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## **PHOTOSENSING DEVICE COMPOSED OF BILAYER MEMBRANES OF POLYMER-PENDANT $\text{Ru}(\text{bpy})_3^{2+}$ AND PRUSSIAN BLUE**

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### **ABSTRACT**

A photosensing device was fabricated based on a photochemical electron transfer reaction. A graphite electrode was coated with bilayer membranes of polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  and Prussian Blue (PB) to give a bilayer-coated device. It was irradiated with visible light in an aqueous electrolyte and the induced photocurrent was measured as a function of the applied potential. The excitation of PB was responsible for the anodic photocurrent, while the excitation of the Ru complex mainly induced the cathodic photocurrent by an electron-transfer mechanism.

### **INTRODUCTION**

Photosensing devices are attracting much notice in conjunction with the future of the data processing and information industry. Most photosensing devices utilize semiconducting or photoconducting properties of materials such as inorganic/organic semiconductors, metals, and dyes. They are therefore based on photophysical processes. It should be possible, however, to construct photosensing devices based on photochemical processes if a photochemical reaction can send an electrical response to the exterior. Such de-

vices must lead not only to new applications in electronics, but also to elucidation of photosynthesis, which is based entirely on photochemical processes.

In order to construct such devices based on photochemical processes, the immobilization of the reaction components as a solid in a specific arrangement is necessary since, in a homogeneous solution, the unavoidable back reaction brings no net response to the exterior. Multilayer structures of thin polymer membranes which contain each reaction component represent one solution to this problem. Another problem that has to be solved toward this objective is the effective occurrence of photochemical reactions in the solid state.

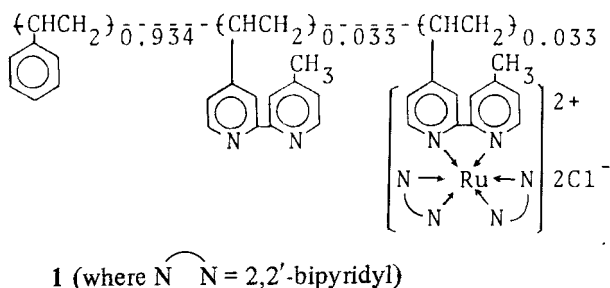
The author has found efficient photochemical electron transfer between tris(2,2'-bipyridine)ruthenium(II) complex (abbreviated  $\text{Ru}(\text{bpy})_3^{2+}$ ) and methylviologen ( $\text{MV}^{2+}$ ) in a solid phase of cellulose [1-3]. Further studies showed that bilayer membranes composed of polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  coated on graphite give a photoelectrochemical response to the exterior [4] although a homogeneous solution of these components shows no response at an electrode dipped in the solution. Such a photoelectrochemical study of multilayer photochemical reaction systems provides fundamental information helpful in constructing photosensing devices.

In the above-mentioned system,  $\text{MV}^{2+}$  works as an electron acceptor. Our study of the water photolysis system composed of  $\text{Ru}(\text{bpy})_3^{2+}$  and Prussian Blue (PB) [5, 6] showed that PB works as an electron relay. Since PB can be formed into a thin membrane [7, 8], it was considered that it might be used instead of  $\text{MV}^{2+}$ . We have succeeded in obtaining a photoelectrochemical response by the bilayer device of graphite/PB/polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  [9]. Since the probable different behavior of the graphite/polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$ /PB system is of interest from a basic standpoint, it has been studied and is reported in this paper.

## EXPERIMENTAL

### Materials

Polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  (1) was prepared as reported previously [10]. Its composition is shown on next page. Basal plane pyrolytic graphite (BPG;  $0.17 \text{ cm}^2$ ) was used as the electrode.



### Device Fabrication

BPG was coated by 1 by casting 1.02  $\mu\text{L}$  DMF solution of 1 (concentration of the pendant Ru complex unit 1 mmol/L). The coated amount of the Ru complex is  $6.0 \times 10^{-9}$  mol/cm<sup>2</sup>. The coating thickness of 1 was estimated to be about 0.16  $\mu\text{m}$  by assuming the density of the polymer complex as 1.0 g/cm<sup>3</sup>.

PB was electrodeposited on top of the polymer layer by dipping the 1-coated BPG into an aqueous mixture of 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  and 10 mM  $\text{FeCl}_3$  and applying -0.5 V (vs Ag-AgCl). The coated amount of PB was estimated as  $6.1 \times 10^{-7}$  equiv/cm<sup>2</sup> from the current flow during the electrodeposition by assuming that all the PB formed was deposited onto the electrode. The coating thickness was then calculated as 1.3  $\mu\text{m}$  from the cubic primitive cell structure of PB ( $a = 1.02$  nm) [11].

### Measurements

The bilayer-coated device, BPG/1/PB, was dipped in 0.5 M  $\text{K}_2\text{SO}_4$  aqueous solution and irradiated under an applied potential. The light source was a 500-W xenon lamp, and cutoff filters (Toshiba VY-42 and IRQ-80) were used to obtain visible light of wavelength 400-800 nm. The photocurrent was measured by a voltammetric analyzer, P-1000, from Yanagimoto Co. The light intensity was monitored by a thermopile, CA-1, from Kipp & Zonen. For most measurements it was 67 mW/cm<sup>2</sup>. Monochromatic light was obtained by using interference filters (KL-42 to 76 from Toshiba Co.).

## RESULTS AND DISCUSSION

The cyclic voltammograms of the bilayer-coated BPG in the dark and under illumination (Fig. 1) show typical waves of PB. PB, whose composition has been reported as  $\text{Fe}_4^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^{4-}$  [8], can take on two other reversible redox states, i.e., Prussian White (PW;  $\text{Fe}^{2+}$ - $\text{Fe}^{2+}$  complex) and Berlin Green (BG;  $\text{Fe}^{3+}$ - $\text{Fe}^{3+}$ ). The very distinct waves of Fig. 1 in spite of the presence of the polymer layer between PB and the electrode might indicate that the PB has grown, maybe partially, directly on the electrode surface through the pores of the Ru polymer, finally forming a uniform layer on the top of the 1 layer. This will be discussed later in relation to the mechanism. Both anodic peaks are shifted under illumination to potentials higher by about 25 mV than those in the dark, and the cathodic peaks to lower potential. These results show that the irradiation induces a shift of the equilibrium of the electrochemical process.

Figure 2 shows typical patterns of current changes induced by switching on and off of the irradiation of the bilayer device dipped in an aqueous solution. A photocurrent was induced repeatedly and reversibly by the irradiation, its direction being dependent on the applied potential. At an applied potential of 1 V, an anodic photocurrent was obtained (Fig. 2a), while at -0.5 V a cathodic photocurrent (Fig. 2b) was obtained. The dependence of the photo-

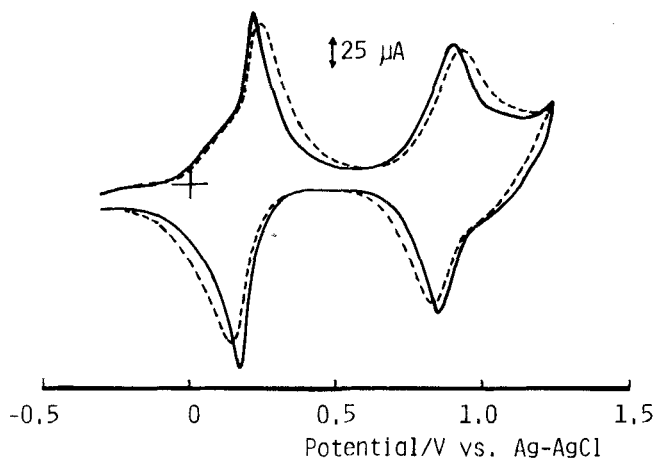


FIG. 1. Cyclic voltammograms of bilayer coated BPG in the dark (—) and under illumination (- -) in aqueous 0.5 M  $\text{K}_2\text{SO}_4$ . Scan rate, 15 mV/s.

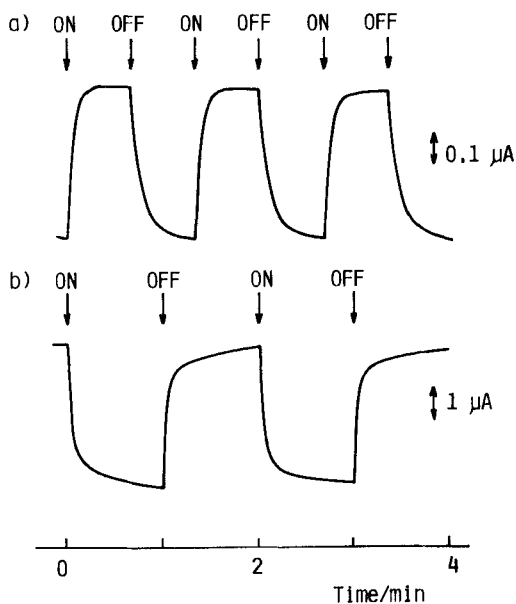


FIG. 2. Current changes induced by switching on and off of the irradiation of BPG/polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}/\text{PB}$  in aqueous  $0.5 \text{ M K}_2\text{SO}_4$  at applied potentials of  $1 \text{ V}$  (vs  $\text{Ag-AgCl}$ ) (top) and  $-0.5 \text{ V}$  (bottom).

current on the applied potential is shown in Fig. 3. An applied potential higher than  $\sim -0.1\text{--}0 \text{ V}$  induced anodic photocurrent, while a cathodic photocurrent was obtained at potentials lower than this. This will be further discussed later. The photocurrent was proportional to the light intensity in the intensity region studied (Fig. 4).

The action spectra for the anodic and the cathodic photocurrent are shown in Fig. 5, where the photocurrent was normalized to the number of incident photons. The absorbances of the polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  and the PB in Fig. 5 almost correspond to the coated amount of the respective species. The action spectra for the anodic photocurrent (at applied potential  $1 \text{ V}$ ) and cathodic one (at  $-0.3 \text{ V}$ ) are quite different. The excitation of PB is responsible for the anodic photocurrent. The cathodic photocurrent involves the excitations of both the Ru complex and the PB, but the excitation of the Ru complex contributes much more than that of PB in spite of the much smaller absorption by the former.

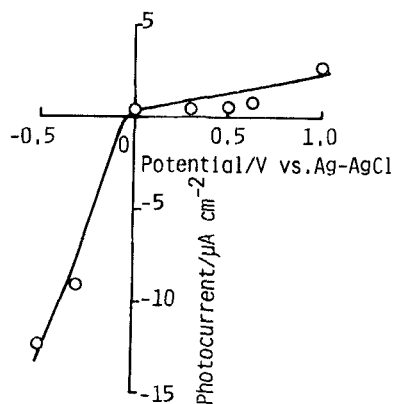


FIG. 3. Dependence of photocurrent on the applied potential.

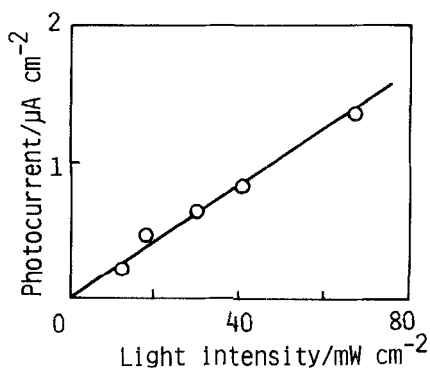


FIG. 4. Dependence of photocurrent on the light intensity (anodic photocurrent obtained at 1 V).

The mechanisms for the anodic and the cathodic photocurrent are shown in Figs. 6 and 7, respectively. As shown by the action spectrum (Fig. 5), the excitation of PB is responsible for the anodic photocurrent. Since the redox reactions of the Ru complex ( $\text{Ru}(\text{bpy})_3^{3+/2+}$  and  $\text{Ru}(\text{bpy})_3^{2+ /+}$ ) cannot mediate the electron transfer from the excited state of PB to the electrode, as shown in Fig. 6, direct injection of the electron from the excited PB to BPG would oc-

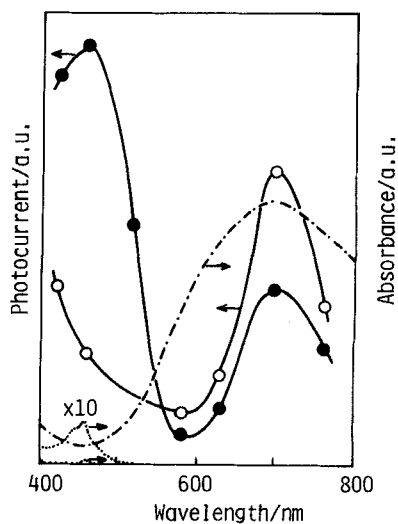


FIG. 5. Action spectra for the anodic (○) and cathodic photocurrent (●) obtained at applied potentials of 1 V (vs Ag-AgCl) and -0.3 V, respectively. Absorbances of Ru(bpy)<sub>3</sub><sup>2+</sup> (···) and PB (- ·).

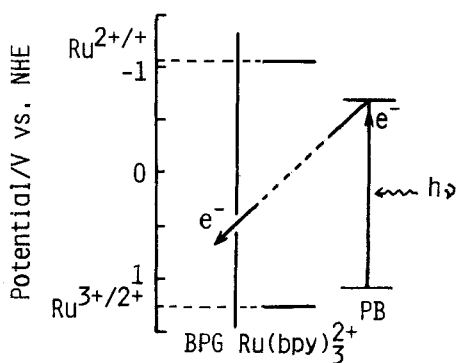


FIG. 6. Mechanism for the anodic photocurrent.



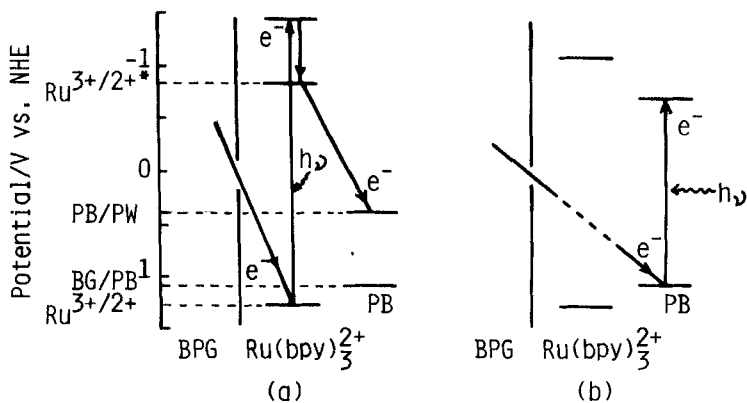


FIG. 7. Mechanisms for the cathodic photocurrent. (a) Major process, (b) minor process.

cur. The growth of PB partially attached to the electrode surface through the pores of the  $\text{Ru}(\text{bpy})_3^{2+}$  polymer membrane would make such a direct injection of electrons possible. The device, BPG/polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$ /PB, is therefore almost the same as the system without **1**, i.e., BPG/PB [12], as far as the anodic photocurrent is concerned.

For the cathodic photocurrent, the major process is the excitation of the polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$  (Fig. 7a). The electron transfer from the excited Ru complex induces the cathodic photocurrent. Such an electron transfer, which is the oxidative quenching of the excited Ru complex by PB, is rationalized by the water photolysis system composed of  $\text{Ru}(\text{bpy})_3^{2+}$  and PB [5, 6]. The minor process for the cathodic photocurrent is the direct electron transfer from the electrode to the excited PB. Such a process, for which the Ru complex layer plays no role, has also been observed for the BPG/PB system [12].

The present device (BPG/polymer-pendant  $\text{Ru}(\text{bpy})_3^{2+}$ /PB) has a *p*-type bilayer character, which gives mainly cathodic photocurrent, as shown in Fig. 3. The process of Fig. 7(a), which is induced by a bilayer photochemical electron transfer, therefore predominates among all the photoinduced processes in the present bilayer-coated device.

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