

Photoelectric Activity of Thylakoid Layer Formed on Gold *via* Aminoalkanethiol Self-Assembled Monolayers

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Energy is the driving force of modern civilization. About 85% of the total energy comes from the fossil fuel. But reserve of fossil fuel is limited and being exhausted rapidly to meet the growing energy demand. Being concerned with the future crisis of energy, scientists are motivated for the development of alternative renewable energy sources. In view of such concerns, solar energy can be the most important energy source: it is abundant, clean, safe, and allows energy generation in remote areas.¹⁻³

For the direct conversation of solar energy to electricity, mimicking photosynthesis (artificial photosynthesis) may be the most efficient way as each component of photosynthesis, being intelligently designed, has already been best adapted to perform its function. The light-harvesting and energy-transducing functions of the chloroplast are performed within an intricate lamellar system of membranes, called thylakoid membranes, which are differentiated into granum and stroma lamellar domains.⁴ The resulting asymmetry in structure has been proposed to serve several functions, including minimization of spillover of excitation energy from photosystem II (PSII) to I (PSI) and regulation of light energy distribution between the two photosystems. In addition, the light harvesting and energy transduction, and the unique organization of the thylakoid membranes are extremely well designed.⁵ In plants, green algae and cyanobacteria, electrons extracted from water by PSII are channeled along the membrane-bound electron transfer chain toward the oxidizing side of PSI.⁶

Different artificial photosynthetic systems using photosynthetic components for the photocurrent generation have been developed. Lebedev *et al.*⁷ genetically engineered poly-histidine tag at the C-terminal end of the M-subunit of the reaction center and oriented it using Ni-NTA (Ni-nitrilotriacetic acid) self-assembled monolayers. Cliffel and coworkers^{8,9} focused on the use of PSI monolayer formed on self-assembled monolayers for the photocurrent generation. Boucher *et al.*¹⁰ used

PSII for the photocurrent generation and showed photocurrent inhibition in the presence of pollutants could be used for monitoring toxicity of sewage sludge. In the meantime, Lin *et al.*^{11,12} developed photosynthetic electrochemical cells (PECs) using thylakoid, in which thylakoid was either suspended in anolyte or immobilized on the surface. In a mediator-type microelectromechanical system PEC, they generated 470 mV and 1.1 $\mu\text{A cm}^{-2}$ at 5.2 μV .

Here we report our results on photocurrent generation by immobilized thylakoid monolayer. Rather than using sub-cellular components, we have used intact thylakoid containing all the components for photosynthesis. Difference between the method by Lin *et al.* and ours is that while they used a relay molecule for the efficient electron transfer, we directly attached thylakoid onto the modified electrode. Fig. 1 explains the principle behind direct electron transfer from thylakoid to the electrode. Since reaction centers are still in thylakoid, water is split to oxygen and protons giving off electrons upon illumination. Some of produced electrons may go to the electrode through chemical bonds between thylakoid and the linker, rather than taking a photosynthetic pathway. Once electrons are transferred to the anode, they can flow through the external load to the cathode.

The thylakoid modification is illustrated in Fig. 2. The gold electrode was modified with amine-functionalized thiols ($\text{HS}-(\text{CH}_2)_n-\text{NH}_2$, $n = 2, 6, 8, 11$) before thylakoid attachment. Then EDC (*N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide) was used to couple between amine groups of thiol and carboxyl groups of thylakoid. Thylakoid was isolated from spinach according to the protocol¹³ and confirmed by the UV-Visible spectrum. Thylakoid was preserved at -20°C .

Fig. 3 shows photocurrent generation from modified electrodes.¹⁴ The $\text{Au/S}(\text{CH}_2)_2\text{NH}_2$ electrode did not give any photocurrent even when light was on. But when thylakoid was attached on this surface ($\text{Au/S}(\text{CH}_2)_2\text{NH-thylakoid}$), large photo-

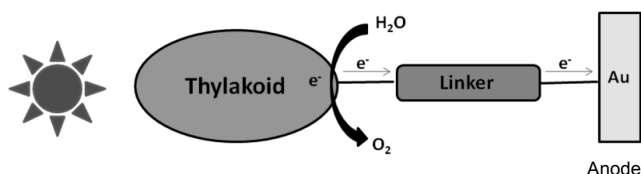


Figure 1. Schematic representation of direct electron transfer from thylakoid to the electrode under illumination. Thylakoid is chemically bonded to the aminoalkanethiol linker on the gold electrode.

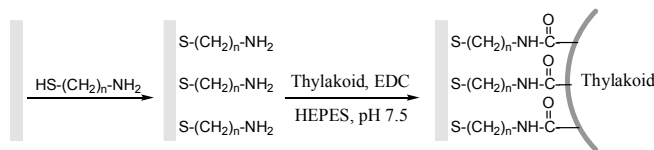


Figure 2. Modification procedure of a gold electrode. Au surface was first modified with self-assembled aminoalkanethiols and then with thylakoid. Thiols of different chain length ($n = 2, 6, 8, 11$) were used. For $n = 2$, cysteamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$) was used.

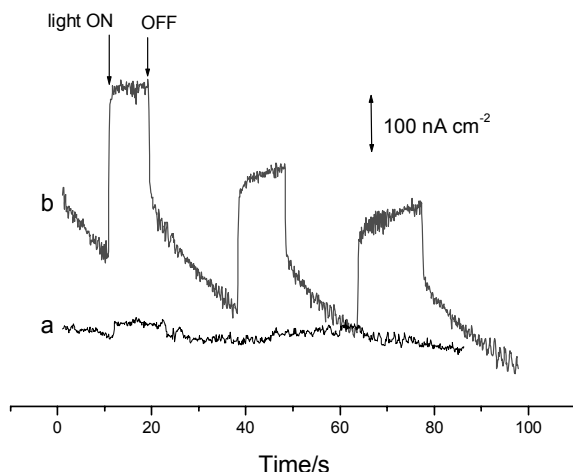


Figure 3. Photocurrent response with time from Au/S(CH₂)₂NH₂ (a) and Au/S(CH₂)₂NH-thylakoid (b) electrodes.

current was observed. The photo response was immediate. This photoeffect lasted at least several hours without any significant decrease, indicating that thylakoid layer was stable on the surface. Tailing in photocurrent may be caused by capacitive effect arising from the charge separation upon illumination.¹⁵ These results tell that thylakoid still properly functions even on the surface and is solely responsible for the photocurrent. Water is split by the reaction center inside thylakoid to oxygen, protons and electrons under illumination. Part of electrons is transferred through the thiol linker to the anode to produce photocurrent. Among linker thiol molecules, NH₂(CH₂)₂SH gave the highest current density of *ca.* 320 nA cm⁻². This value is lower than that of a MEMS fuel cell¹² (1.1 μA cm⁻²) in which thylakoid was suspended and a mediator was used as an electron shuttle, but higher than that of a system (100 nA cm⁻²) constructed using PSI and a mediator.⁹ This result has an important implication that thylakoid itself could be used as a photo-electric component in solar energy harvesting.

If photocurrent flows through the linker molecule, it should decrease with the distance from the electrode to thylakoid. According to Marcus theory, electron-transfer rate constant can be formulated by the equation,

$$k_{\text{app}}(\text{at } d_2) = k_{\text{app}}(\text{at } d_1)\exp[-\beta(d_2 - d_1)]$$

where β is the electron tunnel barrier. Since current is a direct indication of the reaction rate, it is expected that current exponentially decreases with the number of methylene groups. Fig. 4 indeed shows the linear dependence of logarithmic photocurrent density on the number of methylene groups in a linker. The same dependency has been observed in a number of thiol systems having terminal redox centers.^{16,17}

In this communication, we have shown our results of light conversion using thylakoid, a central unit in photosynthesis, rather than devising sophisticated structures or using photosynthetic components. Thylakoid was fixed on the gold electrode already modified with an aminoalkanethiol monolayer. Photocurrent exponentially decreased with the number of methylene groups as expected from the Marcus theory, confirming elec-

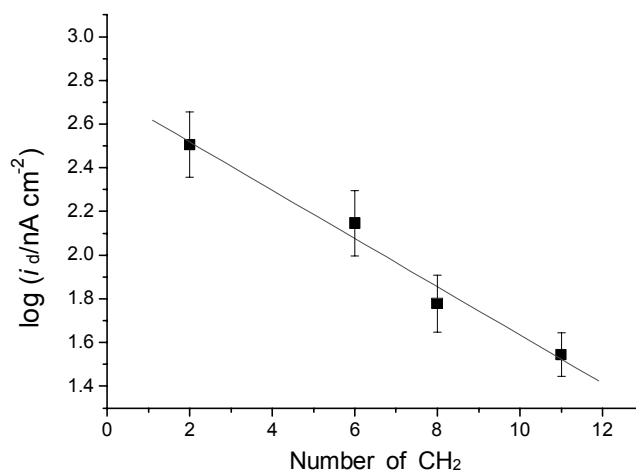


Figure 4. Dependence of photocurrent density on the number of CH₂ units in the linker for Au/S(CH₂)_nNH-thylakoid.

tron tunneling through the linker molecule.

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