

SiO₂ Sol–Gel Composite Films Containing Redox-Active, Polypyridyl–Ruthenium Polymers

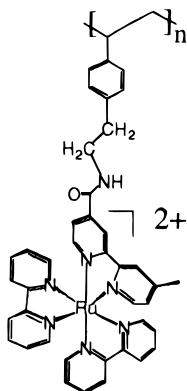
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SiO₂-based sol–gels have been utilized extensively as media for incorporating redox-active, luminescent, or catalytically active molecules.^{1,2} The mild preparative conditions allow for the incorporation of organic and inorganic dyes, and their glasslike optical properties make sol–gel composites attractive media for various optical applications.^{3,4} The high porosities and large surface areas of these materials have led to applications in chemical sensing⁵ and catalysis.⁶ Early studies focused on host–guest interactions of organic dyes^{1,2,7,8} and, to a lesser extent, inorganic chromophores in sol–gel monoliths.⁹ The redox and photophysical properties of [Ru(bpy)₃]²⁺ (bpy = 2,2′-bipyridine) in thin sol–gel films have also been reported.^{8,10–12} In these films the chromophore remains emissive^{8,11,12} and retains the redox activity of the Ru^{II/III} couple.^{10,11} A disadvantage of these composites is an instability toward loss of the chromophore to an external solution.

We report here an approach which is based on the incorporation of Ru^{II}-bpy derivatized polystyrene polymers and results in stable film structures on optically transparent ITO electrodes. The molecular structure of a repeat unit of the polymer is illustrated below with the polymer abbreviated as [PS–CH₂CH₂NHCO–(Ru^{II})_n]Cl_{2n} (*n* = 18 or 20).



The resulting sol–gel/polymer composites are stable in solution and display novel redox properties.

The preparation of the composite films was based on a literature procedure.^{8,11} Briefly, ~20 mg of [PS–CH₂CH₂NHCO–(Ru^{II})_n]Cl_{2n} (*n* = 18 or 20)^{13,14} was dissolved in 1.7 mL of absolute EtOH with stirring. To the continuously stirred solution were added 5

drops (~0.08 g) of the surface active agent Triton-X 100 (Aldrich), 0.1 mL of 0.01 M HCl, and 0.2 mL of TMOS (tetramethyl orthosilicate Si(OCH₃)₄); this composition corresponds to a molar ratio of Si/Ru = 50. The solution was stirred for another 30 min. The sol that resulted was aged, typically for 24 h, and deposited onto an ITO electrode by spreading with a glass slide or by spin coating at 5000–8000 rpm. The film was allowed to dry for 2 h at room temperature and then an additional 24 h at 100 °C in the air. Film thicknesses, 700–1500 nm for films prepared by spreading and 100–400 nm by spin coating, were determined by step profilometry. The concentration of Ru^{II} sites was estimated by UV–visible measurements (from $\epsilon_{456} = 15\,300\text{ M}^{-1}\text{cm}^{-1}$ for [PS–CH₂CH₂NHCO–(Ru^{II})₂₀](PF₆)₃₆ in CH₃CN),¹⁴ which gave [Ru^{II}] ~ 0.2 M.

In Figure 1 is shown a cyclic voltammogram in CH₃CN, 0.1 M in [N(*n*-C₄H₉)₄](PF₆) (TBAH), of an ITO/SG–[PS–CH₂CH₂NHCO–(Ru^{II})₁₈]Cl₃₆ film (SG = sol–gel) of thickness ~300 nm, at a scan rate of 2 mV/s. *E*_{1/2} for the Ru^{III/II} couple appears at 1.26 V (vs SSCE). The figure also illustrates the changes in film absorbance at 456 nm, λ_{max} for the lowest Ru^{II} → bpy metal-to-ligand charge transfer (MLCT) absorption band, during the potential sweep. As indicated by the loss in absorbance following the Ru^{II} → Ru^{III} oxidative sweep, oxidation is complete within a single potential scan at this slow scan rate. Chronoabsorptometry measurements with a potential step to +1.81 V demonstrate loss of the MLCT band concomitant with the appearance of a new band with $\lambda_{\text{max}} \sim 420\text{ nm}$ for Ru(III).¹⁵ The absorbance changes are complete within ~5 min. A reverse step to 0 V resulted in full (>90%) recovery of Ru^{II} consistently with the results shown in Figure 1. Plots of current (*i*) vs *t*^{1/2} are linear (for *t* ≤ 30 s), and from a Cottrell analysis,¹⁶ the apparent diffusion coefficient for Ru^{II} → Ru^{III} oxidation is *D*_{ct} = 1.4 × 10^{−9} cm²/s, which is comparable to *D*_{ct} values obtained in other rigid media.¹⁷ Cyclic voltammetric measurements as a function of scan rate show that the oxidative peak current, *i*_{p,a}, varies as the square root of the scan rate from 2 mV/s to 1000 mV/s, consistent with diffusion-limited charge transfer. The peak-to-peak separation, $\Delta E_p = E_{p,c}$ to *E*_{p,a}, increased from 45 to 370 mV in the same scan rate range. Intrastrand, site-to-site electron transfer within individual poly-

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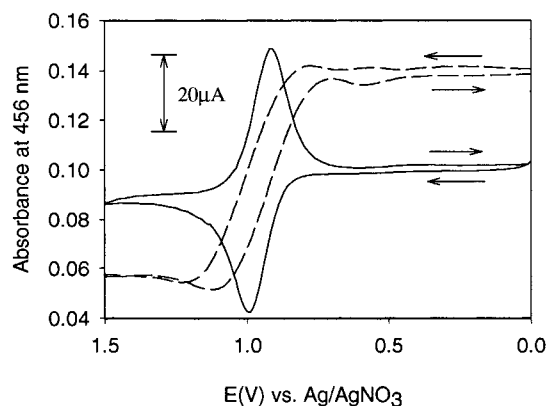


Figure 1. Cyclic voltammogram (solid line) and simultaneous absorbance change (dashed line) for an ITO/SG-[PS-CH₂CH₂NHCO-(Ru^{II})₁₈]Cl₃₆ film with Si/Ru = 50 ([Ru^{II}] ~ 0.2 M), with film thickness ~300 nm at 2 mV/s in CH₃CN, 0.1 M in TBAH.

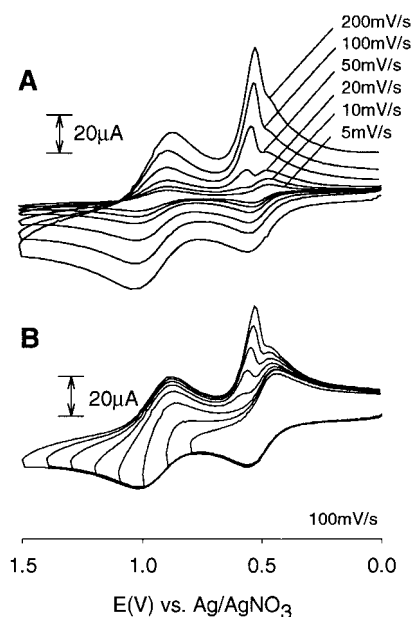


Figure 2. Cyclic voltammograms of ITO/SG-[PS-CH₂CH₂NHCO-(Ru^{II})₂₀]Cl₄₀ with Si/Ru = 50 ([Ru^{II}] ~ 0.2 M) for a film of thickness ~400 nm exposed to 0.1 mM [Os(bpy)₃]²⁺ in CH₃CN, 0.1 M in TBAH, (A) as a function of scan rate and (B) as a function of potential step.

meric strands is expected to be rapid,¹⁸ and either counterion diffusion or interstrand electron transfer hopping or both are presumably rate limiting.

The polymer-doped films are stable toward leaching into an external solution. The instability of SG-[Ru(bpy)₃]Cl₂ composite films toward leaching of the complex under repetitive scan conditions in water has been reported.^{10,11} In CH₃CN, films doped with [Ru(bpy)₃]Cl₂ leach rapidly with ~70% of the chromophore lost within 1 h. The polymer composites are stable under the same conditions for a period of at least 2 weeks. The increased stability is also observed under repetitive scan conditions through the Ru^{III/II} wave at $E_{1/2} = 1.26$ V (vs SSCE) with no decrease in peak current after 50 potential scans between 0.31 and 1.81 V (vs SSCE) in acetonitrile 0.1 M in TBAH or water 0.01 M in NaCl.

We have observed novel mediation effects in the composite films. In Figure 2 are shown series of cyclic voltammograms of an ITO/SG-[PS-CH₂CH₂NHCO-(Ru^{II})₂₀]Cl₄₀ film with [Os(bpy)₃]²⁺ in the external solution. The appearance of the Os^{III/II} wave at $E_{1/2} = 0.50$ V (0.81 V vs SSCE) indicates that the

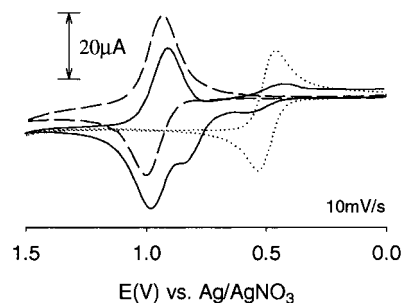


Figure 3. Cyclic voltammograms: (solid line) ITO/SG-[PS-CH₂CH₂NHCO-(Ru^{II})₂₀]Cl₄₀ (Si/Ru = 50; film thickness ~400 nm) exposed to a 0.5 mM solution of [PS-CH₂CH₂NHCO-(Os^{II})₂₀](PF₆)₄₀ in CH₃CN (0.1 M TBAH); (dotted line) blank ITO electrode exposed to the same solution; (dashed line) the composite film exposed to CH₃CN (0.1 M TBAH). Scan rate 10 mV/s, electrode area in all cases 1 cm².

composite films are open to diffusion from the external solution. The scan rate dependence reveals the existence of a “prewave” at the onset of the diffusional Os(III→II) wave with i_p occurring at ~0.53 V (0.84 V vs SSCE). The origin of the prewave is obvious from results of the potential scan experiments shown in Figure 2B. It appears only after a potential scan past the Ru^{III/II} couple. Its origin is in the reduction of a fraction of the Ru^{III} sites (formed during the oxidative scan), by freely diffusing [Os(bpy)₃]²⁺. The fraction of unreacted sites and the magnitude of the prewave depend on scan rate, the potential step, the concentration of [Os(bpy)₃]²⁺ in the external solution, and both film thickness and porosity.

Use of the film as a redox mediator was investigated in experiments in which an ITO/SG-[PS-CH₂CH₂NHCO-(Ru^{II})₂₀]Cl₄₀ film was exposed to a solution containing [PS-CH₂CH₂NHCO-(Os^{II})₂₀](PF₆)₄₀ (Figure 3). The absence of a well-defined diffusional wave for the Os^{III/II} couple at 0.50 V (0.81 V vs SSCE) demonstrates that the polymer is unable to diffuse through the film.¹⁹ Extension of the oxidative scan results in a new wave which appears as a shoulder on the Ru(II→III) wave at $E_{p,a} = 0.85$ V (1.16 V vs SSCE). There is no evidence for Os(III→II) re-reduction on a reverse scan. The same behavior is observed in “bilayer” films containing spatially separated [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ derivatives in electropolymerized films.^{20–22} In the case of [PS-CH₂CH₂NHCO-(Os^{II})₂₀](PF₆)₄₀, diffusion to the underlying ITO electrode is blocked and the multiple Os^{II} sites in the polymer are oxidized at the film–solution interface. Electron transfer to ITO occurs through the film by Ru^{II} → Ru^{III} electron transfer migration at the onset of the Ru^{III/II} wave. Unidirectional Os^{II} → Os^{III} oxidation and the rectifying behavior that results occur because Os(III→II) reduction by Ru^{II} at the film–solution interface is nonspontaneous by 0.45 V.

These initial results show that the SG-[PS-CH₂CH₂NHCO-(Ru^{II})_n]Cl_{2n} composite films form a new class of optically transparent, redox-active membranes. We are currently investigating their redox properties in further detail.

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