Photocurrent Generation *via* Vertical Transport of a Photogenerated Electron through Electron Relay confined within Micropores of an Anodic Aluminium Oxide Film

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A solar to electricity conversion device employing $Ru(bpy)_3^{2+}$ (bpy = bipyridyl) as a sensitizer, octadecyl methyl viologen (ODMV) confined within micropores of an anodic aluminum oxide film as an electron relay, and triethanolamine (TEA) as a donor, was constructed with a gold electrode; when the electrode potential was kept more positive than the redox potential of ODMV, an anodic photocurrent was observed.

Large scale climate changes due to the accumulation of CO_2 in the atmosphere have been attributed to fossil fuel combustion[1] and the development of solar energy conversion technology is now an urgent task. In nature, solar energy is efficiently converted to chemical energy by plant photosynthesis as follows: (i) collection of solar energy, (ii) charge separation, and (iii) synthesis of the energy rich compounds by 'dark reactions'. A high efficiency is achieved because molecules which carry out these functions are efficiently integrated in the membranes of cells.

Research on artificial photosynthesis systems which mimic natural photosynthesis, aiming at solar energy conversion, has been extensive and quite significant results have been obtained. The understanding of the elemental processes involved has also greatly increased. Many problems, however, still exist and the short life-time of the artificial systems is one of the most serious problems to be solved. Although the systems are renewed continually in nature, this is not possible in artificial systems and therefore systems with a long life-time must be constructed. In most of the research done on artificial

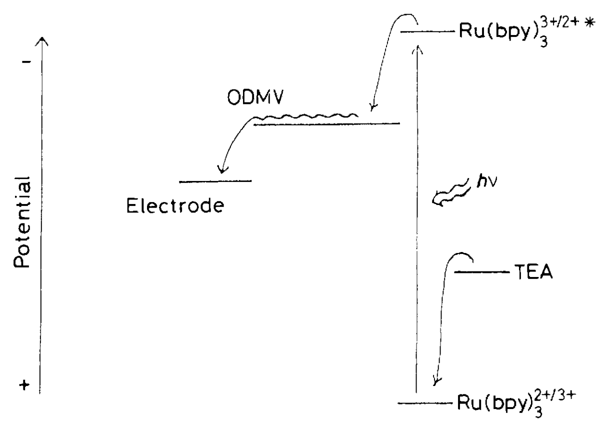

Figure 1. Schematic diagram of proposed photocurrent generation process.

systems, the molecules which play the specific role discussed above are arranged on the micelle or bilayer,[2,3] and it is common that the systems stop functioning within a short time; by using an inorganic membrane, one expects a longer life-time.

Recently, Majda *et al.* demonstrated that vertical electron transport is possible if electrochemically active species are confined within micropores of an anodic aluminium oxide film.[4] In this communication, we report an attempt to construct a solar to electricity conversion device employing $Ru(bpy)_3{}^{2+}$ (bpy = 2,2′-bipyridyl) as a sensitizer, octadecyl methyl viologen (ODMV) confined within micropores of an anodic aluminium oxide film as an electron relay, and triethanolamine (TEA) as a donor. When the electrode potential was kept more positive than the redox potential of ODMV, an anodic photocurrent was observed, as expected from the scheme shown in Figure 1.

The anodic aluminium oxide film was prepared as follows.[5] An aluminium plate (99.99%, 4 × 1.5 cm) degreased with methanol was electro-polished in a mixed acid [acetic acid (780 ml), perchloric acid (60%; 200 ml)] using a two-electrode system with an aluminium counter electrode (bias voltage 30 V, solution temperature 10 °C). Anodic oxidation of the electro-polished aluminium was also carried out using a two-electrode system with an aluminium counter electrode in H_3PO_4 (4%) at 65 V and 20 °C, or in H_2SO_4 (10%) at 15 V and 5 °C. The pore size of the anodic aluminium oxide film obtained under the former conditions was 1 000 Å, and under the latter conditions was 150 Å. For electro-polishing and anodic oxidation of Al, a regulated DC power supply (Takasago, Ltd., GP0110-3) and an electrometer (Takeda Riken Ltd., TR-8651) were used to control the bias voltage and monitor the current passed, respectively. The anodic oxide film was separated from the aluminium substrate by immersing the anodized Al in a saturated aqueous $HgCl_2$ solution. The anodic oxide films thus obtained were washed with water and dried in air. An organic monolayer was formed on the internal wall of the micropores by treatment with octadecyltrichorosilane (OTS). The microporous anodic aluminium oxide film was placed in a freshly made OTS hexadecane solution [2% (v/v)]. The oxide film was kept in the OTS hexadecane solution for 60 min under a dry N_2 atmosphere. The film was then rinsed thoroughly with toluene followed by propan-2-ol and was dried in air. To form an electrode, Au was vacuum deposited onto the open pore side of the film [vacuum evaporation apparatus (Shimadzu Ltd.; EA-400S), 5×10^{-5} mmHg]. A deposition angle of 30° from the surface was employed in order to avoid Au filling the pores.

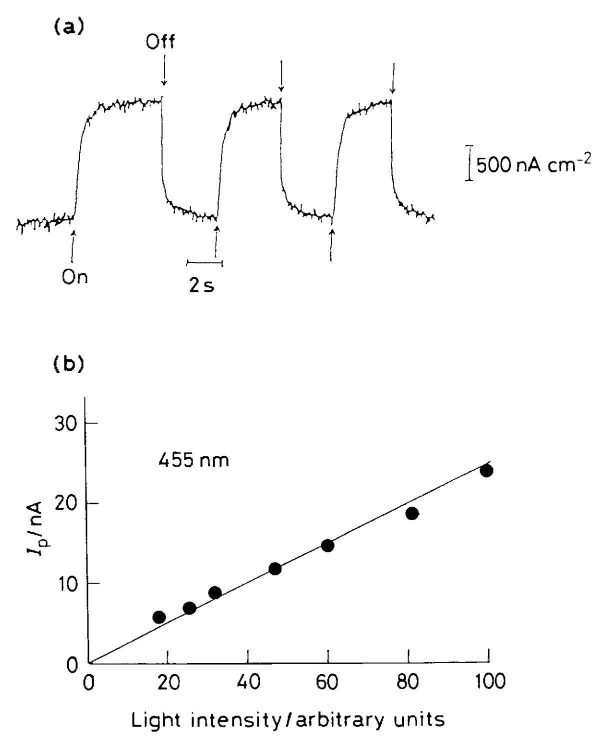

Figure 2. (a) Current response induced by pulsed white light at −30 mV *vs.* SSCE. (b) Intensity dependence of photocurrent measured using monochromatic light at 455 nm.

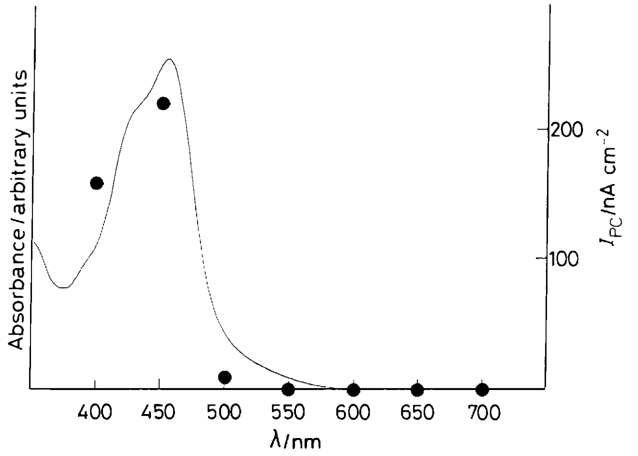

Figure 3. Photocurrent action spectrum of the system Au/Al_2O_3–OTS–ODMV/$Ru(bpy)_3{}^{2+}$/TEA and absorption spectrum of $Ru(bpy)_3{}^{2+}$.

A potentiostat (Hokuto Denko Co. Ltd., HA-301) was used to control the potential of the working electrode with respect to a sodium saturated calomel electrode (SSCE); Pt foil was used as a counter electrode. The external potential was provided by a function generator (Hokuto Denko Co. Ltd., HB-105), and a three-electrode, three-compartment photoelectrochemical cell was employed for both electrochemical and photoelectrochemical measurements. Current–potential and current–time relations were recorded on an *x*-*y*-*t* recorder (Rika Denki Co. Ltd., RW-11T). Since a barrier layer blocks the electrolyte solution from entering the pores, to carry out electrochemical reactions it is necessary to expose the micropores to the solution by dissolving the barrier layer away. By immersing the electrode in an aqueous solution of ODMV (60 µM) containing Na_2SO_4 (0.2 M) as a supporting electrolyte, after the dissolution of the barrier layer and hydrophilic treatment with methanol, ODMV molecules formed a bilayer on the OTS layer in the pores. At first, no waves due to the reduction/oxidation of ODMV were observed by cyclic voltammetry (CV) between −900 and 0 mV *vs.* SSCE, but the waves around −500 mV increased with time and reached a steady value after 3 h. Even after the solution was replaced by an aqueous solution of Na_2SO_4 (0.2 M) without ODMV, the redox waves of ODMV were still observed by CV and the peak current was proportional to the scan rate. Thus, it was confirmed that ODMV molecules were fixed in the micropores as reported by Majda *et al.*, and the amount of ODMV fixed in the micropores decreased only gradually with time (80% remained after 24 h).

The photoelectrochemical conversion was carried out in a solution containing $Ru(bpy)_3^{2+}$ as a sensitizer and triethanolamine (TEA) as an electron donor, and using the microporous anodic aluminium oxide film electrode prepared above, in which ODMV was fixed as an electron relay. Figure 2 shows the current response induced by pulsed white light when the potential was kept at −30 mV *vs.* SSCE, which is much more positive than the redox potential of ODMV. An anodic photocurrent synchronized with the pulsed radiation was obtained and the response was quite fast. Figure 2 (inset) shows that the photocurrent is proportional to the intensity of radiation. These results suggest that the current increase was not caused by a thermal process but by a photoprocess. Only a negligible photocurrent was observed at the electrode without ODMV modification.

Figure 3 shows the absorption spectrum of $Ru(bpy)_3^{2+}$ and the action spectrum of the photocurrent measured using band pass filters. The action spectrum and the absorption spectrum agree fairly well and it is confirmed that $Ru(bpy)_3^{2+}$ acts as the sensitizer.

The photocurrent was constant when the solution [Na_2SO_4 (0.5 M)] contained both $Ru(bpy)_3^{2+}$ and TEA. When the solution was replaced by Na_2SO_4 (0.5 M) containing neither $Ru(bpy)_3^{2+}$ nor TEA, the photocurrent was still observed at first but decreased with time. If TEA was added to this solution, the photocurrent became large again, even larger than the photocurrent observed initially in the solution containing both $Ru(bpy)_3^{2+}$ and TEA. In this case, $Ru(bpy)_3^{2+}$ which was trapped in the micropores during the measurement in the solution containing $Ru(bpy)_3^{2+}$ acted as the sensitizer. These results suggest that TEA really acts as an electron donor. The photocurrent was larger when there was no $Ru(bpy)_3^{2+}$ in the bulk solution because the absorption of light by $Ru(bpy)_3^{2+}$ in solution, the filter effect, became negligible. From these results the mechanism of photocurrent generation can be considered as in equations (1)—(5).

$$Ru(bpy)_3^{2+} + h\nu \rightarrow Ru(bpy)_3^{2+*} \qquad (1)$$

$$Ru(bpy)_3^{2+*} + ODMV^{++} \rightarrow Ru(bpy)_3^{3+} + ODMV^{+\cdot} \qquad (2)$$

$$ODMV^{+\cdot} \rightarrow ODMV^{++} + e \qquad (3)$$

$$Ru(bpy)_3^{3+} + TEA \rightarrow Ru(bpy)_3^{2+} + TEA_{ox} \qquad (4)$$

$$TEA + h\nu \rightarrow TEA_{ox} + e\ (\text{anodic photocurrent}) \qquad (5)$$

The maximum quantum yield of the system, calculated from the action spectrum shown in Figure 3, is ~20% [assuming that the concentration of $Ru(bpy)_3^{2+}$ in the micropores is the same as that in the bulk solution]. The small photocurrent observed despite this high quantum yield is due to small amounts of $Ru(bpy)_3^{2+}$ acting as a sensitizer in the micropores, leading to a very small number of photons absorbed in the pores. To improve the photocurrent, one must increase the number of photons absorbed, by increasing the concentration of $Ru(bpy)_3^{2+}$ or the thickness of the film.

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