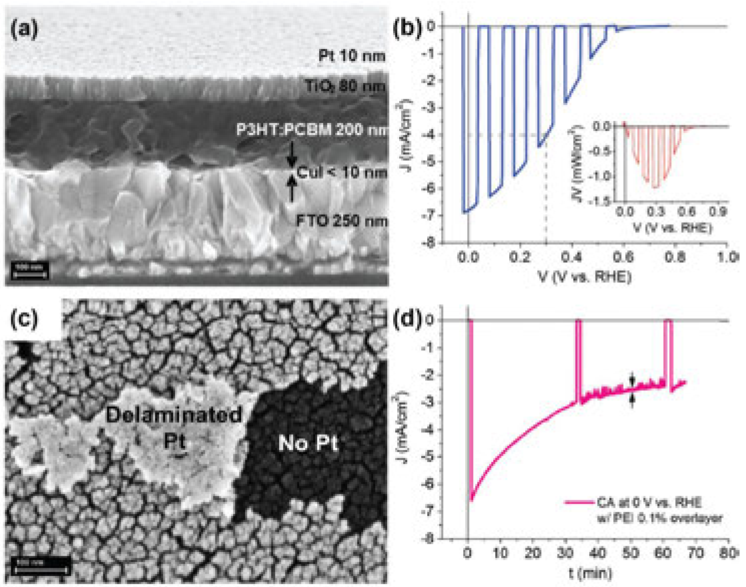
Molecular engineering of chemical structure affords tuning of optoelectronic properties !







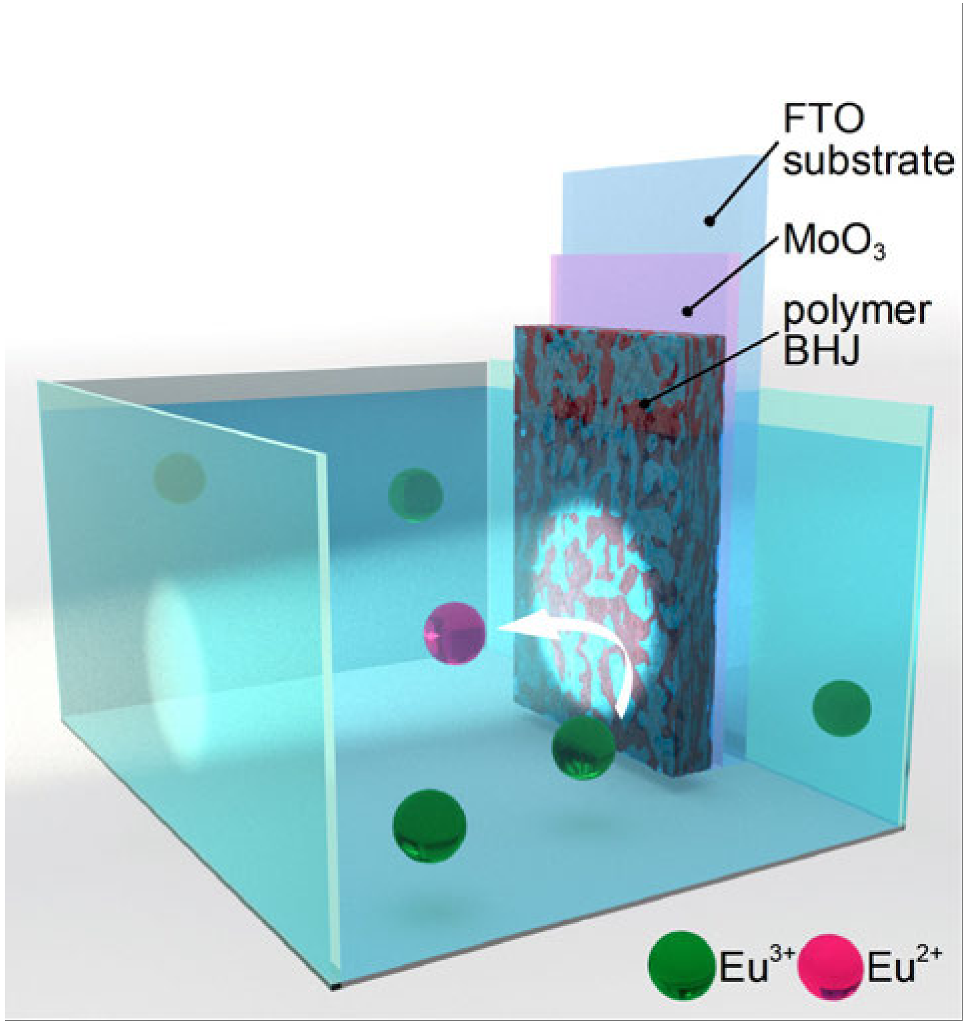
M. Haro, …, A. Guerrero, *J. Phys. Chem. C* **2015**, *119*, 6488.

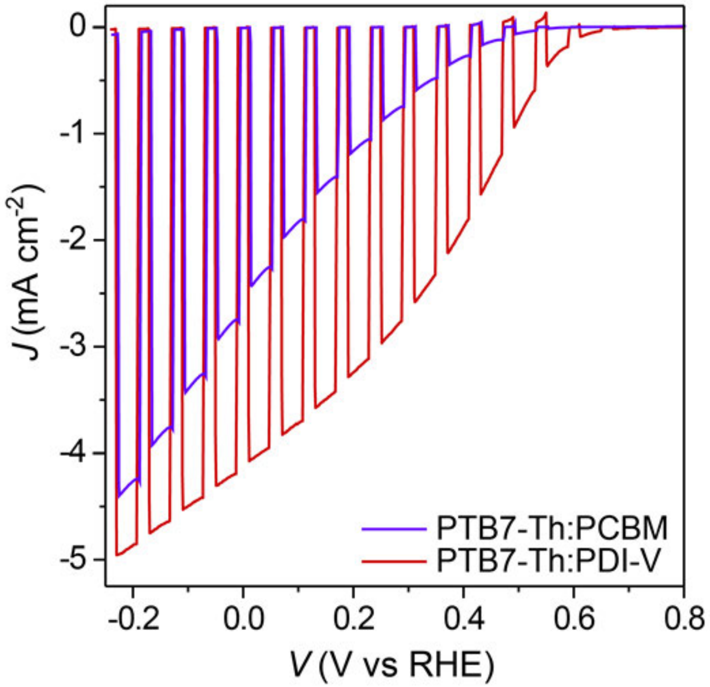


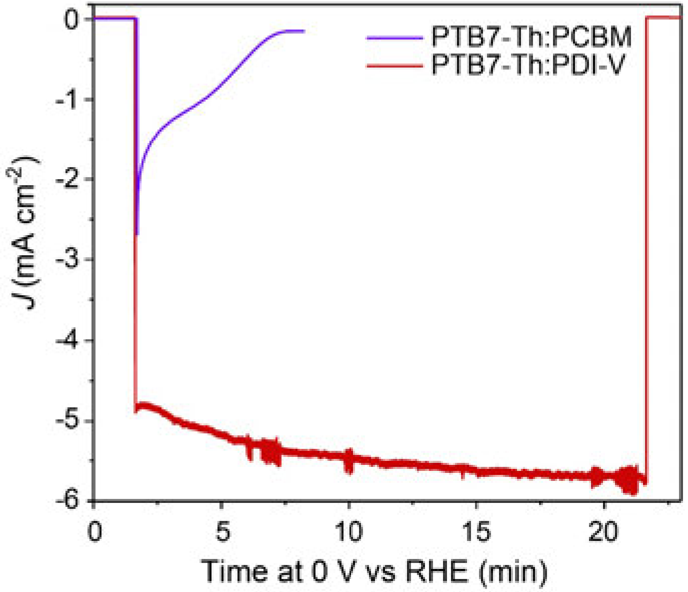
H. Comas Rojas, …, M. R. Antognazza, *Energy & Environmental Science* **2016**, *9*, 3710.

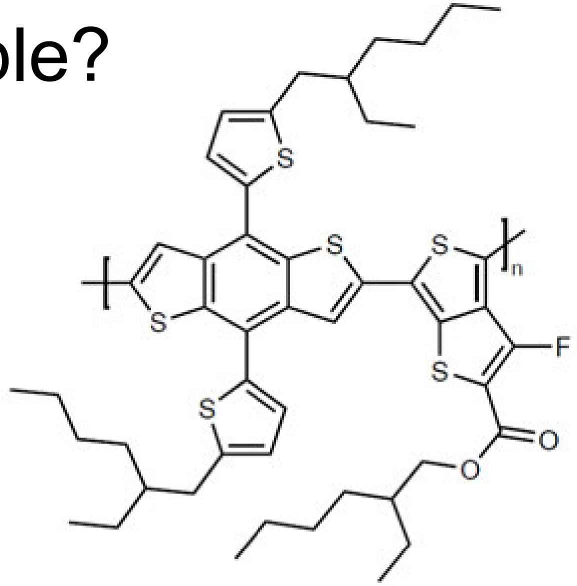
Can organic semiconductors attain stable operation under photocatalytic or photoelectrochemical operation ?

Can a direct BHJ/water junction photocathode be stable?

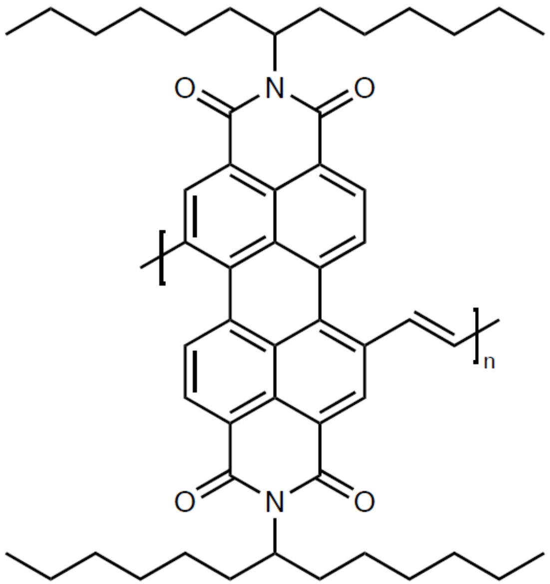






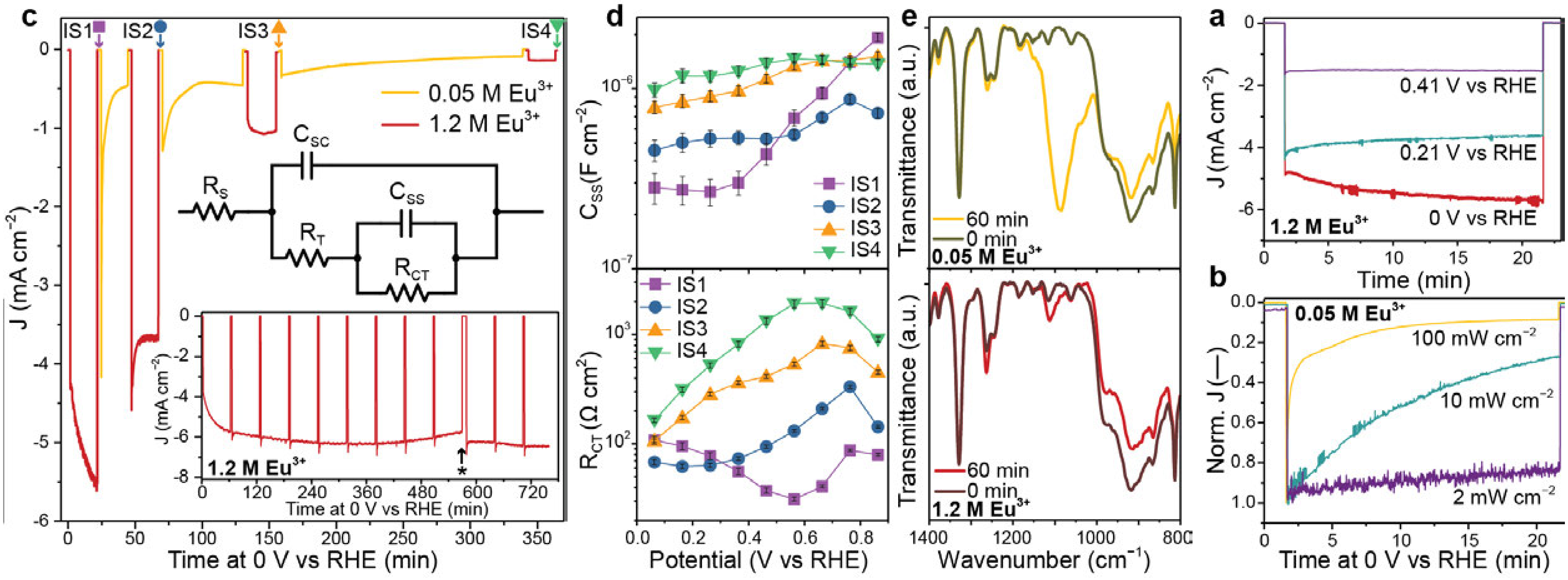


PTB7-Th



PDI-V

Insights into stability of BHJ with electron scavenger



*Photogenerated electron accumulation at the BHJ/electrolyte interface causes chemical damage

*If charge accumulation can be kept low, (order of 100 nC cm^{-2}), stable (>12h) photocathodes are possible

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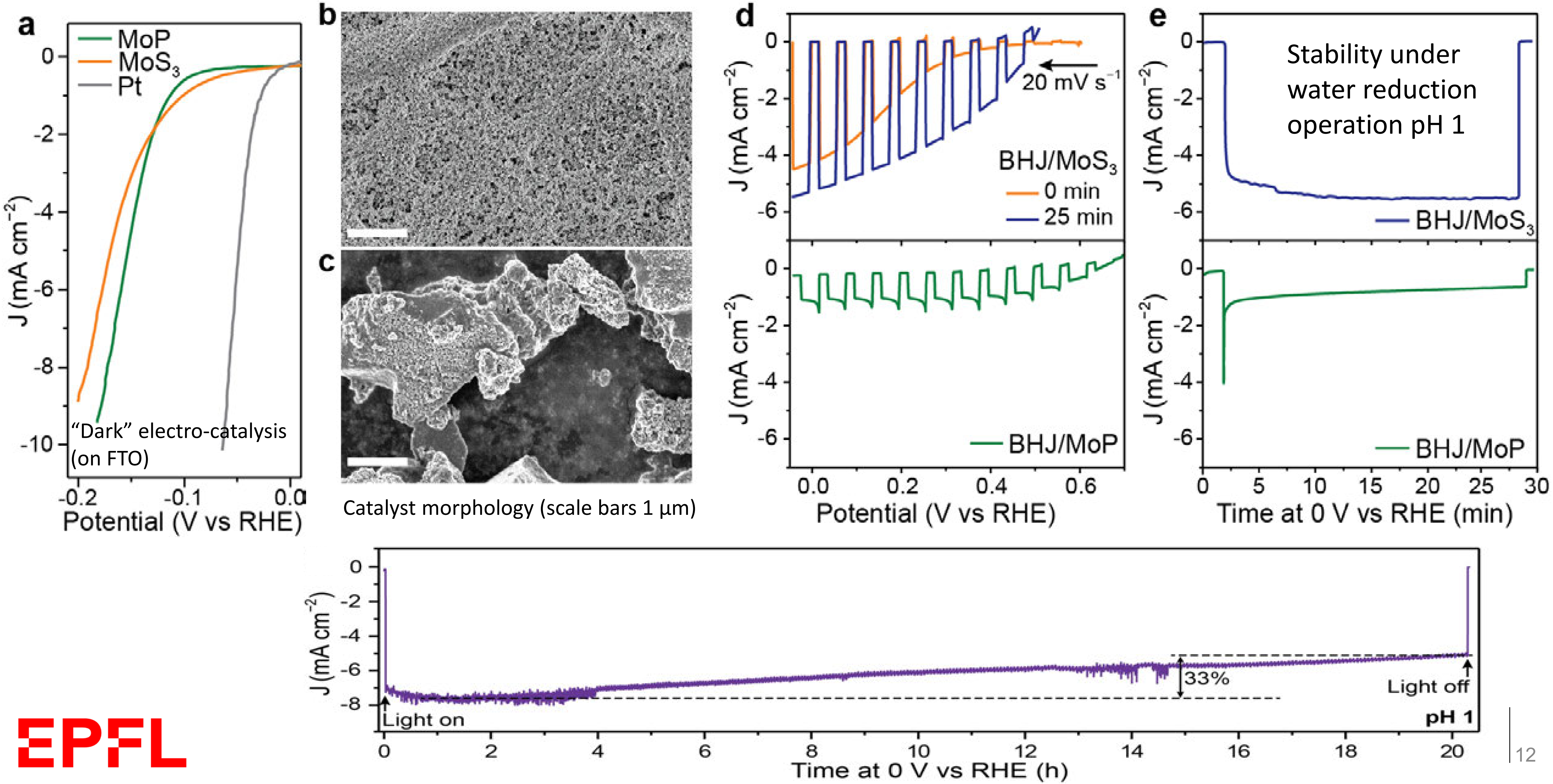
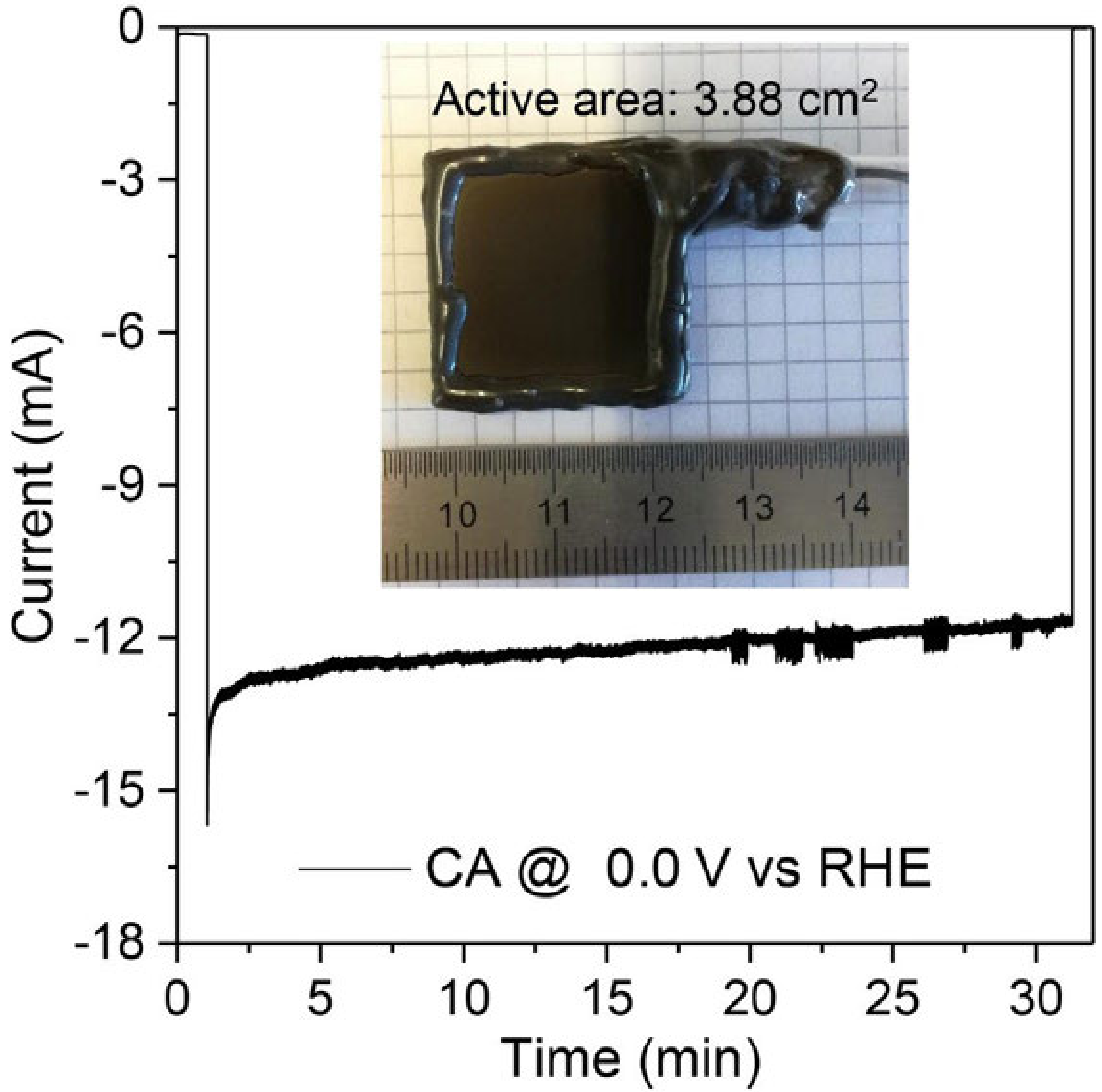
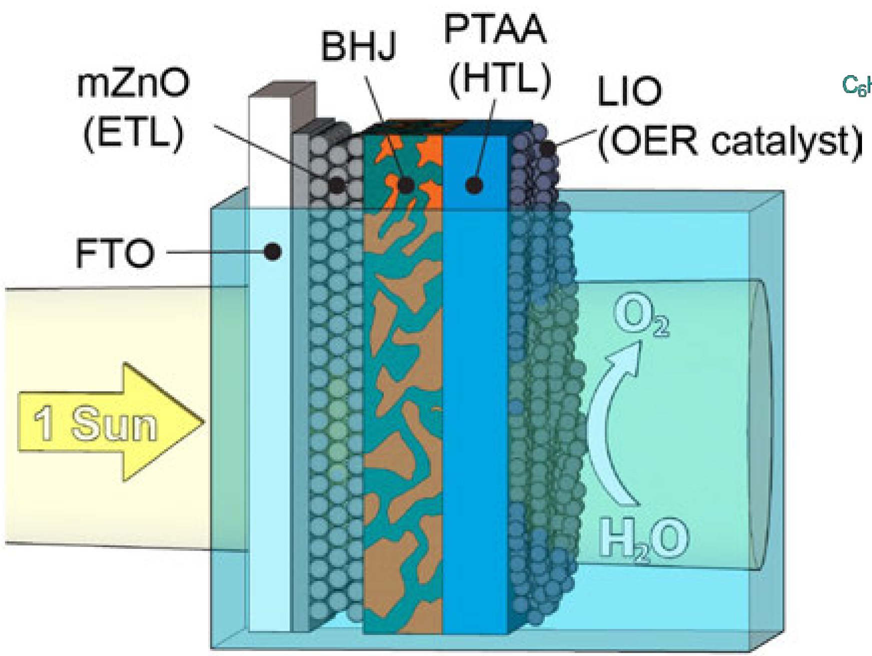
Adding a catalyst to drive H_2 production

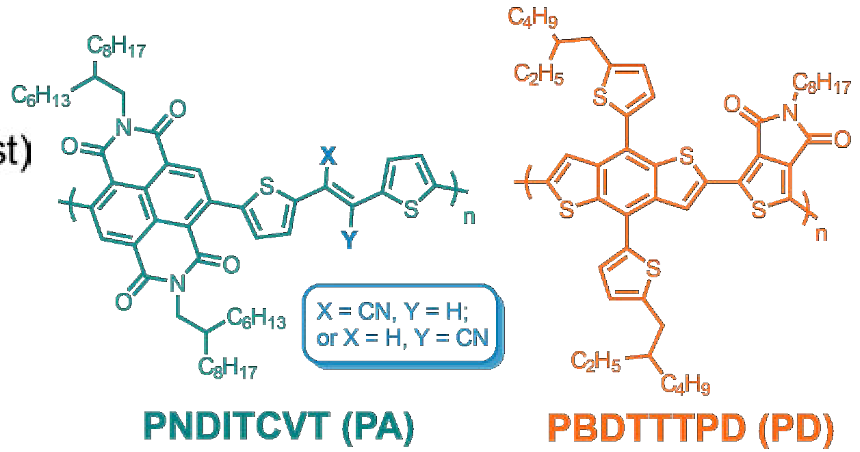


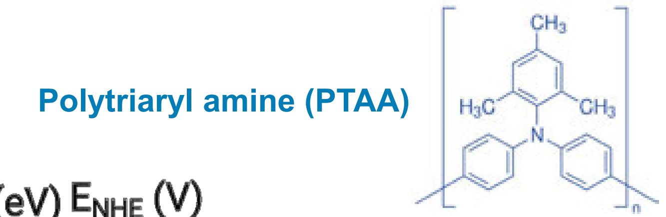
Large area demonstration

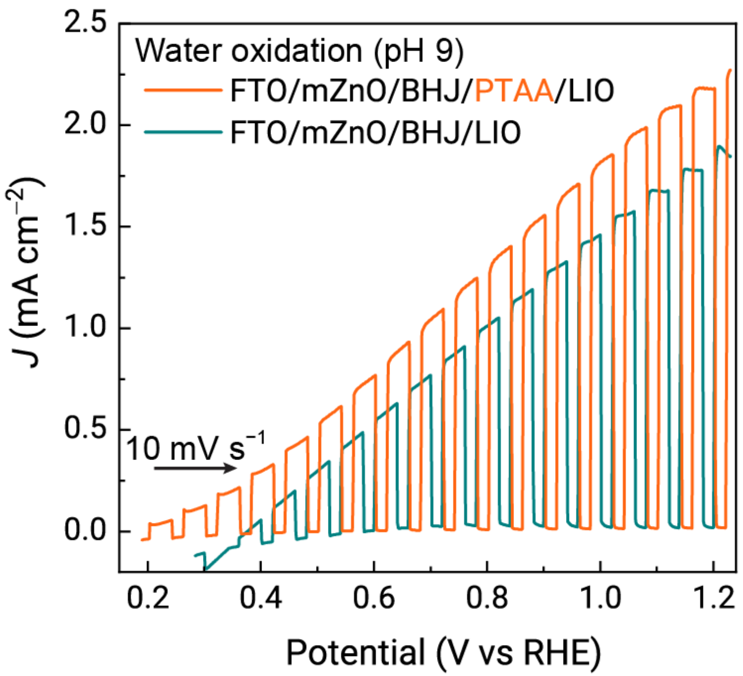


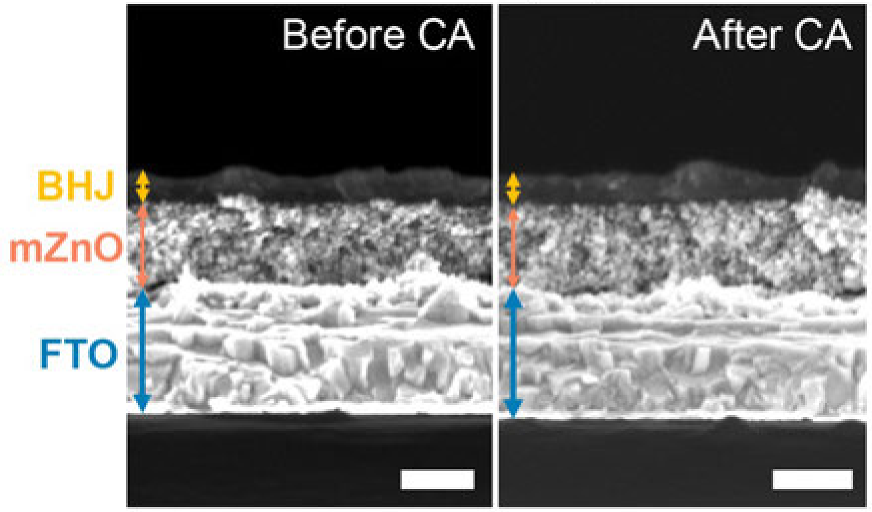
A BHJ photoanode for O_2 evolution



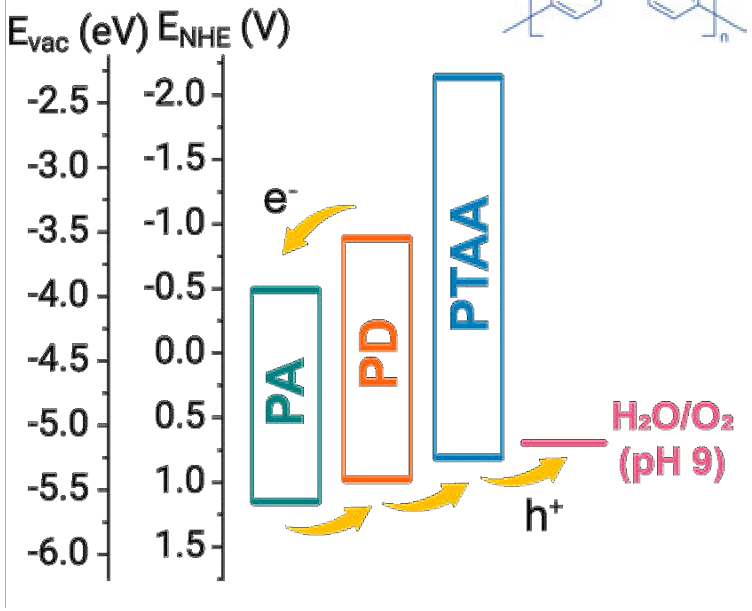


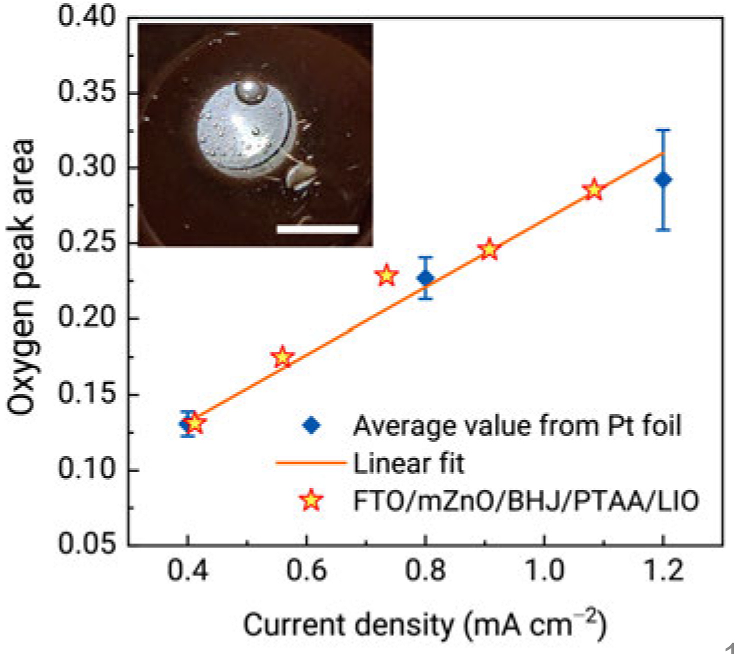




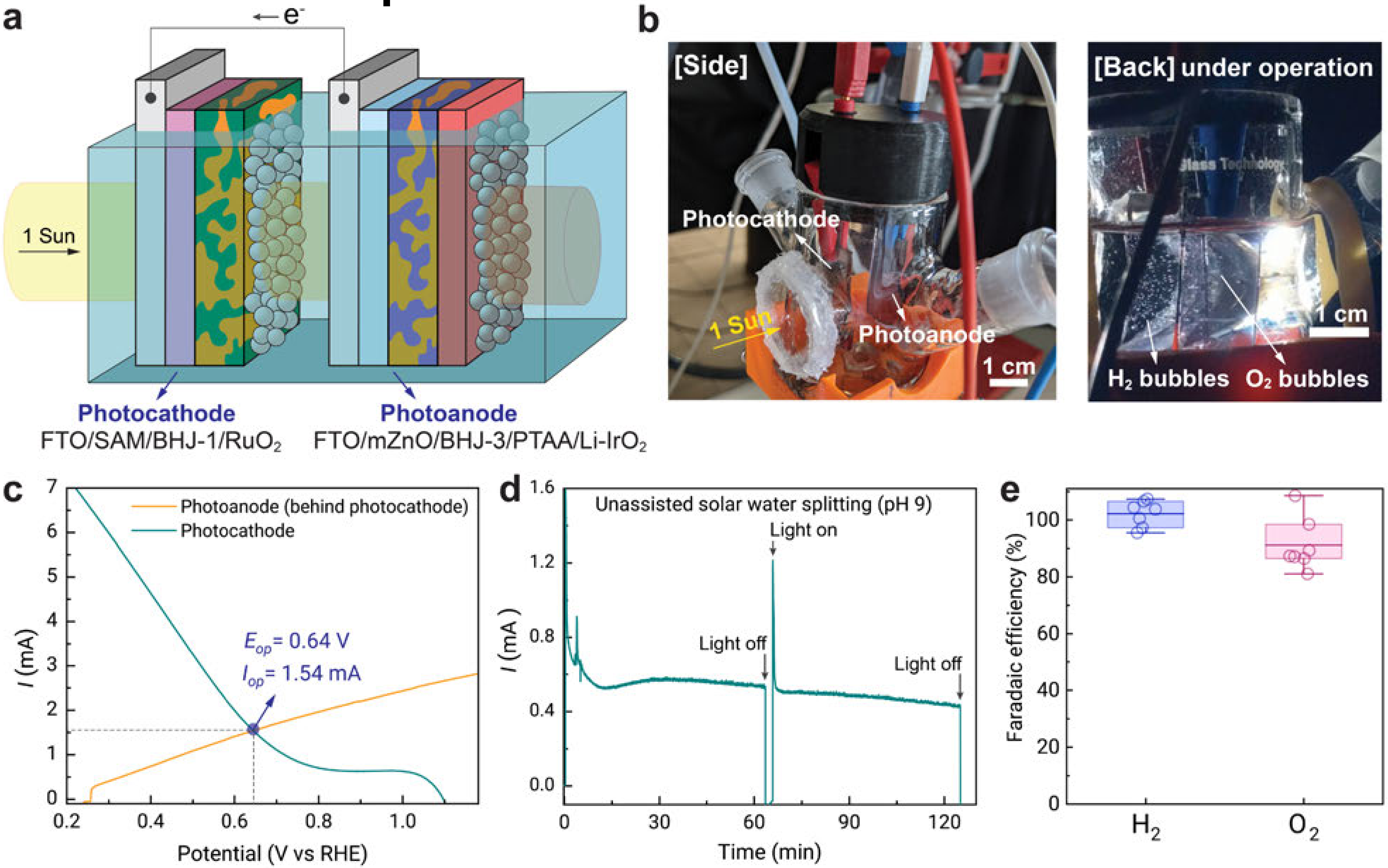


Scale bar = 200 nm

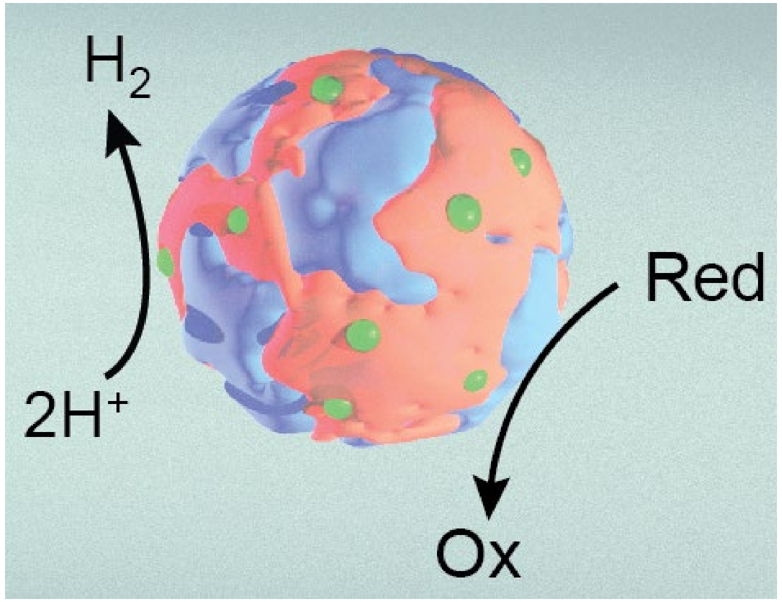


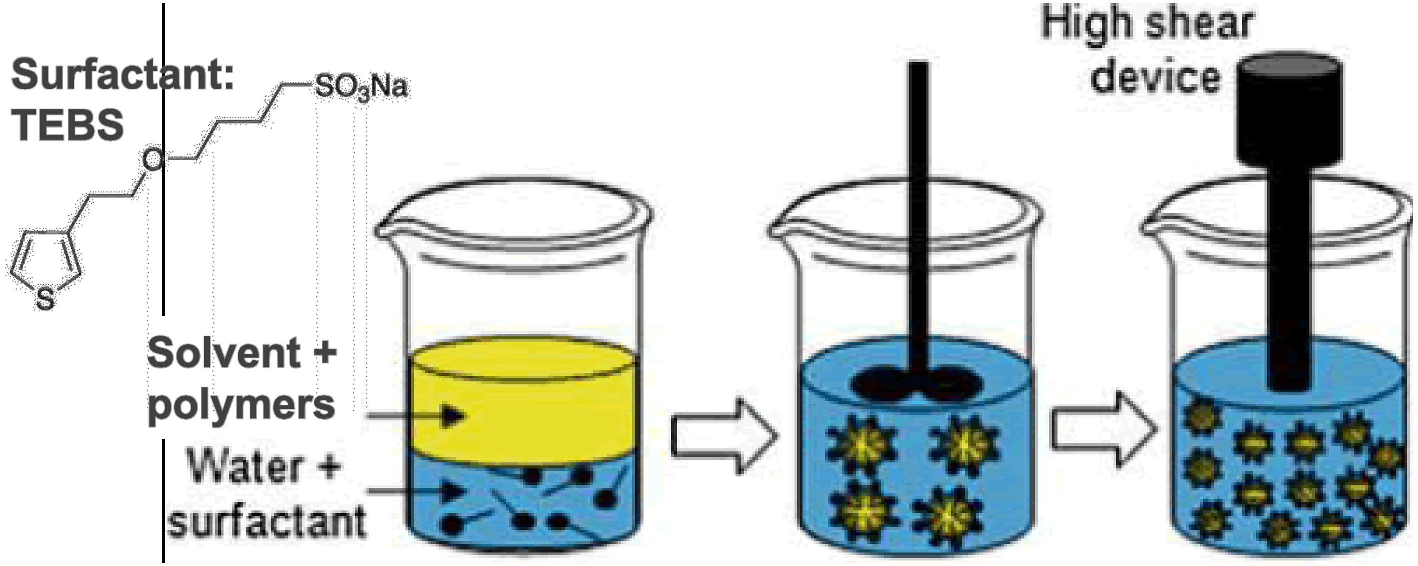


Photocathode/photoanode tandem cells

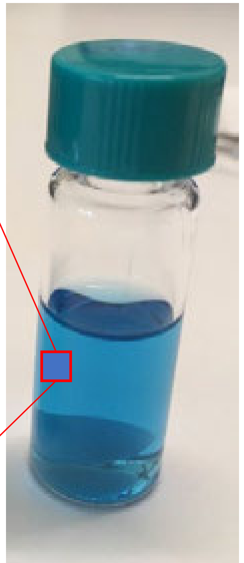


Mini-emulsion synthesis of BHJ nanoparticles





Solvent removal (heat / inert gas purge)



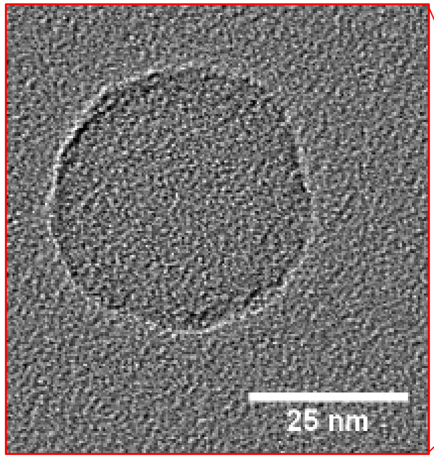
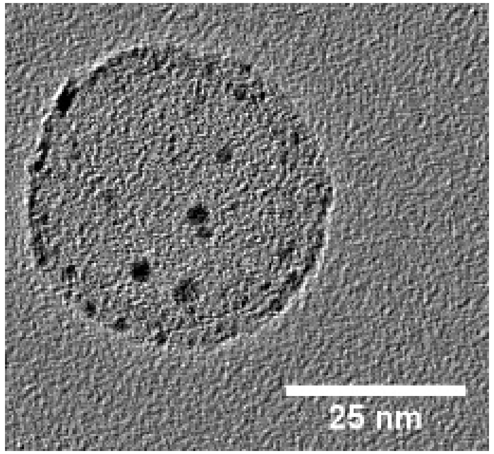


Photo-driven Pt reduction

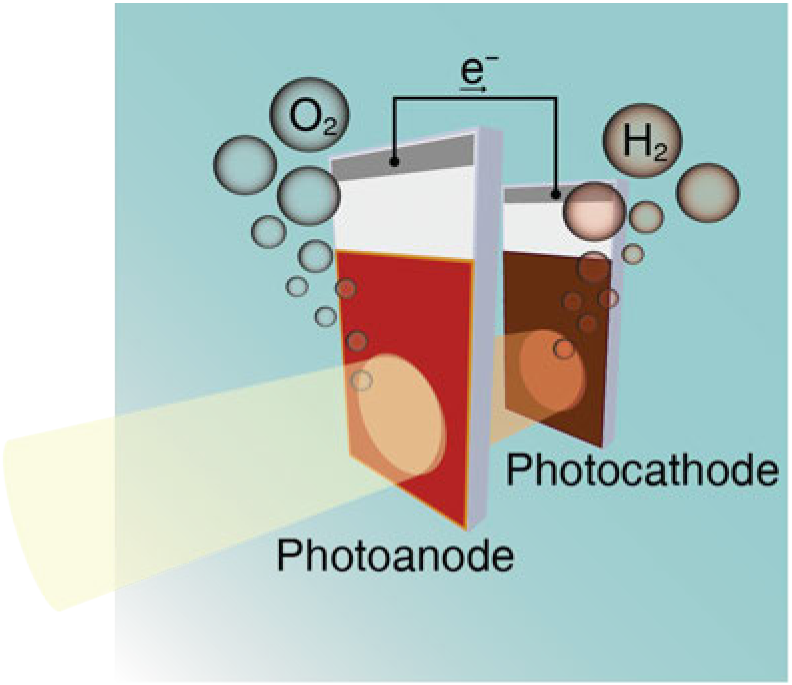
Pt precursor (K_2PtCl_6)

SED (ascorbic acid)

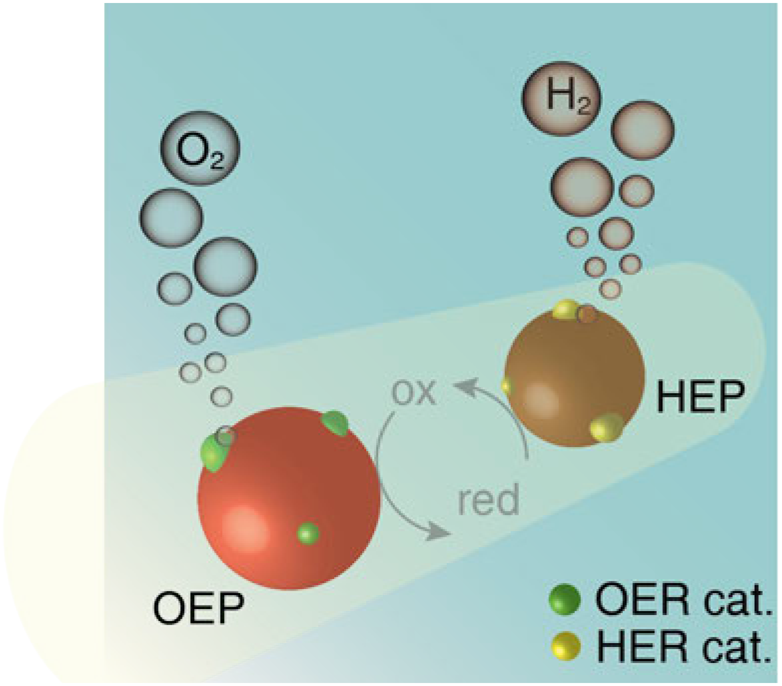


Conclusions and summary

Photoelectrochemical



Photocatalytic



Key factors to advance semiconductors for direct solar-driven water splitting:

- Scalable and high-performance semiconductor systems are needed to realize viable PEC or PC systems
- Optimizing molecular structure, defect concentrations and mechanical/electronic aspects of semiconductor interfaces can drastically improve performance
- Built-in charge separation mechanisms are needed for high-performance PC systems
- For organic semiconductors PC stability on the year timescale has yet to be demonstrated

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Acknowledgements

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