

# Photoelectrochemistry of the water oxidation enzyme Photosystem II: From basic understanding to semi-artificial photosynthesis

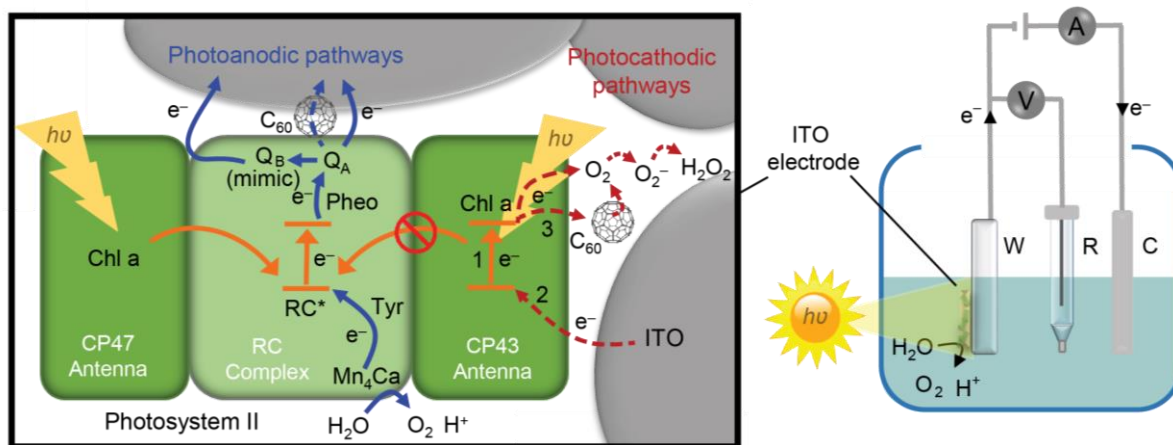
Erwin Reisner

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

E-mail: [reisner@ch.cam.ac.uk](mailto:reisner@ch.cam.ac.uk)

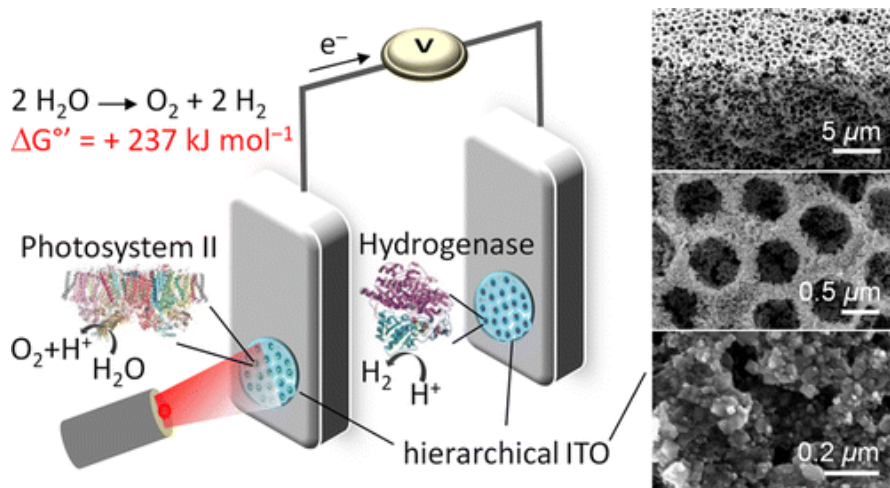
Web: <http://www-reisner.ch.cam.ac.uk/>

In natural photosynthesis, light is used for the production of chemical energy carriers to fuel biological activity and the first protein in the photosynthetic chain is the water oxidation enzyme Photosystem II. This presentation will summarise our progress in the development of protein film photoelectrochemistry as a technique for the light-dependent activity of this enzyme adsorbed onto an electrode surface to be studied.<sup>[1]</sup> Materials design enabled us to develop 'tailor-made' 3D electrode scaffolds for optimised integration of the 'wired' enzyme and these investigations yielded valuable insights into the performance of Photosystem II and interfacial charge transfer pathways. Examples are the identification of unnatural electron escape routes to the electrode and a recently elucidated  $O_2$  reduction pathway that short-circuits the known water-oxidation process (see Figure 1).<sup>[2]</sup>



**Figure 1.** Schematic representation of the energy/charge transfer pathways in Photosystem II adsorbed on a mesoporous ITO electrode connected to a photoelectrochemical three-electrode cell. Taken from reference 2.

The integration of Photosystem II in a photoelectrochemical circuit has also enabled the *in vitro* re-engineering of natural photosynthetic pathways. We succeeded in assembling an efficient enzyme-based full water splitting cell driven by light through the rational wiring of Photosystem II to a [NiFeSe]-hydrogenase (see Figure 2).<sup>[3]</sup> This hydrogenase displays unique properties for water splitting applications as it displays good H<sub>2</sub> evolution activity, little product (H<sub>2</sub>) inhibition and some tolerance towards O<sub>2</sub>.<sup>[4]</sup> The semi-artificial water splitting cell shows how we can harvest and utilise electrons generated during water oxidation at Photosystem II electrodes for the generation of renewable H<sub>2</sub> with a wired hydrogenase through a direct pathway unavailable to biology.



**Figure 2.** Schematic representation of a two-electrode photoelectrochemical cell with Photosystem II wired to a [NiFeSe]-hydrogenase. Water is photo-oxidized and O<sub>2</sub> is generated at a hierarchical ITO electrode loaded with Photosystem II (left), and aqueous protons are reduced at a [NiFeSe]-hydrogenase at the cathode made from the same 3D material (right). Voltage is applied between the two electrodes of the cell to help drive the proton reduction reaction. Taken from reference 3.

### Acknowledgements

This work is currently supported by an ERC Consolidator Grant ‘MatEnSAP’ (682833).

### References

- [1] Kato, Zhang, Paul & Reisner, *Chem. Soc. Rev.*, **2014**, *43*, 6485–6497.
- [2] Zhang, Sokol, Paul, Romero, van Grondelle, & Reisner, *Nature Chem. Biol.*, **2016**, *12*, 1046–1052.
- [3] Mersch, Lee, Zhang, Brinkert, Fontecilla-Camps, Rutherford & Reisner *J. Am. Chem. Soc.*, **2015**, *137*, 8541–8549.
- [4] Wombwell, Caputo & Reisner, *Acc. Chem. Res.*, **2015**, *48*, 2858–2865.