Self-assemblies of light-harvesting core complex and its model complex on an electrode for construction of an artificial photoenergy conversion system

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Abstract

Photocurrent response of light harvesting core complex (LH1-RC) on an ITO electrode upon illumination at near IR area were performed to attempt the construction of an artificial antenna complex toward developing useful nanodevices. Light-harvesting antenna core (LH1-RC) complexes isolated from *Rhodospirillum rubrum* (*R.rubrum*) and *Rhodoseudomonas palustris* (*Rps. palustris*) were successfully self-assembled on an ITO or gold electrode modified with 3-aminopropyltriethoxysilane (APS-ITO) or alkanethiols, respectively. Near infra-red (NIR) absorption, fluorescence and IR spectra of these LH1-RC complexes indicated that these LH1-RC complexes on the electrode were stable on the electrode. An efficient energy transfer and photocurrent responses of these LH1-RC complexes on the electrode were observed upon illumination of the LH1 complex at 880nm. These methodologys are usefull to better understand the suprastrucure of LH1-RC complex as well as to gain knowledge about building an artificial fabrication of LH1-RC complex on solid substrates toward useful nanodevices.

Key words: Light-harvesting complex, Photosynthesis, Electrode, Energy transfer, Photocurrent conversion

1. Introduction

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. At the early stages of purple bacterial light-harvesting complexes, 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 (Figure 1) [1]. 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,photosynsthetic units (PSUs) [2-4]. 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. Recently, the X-ray crystal structure of the LH1-RC core complex has been reported and revealed that it is oval rather than circular as shown in Figure 1.

Integration of photosynthetic proteins or protein-mimics with solar energy devices for tasks of light-harvesting and charge separation will expand current solar energy device technology with novel and inexpensive bio-components. Our goal is to use modified photosynthetic light-harvesting 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 light-harvesting materials [2-7]

We have recently reported that LH1-RC core complexes isolated from *Rs. rubrum* can be assembled a cationically-modified transparent indium tin oxide (ITO) electrode, which exhibits photoinduced current generation [6]. Our current understanding of energy transfer and charge separation reactions in the LH2 and LH1-RC complexes has enabled the first step to be taken towards generating artificial systems from them that convert light energy into usable electrical current. Previous attempts to produce an artificial, energy-converting electrode system used either the LH1 complexes. Until now, there have only been a few attempts to immobilize intact core complexes, consisting of both the LH1 complex and the RC components together, onto an electrode [6,7]. We have recently developed a procedure to create a self-assembled monolayer (SAM) of reconstituted LH1 complexes on a transparent indium tin oxide (ITO) electrode modified with 3-aminopropyltriethoxysilane (APS-ITO) between the electrode surface and the anionic LH1 polypeptides at pH 8.0 [5]. The NIR absorption spectrum showed that the

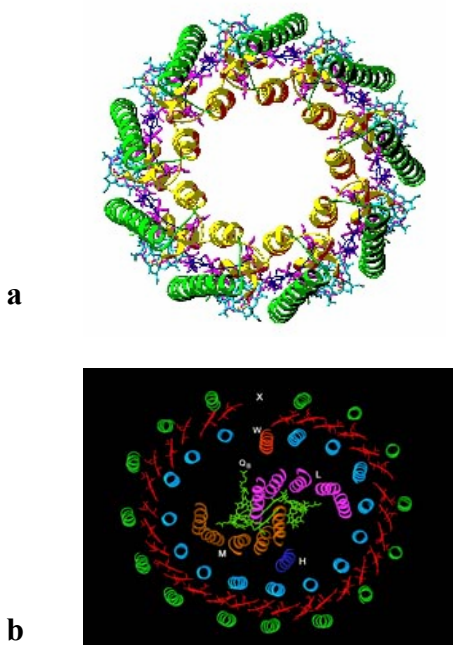

Figure 1. Structure of light-harvesting anntena complex (a) LH2 complex of *Rps. acidophilla* 10050LH2 and (b) LH1-RC complex of *R. palustris.*

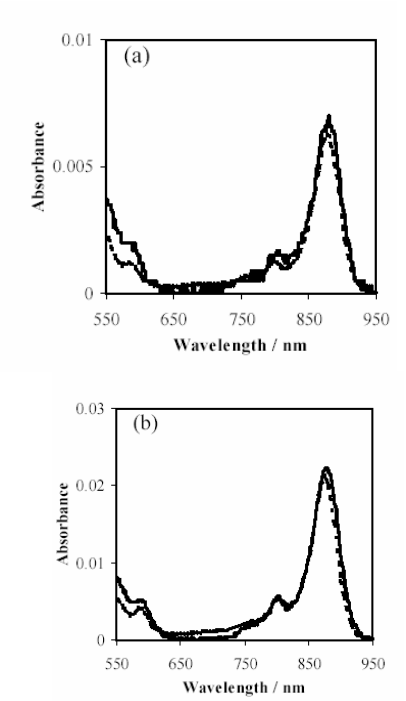

Figure 2. NIR absorption spectra of the isolated *R. rubrum* (a) and *Rps. palustris* (b) core complexes in 20 mM Tris HCl buffer pH 8.0 OG micelle (dotted line) and assembled onto an APS-ITO electrode (solid line)

LH1 complex was stable when immobilized onto these electrodes. This study was extended using native LH1-RC complexes [6]. LH1-RC complexes isolated from *R. rubrum* and *Rps. palustris* were successfully assembled on APS-ITO. Efficient energy transfer and photocurrent responses could be observed upon illumination at 880 nm.

Further, we assembled PSUs, LH1-RC core complex, LH1, RC, and admixed complex of LH1 and RC on a modified Au electrode to investigate assembling manner and to develop photocurrent generation system for these assemblies to attempt the construction of an artificial antenna complex toward developing useful nanodevices.

2. Self-Assembled Monolayerof Light-harvesting Core Complexes of Photosynthetic Bacteria on an Amino-Terminated ITO Electrode

Figure 2 shows the NIR absorption spectra of the isolated *R. rubrum* (a) and *Rps. palustris* (b) core complexes in 20 mM Tris HCl buffer pH 8.0 OG micelle (dotted line) and assembled onto an APS-ITO electrode (solid line), respectively. These spectra show that these core complexes have the absorption maximum at 880 nm with two smaller peaks at 800 nm and 760 nm. The former peak is attributable to the overlap of bacteriochlorophyll *a* (BChl*a*) in the LH1 complex (880 nm) and the reaction center Bchl*a* dimer 'special pair' (870 nm) and the latter two peaks to the BChl*a* called 'accessory' (800 nm) and bacteriopheophytin (760 nm) in the RC, respectively. The NIR absorption spectra of these core complex on the electrode indicate that these complexes are stable when assembled onto an APS-ITO. In the previous study it was apparent that when the RC of *R. rubrum* was assembled, by itself, on the electrode it was relatively labile. Whereas in present study the complete core complex, when assembled onto the electrode, proved to be quite stable. The enhanced stability of the RC surrounded by the LH1 complex probably results from supportive interactions between the two complexes. Interestingly, when illuminating at 880 nm the fluorescence emission of BChl*a* molecules in the LH complex of *R. rubrum* on the APS-ITO was strongly quenched, due to the presence of the RC of *R. rubrum*. This indicates that an efficient energy transfer from BChl*a* in the LH1 complex to the RC in the core complex is still occurring on the electrode (data not shown). FT-IR spectra of the LH complex of *R. rubrum* and the LH1-RC core complexes of *R. rubrum* and *Rps. palustris* assembled on the APS-ITO show the absorptions at 1650 cm^{-1} and 1550 cm^{-1}. These bands can be assigned to the amide I and amide II bands, respectively. These results indicate that the LH polypeptides are in the same *a* helical configurations on the ITO electrode as in OG micelles.

Figure 3 shows the time course of the photocurrent generated from the core complex or the RC of *R. rubrum* assembled onto an APS-ITO when the electrode was illuminated with a pulse of light at 880 nm. It is clear from

Figure 3 that an enhanced photocurrent was observed for the core complex. In contrast no photocurrent was observed for either LH complexes or the RC. Under our experimental conditions a cathodic photocurrent was observed, implying that one-way electron transfer from pigments in the core complex (special pair of BChl*a*, SP in RC) to methyl viologen was occurring as shown in Figure 4.

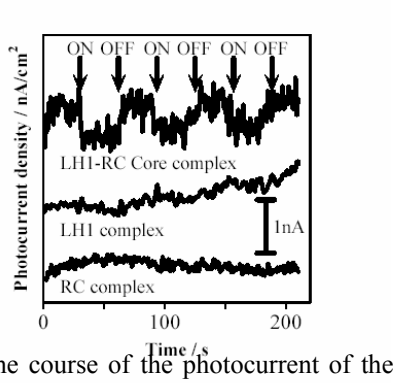

Figure 3. Time course of the photocurrent of the LH1-RC core complex or the RC complex of *R.rubrum* on an APS-ITO electrode when the electrode is illuminated with pulsed light (880nm) firing continuously for 30 seconds.

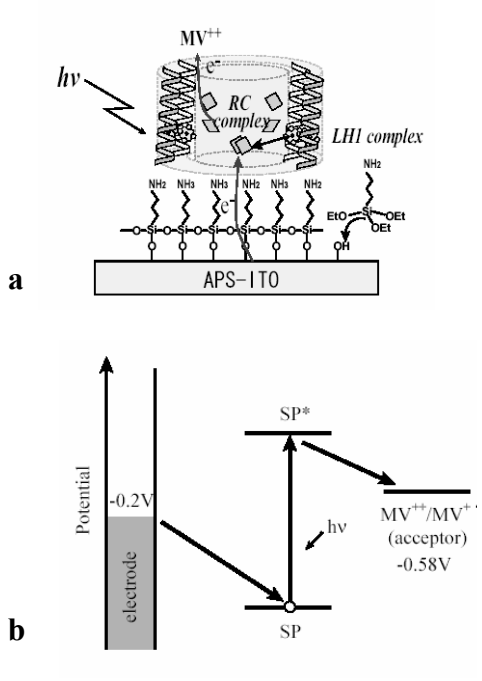

Figure 4. (a) Schematic drawing of LH1-RC core complexes on an APS-ITO electrode generated cathodic photocurrent which shows the electron flow from the complex to methyl viologen according to the cathodic photocurrent as shown in Figure 3. (b) Energy diagram for cathodic photocurrent generation by the LH1-RC core complex.

Figure 5 shows excitation spectrum of the the photocurrent density (dots) and the NIR absorption spectra (solid line) from *R. rubrum* (a) and *Rps. palustris* (b) core complexes assembled onto an APS-ITO, respectively. These photocurrent responses showed a maximum at the wavelength corresponding to the absorption bands of the complex. Interestingly, an enhanced photocurrent was observed especially upon illumination at 880 nm for both *R. rubrum* (a) and *Rps. palustris* (b) core complexes. The quantum yield of the photocurrent was 0.05% for both the *R. rubrum* and *Rps. Palustris* complexes. When the LH1 complex of *R. rubrum* alone, was immobilized on the electrode, the observed photocurrent was mainly generated by light absorbed at 770 nm i.e. from monomeric BChl*a*. Furthermore, when the RC complex of *R. rubrum* only was immobilized on the electrode, an efficient photocurrent was not observed upon illumination at 880 nm as shown in Figure 3. Thus, the enhanced photocurrent observed at 880 nm in the assembled core complex can be ascribed to energy transfer from the LH1 to the RC and then electron transfer from the RC to the electrode as shown in Figure 4. This data indicates that the core complex was well organized on the ITO and the photocurrents were driven by light that was initially absorbed by the LH components.

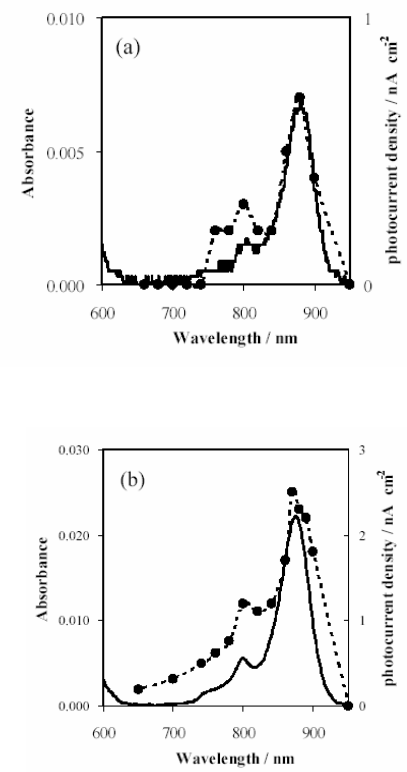

Figure 5. Photocurrent density (dots) and NIR absorption spectrum (solid line) of LH1-RC core complexes form (a) *R. rubrum* and (b) *Rps. palustris* assembled on an APS-ITO electrode.

3. Self-assembled Monolayer of Light-harvesting Core

Complexes from Photosynthetic Bacteria on a Gold Electrode Modified with Alkanethiols

LH1-RC complexes isolated from *Rps. palustris* were self-assembled on a gold electrode modified with self-assembled monolayers (SAMs) of alkanethiols, NH_2-$(CH_2)_n$-SH; n = 2, 6, 8, 11, HOOC-$(CH_2)_7$-SH, and CH_3-$(CH_2)_7$-SH, respectively to attempt the construction of an artificial antenna core complex towards developing useful nanodevices as shown in Figure 6 a. Adsorption of the LH1-RC complexes on the SAMs depended on the terminating group of alkanethiols, where the adsoption increased in the following order for the terminating group, amino group > carboxylic acid group > methyl group. Further, the adsorption on a gold electrode modified with SAMs of NH_2-$(CH_2)_n$-SH, n = 2, 6, 8, 11 depended on the methylene chain length, where the adsorption increased with increasing the methylene chain length. The clear presence of the well known LH and RC peaks NIR spectra of the LH1-RC complexes indicates that these complexes were only fully stable on the SAM gold electrodes modified with the amino group. In the case of modification with the carboxyl group the complexes were partially stable while in the presence of the terminal methyl group the complexes were extensively denatured. An efficient photocurrent response of these complexes on the SAMs of NH_2-$(CH_2)_n$-SH; n = 2, 6, 8, 11 was observed upon illumination at 880 nm as shown in Figure 6 b. The photocurrent depended on the methylene chain length (n), where the maximum photocurrent response was observed at n = 6, which corresponds to a distance between the amino terminal group in NH_2-$(CH_2)_6$-SH and the gold surface of 1.0 nm.

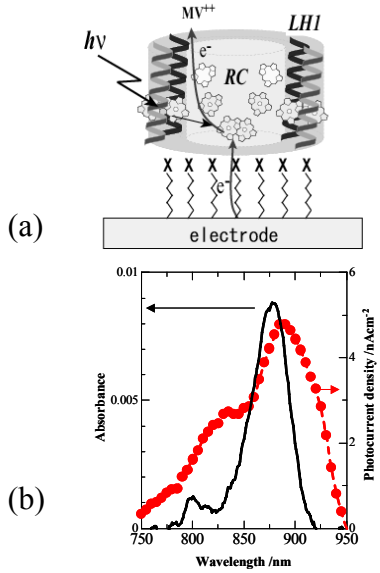

Figure 6. (a) Schematic drawing of LH1-RC core complex on a gold electrode, absorption and (b) action spectra of *Rps. palustris* LH1-RC assembled onto a gold electrode modified with NH_2-$(CH_2)_6$-SH.

In conclusion, the SAM method is clearly successful in allowing assembly of functional core complexes on the electrode. This has been confirmed by NIR absorption spectroscopy, demonstrating that the photocurrent response, which is derived from electron transfer between the RC and the electrode, is enhanced by illumination at 880 nm. These results provide useful methodology to better understand the suprastrucure of LH1-RC complex as well as to gain knowledge about building an artificial fabrication of LH1-RC complex on solid substrates toward useful nanodevices. Various combinations of these complexes are being tested for their usefulness in constructing artificial solar energy conversion devices.

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