

A Photoelectrode based on Visible Photolysis of a Metallopolymer Film

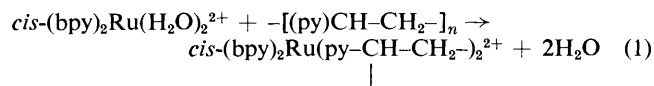
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Visible photolysis of electrodes coated with films of $(2,2'$ -bipyridine) $_2$ Ru[poly(4-vinylpyridine)] $_2^{2+}$ gives large cathodic photocurrents when irradiated in the presence of aqueous $\text{Co}(\text{ox})_3^{3-}$ (ox^{2-} is oxalate anion, $\text{C}_2\text{O}_4^{2-}$).

The photochemical and photophysical properties of Ru-bpy (bpy = 2,2'-bipyridine) chromophores bound to poly(4-vinylpyridine) (PVP) have been reported¹ as has an excited-state photoelectrochemical cell for the production of O_2 based on the oxidative quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by $\text{Co}(\text{ox})_3^{3-}$ (ox^{2-} is oxalate $\text{C}_2\text{O}_4^{2-}$) in acidic solution.² We describe here a photoelectrode which is related to the homogeneous cell but based on visible photolysis of a Ru-bpy containing film.

The metallopolymer used in our experiments was prepared by the reaction between $\text{cis}(\text{bpy})_2\text{Ru}(\text{H}_2\text{O})_2^{2+}$ and PVP $\{ -[\text{CH}_2\text{-CH}(\text{py})-]_n, n = 40 \}$ (py = pyridine) as shown in equation 1. A series of metallopolymers of this type have



been prepared and characterized previously.^{3,4} In the sample used here, the ratio of bound to unbound pyridyl sites in the polymer was 2 to 20 and the sample will be referred to as $(\text{bpy})_2\text{Ru}(\text{PVP})_{2/20}^{2+}$. Thin films of the polymer were prepared by evaporating methanolic solutions onto one side of a platinum flag electrode. Cyclic voltammetry experiments on the polymer-coated electrodes showed the presence of the expected $\text{Ru}^{\text{II/III}}$ couple at +1.0 V vs. standard saturated calomel electrode (S.S.C.E.) in a solution containing 0.1 M Na_2SO_4 with the pH adjusted to 2.0 using H_2SO_4 .^{3a} Surface coverages were estimated by using the areas under the voltammetric waves to determine the total charge passed.

A typical photocurrent of $45 \mu\text{A}/\text{cm}^2$ was observed (Figure 1) upon visible photolysis of a polymer-coated ($\Gamma = 1.8 \times 10^{-8} \text{ mol}/\text{cm}^2$) platinum flag electrode (ca. 1 cm^2) immersed in a solution containing 0.1 M Na_2SO_4 (pH = 2.0, adjusted with H_2SO_4) and 0.01 M $\text{K}_3\text{Co}(\text{ox})_3$. The electrode was adjusted to +0.3 V vs. S.S.C.E. using a potentiostat. The photoresponse of the electrode was independent of the applied potential over the range +0.3 V to +0.6 V vs. S.S.C.E. The cell was pre-purged with nitrogen and was unstirred. The light source was a 300 W Xe lamp with appropriate filters to eliminate u.v. irradiation. A one-compartment cell with an optical flat on one side was employed with the electrode mounted parallel and near to the optical face. Using the same conditions, but with a bare,

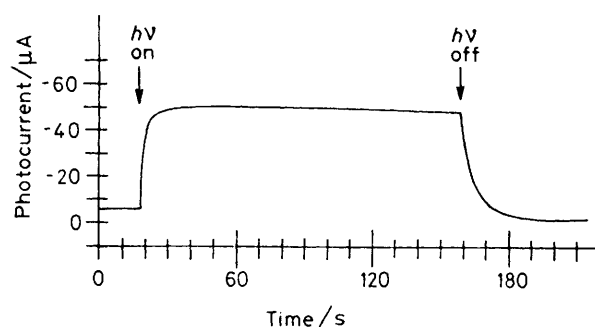
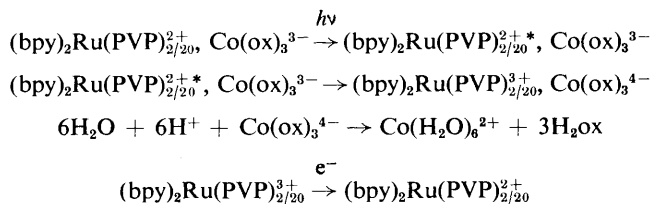


Figure 1. Photocurrent response of a Pt electrode coated with $(\text{bpy})_2\text{Ru}(\text{PVP})_{2/20}^{2+}$ in aqueous solution. Note that since the electrode area is 1 cm^2 , the vertical axis is also the photocurrent density in $\mu\text{A}/\text{cm}^2$.

uncoated platinum electrode, gave essentially zero photocurrent.

The photocurrent rises and reaches a steady-state value quickly. The high current levels can be sustained for at least 1 h. The steady-state current increases with increased concentration of added $\text{Co}(\text{ox})_3^{3-}$ and reaches an upper limit at $[\text{Co}(\text{ox})_3^{3-}] > 0.005 \text{ M}$.

The apparent origin of the photocurrent is in the excitation of the Ru-bpy chromophoric sites within the metallopolymer followed by electron-transfer quenching by $\text{Co}(\text{ox})_3^{3-}$ as shown in Scheme 1.



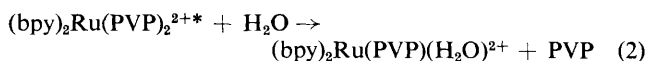
Scheme 1

In acid solution the metallopolymer is polycationic owing to the Ru^{II} and pyridinium sites and $\text{Co}(\text{ox})_3^{3-}$ is sequestered into the film by anion exchange.⁴ Following oxidative quenching and irreversible loss of oxalate from Co^{II} in acid solution,⁵

Ru^{III} sites are created in the film. The Ru^{III} sites are reduced by electron transfer from the electrode which is known to be a relatively facile process from the electrochemical properties of the film.^{3,4} In the related homogeneous cell mentioned above, based on Ru(bpy)₃²⁺ and Co(ox)₃³⁻, the photocurrent was observed to fall with time.⁶ This decrease was attributed to reduction of Ru(bpy)₃³⁺ by released oxalate which is in competition with diffusion to the electrode. Although not a point studied in detail, a similar fall off in photocurrent for the thin-film photoelectrode was not observed.

The proposed mechanism is supported by a number of experimental facts. An analogous scheme based on optical excitation of Ru(bpy)₃²⁺ has been established in homogeneous solution.^{2,5} The Ru-bpy sites in the polymer have been shown to undergo both oxidative and reductive quenching in solution.¹ The photoresponse of the electrode as a function of wavelength in the region 420–650 nm closely follows the absorption spectrum of the chromophore. The steady-state photocurrent increases both with film thickness ($\Gamma = 6.3 \times 10^{-9}$ to 2.8×10^{-8} mol/cm²) and with quencher concentration $\{[\text{Co(ox)}_3^{3-}] = 5.0 \times 10^{-5}$ to 3.7×10^{-3} M\} as noted above.

At low concentrations of Co(ox)₃³⁻ ($< 1.0 \times 10^{-4}$ M) the photocurrent response is an initial burst followed by a relatively low steady-state current. The integrated current for the initial burst is approximately three times that for the surface coverage of ruthenium redox sites as measured by cyclic voltammetry. This result suggests that nearly complete photo-oxidation of Ru^{II} sites to Ru^{III} can occur in the films and at low [Co(ox)₃³⁻] the photocurrent is limited by diffusion of Co(ox)₃³⁻ to or into the film. The films are less stable when photolysed at low [Co(ox)₃³⁻] apparently owing to photochemical loss of PVP (equation 2) which is a known photoreaction for the polymer.^{1,3b} At high [Co(ox)₃³⁻] in



the films the extent of quenching must be high, photochemical ligand loss is not a competitive process, and the films are stable.

The quantum yield per photon for photolysis at 436 nm was determined to be $\phi(436 \text{ nm}) = 11.3 \pm 1.5\%$ $\{[\text{Co(ox)}_3^{3-}] = 0.005 \text{ M}\}$ from the steady-state photocurrent (4.5 μA) after taking into account the absorbance of the film. The absorbance of the film ($A_{\text{film}} = 0.18$) was estimated by preparing a film using identical conditions and evaporating it onto a portion of glass slide of the same area as the electrode. The total light intensity striking the electrode was 2.85×10^{-9} Einstein/s as measured by iron(III) oxalate actinometry.

Although the importance of incorporation of the quencher into the films by ion-pairing has been suggested, it is

important to note that photocurrents can also be observed with cationic quenchers. Photolysis of a thin-film electrode in the presence of Co(NH₃)₅Cl²⁺ also produces a photocurrent. Co(NH₃)₅Cl²⁺ is known to quench Ru(bpy)₃^{2+*} in acidic solution to give Ru(bpy)₃³⁺, Co(H₂O)₆²⁺, NH₄⁺, and Cl⁻,^{5a} a reaction which has also provided a basis for a homogeneous, excited-state photoelectrochemical cell.⁶ The quantum yield per photon for Co(NH₃)₅Cl²⁺ as quencher is $< 3\%$ using the same conditions as described above for Co(ox)₃³⁻.

Although the photocurrents described here are obtained at the expense of the sacrificial reagent Co(ox)₃³⁻, the observations are clearly of value. In this experiment the light into redox energy conversion step is transferred from the more traditional photosensitized semiconductor/solution interface⁷ to a polymer film on a conducting electrode (Pt). In this experiment the electrode acts merely as a collector of photochemically produced electrons or electron holes. The fabrication of a 'device' by evaporation of a chromophoric film becomes trivial and the demands on the composition of the electrode are relatively slight. If sufficiently high separation efficiencies can be realized with reversible quencher systems, the polymer-film electrodes could provide the basis for a series of interesting photovoltaic and photoelectrochemical applications.

Acknowledgements are made for grants from the Army Research Office, Durham (T. J. M.) and the National Science Foundation (R. W. M.).

Received, 1st October 1982; Com. 1152

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