



Mediatorless solar energy conversion by covalently bonded thylakoid monolayer on the glassy carbon electrode



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ABSTRACT

Light reactions of photosynthesis that take place in thylakoid membranes found in plants or cyanobacteria are among the most effective ways of utilizing light. Unlike most researches that use photosystem I or photosystem II as conversion units for converting light to electricity, we have developed a simple method in which the thylakoid monolayer was covalently immobilized on the glassy carbon electrode surface. The activity of isolated thylakoid membrane was confirmed by measuring evolving oxygen under illumination. Glassy carbon surfaces were first modified with partial or full monolayers of carboxyphenyl groups by reductive C–C coupling using 4-aminobenzoic acid and aniline and then thylakoid membrane was bioconjugated through the peptide bond between amine residues of thylakoid and carboxyl groups on the surface. Surface properties of modified surfaces were characterized by cyclic voltammetry, contact angle measurements, and electrochemical impedance spectroscopy. Photocurrent of 230 nA cm^{-2} was observed when the thylakoid monolayer was formed on the mixed monolayer of 4-carboxyphenyl and benzene at applied potential of 0.4 V vs. Ag/AgCl. A small photocurrent resulted when the 4-carboxyphenyl full monolayer was used. This work shows the possibility of solar energy conversion by directly employing the whole thylakoid membrane through simple surface modification.

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1. Introduction

Photosynthesis that occurs in green plants, algae, and cyanobacteria provides a very efficient mechanism to harness solar energy. Light absorbed by light-harvesting complexes of two light reactions located in thylakoid membrane induces electronic transition both in photosystem I (PSI) and photosystem II (PSII). In PSII, excited electrons reduce Q to QH₂ and the resulting P680⁺ has very high oxidizing tendency to extract electrons from water and produce oxygen molecules as by product. The stored electrons in QH₂ are transferred to PSI through cytochrome *b₆f* complex. In PSI, light is used to create reducing power in the form of NADPH. Although about 50% of the incident solar energy in the visible region is accessed by photosynthetic organisms [1], photoprocesses occurring in PSI and PSII are very efficient that quantum yield of PSI, for example, is almost unity [1–3].

Therefore, there have been numerous attempts to develop photoelectrochemical systems by mimicking PSI or PSII of photosynthesis [4–7]. Such systems are composed of many components and individual components are often sophisticatedly designed molecules and nanomaterials whose preparation needs much effort. To function properly, each component should be precisely spatially arranged into the whole system. Recently, another line of research has appeared which

is to directly utilize photosystems as light conversion units that can be isolated from plants or cyanobacteria. This approach has a definite advantage over conventional methods in that one can use already maximally optimized systems rather than designing molecules or nanomaterials, although present conversion efficiency of 2.9% [8] is much lower than 13% of dye-sensitized solar cells [9].

Many researchers have developed solar cells using PSI. For example, Schuhmann et al. used osmium redox polymer and methyl viologen as electron donor and acceptor, respectively, and achieved $29 \mu\text{A cm}^{-2}$ [10,11]. Noteworthy is the work by Cliffel and coworkers. They formed PSI mono- and multi-layer on various electrodes such as gold [12,13], graphene [14], and semiconductors [15,16] for photoconversion using mediators. Although a photocathodic current as high as $875 \mu\text{A cm}^{-2}$ is achieved, sacrificial electron acceptors are needed for the current to continuously flow. The use of a high concentration of mediators is another problem [16]. When electron donors are used, a photoanodic current can be demonstrated. Willner et al. generated appreciable photoanodic currents with ascorbate or dichloroindophenol as sacrificial electron donors [17]. In this regard, using PSII as a light-conversion unit in which electrons are provided from water oxidation has definite merit. As stated above, P680⁺ is such a strong oxidant that water is oxidized to molecular oxygen producing protons and electrons. Ulas and Brudvig showed that electrons can be redirected with the aid of cationic electron mediators that can have access to the Q_A site although the main electron transfer pathway is blocked [18]. Willner and coworkers have developed very sophisticated integrated

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¹ They made an equal contribution to this work.

chemical systems in which PSII and bilirubin oxidase are used at the anode and cathode, respectively [19]. Produced oxygen molecules are used as cathodic fuel. They also showed that layer-by-layer deposition of PSI and PSII on the anode surface enhances photoanodic current and photocathodic current flows by changing the deposition order [20].

Another way of utilizing the photosynthetic unit is to use the thylakoid membrane itself instead of PSI or PSII as the isolation and purification of PSI or PSII are laborious and time-consuming. Both photosystems are spatially optimally situated in the thylakoid membrane for the efficient light utilization and electron transfer. Isolation of thylakoid from chloroplasts can be relatively easily done in a few steps. Allen and Crane were the first to apply thylakoid to photoelectrochemical systems [21]. They suspended a thylakoid membrane in a microelectromechanical system and used a redox mediator. Although current density was about $1 \mu\text{A cm}^{-2}$ under the load, the cell voltage was very small. They obtained the highest power density of only 5.4 pW cm^{-2} . In the meantime, Dewi et al. incorporated thylakoid into an indium tin oxide surface for the photoconversion [22]. About 100 nA cm^{-2} photocurrent was observed in the absence of a mediator. However, $10 \mu\text{A cm}^{-2}$ was obtained in the presence of a mediator. Minter et al. found that the thylakoid system could be stabilized by scavenging oxygen produced by PSII with catalase [23]. Calkins et al. developed a complete photoelectrochemical system with a thylakoid-carbon nanotube-modified anode and a laccase-modified cathode [24]. When a soluble mediator $\text{Fe}(\text{CN})_6^{3-/4-}$ was used, the maximum power density was $5.3 \mu\text{W cm}^{-2}$. Most recently, Gorton's group reported that photocurrent density could be raised to $42.4 \mu\text{A cm}^{-2}$ by applying osmium redox polymer to the thylakoid photoelectrochemical system [25].

In this work, we present a simple method in immobilizing thylakoid membrane on the glassy carbon electrode (GCE) and photocurrent generation from it without using any mediators. The thylakoid monolayer can be readily formed on the GCE via chemical modification through the linker molecule.

2. Experimental

2.1. Isolation of thylakoid from spinach

The process of extracting a pure thylakoid membrane was based on the method of Danielsson et al. [26,27]. The thylakoid membrane, a sub-unit of the chloroplast, was isolated from spinach leaves. 50 g homogenized spinach leaves was ground in 50 mM sodium phosphate buffer (pH 7.4) containing 5 mM MgCl_2 and 300 mM sucrose at 4°C by using a blender for 5 s, and this procedure was repeated five times. The obtained slurry was filtered using 4 layers of nylon mesh (pore size $25 \mu\text{m}$) and centrifuged at $1000 \times g$ for 5 min. After removing the supernatant, the pellet was resuspended in the same buffer and centrifuged again at $2000 \times g$ for 5 min. The collected chloroplast was suspended in 5 mM MgCl_2 for osmotic lysis and then centrifuged at $2000 \times g$ for 5 min. After washing the membrane twice by centrifugation in 10 mM tricine buffer (pH 7.5) containing 5 mM MgCl_2 and 300 mM sucrose, the isolated thylakoid membrane was finally suspended in 10 mM sodium phosphate buffer (pH 7.4) containing 5 mM NaCl, 1 mM MgCl_2 , and 300 mM sucrose. The chlorophyll concentration in the thylakoid membrane was spectrophotometrically determined according to Arnon [28] and handled to be between 3.0 and $4.0 \text{ mg Chl mL}^{-1}$ and stored at -80°C . The total chlorophyll concentration is quantitated by Eq. (1) taking absorbance at 645 and 663 nm.

$$C_{\text{Chl}} \left(\frac{\text{mg}}{\text{mL}} \right) = (0.0202A_{645} + 0.00802A_{663}) \times \text{Dilution factor.} \quad (1)$$

The dilution factor is the ratio of the volume of acetone that was used to dilute thylakoid suspension and the volume of thylakoid suspension, and it was 100.

2.2. Activity measurements of isolated thylakoid

Oxygen evolving activity of the isolated thylakoid was measured by a Clark type O_2 electrode (Hansatech Instruments Ltd., Norfolk, UK) under one sun illumination (100 mW cm^{-2}) using a solar simulator (McScience, Korea). The measurement was done in 15 mM MES(2-(*N*-morpholino)ethanesulfonic acid) buffered at pH 6.5 with 2 mM ferricyanide, 0.5 mM phenyl-*p*-benzoquinone (PpBQ) as an electron acceptor [26]. The isolated thylakoid samples were incubated for 10 min at 20°C in the dark before measurements and the chlorophyll concentration of the isolated thylakoid used was $20 \mu\text{g Chl mL}^{-1}$.

2.3. Modification of electrodes surfaces

Three modified surfaces, benzene, 4-carboxyphenyl (4CP), and mixed monolayers, have been prepared on glassy carbon electrodes for comparison (Scheme 1a). GCE surfaces (0.0314 cm^2) were successively polished with 1.0 and 0.3 and $0.05 \mu\text{m}$ alumina slurries until a mirror finish before modification. The basic idea was to form C-C bonds between the modifiers and the carbon surface [29,30]. For the preparation of a benzene/GCE, 20 mM of aniline was dissolved in 1 M HCl solution containing 100 mM NaNO_2 for 10 min at 4°C , which resulted in diazonium cations. This diazonium solution was then transferred to the three-electrode setup with a potentiostat (CompactStat, Ivium Technologies, Netherlands) where a glassy carbon, Ag/AgCl, and Pt foil were used as working, reference, and counter electrodes, respectively. Single potential cycling between 0.6 and -0.4 V (vs. Ag/AgCl) at scan rate of 50 mV s^{-1} induced reductive C-C coupling to the carbon surface, grafting phenyl (or 4-carboxyphenyl) groups on the surface. The modified electrodes were rinsed with deionized water several times before use. The 4CP/GCE surface was prepared in the same way except that 4-aminobenzoic acid was used instead of aniline. For the mixed monolayer (Benzene-4CP/GCE), 2 mM 4-aminobenzoic acid and 20 mM aniline were used.

2.4. Characterization of the modified surfaces

2.4.1. Quantification of carboxyl groups and electrochemical characterization

The coverage of carboxyl groups in 4CP- and benzene-4CP modified surfaces was determined by bioconjugating dopamine molecules onto the carboxyl groups. The modified surfaces were treated with 0.1 M 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 0.05 M *N*-hydroxysuccinimide (NHS) as coupling agents in 0.1 M phosphate buffer of pH 7 for 1 h at room temperature. Thus, the prepared surfaces were immersed in 0.1 M phosphate buffer solution containing 50 mM dopamine for 1 h at room temperature. Dopamine-immobilized surfaces were rinsed with deionized water before use. Since dopamine undergoes electrochemical oxidation, the coverage by the carboxyl group could be calculated by integrating charge under the oxidation peak.

The modified surfaces may act as a charge transfer barrier to the species on the solution side. Cyclic voltammetry was employed to evaluate electron transfer ability of each electrode using a $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple (1 mM) as a probe in 1 M KCl solution.

2.4.2. Impedance spectroscopy of the modified surfaces

Modified surface-electrolyte interfacial properties are more precisely evaluated by electrochemical impedance spectroscopy (EIS) [31]. Charge transfer resistance and double layer capacitance as well as ohmic resistance were obtained by EIS at a fixed potential of 0.26 V (vs. Ag/AgCl) by superimposing a small AC voltage of 5 mV over a frequency range of 10^4 to 0.01 Hz. 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox couple in 1 M KCl was used as a probe. The measured impedance spectra were fitted to a Randles equivalent circuit.

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