COST Action TD1102

PHOTOSYNTHETIC PROTEINS FOR TECHNOLOGICAL APPLICATIONS: BIOSENSORS AND BIOCHIPS (PHOTOTECH)

2nd PLENARY WORKSHOP AND MANAGEMENT COMMITTEE MEETING

Information, Programme and Abstracts

9-11 April 2014

Istanbul-TURKEY

cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

HACETTEPE UNIVERSITY

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http://cost.hacettepe.edu.tr

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Acknowledgements:
Abdulgafur Mujdeci for the web register system and web design
Hüseyin Efe Genis for the graphic design

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SCIENTIFIC PROGRAMME

DAY 1, Wednesday April 9, 2014

8:30 – 9:00	**Registration**
9:00-9:15	**Welcome Speech:** Ismail Hakki Boyaci, Hacettepe University, Turkey **Opening Speech:** Giuseppina Rea CNR - Institute of Crystallography, Italy

Session 1 Chairman: Fabio Polticelli, University Roma Tre, Italy

9:15 - 10:00	**Invited Lecture 1**: The architecture of native, reconstituted and artificial light-harvesting Garab Gyozo, Biological Research Centre, HAS, Hungary
10:00 - 10:30	**Oral Presentation 1:** Full reduction and full oxidation of the plastoquinone pool with certain wavelengths of visible light Esa Tyystjärvi, University of Turku, Finland

Coffee break (10:30 – 11:00)

11:00 – 11:30	**Oral Presentation 2:** Photosystem II on metal oxides and the nature of the photocurrent Andrea Fantuzzi, Imperial College London, United Kingdom
11:30 - 12:00	**Oral Presentation 3:** Towards Photoelectrochemical Cells based on Photosystem II Integrated in Nanostructured Electrodes Dirk Mersch, University of Cambridge, United Kingdom
12:00 – 12:30	**Oral Presentation 4:** Photocurrents Generated by Langmuir-Blodgett Deposition of Isolated Bacterial RC-LH1 on Bare Gold David Delgado, VU University Amsterdam, Netherlands
12:30 – 13:30	**Lunch**

Session 2 Chairman: Nicolas Plumeré, Ruhr University Bochum, Germany

13:30 - 14:00 **Oral Presentation 5:** Molecular study of *Arthrospira* sp. PCC 8005, a cyanobacterium highly tolerant to ionising radiation
Hanene Badri, Belgian Nuclear Research Center (SCK-CEN), Belgium

14:00 – 14:30 **Oral Presentation 6:** A new designed microbial fuel cell: An electricity production study by *Rhodobacter sphaeroides*
Hilal Bilge Cadirci, Gaziosmanpasa University, Turkey

14:30 - 15:00 **Oral Presentation 7:** Investigation of cbb3-type respiratory oxygen reductase from photosynthetic bacterium *Rhodobacter capsulatus*
Gulgez Gokce Yildiz, Abant Izzet Baysal University, Turkey

15:00 – 15:30 Coffee break

15:30 - 16:00 **Oral Presentation 8:** Reaction Center Optoelectronics In Nano-Hybride Systems
László Nagy, University of Szeged, Hungary

16:00 - 16:30 **Oral Presentation 9:** Redox Interaction In Reaction Center/Porous Silicon Bio-Nanocomposite
Kata Hajdu, University of Szeged, Hungary

16:30 - 17:00 **Oral Presentation 10:**Photocurrent Generated By Photosynthetic Reaction Center Based Nanocomposites
Tibor Szabo, University of Szeged, Hungary

DAY 2, Thursday April 10, 2014

Session 3 Chairman: László Nagy, University of Szeged, Hungary

9:00 - 9:30 **Oral Presentation 11**: Redox hydrogels for biophotovoltaics
Nicolas Plumeré, Ruhr University Bochum, Germany

9:30 – 10:00 **Oral Presentation 12**: Immobilisation of *Rhodobacter sphaeroides* reaction centers on TiO_2 surface for use in solar cells
Rafal Białek, Adam Mickiewicz University, Poland

10:00 - 10:30 **Oral Presentation 13:** The best of both worlds: detergent-free purification of photovoltaic membrane proteins with native bilayer properties
David Swainsbury, University of Bristol, United Kingdom

10:30 – 11:00 Coffee break

11:00 – 11:30 **Oral Presentation 14:** Electronic bridges for contacting photosynthetic proteins to electrode surfaces
Frank Mueller, Ruhr Universitt Bochum, Germany

11:30 - 12:00 **Oral Presentation 15:** Intra-Protein Photodynamics of Photosystem II-Synthetic Hybrid Systems
Nicholas Paul, University of Cambridge, United Kingdom

12:00 – 12:30 **Oral Presentation 16:** Functional reconstitution of photosynthetic reaction centres in polymersomes
Francesco Milano, CNR-IPCF, Italy

12:30 – 13:30 Lunch

Session 4 Chairman: Esa Tyystjärvi, University of Turku, Finland

13:30 - 14:15 **Invited Lecture 2:** Electron transfer pathways in electrochemical biosensors and in some other biodevices
Arunas Ramanavicius, Vilnius University, Lithuania

14:15 – 14:45 **Oral Presentation 17:** Evaluation of a biohybrid photoelectrochemical cell employing engineered purple bacterial reaction centres as a biosensor for herbicides
Michael Jones, University of Bristol, United Kingdom

14:45 - 15:15	**Oral Presentation 18:** Detection of photosynthetic herbicides using PSII biosensors and chlorophyll fluorescence based biotest Karel Klem, Global Change Research Centre, Czech Republic
15:15 – 15:45	**Coffee break**
15:45 - 17:30	**Poster session**
19 :00-	**Dinner (Sur Balik Restaurant)**

DAY 3, Friday April 11, 2014

Session 5 Chairman: Mehmet Mutlu, TOBB ETU, Turkey

09:00 - 9:45	**Invited Lecture 3**: Ellipsometric Biosensors Bora Garipcan, Bogazici University, Turkey
9:45 – 10:15	**Oral Presentation 19**: Laser printing for the fabrication of an aptasensor for environmental monitoring Marianneza Chatzipetrou, National Technical University of Athens, Greece
10:15 - 10:45	**Oral Presentation 20:** Plasma Modified Polycarbonate Nanorod Arrays for Biomedical Applications Mehmet Mutlu, TOBB ETU, Turkey
10:45 – 11:15	**Coffee break**
11:15 - 11:45	**Oral Presentation 21:** A Reaction Center-Based Screen-Printed Photoelectrochemical Cell For The Detection Of Atrazines Maria Rachele Guascito, University of Salento, Italy
11:45 - 12:15	**Oral Presentation 22:** Raman Spectroscopy for Bio-detection: Herbicide detection via chloroplast Ismail Hakki Boyaci, Hacettepe University, Turkey

12:15 – 12:45	**Oral Presentation 23:** Symbiotic Machine Marjolein Shiamatey, VU University of Amsterdam, Netherlands
12:45 – 13:45	**Lunch**
13:45 – 15:30	**MC Meeting**
15:30 – 16:00	**Coffee break**
16:00 – 17:30	**Brainstorming with Joint WGs Meeting**
17:30-	**Closing Remarks**

LIST OF THE PRESENTATIONS

INVITED SPEAKERS

ORAL PRESENTATIONS

POSTER PRESENTATIONS

ABSTRACTS

INVITED LECTURES

IL1

The architecture of native, reconstituted and artificial light-harvesting molecular (macro-) assemblies – as revelaed by polarization spectroscopic and microscopic techniques

Győző Garab

Biological Research Centre, Hungarian Academy of Sciences, Szeged, Hungary

Due to the relatively low photon flux densitiy of sunlight, direct excitation of the photosynthetic reaction centers is a very rare event. In order to increase the efficiency of light-energy conversion all photosynthetic organisms have developed light harvesting antenna complexes, which absorb light in a broad spectral interval and supply excitation energy to the photochemical reaction centers. Feeding photochemically active centers by light-harvesting antennae might also be useful for photocatalytic systems and artificial photosynthesis, especially in low light. The photophysical processes in the antennas depend largely on their spectroscopic properties and molecular architectures. Linear and cicular dichroism (LD and CD) techniques have contributed significantly to our knowledge of the molecular organization of the pigment systems and became indispensable tools in determining the orientation of transition dipole moment vectors of pigment molecules with respect to the protein axes, and in revealing short-range, excitonic interactions between the chromophores as well as certain macroorganizational parameters in molecular aggregates with sizes commensurate with the wavelength of visible light. In my talk, I will be focusing on our recent results using these techniques, with special attention to the anisotropic CD (ACD) technique, used for the first time in photosynthesis research and for excitonic CD (Miloslavina et al. 2012 Photosynth. Res.; P.H. Lambrev, K. Pawlak, P. Akhtar, Y. Miloslavina, A.R. Holzwarth and G. Garab, unpublished), as well as on differential polarization laser-scanning microscopy (Garab et al. 2005 Eur. Biophys J; Chappaz-Gilot et al. 2011 JACS).

IL2

Electron transfer pathways in electrochemical biosensors and in some other biodevices

Arunas Ramanavicius[1,2], Inga Morkvenaite-Vilkonciene[1,2], Asta Kausaite-Mikstimiene[2,3] , Almira Ramanaviciene[2,3]

[1] Department of Physical Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania;
2 Laboratory of NanoBioTechnology, Department of Materials Science and Electronics, Institute of Semiconductor Physics, State Scientific Research Institute Centre for Physical Sciences and Technology. Gostauto 9, LT-01108 Vilnius, Lithuania;
[3] Nanotechnas – Centre of Nanotechnology and Materials Science, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

Significant number of biosensors and other biodevices are based on redox processes and can be easily integrated within electronic circuits. However the efficiency of electron transfer between redox proteins and electrodes is the most limiting step in the development of such biodevices. Therefore this issue is among the most important tasks of bioelectronics. Possible electron transfer pathways in electrochemical biosensors and other biodevices will be overviewed in this presentation. Redox mediators, redox-polymers and conducting polymers will be briefly overviewed as charge carriers. Significant attention in this presentation will be focused on direct electron transfer (DET) between redox proteins and electrodes. The DET is a unique feature of some redox enzymes and other redox proteins and it pave the way in development of superior mediator-free biofuel cells, as it obviates the need for mediators and allows an efficient transduction of electrical signals and electrical current. Therefore the DET is highly beneficial in the development of enzymatic biosensors and biofuel cells [1]. This presentation will be laid on the application of heme containing enzymes (hemoproteins), because the hemoproteins are able to transfer electrons directly to different conducting supports. Some designs of biosensors and some other bioelectronic devices, as well as possible application will be overviewed. Problems and challenges in development and application of electrochemical biodevices will be identified and some possible ways to solve some recent problems will be discussed.

Reference

1. Ramanavicius A., Ramanaviciene A. Hemoproteins in design of biofuel cells. Fuel cells 2009, 9, 25–36.

IL3

Ellipsometric Biosensors

Bora Garipcan

Institute of Biomedical Engineering, Bogazici University, Istanbul, Turkey

Quartz crystal microbalance (QCM), magnetic bead cell sorting, atomic force microscope (AFM), and surface plasmon resonance (SPR) biosensors are label-free methods and commonly used for the detections of biomolecules. Ellipsometry involves measuring the change of polarization state of an elliptically polarized light reflected from thin films and a sensitive technique enough to detect the adsorption of a molecular layer on a solid surfaces (such as glass, silicon and gold surface). Ellipsometry is also a label free method and can be for used biosensing and as a biosensor. Ellipsometry is a non-destructive, sensitive technique and suitable for monitoring the biological interactions (thickness measurement of biological thin films, antibody-antigen interactions, hybridization of oligonucleotides). In the first part of the talk, fundamentals of ellipsometry and in the second part, general applications of ellipsometric technique will be given. In the last part; biological and biosensing applications of ellipsometry will be discussed.

ORAL PRESENTATIONS

O1

Full reduction and full oxidation of the plastoquinone pool with certain wavelengths of visible light

Marja Hakala-Yatkin[1], Heta Mattila[1], Vesa Havurinne[1], Taras Antal1[1,2], Sergey Khorobrykh[1], Taina Tyystjärvi[1], Esa Tyystjärvi[1*]

[1] Molecular Plant Biology, Department of Biochemistry, University of Turku, FI-20014 Turku, Finland.

[2] Biological Faculty, Moscow State University, Vorobyevi Gory, 119992, Moscow, Russia.

The plastoquinone (PQ) pool mediates electron flow from Photosystem II to Photosystem I. The redox state of PQ regulates both photoacclimation responses and expression of nuclear genes. We measured the action spectrum of the redox state of PQ in Arabidopsis leaves using both an indirect chlorophyll fluorescence based method and direct determination with HPLC. The measurements showed that moderate-intensity illumination at 460-500, 560 or 650-660 nm fully reduces PQ, whereas illumination with 420-450, 520, 630 or 680-690 nm light oxidizes PQ. Further in vivo measurements showed that the wavelengths reducing PQ favor Photosystem II and those oxidizing PQ favor Photosystem I, but the effects of the different wavelengths on PQ were much stronger (full oxidation or full reduction) than imbalances in electron transport rates (maximum of 20-30 % imbalance except for far red light). Thus, full reduction of PQ occurs rapidly if the wavelength favors PSII even a little, and full oxidation occurs when a leaf is illuminated with light favoring PSI. White light of the halogen lamp illuminator used for saturating flashes in the pulse amplitude modulation fluorometer was found to oxidize PQ, whereas white light from HQI daylight lamps reduced PQ. Thus, white light can oxidize or reduce PQ, depending on the spectrum, suggesting that that the regulatory effects of PQ on gene expression and photoacclimation are more complicated than earlier assumed.

O2

Photosystem II on metal oxides and the nature of the photocurrent

Andrea Fantuzzi, Katharina Brinkert, A.William Rutherford

Department of Life Sciences, Imperial College London, London, SW7 2AZ, United Kingdom

There are numerous reports of PSII being used as part of photoelectrochemical devices when immobilized onto electrodes. Despite some intrinsic limitations due to the isolated PSII being damaged by light, work on immobilised PSII has continued partly because PSII is seen as the benchmark water splitting catalyst, partly because of applications as biosensors, but also because the immobilization of PSII on an electrode surface may provide a novel method for studying the enzyme. Among the various materials used, mesoporous metal oxides offer two unique advantages: large surfaces on which direct electron transfer from the immobilised protein is possible and the possibility to integrate electrochemical and spectroscopic investigation. PSII has been successfully immobilised on various metal oxides, though a series of controversial results cast doubts over the electrons source and pathway.

Here we investigated the nature of the photocurrent in isolated PSII from *Thermosynechococcus elongatus* when immobilised on nanostructured titanium dioxide on indium tin oxide (TiO_2/ITO). By comparing the behaviour of PSII immobilised as a monolayer *vs* multilayers, we observed that electron transfer occurs from Q_A directly to the electrode surface and that the electron flow through the nanostructured metal oxide is the rate-limiting step. We suggest that when a mobile mediator is present it enhances the photocurrent by taking electrons from the nanostructured semiconductor surface to the ITO electrode surface. We therefore propose a model that describes the electron pathway from the protein to the electrode and that explains the anomalous behaviours previously shown in the literature.

This work was supported by the European Space Agency (ESA-PRODEX) and the Belgian Science Policy (Belspo) through the ARTEMISS project, which is part of the MELiSSA program.

O3

Towards Photoelectrochemical Cells based on Photosystem II Integrated in Nanostructured Electrodes

Dirk Mersch, Jenny Zhang, Erwin Reisner

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

Photosystem II sets the unrivalled benchmark for water oxidation on a 'per active site' basis and has long been an inspiration for artificial photosynthetic systems. This presentation will summarise our recent progress on the immobilisation of photosystem II on nanostructured metal oxide electrodes. Previously, we reported on the direct electronic communication with oriented and covalently attached photosystem II to electrode surfaces. In these studies, we employed Doctor-bladed mesoporous indium-tin oxide electrodes to allow for increased protein loading compared to flat substrates. However, these mesoporous electrodes were not optimised or ideal for high protein loading. We have now optimised the surface morphology of the electrodes and designed conducting and transparent metal oxide electrodes with tuneable and homogeneous pore sizes for the sole purpose of high enzyme loading. These macroporous electrodes allow for enhanced photosystem II loading and substantially increased photocurrent responses per geometric surface area. The resulting electrodes were able to adsorb up to 200 pmol of photosystem II per 1 cm2 of electrode area and achieved direct photocurrents of up to 3 uA/cm2. When additional mediator was introduced, the photocurrent increased more than 30 fold.

Furthermore, this unique approach for electrode design and fabrication can be utilised for other enzymes and thus become a powerful tool in this field of research.

References:

[1] M. Kato, T. Cardona, A.W. Rutherford, E. Reisner, "Photoelectrochemical Water Oxidation with Photosystem II. Integrated in a Mesoporous Indium−Tin Oxide Electrode", J. Am. Chem. Soc. 134, 2012, pp. 8332−8335

[2] M. Kato, T. Cardona, A.W. Rutherford, E. Reisner, "Covalent immobilization of oriented photosystem II on a nanostructured electrode for solar water oxidation", J. Am. Chem. Soc. 135, 2013, pp. 10610−10613.

O4

Photocurrents Generated by Langmuir-Blodgett Deposition of Isolated Bacterial RC-LH1 on Bare Gold

David Delgado[1], Muhammad Kamran[2], Vincent Friebe[1], Thijs J. Aartsma[2], Raoul N. Frese[1]

[1] VU University Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
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Great interest has been given to photosynthetic systems for their potential in future technological applications such as bio-sensors and bio-solar cells. In this context, previous studies have focused on depositing PSI and PSII from plants, and bacterial RCs onto conducting surfaces. In order to make surface adhered protein complexes viable for applications some basic issues need to be addressed, such as, functional integrity on conducting surfaces, efficiency of the electronic communication between the electrode and the protein, and the orientation of these complexes on the electrode. In this respect, photocurrent measurements on an atomically flat electrode in combination with a monolayer of photosynthetic complexes provides a well-defined system. Here we report the Langmuir-Blodgett deposition technique as a promising method to create self assembled monolayers of isolated bacterial RC-LH1 complexes with uniform orientation and minimal distance between the proteins and surface. We show to be able to orient RC-LH1 complexes with a 90% accuracy. We assessed the properties of this system by means of light-induced current generation producing a maximum photocurrent density of 45$\mu A/cm^2$ with an internal quantum efficiency of 32%. This represents the largest photocurrent for a single monoloyer reported to date.

O5

Molecular study of *Arthrospira sp*. PCC 8005, a cyanobacterium highly tolerant to ionising radiation

Hanene Badri [1], Pieter Monsieurs [1], Ruddy Wattiez [2] and Natalie Leys [1]

[1] Expert group for Molecular and Cellular Biology, Belgian Nuclear Research Center SCK•CEN, Mol, Belgium
[2] Proteomics and Microbiology Group, Mons University, Mons, Belgium

Arthrospira (Spirulina) is an edible, oxygenic, water-splitting. photosynthetic cyanobacterium that converts solar light in chemical energy.by fixing carbon from the environment. For these traits, the cyanobacterium Arthrospira sp. PCC 8005 was selected by the European Space Agency (ESA) as part of the life support system MELiSSA for recycling oxygen, water, and food during future long-haul space missions. However, during such extended missions, Arthrospira sp. PCC 8005 will be chronically exposed to artificial illumination and harmful cosmic radiation.

The aim of this study was to investigate how Arthrospira will react and behave when exposed to these stressful conditions. Hence, strain PCC 8005 was exposed to high doses of gamma rays

Test results showed that after acute exposure to high doses of ^{60}Co gamma radiation of up to 3200 Gy, Arthrospira filaments were still able to restart photosynthesis and proliferate normally. However, doses above 3200 Gy clearly had a detrimental effect on the cells as indicated by delayed post-irradiation proliferation. The photosystem activity, measured as the PSII quantum yield immediately after irradiation, decreased significantly at radiation doses above 3200 Gy. Likewise exposure to 3200 Gy caused a significant decrease in phycocyanin content. The extreme high tolerance of this bacterium to ^{60}Co gamma rays triggered our interest to investigate in detail the underlying cellular and molecular mechanisms. Optimised DNA, RNA and protein extraction methods and a novel microarray chip based on Arthrospira sp. PCC 8005 genome data were developed to identify the global cellular and molecular responses after exposure to 3200 Gy and 5000 Gy. Approximately 15 % and 30 % of the 5889

genes studied were found differentially expressed for exposures at 3200 Gy and 5000 Gy, respectively. Some of the induced genes could be confirmed by proteomic analysis. The results enabled us to identify a network of genes involved in the production of antioxidants and the expression of enzymes required for oxidative response- and DNA damage repair mechanisms, and allowed us to map the mechanistic responses deployed by Arthrospira sp. PCC8005 to cope with high doses of ionizing radiation. This advanced integration between transcriptomic data and proteomic analysis led to the identification of a new set of proteins which have never been reported or described before, and which were found to be expressed in a dose dependent manner upon exposure to ionising radiation in Arthrospira sp. PCC8005. The exact role of this new set of genes and proteins in the radiation resistance of Arthrospira is now under investigation.

O6

A new designed microbial fuel cell: An electricity production study by *Rhodobacter sphaeroides*

Emirhan Bozoglan and Bilge Hilal Cadirci

Gaziosmanpasa University

The photosynthetic microbial fuel cell (PMFC) is a bioelectrochemical system capable of converting sunlight into electricity based on the exploitation of biocatalytic reactions within active microbial cells. In a PMFC, the oxidation of a carbon source occurs at the anode while the reduction of O_2 to H_2O occurs at the cathode. Rhodobacter sp. is a model bacterium in PMFC studies. Rhodobacter sphaeroides is a purple non-sulfur bacteria which contains photosystem II and is able to perform anoxygenic photosynthesis under anoxic conditions. Like the other purple non-sulfur bacteria it can grow both aerobically and anaerobically, autotrophically or heterotrophically, chemotrophically or phototrophically. In this study, we design a 50 mL volume PMFC with platin cathode and carbon anode. We used potassium permanganate as electron acceptor in cathodic cell. Acetate was used as carbon source in growth medium for R. sphaeroides anoxygenic photosynthesis. In order to check the efficiency of the fuel cell, we compare the electrical potential producing capacity of R. sphaeroides with the published papers. It was shown that highest electricity potential of R. sphaeroides we gain is 1 Volt with 80 μA current at 48 h. As we know it is the highest electricity potential production level in published papers. The optimization studies are continued to increase the current values.

O7

Investigation of *cbb*$_3$-type respiratory oxygen reductase from photosynthetic bacterium *Rhodobacter capsulatus*

Gulgez Gökce Yildiz, Robert B. Gennis, Fevzi Daldal, Mehmet Ozturk

Department of Biology, Faculty of Literature and Science, Abant Izzet Baysal University, 14280, Bolu, Turkey

Purple bacteria are photosynthetic gram-negative prokaryotes that convert light energy into chemical energy by the process of anoxygenic photosynthesis. This group of bacteria includes an interesting organism, *Rhodobacter capsulatus* due to its versatile metabolic pathways which is an excellent model for studying microbial energy transduction. The heme-copper superfamily are classified into three families (A-, B- and C-families) based on structural and phylogenetic analysis. The C-family, also called the cbb$_3$-type oxygen reductases catalyze the reduction of oxygen to water and drives proton pumping across the membrane in bacteria or mitochondria. All of the heme-copper oxygen reductases require proton-conducting channels. Site-directed mutagenesis experiments and the crystal structures of the A- family oxygen reductases have shown that two channels, D- and K- channels are conserved and essential for this family while B- and C-families have need of only one channel. In this work, the effects of mutations in the K-channel of the *cbb*$_3$-type oxygen reductase from *Rhodobacter capsulatus* were investigated by expressing the mutants in a strain lacking other respiratory oxygen reductases. Proton pumping was evaluated using intact cells, and catalytic oxygen reductase activity was measured in isolated membranes. Two mutations, N346M and Y374F severely reduce the catalytic activity, presumably by blocking the chemical protons required at the active site. One mutation, T272A, results in a substantially lower proton pumping stoichiometry but does not inhibit oxygen reductase activity.

O8

Reaction center optoelectronics in nano-hybride systems

László Nagy

Department of Medical Physics and Informatics, University of Szeged, Hungary

Photosynthetic reaction center (RC) possesses such technical properties that unique applications are possible, for example, its use in nanostructures or in optoelectronic systems. These interesting properties initiated huge efforts for creating bio-nanocomposite materials as well by using RCs and different carrier matrices for several purposes and led to numerous publications in this field. The aim of the experiments in our lab is to see possible directions of creating efficient integrated optoelectronic systems which can be used for several new generations of applications, like biosensors (e.g., for specific detection of pesticides) or light energy conversion (e.g., photovoltaics). RCs are purified from *Rhodobacter sphaeroides* purple bacterial strains and bound to different inorganic carrier matrices (carbon nanotubes, porous silicon, indium tin oxide, conducting polymers). The optical and electric properties of the functional hybrid nanosystems are investigated. An overview of results in our laboratory will be given.

O9

Redox Interaction In Reaction Center/Porous Silicon Bio-Nanocomposite

Kata Hajdu

Department of Medical Physics and Informatics, University of Szeged, Hungary

Photosynthetic reaction center proteins (RCs) are the most efficient light energy converter systems in nature as, during the photosynthesis, they harness light with near to 100% quantum efficiency. Due to their unique properties, combining RCs with nano-structures promising applications can be envisaged in optoelectronic systems. Thanks to the numerous application opportunities, considerable efforts are made to fabricate bio-nanocomposite materials by combining reaction centers with various carrier matrices, like carbon nanotubes, conducting oxides and polymers or silicon-based materials. The aim of our work is to create a system for efficient light energy conversion (e.g. photovoltaics), integrated optoelectronic devices or biosensors (e.g. for specific detection of pesticides). We have shown that RC can be attached to porous silicon microcavities (PSiMc) either physically (through the specific peptide SPGLSLVSHMQT) or chemically by silanization using APTES (3-aminopropyl-triethoxysilane) or MPTS (3-mercaptopropyl-trimethoxysilane). The RC kept its photophysical/-chemical activity after the binding as shown by its transient absorption change in flash photolysis experiments. To prove the direct electrochemical relation between the RC and the PSi, we used our complex as a working electrode in an electrochemical cell, with three-electrode arrangement. Using this set-up, we managed to measure remarkable photocurrent after the light excitation.

O10

Photocurrent Generated By Photosynthetic Reaction Center Based Nanocomposites

Tibor Szabó

Department of Medical Physics and Informatics, University of Szeged, Hungary

Intensive studies have shown recently that photosynthetic proteins purified from plants (PS-I and PS-II) and from purple bacteria bind successfully to nanostructures while their functional activity is largely retained. Current researches are focussing on finding the best bio-nanocomposite sample preparations and experimental conditions for efficient energy conversion and for the stability of the systems. In our studies reaction center proteins (RC) purified from purple bacterium Rhodobacter sphaeroides were bound successfully to amine- and carboxy-functionalized multiwalled carbon nanotubes (MWNTs) immobilized onto the surface of ITO by using specific silane and conducting polymer. Structural (TEM, AFM) and functional (electrochemical measurements) techniques have shown that RCs can be bound effectively to the functionalized carbon nanotubes (CNT). The complexes have high stability and generate fotocurrent in wet and dry conditionas well. An electrochemical cell with three electrodes (reference Ag+/AgCl, counter platinum and the working sample) was designed especially for measuring the photocurrent generated by this composite material. Several hundreds of nA photocurrent was measured with fully active RCs while the current was missing when the RC turnover was disrupted by depleting the electron acceptor quinones. The study of possibility for generating photocurrent in organic solar cell based on RC protein is also under process.

O11

Redox hydrogels for biophotovoltaics

Nicolas Plumeré

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The trend in energy conversion based on bioelectrochemical processes is to aim for direct electron transfer between electrodes and the redox centers of the biocatalyst. The intended outcome is to achieve energy conversion at minimal voltage loss. This strategy is ideal when direct electron transfer is fast (1). However, this is not the case for all redox enzymes and in some cases fast direct electron transfer even induces enzyme deactivation.

Electron relays tethered to hydrogels may be implemented as efficient alternative provided their properties, and in particular their redox potential, are tuned to enable maximal current density at low overpotential. To illustrate the desired parameters of an electron relay and of its polymeric supporting matrix, the example of biophotoelectrochemical cells as well as a full biophotovoltaic cell based on photosynthetic protein complexes will be given (2). In addition various strategies for shielding from oxygen damage will be presented (3).

References

(1) a) N. Plumeré, *Nature Nanotechnology*, **2012**, *7*(10), 616-617; b) D. Gerster, J. Reichert, H. Bi, J. V. Barth, S. M. Kaniber, A. W. Holleitner, I. Visoly-Fisher, S. Sergani and I. Carmeli, *Nature Nanotechnology*, **2012**, **7**, 673–676.

(2) T. Kothe, N. Plumeré, A. Badura, M. M. Nowaczyk, D. A. Gushin, M. Rögner, W. Schuhmann, *Angewandte Chemie International Edition*, **2013**, *52*, 14233 – 14236.

(3) a) N. Plumeré, J. Henig and W. H. Campbell, *Analytical Chemistry* **2012**, *84*, 2141-2146; b) N. Plumeré, *Analytical and Bioanalytical Chemistry* **2013**, *405*(11), 3731-3738; c) M. Swoboda, J. Henig, H.-M. Cheng, D. Brugger, D. Haltrich, N. Plumeré, M. Schlierf, *ACS Nano*, **2012**, *6*(7), 6364-6369.

Acknowledgement: financial support by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.
Projects in cooperation with the following COST TD1102 members: Wolfgang Schuhmann (Ruhr-University Bochum) and Matthias Rögner (Ruhr-University Bochum).

O12

Immobilisation of *Rhodobacter sphaeroides* reaction centers on TiO2 surface for use in solar cells

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One of the biggest problems of the contemporary world is the depletion of fossil fuels. Among the possible solutions for it solar cells based on photosynthetic reaction centers (RCs) of purple bacterium *Rhodobacter sphaeroides* are considered. They have been widely used to study energy and electron transfer in RCs [1]. First steps of photoreaction in photosynthetic reaction centers are absorption of photon and charge separation between chromophores. There are some results suggesting that this process can be used to produce electricity from solar light by binding reaction centers to TiO_2 porous layer [2,3]. This construction is similar to Dye Sensitized Solar Cells (DSSC) invented by Michael Graetzel, but there proteins are used instead of dyes. Process of attaching proteins to the metal oxide semiconductor layer is based mainly on electrostatic interactions [4], so it is important to optimize conditions which have influence on surface charge of either protein or TiO_2. During the presentation some preliminary results of the research on optimization of binding process will be discussed. Studies were conducted on wild type reaction centers and various mutants including those containing special TiO_2 binding amino acids sequence. Some stationary absorption spectra of RCs on TiO_2 and electron micrographs of the surface will be shown.

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O13

The best of both worlds: detergent-free purification of photovoltaic membrane proteins with native bilayer properties

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The use of detergents to solubilise and purify integral membrane proteins is often essential for their characterisation and/or utilisation. However, finding the optimal detergent for stability and function can be a challenging and laborious task, with compromises often having to be made. Alternative vehicles for studying membrane proteins in solution such as liposomes, bicelles or nanodiscs stabilised by a protein scaffold also have their limitations in terms of physical properties and ease of fabrication, and require initial removal of the protein from the native environment using a detergent. In this report we show that a styrene maleic acid (SMA) co-polymer can be used to solubilise the Rhodobacter sphaeroides reaction centre and a portion of associated lipid bilayer, forming a structure termed a SMA-lipid-particle (SMALP). Using a His-tag the protein can be purified by standard methods modified solely by the absence of detergent. The purified RC-SMALP retains functional characteristics typical of the protein when in its native membrane environment, rather than the modified characteristics seen in detergent solution, the lipid composition of the RC-SMALP being close to that of the native membrane. Although RC-SMALPs constitute RCs in a native-like bilayer environment they have optical properties such as low background light scattering typical of RCs in detergent, giving the best of both worlds. In addition the SMALP environment is stabilising with regard to both temperature and light, and does not prevent photocurrent generation when RC-SMALPs are interfaced with an electrode.

O14

Electronic bridges for contacting photosynthetic proteins to electrode surfaces

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Electronic communication between photosynthetic proteins and electrodes is a key requirement for the design and production of efficient biosensors and biophotoelectrochemical cells. We implement redox molecular architecture as an electronic bridge both for electron mediation and specific immibilization of the protein. Dendritic cores are applied as scaffold for the redox molecules and the protein binding moieties. Viologens and quinones as well as metal complexes for affinity binding based on nitrilotriacetic acid or triazacyclononane are attached via isothiocyanate chemistry on the amino head groups on the dendrimer. In addition thiol head-groups are introduced for self-assembly or the redox-active dendritic architecture on gold electrodes. The proteins are genetically modified with terminal or intrachain histidine-tag for the specific binding on the metal complexes. The histidine-tags are located in proximity of the redox site of the protein to allow a low distance with the redox active functionalities of the dendrimer. The redox potential of the redox molecules is tuned to the one of the redox center in the protein to allow for electron transfer at a low overpotential. Only a slight driving force is used to allow for efficient electron transfer limit the energy dissipated as heat. For Ferredoxin NADP+ oxidorecuctase and for photosystem 2, viologen and quinones, respectively are exploited as the mediators.

O15

Intra-Protein Photodynamics of Photosystem II-Synthetic Hybrid Systems

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Photosynthetic proteins such as the water oxidation enzyme, photosystem II, have always been the subject of great curiosity for their subtle, yet complex exciton and charge mechanisms. Photosystem II exhibits phenomenally fast exciton transfer and charge generation/separation, whilst maintaining very low yields of recombination and decay. (1) As the field of hybrid photosynthetic systems, which incorporate natural enzymes for water splitting and/or fuel generation, begins to play more of a role in solar energy based research, questions have to be asked about how these natural systems really perform under such artificial conditions. (2) It is reasonable to hypothesize that the intrinsic photophysical processes can be perturbed due to these new environmental conditions, whether it is induced via steric and/or electronic factors. Here we present initial investigations into the exciton-charge dynamics of solution based photosystem II coated indium tin oxide nanoparticles. This simplistic system looks to see whether the classic transient spectroscopic signatures used for kinetic studies of the natural enzyme show any evidence of perturbed intra-protein kinetics. Room temperature transient absorption and time-resolved photoluminecence spectroscopy has shown evidence for such perturbations occurring on the fs-ps time scale. Such studies could aid in elucidating morphological dependencies of inter-pigment electronic coupling, which is a known pre-requisite for high quantum efficiencies of energy and/or charge transfer.

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O16

Functional reconstitution of photosynthetic reaction centres in polymersomes

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Biological membranes have several roles, but arguably the most important is to form a boundary that separates the inside solution of cells or organelles from the outside milieu. Given the complexity of the biological membranes, numerous model structures reconstituted with the molecular machinery of interest have been introduced, allowing to focus on its activity. Artificial membranes, based on synthetic amphiphilic molecules able to self-assemble in water and possessing higher stability and robustness than lipids, have been looked upon as possible alternative systems to reconstitute and investigate specific membrane and transmembrane proteins. Block co-polymers have drawn attention since they are able to organize in closed vesicles, called polymersomes, in which membrane proteins can be inserted. In this work we prepared polymersomes formed by the hydrophilic poly-(2-methyloxazoline) (PMOXA) linked to the hydrophobic central core poly-(dimethylsiloxane) (PDMS), with a structure $PMOXA_n$-$PDMS_m$-$PMOXA_n$ or $A_nB_mA_n$. The photosynthetic reaction centers (RC) from *Rb. sphaeroides* R26 have been reconstituted in these structures by means of the micelle-to-vesicle transition method that is widely used in the case of phospholipid vesicles[1]. RC integrity and functionality has been investigated and found fully retained. Furthermore, the localization of RC in the polymersomes has been investigated and will be discussed. Our data of charge recombination kinetics and interaction with cytochrome and quinone pools indicate that the protein appears to sit in the external PMOXA moiety of the polymersome structure.

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O17

Evaluation of a biohybrid photoelectrochemical cell employing engineered purple bacterial reaction centres as a biosensor for herbicides

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The *Rhodobacter sphaeroides* reaction centre is a relatively robust and tractable membrane protein that has potential for exploitation in technological applications, including biohybrid devices for photovoltaics and biosensing. We have assessed the usefulness of the photocurrent generated by this reaction centre adhered to a small working electrode as the basis for a biosensor for classes of herbicides used extensively for the control of weeds in major agricultural crops. Photocurrent generation was inhibited in a concentration-dependent manner by the triazides atrazine and terbutryn, but not by nitrile or phenylurea herbicides. Measurements of the effects of these herbicides on the kinetics of charge recombination in photo-oxidised reaction centres in solution showed the same selectivity of response. Titrations of reaction centre photocurrents yielded half maximal inhibitory concentrations of 208 nM and 2.1 μM for terbutryn and atrazine, respectively, with limits of detection estimated at around 8 nM and 50 nM, respectively. Prospects for the use of protein engineering to develop the sensitivity and selectivity of herbicide binding by the Rhodobacter sphaeroides reaction centre will be discussed, as will strategies for genetically-controlling the interaction of reaction centres with conducting materials.

O18

Detection of photosynthetic herbicides using PSII biosensors and chlorophyll fluorescence based biotest

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The photosystem II-based biosensor was developed, using isolated PSII particles from the thermophilic cyanobacterium Synechococcus elongatus as a biosensing element, immobilised on thick-film Pt-Ag/AgCl electrodes printed on corundum. Oxygen evolution produced by PSII during short pulse of red light was monitored and found to be proportional to the herbicide concentration in the medium. When the herbicide is in the medium, a decrease in signal rise during the illumination is observed due to the blocked electron transport between the PSII and electron acceptor. The time of herbicide incidence during a dark period and number of measuring light pulses were optimised to shorten measurement duration and increase the sensitivity. The chlorophyll fluorescence-based bioassay using the analysis of fast fluorescence induction curve in Tripleurospermum inodorum cotyledons was proposed and used for detection of herbicides in soil extracts. The seedlings were grown in Petri dishes with filter paper soaked in soil extract or herbicide solution. After the cotyledons were fully developed, fast chlorophyll fluorescence kinetics were measured with portable chlorophyll fluorometer. The relative variable fluorescence VJ parameter defined as (FJ FO)/(FM FO) provides the most consistent results for description of herbicide dose. Data of field experiment with application of isoproturon showed that both methods correlated with herbicide content in soil determined by HPLC. A gradual decay of isoproturon was demonstrated during the period of measurement (up to 78 days). The degradation patterns at deeper profiles show comparable kinetics to top layer with lower isoproturon activity and small delay in degradation.

O19

Laser printing for the fabrication of an aptasensor for environmental monitoring

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This work presents the development of aptazymes based sensors by means of direct laser printing on micromechanical capacitive sensors, parts of a 8 x 8 array, for the detection of heavy metal ions such as lead (Pb(II)). The sensors are composed of an ultrathin, GOPTS functionalized, flexible silicon membrane passivated by a low temperature oxide (LTO) layer standing at a distance of 0.5 um over the fixed substrate. Aptazymes are similar to aptamers in that they specifically recognise and bind to a single target molecule, although the latter are double stranded, in the presence of a metal ion, a catalytic reaction is caused, leading to the cleavage of the double stranded DNA molecule. The aptazymes were fluorescently taged so as to confirm the immobilization and hybridization procedure.

The DNA(2) aptazyme was fluorescently tagged with fluorescent, while its complementary DNA(1) was tagged with a quencher, so that after their hybridization, the fluorescent signal was decreased. In the presence of Pb(II), the cleavage of the double stranded DNA leads to the increase of the fluorescence.

The synthetic DNA(2) is laser printed and immobilized onto the sensor membranes and subsequently bound to its partially complementary sequence DNA(1) leading to a relatively rigid double stranded DNA complex in the absence of Pb(II). Upon Pb(II) binding, self-cleaving occurs at a specific site of DNA(1), dissociating the complex into three fragments. This event is sensed as a change in stress on the surface of the sensor membrane causing it to deflect, and effectively change the capacitance between the flexible membrane and substrate.

O20

Plasma Modified Polycarbonate Nanorod Arrays for Biomedical Applications

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Nanoporous anodized aluminum oxide (AAO) membranes are a unique class of biomaterials that can be synthesized by two step anodization of high purity aluminium [1,2]. With specific and controllable chemical and topographical features, AAO membranes have wide range of applications from biomedical to electronics.

AAO membranes are also used in nanofeatured polymer surface studies as a mold. The membranes that are modified with chemicals easily and their pore structure can be controlled by voltage and electrolyte concentration provide ordered and uniform nanostructures on polymer surface in large areas (Fig.). Nanostructured polymeric surface are attracting interest due to their wide usage in biomolecular sensing, optics and optoelectronic applications. An important point is that solution based nanofeatured polymer layers substantially mimic AAO mold surface. Therefore, the roughness of the surface increases according to solid based polymer layers. In addition to this point, structure shape is affected to signal quality for SERS application.

Low (50 KHz) or Radio (13.6 MHz) Frequency plasma processing of those surfaces by employing gas (oxygen or argon) [3] or monomeric precursors (Ethylenediamine [4], EDA, AcrylicAcid, AA [5], Hexamethyldisilane, HMDS [6] etc) can lead us to reach different nanostructures or nanocomposites of those nanorod arrays [7]. First, by etching, it is expected to change the physical and morphological properties of the arrays for SERS application. A set of preliminary study result is presented in Figures B and C. Second, by employing monomers as precursor, a very thin layer of porous hydrophilic or hydrophobic polimeric membrane could cover the nanorod array, to be able to use the matrix for controlled drug delivery. Our final target is to create a bacteria antifouling property on the

surface by employing amphoteric precursors [8], for artificial blood compatible vessel surface.

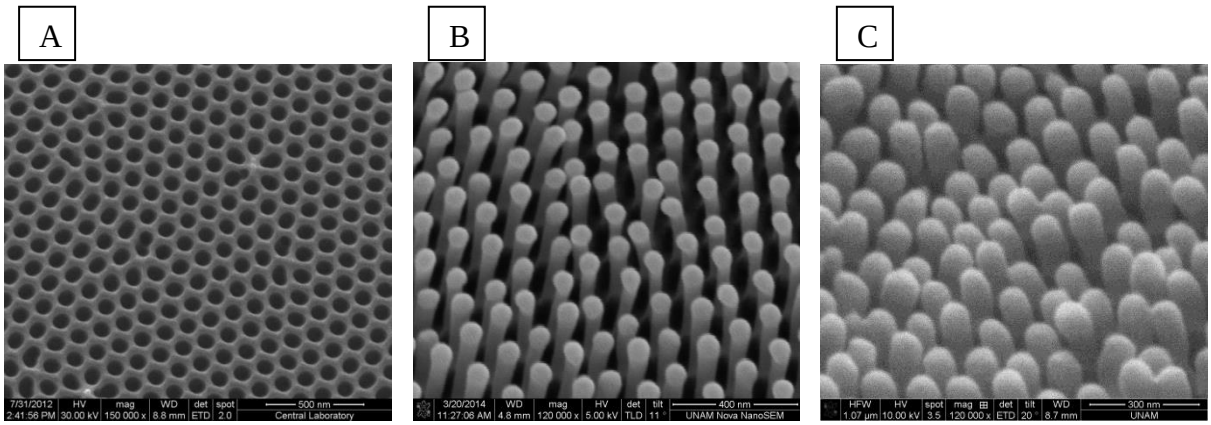

Figure . ***A)*** *SEM images of AAO mold, nanotextured Polycarbonate surface* ***B)*** *before plasma treatment (inset: large area SEM image) and* ***C)*** *after 12 seconds plasma treatment.*

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O21

A Reaction Center-Based Screen-Printed Photoelectrochemical Cell for the Detection of Atrazines

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The primary processes in the photosynthetic apparatus of the purple bacterium Rhodobacter sphaeroides take place in a specialized pigment-protein system called photosynthetic reaction center (RC) [1] embedded in the intracytoplasmic membrane systems (ICM). The reaction center in the native membrane performs a photocycle in which a ubiquinone molecule is eventually reduced to ubiquinol with simultaneous oxidation of two ferricytochrome proteins. The process is promoted by the absorption of two photons. As a consequence of light absorption, an electron is transferred from the singlet excited state of the bacteriochlorophyll special pair (D) through a series of cofactors, to the primary quinone QA, about 25 Å away, in 150 ps and eventually to the secondary quinone QB, 15 Å apart, in 100 μs. The photocycle can be blocked by the addition of atrazine-type herbicides which are known to bind to the QB-site of the reaction centers thereby blocking the electron transfer from QA to QB [2]. The aim of this work is to demonstrate the possible application of this system as herbicide photo-detector in a screen printed electrochemical cell containing the RC, quinone and cytochrome together with suitable mediators. Work supported by project Potenziamento del CENTRO RICERCHE PER LA SALUTE DELL'UOMO E DELL'AMBIENTE (PON 254/Ric., cod. PONa3_00334).

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O22

Raman Spectroscopy for Bio-detection: Herbicide detection via chloroplast

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Raman spectroscopy is a spectroscopic technique used to measure the inelastic scattering of the incident light from a sample and the frequency shift of the scattered light shifts in a manner of characteristic molecular vibrations. The general advantages of Raman spectroscopy over other spectroscopic systems are no interference from water content of the samples, ease of sampling and measurement, and minimal fluorescence interference of sample matrix varying from sample to sample. Combining Raman spectroscopy with chemometric methods and vibrational spectroscopy has enabled enormous progression for both quantitative and qualitative measurements of the samples. Surface Enhanced Raman Spectroscopy (SERS) takes the advantages of strongly increased Raman scattering signal generated by local field enhancements near metallic nanostructures. The internal modes of the reporter molecule can be used as diagnosis signals and appropriate placement of the reporter molecule on the metal nanoparticle surface is a well-appreciated challenge. Several approaches have been suggested for this purpose and multipurpose functionalized hybrid nanoparticles are very promising for the detection of trace amounts of analyte.

The present study aims to development of a novel method using Raman spectroscopy for herbicide detection. Chloroplast form spinach was used as bio-recognition agent and interaction of chloroplast and herbicide (Tribenuronmethyl) was monitored using Raman spectroscopy and SERS. The correlation between the herbicide concentration and Raman signal was found to be linear within the range of 5 ppm to 100 ppm. The limit of detection for the homogeneous assay was determined as 4 ppm.

O23

Symbiotic Machine

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Symbiotic Machine is an autonomous bio-machine that is able to harvest energy by using photosynthetic organisms. This energy is used to make the machine move and search/collect more photosynthetic organisms. The bio-machine is made from floating material that is shaped in a robot-like structure and is able to collect and threat the required organisms autonomously. Therefore the machine creates on symbiotic system with its environment. Symbiotic Machine is developed in co-operation with artist Ivan Henriques, scientists from the VU Amsterdam LaserLab; Raoul Frese and Vincent Friebe, physicists Michiel Overbeek and engineer Leydervan Xavier of Cefet/RJ (Technological School Rio the Janeiro). The project is supported by Stichting Doen. Symbiotic Machine is an example of an invention wherein art and science are combined. This art-science object enables to accelerate the process of knowledge originating from to lab to the public domain. The machine is currently displayed in the Glazen Huis in Amsterdam were it is living in a big pool feeding itself with algae. During the exposition of a total of two months several hands-on workshops and readings will take place. Symbiotic Machine is thus a way to enable best of two worlds. The artist will be able to expose the invention in such a way that is attractive for the public. The scientist are provided with the opportunity to test an invention outside the lab without needing to consider the potential economic benefits.

POSTER PRESENTATIONS

P1

New detectors for metal cations and protons based on PAMAM dendrimers modified with 1,8-naphthalimide units

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Polyamidoamine (PAMAM) is a commercial class of dendrimers finding application in various areas. They are biocompatible, non-immunogenic and possess terminal modifiable amine functional groups.

Yellow-green and blue fluorescent PAMAM dendrimers modified with 1,8-naphthalmide units in their periphery have been investigate recently. Their photophysical properties exhibited in the presence of metal cations make them appropriate for producing very sensitive fluorescent sensors for metal cations and protons in living organisms and the environment.

In this study the synthesis of five new PAMAM dendrimers from first generation modified with 1,8-naphthalimide units has been described. Their photophysical characteristics have been investigated in organic solvents of different polarity in order to investigate their sensor potential. The sensor ability of the dendrimers to detect biological important metal ions has been discussed. The fluorescence intensity of the dendrimers has also been investigated as a pH function of the environment. A cuprum complex of dendrimer has been synthesized and characterized and its antibiotic activity has been investigated in vitro for against eight bacterial cultures.

P2

Photocurrents generated from crude preparations of photosynthetic purple bacterial membranes adsorbed onto a conductive substrate

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The native architecture of photosynthetic membranes adsorbed onto flat surfaces have recently been well characterized using Atomic Force Microscopy to reveal the organizations of the protein-complexes within the network. It was shown that peripheral Light-Harvesting complexes (LH2) formed peculiar domains that further organized with linearly arrayed Light Harvesting -Reaction Centers (LH1-RC's) [1] even after adsorption onto flat gold. Here we reveal the ability to adsorb crude preparations of membranes from Rbl. acidophilus onto a gold substrate and measure considerable light induced currents with appropriate redox mediators cytochrome c and quinones in solution. Photosynthetic membranes are an attractive option for generating photocurrents because they require few steps to isolate relative to isolated reaction center-light harvesting-1 complexes (RC-LH1) and reaction centers only commonly employed in bio-hybrid photoelectrochemical cells. Here we show these simple preparations yield significant photocurrents of (>0.5uA/cm^2 at 45mW/cm^2 illumination intensity). We show the varied contribution of LH1 relative to LH2 to photocurrent output by measuring action spectra, and reveal lasting durability of the proteins via photocurrents that were generated over many days. These results show promise for cheap and easily isolated photosynthetic materials that may be used in bio-hybrid solar cells.

P3

From whole cells towards photosynthetic reaction centres: "functional" and intrinsic dynamic properties

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The core of the reaction center protein is dominated by the D1/D2 heterodimer hosting all the redox cofactor involved in charge separation and electron transfer processes. The D1 protein is the subject of intense research being either the main actor in Photosystem II (PSII) assembly and repair cycle. Several studies demonstrated that even single point mutations in the D1 primary structure could affect PSII photochemistry and the physiological performance of the hosting organisms.

Here, we address the question if there is a "functional" dynamics in addition to the intrinsic dynamical behaviour common to all proteins and how do they couple. In particular, understanding if "rigidity" is essential for the charge transfer process and if this property is shared by all the photosynthetic systems and how this information can be apply to design high performant bio-sensors.

To this end a comparison between *Chlamydomonas* cells carrying both native and mutated D1 protein (hosted in the PSII of the cell) has been undertaken using neutron scattering experiment. Mutation were located in the functionally important regions D1 protein All the mutants had a lower chlorophyll content indicating a possible modified antenna size. However, the mutation's type and localization impacted photosynthetic performance in a different manner. Mutants displayed reduced electron transport efficiency in physiological conditions, and increased photosynthetic performance stability and oxygen evolution capacity in stressful high-light conditions.

Results show that point genetic mutations may notably affect not only the biochemical properties but also the T dependence of the whole complex dynamics in particular suggesting the wild type more rigid than mutants. We highlight non negligible differences at longer time scale, rather than short, and large scale. We defined an intrinsic soft matter dynamics (Td ..) and a "functional dynamics" We bring to light for the first time that hydration water collective density fluctuations can provide also a measurement of "functional dynamics".

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P4

Interaction between *Rhodobacter sphaeroide*s reaction centers and TiO_2

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Nowadays one can observe intensified development in field of alternative sources of energy, which is caused by the depletion of fossil fuels. One of the most promising is the solar energy. The invention of Dye Sensitized Solar Cells (DSSCs) by Michel Graetzel was a breakthrough in solar cells technology. In the classical DSSC cell what is used for photon – electron conversion are dyes such as ruthine complexes or porphirines (with efficiencies up to 11,7 % [1]). However one of the proposed modifications of DSSCs is replacing those dyes with photosynthetic reaction centers (RCs) from different organisms, for example purple bacterium *Rhodobacter sphaeroides* [2]. In such cases RCs may be treated as solar cells in nanoscale. First steps in photosynthetic reaction centers are absorption of photon and charge separation between chromophores [3]. Process of producing described construction consists of positioning protein on the titanium dioxide porous layer. Implementation of the RCs in the pores of TiO_2 enables to acquire many layers of those proteins, thus enlarging the probability of photon absorption. Since binding of RCs is mainly based on electrostatic interactions, it can be affected by even slight environmental changes [4]. The aim of the research was to optimize conditions of attaching proteins to the TiO_2, regarding RCs / TiO_2 ratio, concentration of detergent or pH of the buffer. For this purpose Fluorescence Correlation Spectroscopy (FCS) of RCs with TiO_2 nanoparticles in solutions was performed.

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P5

Adsorption Of Proteoliposomes At The Air-Water Interface As A Tool For The Preparation Of Supported Photoactive Membranes

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The active layer deposition on the surface of a suitable transducer represents a critical step in the definition of the final performance of a chemical sensor. Moreover, to achieve the high sensitivity and selectivity of a biosensor, it is important to preserve full functionality of the biomolecules after their immobilization onto the sensor surface. Supported lipid membranes have attracted much attention since they can provide a biomimetic environment, which may prevent denaturation and loss of activity, thus improving biosensor performance. We propose a new strategy for attaining the controlled deposition onto solid supports of lipid layers where photosynthetic reaction centers (RCs) from R. sphaeroides are embedded. RCs where first integrated in small unilamellar vesicles (SUVs) made of phospholipids, using the micelle to vesicle transition (MVT) method. The Langmuir-Blodgett technology was then exploited for achieving the transition from the three-dimensional (vesicles) to the two-dimensional (floating layer) organization of phospholipids. Surface pressure in Langmuir troughs was monitored for following proteoliposomes adsorption at the air-water interface. The equilibrium surface pressure proved to depend strongly on the presence of incorporated proteins into the vesicle bilayers, thus suggesting the higher instability of these structures and their attitude to evolve towards the planar architecture. Langmuir-Schafer techniques were eventually employed for achieving the transfer of floating RCs/lipids films onto solid surfaces. The characterization of transferred layers by means of different spectroscopic techniques confirmed the successful deposition of RCs into a biomimetic lipid environment.

Work supported by the grant PON 254/Ric., cod. PONa3_00334.

P6

Oxygen Plasma Etched Polycarbonate Nanorod Arrays for Surface-Enhanced Raman Scattering (SERS) Applications

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Functionalized multicomponent nanorods are utilized in applications ranging from multiplexing, protein sensing, glucose sensing, imaging, biomolecule-associated nanocircuits, gene delivery and vaccinations [1]. The manufactured nanorod arrays have manifested superior omnidirectional antireflection behavior (up to 70) with an average reflectance staying below 2% in the visible spectrum (400–800 nm) [2,3]. These structures have also potential use as Surface-enhanced Raman Scattering (SERS) substrates and superhydrophobic surfaces [4]. The etching of polymeric surfaces has been shown to improve wettability according to increasement of the surface energy.

Polymeric nanorod arrays with ordered nanotopographies can be fabricated by using nanoporous silicon molds through nanoimprint lithography or drop casting. The silicon molds are made by using Anodized Aluminum Oxide (AAO) etch masks under Inductively Coupled Plasma (ICP) condition [1,2]. We have recently discovered an approach to produce large (~ 50 cm^2) area polycarbonate nanorod arrays directly by drop casting onto AAO molds hence alleviated the requirement for plasma processing for mold fabrication.

This research will focus on the affects of low pressure/low frequency oxygen plasma on the rod-to-rod distance, hydrophobic to hydrophilic transition as well as physical composition of PC nanorod surfaces. 50 kHz capasitively coupled plasma generator will be employed at different parameters such as power, oxygen flow rate and exposure time. The effect of oxygen plasma etching [5] on the physical, physicochemical and morphological changes will be determined by contact angle, XPS, FTIR-ATR, SEM and AFM techniques.

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P7

Photoelectrochemical Water Oxidation using Photosystem II on Mesoporous Indium-Tin Oxide Electrodes

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In photocatalytic water splitting, water oxidation is the most difficult step since it is both energetically demanding and mechanistically complex. Photosystem II (PSII), a highly efficient enzyme for light-driven water oxidation, is a benchmark O2-evolution catalyst and a blueprint for chemists to develop improved synthetic water oxidation catalysts. Here, we present work where we have integrated PSII (Thermosynechococcus elongatus) into a mesoporous indium-tin oxide (ITO) photoanode (Figure 1). The generated photocurrent densities were optimised using rational strategies to control the orientation and immobilisation of the PSII to the electrode, allowing for more efficient electron injection from the reducing sites of the enzyme to the anode. The addition of a PSII QB inhibitor to block electron transfer at the last step of the electron transfer pathway resulted in significant residue photocurrents, consistent with the existence of an alternative electron transfer pathway from the PSII to the anode, presumably via QA (Figure 1). The photoelectrochemical profile of the PSII-ITO electrode was compared against a promising synthetic photocatalytic system comprising of nanostructured WO3 modified with a layer of TiO_2 and a NiOx electrocatalyst. The strengths and weaknesses of the enzymatic and synthetic systems will be discussed.