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Photoelectrochemical Behavior of the Fe(CN)$_5^{2-}$ Complexes Coordinated to the Poly(4-vinylpyridine) Film on Graphite Surfaces

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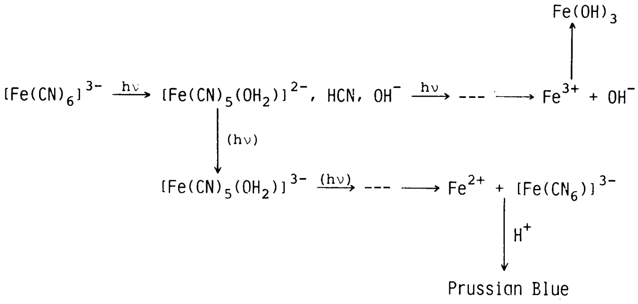
Photoelectrochemical reaction of the Fe(CN)$_5^{2-}$ complex (PVP[Fe(CN)$_5^{2-}$]$_n$) coordinated to the unprotonated poly(4-vinylpyridine) (PVP) film on a graphite electrode was examined in an aqueous solution. It was found that the carbon electrode coated with the PVP[Fe(CN)$_5^{2-}$]$_n$ generates the long-time responses of the photocurrents under irradiation of visible light and that the mechanism of its photochemical reaction is different from that for the photochemical reaction of [Fe(CN)$_6$]$^{3-}$ in a bulk solution, where the dissociation reaction of [Fe(CN)$_6$]$^{3-}$ to its aqua ion occurs.

Recently, the present authors have reported that the carbon surfaces coated with a couple of tris (2,2′-bipyridine)ruthenium(II) and methylviologen can generate the photocurrent.[1—3] As a series of papers regarding photoresponsive electrode prepared by coating of the photochemically active polymer, the present paper reports the photoelectrochemical investigation of the Fe(CN)$_5^{2-}$ complex (abbreviated as PVP[Fe(CN)$_5^{2-}$]$_n$) which is coordinated to the unprotonated poly(4-vinylpyridine) film coated on a basal plane pyrolytic graphite electrode in an aqueous solution. The photosensitivity of [Fe(CN)$_6$]$^{3-}$ and [Fe(CN)$_6$]$^{4-}$ was already known in 19th century and since then, a number of reports dealing with the photochemistry of [Fe(CN)$_6$]$^{3-}$ and [Fe(CN)$_6$]$^{4-}$ in aqueous solutions have appeared.[4] Moggi *et al.*[5] have studied the photochemical behavior of some cyanide complexes at various wavelengths in the ligand field spectral region and proposed a reaction mechanism involving a primary photoaquation reaction for the photolysis of the [Fe(CN)$_6$]$^{3-}$ ion both in neutral and in acidic solutions (see Scheme 1). Recently, Bowen and Hurlen[6] have studied the effect of irradiation on the electrode reactions of the [Fe(CN)$_6$]$^{4-}$/[Fe(CN)$_6$]$^{3-}$ couple at passive iron electrodes in borate solution and suggested that the rate of oxidation of [FeCN)$_6$]$^{4-}$ is markedly increased on irradiation, whereas the reduction of [Fe(CN)$_6$]$^{3-}$ is not affected. The overall photochemical reactions of [Fe(CN)$_6$]$^{3-}$ and [Fe(CN)$_6$]$^{4-}$ in aqueous solutions are composed of photoaquation, photooxidation-reduction and photosubstitution processes which sometimes occur simultaneously or successively. The photochemical reactions of these complexes are thus complicated, so that their photolysis has not been completely understood yet.



Scheme 1. [Fe(CN)$_6$]$^{3-}$ photolysis schematized by Ref. 5

The electrode reaction of Fe(CN)$_5^{2-/3-}$ redox couple, which is coordinated to the unprotonated PVP film coated on a graphite electrode, at the electrode/PVP film interfaces and the electron transfer reaction within the PVP film have been examined in previous papers,[7,8] where the special effect of the domain of the polymer film upon the electron transfer reactions has been demonstrated. Therefore, it is of interest to examine whether the polymeric domains influence upon the photochemical reaction of the Fe(CN)$_5^{2-/3-}$ complexes which are coordinated to the unprotonated PVP film or not.

Experimental

Electrochemical measurements were performed with a voltammetric analyzer (Model P-1000, Yanaco Co.). A 500 W Xenon lamp power supply (Model UI-501C, Ushio Electric Co.) was used as an irradiation source. The irradiation on the graphite electrode was performed with visible light (400—800 nm) through UV (Toshiba VY-42) and IR (Toshiba IRQ-80) cut-off filters. The intensity of the light could be varied by means of neutral density filters, and the wavelength could be varied using interference filters of band-pass 10 nm. IR spectra of PVP[Fe(CN)$_5^{2-}$]$_n$ film coated on electrode surface was measured by infrared spectrophotometer (A-302, Japan Spectroscopic Co., LTD.).

Poly(4-vinylpyridine) (PVP) (Bordon Inc., Philadelphia, PA) which was used in the present experiment unless otherwise described was reprecipitated twice from methanol-diethyl ether and its average molecular weight was 7.4×10^5.[9] Solutions containing PVP to which various quantities of Fe(CN)$_5^{2-}$ groups were coordinated were prepared, as described previously,[7] by mixing methanolic solutions of PVP having appropriate concentrations and aqueous solutions of [Fe(CN)$_5$(OH$_2$)]$^{3-}$ which were prepared by dissolving Na$_3$[Fe(CN)$_5$(NH$_3$)]·3H$_2$O (Tokyo Kasei Kogyo Co., Ltd.) in aqueous solutions under conditions where substitution of the NH$_3$ ligand by H$_2$O proceeds rapidly. Aliquots of the resulting solution of the polymer were transferred to the surface of a freshly cleaved basal plane graphite electrode (BPG, Union Carbide Corp.) and then the evaporation of the solvent was carried out at room temperature. The resulting coatings were swelled in an aqueous solution but remained insoluble. The thickness of the coating was calculated from the polymer densities (0.65 g cm^{-3}) estimated from the solvent-swelling measurements. The quantities of Fe(CN)$_5^{2-}$ moiety present in the coatings were measured by integrating the current from cyclic voltammograms which were observed at a low scan rate of 1—4 mV s^{-1}.[10] The exposed area of each electrode was 0.17 cm^2.

The test solution was made of a distilled water and a supporting electrolyte (0.2 M (1 M=1 mol dm^{-3}) CF$_3$COONa) and its pH was adjusted to desired pH value with NaOH and CF$_3$COOH solutions. Solutions were deaerated with prepurified argon and experiments were conducted at 25 °C under an atmosphere of argon. All potentials are reported with respect to a sodium chloride saturated calomel electrode (SSCE).

Results and Discussion

In previous papers,[7,8] we have succeeded in evaluation of the kinetic parameters of the electron-transfer reactions within the PVP[Fe(CN)$_5^{3-/2-}$]$_n$ film coated on a BPG and at the BPG/film interface in a solution containing only supporting electrolyte. Such a success depended upon the insolubility of the PVP[Fe(CN)$_5^{3-/2-}$]$_n$ film coated on electrodes in an aqueous solution. Figure 1 shows typical voltammetric response which is obtained with a pyrolytic graphite electrode coated with PVP[Fe(CN)$_5^{3-/2-}$]$_n$ film in a 0.2 M CF$_3$COONa solution adjusted to pH 3.0 in dark or under irradiation. The anodic and cathodic peak potentials under irradiation were the same as those in dark. The voltammograms remained unchanged for several hours of continued cycling of the electrode potential in an acidic solution (pH 3.0) under the usual diffuse light, although the peak currents decreased gradually with increasing the irradiation time of visible light as mentioned below.

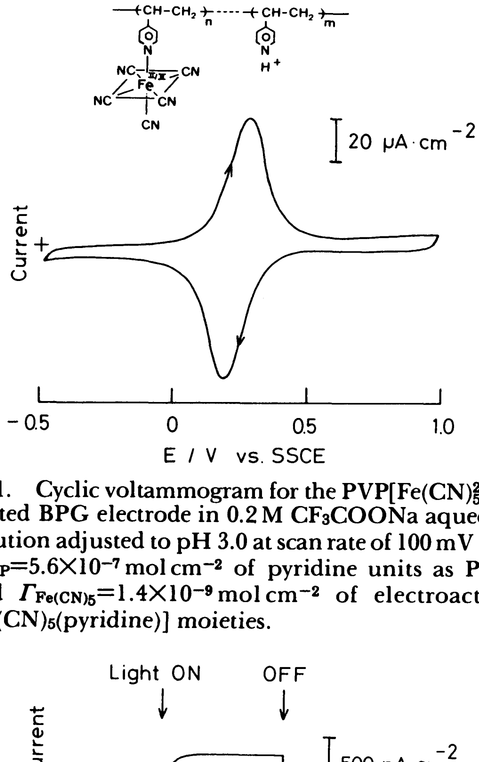


Fig. 1. Cyclic voltammogram for the PVP[Fe(CN)$_5^{2-}$]$_n$-coated BPG electrode in 0.2 M CF$_3$COONa aqueous solution adjusted to pH 3.0 at scan rate of 100 mV s^{-1}. Γ_{PVP}=5.6×10^{-7} mol cm^{-2} of pyridine units as PVP and $\Gamma_{Fe(CN)_5}$=1.4×10^{-9} mol cm^{-2} of electroactive [Fe(CN)$_5$(pyridine)] moieties.

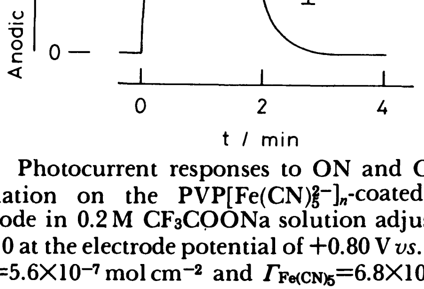


Fig. 2. Photocurrent responses to ON and OFF of irradiation on the PVP[Fe(CN)$_5^{2-}$]$_n$-coated BPG electrode in 0.2 M CF$_3$COONa solution adjusted to pH 3.0 at the electrode potential of +0.80 V *vs.* SSCE. Γ_{PVP}=5.6×10^{-7} mol cm^{-2} and $\Gamma_{Fe(CN)_5}$=6.8×10^{-9} mol cm^{-2}. Photocurrents were measured as the difference between the total current and its residual current measured with an uncoated BPG electrode at the same potential. Intensity of the visible light (400—800 nm) through UV and IR cut-off filters is 140 mW cm^{-2}.

Figure 2 demonstrates the photoresponses induced by ON and OFF of the irradiation of visible light (400—800 nm) on the PVP[Fe(CN)$_5$]$_n$ coated BPG electrode in a 0.2 M CF$_3$COONa solution (pH 3.0) at +0.80 V *vs.* SSCE. The same photocurrent response to ON and OFF of irradiation was obtained repeatedly. The anodic photocurrent responses were observed at the positive-side potential more than *ca.* 0.3 V and the values increased as the applied potential shifts to the positive side. The photocurrent was also influenced by pH of the solution in which the electrode is soaked, and its maximum was observed in the solution of pH 3.0. In the case of the electrode coated with PVP film (Γ_{PVP}=5.6×10^{-7} mol cm^{-2}) to which the Fe(CN)$_5^{2-}$ moieties of $\Gamma_{Fe(CN)_5}$=6.8×10^{-9} mol cm^{-2} were coordinated, the anodic photocurrent of 0.9 μA cm^{-2} was obtained at the potential of 0.80 V under the irradiation with the intensity of 140 mW cm^{-2} in a 0.2 M CF$_3$COONa solution (pH=3.0). No photocurrent response under irradiation were observed with a bare BPG electrode and the BPG electrode coated with PVP coordinating no Fe(CN)$_5^{2-}$ complexes. The cathodic photocurrents were also observed at the negative-side potential more than about 0.2 V, although their values were smaller than the values of the anodic ones.

Figure 3 shows the action spectrum of the anodic photocurrent obtained with the coated electrode, coverages of which are Γ_{PVP}=1.1×10^{-6} mol cm^{-2} and $\Gamma_{Fe(CN)_5}$=3.6×10^{-8} mol cm^{-2}, at the electrode potential of 0.80 V under irradiation of monochromatic light. The shift (about 20 nm) of the action spectrum to longer wavelengths than the absorption spectrum in water

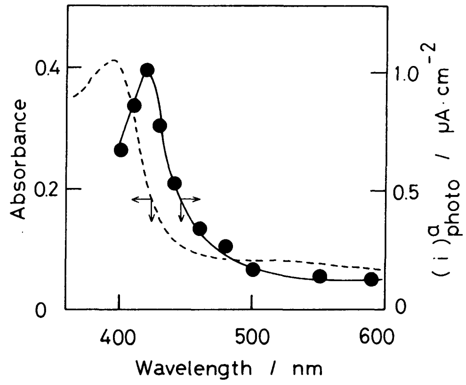


Fig. 3. Action spectrum for the anodic photocurrent observed with the PVP[Fe(CN)$_5^{2-}$]$_n$-coated electrode, coverages of which are Γ_{PVP}=1.1×10^{-6} mol cm^{-2} and $\Gamma_{Fe(CN)_5}$=3.6×10^{-8} mol cm^{-2}. (●) experimental; (----) absorption spectrum of 0.46 mM [Fe(CN)$_5^{2-}$]$_n$ coordinated to PVP of the average molecular weight 1980 in 0.2 M CF$_3$COONa aqueous solution adjusted to pH 3.0.

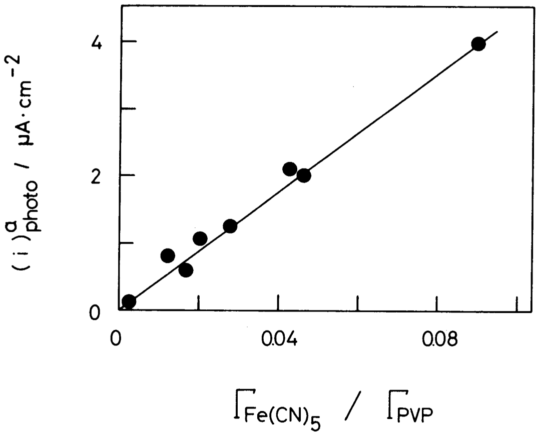


Fig. 4. Anodic photocurrent *vs.* $\Gamma_{Fe(CN)_5}/\Gamma_{PVP}$. Γ_{PVP} is constant (5.6×10^{-7} mol cm^{-2}). Other experimental conditions are the same as in Fig. 2.

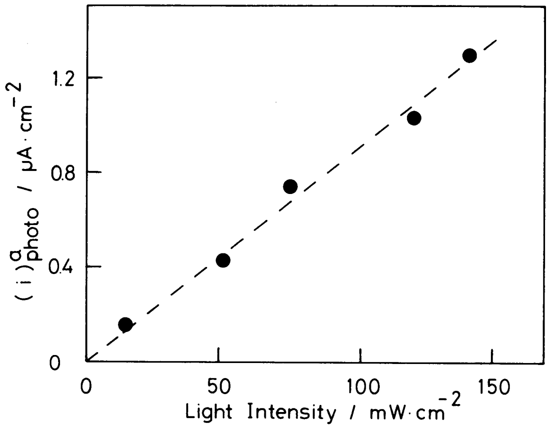


Fig. 5. Anodic photocurrent *vs.* light intensity. $\Gamma_{PVP}=5.6\times10^{-7}$ mol cm^{-2} and $\Gamma_{Fe(CN)_5}=1.6\times10^{-8}$ mol cm^{-2} at electrode potential +0.80 V *vs.* SSCE. Other experimental conditions are the same as in Fig. 2.

suggests some strong interaction[11] between the metal complex and PVP. Its shape almost agrees with that of the spectrum of the PVP[Fe(CN)$_5^{2-}$]$_n$ complexes formed with PVP of the average molecular weight 1980 in aqueous solutions, indicating that the excitation of the Fe(CN)$_5^{2-}$ complexes coordinated to the unprotonated PVP film is responsible for their photoelectrochemical behaviors.

Figure 4 shows the dependence of the anodic photocurrent, $(i)^a_{photo}$, upon the ratio $\Gamma_{Fe(CN)_5}/\Gamma_{PVP}$ at the constant concentration of pyridine ligand as PVP ($\Gamma_{PVP}=5.6\times10^{-7}$ mol cm^{-2}). The measurements were made in a 0.2 M CF$_3$COONa (pH 3.0) at the electrode potential of 0.80 V *vs.* SSCE under the irradiation of visible light with the intensity of 140 mW cm^{-2}. $(i)^a_{photo}$ was proportional to $\Gamma_{Fe(CN)_5}/\Gamma_{PVP}$. The dependence of the anodic photocurrent on the light intensity at the electrode potential of 0.80 V *vs.* SSCE was also measured and is shown in Fig. 5. $(i)^a_{photo}$ exhibits essentially linear dependence on the light intensity. The similar dependence of photocurrent on the light intensity has been reported in the photochemistry of an aqueous solution of [Fe(CN)$_6$]$^{4-}$.[6] At constant values of $\Gamma_{Fe(CN)_5}/\Gamma_{PVP}$, $(i)^a_{photo}$ increased with an increase in Γ_{PVP}.

Moggi *et al.*[5] have suggested that [Fe(CN)$_5$(OH$_2$)]$^{2-}$ is the main primary product of the photoreaction of [Fe(CN)$_6$]$^{3-}$ and the photochemical aquosubstitution reaction of [Fe(CN)$_5$(OH$_2$)]$^{2-}$ occurs simultaneously with the oxidation-reduction reaction which yields [Fe(CN)$_5$(OH$_2$)]$^{3-}$. They have confirmed that the products formed by a series of these reactions under long irradiation periods are Fe(OH)$_3$ (in neutral solution), prussian blue (in acidic solution), [Fe(CN)$_5$(OH$_2$)]$^{3-}$, Fe^{2+} and Fe^{3+}, and further that the pH of aqueous solutions slowly increases during irradiation in neutral solution and after some time tends to reach a constant value. On the basis of the mechanism (Scheme 1) proposed previously for photochemical reaction of the aqueous solution of [Fe(CN)$_6$]$^{3-}$, the mechanism of the photoelectrochemical reaction of PVP[Fe(CN)$_5$]$_n$ coated on the BPG can be expressed as follows:

$$\mathrm{PVP[Fe(CN)_5^{3-}]}_n - \mathrm{e} \rightleftharpoons \mathrm{PVP[Fe(CN)_5^{2-}]}_n, \tag{1}$$

$$\mathrm{PVP[Fe(CN)_5^{2-}]}_n \xrightarrow{h\nu} \mathrm{PVP[Fe(CN)_5^{2-}]}_n^*, \tag{2}$$

$$\mathrm{PVP[Fe(CN)_5^{2-}]}_n^* \longrightarrow \mathrm{PVP[Fe(CN)}_{5-x}\mathrm{(OH_2)}_x^{(2-x)-}]_n, \tag{3}$$

$$\mathrm{PVP[Fe(CN)}_{5-x}\mathrm{(OH_2)}_x^{(2-x)-}]_n \xrightarrow{\mathrm{OH^-}} \mathrm{PVP,\ Fe(OH)_3,\ CN^-}, \tag{4}$$

$$\mathrm{PVP[Fe(CN)}_{5-x}\mathrm{(OH_2)}_x^{(2-x)-}]_n \xrightarrow{\mathrm{H^+}} \mathrm{PVPH^+,\ Fe^{2+},\ HCN}, \tag{5}$$

$$\mathrm{PVP[Fe(CN)}_{5-x}\mathrm{(OH_2)}_x^{(2-x)-}]_n \longrightarrow \mathrm{PVP[Fe(CN)}_{5-x}\mathrm{(OH_2)}_x^{(3-x)-}]_n, \tag{6}$$

where, Eq. 1 shows the electrode reaction of PVP[Fe(CN)$_5^{3-/2-}$]$_n$ couple, PVP[Fe(CN)$_5^{2-}$]$_n^*$ is the excited species formed from PVP[Fe(CN)$_5^{2-}$]$_n$ by the irradiation of visible light, PVPH$^+$ is the protonated PVP, Eqs. 3 and 6 denote aqua-substitution and thermal reduction reactions, respectively, and Eqs. 4 and 5 show the decomposition reactions in neutral and acidic solutions, respectively. If this series of the reaction mechanism is applicable to the present system, anodic photocurrent could not be observed for the longer irradiation time than that which is enough for the reaction expressed by Eq. 2 to be terminated. However, when the PVP[Fe(CN)$_5^{2-}$]$_n$ coated on electrode, the coverages of which were $\Gamma_{PVP}=2.8\times10^{-7}$ mol cm^{-2} and $\Gamma_{Fe(CN)_5}=1.9\times10^{-9}$ mol cm^{-2}, was irradiated with visible light for 30 h in a 0.2 M CF$_3$COONa solution (pH 3.0) at the electrode potential of 0.80 V *vs.* SSCE, total amount of electricity, Q_p, that flowed during irradiation was estimated to be 1.8×10^{-3} coulomb cm^{-2}, which corresponds to 1.9×10^{-8} mol cm^{-2}. After 30 h, PVP[Fe(CN)$_5^{2-}$]$_n$ of $\Gamma_{Fe(CN)_5}=2.0\times10^{-10}$ mol cm^{-2} remained still confined in the PVP film on electrode surface. The concentration of Fe(CN)$_5^{2-}$ moiety decreased to about 10% of its initial value, nevertheless the value of Q_p corresponded to about ten times the initial concentration of Fe(CN)$_5^{2-}$ moiety. The anodic photocurrent after 30 h was also about 10% of its initial value, although about 80% of its initial value was lost within 1 h of irradiation. The decays in the current and in the concentration of the $\mathrm{Fe(CN)_5}$ complex are rapid and almost exponential. Judging from the fact that the redox potentials of $\mathrm{[Fe(CN)_6]^{4-/3-}}$ and $\mathrm{[Fe(CN)_5(py)]^{3-/2-}}$ (where py=pyridine) couples were 0.20 V *vs.* SSCE and that of $\mathrm{[Fe(CN)_5(OH_2)]^{3-/2-}}$ was 0.09 V *vs.* SSCE at a bare BPG in aqueous solutions, if the aquoated complex, *i.e.*, $\mathrm{[Fe(CN)_{5-\mathit{x}}(OH_2)_\mathit{x}]^{(2-\mathit{x})-}}$ formed during the photochemical reaction of $\mathrm{Fe(CN)_5^{2-}}$ remains in the PVP film without any dissociation, the peak potentials of voltammograms would be different from those for $\mathrm{Fe(CN)_5^{3-/2-}}$ couple coordinated to the unprotonated PVP film. However, the redox potential estimated from cyclic voltammogram obtained with the $\mathrm{PVP[Fe(CN)_5]_\mathit{n}}$-coated electrode which was irradiated with visible light for 30 h was the same as that (0.2 V *vs.* SSCE) obtained with the same electrode before irradiation (see Fig. 1). Further, $\mathrm{Fe^{2+}}$ aqua ion as Prussian blue was undetected.

From these results, it seems unlikely that the similar mechanism (Eqs. 1—6) to the photochemical reaction of $\mathrm{[Fe(CN)_6]^{3-}}$ in aqueous solution is applicable to the photoelectrochemical reaction of $\mathrm{PVP[Fe(CN)_5]_\mathit{n}}$ coated on the BPG. In the place of reactions expressed by Eqs. 3—6, we can consider the following reaction mechanisms for the photochemical reaction under consideration:

$$\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}^{*} + H_2O \longrightarrow PVP[Fe(CN)_5^{2-}]_\mathit{n} + 1/2O_2 + 2H^+}, \qquad (7)$$

$$\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}^{*} \longrightarrow PVP^+[Fe(CN)_5^{3-}]_\mathit{n}}, \qquad (8)$$

$$\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}^{*} + (BPG) \longrightarrow PVP[Fe(CN)_5^{3-}]_\mathit{n} + (BPG)^+}, \qquad (9)$$

where, $\mathrm{PVP^+[Fe(CN)_5^{3-}]_\mathit{n}}$ denotes the species resulting from oxidation of pyridine ring and/or vinyl group of PVP, $\mathrm{(BPG)^+}$ denotes the product obtained from oxidation of the BPG material itself by the $\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}^{*}}$. IR absorption spectra of the $\mathrm{PVP[Fe(CN)_5]_\mathit{n}}$ coated on the BPG after long-time irradiation (30 h) demonstrated the new absorption peak which seems to be characteristic of carbonyl group at 1670 $\mathrm{cm^{-1}}$. This suggests the formation of carbonyl group which is caused by Eq. 8 during the irradiation of visible light, although the details of this reaction mechanism are not clear. From the reaction expressed by Eq. 7, the evolution of oxygen is expected under long-time irradiation but has not been detected by gas chromatography. Figure 6 demonstrates the decay in the anodic photocurrent under the irradiation. As seen from this figure, the electricity, Q_p, that flows as a photocurrent during 35 h irradiation is estimated to be 9.4×10^{-3} coulomb $\mathrm{cm^{-2}}$, which corresponds to 9.7×10^{-8} mol $\mathrm{cm^{-2}}$. This value of Q_p corresponded to fifty times the initial concentration of the $\mathrm{Fe(CN)_5^{2-}}$ complexes and about five times the initial concentration of pyridine ligand as PVP. Therefore, the process expressed by Eq. 9 (*i.e.*, the oxidation of the BPG electrode used as an anode) seems to be mainly responsible for the photochemical responses, since vinylpyridine moiety of PVP, not oxidized, is still on the BPG surfaces.

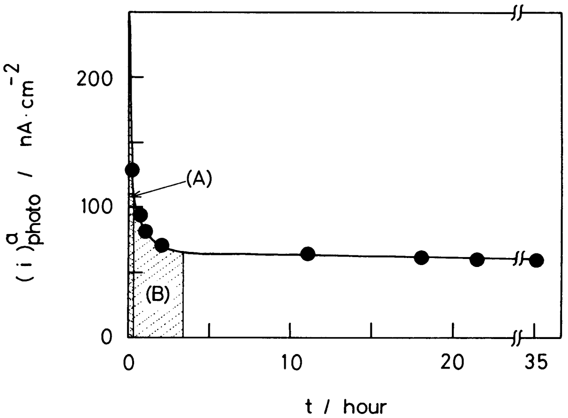


Fig. 6. Anodic photocurrent *vs.* irradiation time. Initial value of $\Gamma_\mathrm{PVP}=1.8\times10^{-8}$ mol $\mathrm{cm^{-2}}$ and initial value of $\Gamma_\mathrm{Fe(CN)_5}=1.9\times10^{-9}$ mol $\mathrm{cm^{-2}}$. Other experimental conditions are the same as in Fig. 2. Area (A) corresponds to the initial value of $\Gamma_\mathrm{Fe(CN)_5}$; area (B) corresponds to the initial value of Γ_PVP.

The present results conclude that the mechanism of the photochemical reaction following the oxidation of $\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}}$ coated on the BPG surfaces is different from that of an aqueous solution of $\mathrm{[Fe(CN)_6]^{3-}}$ [5] and photochemical processes are oxidation-reduction reactions expressed by Eqs. 8 and 9. Further, it became to be clear that the photoaquation and the subsequent dissociation reactions, which are very familiar in the photochemistry of aqueous solutions of $\mathrm{[Fe(CN)_6]^{3-}}$ and $\mathrm{[Fe(CN)_6]^{4-}}$,[4,5] seem to be suppressed in the polymer domains. However, some unsolved problems still remain: (1) A rapid, almost exponential decay in the anodic photocurrent occurred during the short-time (less than 1 h) irradiation. We have no idea to explain such a behavior at present. (2) Anodic photocurrents were influenced by pH of the solution in which the $\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}}$-coated electrode was soaked, and their maxima were observed for the solution of pH 3.0. It seems to be considered that the change of morphology of the $\mathrm{Fe(CN)_5^{2-}}$ complex polymer with pH results in the pH-dependence of the photocurrent. (3) The cathodic photocurrents were also observed at the negative-side potential more than about 0.20 V and their values were smaller than the anodic ones at the same coating electrode. The reduction of the BPG electrode by the $\mathrm{PVP[Fe(CN)_5^{2-}]_\mathit{n}^{*}}$ may result in the cathodic photocurrents but we have no direct evidence to support this interpretation.

In conclusion, we emphasize that modification of the carbon electrode by coating the photosensitive species on it can generate the photocurrent.

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