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Energy from Photosynthesis

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2) Efficient usage of light energy. photosynthetic antennas can collect light energy in the entire region from ultraviolet to near infrared.
3) Key to solve the energy and environmental crisis. The development of a safe and economical system for conversion of light energy into electricity is crucial in order to solve the energy and environmental crisis.
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Development of "Biosolar Devices" for Sustainable Energy from Photosynthesis

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Contents

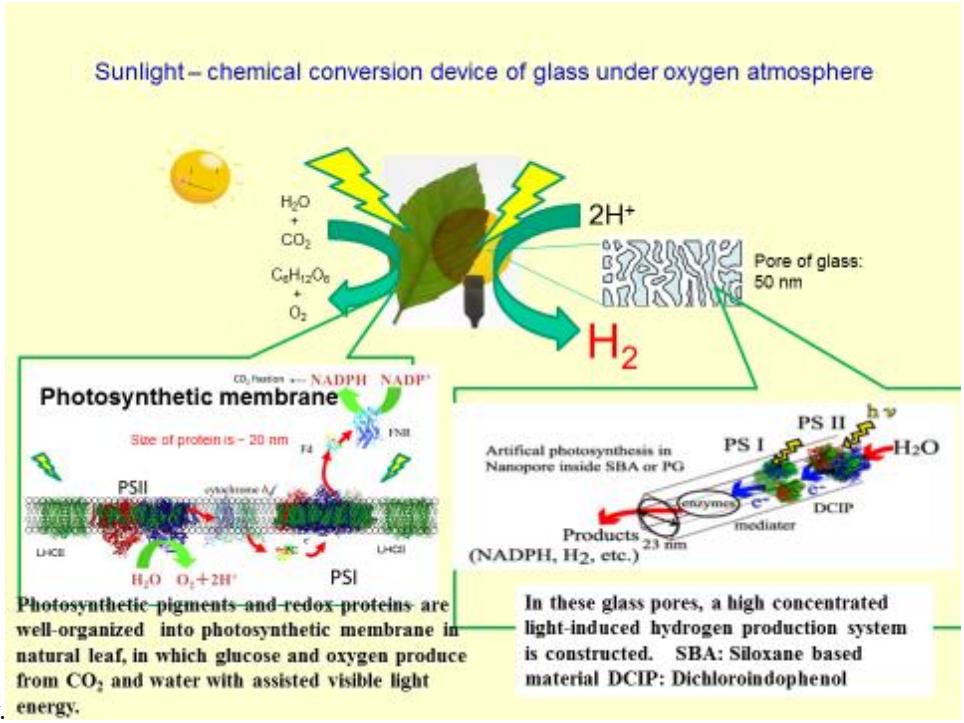
I. Abstract of the project results

Abstract:

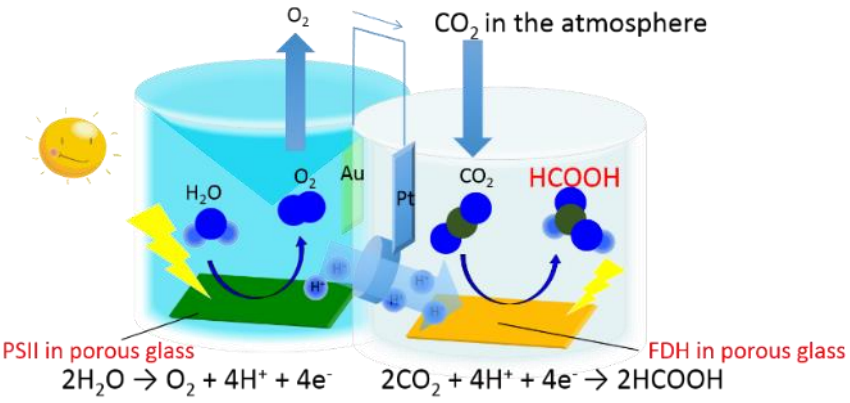
Our goal is to construct efficient energy transfer systems for development of new type of "biosolar devices" as well as to provide insight into the systems of photosynthetic reaction, "how nature establish the efficient energy transfer systems from solar to fuel production". The purpose of this proposal is to use conjugated photosynthetic complexes to develop biosolar materials for sustainable energy. The advantage of conjugated photosynthetic complexes (LHCII, PSII and PSI in Scheme 1) is their efficient capture of photons throughout the near UV to near IR region and much higher durability than ordinary isolated dyes supported by their inherent photo-protective function under oxygen atmosphere (Refs. (1)-(5)).

In this proposal, we focused the assembly of LHCII and PSI from photosynthetic membrane into the porous glass for photocurrent generation and H_2 production in Scheme 1(Refs. (6)-(9)). Combinations of antenna pigments with PSI and of metal complexes with LHCII which have the unique ability to yield high photocurrent and H_2 productivity were assembled into the pore of glass to construct the biosolar materials. Further, the systems from carbon dioxide to low carbon such as formic acid (HCOOH) using formate dehydrogenase (FDH) conjugated oxygen evolution (in Scheme 2) were developed (Ref.10). These methods of approach using photosynthetic complexes assembled on electrodes will be very useful for construction of biosolar devices with the functions of solar to fuels for sustainable

energy.



Scheme 1. Concept of biosolar devices



Scheme 2. Oxygen evolving system conjugated CO_2 reduction electrodes, where PSII into the pore glass conjugated electrode (green color) and integrated molecular catalysts (FDH: formate dehydrogenase) conjugated electrode (orange color) are constructed, respectively.

II. Result of the project

1 Introduction

Solar fuel production from carbon dioxide and water based on biological design principles of photosynthesis has received significant attention in recent years. Nature photosynthesis provides a number of examples, in which processes of energy conversion, storage and transport

are combined and optimized through 'smart matrices' at various levels, going from molecular to cellular or higher organisms. Based on biological design principles of photosynthesis, future biology-based photonics could form clean and inexpensive future alternatives for constructing the system of "solar to fuels" for sustainable energy. Our goal is to construct efficient energy transfer systems" for development of new type of biosolar devices (Ref. (1)) as well as to provide insight into the systems "how nature establish the efficient energy transfer systems from solar to fuel production". In this project on the experiments using the native photosynthetic antenna complexes (LHII and PSI in Scheme 1), a variety of modified complexes were prepared and tested for their usefulness in artificial photosynthetic materials forward to "solar to fuels". Combinations of antenna pigments with PSI and of metal complexes with LHCII which have the unique ability to yield high photocurrent and H_2 productivity were assembled into the pore of glass to construct biosolar materials. Further, the systems from carbon dioxide to low carbon such as formic acid (HCOOH) using formate dehydrogenase (FDH) (in Scheme 2) were developed (Ref.10). These modified photosynthetic protein complexes and enzymes for CO_2 reduction were introduced on electrodes to produce a new type of biosolar devices for sustainable energy (Scheme 2).

Statement of Objectives:

In this project, we proposed a scenario of the construction of electron transfer system analogous to nature photosynthetic system as for an example illustrated in Schemes 1. This system is expected to start from molecular and supra-molecular entities in a variety of smart matrices that collect light energy and separate charge for development of new types of biosolar devices from solar to fuels for sustainable energy.

2.Experiment

More details are presented in our papers in the list of publications (Refs.(6)-(10)) below.

3.Results & Discussion

In this proposal, we focused to the assembly of photosynthetic pigment complexes (LHCII and PSI) into the porous glass connected on electrodes as shown in Schemes 1 & 2. As indicated by Tasks below, photoinduced electric current production and hydrogen evolution as well as O_2 evolution systems conjugated with carbon dioxide to formic acid (HCOOH) were performed in the proposed project period.

Approach or Research Effort:

Tasks. **Artificial domain assembly of conjugated photosynthetic systems with artificial antenna complexes on electrodes to construct biosolar materials on sustainable energy transfer systems**.

In the current of our previous study (Refs. (1)- (5)), combinations of the antenna model pigments with PSI and of metal complexes with LHCII which have the unique ability to yield high photocurrent

and H_2 productivity were assembled into the pore of glass to construct the biosolar materials as Tasks bellow (Tasks 1-2). Further, we had a plan to prepare several originally designed electrochemical measurement systems from carbon dioxide to low carbon such as formic acid (HCOOH) conjugated from water to O_2 evolution as shown in Scheme 2 (Task 3).

Task 1: Light-induced photocurrent production of conjugated photosynthetic system on the nanopore glass conjugated on electrodes (Refs. (6)-(7)).

i)Enhancement of photocurrent by integration of an artificial light-harvesting antenna with a photosystem–I photovoltaic device(Ref.(6)).

Photosynthetic pigment-protein-based bio-photovoltaic devices are attracting interest as environmentally friendly energy sources. One of the photosynthetic pigment-protein, photosystem I (PSI), has been demonstrated as bio-photovoltaic materials because of the abundance and the high charge separation quantum efficiency. However, the photocurrent of these bio-photovoltaic devices is not high because of their low spectral response. We integrated an artificial light-harvesting antenna into PSI-based bio-photovoltaic device to expand the spectral response. To fabricate the device, perylene di-imide derivative (PTCDI) was introduced onto a TiO_2 surface as an artificial antenna. In the photovoltaic cells formed by the PTCDI/PSI assembled TiO_2 electrode (Figure 1), the incident photon-to-current conversion efficiency spectrum is greatly increased in the range of 450–750 nm and the photocurrent increased to 117 $\mu A/cm^2$. The result indicates that the photons absorbed by the PTCDI transfer to PSI via Förster resonance energy transfer.

This study indicates that the bio-inspired approach that imitates the light-harvesting process of photosynthesis can lead to the development of more efficient bio-photovoltaic devices.

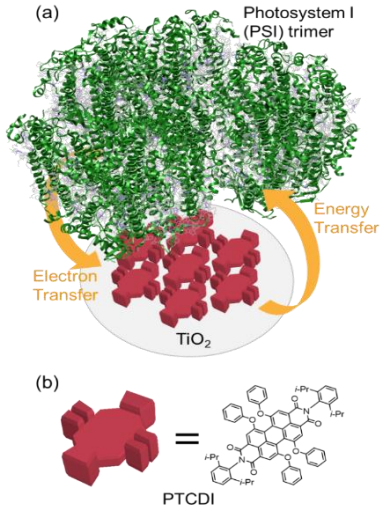


Figure 1. (a) Schematic representation of fabricating the electrode surface. PTCDI was adsorbed parallel to the TiO_2 surface, and PSI was deposited on the PTCDI occupied TiO_2. The photo-energy was absorbed by the PTCDI transfer to PSI via Förster resonance energy transfer (FRET), and then the photons are converted to electrons by PSI. The structure of PSI was drawn with a PDB ID 1JB0 file. (b) Structure of PTCDI.

ii)Photocurrent generation by photosystem I-NiO photocathode for *p*-type biophotovoltaic and tandem cell (Ref.(7)).

We fabricated a PSI-adsorbed NiO electrode for utilization as a component in a tandem cell and demonstrated *p*-type biophotovoltaics based on DSSCs using the PSI-NiO electrode (Figure 2). Under visible light illumination, the electrode showed a cathodic photocurrent, and the photovoltaic was powered by PSI, which indicates that the PSI-NiO electrode acts as a photocathode. Moreover, we demonstrated a tandem cell consisting of the PSI-NiO photocathode and a PSI-TiO_2 photoanode. The tandem cell exhibited a high V_{OC} of over 0.7 V under illumination on the TiO_2 side. Tandem cells have the advantages of a simple fabrication method employed by changing the Pt counter electrode and a high V_{OC} since it does not depend on the redox potential of the redox agents but instead on the conduction band minimum of the photoanode and valence band maximum of the photocathode. Therefore, selection of appropriate redox agents could lead to more efficient photovoltaic performances. Moreover, controlling the PSI orientation to match the current flow and using other photosynthetic proteins that can absorb a broad spectral region could also lead to further improvements to the efficiency of these biophotovoltaics.

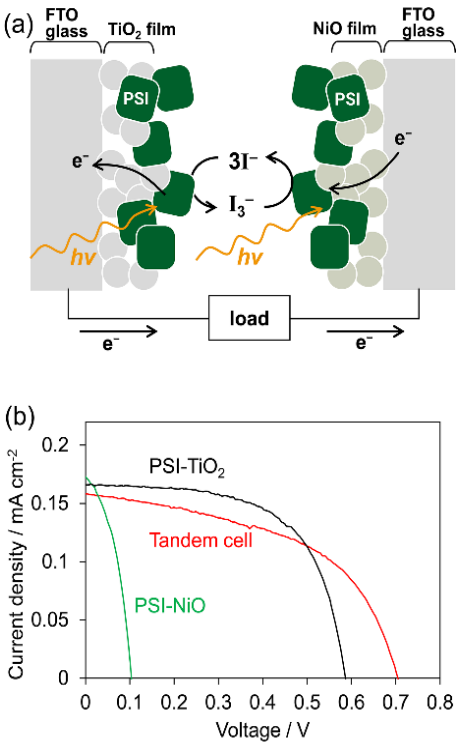


Figure 2 (a) Schematic representation of the tandem cell power generation mechanism. (b) *J*–*V* curves under AM 1.5G (100 mW cm^{-2}) of the tandem cell and individual *n*- and *p*-biophotovoltaic cells.

Task 2: Light-induced hydrogen production of Photosystem LHCII or PSI -Pt nanoparticle

conjugate on pores of porous glass plate (Refs. (8)-(9)).

i)Hydrogen production activity of the Light-harvesting complex of Photosystem II (LHCII) monomer((Ref. (8)).

Light-harvesting complex of photosystem II (LHCII) is the most abundant membrane protein-chlorophyll complex in chloroplasts. In this study, we evaluated photocatalytic hydrogen production activity of LHCII in the native-trimer and the enzymatically-treated monomer forms (Figure 3). The fluorescence lifetime in the presence of MV^{2+} is significantly shortened for the monomer than that for the trimer, indicating quenching through more efficient electron transfer from LHCII monomer to MV^{2+}. In the presence of Pt nanoparticle in a catalytic solution system, the significant hydrogen production activity was also observed for the LHCII monomer compared to the trimer (Figure 4). Therefore, the monomeric LHCII can be expected to be a potential photocatalyst for a solar energy conversion device.

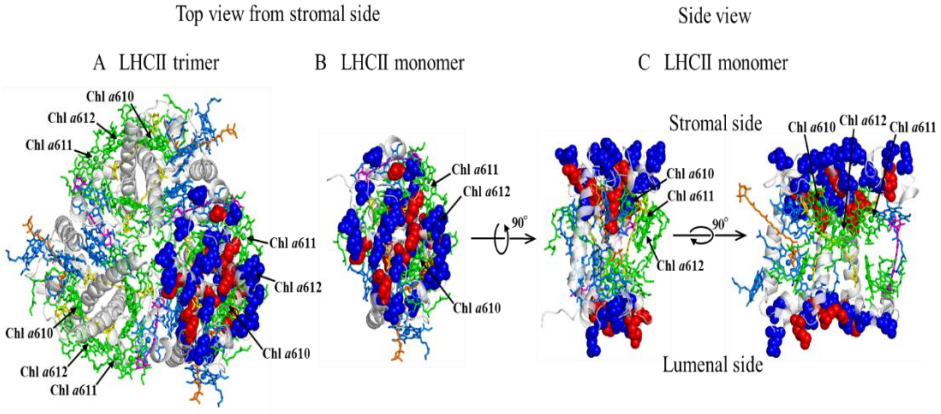


Figure 3. Structure of the LHCII trimer and monomer based on X-ray crystallography data (PDB ID 1rwt). A, B, Top view from stromal side. C, side view. Chl *a* (green), Chl *b* (blue), luteins (yellow), neoxanthin (orange), and violaxanthin (magenta), presented as a stick model. Protein (gray) ribbon diagram. Anionic amino acid residues, Asp and Glu, and cationic amino acid residues, Lys and Arg, are shown in blue and red in the LHCII monomer.

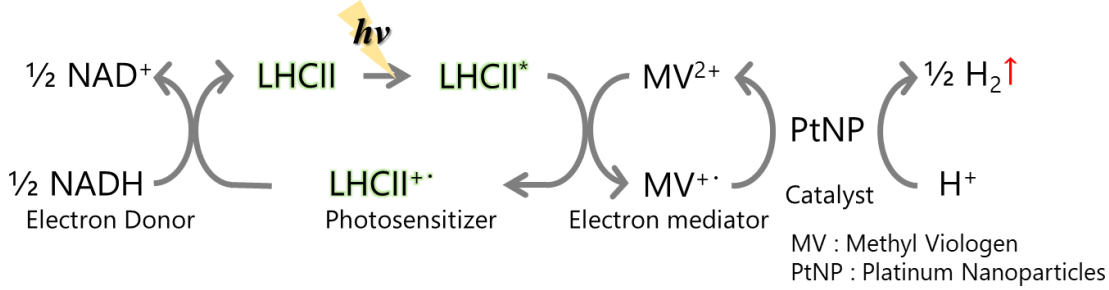


Figure 4. Photoinduced hydrogen production with Pt nanoparticles via photoreduction of methylviologen (MV^{2+}) using sensitization of the LHCII monomer or trimer in the presence of NADH.

ii)Efficient hydrogen production using photosystem I/Pt nanoparticle enhanced by artificial light harvesting dye, Lumogen Red (LR) composite under visible light by fluorescence resonance energy transfer (Ref.(9)).

We have achieved hydrogen production under visible light by using a PSI/PtNP/LR composite. Our experiments revealed that PSI, PtNPs, and LR were essential for the hydrogen production reaction. As per the reaction scheme, light energy from LR is transferred to PSI by FRET. Thereafter, the excited electrons which are charge-separated by the reaction centre of PSI are efficiently transported by the energy levels and tertiary structure of the PSI electron transport system, and recombination is prevented. Electrons moved to the stromal side are transported to PtNPs as active sites for hydrogen production. This strategy is expected to be used to improve the efficiency of PSI composite devices in the future.

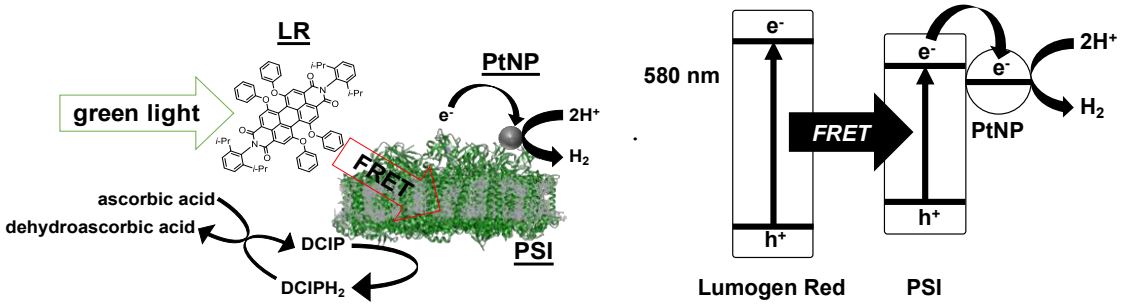


Figure 5. Schematic illustration of the hydrogen evolution mechanism using the PSI/PtNP+LR composite.

Now, light-induced oxygen-hydrogen production systems via optimization of LHCII, PSI and PSII into the pore glass conjugated electrodes are ongoing for development of "bio solar devices".

Task 3: Artificial assembly of biosolar devices for oxygen evolution as well as for fixation of carbon dioxide to fuels in the pore glass conjugated with electrodes collaborated with Prof. Y. Amao (Refs. (10)-(11)).

Photoelectrochemical CO_2 reduction to formate with the sacrificial reagent free system of semiconductor photocatalysts and formate dehydrogenase (FDH)(Ref.(10)).

The development of the efficient sacrificial reagent free and no external bias photoelectrochemical CO_2 reduction to formate system with a hybrid system consisting of semiconductor-based photocatalytic TiO_2 nanoparticles, MV, and FDH was attempted as shown in Figure 6. The photoanode based on TiO_2 film and cathode based on the CFP were separated into two compartments using a proton-permeable Nafion film. When the photoanode was irradiated with Xenon

lamp, MV reduction and CO_2 reduction to formate with FDH on the cathode side proceeded in this system without external bias. For MV reduction with photoelectrochemical cell, pH dependent MV reduction was observed and effective MV reduction proceed at pH 8. For CO_2 reduction to formate in the presence FDH on the cathode side with photoelectrochemical cell, the formate production rate was estimated to be 31.9 $nmolh^{-1}$ at pH 8 under continuous irradiation without bias. We have succeeded in constructing semiconductor based photocatalyst and biocatalyst hybrid CO_2 reduction to formate using water as an electron donor, which does not require a sacrificial reagent.

Now we are trying to develop the hybrid system using photosynthetic antenna complexes, LHCII /PSII with various visible-light responded semiconductor photocatalyst, MV and FDH for more effective CO_2 reduction to formate system.

These methods of approach using enzyme model assembled in the pores of glass conjugated on electrode will be very useful for construction of biosolar devices with the functions of solar to fuels.

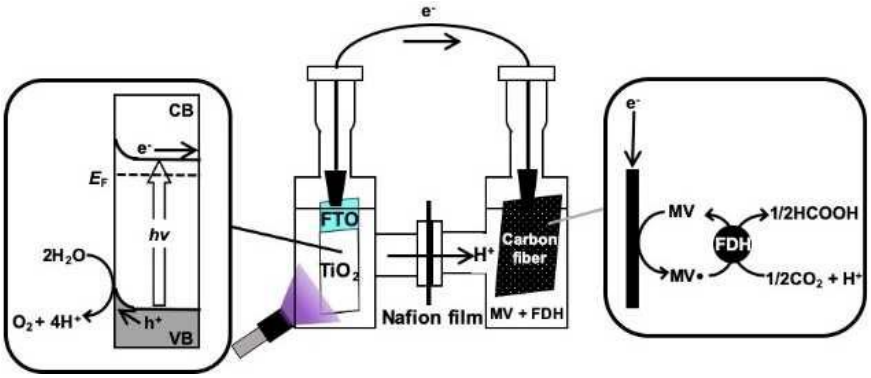


Figure 6. Light-driven O_2evolution and CO_2 reduction system consisting of TiO_2 based photoanode and carbon fabric paper electrode (CFP) based cathode with Nafion film (TiO_2/ CFP).

Summary:

In this project, we propose a scenario for construction of artificial photosynthetic system on "biosolar devices" for sustainable energy as well as for providing insight into the systems "how nature establish the efficient energy transfer systems from solar to fuel production". With the subject options, starting from molecular and supramolecular entities in a variety of smart matrices to lead an electrochemical potential for development of new types of biodevices for "solar to fuels". These methods of approach using photosynthetic antenna complexes and their enzyme model assembled in the pore glass and on several electrodes with pattern will be very useful for construction of biosolar devices with the functions of solar to fuels for sustainable energy .

Pay-off

Effects of dissemination of research results are as follows,

1) **Assembly of photosynthetic antennas on electrodes and into the pore glass.** This proposal aims to assemble photosynthetic core complexes (PSI) and the antenna complex (LHCII), and their model complexes into the pore glass for solar to fuel production from water, conjugated with the reduction of carbon dioxide. If this trial becomes successful, it can be trigger the development of a new information technology (IT), IT industry as well as the development of a new type of biodevices,**"artificial leaf"**.
2) **Efficient usage of light energy. photosynthetic antennas can collect light energy in the entire region from ultraviolet to near infrared.** It has a unique property to harvest a small number of photons from all the different directions and to concentrate them for usage. This mechanism to enable high sensitivity in a wide spectral region can be used as a guiding principle in designing **"artificial antenna**".
3) **Key to solve the energy and environmental crisis.** The development of a safe and economical system for conversion of light energy into electricity is crucial in order to solve the energy and environmental crisis. The photosynthetic system is a best refined material in harmony with the global environment, and the present project aims to create **"Solar to Fuels"** as well as the reduction of carbon dioxide for the next generation using the solar energy which is exhaustible, clear and free of pollutant.

4.List of Publications (Ref.):

(1) "Electric Device Approach Using Photosynthesis Assembly for the Development of Nanobiodevices, *Springer Series in Material Science, Lecture Note in Energy* 32, 437-454 (2016); "Solar to Chemical Energy Conversion"; "Theory and Application", M.Sugiyama, K.Fujii, S. Nakamura Ed..

(2) "Light-Driven Hydrogen Production by Hydrogenases and a Ru- Complex inside a Nanoporous Glass Plate under Aerobic External Conditions" *J. Phys. Chem. Lett.*, 5, 2403-2407 (2014).

(3) "Extension of Light-Harvesting Ability of Photosynthetic Light-Harvesting Complex 2 (LH2) through Ultrafast Energy Transfer from Covalently Attached Artificial Chromophores", *J. Am. Chem. Soc.,* 137, 13121-13129 (2015).

(4) "Oxygen-Evolving Porous Glass Plates Containing the Photosynthetic Photosystem Pigment−Protein Complex", *Langmuir*, 32, 7796 -7805 (2016).

(5) ” Light-Driven CO_2 Reduction to Formic Acid by Formate Dehydrogenase with a Ru-Complex inside a Nanoporous Glass Plate”, *ACS Appl. Mater. Interfaces,* 9, 3260-3265 (2017).

(6) “Enhancement of Photocurrent by Integration of an Artificial Light-Harvesting Antenna with a Photosystem –I Photovoltaic Device”, *ACS Appl.Energy. Materials*, 2, 3986-3990 (2019).

(7) ”Photocurrent Generation by Photosystem I-NiO Photocathode for *p*-Type Biophotovoltaic and Tandem Cell”, *RSC Advances,* in press.

(8) “Hydrogen Production Activity of the Light-harvesting complex of Photosystem II (LHCII) Monomer”, *Photochem. & Photobio., A:Chemistry.*, submitted.

(9) “Efficient Hydrogen Production using Photosystem I enhanced by Artificial Light Harvesting Dye”, *Photochem. & Photobio. Sci.,*18, 309-3158 (2019).

(10) “Photoelectrochemical CO2 Reduction to Formate with the Sacrificial Reagent Free System of Semiconductor Photocatalysts and Formate Dehydrogenase”, *ChemCatChem,*11,6277-6235(2019).

(11) Conference presentations:

1)”Visible Light Driven Carbon Dioxide Reduction to Methanol with Photo/Biocatalysts Hybrid System”, 8th Asia-Pacific Congress in Catalysis (APCAT) 2019.8.4-7, Centara Grand & Bangkok Conventional Centre, Bangkok, Thailand.

2)“Visible-Light Driven C-H Bond Activation and Carboxylation with CO_2 in the System of Bio/Photo-hybrid Catalysts”,18th Asian Chemical Congress (18th ACC) 2019.12.8-12 , Taipei, International Convention Center, Taipen, Taiwan.