Electrochemistry and Photocurrents of the Tris(bipyridine)ruthenium(II) and Methyl Viologen Cations Immobilized in Carrageenan Hydrogel

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A procedure for immobilization of both a photochromophore, tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$), and a quencher, methyl viologen (MV^{2+}), within a carrageenan hydrogel matrix at an electrode surface is described. $Ru(bpy)_3^{2+}$ and MV^{2+} exhibited diffusion coefficients that ranged from 10^{-7} to 10^{-6} cm^2/s in the hydrogel, which represents an improvement over other immobilization matrices. Photolysis of the resulting hydrogel surface modified electrodes gave rise to a significant photocurrent which depended on the concentrations of $Ru(bpy)_3^{2+}$, MV^{2+}, and triethanolamine and resulted in a maximum value of 12 $\mu A/cm^2$ after the hydrogel was cured with a solution containing 5 mM $Ru(bpy)_3^{2+}$ and 50 mM MV^{2+}. The photocurrent was the result of reoxidation of MV^+ at the electrode surface following reduction of MV^{2+} by photoexcited $Ru(bpy)_3^{2+}$. The quenching rate constant of $Ru(bpy)_3^{2+*}$ by MV^{2+} in the hydrogel was 4.2×10^8 M^{-1} s^{-1}. The photocurrent action spectrum was consistent with $Ru(bpy)_3^{2+}$ acting as the photochromophore. Offsetting the potential of the hydrogel electrode verified the role of the $MV^{2+/+}$ redox couple as the source of the current.

Introduction

In this paper we focus our attention on the electrochemical behavior of tris(2,2'-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, and methylviologen, MV^{2+}, cations in a hydrogel matrix and then examine the potential uses of this modified electrode surface for photochemical applications. The electrochemical behavior of $Ru(bpy)_3^{2+}$ and MV^{2+} has been investigated in other matrices, such as Nafion and montmorillonite clay.[1,2] On the basis of the $Ru(bpy)_3^{3+/2+}$ couple, diffusion coefficients in both media range from 10^{-9} to 10^{-11} cm^2/s compared to 10^{-5} to 10^{-6} cm^2/s in water.[1,2] The diffusion coefficient of MV^{2+} was 1 order of magnitude larger in Agarose impregnated with Nafion[3] but still lacked good electrolytic permittivity.

Recently[4] we reported the electrochemical behavior of a number of cations in carrageenan hydrogel and found that the diffusion coefficient of $Ru(bpy)_3^{2+}$ was within an order of magnitude of that obtained in water. Here we extend those studies to include MV^{2+} and a mixed $Ru(bpy)_3^{2+}/MV^{2+}$ system. In addition, we examine the combination of $Ru(bpy)_3^{2+}$, MV^{2+}, and the scavenger triethanolamine for generating photocurrent, as has been done in the past at other surface-modified electrodes.[5]

Experimental Section

Materials. κ-Carrageenan powder was obtained as a gift from FMC (research grade, 25% by weight sulfate groups). Methyl viologen (MV^{2+}) dichloride, tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ([Ru(bpy)_3]Cl_2·6H_2O), silver trifluoromethanesulfonate ($AgCF_3SO_3$), ethylenediamine dihydrochloride, potassium nitrate, and triethanolamine (TEOA) were purchased from Aldrich. Sodium perchlorate was purchased from Fisher and was also prepared by neutralization of $HClO_4$ (Fisher) with Na_2CO_3 (Fisher) and was recrystallized from water prior to use.

Preparation of Compounds. The trifluoromethanesulfonate (triflate) salts of $Ru(bpy)_3^{2+}$ and MV^{2+} were prepared by metathesis. An aqueous solution of silver triflate was slowly added to an aqueous solution of the appropriate dichloride salt in a 2:1 mole ratio. The resulting AgCl precipitate was removed by filtration, and the filtrate was concentrated in vacuo until the triflate precipitate began to form. After the solution was cooled to 0 °C to effect further precipitation, it was filtered and the precipitate was washed with cold ether and dried in a vacuum desiccator. Elemental analyses of the compounds were performed by MHW Laboratories. Anal. Found (calcd) for [Ru(bpy)_3](CF_3SO_3)_2: C, 44.36 (44.25); H, 3.28 (2.77); N, 9.78 (9.68). Found (calcd) for MV-(CF_3SO_3)_2: C, 34.95 (34.69); H, 3.28 (2.89); N, 5.76 (5.78).

Preparation of the Working Electrodes. Two different types of working electrodes were used in our studies. The first was a platinum-gauze electrode (Fisher, 52 mesh, 0.26-cm^2 area) which was cleaned by applying a potential of +1.2 V (vs Ag/AgCl) for 30 min in 1.0 M H_2SO_4. The second electrode was a platinum disk (area 0.147 cm^2) which was cleaned on a buffing wheel followed by sonication. A cylindrical Teflon

shroud was then slipped around the disk. Normally a 4% (w/v) carrageenan/aqueous solution (sulfate groups $\leq$0.1 M) was prepared by warming. The Pt gauze was then dipped into the 4% carrageenan solution, withdrawn, dipped into a curing solution for 30 min, and rinsed with water. The Pt-disk electrode was inverted, and the well was filled with 4% carrageenan solution; after cooling, the electrode was dipped into the curing solution for 30 min and rinsed with water. Normally the curing solution contained either 100 mM ethylenediamine dihydrochloride (defined as method 1 in ref 4), or 20 mM $Ru(bpy)_3^{2+}$ or 20 mM MV^{2+} (defined as method 2 in ref 4). The coatings on both electrodes were ca. 2 mm thick; total hydrogel volume was ca. 0.05 mL for the gauze electrode and ca. 0.03 mL for the disk electrode.

$Ru(bpy)_3^{2+}$ and MV^{2+} were immobilized in the carrageenan hydrogel on an electrode surface by two methods. In method 1, an ethylenediamine dihydrochloride cured hydrogel coated on a Pt electrode was placed in an aqueous solution of $Ru(bpy)_3^{2+}$ or MV^{2+} containing 0.10 M KNO_3 and repeatedly cycled through the 3+/2+ ($Ru(bpy)_3^{2+}$) or 2+/1+ (MV^{2+}) redox couple until a steady-state cyclic voltammogram was achieved and remained constant over a 6-h period. In method 2, a hydrogel-coated Pt electrode was cured in a solution containing $Ru(bpy)_3^{2+}$ or MV^{2+}, followed by current/voltage cycling in a solution containing only background electrolyte until a steady-state cyclic voltammogram was obtained. The method used to determine the concentrations of redox-active species in the hydrogel has been described previously.[4] The following $Ru(bpy)_3^{2+}$;[6] λ = 450 nm, ϵ = 1.3 $\times 10^4$ M^{-1} cm^{-1}; λ = 288 nm, ϵ = 6.0 $\times 10^4$ M^{-1} cm^{-1}; λ = 260 nm, ϵ = 2.0 $\times 10^4$ M^{-1} cm^{-1}. MV^{2+};[7] λ = 288 nm, ϵ = 6.3 $\times 10^3$ M^{-1} cm^{-1}; λ = 260 nm, ϵ = 1.9 $\times 10^4$ M^{-1} cm^{-1}. Concentrations are precise to $\pm$5%. The concentration of cationic redox species in the hydrogel was found to be higher than its concentration in the cyclic voltammetry solution (method 1) or curing solution (method 2) for both methods of immobilization. The hydrogel-coated electrode with an immobilized cationic redox species can be removed from a solution containing the cationic redox species and placed in a solution containing only background electrolyte without any loss in the steady-state redox signal after continuous use for over 6 h. Optimum results were obtained using 100 mM KNO_3 as the background electrolyte when method 1 was used

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Table I. Electrochemical Parameters for MV^{2+}/Carrageenan Hydrogel Electrodes[a]

electrode	immob method[b]	[MV^{2+}], mM		D_{exp},[d] cm^2/s	$E_{1/2}$,[e] V	ΔE_p,[f] V
		hydrogel[c]	soln			
Pt disk	NA[i]	NA	5.0	1.9×10^{-5} [g,h]	−0.62	0.058
Pt gauze	NA	NA	5.0	1.8×10^{-5} [g]	−0.62	0.102
Pt gauze/gel	1	20	5.0	9.3×10^{-7} [g]	−0.60	0.102
Pt gauze/gel	2	14	0.0	4.4×10^{-7} [g]	−0.56	0.125
Pt disk/gel	2	16	0.0	1.9×10^{-6} [h]	−0.64	0.140

[a] Background electrolyte 0.10 M KNO_3 for nongel electrode cyclic voltammetry and immobilization method 1; background electrolyte 0.05 M KNO_3/0.05 M $NaClO_4$ for immobilization method 2. [b] Immobilization methods 1 and 2 are defined in the Experimental Section. [c] Concentration of redox-active species in the hydrogel measured as described in the Experimental Section. [d] Standard deviation $\leq 10\%$ of reported value obtained from standard deviation of i_p vs $v^{1/2}$ (cyclic voltammetry) and Q vs $t^{1/2}$ (chronocoulometry) plots. [e] Reference Ag/AgCl; ±0.02 V. [f] For a scan rate of 10 mV/s. [g] Cyclic voltammetry. [h] Chronocoulometry. [i] Not applicable.

for immobilization and 50 mM $NaClO_4$/50 mM KNO_3 as the background electrolyte when method 2 was used for immobilization.[4]

Physical Measurements. UV–vis spectra were determined with a Perkin-Elmer Lambda Array 3840 UV–vis spectrophotometer and a Beckman Acta III spectrophotometer. Uncorrected excitation and emission spectra as well as emission quenching results were obtained with a Hitachi Perkin-Elmer 650-40 luminescence spectrophotometer. Luminescence lifetimes were determined in the hydrogel at room temperature using a PRA LN1000 pulsed N_2 laser, a PRA LN102 dye laser, a LeCroy 6880A transient digitizer, and an IBM PS/2 Model 60 microcomputer.

Cyclic voltammetry measurements were carried out with a BAS CV-27 potentiostat and with a unit that consisted of a PAR 173 potentiostat, a PAR 179 digital current converter, and a PAR 175 universal programmer, and the voltammograms were recorded with a Houston Instruments Model 100 X-Y recorder. Photocurrent measurements were made with a Pine RDE4 potentiostat, and the results were plotted with an IBM X-Y-T recorder. Chronocoulometry was performed with a PAR 273 potentiostat controlled by an IBM PS/2 Model 30 microcomputer.

The electrochemical experiments were conducted in a three-electrode cell with both modified and unmodified Pt-disk and Pt-gauze working electrodes, either a Ag/AgCl or a saturated sodium chloride calomel electrode (SSCE) as the standard electrode, and a Pt wire as the counter electrode. Solutions containing the appropriate electrolyte (0.1 M KNO_3, 0.1 M $NaClO_4$, or 0.05 M KNO_3/0.05 M $NaClO_4$) were deaerated with N_2 or Ar prior to use in electrochemical measurements. The polarographic redox potential, $E_{1/2}$, was taken as the average between the anodic and cathodic peak potentials $((E_{pc} + E_{pa})/2)$. The difference $E_{pa} - E_{pc}$ was taken as ΔE_p. Diffusion coefficients were determined by analyzing the scan rate dependence of the cyclic voltammograms over the range 5–250 mV/s using published procedures.[8,9] Plots of peak current (i_p) vs $v^{1/2}$ were linear with $R \geq 0.99$, and the experimental diffusion coefficients (D_{exp}) were calculated from the slopes of these plots.[8] D_{exp} determinations were also made by chronocoulometry from the slope of Q vs $t^{1/2}$ plots and were found to agree with values obtained by cyclic voltammetry. Diffusion coefficient data obtained for a bare Pt-disk electrode were found to be consistent with values reported in the literature for $Ru(bpy)_3^{3+/2+}$.[10] The influence of uncompensated solution resistance on our results was judged to be insignificant on the basis of the following observations. In cyclic voltammetry experiments, the observed peak to peak separations were found to be independent of the redox couple concentrations and electrode area and the heterogeneous electron transfer rate constant was found to be independent of scan rate. The experimental diffusion coefficients (D_{exp}) did not change with electrode area, and values obtained from cyclic voltammetry and chronoamperometry experiments agree to within experimental error.

Photolysis was effected with a Schoeffle system consisting of a 1000-W xenon lamp in an LH 151 N lamp housing, a Model LPS 255 HR universal arc lamp power supply, and a GM 252 dual-grating monochromator. The optical components and electrochemical cell were mounted on an optical rail, the appropriate electrodes were connected to the potentiostat, and the shutter was removed to measure the photocurrent.

In a typical experiment, the well of the Pt-disk electrode was filled with carrageenan and the electrode was cured in a 5 mM $Ru(bpy)_3^{2+}$ solution (method 2).[4] After this step, it was placed in an electrochemical cell containing a solution of 20 mM MV^{2+}, 50 mM KNO_3, and 50 mM $NaClO_4$. Continuous scanning by cyclic voltammetry was commenced

between +1.25 and −0.90 V vs SSCE at 50 mV/s. Scanning was allowed to proceed uninterrupted until a steady-state current of the $MV^{2+/+}$ couple was noted. The electrode was then rinsed with water, placed in the center compartment of the H-cell which contained 50 mM KNO_3, 50 mM $NaClO_4$, and 1 M TEOA, and then irradiated with 436-nm light.

Results and Discussion

Electrochemistry of $Ru(bpy)_3^{2+}$ or MV^{2+} Immobilized in Carrageenan Hydrogel. $Ru(bpy)_3^{2+}$ was successfully immobilized in a carrageenan hydrogel coating on Pt-gauze and Pt-disk electrodes by methods 1 and 2. Stable electrodes were produced in which the redox couple exhibited quasi-reversible electrochemistry with $E_{1/2} = 1.06$ V (vs Ag/AgCl).[4]

The redox-active quencher MV^{2+} was also immobilized in a carrageenan hydrogel on an electrode surface by methods 1 and 2. Table I lists D_{exp}, $E_{1/2}$, and ΔE_p values and the concentrations of MV^{2+} in the hydrogel. The observed electrochemistry is quasi-reversible. For both methods of immobilization, the concentration of MV^{2+} in the hydrogel was higher than the concentration in the bulk solution. The hydrogel-modified electrode with immobilized MV^{2+} can be removed from a solution containing MV^{2+} and placed in a solution containing only background electrolyte with minimal leakage and retention of the $MV^{2+/+}$ redox signal. Both of these observations provide evidence for exchange of the MV^{2+} cation into the carrageenan matrix, as opposed to simple diffusion into and out of the matrix.

The small decrease in D_{exp} for MV^{2+} on going from aqueous solution to a carrageenan hydrogel immobilization matrix is comparable in magnitude to the corresponding decrease observed for $Ru(bpy)_3^{2+}$.[4] This is consistent with our report[4] that electron hopping may contribute to charge propagation in a carrageenen hydrogel when the immobilized redox couple has a large self-exchange rate constant. The self-exchange rate constant for $Ru(bpy)_3^{2+/3+}$ is 10^9 M^{-1} s^{-1},[11] and the estimated value for $MV^{2+/+}$ is $>10^8$ M^{-1} s^{-1}.[12]

The D_{exp} values for $Ru(bpy)_3^{2+}$ and MV^{2+} immobilized in carrageenan were 2–3 orders of magnitude larger than those found previously for the same redox species in the cation-exchange matrix Nafion[2,12] and were 4–5 orders of magnitude larger than those found for montmorillonite clay.[3,13] This further illustrates that carrageenan hydrogel provides a very open and porous matrix for the immobilization of one or more redox-active species.

Electrochemistry of $Ru(bpy)_3^{2+}$ and MV^{2+} Coimmobilized in Carrageenan. As we have shown previously, one of the advantages of carrageenan is that two redox couples can be immobilized simultaneously without degradation of their electrochemical properties or stability.[4] In this work, $Ru(bpy)_3^{2+}$ and MV^{2+} were coimmobilized in carrageenan hydrogel on an electrode surface. This allowed the immobilization of both the photocatalyst and the quencher near the electrode surface, where they are preconcentrated for optimization of photochemical applications. Coimmobilization was accomplished by using a $Ru(bpy)_3^{2+}$-cured

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Table II. Electrochemical Parameters for $Ru(bpy)_3^{2+/3+}$ and MV^{2+} Coimmobilized in Carrageenan Hydrogel Electrodes[a]

electrode	couple	D_{exp},[b] cm²/s	$E_{1/2}$,[c] V	ΔE_p,[d] V	[gel],[e] mM
Pt gauze	$Ru(bpy)_3^{3+/2+}$	6.6 × 10⁻⁷	1.06	0.075	15
Pt gauze	$MV^{2+/+}$	4.0 × 10⁻⁷	−0.59	0.122	22
Pt disk	$Ru(bpy)_3^{3+/2+}$	1.7 × 10⁻⁶	1.06	0.090	16
Pt disk	$MV^{2+/+}$	1.9 × 10⁻⁶	−0.63	0.150	12

[a] Cured in 20 mM $Ru(bpy)_3^{2+}$; current/voltage to steady state in 5.0 mM MV^{2+}; electrolyte 0.05 M $NaClO_4$ and 0.05 M KNO_3. [b] Results obtained by cyclic voltammetry for Pt-gauze electrode and by chronocoulometry for Pt-disk electrode; standard deviation ≤10% of reported value obtained from standard deviation of i_p vs $v^{1/2}$ (cyclic voltammetry) and Q vs $t^{1/2}$ (chronocoulometry) plots. [c] Reference Ag/AgCl; ±0.02 V. [d] For a scan rate of 10 mV/s. [e] Concentration of redox-active species in the hydrogel measured as described in the Experimental Section.
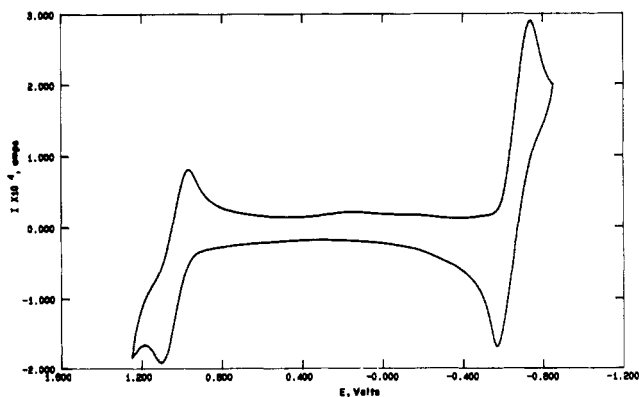
Figure 1. Cyclic voltammogram of an aqueous solution containing 50 mM $NaClO_4$ and 50 mM KNO_3 obtained by using a Pt-disk hydrogel electrode cured with 20 mM $Ru(bpy)_3^{2+}$ and 20 mM MV^{2+} as described in the text (scan rate 50 mV/s; potential on the horizontal axis in volts vs SSCE).

Figure 2. Spectra of a carrageenan hydrogel cured with 5.0 mM $Ru(bpy)_3^{2+}$: (a) excitation spectrum obtained with λ_{em} = 617 nm; (b) emission spectrum obtained with λ_{ex} = 436 nm. Inset: Action spectrum for the photocurrent observed with a Pt-disk hydrogel electrode cured with a 5 mM $[Ru(bpy)_3]Cl_2/10$ mM KNO_3 solution. MV^{2+} was incorporated into the hydrogel by the scanning technique outlined in the text. The light intensity at each wavelength was adjusted to a constant level by adjusting the slits of the monochromator. The value of the photocurrent at each wavelength was the maximum obtained at the diffusion-controlled limit.

carrageenan hydrogel (method 2) on a Pt-gauze electrode for cyclic voltammetry experiments in a 5.0 mM MV^{2+} solution containing the mixed background electrolytes (0.05 M KNO_3 and 0.05 M $NaClO_4$). The $Ru(bpy)_3^{2+}$/carrageenan hydrogel electrode was repetitively scanned from +1.40 to −0.85 V (vs Ag/AgCl) until the currents for both the $MV^{2+/+}$ and $Ru(bpy)_3^{2+/3+}$ couples remained constant. A representative cyclic voltammogram for this system is shown in Figure 1. The values of D_{exp}, $E_{1/2}$, and ΔE_p and the concentration of each redox species in the hydrogel are given in Table II. The excellent diffusion properties found for each individual redox species within the hydrogel were retained in the combination $Ru(bpy)_3^{2+}$/MV^{2+}/carrageenan hydrogel electrode.

Photophysical Behavior of Ru(bpy)₃²⁺ in the Hydrogel. Carrageenan hydrogel is also transparent to visible light. We have shown electrode stability and excellent diffusion properties for the photocatalyst, $Ru(bpy)_3^{2+}$, and the quencher, MV^{2+}, coimmobilized in carrageenan hydrogel on a Pt-gauze or -disk electrode. This hydrogel modification preconcentrates the photocatalyst at the electrode surface, where it can be easily regenerated for further use. As a result, this electrode with a transparent hydrogel coating containing immobilized $Ru(bpy)_3^{2+}$ and MV^{2+} is ideal for photochemical studies. A platinum-disk substrate was used for the photochemistry experiments.

The photophysical behavior of $Ru(bpy)_3^{2+}$ in the carrageenan hydrogel matrix was found to be similar to that in aqueous solution. The absorption spectrum of the hydrogel, cured with 1 mM $Ru(bpy)_3^{2+}$, on a quartz slide was determined by transmission. Maxima were located at 459, 290, and 248 nm compared to 450, 290, and 250 nm in water.[14] The excitation and emission spectra obtained by reflection from the hydrogel cured with 5 mM $Ru(bpy)_3^{2+}$ (method 2) are shown in Figure 2. The excitation spectrum followed the profile of the low-energy absorption manifold, although the maximum was shifted to 468 nm. The emission maximum at room temperature was located at 617 nm, an energy similar to that found in water.[15]
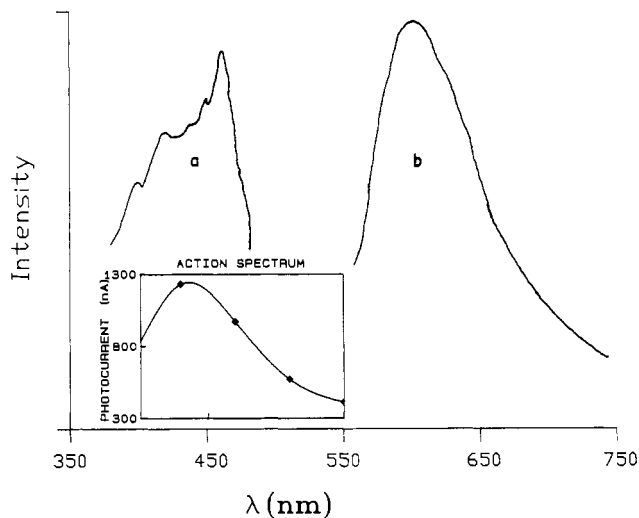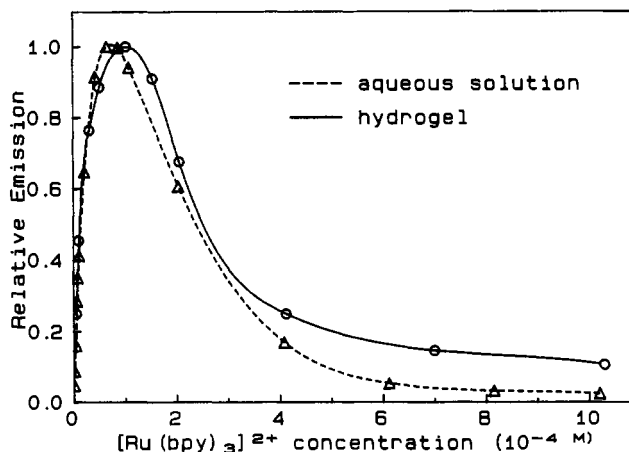

Figure 3. Excited-state self-quenching by $Ru(bpy)_3^{2+}$ in water and the hydrogel. For illustrative purposes, relative emission on the vertical axis was used.

The excited-state lifetime of $Ru(bpy)_3^{2+*}$ in a carrageenan hydrogel cured with 1 mM $Ru(bpy)_3^{2+}$ was found to be 626 ns. This value is comparable to that found in aqueous solution.[16] In addition, incorporation of MV^{2+} in the hydrogel quenched the emission of $Ru(bpy)_3^{2+*}$. A Stern–Volmer constant of 260 ± 16 M⁻¹ was obtained over the 0–2.5 mM MV^{2+} concentration range

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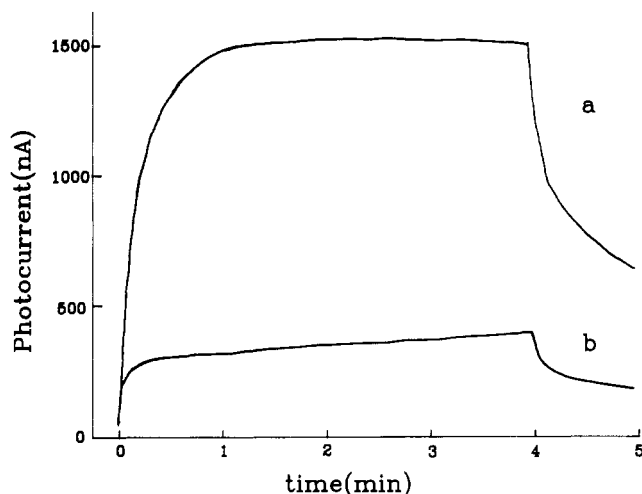
Figure 4. Typical photocurrent response obtained for a Pt-disk hydrogel electrode. (a) The hydrogel electrode coating was cured with 1 mM [Ru(bpy)$_3$]Cl$_2$. MV^{2+} (20 mM) was incorporated into the hydrogel by the scanning technique outlined in the text. The electrolyte was 50 mM NaClO$_4$, 50 mM KNO$_3$, and 1 M TEOA. λ_{ex} = 436 nm. (b) The electrode was cured with 20 mM [Ru(bpy)$_3$]Cl$_2$. MV^{2+} (20 mM) was incorporated into the hydrogel by the scanning technique outlined in the text. The electrolyte was 50 mM NaClO$_4$, 50 mM KNO$_3$, and 1 M TEOA. The offset potential was 0 V vs SSCE. λ_{ex} = 436 nm.

resulting in a quenching rate constant of k_q = 4.2 × 10^8 M^{-1} s^{-1}. This value is approximately 1 order of magnitude less than the quenching constant found in aqueous solution.[17] As illustrated in Figure 3, self-quenching processes in the hydrogel and water were similar. Appreciable self-quenching is noted at concentrations greater than 0.10 mM.

Since our observed diffusion coefficients are lower in the hydrogel than in solution, the Smoluchowski equation has been invoked to determine if k_q was diffusion-limited. The diffusional bimolecular rate constant, k_0, was calculated using eq 1,[18] where

$$k_0 = \frac{4\pi N}{1000}(R_{Ru} + R_{MV})(D_{Ru} + D_{MV}) \quad (1)$$

R_{Ru} is the molecular radius of Ru(bpy)$_3^{2+}$, R_{MV} is the molecular radius of MV^{2+}, D_{Ru} is the diffusion coefficient of Ru(bpy)$_3^{2+}$, and D_{MV} is the diffusion coefficient of MV^{2+}. The radius (5.6 Å) of Ru(bpy)$_3^{2+}$ was obtained from the crystal structure of Ru(bpy)$_3$(PF$_6$)$_2$.[19] The radius of MV^{2+} (3.6 Å) was calculated from the methyl group to the center of the attached pyridine ring using published bond lengths for organic compounds.[20] The k_0 value ranged from 7.4 × 10^8 to 2.5 × 10^9 M^{-1} s^{-1}, depending on the diffusion coefficients chosen from Table II. The k_0 value was greater than k_q, indicating that k_q was not diffusion-limited.

Photocurrent. Oxidative photocurrent was observed upon visible-light excitation (λ_{ex} = 436 nm) of a carrageenan hydrogel electrode containing immobilized Ru(bpy)$_3^{2+}$ and MV^{2+} and immersed in an electrolyte solution containing 1 M TEOA (pH = 11). The photocurrent response is illustrated in Figure 4. As noted in the figure, the photocurrent rapidly builds to a maximum and continues at a near steady state until the light is turned off. At this point, the current diminishes exponentially at first and then slowly recedes to the baseline as diffusion becomes limiting in the hydrogel as described below. The source of the photocurrent is derived from the reaction of MV$^+$ at the electrode surface. MV$^+$ is formed by the photoreaction of MV^{2+} with Ru(bpy)$_3^{2+*}$, and
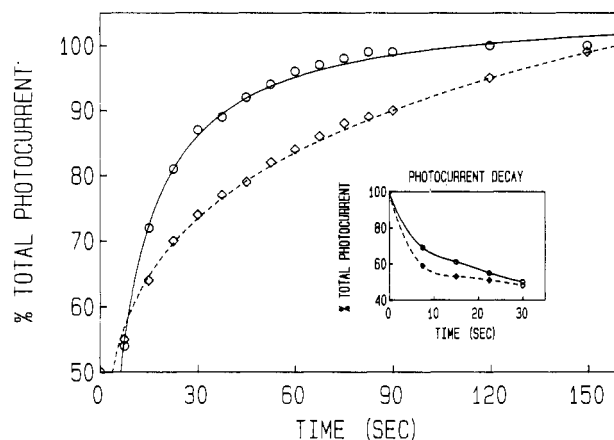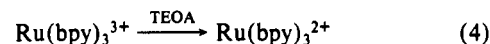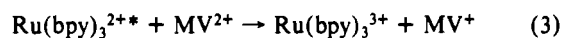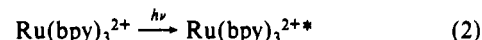

Figure 5. Comparison of an initial photocurrent response and decay (inset) for hydrogel electrodes (O) cured with a solution containing 1 mM Ru(bpy)$_3^{2+}$ and 20 mM MV^{2+} and (◇) cured with a solution containing 20 mM Ru(bpy)$_3^{2+}$ and 20 mM MV^{2+}.

MV$^+$ remains in solution after the scavenging of Ru(bpy)$_3^{3+}$ with TEOA (eqs 2–4). MV$^+$, then, can be used to drive reactions such

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad (2)$$

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^+ \quad (3)$$

$$Ru(bpy)_3^{3+} \xrightarrow{TEOA} Ru(bpy)_3^{2+} \quad (4)$$

as the reduction of H$^+$ to $^1/_2$ H$_2$,[13] or it can be used to generate oxidative current at an electrode surface according to eq 5.

$$MV^+ \rightarrow MV^{2+} + e^- \quad (5)$$
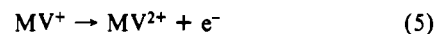
Control experiments were run to verify the necessity of the three components, Ru(bpy)$_3^{2+}$, MV^{2+}, and TEOA, to generate a photocurrent. The absence of TEOA from the solution resulted in a photocurrent of about 40 nA compared to a typical value of 1000 nA with TEOA present. Clearly, the role of TEOA is crucial in obtaining significant photocurrent. It acts as a scavenger, inhibiting the wasteful back-reaction of Ru(bpy)$_3^{3+}$ with MV$^+$ to reproduce the starting reagents. The oxidized TEOA$^+$ is known to undergo rapid, irreversible decomposition.[21] Removal of MV^{2+} or Ru(bpy)$_3^{2+}$ also had a detrimental effect, as negligible photocurrents were obtained in these situations. Thus, all three reagents were necessary for the observation of significant photocurrent.

Several variations were made to maximize the photocurrent. The photocurrent was found to increase as the concentration of TEOA increased and reached a plateau after its concentration was 0.1 M. Another well-known scavenger, Na$_2$EDTA,[22] was used as a substitute for TEOA. However, the photocurrent dropped by a factor of 2 compared to that found with TEOA as the scavenger.[23] Thus, TEOA was used in all experiments as the scavenger.

The photocurrent dependence of the Ru(bpy)$_3^{2+}$ concentration was deduced by changing the Ru(bpy)$_3^{2+}$ concentration of the hydrogel-curing solution (method 2). The photocurrent response comparison of a hydrogel electrode cured with a 1 mM Ru(bpy)$_3^{2+}$/20 mM MV^{2+} solution (upper trace) to one cured with a 20 mM Ru(bpy)$_3^{2+}$/20 mM MV^{2+} solution (lower trace) is shown in Figures 4 and 5. Figure 5 allows one to compare the time necessary for each system to achieve maximum photocurrent. The hydrogel containing the more concentrated Ru(bpy)$_3^{2+}$ (20 mM) responds less rapidly to light than the less concentrated one (1 mM). The more sluggish response in the more concentrated

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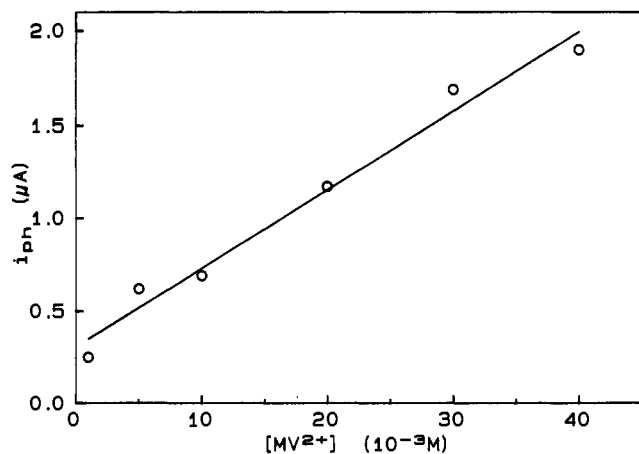(23) The drop may have been due, in part, to the lack of solubility of Na$_2$EDTA in the electrolyte solution.

Figure 6. Graph illustrating the photocurrent dependence on the MV²⁺ concentration used to cure the hydrogel. The electrolyte was 50 mM NaClO₄, 50 mM KNO₃, and 1 M TEOA. The slope was 42 μA/M, and the correlation coefficient was 0.99. The offset potential was 0 V vs SSCE. λ_{ex} = 436 nm.
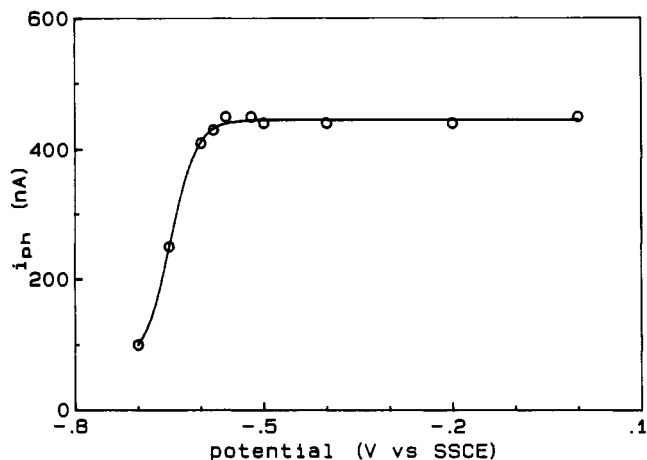

Figure 7. Graph illustrating the photocurrent dependence on the offset potential applied to the Pt-disk hydrogel working electrode. The electrode was cured with 20 mM [Ru(bpy)₃]Cl₂. MV²⁺ was incorporated into the hydrogel by the scanning technique outlined in the text. The electrolyte was 50 mM NaClO₄, 50 mM KNO₃, and 1 M TEOA. The photocurrent was the maximum obtained at λ_{ex} = 436 nm.

Ru(bpy)₃²⁺ hydrogel results from less efficient excited-state electron transfer due to self-quenching and masking of photochemical processes near the electrode surface. The photocurrent decay shown in the inset of Figure 5, however, is more rapid for the hydrogel electrode containing more Ru(bpy)₃²⁺. While greater photocurrents were observed in the less concentrated Ru(bpy)₃²⁺ hydrogel electrodes, sustained photocurrents were obtained with hydrogel electrodes cured with the more concentrated Ru(bpy)₃²⁺ solution (≥5 mM Ru(bpy)₃²⁺).

The photocurrent dependence on the MV²⁺ concentration is illustrated in Figure 6. In this series of experiments, the hydrogel was cured with a 5 mM Ru(bpy)₃²⁺ solution containing variable concentrations of MV²⁺. Electrolyte was then incorporated into the hydrogel by scanning the potential region from +1.25 to –0.9 V vs SSCE by cyclic voltammetry. A linear photocurrent response over the concentration range from 1 to 40 mM MV²⁺ was observed. The correlation coefficient was 0.99 and the slope was 42 μA/M. The plot indicates that substantial photocurrents are possible with the hydrogel electrode.

The photocurrent action spectrum is shown as an inset in Figure 2. The slits of the monochromator were adjusted for constant power output at each wavelength setting. The line through the points was constructed with a cubic spline curve fitting routine. The action spectrum closely resembles the excitation spectrum shown in Figure 2.

The offset potential of the working electrode was also varied. As illustrated in Figure 7, the break in the photocurrent response occurred approximately at –0.6 V (vs SSCE). This is in accord with the oxidative photocurrent assignment of MV⁺ → MV²⁺ + e⁻, as suggested earlier by eq 5.

In summary, the photophysical behavior of the Ru(bpy)₃²⁺/MV²⁺/hydrogel electrode was consistent with eqs 2–5. (1) The photochemical action spectrum coincided with the excitation and absorption spectrum of Ru(bpy)₃²⁺. (2) The falloff in photocurrent

as the offset potential approached that of the MV²⁺/MV⁺ redox couple was consistent with MV⁺ as the electron carrier. (3) Control experiments where MV²⁺ or TEOA was omitted from the solution resulted in negligible photocurrent. (4) Photocurrents increased as the concentrations of TEOA and MV²⁺ increased. (5) Emission in the hydrogel was quenched by the presence of MV²⁺. (6) The photocurrent response was greatest in the more dilute Ru(bpy)₃²⁺ hydrogels, but more sustained photocurrents were obtained in the more concentrated Ru(bpy)₃²⁺ hydrogels. This may be due to the competitive back-reaction of Ru(bpy)₃³⁺ with MV⁺ in the more concentrated hydrogel playing a greater role than in the more dilute one, which then gives rise to a better steady-state response but a lower photocurrent than in the case of the more dilute one.

The carrageenan hydrogel electrode offers a number of advantages compared to polymer-coated electrodes. The electrode can be constructed of readily available materials, it can be easily fabricated by dipping a platinum screen into a carrageenan solution or by applying the hydrogel to a platinum disk and cured in layers of 2 mm or less, and the components of the curing solution can be varied to maximize the photocurrent desired. Finally, the material can be redissolved in hot water and a fresh modified electrode can be readily prepared.