



**SOLAR ENERGY FOR A
CIRCULAR ECONOMY**



CeNT CENTRE
OF NEW
TECHNOLOGIES



**SUNRISE POLAND
Stakeholder Workshop
CeNT UW**

**5-6 June 2019
Warsaw, Poland**

Organizers



Joanna Kargul

Solar Fuels Laboratory, CeNT UW

j.kargul@cent.uw.edu.pl



Renata Solarska

Laboratory of Solar Energy Innovations, CeNT UW

r.solarska@cent.uw.edu.pl

Programme

SUNRISE POLAND Stakeholder Workshop

Centre of New Technologies, University of Warsaw, Banacha 2C
Warsaw, 5 – 6 June 2019

Wednesday, 5th June

08:00 – 08:55 **Registration (CeNT Atrium)**

Day 1 Venue: Lecture Hall 0142

Welcome

09:00 – 09:10 **Organisers**, Joanna Kargul and Renata Solarska (CeNT UW, PL)

09:10 – 09:15 **CeNT UW Director**, Ewa Bulska

Session 1: **SUNRISE Coordination and Support Action**

Chair: **Renata Solarska (CeNT UW)**

09:15 – 09:55 **Plenary: Jacinto Sá** (Uppsala Uni., SE; IPC PAS, PL)

Solar fuels with plasmonic nano-hybrid structures

09:55 – 10:15 **Hervé Bercegol** (Deputy Coordinator of SUNRISE CSA; CEA Saclay, FR)

Overview of the SUNRISE action

10:15 – 10:35 **Joanna Kargul** (SUNRISE Partner, CeNT UW, PL)

Task Forces: How to get involved?

10:35 – 11:00 **Coffee break**

11:00 – 12:00 **Q&A session** (Panel: **Hervé Bercegol**, CEA, FR; **Yagut Allahverdiyeva-Rinne**, Uni. of Turku, FI, **Tomasz Podgajniak**, Vice-President of PIGEOR, PL; **Wojciech Macyk**, Dean of Chemistry Dept., UJ, PL; **Dorota Rutkowska-Żbik**, Haber Inst., PAS, PL, ENERGY-X Partner; **Marcin Opałło**, Director of IPC PAS, PL).

Moderator: Joanna Kargul (CeNT UW, PL)

12:00 – 13:00 **Lunch**

Session 2:	Photoconversion and solar-driven CO₂ reduction
Chair:	Květoslava Burda (AGH UST, PL)
13:00 – 13:40	Plenary: Nicolas Plumeré (Ruhr-Universität Bochum, DE) <i>Semi-Artificial Photosynthesis</i>
13:40 – 14:00	Dorota Rutkowska-Żbik (Haber Inst., PAS, Partner of Energy-X Consortium, PL) <i>Hydrogenation of CO₂ to Methanol over Cu-Ag/ZrO₂ Catalyst: Influence of Polymorphic Zirconia Phases, Copper Electronic State, and Silver Doping</i>
14:00 – 14:20	Renata Solarska (CeNT UW, PL) <i>Development and Photoelectrochemical Performance of Copper Oxide-Based Heterojunctions for Activation of CO₂ Molecule</i>
14:20 – 14:40	Marcin Opałło (Inst. of Physical Chemistry, PAS, PL) <i>SECM study of hydrogen photogeneration at liquid/liquid interface with electrochemical regeneration of electron donor</i>
14:40 – 15:00	Bartłomiej Witkowski (Inst. of Physics, PAS, PL) <i>Innovative solution for photovoltaics</i>
15:00 – 15:30	Coffee break
15:30 – 15:50	Wojciech Macyk (Dept. of Chemistry, UJ, PL) <i>On selected factors governing the photocatalytic CO₂ reduction</i>
15:50 – 16:10	Janusz Lewiński (Warsaw Technical Uni. and Inst. of Physical Chemistry, PAS, PL) <i>Mechanoperovskites for Photovoltaic Applications</i>
16:10 – 16:30	Paweł Kulesza (Faculty of Chemistry, UW, PL) <i>Toward Effective Photoelectrochemical Water Splitting and Electrocatalytic Reduction of Carbon Dioxide</i>
16:30 – 17:30	Poster and Networking Session
18:30 – onwards	Conference Dinner, Polka Restaurant, ul. Świętojańska 2, Warsaw

Thursday, 6th June

Centre of New Technologies, University of Warsaw, Banacha 2C

Day 2 Venue: Lecture Hall 1130

Session 3: Biohybrid electrodes and plasmonic nanostructures (POLTUR session)

Chair: *Yagut Allahverdiyeva-Rinne (Uni. of Turku, FI)*

09:00 – 09:20 **Joanna Kargul** (CeNT UW, PL) *GraphESol Partner*

Photosystem I as the robust component of solar cells and solar-to-fuel devices

09:20 – 09:40 **Marcin Szalkowski** (Nicolaus Copernicus University, PL) *GraphESol Partner*

Fluorescence imaging of plasmonically active PSI-graphene bioelectrodes

09:40 – 10:00 **Kasim Ocakoglu** (Tarsus Uni., TR) *GraphESol Partner*

Photosystem I Integrated Nanostructured Architectures for Solar Fuel Production

10:00 – 10:20 **Silvio Osella** (CeNT UW, PL) *GraphESol Supporter*

Hybrid materials for artificial photosynthesis: a computational approach

10:20 – 11:00 **Coffee break**

Session 4: Natural photosynthesis in SUNRISE POLAND

Chair: *Joanna Kargul (CeNT UW, PL)*

11:00 – 11:40 **Plenary: Yagut Allahverdiyeva-Rinne** (Univ. of Turku, FI)

Photosynthetic microorganisms as biocatalysts for the production of chemicals

11:40 – 12:00 **Wiesław Gruszecki** (UMCS, Lublin, PL)

Thermal energy dissipation in plants: Is it good or is it bad for photosynthesis?

12:00 – 12:20 **Marcin Sarewicz** (UJ, Cracow, PL)

Molecular mechanisms of regulation of photosynthetic electron flow

12:30 – 13:30 **Lunch**

13:30 – 13:50 **Stanisław Karpiński** (SGGW, Warsaw, PL)

Challenges, Technologies and Innovative Potential of Photosynthesis

- 13:50 – 14:10 **Leszek Fiedor** (UJ, Cracow, PL)
Chlorophylls – sophisticated self-protecting photodevices
- 14:10 – 14:30 **Rafał Białek** (UAM, Poznań, PL)
Rhodobacter sphaeroides Reaction Centers as an Active Material for a Biohybrid Photovoltaic Device
- 14:30 – 14:50 **Radosław Mazur** (Faculty of Biology, UW, PL)
Three-dimensional thylakoid network – biogenesis, dynamics, and reorganizations in response to the environmental factors
- 14:50 – 15:10 **Květosława Burda** (AGH, Cracow, PL)
Involvement of non-heme iron in long range regulatory mechanisms of electron and proton transfer within photosystems of type II
- 15:10 – 15:30 **Patrycja Haniewicz** (CeNT UW, PL)
Extreme Photosynthesis: Molecular mechanisms of photoprotection in photosynthetic apparatus of an extremophilic red microalga Cyanidioschyzon merolae
- 15:30 – 16:00 **Coffee break**
- 16:00 – 17:00 **Poster and Networking Session/GraphESol Consortium meeting**
- 17:00 **Closing remarks: Joanna Kargul and Renata Solarska** (CeNT UW, PL)

Abstracts

Invited talks

Solar fuels with plasmonic nano-hybrid structures

Jacinto Sá

*Department of Chemistry, Ångström laboratory, Uppsala University, Sweden
Institute of Physical Chemistry, Polish Academy of Sciences, Poland*

jacinto.sa@kemi.uu.se

The efficient conversion of light energy into chemical energy is key for sustainable human development. This lecture will cover general aspects of solar fuel productions as well recent development on the applications of plasmonic based nano-hybrid assemblies to solar fuels. I report on the concomitant reductive hydrogen production and pollutant oxidation using visible light as energy source, thus increasing the economical viability of the process and green credentials. The modular architecture of this silver plasmonic nano-hybrid material allows the fine-tuning of its properties by simple manipulation of a reduced number of basic components. The synthetic routes are scalable and green, ensuring fast knowledge transfer. I also talk about stabilization mechanisms underpinning system high activity.

Overview of the SUNRISE action

Hervé Bercegol

Deputy Coordinator of SUNRISE CSA; CEA Saclay, France

herv.bercegol@cea.fr

SUNRISE is a European action currently elaborating a Science and Technology roadmap (2020-2030) for artificial photosynthesis in a broad sense: electrochemistry with renewable current, photo-electrochemistry and biosynthetic and biohybrid approaches. Our vision is to enable the production of renewable fuels, chemicals and materials on a global scale using abundant molecules as feedstocks (e.g., H₂O, CO₂, N₂) and sunlight as the primary energy source. We aim at solar to products yields tenfold to hundredfold higher than current biomass-based solutions.

With the rapid growth of zero-carbon power capacity, electrocatalysis is the first process being used and promoted for the production of e-fuels and commodity chemicals. By solving fundamental bottlenecks and fostering industry-academia collaboration, SUNRISE aims at improving the efficiency and sustainability of existing chemical routes. Direct conversion and storage of solar energy into chemical bonds, today at lower readiness levels, could give access to even higher performance. The new technologies will provide the opportunity to deploy decentralized facilities converting CO₂ into environmentally friendly chemicals and materials of various lifetime. Long lasting materials storing CO₂ on the long run would lead to an important negative emission technology.

The core consortium of 20 partners is open to contributions from the more than 200 supporting institutions. SUNRISE Stakeholder workshop (June 17-18) will welcome strategic views and ideas from the whole community, especially European scientists and industrialists involved in similar projects.

Task Forces: How to get involved?

Joanna Kargul

SUNRISE Founding Partner and National Contact Point for Poland; Centre of New Technologies, University of Warsaw, Banacha 2C, Warsaw, Poland

j.kargul@uw.edu.pl

With the launch of the SUNRISE CSA large research initiative in March of this year, the research and innovation community in Europe holds a unique opportunity to make a real difference the way energy is produced from the Sun to drive a circular economy. This is the momentous time when academic researchers join forces with industry, non-governmental organisations, public and private funding bodies and citizens to release the society from nearly total dependence on fossil fuels. It is not a trivial task and it requires a wide participation of science and technology experts to provide leadership in this ambitious quest. SUNRISE relies on active involvement of such expert supporters to develop optimal break-through technology solutions for production of solar fuels, commodity and high value chemicals and CO₂ capture. For SUNRISE roadmap currently in the making, several task forces have embarked on in-depth analysis of the main challenges and optimal strategies for solar-driven fuel and chemicals production using 3 approaches: electrochemical with renewable power, photoelectrochemical and biosynthetic/biohybrid. We now call upon the SUNRISE supporters to join the coalition through active engagement during public consultation on identifying the main gaps in knowledge for each approach and providing the most promising solutions to fill in these gaps, with the ultimate aim of formulating a long-term multi-angled strategy for a viable solar-driven circular economy.

Semi-Artificial Photosynthesis

Nicolas Plumeré

Ruhr-Universität Bochum, Center for Electrochemical Sciences, Bochum, Germany

nicolas.plumere@rub.de

The integration of photosynthetic proteins in biophotoelectrodes is envisioned for the production of electricity^[1] or chemical fuels. Redox hydrogels proved particularly suitable as matrices for the immobilization and electrical contacting of photosynthetic proteins to electrodes. We tuned the redox potentials of the electron relays and the properties of the polymeric supporting matrix to enable benchmark photocurrent densities (300 $\mu\text{A cm}^{-2}$ for PS1^[2] and up to 400 $\mu\text{A cm}^{-2}$ for PS2^[3]) at low overpotential.^[4] In analogy to the working principle of dye sensitized solar cells, an important feature of biohybrid solar cells for conversion of light to electricity is the charge carriers needed for collection of the high-energy electron from the photosystem.^[5] The main limitation in energy conversion efficiency is the recombination of this charge carrier at the photoelectrode, a process that decreases both the photocurrent and the open circuit voltage. Moreover, this charge recombination process is suspected to induce degradation of the photosynthetic protein.^[6] We demonstrate that the hydrogel film properties as well as the electrode surface chemistry can be tuned to minimize the various charge recombination pathways. In addition, photodegradation directly correlates with the generation of reactive oxygen species.^[7] To avoid degradation of PS1 during illumination and hence to enhance the long-term stability, the operation of biophotocathodes under anaerobic conditions is advantageous.

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Hydrogenation of CO₂ to Methanol over Cu-Ag/ZrO₂ Catalyst: Influence of Polymorphic Zirconia Phases, Copper Electronic State, and Silver Doping

Dorota Rutkowska-Żbik¹, Agnieszka Kornas¹, Michał Śliwa¹, Katarzyna Samson¹, Ryszard Grabowski¹, Małgorzata Ruggiero¹, Kinga Góra-Marek²

¹Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Krakow, Poland

²Faculty of Chemistry, Jagiellonian University, Krakow, Poland

nczbik@cyf-kr.edu.pl

Methanol is considered a key material for C1 chemistry. It is produced on a large scale from synthesis gas with the use of heterogeneous catalysts. Carbon dioxide is also used in the feed. From the perspective of protection of natural environment, it would be highly desirable to replace CO by CO₂, as carbon dioxide is considered a greenhouse effect gas. Usually, copper catalyst on ZnO or ZrO₂ is used, supported on Cr₂O₃, Al₂O₃ or BeO to increase its thermal stability. Recently, it was observed that the Cu/ZrO₂ catalytic activity in CO_x hydrogenation depends on the polymorphic structure of zirconium oxide. Another factor which influences the catalytic activity of Cu/ZrO₂ systems, is the electronic state of copper phase. While many attribute copper activity to positively charged copper ions, some argue that metallic copper is responsible for efficient hydrogenation of CO₂.

Our aim was to study i) the influence of the type of polymorphic ZrO₂ phase, ii) copper electronic state on the catalytic activity of Cu/ZrO₂ in hydrogenation of CO₂, and iii) influence of the catalyst doping with silver. The Cu/ZrO₂ catalysts were obtained by co-precipitation and complexation, so that the t-ZrO₂/m-ZrO₂ ratio varied in the range 0–100%. In addition to catalytic tests, investigations of the crystallographic structure by XRD method, studies of the catalysts surface structure by XPS and Auger, a reactive adsorption of N₂O, and the acidity measurements using pyridine adsorption were carried out. Quantum chemical calculations concerning oxygen vacancies with the participation of different crystallographic facets in both ZrO₂ polymorphs and on the influence of the electronic state of copper and silver were done.

It was found that variation of catalyst preparation conditions influences copper dispersion, its electronic state, and contents of the zirconia polymorphic phases [1]. The presence of oxygen vacancies stabilizes both the thermodynamically unstable t-ZrO₂ phase and Cu⁺ cations. The catalytic activity toward

methanol increases with increasing t-ZrO₂ content. Partial positive charge accumulated on copper greatly enhances interaction of the catalyst active phase with reactants [2]. The presence of silver as the dopant increases the internal surface area of the catalyst and enhances its reducibility as seen by H₂-TPR measurements. The latter can be explained in view of the DFT calculations showing a facilitated H₂ activation in the Cu-Ag bimetallic systems as compared to the copper one.

Keywords: CO₂ valorization, ZrO₂ phases, Cu catalyst, Cu-Ag systems, hydrogenation

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Development and Photoelectrochemical Performance of Copper Oxide Based Heterojunctions for Activation of CO₂ Molecule

Renata Solarska, Krzysztof Bienkowski, Michał Jadwiszczak, Monika Arasimowicz

*Laboratory of Solar Energy Innovations, Centre of New Technologies
University of Warsaw, Banacha 2c, 02-097 Warsaw*

r.solarska@cent.uw.edu.pl

The need for renewable and sustainable energy might be a concern for the society if we are not able to provide this energy with concomitant environmental protection and economic competitiveness. A technology which allows exploiting sunlight, water, and CO₂ to produce solar fuels will certainly contribute to high rate of solar energy conversion and reduction of global warming. Therefore, major considerations are paid to the construction of heterogenous junctions & surfaces allowing better charge transport kinetics and selective simulative proceeding of desired products in appropriate ratios. For that reason, design and construction of different types of joined semiconductor systems aiming enhancement of charge carrier excitation, separation and their transport dynamics followed by recognition of their intrinsic limitations and enhanced efficiency towards CO₂ conversion, becomes a priority in terms of global advancement in the field.

Recent advances regarding construction of a such heterojunction, consist of coupling of high photocatalytic activity of Cu₂O towards CO₂ reduction with high stability and electric conductivity of defective titanium oxide. This approach allowed to convert the CO₂ to methanol with high efficiency and at relatively positive potential of 0.1 V vs RHE. The stable and reproducible photocurrents that reached more than 1.2 mA/cm² were attained at standard conditions. Then, the substoichiometric titanium oxide has been replaced by the nanoneedles of WO₃ containing more than bare one, oxygen deficiencies. Further, change in its crystal lattice system allowed better stabilization of the overall working system and higher rate of solar energy conversion to CO₂ reduction products. The mechanism which has been pointed as responsible for better charge separation in the junction relied onto indirect charge transfer between components and could be diversified by the content of carbon in the upper layer. Design, construction and performance of those systems will be an objective of this presentation.

Keywords: solar energy conversion, copper oxide, heterojunction, CO₂ photoreduction

SECM study of hydrogen photogeneration at liquid|liquid interface with electrochemical regeneration of electron donor

Marcin Opałło¹, Justyna Jedraszko¹, Wojciech Adamiak¹, Wojciech Nogala¹, Hubert H. Girault²

¹*Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*

²*EPFL Valais Wallis, EPFL SB ISIC LEPA, Sion, Switzerland*

mopallo@ichf.edu.pl

Generation of H₂ using metallocenes and their derivatives as electron donors has been studied since the late 1980s. Three decades later it has been shown that light driven hydrogen evolution reaction (HER) also occurs at polarized liquid|liquid interface with sacrificial electron donor. We will demonstrate light driven (HER) at the interface between two immiscible electrolyte solutions (ITIES), namely 1,2-dichloroethane|water (DCE|W) interface using photoexcited decamethylruthenocene (DMRc) as electron donor using scanning electrochemical microscopy (SECM) setup. In particular in our system DMRc is *in situ* regenerated by electroreduction of its oxidized form (DMRc⁺) formed during HER as a by-product, at the electrode positioned close to DCE|W. This reaction is followed by anion insertion from water to organic phase. Such regeneration enables continuous hydrogen generation using small amount of DMRc. Proton transfer from the acidic aqueous phase to the DCE phase is ensured by negative chemical polarization of the liquid|liquid interface. The reduction of protons in DCE occurs only after excitation of DMRc by light. Most importantly significant flux of hydrogen is detected only when SECM tip is positioned in front of the electrode, where DMRc is regenerated.

Keywords: *hydrogen evolution reaction (HER), photogeneration, scanning electrochemical microscopy, liquid|liquid interface, decamethylruthenocene, 1,2-dichloroethane*

Innovative solution for photovoltaics

Bartłomiej S. Witkowski, Rafał Pietruszka, Monika Ożga, Jarosław Kaszewski, Piotr Sybilski, Marek Godlewski

Institute of Physics of the Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

bwitkow@ifpan.edu.pl

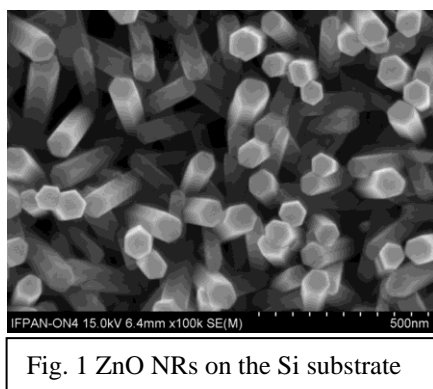


Fig. 1 ZnO NRs on the Si substrate

Semiconductors nanostructures such as nanowires, nanorods (NRs) and thin films have attracted increasing attention recently, largely as a result of their great potential in application in optoelectronic nanodevices and functional materials i.e. for photovoltaics (PV) [1]. One of the most studied recently material in this field is ZnO - a semiconductor with a direct band gap of 3.37 eV at room temperature of high transparency and high n-type conductivity [2].

The second material very intensively studied regarding PV applications is copper oxide. As in the case of ZnO, despite the huge financial outlays, CuO is not commercially used in the production of photovoltaic cells.

Our group has presented a new extremely fast, efficient and also low-cost growth method of ZnO NRs [2], based on the hydro-thermal method. This fully reproducible method allows growth of nanorods without any catalyst or complexing agent on various substrates (silicon, GaAs, quartz, sapphire), as shown in Fig. 1. These NRs were successfully used in construction of simple PV cells with efficiency of 14%. What is important, all technologies used in this approach are very inexpensive and easy scalable to industrial size.

Our group has also attempted to develop a technology for the growth of CuO layers by hydrothermal method by the similar approach as for ZnO NRs. The first results are very promising. We managed to obtain homogeneous layers with controlled thickness. In the next stage, attempts will be made to optimize the electrical parameters of the layers, and then a prototype photovoltaic cell will be constructed.

Keywords: *PV cells, nanorods, nanolayers, hydrothermal, crystal growth*

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On selected factors governing the photocatalytic CO₂ reduction

Wojciech Macyk

Faculty of Chemistry, Jagiellonian University, ul. Gronostajowa 2, 30-387 Kraków, Poland

macyk@chemia.uj.edu.pl

The photocatalytic carbon dioxide reduction is a challenging process in which, similarly to photosynthesis, light can be converted to a chemical energy. The energetics of this reaction is very different from the most commonly studied photocatalytic reactions in which pollutants are photooxidized to CO₂. Although these two processes are, in principle, opposite to each other, usually the same photocatalysts (mainly oxides, including TiO₂) are considered in both cases. Most of metal oxides, being *n*-type semiconductors, upon excitation offer strong oxidation properties, but at the same time they are relatively mild reductants. We propose another approach to a photocatalytic CO₂ reduction, involving application of *p*-type semiconductors, offering, contrary to *n*-semiconductors, better reduction and worse oxidation properties. As an example, the photocatalytic activity of *p*-CuI towards carbon dioxide photoreduction (mainly to CO and HCOOH) can be compared to that of TiO₂ (P-25).¹ The applicability of *p*-type semiconductors for carbon dioxide valorization will be discussed.^{1,2}

Other important parameters influencing the photocatalytic CO₂ reduction process encompass redox properties of the material, adsorption of reactants, number of electrons participating in the reduction reaction, the oxidation counterpart of the reaction, and several others. Redox properties of the photocatalysts can be easily determined using spectroelectrochemical methods developed recently in our laboratories.³ The number of electrons participating in reduction reactions should also be taken into account – methane formation requires eight electrons in total,⁴ but carboxylic acids can be synthesized in the process of CO₂⁻ (one-electron reduction of CO₂) and R• radicals (one-hole oxidation of RH) coupling.⁵⁻⁷

Do we know how to design photocatalysts for CO₂ reduction? Can we control the redox properties of photocatalysts? Do we understand which factors determine the photocatalytic activity of photocatalysts? These questions will be briefly discussed during the presentation.

Acknowledgement: The work was supported by the National Science Center (Poland) within the 2015/19/B/ST5/00950 project.

Keywords: *CO₂ reduction, photocatalysis, photocatalytic synthesis of chemicals*

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Mechanoperovskites for Photovoltaic Applications

Janusz Lewiński^{1,2}

¹*Institute of Physical Chemistry, PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*

²*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw*

lewin@ch.pw.edu.pl

The recent discovery of hybrid organic-inorganic metal halide perovskites led to a renaissance of thin film photovoltaics.¹ The great diversity of hybrid perovskite compositions and preparation pathways makes them an excellent candidate for novel photovoltaic materials with unique combination of properties, the potential for low cost and easy processing along with relatively high power conversion efficiencies.² Notably, the optoelectronic properties and the influence on the photovoltaic parameters of perovskite materials are highly sensitive to the adopted synthetic strategy. Therefore, it is of great interest to provide simple and feasible approaches to high quality hybrid perovskites and the respective thin films. In that context, the synthetic approach induced by mechanical forces has appeared as a new emerging methodology in materials science. The mechanochemical reactions in solid state offer a significant advance by avoiding the use of solvents, dramatically shortening synthesis times and simultaneously increasing the purity and amount of product.

Herein, we have developed a facile mechanochemical route for the preparation of various organic-inorganic hybrid lead halide perovskites and lead-free perovskite materials for high-efficiency thin-film photovoltaics.³ Strikingly, this procedure can pave the way for new compositions and phases, which are not otherwise obtainable.⁴ The mechanochemical approach for preparation of perovskite materials has also advantage over a solution-based synthetic routes in terms of hysteresis and device performance.⁵ Our studies highlight the essential need for atomic-level characterization of photovoltaic perovskite materials and provided fundamental understanding of photovoltaic parameters in these systems and their superior stability.

Keywords: *green chemistry, mechanosynthesis, lead halide perovskites, lead-free perovskites, solar cells, preparation, characterization*

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Toward Effective Photoelectrochemical Water Splitting and Electrocatalytic Reduction of Carbon Dioxide

Pawel J. Kulesza, Iwona A. Rutkowska

Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland.

pkulesza@chem.uw.edu.pl

The reduction of carbon dioxide is a very inert process that requires breaking the double C=O bond in the stable CO₂ molecule. There is a need for conversion of carbon dioxide, a potent greenhouse gas and a contributor to the global climate change, to useful carbon-based fuels or useful chemicals. Our contribution addresses the low-temperature CO₂-conversion processes based on electrocatalytic and photoelectrochemical approaches. In the realistic electrolysis cells, the reduction of CO₂ (at cathode or photocathode) would have to be accompanied by water oxidation (at anode or photoanode).

Our interest is in the PEM electrolyzers utilizing the proton exchange polymer electrolyte membranes (as separators between anode and cathode compartments) allowing electrolysis at low pH's and, in principle, capable of yielding higher current densities than alkaline electrolyzers. Nevertheless, under such conditions, the parasitic hydrogen evolution reaction is likely to become predominant and complicate formation of any CO₂-reduction products. Our preliminary results with the copper or ruthenium containing tungsten oxide nanorods as catalytic materials are promising with respect to the investigations in acid media.

Recent advances (including our studies) in photoelectrochemical water splitting are based on semiconducting photoanodes (typically n-type semiconducting metal oxides) combined either with a metallic cathode (e.g. Pt) or with a p-type semiconductor as a photocathode should be mentioned here in a context of the development of the CO₂-electrolyzers exploring photoelectrocatalytic properties and operating under illumination. Among representative examples of metal oxides with n-type semiconducting and promising photoelectrocatalytic properties, tungsten oxide (WO₃) should be mentioned. The WO₃-based semiconductors are highly stable in acid media, and they are characterized by an energy band gap of 2.5-2.7 eV thus allowing absorption of a reasonable fraction of the solar spectrum up to ca. 500 nm. It comes from our research that, upon illumination, the onset potential for photooxidation of water (in acid medium) is as low as 0.45 V (vs. RHE) what is of practical importance to the energy efficient photoelectrolysis. Further improvement of performance of photoactive metal oxides, e.g. through doping with certain anions or oxo-species will be discussed. Utilization of such systems in the CO₂-electrolyzers

would require, however, development of practical cathodes (CO₂-reduction) operating in acid media that will be addressed during presentation. In our work, the solar energy will be absorbed by a suitable semiconductor to drive water oxidation to oxygen and protons, whereas the reduction of CO₂ will be achieved electrochemically with use of a proper (selective) catalyst. By utilizing the aqueous acidic medium, no external hydrogen is required for the CO₂-reduction process because the H⁺ ions not only exist at sufficiently large population, but they are generated in situ during the anodic reaction. Coupling of the two processes in a single unit leading to one-step photoelectrochemical/electrocatalytic approach should be possible (e.g. with use of a tandem cell) but, in practice, physical separation of the two reactions in photoanodic (photoelectrochemical water oxidation) and cathodic (carbon dioxide electroreduction) compartments is necessary to increase efficiency and to limit charge recombination. Conversion of CO₂ to CO (accompanied by H₂-evolution) is an attractive target because syngas (CO + H₂) can be utilized for manufacturing of many useful chemicals including synthetic fuels via the Fischer-Tropsch type process.

Photosystem I as the robust component of solar cells and solar-to-fuel devices

Joanna Kargul¹, Małgorzata Kiliszek¹, Ersan Harputlu², Marcin Szalkowski³, Dorota Kowalska³, C. Gokhan Unlu⁴, Patrycja Haniewicz¹, Mateusz Abram¹, Kamil Wiwatowski³, Silvio Osella⁶, Bartosz Trzaskowski⁶, Sebastian Maćkowski³, Kasim Ocakoglu^{2,5}

¹*Solar Fuels Lab, Centre of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland*

²*Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR33343, Yenisehir, Mersin, Turkey*

³*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Torun, Poland*

⁴*Department of Biomedical Engineering, Pamukkale University, TR-20070 Denizli, Turkey*

⁵*Department of Energy Systems Engineering, Mersin University, Tarsus Faculty of Technology, 33480 Mersin, Turkey*

⁶*Chemical and Biological Systems Simulation Lab, Centre of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland*

j.kargul@uw.edu.pl

A major bottleneck in the fabrication of efficient bio-organic nanoelectronic devices resides in the strong charge recombination that is present at the different interfaces forming the complex system. An efficient way to overcome this limitation is to add an optimized self-assembled monolayer (SAM) of molecules between the biological material and the electrode that promotes an efficient direct electron transfer whilst minimising wasteful processes of charge recombination. Another approach is to include plasmonic nano-architectures that interact with photoactive components often leading to an improved photocurrent density obtained from biophotoelectrodes. Here we show that coupling extremophilic robust photosystem I (PSI) reaction centers¹ with plasmonically active silver island film (SIF) leads to enhancement of both fluorescence intensity as well as photocurrent generation. The nanostructure is assembled by the controlled attachment of PSI to a monolayer graphene deposited on the SIF layer, using cytochrome *c*₅₅₃ as the conductive orienting biomolecule²⁻⁴. The molecular organic interface between PSI and electrode surface is based on a pyrene-nitrilotriacetic acid SAM containing various metallic redox centers for oriented coupling of the biophotoactive layer of PSI. A combination of theoretical calculations, field emission scanning electron microscopy, and photoelectrochemical characterization reveals that the metal center at the or-

ganic conductive interface holds the key role for both, improved direct electron transfer at the interface and SIF-mediated plasmonic enhancement of fluorescence in the PSI layer.^{5,6}

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Keywords: *biophotoelectrodes, biocatalysts, biohybrid solar-to-fuel nanodevices, photosystem I, single layer graphene, plasmonic interactions*

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Fluorescence imaging of plasmonically active PSI-graphene bioelectrodes

Marcin Szalkowski¹, Dorota Kowalska¹, Ersan Harputlu², Małgorzata Kiliszek³, C. Gokhan Unlu⁴, Kamil Wiwatowski¹, Kasim Ocakoglu^{2,5}, Joanna Kargul³, Sebastian Maćkowski¹

¹ *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland*

² *Advanced Technology Research & Application Center, Mersin University, Cilikkoy Campus, TR33343, Yenisehir, Mersin, Turkey*

³ *Center of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland*

⁴ *Department of Biomedical Engineering, Pamukkale University, TR-20070 Denizli, Turkey*

⁵ *Department of Energy Systems Engineering, Faculty of Technology, Tarsus University, 33400 Tarsus, Turkey*

marszal@fizyka.umk.pl

Photosynthetic reaction centers, the essential components of photosynthetic apparatus, are huge pigment-protein complexes capable of performing electric charge separation. This process, powered by the sunlight energy, is characterized by high quantum efficiency of almost 100% – hence each captured quanta of light triggers production of a pair of separated charges. This feature promotes such biocomplexes to be considered as building blocks of solar fuel cells [1]. Nevertheless, it has proven to be rather challenging to construct electrodes featuring all of the benefits of photosynthetic reaction centers.

Recently, we have demonstrated a bioelectrode based on robust photosystem I (PSI) supercomplexes isolated from extremophilic red algae *Cyanidioschyzon merolae* interfaced with atomically thin lattice of

carbon atoms – graphene [2]. Graphene is an efficient energy and electron acceptor. Due to directional charge flow in PSI complexes it is critical from the point of view of optimizing its electrochemical performance to achieve their uniform assembly at the interface. It has been achieved by chemical modification of graphene with nitrilotriacetic acid (NTA) followed by binding of cytochrome (cyt) *c553*. The cyt *c553* molecules furthermore facilitate specific binding of PSI and play a role as their electron donors [3].

In the present work we aimed at improving the performance of the PSI-based electrodes by coupling them with a metallic nanostructure – silver island film (SIF). The SIF layers were prepared both on conductive FTO substrates and on glass coverslips. In such a nanostructure there emerge collective oscillations of electrons induced by incoming light, which are called plasmons. The plasmons can strongly modify the optical properties of fluorophores in their vicinity, resulting particularly in enhancing of the absorption efficiency or changes in the emission dynamics [4]. As a result, the electrode composed of PSI complexes interfaced via *c553* to a graphene layer deposited on SIF, was fabricated and thoroughly characterized. In particular, we focused on investigating the optical properties of such electrodes using excitation wavelength-dependent fluorescence microscopy. It is a low-invasive technique, which provides insight into microscale homogeneity of the samples and enables spectrally- and time-resolved measurements, which are essential for determination of impact of plasmonically active nanostructures on fluorophores.

We found that by including the SIF layer it is possible to strongly enhance fluorescence intensity of PSI complexes assembled on graphene, even though this effect is reduced by the energy transfer from PSI to graphene. Observed fluorescence enhancements depend on both, excitation wavelength and silver island deposition density, and can reach values exceeding 20. Moreover, clear shortening of fluorescence decay of PSI confirms the plasmonic origin of the observed effects. We found that the enhancement of the PSI fluorescence is a direct result of plasmonically-increased absorption efficiency of PSI complexes and, presumably, also activation of internal energy transfer pathways.

The results prove that control of the nanoscale spatial arrangement of components and implementation of plasmonically active metallic nanostructures are crucial for improving performance of PSI-based photoelectrodes for energy conversion.

Acknowledgement: Research was supported by project DZP/POLTUR-1/50/2016 funded by the National Centre for Research and Development.

Keywords: *fluorescence imaging, plasmonics, graphene, photosystem I, bioelectrode, solar cell*

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Photosystem I-Integrated Nanostructured Architectures for Solar Fuel Production

Kasim Ocakoglu¹, Ersan Harputlu², Cumhuri Gokhan Unlu³, Małgorzata Kiliszek⁴, Patrycja Haniewicz⁴, Mateusz Abram⁴, Marcin Szalkowski⁵, Dorota Kowalska⁵, Sebastian Mackowski⁵, Joanna Kargul⁴

¹Department of Energy Systems Engineering, Faculty of Technology, Tarsus University, 33400 Tarsus, Turkey.

²Advanced Technology Research&Application Center, Mersin University, Ciftlikkoy Campus, TR33343, Mersin, Turkey.

³Department of Biomedical Engineering, Pamukkale University, TR-20070, Denizli, Turkey.

⁴Solar Fuels Laboratory, Centre of New Technologies, University of Warsaw, Warsaw, Poland.

⁵Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland.

kasim.ocakoglu@tarsus.edu.tr

The solar energy conversion and storage with chemical process take place in the nature by photosynthesis. In order to use same analogous mechanism of natural photosynthesis in the novel artificial solar energy conversion devices, it should require to understand the nature of photosynthesis mechanism. It is well known that in photosynthesis, photo-induced electron transfer and charge separation occurs in Photosystem I (PSI). Recently, researchers have concentrated their efforts to integrate PSI into functional devices to systematically construct appropriate artificial solar energy conversion devices and simulate similar natural systems (1-2). The aim of this work is to design superior electrodes for new solar-fuel devices compared to presently studied structures for photo-conversion and solar fuel generation. Therefore, single-layer graphene (SLG) structures have been used in this electrode structure owing to its unique properties in the transmission of electricity and a flat surface. SLG acts as an ideal electrode for transferring energy from natural photosynthetic systems such as *Cyanidioschyzon merolae*. Based on this objective, highly stable natural photosynthetic complexes are specifically bound to the modified SLG coated electrode surface with functional groups. In this context, the SLG-based electrode was functionalized with PSI using a linker such as pyrene derivative (pyrene-nitrilotriacetic acid) to build ordered biohybrid devices for solar energy conversion.

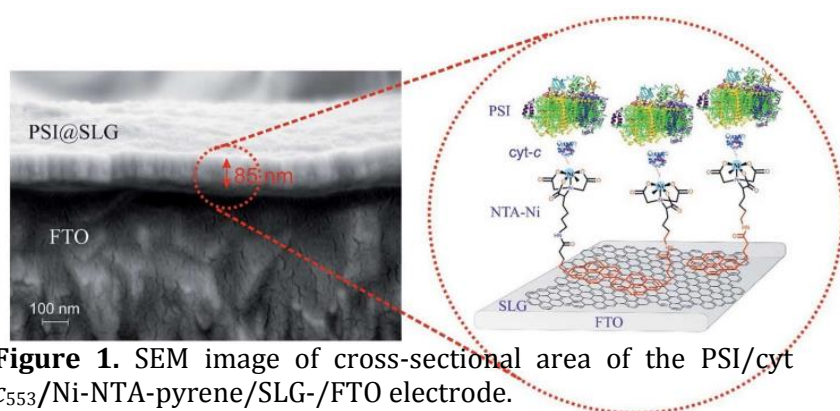


Figure 1. SEM image of cross-sectional area of the PSI/cyt *c*₅₅₃/Ni-NTA-pyrene/SLG-/FTO electrode.

SLG surface (3-4). The specific conjugation of cyt *c*₅₅₃ with the Ni-NTA-pyrene/SLG-/FTO electrode was performed using the molecular interaction between the donor (P700) side of the PSI and cyt *c*₅₅₃ (Fig. 1). Figure 1 shows the SEM image of cross-sectional area of the PSI/cyt *c*₅₅₃/Ni-NTA-pyrene/SLG-/FTO electrode, including the 3D organization of the PSI/cyt *c*₅₅₃ on the electrode surface.

Keywords: Energy, Photosynthesis, Photosystem I, PSI, Single Layer Graphene, Biophotoelectrode, Photosynthetic Complex.

Acknowledgment: This research was financially supported by The Scientific and Technological Research Council of Turkey, TUBITAK (grant no. 215M389 to KO) and The Polish National Centre for Research and Development (grant no. DZP/POLTUR-1/50/2016, agreement no. 5/POLTUR-1/2016 to JK and SM) within the framework of Bilateral Polish-Turkish POLTUR program.

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Hybrid materials for artificial photosynthesis: a computational approach

Silvio Osella, Bartosz Trzaskowski

Chemical and Biological Systems Simulation Lab, Center of New Technologies, University of Warsaw, Banacha 2C, 02-097 Warsaw, Poland.

s.osella@cent.uw.edu.pl

In recent years, research effort has been devoted to the generation of hybrid materials which change the electronic properties of one constituent by changing the optoelectronic properties of the other one. The most appealing and commonly used approach to design such novel materials relies on combining organic materials or metals with biological systems like redox-active proteins. Such hybrid systems can be used e.g. as bio-sensors, bio-fuel cells, biohybrid photoelectrochemical cells and nanostructured photoelectronic devices. Although experimental efforts have already resulted in the generation of a number of hybrid bio-organic materials, the main bottleneck of this technology is the formation of a stable and efficient (in terms of electronic communication) interface between the biological and the organic/metal counterparts. In particular, the efficiency of the final devices is usually very low due to two main problems related to the interfacing of such different components: charge recombination at the interface and the high possibility of losing the function of the biological component, which leads to the inactivation of the entire device.

Here, we present a multiscale computational design which allows the study of complex interfaces for stable and highly efficient hybrid materials for biomimetic application, consisting of single layer graphene (SLG) as organic material/metal and light harvesting protein complex (Photosystem I) as biological counterpart, linked together via a self-assembly monolayer (SAM) and a biological linker (cytochrome *c*₅₅₃) to allow flexibility of the whole system, in order to create novel biomimetic materials for solar-to-fuel, bio-transistors or bioorganic electronic applications. In particular, we focus on the SAM/SLG and cytochrome *c*₅₅₃/SLG interfaces as models to validate our theoretical approach. [1-5]

Keywords: *multiscale modelling, graphene, self-assembly monolayers, artificial photosynthesis, electron transfer*

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Photosynthetic microorganisms as biocatalysts for the production of chemicals

Yagut Allahverdiyeva-Rinne

Molecular Plant Biology unit, University of Turku, Turku, Finland

allahve@utu.fi

The structure and function of photosynthetic machinery have been well-studied throughout recent decades. However, regulation of this machinery is complex and new players are still being revealed. Photosynthetic organisms possess, among other protection mechanisms, an extensive network of auxiliary electron transport pathways to regulate photosynthesis. On the one hand, these routes can be considered necessary for the survival of cells under extreme changes in environmental conditions, whereas on the other hand, the resulting physiological changes can be thought of as a “waste” of photosynthetic electrons or reducing power. Our research is focused on auxiliary electron transport pathways, particularly on flavodiiron proteins (FDPs or Flv) in cyanobacteria and algae (*e.g.* Allahverdiyeva et al 2013, Ermakova et al. 2014, Mustila et al. 2016, Jokel et al. 2018, Sanchez et al. 2019). FDPs function as powerful electron sink by photo-reducing O₂ in the Mehler-like reaction downstream of Photosystem I. The FDP pathway(s) is important to consider in future high-yield crop development and design living factories producing targeted end-chemicals.

Our applied photosynthesis research aims to optimize photosynthetic performance for improved chemical and bioenergy production, as well as waste-water treatment. We have developed a novel protocol for improved H₂ photoproduction yields in *C. reinhardtii* under periodic light conditions, which does not require severe stress conditions (Kosourov et al. 2018). This study has clearly shown that a major obstacle to efficient H₂ photoproduction is a strong competition between two metabolic pathways: CO₂ fixation leading to the biomass accumulation and the hydrogenase enzyme catalysing photoproduction of H₂. This finding opens up new opportunities for construction of highly-efficient cell factories for production of biofuels and chemicals directly from solar energy. It provides important information how to avoid ‘wasting’ of solar-driven energy to biomass production and how to apply this energy for direct production of useful bio-products.

Moreover, the tailored solid-state cell factories, where algal (cyanobacterial)-based cell factories (biocatalysts) function with high catalytic turn-over time and novel immobilization approaches (Jamsa et al. 2018) permitting higher light-to-product conversion efficiency will be discussed.

Keywords: *photosynthetic electron-transport, cyanobacteria, algae, auxiliary electron-transport, flavodiiron, photohydrogen, ethylene, immobilization, bioproduction*

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Thermal energy dissipation in plants: Is it good or is it bad for photosynthesis?

Wiesław I. Gruszecki¹, Monika Zubik¹, Rafal Luchowski¹, Dariusz Kluczyk¹,
Wojciech Grudzinski¹, Magdalena Maksim², Artur Nosalewicz²

¹ *Department of Biophysics, Institute of Physics, Maria Curie-Skłodowska University, Lublin Poland*

² *Institute of Agrophysics, Polish Academy of Sciences, Lublin, Poland*

wieslaw.gruszecki@umcs.pl

Thermal dissipation of a fraction of excitation energy in the photosynthetic apparatus of plants is considered as one of the mechanisms operating to protect plants against photo-damage. On the other hand, conversion of a fraction of excitation energy to heat obviously decreases an overall energy yield of photosynthesis. We will present an intriguing observation that thermal excitation energy dissipation in chloroplasts is highly efficient not exclusively under overexcitation conditions that can be referred to high light stress, but equally efficiently at very low light intensities. Is such a mechanism relevant from the physiological standpoint or rather it represents an imperfect nature of Nature? We will try to discuss this problem during the seminar.

Keywords: *photosynthesis, Photosystem II, Photosystem I, LHCII, thermal energy dissipation*

Molecular mechanisms of regulation of photosynthetic electron flow

Marcin Sarewicz, Łukasz Bujnowicz, Sebastian Pintscher, Robert Ekiert, Patryk Kuleta,
Arkadiusz Borek, Rafał Pietras, Artur Osyczka

¹*Department of Molecular Biophysics, Faculty of Biochemistry, Biophysics and Biotechnology,
Jagiellonian University, Kraków*

marcin.sarewicz@uj.edu.pl, artur.osyczka@uj.edu.pl

Our group investigates molecular mechanisms of operation of enzymes involved in photosynthetic and respiratory electron transport chains. We aim at understanding the nature of their energetic efficiency and physiological regulation. Toward this aim we ask how the electron transport systems are designed to secure both the recognition of the reacting partners and catalysis while avoiding deleterious side reactions. The latter ones not only dissipate energy, but can also be associated with production of reactive oxygen species (ROS).

We focus on cytochrome *bc* complexes, crucial and ubiquitous energy-conserving enzymes. Operation of these enzymes involves unstable radical intermediates which in oxygenic atmosphere present a danger of becoming a source of electrons for generation of ROS. Using genetic approaches combined with optical and electron paramagnetic spectroscopies we provided knowledge on several important molecular elements of the operation of cytochrome *bc* complexes. This includes a description of dynamics of interaction between cytochrome *bc*₁ and its physiological partner, cytochrome *c* [1], an experimental evidence for catalytically relevant electron transfer between the monomers of cytochrome *bc*₁ [2], a proposal of molecular mechanism of ROS generation by the quinol oxidation site of this enzyme [3]. Most recently we discovered a metastable state associated with operation of both the respiratory cytochrome *bc*₁

and photosynthetic cytochrome *b₆f* [4,5]. In this state, which appears nonreactive with oxygen, a radical intermediate interacts with a metal cofactor of a catalytic site via spin-spin exchange.

Based on this discovery we proposed a new concept explaining how cytochrome *bc* complexes adjust electron transfer rates for efficient catalysis under different oxygen tensions to minimize ROS generation. We also hypothesized that formation of this metastable state in cytochrome *b₆f* is one of the means for kinetic control to balance between cyclic and linear electron flow (CET and LET, respectively) in photosynthesis needed for efficient reduction of CO₂ into the organic form.

From this perspective, in our current research we intend to explore structural basis and dynamics of interaction between cytochrome *b₆f* and its plausible CET protein partners, define the sequence of electron transfer steps that engage cytochrome *b₆f* into CET and describe thermodynamic basis for control of CET. In this project we will utilize the methodology and knowledge gathered during studies on cytochrome *bc₁* in photosynthetic bacteria. We hope that this will provide fundamentals for understanding regulation of photosynthesis on molecular level, as a step towards development of enhanced photosynthetic organisms to increase efficiency in plant production.

Keywords: *electron transfer, photosynthesis, cytochromes, quinones, reactive oxygen species (ROS), electron paramagnetic resonance spectroscopy, freeze-quench*

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Challenges, Technologies and Innovative Potential of Photosynthesis

Stanisław Karpiński

*Warsaw University of Life Sciences, Department of Plant Genetics, Breeding and Biotechnology,
Nowoursynowska Street 159, 02-776 Warszawa, Poland*

stanislaw_karpinski@sggw.pl

It is well known that PsbS is a key protein for the proper management of excessive energy in plants. Plants without PsbS cannot trigger non-photochemical quenching, which is crucial for optimal photosynthesis under variable conditions. Our studies showed wild-type plants had enhanced tolerance to UV-C-induced cell death (CD) upon induction of light memory by a blue or red light. We will show a novel, substantial role for PsbS in the retrograde regulation of light memory and light acclimation, electrical signalling, and cross-tolerance of light acclimatory and defence processes such as CD and play a role in the regulation of cross-tolerance between high-light acclimation and UV responses. Furthermore, PsbS play important role in regulation of electrical signal that link in a communication network of the photosystems II, within and between transmitter and receiver plants. For the first time, we report collective aboveground communication of stress electrical signals that are conveyed in the plant population to induce (so-called by us) the network acquired acclimation. Inventive potential of these findings for amelioration of photosynthesis, plants productivity, plants breeding and biofuels production will be presented.

Chlorophylls – sophisticated self-protecting photodevices

Leszek Fiedor^a, Mariusz Pilch^{a,b}, Alina Dudkowiak^c

^a*Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University,
Gronostajowa 7, 30-387 Krakow, Poland*

^b*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland*

^c*Faculty of Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland*

leszek.fiedor@uj.edu.pl

Various experimental and theoretical approaches have been applied to investigate the properties of a series of metallochlorophylls (complexes Mg^{2+} , Zn^{2+} , Ni^{2+} and Pd^{2+} , and Pt^{2+}), to reveal how the central metal ion affects the chemical and photophysical features of the chromophore.¹⁻³ Depending on the valence configuration of the central metal ion and symmetry of the macrocyclic system, three different types of chemical bonds can be formed to the core nitrogens. This model challenges the common view of (metallo)chlorophylls as coordination complexes. The influence of the central metal ion on the pigment properties is largely dictated by the type of the bond formed. High pressure and optical spectroscopy studies, supported by DFT calculations, show that in the Mg^{2+} complexes, the metal ion–macrocycle interaction is mostly electrostatic, and the chelation of Mg^{2+} has a flattening effect on the macrocycle. Also, among various metallocomplexes, the lowest quantum yield of the T_1 state is always observed in the Mg complex, which shows the least efficient energy transfer to molecular oxygen, as determined using time-resolved laser-induced optoacoustic spectroscopy. These results point to the existence of intrinsic photoprotective mechanisms in chlorophylls. The transition metal ions, due to the unfilled d shell, bind very strongly via mixed coordinative-covalent interactions. Only in the Zn^{2+} complexes, classical coordination bonds are present. The model of three modes of metal ion bonding consistently explains also other features of metallochlorophylls, such as their stability/lability and their preferences for axial ligand coordination.

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***Rhodobacter sphaeroides* Reaction Centers as an Active Material for Bio-hybrid Photovoltaic Device**

Rafał Białek¹, Vincent M. Friebe^{2,3}, Adrian Ruff³, David Swainsbury^{4,#}, Michael R. Jones⁴, Maciej Wiesner^{1,5}, Raoul Frese², Krzysztof Gibasiewicz¹

¹*Faculty of Physics, Adam Mickiewicz University in Poznań,
ul. Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland*

²*Department of Physics and Astronomy, LaserLaB Amsterdam, VU University Amsterdam,
De Boelelaan 1081, Amsterdam 1081 HV, The Netherlands*

³*Center for Electrochemical Sciences, Faculty of Biochemistry and Chemistry,
Ruhr-University Bochum, Universitätsstrasse 150, D 44780 Bochum, Germany*

⁴*School of Biochemistry, Biomedical Sciences Building, University of Bristol,
University Walk, Bristol BS8 1TD, UK*

⁵*NanoBioMedical Center, Adam Mickiewicz University in Poznań,
ul. Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland*

[#]*Present address: Department of Molecular Biology and Biotechnology,
University of Sheffield, Sheffield S10 2TN, UK*

rafal.bialek@amu.edu.pl; krzysztof.gibasiewicz@amu.edu.pl

One of the biggest problems of the contemporary world is the depletion of fossil fuels. Among possible solutions for meeting future energy demands, solar cells based on photosynthetic reaction centers (RCs) of the purple bacterium *Rhodobacter sphaeroides* are considered. These proteins can be used in various cell designs. During the presentation two of those will be presented: protein in semi-conducting matrix of mesoporous TiO₂¹⁾ and in redox active hydrogel matrix.²⁾ In these systems, RCs show ability to generate both cathodic and anodic photocurrents depending on the applied potential, mediators and substrate used.

Our main research goal is the description of the mechanism of operation of studied systems and finding bottle-necks in photocurrent generation. For this purpose, we use modelling with computer simulations and spectroelectrochemical methods for *in situ* redox potential determination. Hopefully this research will enable further optimization of prototype biosolar cell.

Keywords: *biophotovoltaics; reaction centers; spectroelectrochemistry; electron transfer; Rhodobacter sphaeroides*

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Three-dimensional thylakoid network – biogenesis, dynamics, and reorganizations in response to the environmental factors

Mazur Radosław¹, Kowalewska Łucja², Gieczewska Katarzyna², Samól Iga¹, Wójtowicz Joanna², Szach Joanna², Łazicka Magdalena¹, Piotrowska Paulina¹, Bykowski Michał², Krysiak Małgorzata¹, Mostowska Agnieszka², Garstka Maciej¹

rmazur@biol.uw.edu.pl

The chloroplast thylakoid network, a site of photochemical reactions, forms an intricate spatial structure assembly of proteins, polar lipids, and pigments. This system develops upon illumination during chloroplast biogenesis and its possible rearrangements play a crucial role in the photosynthesis regulation. Moreover, this system evolved multiple regulatory mechanisms which can trigger dynamic rearrangement of the chlorophyll-protein (CP) complexes in response to diverse environmental factors. Our research is focused on the relationship between composition, structure, and function of the thylakoid membranes network. In particular we study: (i) three-dimensional tubular-lamellar transformation of the internal plastid membrane network during biogenesis and its modifications in different species/mutants/environmental conditions; (ii) three-dimensional visualization of the thylakoid membrane stacking dynamics; (iii) role of plastoglobules in plant chilling response; (iv) regulation of LHCII phosphorylation during low-temperature stress in plants with different chilling tolerance; (v) changes of protein, lipid and CP complexes organization during chilling stress in chilling sensitive and chilling tolerant plant species; (vi) electrochemical properties of LHCII complexes immobilized on screen-printed graphite electrodes.

Involvement of non-heme iron in long range regulatory mechanisms of electron and proton transfer within photosystems of type II

K. Burda¹, A. Halas¹, A. Orzechowska¹, V. Derrien², A. Chumakov³, P. Sebban², J. Fiedor¹, M. Zając⁴, T. Ślęzak¹, J. Korecki¹

¹*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Kraków, Poland*

²*Laboratoire de Chimie Physique, CNRS, University of Paris-Sud, Orsay, France*

³*European Synchrotron Radiation Facility, Grenoble, France*

⁴*Solaris, Jagiellonian University, Krakow, Poland*

kvetoslava.burda@fis.agh.edu.pl

Non-hem iron is intrinsically involved in photosynthesis, a fundamental biological process. It is a very conservative component of type II photosynthetic reaction centers (RCs). In reaction centers from purple bacteria, so far structurally best characterized pigment-protein complexes [1], the electron transfer cofactors are symmetrically (along pseudo C2 axis) organized in two branches which comprise a special pair of bacteriochlorophyll (P860), serving as a primary electron donor, two bacteriochlorophyll monomers, two bacterio-pheophytins, a non-heme iron and two ubiquinones Q_A and Q_B, which are the final electron acceptors. Although the tertiary structure of RCs is presently known with 1.87 Å [1] resolution, the molecular mechanism of some reactions occurring within the photosynthetic centers is not completely understood. For example, the Q_A to Q_B ET process is gated by mechanisms coupled to rearrangements of hydrogen bond networks in the vicinity of the Q_A-Fe-Q_B complex [2,3] and therefore a proper flexibility of the acceptor side of RCs is required to ensure its efficient functioning [4-6].

Our aim was to investigate long range regulatory mechanisms controlling the activity of the photosynthetic bacterial reaction centers (BRC) of type II (having iron-quinone complex at the acceptor side). They are governed by the flexibility of the BRC core proteins which contain cofactors participating in

electron transport (ET) and residues involved in forming hydrogen network and in tuning the redox potential of these cofactors. We concentrate on the role of the non-heme iron (NHFe) in these processes. The use of the Nuclear Inelastic Scattering (NIS) method allowed us to show that the stoichiometry of proton uptake and reduction of proton transfer in mutated BRC close to the Q_B, when two hydrogen bonds were removed (L212Glu/L213Asp to Ala/Ala), and close to the Q_A site, when additionally its hydrophobic character was changed (+M249Ala to Tyr), were directly related to the modification of the partial phonon density of NHFe states [7]. It became clear that the high spin state of NHFe is important for the optimal transfer of fast collective motions on the acceptor side of BRCs of type II and effective ET between the quinones Q_A → Q_B [6,7].

We believe that the long-range coupling of NHFe to protein matrix, regulated by thermal motions, might be crucial for optimal functioning of the BRCs. Understanding how NHFe in BRCs minimizes promiscuity of paths of electron and proton transfer is of great importance for designing artificial reaction centers, which would perform the fundamental process of photochemical charge separation with comparable efficiency.

Keywords: *bacterial reaction centers, non-heme iron spin states, collective motions, electron transfer,*

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Extreme Photosynthesis: Molecular mechanisms of photoprotection in photosynthetic apparatus of an extremophilic red alga *Cyanidioschyzon merolae*

Patrycja Haniewicz¹, Mateusz Abram¹, Rafał Białek², Sebastian Szewczyk², Jerzy Karolczak², Krzysztof Gibasiewicz, Lukáš Nosek³, Joanna Kirkpatrick⁴, Roman Kouřil³, and Joanna M. Kargul¹

¹*Solar Fuels Laboratory, Center of New Technologies, University of Warsaw, Warsaw, Poland*

²*Faculty of Physics, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 2, Poznań, Poland*

³*Centre of the Region Haná for Biotechnological and Agricultural Research, Department of Biophysics, Faculty of Science, Palacký University, Olomouc, Czech Republic*

⁴*Leibniz Institute on Aging-Fritz Lipmann Institute, Jena, Germany*

p.haniewicz@cent.uw.edu.pl

Life can develop in environments that seem impossible to be inhabited. Extremophiles have evolved remarkable strategies that allow them to thrive beyond some daunting physical and chemical limits of life on Earth. In the era of global climate change, there is a strong need to understand photosynthetic processes and their regulatory basis, particularly as they relate to extreme conditions.

Our research is focused on *Cyanidioschyzon merolae* that is a thermo-acidophilic unicellular red microalga isolated from acidic hot springs rich in sulphate and moderately high temperatures. The photosynthetic

apparatus of *C. merolae* is considered to be an evolutionary intermediate between the photosynthetic apparatus of prokaryotic cyanobacteria and the eukaryotes.

We show that the *C. merolae* PSI-LHCI supercomplex is characterized by robustness in various extreme conditions. By a combination of biochemical, spectroscopic, mass spectrometry, and electron microscopy/single particle analyses, we dissected three molecular mechanisms underlying the inherent robustness of the *C. merolae* PSI-LHCI supercomplex: (1) the accumulation of photoprotective zeaxanthin in the LHCI antenna and the PSI reaction center; (2) structural remodeling of the LHCI antenna and adjustment of the effective absorption cross section; and (3) dynamic readjustment of the stoichiometry of the two PSI-LHCI isomers and changes in the oligomeric state of the PSI-LHCI supercomplex, accompanied by dissociation of the PsaK core subunit. We show that the largest low light-treated *C. merolae* PSI-LHCI supercomplex can bind up to eight Lhcr antenna subunits, which are organized as two rows on the PsaF/PsaJ side of the core complex. Under our experimental conditions, we found no evidence of functional coupling of the phycobilisomes with the PSI-LHCI supercomplex purified from various light conditions, suggesting that the putative association of this antenna with the PSI supercomplex is absent.

Recently we explored different biological strategies optimizing the light conversion by photosynthetic pigment-containing proteins depending on the illumination light intensity during growth of photosynthetic organisms. Our time-resolved fluorescence decay analysis has revealed the remarkable functional flexibility of light harvesting strategies in an extremophilic red microalga *C. merolae*. The foundation of the photosynthetic optimization strategy is most likely supported by the structural and functional rearrangement of LHCI antenna associated with the photochemical reaction center of PSI. Under extreme high light conditions, some of the Lhcr subunits, forming the LHCI antenna in *C. merolae*, are equipped with low-energy 'red' chlorophylls (Chls) that trap the excitation. As part of photoprotection strategy under such harsh conditions these Chls are likely to increase their distance from the photochemical reaction center of PSI leading to excitonic decoupling. Under standard illumination conditions, the LHCI antenna, devoid of any low-energy Chls, is tightly coupled to the PSI reaction center, while under light-limiting conditions large contribution of the low-energy Chls in LHCI antenna maximizes the amount of the absorbed far-red light characteristic for the shaded environment.

Keywords: *photosynthesis, Photosystem I, photoprotection, LHCI*

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Posters

Theory meets experiment in biohydrogen production: aerobic damage of the [FeFe] hydrogenases

Adam Kubas¹, Christophe Orain, David De Sancho, Laure Saujet, Matteo Sensi, Charles Gauquelin, Isabelle Meynial-Salles, Philippe Soucaille, Hervé Bottin, Carole Baffert, Vincent Fourmond, Robert B. Best, Jochen Blumberger, Christophe Léger

¹Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw

akubas@ichf.edu.pl

[FeFe]-hydrogenases are the best natural hydrogen producing enzymes¹ but their biotechnological exploitation is hampered by the extreme oxygen sensitivity of these proteins. Most of the previous theoretical studies put emphasis on explanation of the irreversibility of this process as they were related to experiments carried out under constant O₂ concentration. However, we have recently shown experimentally that such aerobic inactivation is partially reversible.^{2,3} Here we combined the molecular dynamic (MD) simulations of the the dioxygen diffusion in the [FeFe] hydrogenase, extracted from *Clostridium Pasteurianum*, with the high level *ab initio* calculations of the O₂ binding and its transformations at the active site of the protein.^{3,4}

We found that the partial reversibility results from the four-electron reduction of O₂ to water.³ The third electron/proton transfer step is the bottleneck for water production, competing with formation of the highly reactive hydroxyl radical (-OH) and cysteine sulfenic acid (Cys299-SOH), consistent with the recent crystallographic evidence.⁵ The rapid delivery of electrons and protons to the active site is therefore crucial to prevent the accumulation of these harmful species upon exposure to oxygen. Moreover, our Markov state modelling⁶ of the diffusion process identified key residues that should be the target of the future mutational studies aiming to restrict O₂ access to the active site of the [FeFe] hydrogenases.

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Application of an extremophilic red alga *Cyanidioschyzon merolae* in phytoremediation

Ewa Borowska¹, Mateusz Abram^{1,2}, Małgorzata Wierzbicka², Joanna Kargul¹

¹Center of New Technologies, University of Warsaw, Banacha 2C, Warsaw, Poland

²Faculty of Biology, University of Warsaw, Miecznikowa 1, Warsaw, Poland

e.borowska@cent.uw.edu.pl

Phytoremediation attracted a lot of attention as a result of different kinds of applications towards removal of environmental water pollutants in acid mine drainage and other types of wastewater. These sludges cause massive environmental concerns worldwide. In this study, *Cyanidioschyzon merolae*, a model red thermo-acidophilic red microalga, was applied to reduce elevated concentrations of selected salt compounds associated with eutrophication: NH_4^+ NO_3^- PO_4^- and NaCl at two distinct growth temperatures: 25°C and standard 42°C, under standard illumination conditions (90 $\mu\text{moles photons/m}^2/\text{s}$). The salt compounds were added at standard (100 mM and 200 mM NaCl) or double concentration (19.8 mM NH_4^+ , 39.7 mM NO_3^- , 4 mM PO_4^{3-}) compared to that used in Allen-2 medium at pH 2.5. After 7-day exposure to elevated salt concentration the cell growth kinetics was analysed by RT absorbance and 77K fluorescence. In the presence of salt concentrations applied cell growth at a lower growth temperature of 25°C was slightly inhibited in the first 4 days of the experiment. It was observed that the cells adapt the salt stress factor and from day 5 show a similar growth kinetic as in the control sample (at the standard temperature of 42°C in the absence of elevated salt concentration). 77K fluorescence measurements indicate that during adaptation of the *C. merolae* cells to the applied salt stressors, both rearrangement of the light harvesting antenna and changes of photosystem I/photosystem II ratio occur. These changes in photosynthetic functionality may reflect the changes in the energy consumption required for the transmembrane ion transfer. Overall, our study confirms the potential of *C. merolae* for bioremediation of increased salinity in ground water, which will be addressed in future research.

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Optimization of electron transfer in PSI-based biophotoelectrodes using terpyridine molecular wires

Margot Jacquet^a, Miriam Izzo^a, Jaroslaw Sar^a, Mateusz Abram^a, Małgorzata Kiliszek^a,
Daniel Gryko^b, Joanna M. Kargul^a

^aSolar Fuels Laboratory, Center of New Technologies, University of Warsaw, Warsaw, Poland

^bInstitute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

m.jacquet@cent.uw.edu.pl

Biomimicry is of key importance for developing green chemistry innovations, also in the context of technological solutions for solar-driven chemistry. Artificial photosynthesis is a promising way to produce electricity and fuels using the most abundant renewable energy source: solar energy. To apply this idea for our technology, scientist are trying to develop efficient biophotoelectrodes based on the light-harvesting

macromolecular machine present in cyanobacteria, algae and higher plants, photosystem I (PSI). Indeed, this large pigment-protein complex is an efficient light energy converter with a quantum yield close to unity (for $\lambda < 680$ nm), and also functions as a charge separator generating long live e^- /hole pairs ($P700^+F_B^-$) upon light activation^{1,2}.

In our lab, we develop biophotoelectrodes with a highly robust PSI obtained from an extremophilic red microalga *Cyanodioschyzon merolae*, showing the highest robustness and photochemical activity compared to other photosynthetic systems. Our previous results on PSI-cyt *c*₅₅₃-based graphene electrodes revealed that a significant enhancement of photocurrent output can be obtained through a controlled orientation of PSI towards the electrode surface³. In order to develop more efficient direct electron transfer in biophotoelectrodes, we have decided to improve the architecture of the whole system by introducing a novel terpyridine conductive interface between PSI and the electrode surface. Currently, we have embarked on an ambitious quest to synthesise and nanostructure the library of derivatives of highly-conjugated terpyridine wires and ditopic ligands containing redox-active metal centers to study their electron transfer properties upon functionalization of various types of electrode materials.

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Optimization of the molecular interface for oriented immobilization of electroactive proteins in biosolar nanodevices

Miriam Izzo^{1,2}, Małgorzata Kiliszek¹, Ersan Harputlu³, Mateusz Abram^{1,2}, Marcin Szalkowski⁴, Dorota Kowalska⁴, C. Gokhan Unlu⁵, Patrycja Haniewicz^{1,7}, Margot Jaquet¹, Jarosław Sar¹, Sebastian Maćkowski⁴, Kasim Ocağolu^{3,6}, Takayuki Fujiwara⁸, Shin-ya Miyagishima⁸ and Joanna Kargul¹

¹*Solar Fuels Laboratory, Centre of New Technologies, University of Warsaw, Warsaw, Poland;*

²*Faculty of Biology, University of Warsaw;*

³*Advanced Technology Research & Application Centre, Mersin University, Mersin, Turkey;*

⁴*Institute of Physics, Faculty of Physics, Astronomy and Informatics,*

Nicolaus Copernicus University, Toruń, Poland;

⁵*Department of Biomedical Engineering, Pamukkale University, Denizli, Turkey;*

⁶*Department of Energy Systems Engineering, Tarsus Faculty of Technology, Mersin, Turkey;*

⁷*Laboratory of Molecular Research for Solar Energy Innovations, Centre of New Technologies;*

⁸*Division of Symbiosis and Cell Evolution, National Institute of Genetics, Japan*

m.izzo@cent.uw.edu.pl

Nowadays the world produces energy primarily from fossil fuels. These, however, are predicted to be exhausted by the end of the century. The main challenge for the present civilization is to create innovative technologies aiming at fulfilling the increasing energy consumption while at the same time reducing the carbon footprint. The production of high-efficiency biohybrid photoelectrodes is a highly promising

approach to meet these challenges. Indeed, it has been estimated that the energy captured in one hour of sunlight is equivalent to annual global energy produced by human population. This project focuses on the production of solar fuels by the construction of biohybrid photoelectrodes of increased efficiency compared to the present-day biophotovoltaic technologies. The device will be composed of graphene substrate and robust (photo)electroactive proteins (photosystem I and cytochrome *c553*) to combine them into an entire fuel cell, that would use water as a source of photogenerated electrons and protons. The aim of the current project is to improve the direct electron transfer (DET) within a novel class of biophotoelectrodes. In fact, the limited DET, which negatively affect the efficiency of such devices, is often found to be the major bottleneck for practical applications. In contrast with the previous engineered electrodes, the new designed devices will allow for a more homogenous coverage of the electrode as well as better control of the orientation of the electrochemical proteins. One of the proteins of choice as the biocomponents is cytochrome *c553* (cyt *c553*), the soluble electron donor to the photo-oxidized reaction centre of photosystem I (PSI).

A library of novel His-tagged cyt *c553* variants is currently genetically engineered to contain 7-amino acid peptide linkers, optimised for Gibbs free energy levels, at carboxyl terminus between the cyt holoprotein and a His₆-tag. The peptide linkers will allow for optimisation of both the distance and orientation of the redox-active heme center of cyt *c553* with respect to the electrode surface, ultimately leading to improved DET and better cathodic photocurrent output. The second device will generate anodic photocurrent by using modified His-PsaD-PSI as the photoelectroactive protein layer.

Here, we show the results of the genetic engineering, as well as the biochemical expression and purification of the abovementioned protein components of the biophotocathodes and biophotoanodes that ultimately will be incorporated in the full solar-to-fuel devices.

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Influence of Cd²⁺ ions on properties of non-heme iron in bacterial reaction centers of type II

S. Krysiak¹, A. Halas¹, A. Orzechowska¹, A. Chumakov², D. Bessas², V. Derrien³, P. Sebban³, J. Korecki¹, T. Slezak¹, K. Burda¹

¹*AGH University of Science and Technology, Kraków, Poland*

²*European Synchrotron Radiation Facility, Grenoble, France*

³*University of Paris XI, Orsay, France*

Sonia.Krysiak@fis.agh.edu.pl

Bacterial photosynthetic reaction centers (BRCs) of type II use light energy to drive electron transfer between two quinone molecules (Q_A and Q_B). Efficient electron flow requires the reduction of a bound quinone molecule Q_B to quinol Q_BH₂. In BRCs from *Rhodobacter sphaeroides* the protons involved in this process come from the cytoplasm and travel through pathways that involve His-H126 and His-H128 located near the proton entry point as well as Glu212 and Asp213 located on the protein L. It has been shown that Cd²⁺ inhibits the BRC function by binding to these functionally important histidines, Fig.1 [1-4].

Because the non-heme iron (NHFe) forming Q_A -Fe- Q_B complex triggers the electron transfer between the two quinones [5, 6] we searched for possible changes of the NHFe valence and spin states and rigidity of its binding site in mutated BRCs in which L213Asp and L212Glu were exchange for hydrophobic alanine (AA mutant).

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Cytochrome c_{553} -photosystem I interaction for an improved photocurrent generation in a single layer graphene electrode

Mateusz Abram^{1,2}, Małgorzata Kiliszek¹, Ersan Harputlu³, Marcin Szalkowski⁴, Dorota Kowalska⁴, C. Gokhan Unlu⁵, Patrycja Haniewicz¹, Kamil Wiwatowski⁴, Joanna Niedziółka-Jönsson⁶, Sebastian Maćkowski⁴, Kasim Ocakoglu^{3,7}, and Joanna Kargul¹

¹*Solar Fuels Lab, Centre of New Technologies, University of Warsaw, Banacha 2C, Warsaw, Poland;*

²*Faculty of Biology, University of Warsaw, Miecznikowa 1, Warsaw, Poland;*

³*Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, Yenisehir, Mersin, Turkey;*

⁴*Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, Torun, Poland;*

⁵*Department of Biomedical Engineering, Pamukkale University, Denizli, Turkey;*

⁶*Institute of Physical Chemistry Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, Poland;*

⁷*Department of Energy Systems Engineering, Mersin University, Tarsus Faculty of Technology, Mersin, Turkey.*

m.abram@cent.uw.edu.pl

Photosynthesis evolved on Earth over 3.5 billion years ago. For the efficient conversion of solar energy into energy of chemical bonds, several specialized protein-pigment complexes act in concert to capture solar light, then initiate and convey proton-coupled electron transfer that ultimately produces cellular metabolic energy in the form of ATP. One of the crucial components in this process is Photosystem I (PSI) – a natural solar-powered biological photodiode.¹ In our studies on construction of efficient biophotocatalytic electrodes, we implemented PSI as the photoactive biological component within the single layer graphene/fluorine-doped tin oxide (SLG/FTO) electrode in order to enhance solar energy conversion. Here, we report fabrication of a bioelectrode in which a highly robust PSI complex isolated from a red microalga *Cyanidioschyzon merolae* was successfully immobilized on SLG/FTO electrode in an oriented manner.² We demonstrate the improved photocurrent generation due to incorporation of another electroactive protein: cytochrome c_{553} (cyt c_{553}). Cyt c_{553} is an electron donor that specifically binds to PSI, in the vicinity of the photochemical reaction centre, P700 (a special pair of Chl a molecules). We applied the specific protein-protein interaction between His₆-tagged cyt c_{553} and PSI to orient the latter complex with its oxidizing (donor) side towards the SLG/FTO surface.²⁻⁴ The conductive interface between the PSI and SLG was formed by π - π stacked pyrene functionalized with Ni²⁺-NTA moiety forming an organic monolayer that binds the biological monolayer of His₆-cyt c_{553} .²⁻⁵ Uniformity of the PSI coverage of the electrode was confirmed by cross-sectional scanning electron microscopy. Efficient electronic coupling between PSI layer

and SLG was demonstrated by efficient quenching of fluorescence.² Such a highly oriented PSI layer resulted in the photocurrent generation even at an open circuit potential, and a further increase of the currents with a negative potential applied to the photoelectrode. We measured over 5-fold increase of the cathodic photocurrents at the highest negative potential applied (-0.3 V), as compared to the randomly oriented structure, where PSI is physisorbed on SLG.² Our results point towards the key role of a strict uniformity of the biological photoactive component in this type of biophotoelectrode architecture for the efficient solar energy conversion.

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List of Participants

1. **Abram Mateusz**, University of Warsaw, Poland m.abram@cent.uw.edu.pl
2. **Allahverdiyeva-Rinne Yagut**, University of Turku, Finland allahve@utu.fi
3. **Bercegol Hervé**, CEA Saclay, France herve.bercegol@cea.fr
4. **Białek Rafał**, Adam Mickiewicz University, Poland rafal.bialek@amu.edu.pl
5. **Bieńkowski Krzysztof**, University of Warsaw, Poland k.bienkowski@cent.uw.edu.pl
6. **Bojanowski Gawel**, University of Warsaw, Poland gawel.bojanowski@cent.uw.edu.pl
7. **Bojarska Zuzanna**, Warsaw University of Technology, Poland zuzanna.bojarska.dokt@pw.edu.pl
8. **Borowska Ewa**, University of Warsaw, Poland e.borowska@cent.uw.edu.pl
9. **Bulska Ewa**, University of Warsaw, Poland ebulska@chem.uw.edu.pl
10. **Burda Květoslawa**, AGH University of Science and Technology, Poland kveta.burda3@gmail.com
11. **Ekiert Robert**, Jagiellonian University, Poland robert.ekiert@uj.edu.pl
12. **Fiedor Leszek**, Jagiellonian University, Poland leszek.fiedor@uj.edu.pl
13. **Garstka Maciej**, University of Warsaw, Poland garstka@biol.uw.edu.pl
14. **Grudziński Wojciech**, Maria Curie-Skłodowska University, Poland wojciech.grudzinski@umcs.pl
15. **Gruszecki Wiesław**, Maria Curie-Skłodowska University, Poland wieslaw.gruszecki@umcs.pl
16. **Haniewicz Patrycja**, University of Warsaw, Poland p.haniewicz@cent.uw.edu.pl
17. **Henryk Szymczak**, Institute of Physics, PAS, Poland szymh@ifpan.edu.pl
18. **Horeglad Paweł**, Warsaw University of Technology, Poland phoreglad@ch.pw.edu.pl
19. **Izzo Miriam**, University of Warsaw, Poland m.izzo@cent.uw.edu.pl
20. **Kargul Joanna**, University of Warsaw, Poland j.kargul@cent.uw.edu.pl
21. **Karpiński Stanisław**, Warsaw University of Life Sciences, Poland stanislaw.karpinski@sggw.pl
22. **Kolwas Krystyna**, Institute of Physics, PAS, Poland Krystyna.Kolwas@ifpan.edu.pl

23. **Kowalska Dorota**, Nicolaus Copernicus University, Poland dorota@fizyka.umk.pl
24. **Krysiak Małgorzata**, University of Warsaw, Poland mkrysiak@biol.uw.edu.pl
25. **Krysiak Sonia**, AGH University of Science and Technology, Poland Sonia.Krysiak@fis.agh.edu.pl
26. **Kubas Adam**, Institute of Physical Chemistry, PAS, Poland akubas@ichf.edu.pl
27. **Kulesza Paweł**, University of Warsaw, Poland pkulesza@chem.uw.edu.pl
28. **Łazicka Magdalena**, University of Warsaw, Poland lazicka@biol.uw.edu.pl
29. **Lewiński Janusz**, Warsaw University of Technology, Poland lewin@ch.pw.edu.pl
30. **Macyk Wojciech**, Jagiellonian University, Poland macyk@chemia.uj.edu.pl
31. **Ocakoglu Kasim**, Tarsus University, Turkey kasim.ocakoglu@tarsus.edu.tr
32. **Opałło Marcin**, Institute of Physical Chemistry, PAS, Poland mopallo@ichf.edu.pl
33. **Osella Silvio**, University of Warsaw, Poland s.osella@cent.uw.edu.pl
34. **Plumeré Nicolas**, Ruhr-Universität Bochum, Germany Nicolas.Plumere@rub.de
35. **Podgajniak Tomasz**, PIGEOR, Poland tp@enerco.pl
36. **Puźniak Roman**, Institute of Physics, PAS, Poland puzni@ifpan.edu.pl
37. **Radosław Mazur**, University of Warsaw, Poland rmazur@biol.uw.edu.pl
38. **Rutkowska-Żbik Dorota**, Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Poland nczbik@cyf-kr.edu.pl
39. **Sá Jacinto**, Uppsala University, Sweden and Institute of Physical Chemistry, PAS, Poland jacinto.sa@kemi.uu.se
40. **Sar Jarosław**, University of Warsaw, Poland j.sar@cent.uw.edu.pl
41. **Sarewicz Marcin**, Jagiellonian University, Poland marcin.sarewicz@uj.edu.pl
42. **Sobolewski Andrzej**, Institute of Physics, PAS, Poland sobola@ifpan.edu.pl
43. **Solarska Renata**, University of Warsaw, Poland r.solarska@cent.uw.edu.pl
44. **Śrębowata Anna**, Institute of Physical Chemistry, PAS, Poland asrebowata@ichf.edu.pl
45. **Staicu Lucian**, University of Warsaw, Poland staicu@biol.uw.edu.pl
46. **Szalkowski Marcin**, Nicolaus Copernicus University, Poland marszal@fizyka.umk.pl

47. **Trzaskowski Bartosz**, University of Warsaw, Poland trzask@cent.uw.edu.pl
48. **Witkowski Bartłomiej**, Institute of Physics, PAS, Poland bwitkow@ifpan.edu.pl
49. **Zubik Monika**, Maria Curie-Skłodowska University, Poland monika.zubik@umcs.pl