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 conversion 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 grana 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. Some of produced electrons may go to the electrode split to oxygen and protons giving off electrons upon illumination. 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 (HS-(CH2)n-NH2, 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 leaves and oriented it using Ni-NTA (Ni-nitrilotriacetic acid) dinine tag at the C-terminal end of the M-subunit of the reaction center and oriented it using Ni-NTA (Ni-nitrilotriacetic acid) 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 Au/S(CH2)n-NH2 electrode did not give any photocurrent even when light was on. But when thylakoid was attached on this surface (Au/S(CH2)n-NH-thylakoid), large photo-

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**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 (NH2CH2CH2SH) was used.
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. 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 cell (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.  This result has an important implication that thylakoid itself could be used as an electron shuttle, but higher than that of a system (100 nA cm⁻²)

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,

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

where \( \beta \) 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.

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 electron tunneling through the linker molecule.

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References

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14. We used a gold bead electrode (0.1 cm²) prepared by melting a gold wire. It was cleaned in piranha solution (3:1 mixture of conc. H₂SO₄ and 30% H₂O₂) and then electrochemically treated in 0.5 M H₂SO₄ until a typical voltammogram was obtained. The surface area was measured as described in ref. 20. Photocurrent measurement was done in a potentiostatic mode by applying 0.7 V. A 150 W tungsten lamp was used as a light source. An aluminum reflector was placed behind the Au bead electrode.

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

Figure 4. Dependence of photocurrent density on the number of CH₂ units in the linker for Au/S(CH₂)₂NH-thylakoid.