Artificial Photosynthesis - Investigation of the Bio-inorganic Interface

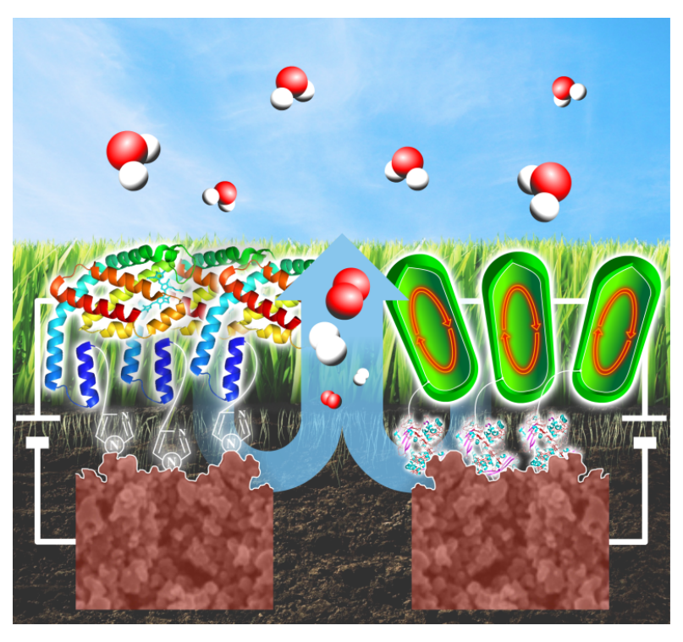
Materials Science & Technology

Niels Burzan[1], Artur Braun[2]

[1] Swiss Nanoscience Institute, University of Basel, CH-4056 Basel, Switzerland

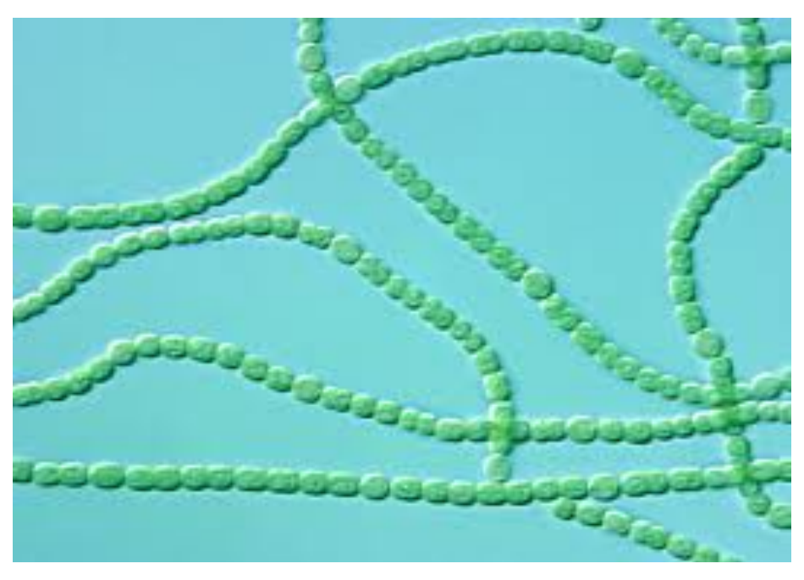
[2] Swiss Federal Laboratories for Material Science and Technology, CH-6800 Dübendorf, Switzerland

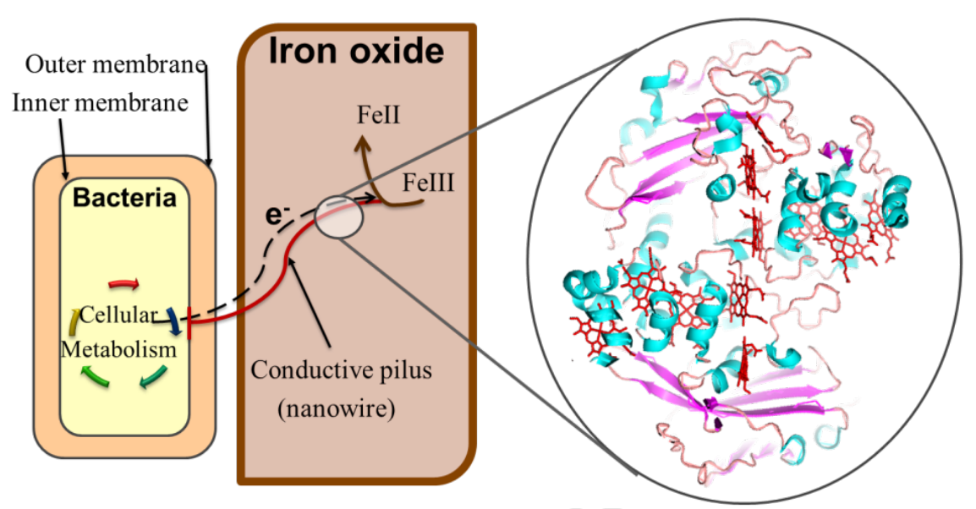
Introduction & Socio-Economic Context



The sun delivers 1000 x the world energy use. Solar electricity is readily established in photovoltaics. 80% of the world energy use in fuels, and only 20% in electricity. Solar fuels can be produced by artificial photosynthesis (AP) [1] in photoelectrochemical cells (PEC). Artificial photosynthesis is inspired by photosynthesis in nature. Inspired by semiconductor based solar hydrogen producing PEC, we investigated the possibilities for bio-hybrid water splitting PEC's. While PEC photoelectrodes are typically inorganic semiconductors such as 3d metal oxides, light harvesting proteins and bio-catalysts can be coupled with such electrodes and enhance the hydrogen production [2,3]. We expand this concept toward PEC devices with vital or dead photosynthetic organisms.

From natural to artificial Photosynthesis

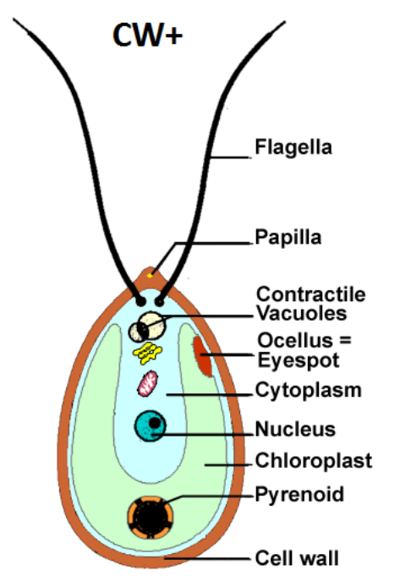


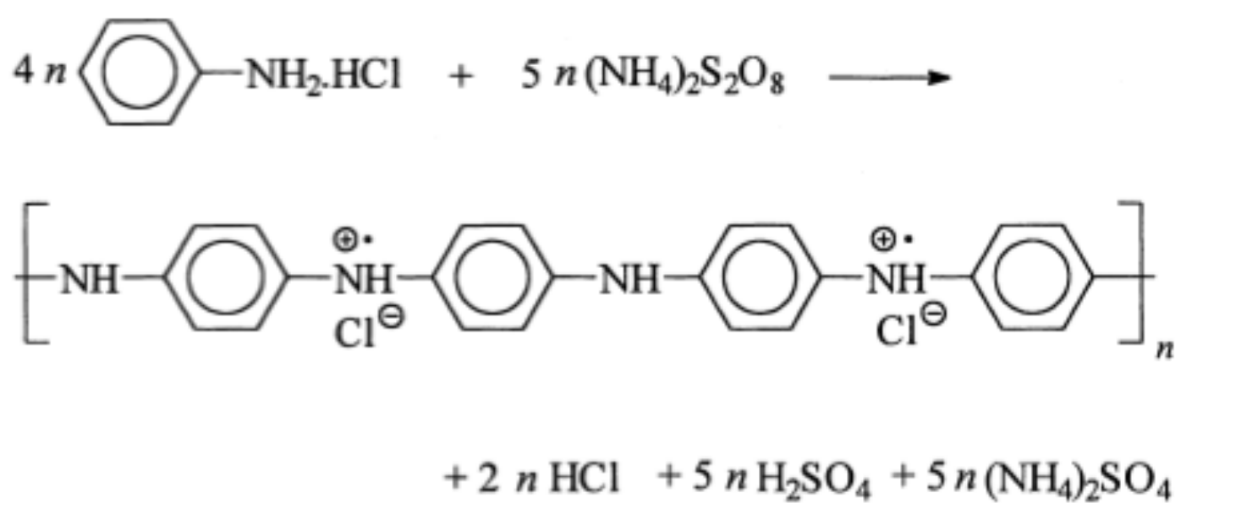


$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2 \qquad \Delta H^0 = +2870\ \frac{kJ}{mol}$$

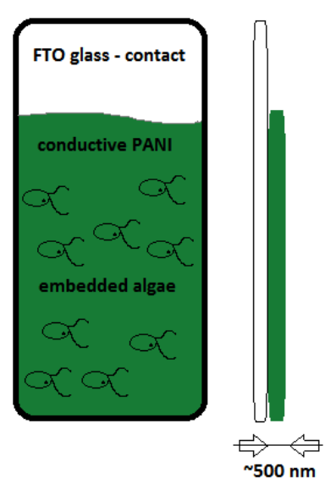
■ The holy grail of sustainable energy supply is by artificial photosynthesis (AP). AP has the most environmental friendly and sustainable operation principle. Nature evolved highly sophisticated protein complexes to transform radiation into chemical energy using water and carbon dioxide. The only waste, oxygen, is used by a great variety of lifeforms for their metabolism. With AP, the harvested solar energy can be used for the production of fuels and basic chemicals in tailored reactions without compromising our environment. Exploiting earth abundant elements for sophisticated, bio-hybrid systems may solve the frequently recurring energy and resource crises [2].

C. reinhardtii embedded in a conductive polymer

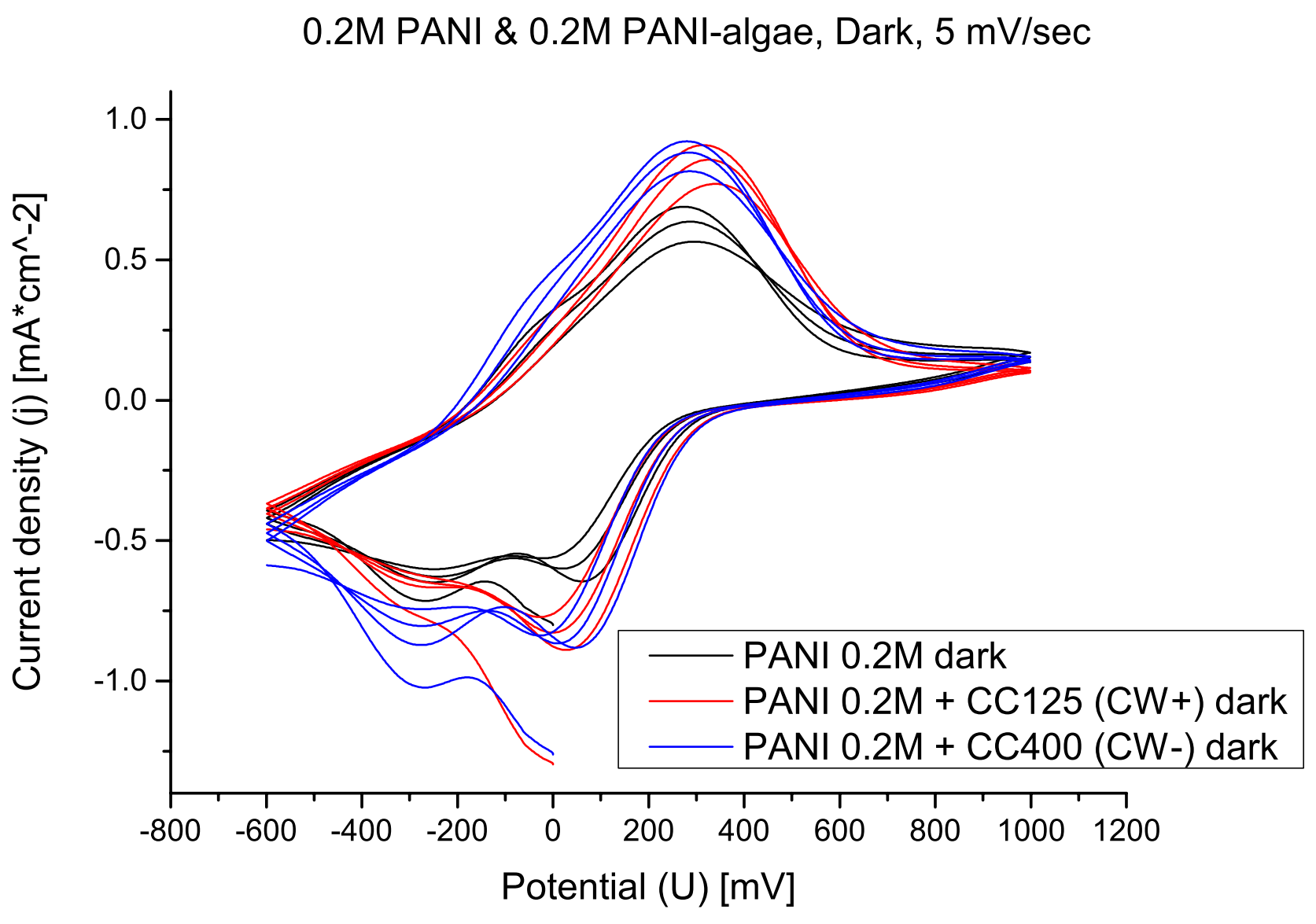


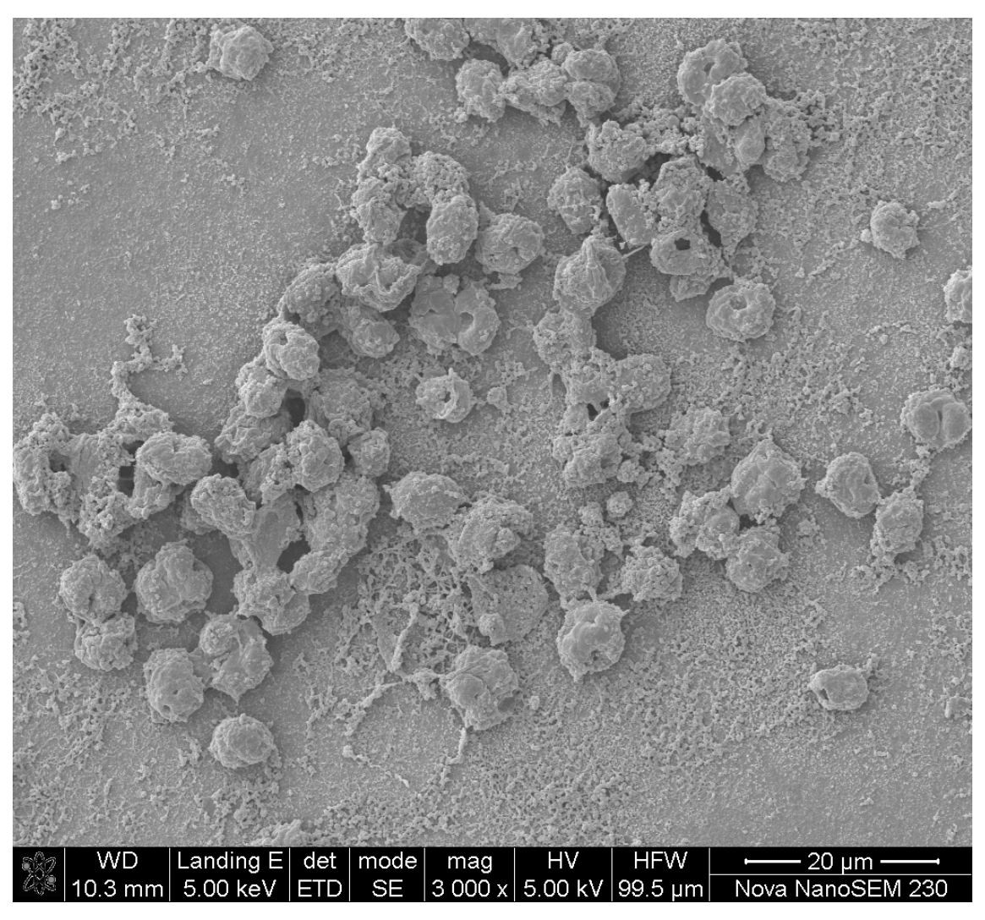


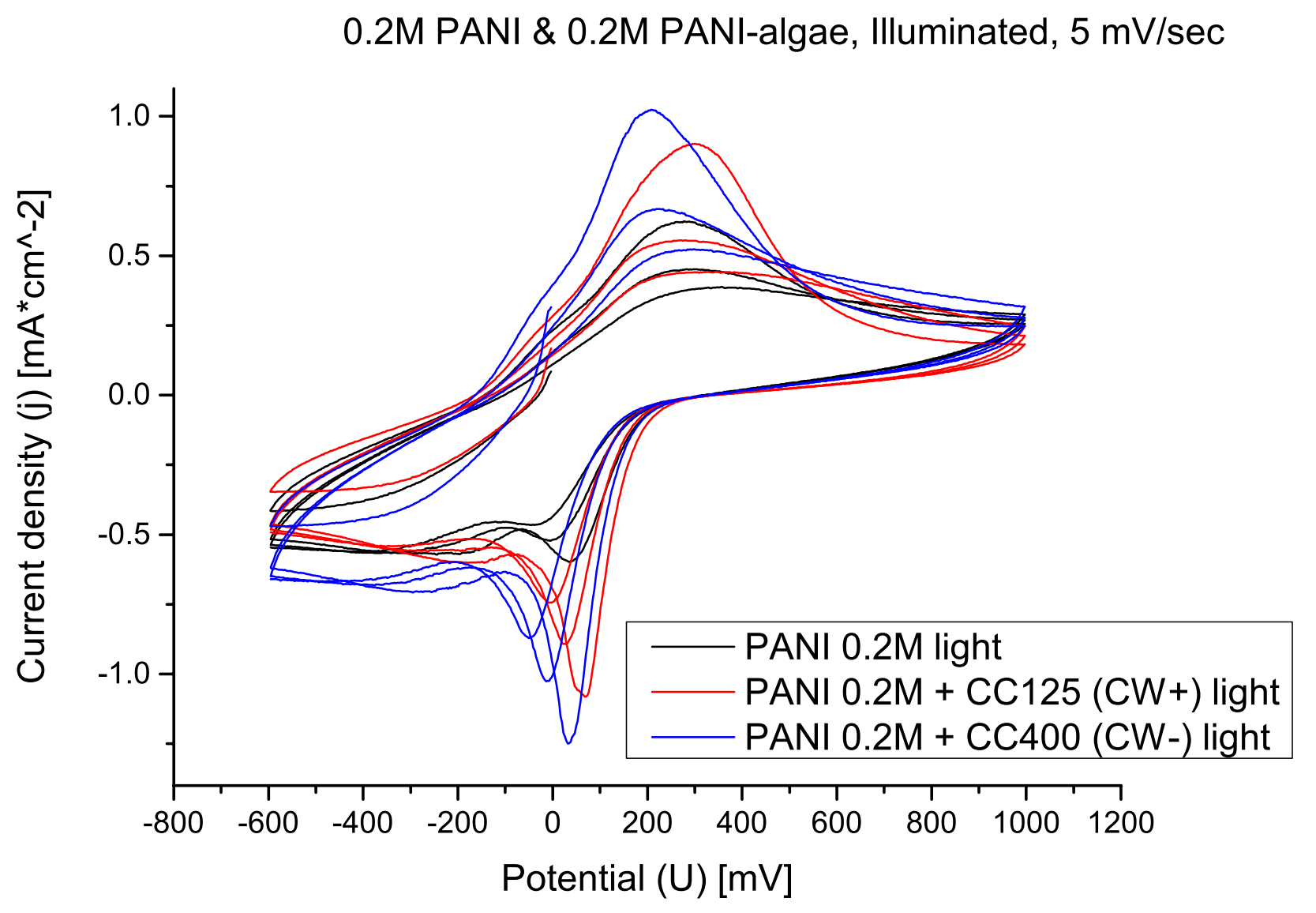
$$4\,n\ C_6H_5NH_2{\cdot}HCl + 5\,n\,(NH_4)_2S_2O_8 \longrightarrow [\ldots]_n + 2\,n\,HCl + 5\,n\,H_2SO_4 + 5\,n\,(NH_4)_2SO_4$$



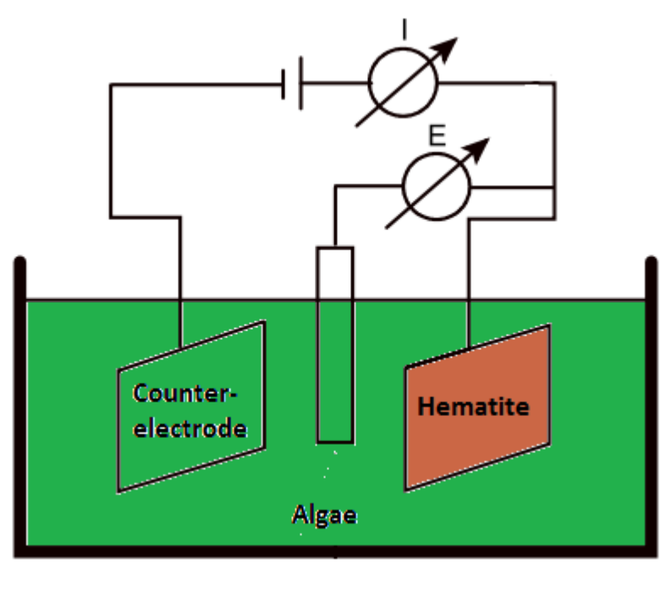
■ Hot spring cyanobacteria have been investigated in 1980 and proposed as a living photoconverter for biophotoysis of water [4]. Only during the last years, theses concept attracts the attention of the scientific community. On basis of that work, the eucaryotic algae *Chlamydomonas reinhardtii* (top left) was embedded within a thin layer of polyanilin (PANI), a conductive polymer, to ensure a electric contact to the fluoride-doped tin oxide (FTO) glass substrate. Both *C. reinhardtii* strains with and without cell wall (CW+/-) were investigated using cyclic voltametry and impedance spectroscopy in a three-electrode setup.
The polymerization reaction occurred in algae containing solution, despite the harsh reaction condition (exothermic reaction, evolution of hydrochloric acid and sulfuric acid), electron microscopy revealed intact clusters of algal cells at the surface (below).

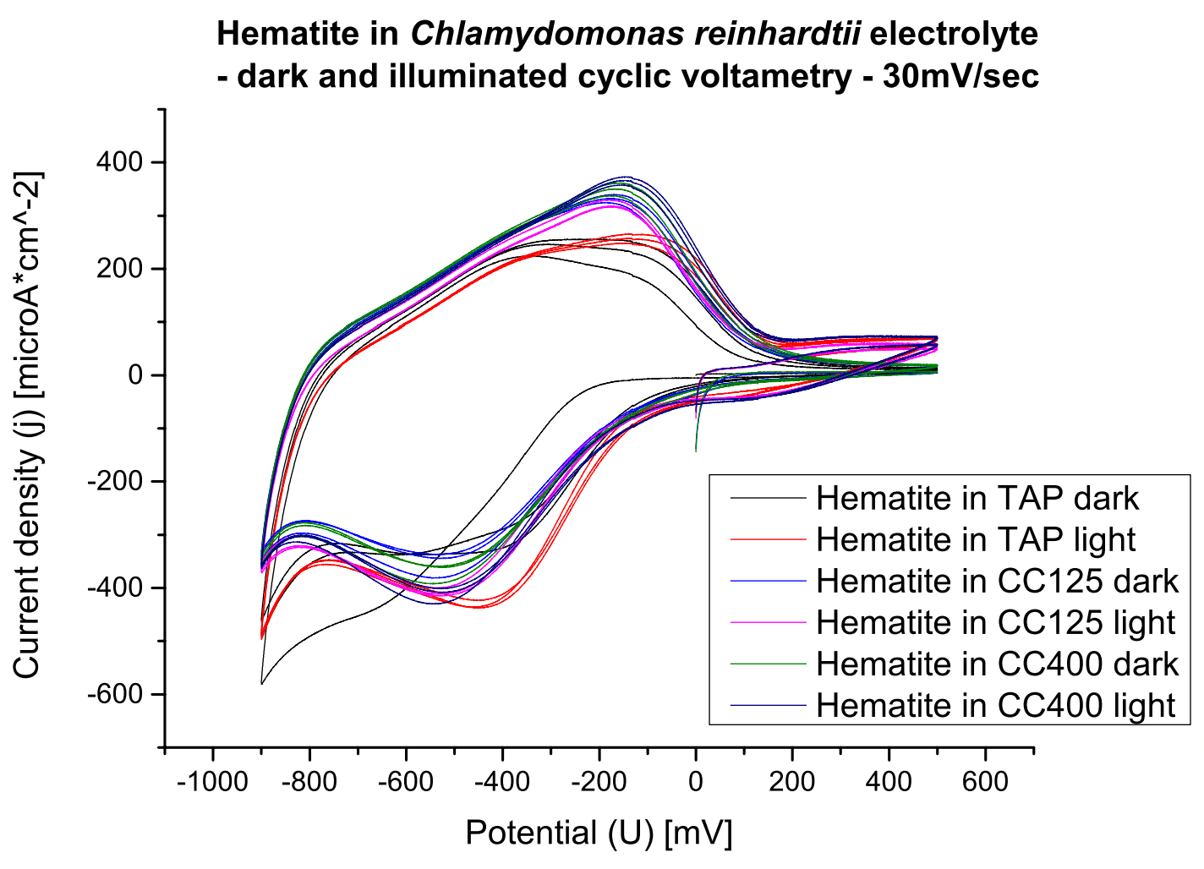


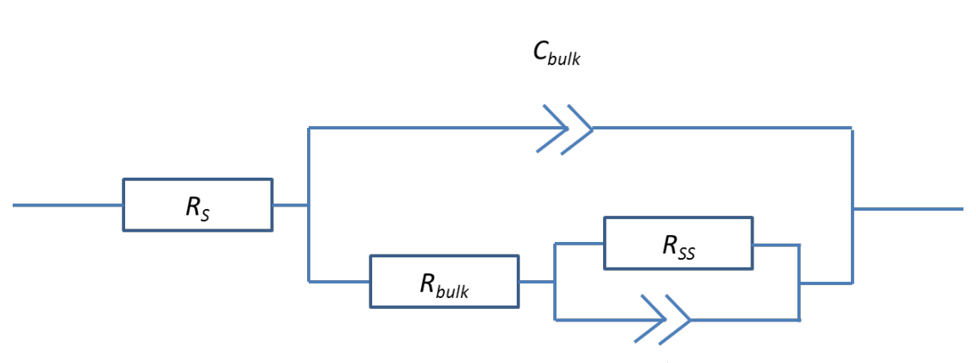


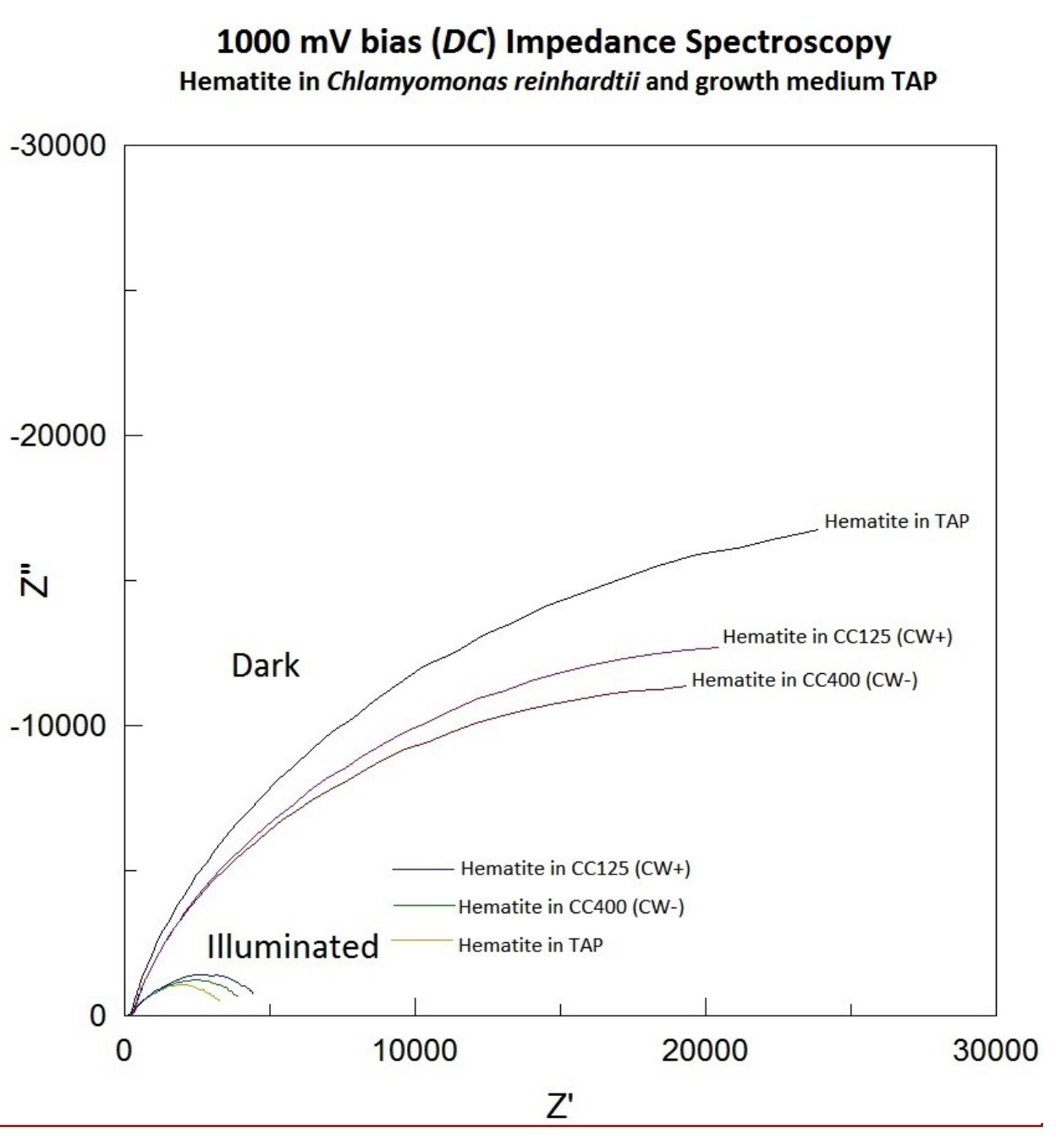


■ Graphs right above - Cyclic voltametry was carried out without (top) and with illumination (bottom), each 3 cycles . In both dark and light conditions, the PANI containing algae show higher current peaks the PANI control. Most prominent feature is a increased cathodic peak at 50 mV (0.487 V vs. RHE) when light was shined on the electrode. This may be indicate, that intact photoactive remainments of the dead algae increase the measured current. Potential candidates are light-induced electron transfer protein complexes as the photosystem I & II and cytochrome b6f, plastoquinone and ferredoxin. These findings indicate, that even inaccurate film processing using cheap precursors could exploited for solar applications.



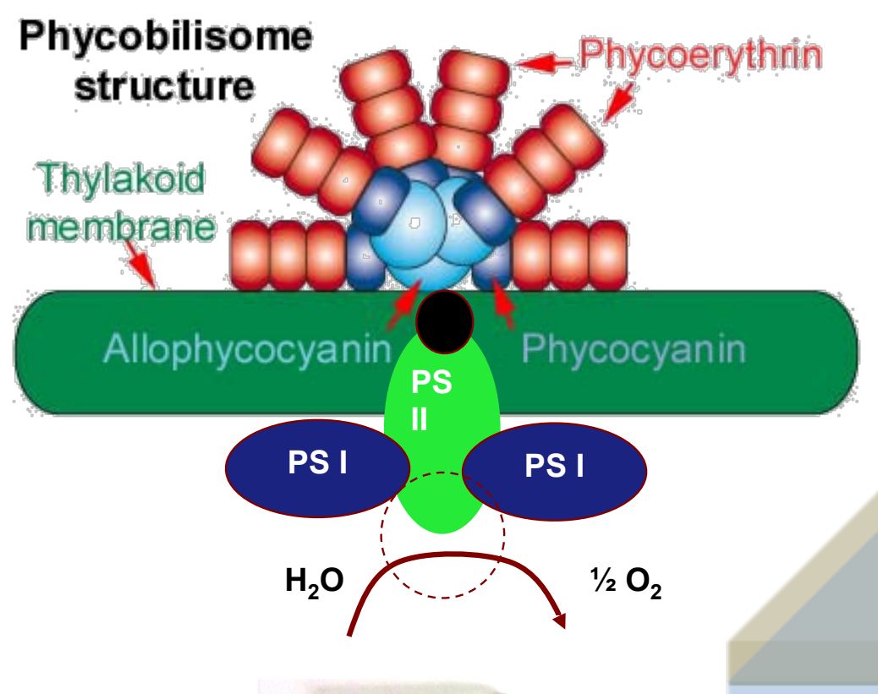


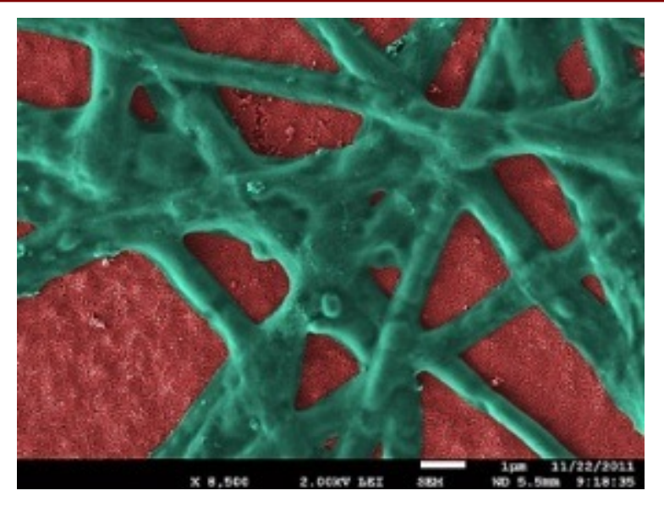


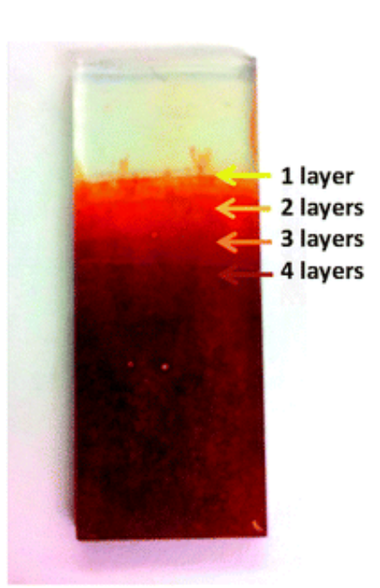


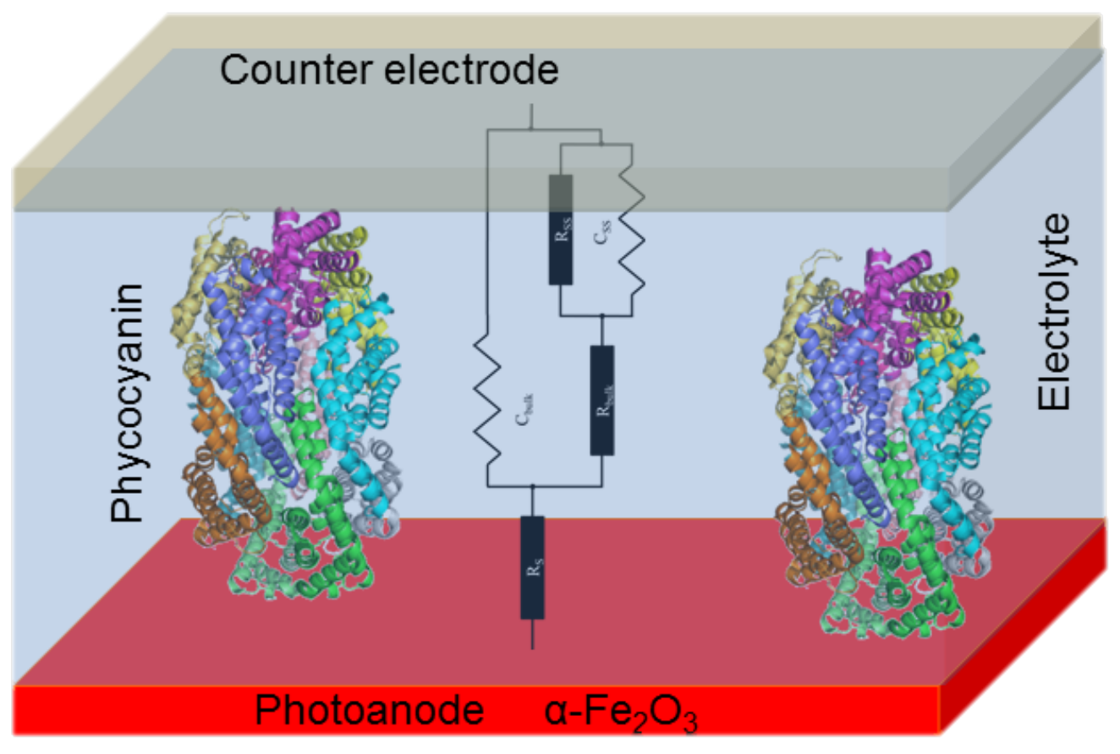
■ Further investigations with living algal cells were carried out in terms of a electrolyte consisting of growth medium (TAP) with and without algae. Electrochemical impedance spectroscopy (EIS) is employed for the investigation of charge carrier dynamics and charge transfer resistances. The Nyquist plot, on the right, demonstrate how the charge transfer resistance decreases when the electrodes are illuminated and when living algae are used as electrolyte in dark conditions. This effect is opposite when light is turned on but due to the algal suspension, less light hits the hematite surface (see experimental setup above). The findings suggest an intensified cooperation between the semiconductor electrode and the electrolyte, mediated by living algae.

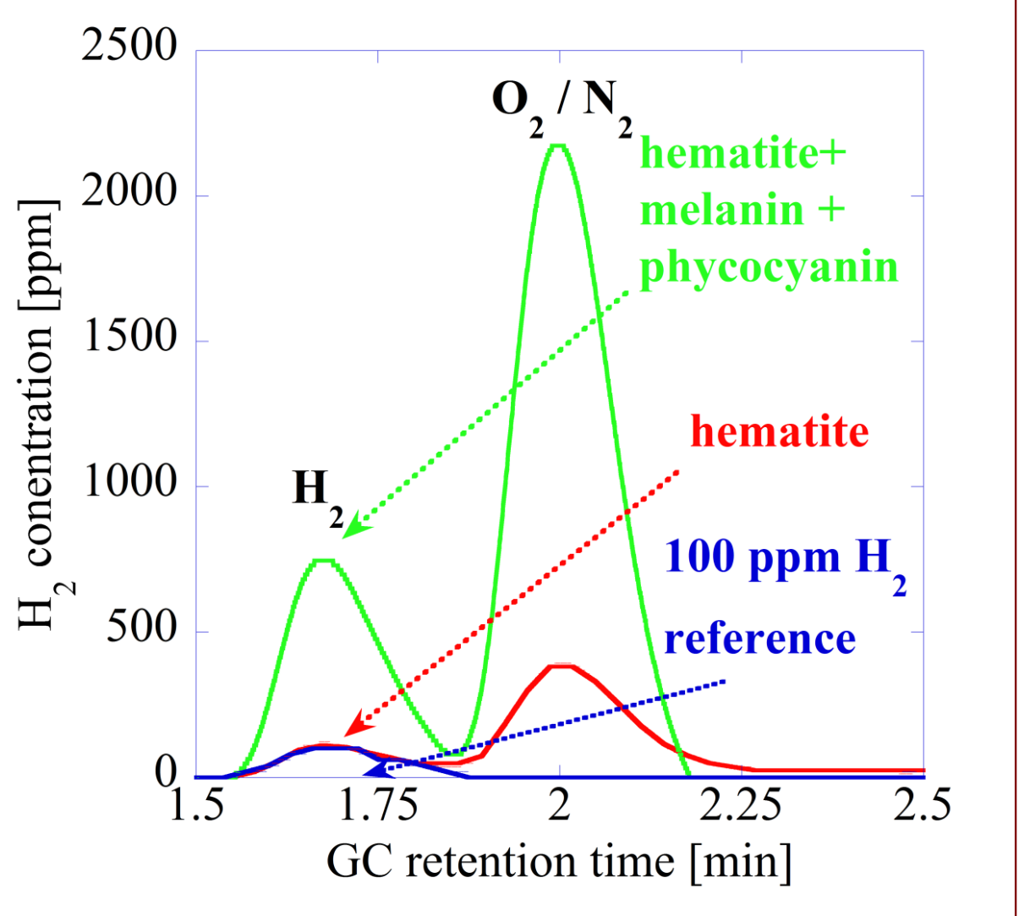
Light harvesting protein coated iron oxide semiconductor electrodes





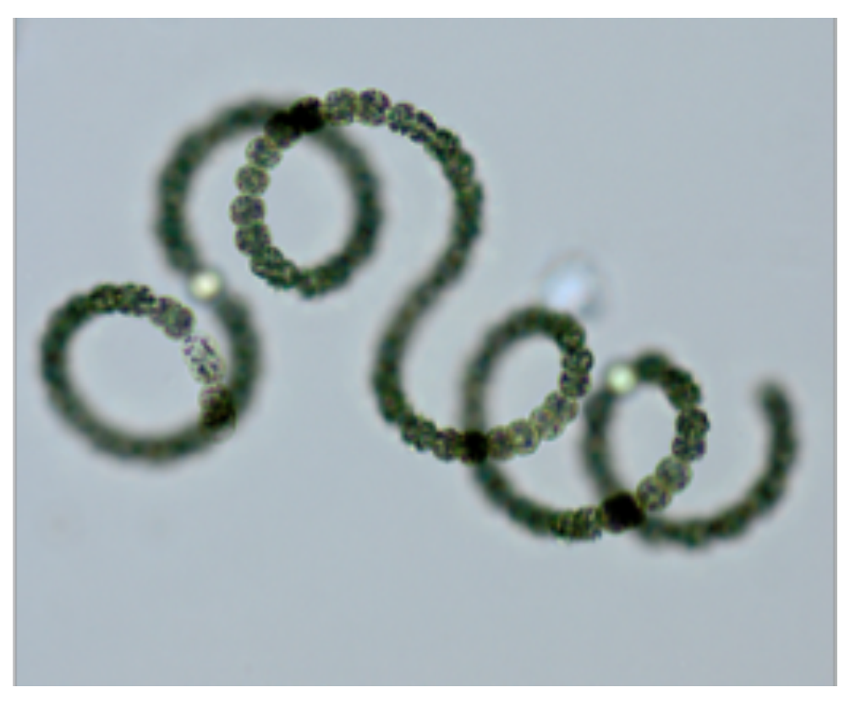


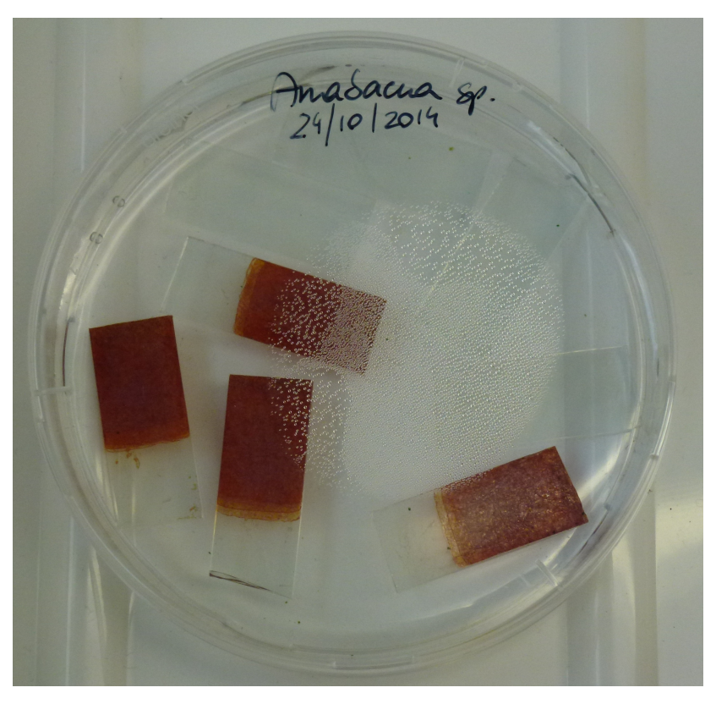


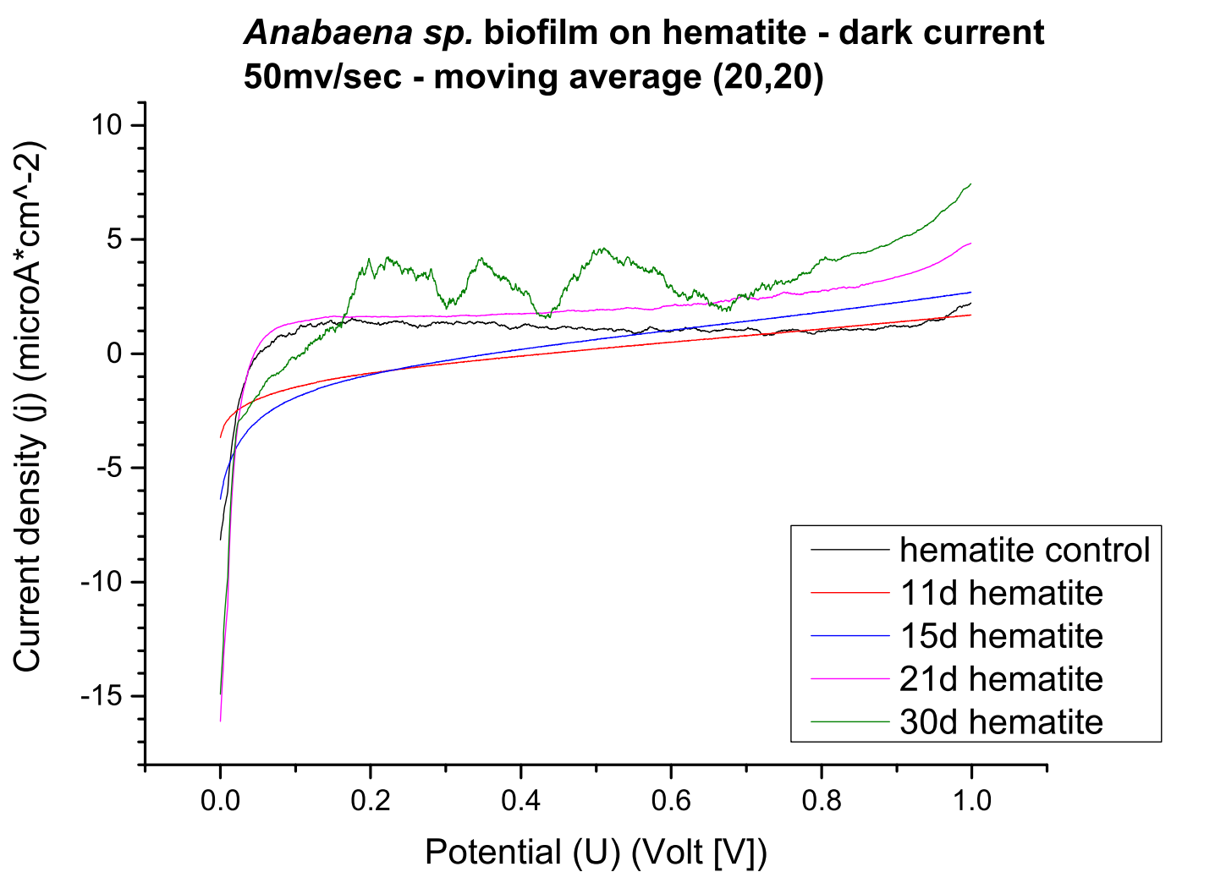


■ Left - Cyanobacteria (blue green algae) have a hydrogen and an oxygen evolving complex [5]. They also contain the light harvesting antenna protein C-phycocyanin which can be covalently attached to iron oxide semiconductor electrodes in PEC cells (middle) so as to provide optimum charge transfer between them for efficient energy conversion. Such bio-hybrid electrodes (graph on the right) demonstrates how the functionalization of a hematite electrode with phycocyanin yields a 6-fold increase of the hydrogen yield [6]. Inspired by the enhanced photocurrent of a C-phycocyanine (PC) coated hematite (alpha-Fe2O3) thin-film electrode used in an artificial photosynthesis approach to split water into hydrogen and oxygen [7], a two-month student project was performed to find alternatives to the complicated protein handling.

Anabaena sp. biofilm on hematite electrodes

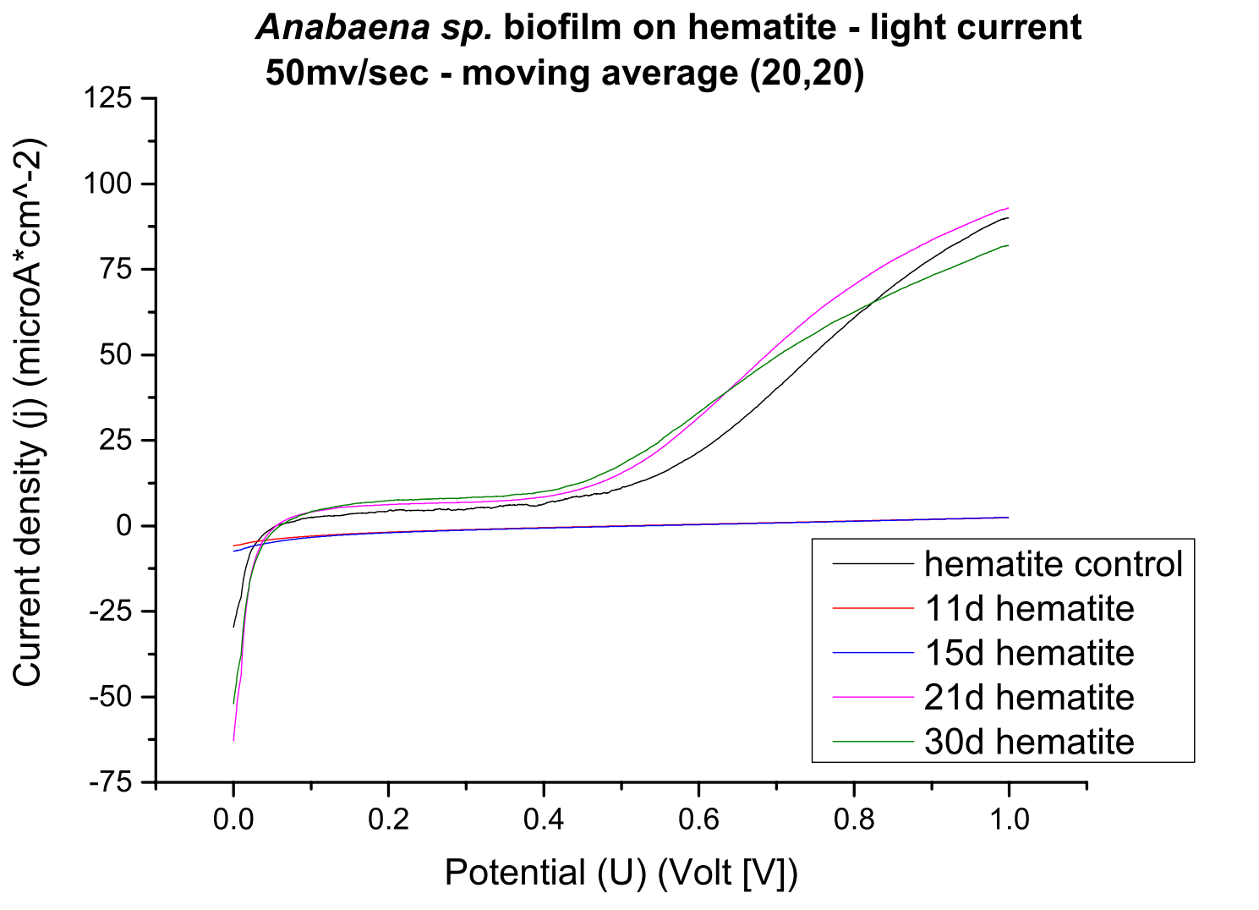


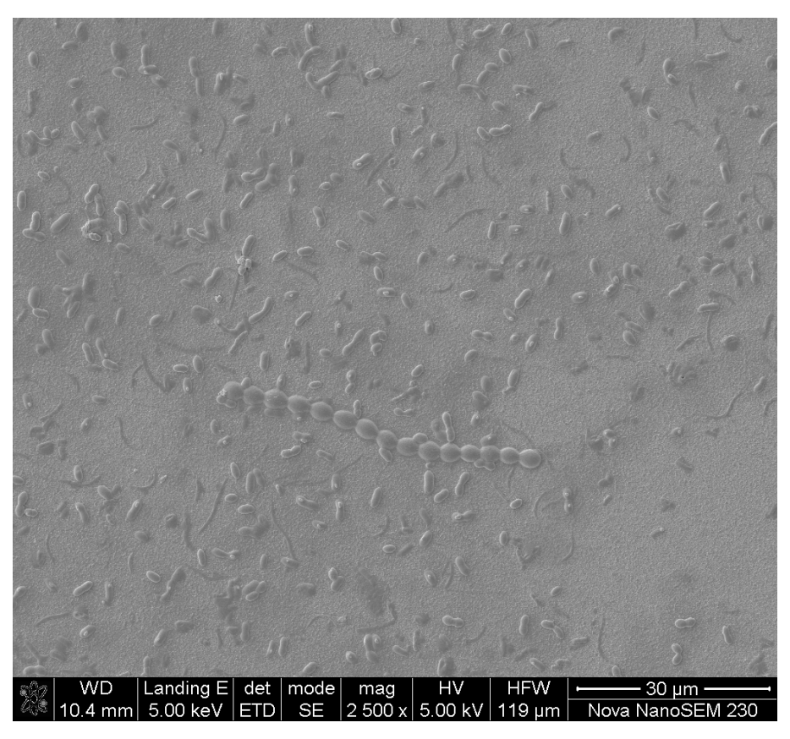


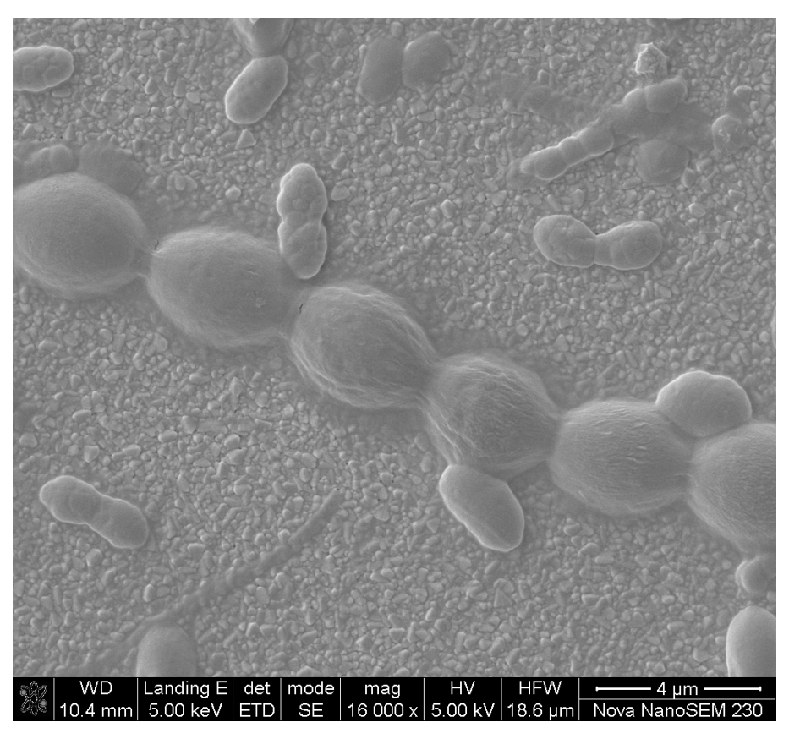


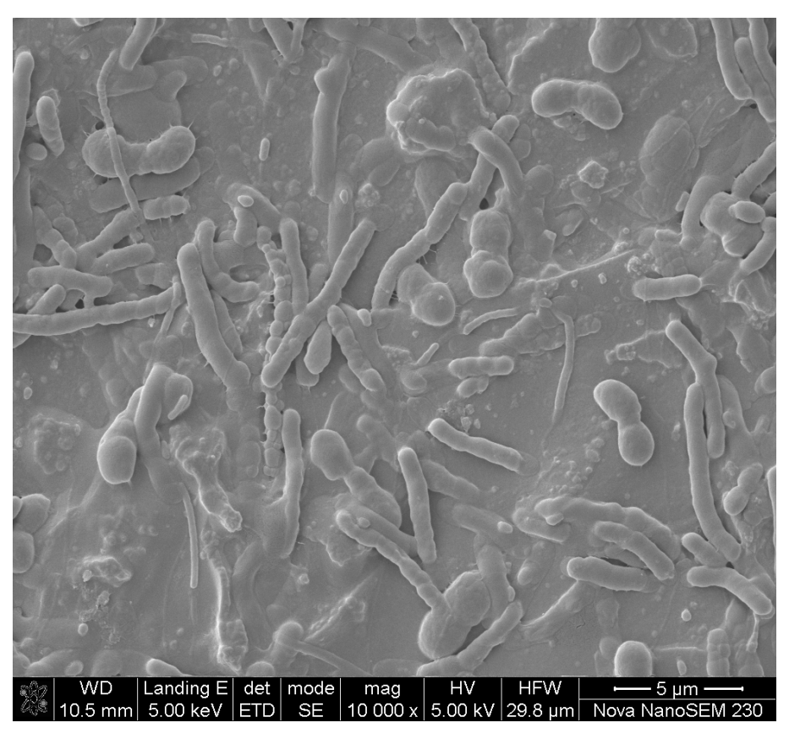
■ The filamentous, biofilm forming cyanobacteria *Anabaena sp.* were grown 11, 15, 21 and 30 days on hematite electrodes and air dried to receive an intact biomaterial coating compared to the PANI embedded *C. reinhardtii*. Cyclic voltametry reveals a bio-related dark current (top right) which increases with the maturity of the biofilm. The source of this current remains unclear: Destructive processes due to the applied potential would „burn“ the biofilm in layers and no increase depending of the growth time would have been observed. Once again, that indicates an electronic mediation by bio materials which should investigated further and may enhance todays semiconductor applications.

In illuminated conditions, the photo induced effect on hematite is dominating and no clear trend is observed with the used methods.









Acknowledgment

We gratefully thank Prof. Housecroft and Prof. Constable (Uni Basel) for advice and mentoring the project. Cultures of *Chlamydomonas reinhardtii* and *Anabaena sp.* as well as growth media were contributed by Dr. Kroll (EAWAG). Electron-microscopy pictures were taken at the Microscopy Centre (Uni Basel) with the help of Dr. Dürrenberger's group. Also we would like to thank the whole „Functional Ceramic Materials for Energy and Environment“ group at EMPA for constant support during the experimental part of the project and Dr. Faccio (EMPA St. Gallen) for her expertise in the C-phycocyanine protein coating.

Related Publications

[1] Artificial Photosynthesis for Solar Fuels – an Evolving Research Field within AMPEA, a Joint Programme of the European Energy Research Alliance, Green 2013; 3(1): 43–57.
[2] “In rust we trust”. Hematite the prospective inorganic backbone for artificial photosynthesis, Energy & Environmental Science, 2013, 6: 407-425.
[3] Functionalization of Nanostructured Hematite Thin-Film Electrodes with the Light-Harvesting Membrane Protein C-Phycocyanin Yields an Enhanced Photocurrent, Advanced Functional Materials 2012, 22 (3): 490–502.
[4] „Living electrode“ as a long-lived photoconverter for biophotoysis of water, Proceedings of the National Academy of Sciences, 1980; 77(5): 2442-2444.
[5] Hydrogen production by Trichodesmium erythraeum Cyanothece sp. and Crocosphaera watsonii, Aquatic Microbial Ecology 2010, 59: 197-206.
[6] J. Ihssen, A. Braun, G. Faccio, K. Gajda-Schrantz, L. Thöny-Meyer; Light harvesting proteins for solar fuel generation in bioengineered photoelectrochemical cells; Current Protein & Peptide Science, 2014, 15 (4): 374-384
[7| Biological Components and Bioelectronic Interfaces of Water Splitting Photoelectrodes for Solar Hydrogen Production, Chemistry - A European Journal, 2015; 21(11): 4188-4199