

太陽光エネルギーの有効利用に関するワークショップ

主催：大阪市立大学学内重点研究：
都市環境の再生に向けた戦略的新展開
研究代表者：橋本秀樹

12月15日(月)11:00-17:00
大阪市立大学 文化交流センター ホール
(大阪駅前第二ビル6F)

はじめに

橋本 秀樹 (プロジェクトリーダー)



現在人類が地球規模で遭遇しており、早急な解決が切望される問題として、エネルギー不足、水資源の不足 (=食糧生産の不足)、地球温暖化の問題が上げられる。これらは全て近代都市が生み出した問題であるとともに、都市そのものにその甚大な影響が及ぼされており、正に現代における都市問題を象徴していると言える。大都市、大阪に生きる我々にとっても、これらの問題は単純に無視することのできない切実な問題であるばかりでなく、一大政令指定都市として、上述の問題に正当に対処するための方策・指針を、世界にさきがけて提案・提言して行くことは極めて本質的かつ重要な課題であると考えられる。

大阪市立大学杉本キャンパスには、理学部・工学部・生活科学部の理系3学部が存在し、これらは正に大阪市における理科系分野における知の宝庫を形成している。対象となる研究課題が地球規模におよぶことを熟慮し、これら理科系研究分野における個別の英知を戦略的に融合し、地球規模での急務な課題に対応するために、新研究機構を設立することが必須である。そこで、都市圏におけるエネルギー・水・生態系の健全かつ斬新な循環・活用に関して、理系3学部における研究者より構成される「複合先端研究機構」(理系共同研究新機構)を設立し、以下に掲げる3つの研究課題(喫緊の都市問題)に対して、戦略的に研究を展開することとなった。

戦略課題 A : 次世代エネルギーの開拓と産業応用

戦略課題 B : 都市圏の環境保全と地盤防災のための地下水資源の健全な活用法の構築

戦略課題 C : 都市圏における環境・生態系の時空間変動

これらの課題は、微視的な空間から巨視的な予測を含む包括的なものである。その成果を有効に活用するためには、分野間の垣根を越えた相互のコミュニケーションが非常に重要であり、それなくしては都市圏における環境問題や地球規模での諸問題に正当に対処することは不可能である。また、得られた成果を広く世に伝えて行くことが必須である。

今回のワークショップは、前述の戦略課題 A において世界的に活躍されている著名な研究者を講師としてお招きした。活発な意見交換を行うことにより、問題解決に向けての認識を共有すると同時に、「大阪発世界を救う」を合い言葉として、情報発信の第一歩としたい。

Preface

Shortage of energy and water resources (= food production) and the global warming are the grave crises that the human beings on this planet are currently facing. These crises are generated during the course of the development of cities. And now they are seriously affect the life of the people, who are living in the modern cities. In this sense, the global crises can be regarded as a symbolic matter of civic problems. They cannot be simply ignored by us, who are living in one of the major ordinance-designed cities "Osaka". Therefore it is a challenging subject to find out possible ways to suggest powerful measures to cope well with these problems.

There are three scientific faculties (Faculties of Science, Engineering, and Human Life Science) in the Sugimoto campus of Osaka City University. These faculties are accounted to be the treasure troves of Osaka city in the scientific field. Since the issue of global crisis extends over the whole planet, it is required to assimilate the knowledge accumulated by the scientists in these three independent faculties to correctly deal with the urgent issue of the global crises. This is an exact reason why we have launched a new research institute whose members are carefully selected from the above three faculties. The new research institute is named as "Integrated Advanced Research Institute". The first approved research project in this institute is the one that challenges the regeneration of the urban environment, and it tries to tackle the problems of biological systems and the sound and innovative use and circulation of energy and groundwater. The project is constituted with three strategic research subjects and is guided by three research teams as listed below.

- Subject of Team A: Development and Industrial Application of the Next Generation Energy Resources
- Subject of Team B: Utilization of Groundwater for the Preservation of Civil Environment and for the Prevention against Geo-hazard
- Subject of Team C: Space and Time Evolution of the Environment and Biological Systems in the Urban Area

These subjects cover the broad area of scientific research ranging from microscopic space to macroscopic prediction. In order to effectively use the outcome of the project it is very important to facilitate the mutual communication among the three research groups. Without mutual understandings it is impossible to meet the problems of the urban environment and the global issues. Furthermore, the outcomes of the project should be informed toward all over the world.

This international workshop is held on the subject of Team A. Eminent active researchers at home and abroad in the relevant research fields are invited as keynote speakers of this workshop. I hope that, through an animated discussion, we can share common realization toward the resolution of worldwide affair. Finally, I strongly wish that this symposium becomes small but great first step for the dispatch of intelligence under the slogan of "Saving the World Starting from Osaka".

Hideki Hashimoto (Project Leader)

List of Invited Speakers

Richard J. Cogdell

Fellow of Royal Society

Division of Biochemistry and Molecular Biology, IBLS, University of Glasgow, UK

Mamoru Nango

Department of Life and Materials Engineering, Nagoya Institute of Technology, Japan

Shunichi Fukuzumi

Department of Material and Life Science,

Division of Advanced Science and Biotechnology,

Graduate school of Engineering,

Osaka University, SORST, JST, Japan

Tsutomu Miyasaka

Graduate School of Engineering, Toin University of Yokohama, Japan

Yutaka Amao

Department of Applied Chemistry, Oita University, Japan

Hideki Hashimoto (Chair)

CREST-JST and Department of Physics, Graduate School of Science, Osaka City University, Japan

Keiji Okada (Workshop coordinator)

Department of Chemistry, Graduate School of Science, Osaka City University, Japan

Isamu Kinoshita

Department of Material Science, Graduate School of Science, Osaka City University, Japan

太陽光エネルギーの有効利用に関するワークショップ

平成20年(2008年)

開催日時：12月15日 11:00-17:00

会場：大阪市立大学 文化交流センターホール（大阪駅前第2ビル6階）

主催：大阪市立大学学内重点研究：「都市環境の再生に向けた戦略的新展開」

研究代表者：橋本秀樹

Programme

- 11:00-11:10 開会 (Opening remark) 橋本秀樹 (大阪市立大学)
- 11:10-12:00 **Richard J. Cogdell** (University of Glasgow)
Towards Building Systems to Convert Solar Energy into Fuels
- Lunch---
- 13:20-14:00 南後 守 (名古屋工業大学大学院 つくり領域)
Molecular Assembly of Artificial Photosynthetic Antenna Core Complex
on Electrodes
- 14:00-14:40 橋本秀樹 (大阪市立大学大学院理学研究科)
Solar to Fuels; Natural Tactics of Solar Energy Conversion by
Photosynthesis
- 14:40-14:50 Break (休憩)
- 14:50-15:30 福住俊一 (大阪大学大学院工学研究科、SORST)
Artificial Photosynthetic Systems
- 15:30-16:10 宮坂 力 (桐蔭横浜大学大学院工学研究科)
Design of Green Printable and Flexible Dye-sensitized Photovoltaic Cells
- 16:10-16:50 天尾 豊 (大分大学工学部)
Photoinduced Hydrogen and Methanol Production based on Artificial
Photosynthesis
- 16:50-17:00 閉会 (Closing remark) 橋本秀樹 (大阪市立大学)

Towards building systems to convert solar energy into fuels

Richard J. Cogdell and Hideki Hashimoto

Division of Biochemistry and Molecular Biology, IBLS,
University of Glasgow, Glasgow G12 QQ, UK and CREST-JST and
Dept. of Physics, Graduate School of Science,
Osaka City University, Osaka 558-8585, Japan

For its long term survival mankind needs to produce clean sustainable ways of converting solar energy into fuels. At present most of our energy comes from burning fossil fuels such as oil, natural gas and coal. This is not sustainable, even in the middle term, since oil and gas resources are quite limited and the environmental consequences of doing this would be unacceptable. Where then can we get our energy and, more particularly, where can we get our fuel from? At present ~70% of our energy comes from fuel. The provision of fuel is the really big issue. In principal there are two possible, long-term, sustainable energy sources that have the capacity to achieve this. One is nuclear fusion and the other is the sun. The aim of this lecture is to present a possible road map of how we can begin to learn from the one process on Earth that already successfully converts solar energy into fuels, namely photosynthesis, to begin to design solar energy to fuel conversion systems based on a biological blueprint. This lecture will also illustrate then need to include the Social Sciences in this type of long-term research effort to ensure that any practical solutions will be socially acceptable.

<http://nsl.caltech.edu/energy.html> (This web-site provides all the background information for this presentation.

Molecular Assembly of Artificial Photosynthetic Antenna Core Complex on Electrodes

Mamoru Nango

Department of Life and Materials Engineering, Nagoya Institute of Technology,
Gokiso-cho, showa-ku, Nagoya 466-8555, Japan. E-mail: nango@nitech.ac.jp

At the early stages of the photosynthetic process, light-harvesting complexes, called LH1 and LH2, absorb solar energy and transfer it to the reaction center (RC), whereupon the absorbed energy is efficiently converted into electrochemical energy. These reactions take place within a 'core complex' consisting of a RC located inside the LH1 complex, where porphyrin complexes play important roles on these reactions. We are interested in the rapid and efficient energy transfer between porphyrins in these complexes. Porphyrin complexes have been aiming to construct an artificial solar energy device based on a natural solar energy conversion system such as the core complex. The core complex, isolated from the photosynthetic bacterium, *Rps. palustris*, was successfully assembled onto an Au electrode modified with various terminated alkanethiol by using an electrostatic interaction. (Figure 1a). Efficient energy transfer and photocurrent responses of the complexes were observed upon illumination at 880 nm. Interestingly, the fluorescence of bacteriochlorophyll *a* (BChl *a*) molecules in the LH complex was strongly quenched due to the presence of RC when illuminated at 880 nm, implying that an efficient energy transfer from BChl *a* in the LH1 complex to RC in the core complex occurred. Furthermore, the photocurrent generated from the core complex assembled onto an Au electrode depended on the wavelength of the exciting light (Figure 1b). This action spectrum revealed a maximum at the wavelength corresponding to the absorption band of the complex. At this wavelength an enhanced photocurrent was observed for the core complex of *Rps. palustris*. On the other hand, photocurrents were observed for molecular assembly of LH 1 model polypeptides with porphyrin derivatives on a gold electrode. The photocurrent response depended on the structure of the model complex. Thus, various combinations of these complexes will be useful for the self-assembling monolayer of the model LH1-RC core complex to provide insight into the function of photosynthetic membrane proteins as well as for constructing artificial solar-energy converters (Figure 2).

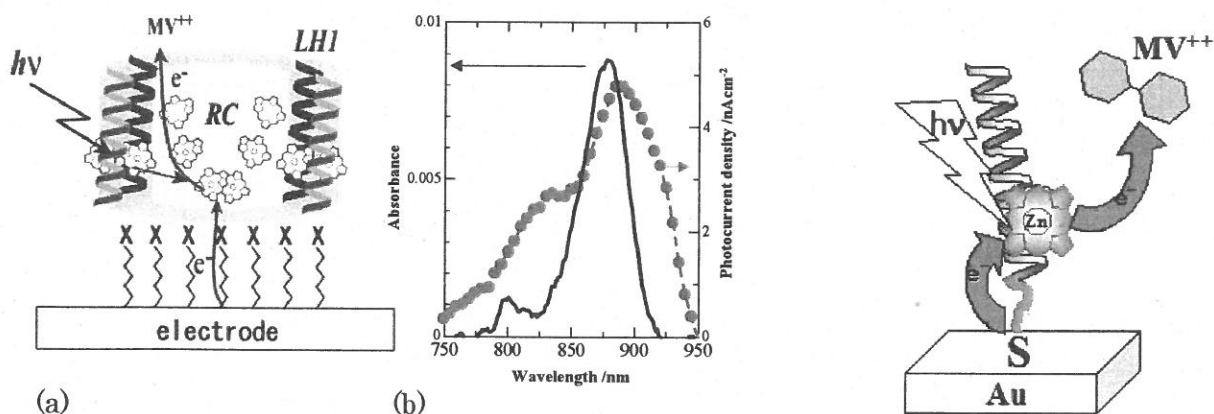


Figure 2. Schematic drawing of LH1 model polypeptides with porphyrin on an electrode.

Solar to Fuels; Natural Tactics of Solar Energy Conversion by Photosynthesis

Hideki Hashimoto

CREST-JST and Department of Physics, Graduate School of Science,
Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

70% of mankind's current energy needs are met by burning fossil fuels. This is already problematic since oil and gas supplies are limited and because of the adverse environmental effects of rising levels of carbon dioxide in the atmosphere. Moreover this situation is set to get worse as current predictions estimate that our energy needs will double by 2050. Mankind is, therefore, facing a major challenge to find new ways of creating clean, renewable fuels. One potentially abundant source of energy is solar radiation. More energy strikes the earth surface every hour than mankind uses each year. The problem is how to harness such an abundant yet diffuse source of energy. Photosynthesis has evolved mechanisms to achieve this. Conceptually photosynthesis can be divided into the following partial reactions, light-harvesting (concentration), charge-separation (conversion of solar energy into chemical energy) and finally multi-electron catalysis that takes electrons from water and uses them to reduce carbon dioxide to carbohydrates (fuel).

Any proposed strategies that set out to mimic this process in order to make solar fuels must begin with a light-harvesting or light-concentration step. We know a great deal about the structure and function of photosynthetic light-harvesting complexes as individual molecules, but rather little is known about how their supra-molecular organization within their photosynthetic membranes affects their overall function *in vivo*. We wish to understand how the supra-molecular arrangement of the light-harvesting apparatus relates to overall light-harvesting efficiency and to be able to translate this information to inform the design of robust artificial light-harvesting arrays that can, in the long term, be used in devices for producing solar fuels. Photosynthetic antenna complexes are organised on the nanoscale (see Figure 1) and a major question is how to translate this information into the design of meso- to macroscale light-harvesting devices.

This lecture will outline how photosynthesis achieves 'Solar to Fuels' conversion concentrating on the general principles involved. Recent progress on understating the molecular details of the key reactions in the photosynthetic process has been remarkable. We are now at the stage where it is realistic to start to use this 'biological blueprint' to begin to construct devices that have the capability to mimic the key steps in the natural process. This is one of the grand scientific challenges of our time.

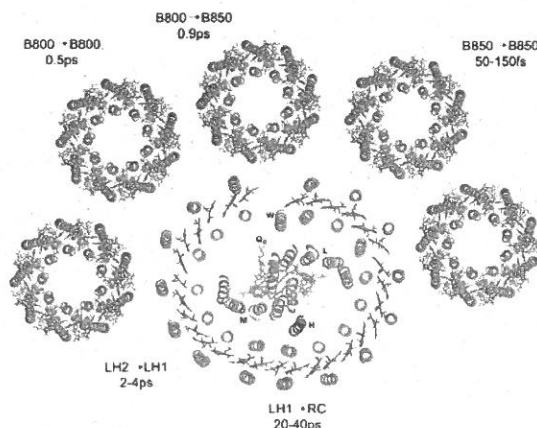


Figure 1. A cartoon of the purple bacterial photosynthetic unit (PSU) with the times of the major Bchl → Bchl energy transfer reactions indicated. This is a hypothetical model of the PSU designed to help the reader visualised the various energy transfer steps that have been time-resolved. It is not meant to represent how these complexes are organised relative to each other in the natural photosynthetic membrane.

Artificial Photosynthetic Systems

Shunichi Fukuzumi

Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, SORST, JST, Suita, Osaka, Japan
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp, home page: <http://www-etchem.mls.eng.osaka-u.ac.jp/>

The rapid consumption of fossil fuel has already caused unacceptable environmental problems such as the greenhouse effect by CO₂ emission, which is predicted to lead to disastrous climatic consequences. Thus, renewable and clean energy resources are urgently required in order to solve global energy and environmental issues. Among renewable energy resources, solar energy is by far the largest exploitable resource.

The specific objective of this presentation is to demonstrate recent development of bioinspired artificial photosynthetic systems and their applications. The design of such systems can be guided by the key steps of natural photosynthesis such as the efficient capture of visible light photons and electron/hole separation via electron transfer to give energetic oxidizing and reducing equivalents with long lifetime. First, multi-step electron-transfer systems composed of electron donor-acceptor ensembles are presented, mimicking functions of the photosynthetic reaction center. However, a significant amount of energy is lost during the multi-step electron-transfer processes. Then, as an alternative to conventional charge-separation functional molecular models based on multi-step long-range electron transfer within redox cascades, simple electron donor-acceptor dyads linked by covalent or non-covalent bonding have been developed to attain a long-lived and high-energy charge-separated state without significant loss of excitation energy. Such simple molecular dyads, capable of fast charge separation but extremely slow charge recombination, have significant advantages with regard to synthetic feasibility, providing a variety of applications including construction of organic solar cells and development of efficient photocatalytic systems for the photocatalytic generation of hydrogen.

Hydrogen is a clean energy source for the future to reduce dependence on fossil fuels and emissions of greenhouse gases in the long-term. Low-cost, energy efficient storage of hydrogen is needed for stationary and portable applications in the hydrogen delivery infrastructure. In this context, the conversion of H₂ with CO₂ to formic acid (HCOOH) merits special attention, because HCOOH is liquid that is easy to store and carry. The efficient catalytic systems for inter-conversion between H₂ and HCOOH are presented.

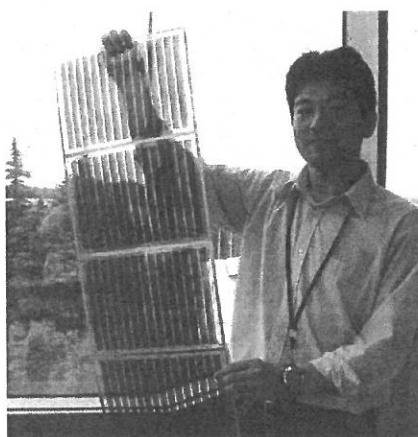
Design of Green Printable and Flexible Dye-sensitized Photovoltaic Cells

Tsutomu Miyasaka

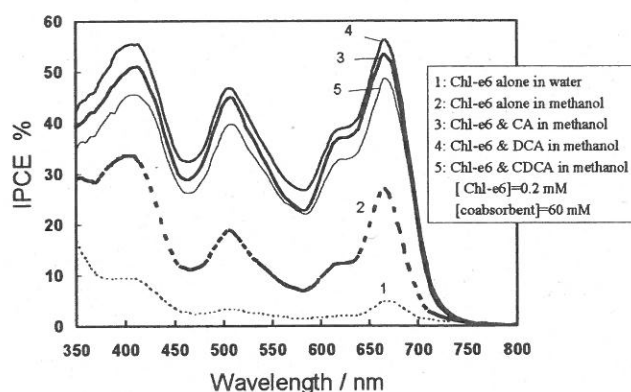
Graduate School of Engineering, Toin University of Yokohama
1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8502, Japan

Email: miyasaka@cc.toin.ac.jp

A major advantage for commercialization of the dye-sensitized solar cell (DSC) is environmentally benign materials and processes, which become especially important when the cell technology watch an increasing market of consumer electronics where lowest cost and use of non-hazardous materials are key to design a device. The target in the light source is not necessarily sunlight but also includes indoor lighting (for this reason dye-sensitized photovoltaic cell (DSPV) is more suitable wording). We have investigated use of non-ruthenium complex sensitizers including organic dyes. Using chlorine-e6, a metal-free derivative of chlorophyll, as sensitizer, and co-absorbent system, DSC of 4.4% conversion efficiency are obtained, which exhibits an action spectrum similar to that of natural photosynthesis (see figure). High absorption coefficient ($>40000 \text{ mol}^{-1}\text{cm}^{-1}$ for Chl-e6) enables use of least loading (thinnest film) of TiO_2 . Plastic substrate for electrode fabrication can minimize the device cost by utilizing printable materials. Exploring suitable printable materials that can work with low temperature, however, is a difficult issue. TiO_2 coating paste that works without binder greatly helps rapid making of cells by non-sintering process. The DSPV structure sandwiched by flexible electrodes can significantly reduce the volume of electrolyte (minimize electrolyte thickness) to save cost and to increase efficiency (decrease internal resistance). ITO conductive layer can be replaced by other transparent printable materials by plastic-processing technology. Our estimation shows plastic-based DSPV module could achieve a cost 1/5 that required to glass-based ones. Although efficiency and lifetime are eternal subjects, extremely low cost will contribute to promotion of a life style based on easy-to-exchange PV systems.



Full-plastic DSPV module fabricated with minimum loading of electrolyte



Chlorin-e6 sensitized TiO_2 cell mimicking photosynthesis of a maximum 4.4% power efficiency

Ref: M. Ikegami, et. al., *Electrochem.*, 76, 140 (2008); Miyasaka, et. al, *J. Electrochem. Soc.*, 154, A455 (2007).

Photoinduced Hydrogen and Methanol Production based on Artificial Photosynthesis

Yutaka Amao

Department of Applied Chemistry, Oita University

Solar energy conversion system based on the photosynthesis reaction is paid much attention for future energy innovation. In this work, two solar energy conversion systems based on the photosynthesis reaction are introduced. One is the photoinduced hydrogen production system coupling the methylcellulose as a cellulose derivative hydrolysis using the cellulase, with GDH and photoinduced hydrogen production with Mg chlorophyll-*a* (Mg Chl-*a*) and platinum colloid. The other is the visible light-induced methanol synthesis from HCO_3^- with the system formate (FDH), aldehyde (AldDH), and alcohol (ADH) dehydrogenases, and methylviologen (MV^{2+}) photoreduction by the visible light photosensitisation of chlorophyll analogue zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) in the presence of triethanol amine (TEOA) as an electron donor.

Hydrogen Production

When the sample solution containing methylcellulose (10 mM), cellulase (5.0 units), nicotinamide adenine dinucleotide (NAD^+) (5 mM), GDH (5.0 units), Mg Chl-*a* (9.0 μM), methylviologen (MV^{2+} , an electron carrier reagent, 5 mM) and platinum colloid is irradiated, continuous hydrogen production is observed with irradiation time. The amount of hydrogen production is more than 10 μmol after 4 h irradiation. The yield of hydrogen from methylcellulose is more than 30% after 4 h irradiation.

Methanol Synthesis

When the sample solution containing ZnTPPS (0.1 μM), MV^{2+} (0.1 mM), TEOA (0.3 M) FDH (12.5 units), AldDH (12.5 units), ADH (12.5 units) and NaHCO_3 (0.01 mM) was irradiated, methanol is produced with irradiation time. The methanol production was 0.55 μM after 4 h irradiation. The conversion yield of HCO_3^- to methanol was estimated to be 5.5% after 4 h irradiation. In contrast, no methanol production was observed without irradiation. Moreover, no methanol production was also observed in the absence of HCO_3^- . Thus, the produced methanol is not the oxidized TEOA but the origin from HCO_3^- reduction with three dehydrogenases. These results indicate that the photochemical synthesis of methanol from HCO_3^- with FDH, AldDH and ADH via the photoreduction of MV^{2+} using ZnTPPS photosensitisation.