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LIGHT ENERGY CONVERSION WITH *ANABAENA CYLINDRICA* COATED METHYL VIOLOGEN–POLYSTYRENE SULFONATE–COATED ELECTRODE

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A blue-green alga, *Anabaena cylindrica*, immobilized on the methyl viologen–polystyrene sulfonate–polyvinyl alcohol coated SnO_2 electrode showed a remarkable photoanodic current. The photocurrent onset potential corresponded to the energy level of the redox potential of methyl viologen, which was sufficient to generate hydrogen at a cathode.

Photoelectrochemical behavior of chlorophyll, chloroplast, and living blue-green algae on optically transparent electrodes (OTE) has been studied extensively in connection with the electrochemical simulation of the photosynthesis and with the light energy conversion. In the chloroplast photosystem, an electron in the photosystem II (PS II) is excited from the level of the water oxidation at +0.81 V (*vs.* NHE) in neutral solutions to that of the redox potential of ferredoxin at -0.43 V through the photosystem I (PS I). It has been well known that methyl viologen (MV), whose redox potential is -0.44 V at pH 7.0, blocks the flow of electrons from PS I to nicotinamide adenine dinucleotide phosphate (NADP), whose redox potential is -0.32 V, through ferredoxin.

The photocurrent onset potential of chlorophyll *a* monolayer on SnO_2 OTE was about +0.07 V,1) and that of blue-green algae on SnO_2 OTE was +0.68 V.2) In the case of a chloroplast-polyvinyl alcohol (PVA) coated electrode it was about +0.44 V.3,4) A mixture of MV and spinach chloroplast sandwiched between SnO_2 OTEs was used as a photoanode and photocurrent onset potential was +0.04 V.5) The photocurrent onset potential of these photoanodes was at most +0.04 V, which was inadequate for the photolysis of water. It is necessary to use a photoanode whose photocurrent onset potential is about -0.41 V to generate hydrogen at platinum counter electrode at pH 7.0. In principle, we can trap electrons at the level of the redox potential more negative than that of ferredoxin, -0.43 V, by using an electrode coated by a redox polymer that can reversibly exchange electrons with an electron carrier in the electron transfer process from PS I to ferredoxin.

The purpose of this experiment is to demonstrate that the MV–polystyrene sulfonate (PSS) polymer coated electrode blocks the electron flow from PS I to NADP and that the photocurrent onset potential of this photoanode is the level of the redox potential of MV–PSS polymer, -(0.41—0.44) V,6) which is adequate to generate hydrogen at pH 7.0 with an appropriate counter electrode.

Anabaena cylindrica was cultured under the usual condition and separated by centrifugation. A mixture of PSS ($\overline{MW}$ = 7 500, 73.4 % sulfonated), 0.69 g and MV, 0.20 g was dissolved in water. Then, 2.97 g of PVA (average degree of polymerization 1 700) was added to it and was gently dissolved at 80 °C. After that, 0.3 wt% of bovine serum albumin was added to stabilize the redox polymer at the electrode surface. This mixture was spread uniformly on a SnO_2 OTE (Matsuzaki Shinku Ltd., 20 ohm/square, 500 Å film thickness) and dried under a reduced pressure over phosphorus pentaoxide for a day. Then, the film-coated electrode was heat-treated at 190 °C for 15 min. Methyl viologen was stable in the polymer film when the mole ratio of MV to the sulfonate group in PSS was smaller than 0.25.6) The dissolution of MV was not detectable during the experiments. A MV–PSS–PVA polymer coated pyrolytic graphite electrode was used to study the voltammetric behavior of the polymer film. *Anabaena cylindrica* was spread on the MV–PSS–PVA polymer coated SnO_2 OTE. Then, the electrode was dried in air and was subjected to the photoelectrochemical measurement. The photoelectrochemical cell used in the present experiments was described elsewhere.1,4) The supporting electrolyte was 0.05 M7) tris(hydroxymethyl)aminomethane + 0.01 M NaCl (pH 10.2), in which we were able to polarize the photoanode up to -0.3 V. The current-potential relations of photoanodes were determined under the potentiostatic condition. A platinum plate was used as a counter electrode and a Ag/AgCl electrode8) was used as a reference electrode and the solutions were deaerated by bubbling purified nitrogen. The light source was a 500 W

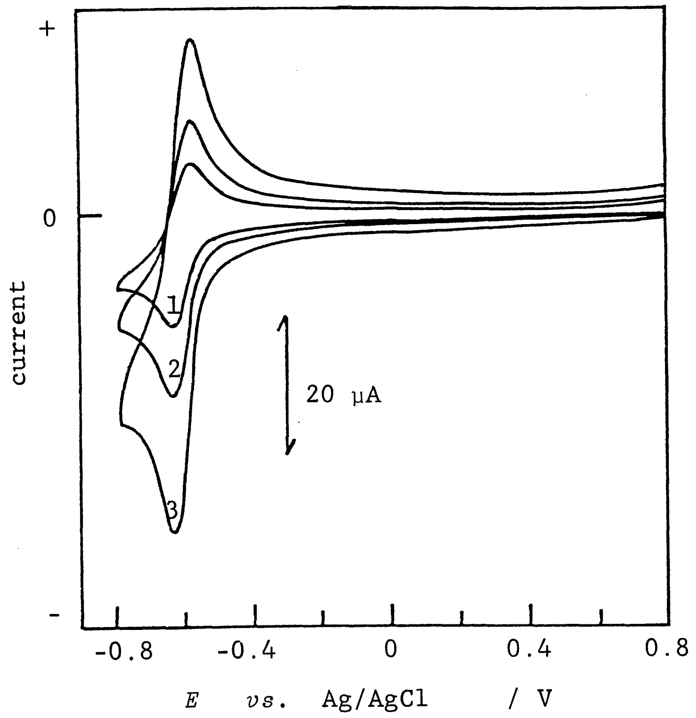

Fig. 1. Cyclic voltammograms of the MV-PSS-PVA polymer coated pyrolytic graphite electrode in 0.1 M phosphate buffer (pH 7), film thickness: 3.5 µm.
scan rate; 1: 10 mV/s, 2: 20 mV/s, 3: 50 mV/s.

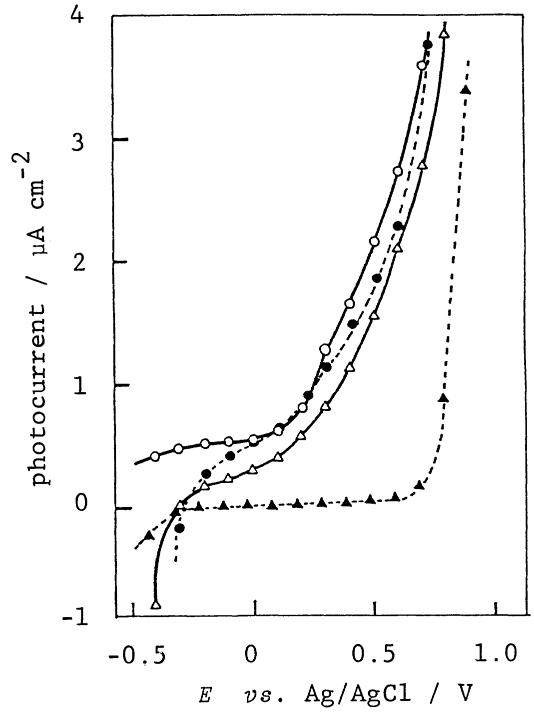

Fig. 2. Photocurrent-potential curves at various photoanodes in 0.05 M tris(hydroxymethyl)aminomethane + 0.01 M NaCl (pH 10.2).
○ : SnO_2/MV–PSS–PVA/*Anabaena cylindrica*,
● : SnO_2/*Anabaena cylindrica*,
△ : SnO_2/MV–PSS–PVA,
▲ : SnO_2 (dark).

xenon arc lamp (Ushio Electric Ltd., PSR-501A). The action spectra of the photoanodes were measured with a 500 W xenon arc lamp (UI-501C), a Nikon G250 monochrometer, a thermopile radiometer and a picoammeter. A cut-off filter (Toshiba Kasei, V-48) was used to eliminate the photoresponse of SnO_2 OTE.

The polarographic behavior of the MV–PSS couple dissolved in the aqueous solution is reversible and the half-wave potential shifts toward positive potential with the increase in the mole ratio of methyl viologen to sulfonate group in PSS.6) Figure 1 shows the cyclic voltammograms of the MV–PSS–PVA polymer coated pyrolytic graphite electrode (the polymer was spin-coated on the electrode and the thickness ranged from 3.5 μm to 40 μm). Methyl viologen in the polymer film showed a well-defined voltammogram and the mid-point potential of the current peaks was -0.61 V (*vs.* Ag/AgCl), which corresponded to the half-wave potential of the MV–PSS couple in the bulk solution. Figure 2 shows the current-potential relations of the various photoanodes (a cut-off filter was not installed). The current-potential characteristics of both MV–PSS–PVA polymer coated and *Anabaena cylindrica* coated SnO_2 electrodes were almost the same and the photocurrent onset potential was about -0.3 V (*vs.* Ag/AgCl). On the other hand, the MV–PSS–PVA polymer coated SnO_2 OTE covered by *Anabaena cylindrica* (MV, 2.4×10^{-7} mol cm^{-2}; PSS, 8.8×10^{-7} mol cm^{-2}; PVA, 0.9 mg cm^{-2}; *Anabaena cylindrica*, 0.4 mg cm^{-2}) showed a marked enhancement of the photoanodic current, especially, at negative potentials. When the MV–PSS–PVA polymer coated SnO_2 OTE covered by *Anabaena cylindrica* was illuminated at open circuit, the polymer film became deep blue, suggesting the reduction of MV^{2+} to $MV^{+\cdot}$ by the electron from the photosystems in *Anabaena cylindrica*.

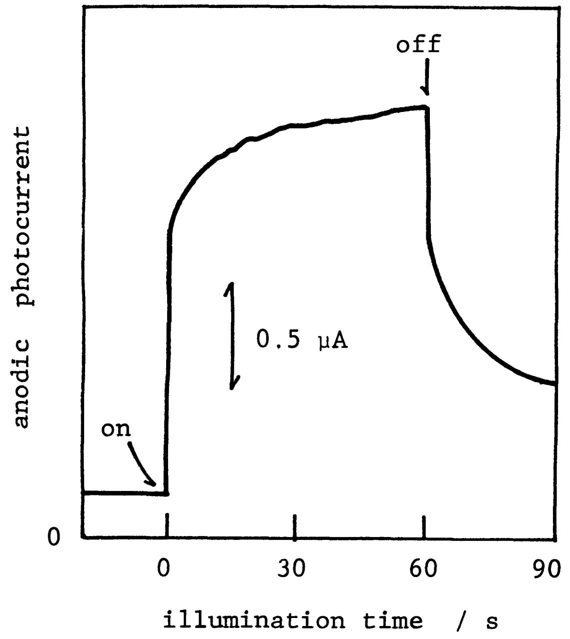

Fig. 3. Response of a SnO_2/MV–PSS–PVA/*Anabaena cylindrica* photoanode to illumination at the rest potential. Conditions are given in Fig. 2.

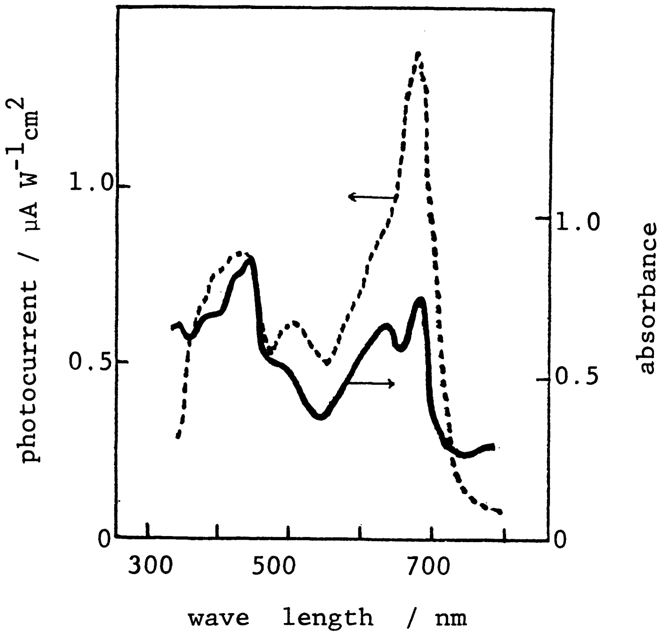

Fig. 4. Spectra of *Anabaena cylindrica*.
▬▬ UV-Vis. spectrum (in Triton X-100 aqueous solution),
- - - - action spectrum (SnO_2/MV–PSS–PVA/*Anabaena cylindrica*, the same conditions as given in Fig. 2).

These results revealed that electrons were ejected from *Anabaena cylindrica* to MV immobilized in PSS polymer and then to the electrode at the energy level of the redox potential of the MV–PSS couple. That is, the onset potential of the *Anabaena cylindrica*/MV–PSS–PVA/SnO_2 photoanode is expected to be about -0.61 V (*vs.* Ag/AgCl), which is sufficient to generate hydrogen when this photoanode is coupled with a platinum cathode. Figure 3 shows a response of the photoanode to the illumination. A typical photoanodic current spectrum of the *Anabaena cylindrica*/MV–PSS–PVA/SnO_2 photoanode is shown in Fig. 4 together with the absorption spectrum of *Anabaena cylindrica* suspended in aqueous solution (Triton X-100 was added). The photoanodic current spectrum accorded with the absorption spectrum. The maxima at 480 nm, 630 nm, and 680 nm corresponded to carotenoids, phycobilisome, and chlorophyll *a*, respectively. These present results have revealed that MV in the polymer coated electrode is probably reduced by the electron from an electron carrier in the electron transfer process from PS I to ferredoxin, and then the electron is ejected from the MV–PSS–PVA polymer layer to SnO_2 OTE. This type of photoanode will be also useful in the study of the activity of the photosystem by selecting an appropriate mediator as an electrode material.

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7) 1 M = 1 mol dm^{-3}.

8) The electrode potential *versus* a Ag/AgCl electrode in a saturated KCl aqueous solution (+0.198 V at 25 °C *vs.* NHE).

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