The Final Research Report of FA4869-08-1-4030 (AOARD084030)

Title of Proposed Research:
Bioinspired Organic PV Cells Using Photosynthetic Pigment Complex for Energy Harvesting Materials

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14. ABSTRACT

This is the report of a research project that used the photosynthetic pigment complex of purple bacteria or green plants and their model complexes to control the direction and orientation of complex on electrodes for developing dye-sensitized solar PV cells.

15. SUBJECT TERMS

Bio-mimetic materials, Solar Cells
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I. Abstract of the project results

The purpose of this proposal is to use photosynthetic pigment complex of purple photosynthetic bacteria or green plant and their model complexes in order to control the direction and orientation of the complex on electrodes for developing dye-sensitized solar PV cells. The advantage of these pigment complexes is its high efficiency of light-energy conversion throughout the near UV to near IR region and much higher durability using these methods than ordinary light-harvesting (LH) complex isolated from photosynthetic bacteria or green plant. The present generations of PV solar cells are twenty to thirty times too expensive to be cost-effective compared to other existing energy technologies. Expanding existing PV technologies by incorporation of modified photosynthetic protein/pigments complexes or their protein-mimic materials to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, meanwhile reducing the cost aspect by the use of bio-materials and their synthetic protein-mimic materials. The majority of the aim in this report is construction of the array of artificial photosynthetic system with patterning substrate and building solar batteries using modified photosynthetic protein materials prepared from modern biosynthetic manufacturing methods and photosynthetic pigments for energy harvesting materials.

II. Result of the project.

Introduction

Nature 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, future biology-based solar cells or their synthetic organic cells could form clean and inexpensive future alternatives for electricity production.

The past 10 years have seen tremendous progress in our understanding of the structure and function of the pigment-protein complexes involved in the primary reactions of bacterial photosynthesis. The structure of the reaction center (RC, the first membrane protein to have its structure determined to high resolution) revealed the nearly C_2 symmetrical arrangement of the redox centers and this system has now been extensively studied by ultrafast laser spectroscopy. More recently the structures of the LH2 complexes has revealed the nonamer or octameric arrangement of repeating units consisting of two apoproteins and one or two carotenoids and three BCHls while the recent crystal structure of the LH1-RC core complex reveals that the LH1 complex surrounds the contours of the RC although a high-resolution structure has not yet been determined for the LH1 complex (Scheme 1).
Scheme 1. Compartimentalization of light harvesting and charge separation.

The antenna complexes (LH2, LH1-RC) efficiently realize various photosynthetic functions using cofactors (BChl α and carotenoid) assembled into the apoproteins (LH1 and LH2).

The light-harvesting mechanisms in these light-harvesting complexes have been studied both spectroscopically and theoretically. These advances put us in a unique position of being able to exploit this information to design artificial antenna systems based on 'biological blueprint'. Our aim is to see if we could produce an antenna module, which acts as a ‘sensitizer’, and a light-induced redox component for solar batteries. As well as using LH2 complexes this summary also proposed to use LH1-RC complexes.

One of its unique features is that it works over a large dynamic range of incident light intensities. It has a remarkable ability to capture efficiently photons even at very low light fluxes, yet at the same time to withstand very high light fluxes by efficiently dissipating the excess photons, thereby protecting itself against the potential harmful effects of over-excitation.

It is important to understand not only the mechanisms of efficient light-harvesting but also those of photo-protection. In order to understand these reactions both structural and functional information is required. The data on how the energy levels and intermolecular interactions of the pigments affect their energy-transfer properties, and how the ‘durability’ of the complexes is required for rational design of novel solar-cells. Based on the experiments using the native antenna complexes, a variety of modified complexes
were also synthesized and tested for their usefulness in artificial solar-cells. After elucidation of the mechanisms of harvesting, transferring, usage and dissipation of light energy, our aim is to optimize under a given light intensity the energy-conversion efficiency and the durability of the core and the antenna complexes by modifying the pigment Car and BChl or chlorophyll as well as the supporting peptides. In this report, these modified photosynthetic protein-mimic complexes were introduced into a membrane system on electrodes as a light-induced redox component, and the antenna complexes were attached to a solar cell as a UV and Vis light harvester modules to produce a new type of PV cells. These approaches will provide a foundation for using the artificial domains of photosynthetic core-antenna and antenna complexes with patterning substrate and the development of new methods of dye-sensitized PV solar cells.

The present generations of PV solar cells are, though quite efficient, are too expensive to be cost-effective compared to other existing technologies. Hence there is a need for PV electricity generation using novel-low-cost, systems with the inherently high photon-capturing and charge separation efficiency of natural photosynthetic systems to supply the national grids. Integration of photosynthetic proteins or its pigments complexes with PV devices for tasks of light-harvesting and charge separation were expanded by current PV technology with novel and inexpensive bio-components. Design principles of natural photosynthetic units formed the guideposts for the design and development of native light-harvesting and photoconversion matrix modules as described in the section of Results and Discussion below. A critical step was creating functional supramolecular assembly of small organic building blocks that co-operate to create a directional flow of energy using the operational principles of the natural systems. Properties of the building-block molecules intrinsically had the capacities to direct their co-operative assembly into structures with specific orientation and alignment. The advantages of the large scale of modern biosynthetic manufacturing methods offered a promising route to economically viable devices.

Our goal is to use photosynthetic pigment complex or its model complex as a light harvester of the well-established cell to convert light energy in the ultraviolet and visible region into that in the near infrared region for the development of energy harvesting materials. The advantage of the light-harvesting complex is its high efficiency of light-energy conversion throughout the near UV to near IR region and much higher durability than ordinary isolated dyes supported by its inherent photo-protective function. Thus, the results of the above grounds can be directly applied to the development of solar cells using modified photosynthetic pigments or their model light-harvesting materials with patterning substrate using developing modern nanotechnology.
Experiment

More details are presented in our previous papers in the list of publications. LH and its model compounds are prepared as described in the reference, No. 2 and No. 3, respectively. Molecular assembly of these complexes onto electrodes are described in the reference, No. 4, No. 11 and No. 12. Photocurrents of these complexes on electrodes are measured as described in the reference No.12.

Results and Discussion

1. Artificial domains of LH2 and LH1-RC and their model complexes for the development of antenna-mimics PV cells

Please see the manuscript for example as follows;


Molecular self-assembly of LH1-RC core complexes and LH2 complex as shown in Scheme 1 and its model complexes onto various electrodes were used to develop new types of antenna-mimics PV cells. In the current of our previous study, we used modified photosynthetic antenna complex with His-tag or modifiers at the LH polypeptide with thiol group (SH) using molecular biological methods to control the orientation and direction of the complex onto electrodes as shown in Scheme 2.

The pigment-protein complexes of the modified LH1-RC or LH2 complex was be laid down onto functionalized electrodes, such as ITO or Au electrode. Upon illumination photocurrents were successfully measured. Excitation spectra confirmed that these photocurrents were produced by light absorbed by the pigment-protein complexes as shown in our previous data (M. Ogawa, M. Nango, et.al., Chem. Lett., 772-773 (2004), M. Nagata, M. Nango, et.al., Trans. MRS-J, 30, 655-658 (2005), Y. Suemori, M. Nango, Colloids and Surfaces B: Biointerfaces, 56, 182-187 (2007), M. Kondo, M. Nango, Biomacromolecules, 8, 2457-246(2007).
Scheme 2 Artificial domains of LH2 & LH1-RC with patterning substrate: Schematic model of the assembly of LH1-RC complex with His-tag and LH2 with thiol group (SH) on an electrode (a) and electron transfer pathway of RC (b). (a) The C-terminal of LH1-RC complex and SP side of RC is oriented to hydrophilic SAMs on the electrode and the H-chain is oriented to aqueous phase (C-His), and in contrast, the H-chain is oriented to the electrode (N-His). LH2 with SH is selectively assembled onto the electrode modified with thiol goups.

(b) Electrons are transferred along the pigments associated with the L-subunit of the RC i.e. from SP to BChl $a$ (0.47 nm transfer distance), to Bpheo (0.38 nm transfer distance) and finally to Q (0.9 nm transfer distance).

1) Molecular assembly of modified photosynthetic antenna core complex with His-tag and LH2 with SH to control the orientation and direction of the complex on electrodes

It proved critical in these studies to capitalize on our knowledge of the behavior of these complexes to select those that are the most stable and well organized. The best results were only obtained with the subset...
of the most stable complexes which the orientation and direction were controlled. These studies were examined to correlate the supramolecular organization of the complexes on the electrodes with the efficiency of photocurrent.

AFM and EM studies resolved the organization of antenna complexes both in reconstituted lipid bilayers and in native photosynthetic membranes. These techniques are now being applied to investigate the organization of the antenna complexes and their synthetic model complexes on the electrodes. This work requires very careful attention to detail and the current pictures are very exciting.

2) Molecular assembly of synthetic LH 1-RC core model polypeptides with pigments on Au or ITO electrode


In the current of our previous study, LH1 synthetic model polypeptides with cysteine group or His-tag at the C- or N-terminal, analogous to the native LH polypeptide were assembled on Au or ITO electrode. Then pigments such as native and chlorophyll or carotenoid derivatives were further selected and assembled on the specific site of the LH1 synthetic model polypeptides to control the organization of the pigments on electrodes as shown in Scheme 3. The structural effects of the pigments and the synthetic polypeptides on the production of the efficient photocurrent were further examined.

Scheme 3. Schematic model of the assembly of synthetic LH model polypeptides with pigments on Au electrode.

Molecular assembly of Zn porphyrin pigments on a gold electrode or ITO electrode using synthetic 1α-helix hydrophobic polypeptide which have similar amino acid sequences to the hydrophobic core in the
native photosynthetic light-harvesting (LH) 1-β polypeptide from *Rhodobacter sphaeroides* as well as lipid components, has been achieved. These methods were clearly successful in allowing assembly of porphyrins together with a defined distance and orientation on the electrode. In this case, the switching of photocurrent direction by changing the applied potential was successfully demonstrated (such as in T. Ochiai, M. Nango, et al., *Tetrahedron Lett.*, 48, 8468-8471(2007), T. Ochiai, M. Nango, et al., *Photosynth. Res.* 95, 353-361(2008)). These methods were useful for the self-assembly of these complexes in order to study the energy transfer and electron transfer reactions between individual pigments in the supramolecular complexes on the electrode as well as to provide insight into the effect of the structure of 1α-helix hydrophobic polypeptide on the energy transfer and electron transfer reactions in the LH1-RC core complex.

2. Development of dye-sensitized solar PV cells using photosynthetic polypeptide-pigments complexes

A dye-sensitized solar cell was fabricated using modified LH1-RC complex with His-tag and its model complexes with His-tag or SH group (or protein-mimic materials) as described above. The effect of modifier of the His-tag or SH group and adding carotenoids or their mimic pigments was examined to see electron transfer from the carotenoid to the radical cation of the dye sensitizer (Chl+) blocks the reverse electron transfer from TiO2− and stabilizes the resultant charge-separated state between TiO2− and carotenoid++. No dye-based PV solar cells have built-in photoprotection mechanisms. However, in protein-mimicking devices photoprotection could easily be achieved by incorporating carotenoid or carotenoid-mimicking components, through co-assembly with the chlorophyll/protein components. For effective energy triplet-triplet energy transfer, their absorption band should have spectral overlap and the co-assemblies should be tightly connected for strong excitonic coupling.

We are now ready to fabricate several types of dye-sensitized solar PV cell by combining the two different LH complexes, i.e. LH 1 and LH 2, on various electrodes such as TiO2 as shown below, collaborated with Prof. Minoru Taya, University of Washington in Seattle, US.
Scheme 4. Schematic model of dye sensitized solar cell (DSSC)

Design of Dye using tandem system

Electronic integration of devices were achieved by self-assembled monolayers with various dyes as shown below (Dye 1, Dye 2 and Dye 3) using LH1-RC core complexes (as shown in Scheme 2) and its model complexes (as shown in Scheme 3) on TiO$_2$ coated plastic films using tandem system for MURI, collaborated with Prof. Minoru Taya group, University of Washington, Seattle, US.

One testable example for plastic films using chlorophyll derivatives was prepared last year as shown in Scheme 5.

Scheme 5. Schematic model of energy transfer and electro transfer between dyes using tandem system and TiO$_2$ plastic films

Pay-off

Effects of dissemination of research results are as follows,

1) Incorporation of photosynthetic antennas and their protein-mimic complexes on electrodes and into solar cells. This proposal aims to incorporate modified core complex (LH1-RC) and the antenna (LH2 and LHCII) complexes, and their model complexes onto Au, ITO or TiO2 and polymer matrix as well as Gräzel and silicon solar cells. If this trial becomes successful, it can trigger the development of a new information technology, IT industry as well as a new evolution battery industry.
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 photo-electronic materials.
3) Key to solve the energy and environmental crisis. 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 a novel battery for the next generation using the solar energy which is exhaustible, clear and free of pollutant.

**Summary**

The present generations of PV solar cells are twenty to thirty times too expensive to be cost-effective compared to other existing energy technologies. Expanding existing PV technologies by incorporation of modified photosynthetic proteins or protein-mimics to perform tasks of light-harvesting and charge separation, is currently explored as a novel concept, which makes use of natural protein environments to create a directional flow of light energy and electronic charge separation, even under dim or diffuse light condition, meanwhile reducing the cost aspect by the use of bio-materials. Based on biological design principles, future biology-based solar cells or model synthetic organic PV cells could form clean and inexpensive future alternatives for electricity production. We propose a scenario where construction of artificial photosynthetic systems with patterning substrate is expected to start from molecular and supramolecular entities in a variety of smart matrices that collect light energy and separate charge, leading to an electrochemical potential that can be used to produce current for developing new types of light harvesting organic PV cells for energy harvesting materials.

These results were presented in the list of publications and at several international conferences as described bellow;

**List of Publications:**

**Publications:**

4. Takeshi Mikayama, Kouji Iida, Yoshiharu Suenori, Takehisa Dewa, Tokui Miyashita, Mamoru Nango, Alastair T. Gardiner and Riciard J. Cogdell, The Electronic behavior of a Photosynthetic Reaction Center


Conference presentations:


2. Yoshito Takeuchi, Takashi Joke, Kotaro Kuzuya, Syuichi Ishigure, Katsuichi Kanemoto, Takehisa Dewa, Mitsuru Sugisaki, Keiji Yamashita, Hideki Hashimoto, and Mamoru Nango, ”Characteristic Intramolecular Electron or Energy Transfer of Chlorin Dimers” The 8th International Porphyrin-Heme Symposium, Matsue, Japan (Oct. 16-17 2008).


