PHOTORESPONSIVE GRAPHITE ELECTRODE COATED WITH BILAYER MEMBRANES OF PRUSSIAN BLUE AND POLYMER-PENDANT Ru(bpy)$_3^{2+}$

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Abstract—Graphite electrode was made photoresponsive by coating with bilayer membranes of Prussian blue (PB) and polymer-pendant Ru(bpy)$_3^{2+}$. Photocurrent was induced by irradiating the coated electrode which was dipped in aqueous electrolyte. The photocurrent was dependent on the applied potential. Action spectra showed that the major process for the photocurrent generation concerns the excitation of the Ru complex, and the role of PB as electron mediator was strongly suggested. The minor process for the photocurrent generation concerns the excitation of PB and the following electron transfer between the excited PB and the electrode.

INTRODUCTION

Photoresponse of electrode is recently receiving much attention in relation to sensors and solar energy conversion. Although most of the photoresponsive electrodes are based on photophysical process in semiconductors made of inorganic and organic materials, photochemical processes between two compounds can also be utilized to obtain photoresponsive electrodes if the reaction components are coated on the electrode as membrane[1-3].

The authors have reported photoresponsive graphite electrodes which utilize photo-induced electron transfer from tris(2,2'-bipyridine)ruthenium(II) complex [Ru(bpy)$_3^{2+}$] to methylviologen (MV$^2+$) occurring in a membrane coated on the graphite[1, 2, 3]. In such systems, when the photochemical reaction components [eg Ru(bpy)$_3^{2+}$ and MV$^2+$] are incorporated as a mixture into a membrane coated on an electrode, both cathodic and anodic photocurrent are obtained depending on the applied potential because both the photochemical reaction products derived from the initial compounds can react at the electrode. When the two components are present separately in different layers of bilayer coating, however, the direction of the photocurrent is fairly well controlled because the photochemical reaction product located in the layer directly attached to the electrode can react preferentially at the electrode[3]. In order to fabricate such bilayer modified devices, the reaction components must be coated on an electrode as thin films. Polymeric compounds are of great use in this viewpoint[4].

The Ru(bpy)$_3^{2+}$ has been markedly noticed in these more than ten years because it is one of the promising candidates as a sensitizer to photolyze water under visible light irradiation[4-8]. The authors have found that the irradiation of water containing Ru(bpy)$_3^{2+}$ and Prussian blue (PB) gave simultaneous evolution of hydrogen and oxygen by water photolysis[9, 10]. One important point of this photolysis system is the electron transfer from the excited state of the Ru complex to PB. Since PB can be coated on many types of electrode very easily by electrodeposition[11, 12], the photo-induced electron transfer between PB and Ru(bpy)$_3^{2+}$ must provide a new photoresponsive electrode composed of bilayer coating. In addition, the appearance of such photoresponse of the electrode coated by bilayer of PB and the Ru complex must give direct evidence on the photochemical reaction between the two compounds. From these viewpoints, photoresponse of the graphite electrode coated with bilayer of PB and Ru(bpy)$_3^{2+}$ was studied.

EXPERIMENTAL

Basal plane pyrolytic graphite (BGP; 0.17 cm$^2$) was used as the electrode. Ru(bpy)$_3^{2+}$ was used as a polymer-pendant type which was prepared by reaction of the copolymer of styrene and 4-methyl-4'-vinyl-2,2'-bipyridine with cis-Ru(bpy)$_3$Cl$_2$ as reported[13].

PB was electrodeposited on the BGP by dipping it into an aqueous mixture of 10mM K$_3$Fe(CN)$_6$ and 10mM FeCl$_3$ and applying -0.6V (vs Ag-AgCl) usually for 180s. Polymer-pendant Ru(bpy)$_3^{2+}$ was coated on the top of the PB layer by casting from 1.02% DMF solution of the polymer complex (the concentration of the Ru complex unit; 1 mM).

The bilayer coated BGP was irradiated in a 4ml aqueous solution containing 0.5M K$_3$SO$_4$ under an applied potential (vs Ag-AgCl) with platinum counter electrode, and the photocurrent was measured by the voltammetric analyzer, P-1000, from Yanagimoto Co. Ltd. The irradiation was made by a 500 W xenon lamp through cutoff filters (Toshiba YY-42 and IRQ-80). The light intensity was monitored by the thermopile, CA-1, from Kipp & Zonen. It was usually 67 mW cm$^{-2}$. Monochromatic light was obtained by using interference filters (KL-42 to 76 from Toshiba Co. Ltd).
RESULTS AND DISCUSSION

The composition of the polymer-pendant Ru(bpy)$_2^{+}$ used was as follows:

\[ \begin{array}{c}
\text{Ru}^{2+} \quad \text{N-N = 2, 2'-bipyridine}
\end{array} \]

The ground and the excited levels and the redox reactivity of the excited state of the polymer-pendant Ru(bpy)$_2^{+}$ were very similar to the low molecular Ru(bpy)$_2^{2+}$ as reported[1, 4, 13].

The composition of electrodedeposited PB has been reported as Fe$_2^{2+}$[Fe$_{11}$(CN)$_{14}]^{2-}$ [14]. The PB coated on BPG showed almost reversible two redox waves at 0.17 V and 0.86 V (vs Ag-AgCl) due to three redox states of PB (Fe$^{2+}$-Fe$^{3+}$ complex), Prussian white (PW, Fe$^{2+}$-Fe$^{3+}$ complex) and Berlin green (BG, Fe$^{3+}$-Fe$^{3+}$ complex)[15]. The amount of coated PB was estimated as $6.1 \times 10^{-7}$ equivalent cm$^{-2}$ from the current flow ($1.0 \times 10^{-2}$ C) at the electrodeposition (180s) when assuming that all the PB formed was deposited onto the electrode. The coating thickness is then calculated to be 1.3 μm from the cubic primitive cell structure of PB (a = 1.02 nm)[16]. The coverage of PB (amount of redox response of the coated PB) was obtained from the area of the redox peaks of its cyclic voltammogram to be $1.6 \times 10^{-7}$ equivalent cm$^{-2}$.

The polymer pendant Ru(bpy)$_2^{+}$ was coated on the top of this PB layer to give a bilayer coated BPG. Its coated amount was $6.0 \times 10^{-9}$ mol of the Ru complex per cm$^2$. The coating thickness was estimated to be about 0.16 μm by assuming the density of the coated polymer layer as ca 1.0 g cm$^{-3}$.

Figure 1 shows typical patterns of the current changes induced by switching on and off of the irradiation on the bilayer coated BPG dipped in 0.5 M K$_2$SO$_4$ aqueous solution. Photocurrent was induced reversibly by irradiation. The direction of the photocurrent was dependent on the applied potential. At the applied potential of 1 V (vs Ag-AgCl) [Fig. 1(a)], anodic photocurrent was obtained, while at −0.3 V the photocurrent was cathodic [Fig. 1(b)]. The dependence of the photocurrent on the applied potential is shown in Fig. 2. The applied potential higher than ca 0.4 V (vs Ag-AgCl) induced anodic photocurrent, and the potential lower than this value cathodic photocurrent. The photocurrent was proportional to the incident light intensity (Fig. 3).

Action spectra of the photocurrent are shown in Fig. 4, where the photocurrent is normalized to the incident light intensity.

\[ \text{Anodic photocurrent/A cm}^{-2} \]

\[ \text{Cathodic photocurrent/A cm}^{-2} \]

Fig. 2. Dependence of photocurrent on the applied potential at bilayer coated BPG dipped in 0.5 M K$_2$SO$_4$ aqueous electrolyte.

Fig. 3. Dependence of photocurrent on light intensity. Applied potential, 1 V (vs Ag-AgCl).

Fig. 4. Action spectra of anodic and cathodic photocurrent obtained at the bilayer coated BPG with the applied potential of 1 V (o) and −0.3 V (c) (vs Ag-AgCl). The photocurrent is normalized to incident photon numbers. The absorbances of PB (---) and polymer-pendant Ru(bpy)$_2^{+}$ (-----) are corresponding approximately to the coated amount described in the text.
Fig. 6. Mechanism of cathodic photocurrent generation at photocurrent is induced by the excitation of the Ru complex (vide supra). Since a monolayer coating of polymer pendant Ru(bpy)$_2^+$ induced only a small photocurrent of the order of nA cm$^{-2}$ even under white light illumination, the PB layer of the present bilayer system must play an important role. Effective quenching of the excited state of Ru(bpy)$_2^+$ by PB in the water photolysis system by which photoredox products of water are given[10,17] indicated the occurrence of electron transfer between Ru(bpy)$_2^+$* and PB. The PB, which has three redox states as described before, is an excellent reversible redox reagent both for reduction and oxidation. From these considerations, the PB in the present photoelectrochemical system must work as an electron mediator by accepting or donating electrons from or to the excited state of Ru(bpy)$_2^+$*. For the anodic photocurrent, PB would work as an acceptor from the excited state of the Ru complex [Fig. 5(a)], while for the cathodic one as a donor to Ru(bpy)$_2^+$* [Fig. 6(a)]. In both the cases, the accepting and donating redox levels of PB are different according to the two-step redox reactions. The minor process to produce photocurrent is concerning the excitation of PB (see Fig. 4). As was reported[15], the PB coating alone can induce photocurrent by donating or accepting electron to or from BPG electrode [Figs 5(b) and 6(b)].

Thus, the graphite electrode coated with a bilayer of PB and Ru(bpy)$_2^+$ gave photoresponse. It also gave a support to the electron transfer between PB and the excited Ru(bpy)$_2^+$* which must occur in the water photolysis system composed of the two components.

**REFERENCES**