A Mediator-Free Integrated Chemical System for Efficient Energy Conversion Using Thylakoid Membrane-Based Composite Film

Jinhwan Lee and Sungyun Kim*‡

Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, Korea

There are numerous attempts to mimic or directly utilize photosynthetic light reactions taking place in a thylakoid membrane to convert solar energy to electricity as they provide highly efficient electron transfer mechanisms. In this study, we develop a mediator-free integrated system in which whole thylakoid membranes are incorporated into polyaniline and reduced graphene oxide. Each component plays its own role in electron transfer from thylakoid to the electrode. Polyaniline acts like a molecular wire that has access to reaction centers from which it takes electrons, delivering them to reduced graphene oxide and eventually to the electrode. Graphene oxide needs to be electrochemically reduced due to its low electrical conductivity. Lacking any component causes smaller photocurrent than when all three components are present. System optimization between graphene oxide, polyaniline, and the number of potential cycling is made for the enhanced photocurrent. The maximum power density of 10.5 μW cm⁻² with current density of 24.7 μA cm⁻² under one sun illumination is achieved. The turnover frequency is calculated to be 0.3 water molecule per photosystem II per second. This result shows the possibility of using whole thylakoid membranes as a solar energy conversion unit with proper means of electron transfer.

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Manuscript submitted July 2, 2018; revised manuscript received August 28, 2018. Published September 7, 2018.

Photosynthesis is a highly sophisticated system for the light harvesting and its utilization. Harvested solar light energy is transferred to the reaction center of photosystem II (PSII) to induce charge separation and water oxidation. Excited electrons undergo a series of electron transfer reactions through PSII, cytochrome b₆f-complex, and photosystem I (PSI) embedded in a thylakoid membrane (TM), and stored in the form of NADPH for CO₂ reduction. Since quantum yields of PSI and PSII are very high with almost unity for PSI in particular, intensive research has been done to electrochemically use these photosynthetic units, individually or in combination, to convert light energy into electricity.¹⁻⁵ Aiming at achieving as high photocurrent as possible, a lot of ingenious methods have been invented to divert electrons from the electron transfer pathway of Z-scheme to the electrode. For example, Cai et al.⁶ assembled PSI with reduced graphene oxide and polyethylene imine for the effective electron transfer. They obtained about 50 nA cm⁻² without external mediators. Much better result was reported by Wilner et al.⁷ when they wired the anode with PSI via mercaptobenzoquinone polymer. In combination with bilirubin oxidase as an oxygen reduction catalyst, power density of 17 μW cm⁻² was obtained. The highest photocurrent close to 1 mA cm⁻² has been achieved at a single wavelength by Reisner and coworkers when they employed redox polymers⁸ or soluble redox mediators.⁹ PSI has also been widely used as a light energy conversion unit despite the fact that sacrificial electron donors or acceptors are usually needed. Jennings and Clifffel groups have applied graphene oxide,¹⁰ polyaniline,¹¹ and semiconductor materials¹² to enhance photocurrent even to 875 μA cm⁻² when PSI film was formed on the p-doped Si with methyl viologen as a mediator. Schumann and Rögen¹³,¹⁴ have employed reduced hydrogels such as Os complex-containing polymers functioning as immobilizing matrices and as redox mediators. PSI and PSII wired to the electrode by redox hydrogels showed higher photocurrent than not wired.

The whole TM has also been used as a conversion unit for solar energy to electricity. Use of TM offers many advantages. Since PSI, PSII and other components are already best arranged in the membrane for light harvesting and a series of electron transfer, TM provides ideal environment and high structural stability for the solar energy utilization. The simpler and faster procedure for isolation and purification adds them another advantage. Because of these advantages, many researchers have tried to utilize TM as a photobiocatalyst for solar energy conversion, with still lower efficiency than PSI and PSII, however.

Since Allen and Crane¹⁵ published photocurrent generation from TM suspension, numerous efforts have been made to increase photocurrent. For instance, Lam et al.¹⁶ developed a microelectromechanical system using TM suspension and a redox mediator. However, they only achieved a very small power density of 5.7 pW cm⁻². Chemically immobilized TM monolayers on the functionalized electrode have also been used without mediators but photocurrent was as small as 0.63 μA cm⁻².¹⁷ Minteer et al.¹⁸ in the meantime developed a stabilizing method of adsorbed TMs on the electrode employing catalase as O₂ scavenger. They obtained photocurrent of 1.53 μA cm⁻². Dewi et al.¹⁹ observed a large increase in photocurrent in the presence of a soluble mediator. With TM deposited on the ITO surface with a mediator, photocurrent density of 10 μA cm⁻² was observed. However, without a mediator photocurrent was dropped to 100 nA cm⁻². Large enhancement in photocurrent has been made by Calkins et al.²⁰ when TM-carbon nanotube composite was used as a conversion unit with a soluble mediator. Steady-state current of 38 μA cm⁻² was observed. In a complete cell using a laccase cathode for O₂ reduction, the maximum power density of 5.3 μW cm⁻² was obtained. Most notable progress has been made by Gorton and coworkers who have sought enhancement methods of photocurrent from TMs. They found that photocurrent could be greatly increased with use of mediators such as Os-redox polymers and soluble mediators.²¹⁻²³ 130 μA cm⁻² that was achieved with p-benzoquinone as a mediator is the highest value ever reported.

In this study, we have pursued a simple but useful way of enhancing photocurrent from TMs without soluble mediators. An integrated system consisted of thylakoid membrane (TM), polyaniline (PANI), and reduced graphene oxide (RGO) that was constructed on the electrode surface was proven an effective way to convert solar energy to electricity.

Experimental

Isolation of thylakoid membrane and calculation of chlorophyll concentration.—TM, a subunit of chloroplast, was isolated from spinach according to the method of Danielsson et al.²⁴,²⁵ Chlorophyll concentration in the isolated TM was spectrophotometrically determined according to Arnon.²⁶ The isolated TM samples were diluted to a chlorophyll concentration of approximately 3 mg Chl mL⁻¹ and...
stored at −80 °C. The chlorophyll concentration was calculated from TM absorbance at 645 and 663 nm by the following equation:

\[
\text{Chlorophyll concentration (mg mL}^{-1} = (0.0202A_{645} + 0.00802A_{663}) \times \text{Dilution factor}
\]

Activity measurements of thylakoid membrane.—Oxygen evolving activity of photosystem II in isolated TM was measured by a Clark-type O2 electrode (Hansatech Instruments Ltd., Norfolk, UK) at 20 °C under one sun illumination (100 mW cm \(^{-2}\)) using a solar simulator (Model K201 LBA50, McScience, Korea). Oxygen evolution from isolated TM was measured in 15 mM MES (2-(N-morpholino)ethanesulfonic acid) solution buffered at pH 6.5 with 2 mM ferricyanide, 0.5 mM phenylmorpholino)ethanesulfonic acid) solution and subject to potential cycling in the range of 0.4 V and −1.3 and 0.6 V (vs. Ag/AgCl) at 50 mV s\(^{-1}\) in a typical three-electrode setup.

Surface characterization.—The morphology of TM/PANI/RGO film on AP-modified GCE was observed with a scanning electron microscopy (SEM, TESCAN, Mira II LMU, Czech Republic). Raman analysis was carried out to confirm the production of RGO using a confocal Raman microscope (WiTec, Alpha300 R). A 532 nm Nd:YAG laser and x100 objective (NA: 0.9) were employed for measurements. Acquisition time for each sample was 30 s by about 1 mW laser power. X-ray photoelectron spectroscopy (XPS, VG Multilab ESCA 2000 System) with an Al Kx X-ray source (\(\lambda = 1486.6\) eV) was also performed on GO and RGO samples.

Photocurrent measurements.—Photocurrents were measured in a chronoamperometric mode with a typical three-electrode setup using a potentiostat (Ivium Compactstat, The Netherlands) in 0.1 M sodium phosphate buffer (pH 7). The working electrode was positioned in a cell that had a water jacket through which water circulated and temperature was maintained at 20 °C. Sun light of one sun (100 mW cm \(^{-2}\)) intensity from a solar simulator (Model K201 LBA50, McScience, Korea) impinged on the working electrode surface from the top. The working electrode was poised at 0.4 V with respect to Ag/AgCl reference electrode. A Pt foil was used as a counter electrode.

Action spectrum measurements.—The action spectrum was constructed by measuring photocurrent at selected wavelengths. 11 narrow bandpass filters (380, 410, 430, 450, 480, 530, 590, 650, 660, and 700 nm, Asahi Spectra Co., Tokyo, Japan) were used with full width at half maximum (FWHM) of 10−13 nm and transmission of 45−65%. These filters were placed above the working electrode.

Results and Discussion

Fabrication and characterization of TM/PANI/RGO film on the AP-modified GC.—Figure 1 shows a fabrication step of an integrated system of a TM/PANI/RGO composite film formed on an aminophenyl (AP)-modified glassy carbon surface and its cross-sectional SEM image.

![Diagram of TM/PANI/RGO film](image)

**Figure 1.** Schematic representation of the preparation of an integrated system of a TM/PANI/RGO composite film formed on the aminophenyl (AP)-modified glassy carbon surface and its cross-sectional SEM image.
surface modification, composite film preparation, and photocurrent measurements are found in Experimental and Supplementary Material (Figures S1-S3). It is important to apply small vacuum (ca. 0.3 atm) so that the composite film can be securely settled on the surface. Since the electrical conductivity of GO is poor due to the oxygen-containing functional groups, GO was reduced to RGO by potential cycling before photocurrent measurements. Simple drop casting of a composite film on the bare GC surface was found not to be stable upon potential cycling. A uniform film with ca. 8 μm thickness was formed over the surface.

Various spectroscopic methods have been employed to confirm RGO formation. The redshift of the main absorption peak at 232 nm of GO to 268 nm and the increased absorbance over the entire spectral region are an indication of conjugated C= C bonds by reduction (Figure 2a). An increase in the intensity ratio of two Raman peaks D and G, I_D/I_G, from 1.01 to 1.65 upon reduction indicates the formation of RGO. The increase in I_D/I_G is attributed to the recovery of sp² domain by reduction (Figure 2b). Detailed aspects of reduction can be seen by C1s XPS. After deconvolution, GO shows four different carbon peaks at 284.6, 286.7, 287.7, and 288.8 eV which, respectively, correspond to non-oxygenated ring C, C-O bonds, carbonyl C, and carboxyl C. Upon reduction all carbon peaks that are related to oxygen atoms noticeably decreased, indicating most though not all of oxygen atoms are removed from the surface (Figures 2c and 2d).

Optimization of TM/PANi/RGO film for enhanced photocurrent.—It was found that the highest photocurrent was resulted when all the components of the film were present on the AP-modified surface. An omission of any components led to lower current. Optimization between components has been made to obtain enhanced photocurrent as possible. Figure 3a shows that polyaniline is an inevitable component for achieving high photocurrent. Without polyaniline, electrons produced from water oxidation are not readily transferred to the electrode. As a conductive, redox-active polymer, polyaniline freely accesses to the reaction center of TM. Functioning as a molecular wire, it transfers electrons from the TM to RGO then to the electrode. The role of PANi in PANi/RGO, TM/RGO, and TM/PANi/RGO composite films was further elucidated by cyclic voltammetry (Figure 3b). PANi/RGO shows a main redox pair at 0.095 and −0.06 V (E⁰ = 0.02 V) which has been known as a redox process between emeraldine base and pernigraniline base form. This redox characteristics is still visible even in the presence of TM. Since the electrode was poised at +0.4 V, the pernigraniline form was ready to accept electrons from various components in PSII or PSI whose formal potentials are more negative than +0.4 V. When less positive potential was applied, smaller photocurrent was resulted. This indicates that the redox process between emeraldine base and pernigraniline base forms are involved in the electron transfer. A couple of small redox peaks at −0.18 and 0 V are attributed to...
the oxygen-containing species present in RGO.33,34 Direct electron transfer from TM to the electrode via RGO gives rise to only 5 μA cm−2, implying that simple mixing of TM and RGO is not a good way of transferring electrons.

Figure 3c shows the dependence of photocurrent on the RGO:Chlorophyll ratio. RGO was prepared from GO by 50 potential cycling between −1.3 V and 0.6 V. The amount of polyaniline was fixed at a value that the number of polyaniline molecules was 18 times higher than that of TM units assuming that one TM unit contains a trimeric PSI and a dimeric PSII complexes. The highest current was observed at a 3:1 ratio. At lower ratios than this, RGO particles are not sufficient to function as an electron sink connecting polyaniline molecules and the anode, and at higher ratios, the presence of too many RGO particles may hinder light from penetrating into the TM to generate photoelectrons. The ratio was fixed at 3:1 throughout the experiments. Since GO has limited electrical conductivity which makes photocurrent negligible, it is crucial to impart high electrical conductivity to the TM/PANI/GO film by reducing GO to RGO. As mentioned above, it has been done through the electrochemical reduction of GO to RGO by potential cycling. Figure 3d shows the photocurrent dependence on the number of potential cycling between −1.3 and 0.6 V vs. Ag/AgCl. A dramatic increase in photocurrent was observed after GO reduction. Upon 25 cycles 4.5 μA cm−2 was resulted and it kept increasing reaching maximum of 14.8 μA cm−2 at 100 cycles. However, more potential cycles gave smaller photocurrent.

In order to understand the relationship between photocurrent and the degree of reduction of GO, we examined the oxygen-evolving activities of three samples, TM/PANI/GO, TM/PANI/GO-RGO, and TM/PANI/RGO with time under 1 sun illumination (Figure 4). Each sample contained the same amount of TM, polyaniline, and the same total amount of graphene (oxidized + reduced). The TM/PANI/GO-RGO sample was prepared by mixing TM suspension, PANi, and half-reduced GO. The highest oxygen-evolving activity was observed for the pure TM suspension. This is because oxygen evolved complex (OEC) in PSII is well preserved. A decrease was found as the RGO portion increased. TM/PANI/GO showed about 91% activity of pure TM even after 1 hr. This indicates that the presence of PANi and GO does not significantly affect the oxygen-evolving activity of TM. It is concluded, therefore, that very low photocurrent observed for TM/PANI/GO could be ascribed to the poor electrical conductivity of GO to transfer electrons from TM to the electrode. However, with RGO on the TM surface, less oxygen is produced. For TM/PANI/GO-RGO, about 15% decrease was observed. For the TM/PANI/RGO sample, only 29% of activity was maintained compared to the pure TM sample. One possible reason for the decreased oxygen-evolving activity when RGO is present is that RGO, having higher absorptivity than GO, blocks the light from reaching the OEC in a TM (Figure 2a). Another possible explanation is the increased hydrophobicity of RGO induced by GO reduction.34 As evidenced by XPS spectra, many of oxygen-containing functional groups are removed from the GO surface upon reduction, leaving the RGO surface more hydrophobic.
which prevents water from approaching the OEC to be oxidized. In the meantime, photocurrent depends on how well electrons are transferred to the anode. Without any means of transferring electrons to the anode, photocurrent will be very small although more electrons are produced from more water oxidation as evidenced in the case of a pure TM film (Figure 5a). Therefore, the degree of reduction of GO needs to be controlled to achieve as high photocurrent as possible. It is concluded that electron transfer in the TM/PANi/RGO film is essentially through the reduced part of graphene oxide via polyaniline. Since too much production of RGO may hinder light absorption by TMs, some balance should be made between the degree of reduction and photocurrent generation. In our system, 100 potential cycles were found optimum to generate highest photocurrent.

**Photocurrent generation of TM/PANI/RGO film**—In the discussion thus far, it was assumed that each component in TM/PANi/RGO is essential for achieving high photocurrent. Figure 5a compares photocurrents when this system is devoid of some components or TM is deactivated. The highest photocurrent of 14.8 μA cm⁻² was obtained for the TM/PANi/RGO film. It is rather surprising that without TM, the PANi/RGO film also exhibits appreciable photocurrent of 5.7 μA cm⁻². It has been reported that PANi and graphene exhibit photoeffect in UV-vis and near IR regions. Cliffl and co-workers showed in their biosolar cell using PSI-PANI composite films that PANi considerably contributed to the total photocurrent. Graphene materials such as pristine graphene, graphene oxide, and reduced graphene are also knowns to have photoelectrochemical properties. The TM/PANi/RGO film only produces negligible photocurrent of 0.16 μA cm⁻². This value is even smaller than that of AP-modified glassy carbon which is 0.34 μA cm⁻².

The electron transfer pathway from PSII to the electrode could be determined by the blocking experiment. DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea) has been known as an inhibitor of electron transfer from excited P₆₈₀ to QA, and subsequently to cytochrome b₅₆₃-complex and PSI. When TMs were treated with DCMU before forming a TM/PANi/RGO film, no oxygen gas was evolved, indicating that DCMU effectively blocked the electron transfer (Figure S4). It is, however, surprising that appreciable photocurrent of 9.0 μA cm⁻² was still observed from a film using DCMU-treated TM film (DCMU-TM/PANi/RGO). This means that water photolysis by the OEC attached to PSII still occurs, strongly indicating that a new electron transfer channel is formed from the QA site to the electrode through polyaniline. A similar phenomenon was observed in our previous experiments in which TM was formed on the anthracene-modified electrode. Polyaniline can have access to the QA site, playing as an electron conduit to take electrons from QA to the electrode. The remaining photocurrent of 5.8 μA cm⁻² (14.8–9.0) is therefore believed to flow to the electrode from other components such as plastoquinone pool, cytochrome b₅₆₃-complex, or PSI.

Highest photocurrent observed in TM/PANi/RGO system could be explained by the synergistic effect of each component. Positively charged polyaniline can easily access to the negatively charged TM. Photoexcitation of polyaniline creates delocalized polarons in the polymer backbone that function as electron acceptors. Cliffl and co-workers showed in their biosolar cell using PSI-PANI composite films that PANi considerably contributed to the total photocurrent. Graphene materials such as pristine graphene, graphene oxide, and reduced graphene are also knowns to have photoelectrochemical properties. The TM/PANi/RGO film only produces negligible photocurrent of 0.16 μA cm⁻². This value is even smaller than that of AP-modified glassy carbon which is 0.34 μA cm⁻².

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Construction and performance of photoelectrochemical cell.— A complete photoelectrochemical cell comprised of a TM/PANi/RGO photoanode and Pt/C air-cathode was constructed and its performance was tested in pH 7 phosphate buffer (Figure 6a). Upon illumination of visible light, electrons and protons produced by the water photolysis are transferred to the cathode through the external circuit and the electrolyte respectively to reduce oxygen to water. In this system, water and oxygen are used as anodic and cathodic fuels, not requiring artificial sacrificial electron donors which are needed in PSI-based systems.

Figure 6. (a) Schematic representation of a complete photoelectrochemical cell made of a TM/PANi/RGO photoanode and a Pt/C air-cathode. (b) A polarization curve (black) derived from a complete photoelectrochemical cell. Potential was scanned from open circuit voltage toward zero at 5 mV s⁻¹ scan rate. The power density curve (green) was constructed from a polarization curve.

small contribution from polyaniline. Quantum efficiencies at 430 nm and 660 nm are calculated to be 0.49% and 0.14%, respectively according to the Equation S6 (Supplementary Material 1). These values are favorably compared with the reported ones. Gorton et al. reported that in their photoanode systems where TMs are wired with co-deposited Os redox polymers, QEs are 0.09% and 0.01% for 400 and 660 nm respectively to reduce oxygen to water. In this system, water oxidation per second. TOF was 0.3 water molecule per PSII unit per second. This number is much smaller than the theoretical value of 100–150 and even smaller than our previously obtained value for TM monolayer. This is attributed to the limited water supply within the film and hindered light penetration by the RGO layer. Higher power density is therefore expected if the system is constructed using transparent, conductive and hydrophilic materials.

Conclusions

In summary, we have successfully developed an integrated system consisted of the whole TM, polyaniline, and reduced graphene oxide for the solar energy conversion. When constructed on the AP-modified GC surface, photocurrent was greatly enhanced. Each component in the composite film of TM/PANi/RGO plays its role in the electron transfer. Polyaniline functioning as an immobilized molecular wire can take electrons from PSII or PSI to the anode via RGO. It is important to increase electrical conductivity of RGO by reducing GO. After optimization between components, the maximum power density of 10.5 μW cm⁻² was obtained at 24.7 μA cm⁻². Low TOF of 0.30 for water oxidation could be improved by using transparent and yet conductive nanoparticles such as indium tin oxide. The concept developed in this work can be extended to systems to achieve higher photocurrent.

Acknowledgments

This work was supported by Konkuk University (No. 2016-A019-0223) in 2016.

ORCID

Sunghyun Kim https://orcid.org/0000-0001-6632-011X

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