Electrogenerated chemiluminescence from Ru(II) bipyridylphosphonic acid complexes adsorbed to mesoporous TiO_2/ITO electrodes

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Ru(II) diimine complexes having phosphonic acid substituents adsorb to TiO_2 modified ITO electrodes and exhibit electrogenerated chemiluminescence when potentiostated at positive voltages in the presence of oxalate in buffered aqueous solutions.

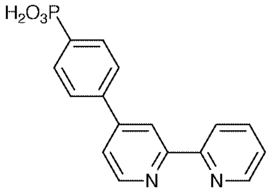
Luminescence is often observed from chromophores excited by highly exoergic redox reactions that generate excited states without direct photonic excitation.[1] When the redox reaction is driven electrochemically the process (electrogenerated chemiluminescence, ECL) has several potential applications including electroactive display development and trace analysis.[2] Many potential applications of ECL can be optimized by using luminescent electroactive species that are immobilized at an electrode surface. A number of approaches to surface modification for ECL have been developed including (a) covalent or ionic attachment of the chromophore to a surface bound polymer,[3] (b) formation of thin polymer films from a monomer containing an ECL active chromophore,[4] (c) attachment of a chromophore to a substrate capable of binding to the surface *via* specific molecular recognition (*i.e.* antibody/antigen interaction)[5] and (d) direct incorporation of the redox active species into the electrode material.[6,7] For many applications it is desirable for the ECL active chromophore to be bound to a highly robust support which is also porous enough to allow for rapid ion and substrate uptake. This report describes ECL of Ru(II) diimine complexes adsorbed onto mesoporous TiO_2 films on optically transparent ITO electrode supports.

Among the chromophores most commonly used for ECL are Ru(II) diimine complexes.[8] They are stable upon one-electron oxidation and reduction and annihilation of the radical ions leads to formation of a metal-to-ligand (MLCT) charge transfer excited state. Electrogenerated luminescence can also be obtained from these complexes by reducing the complex in the presence of a species which can be reduced to produce a strong oxidizing agent (such as $S_2O_8^{2-}/SO_4^{\cdot -}$)[9] or oxidizing the complex in the presence of a species which can be oxidized to produce a strong reductant (such as $C_2O_4^{2-}/CO_2^{\cdot -}$).[10]

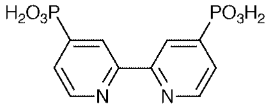
Several examples exist of ECL from surface bound Ru(II) diimine complexes[2–7] and recent work has shown the potential of these complexes in electroluminescent displays.[11] The most chemically flexible and durable of the modified surface ECL systems consists of ITO with a thin film of Nafion into which the Ru(II) diimine complex is adsorbed. This system involves a polymer support for which the porosity, solubility and ion transport characteristics are intimately dependent on the medium. The development of porous, insoluble, inert supports for ECL would expand the opportunities for applications of ECL in sensing and display development. Very recently Sykora and Meyer reported ECL from a polymer/SiO_2 sol–gel composite, which has the potential to meet the above criteria.[12] We report here, the observation of ECL from Ru(II) diimine complexes adsorbed onto mesoporous TiO_2 films deposited on ITO optically transparent electrodes. The TiO_2 films provide an inert, robust support for the ECL active Ru(II) complex. Gratzel and coworkers have recently observed ECL in a similar system involving reduction of $S_2O_8^{2-}$ in DMF at ITO/TiO_2 surfaces having an adsorbed Ru(II) diimine complex; the $SO_4^{\cdot -}$ radical ion produced oxidizes surface bound Ru(II) which then annihilates with conduction band electrons to yield luminescence.[7]

TiO_2 modified ITO electrodes were initially prepared as a means of increasing the photoactive surface area of electrodes used in dye sensitized photoelectrochemical cells.[13] Films are prepared by deposition of a colloidal suspension of TiO_2 onto ITO surfaces, evaporation and sintering of the subsequent film.[14] Surfaces prepared in this way are typically 1–10 μm thick and appear by SEM and AFM as packed spherical particles of the order of 20–50 nm in diameter.[15] The films are known to adsorb dyes having negatively charged substituents (carboxylates, phosphonates, *etc.*). In two electrode cells consisting of the dye modified ITO/TiO_2 electrode and a noble metal counter electrode excitation of particular dyes results in charge injection into the TiO_2 with high efficiency.[8] However, other dyes often exhibit strong photoluminescence when adsorbed.[16,17] The observation of luminescence from Ru(II) diimine complexes on ITO/TiO_2 photoelectrodes is believed to result from either (a) complex which has desorbed from the surface[16b] or (b) complex adsorbed to surfaces for which charge injection is thermodynamically unfavorable.[17]

The Ru(II) complex dyes used in this work are adsorbed to the surface through interaction of phosphonic acid moieties on 2,2′-bipyridyl ligands. The ligands used are $bpppH_2$ and $bpdpH_4$. The complexes prepared from these ligands are $[(bpy)_2Ru(bpppH_2)]^{2+}$, $[(bpy)_2Ru(bpdpH_4)]^{2+}$ and $[Ru(bpppH_2)_3]^{2+}$, having one, two and three phosphonic acid substituents, respectively. The ligand and complex syntheses are reported elsewhere.[18] The complexes were deposited on ITO/TiO_2 surfaces by immersion of electrodes in DMSO–H_2O (90 : 10) solutions of the complex for 12 h.



$bpppH_2$



$bpdpH_4$

Observation of ECL from the dye modified ITO/TiO_2 surfaces requires that three conditions are met: (a) the adsorbed Ru(II) complex is oxidized by the electrode, (b) oxidation of the oxalate occurs in the film and (c) emission is observed from the adsorbed Ru(II) complex following reaction of Ru(III) with $CO_2^{\cdot -}$. Fig. 1 shows an oxidative cyclic voltammogram for a ITO/TiO_2/$[Ru(bpppH_2)_3]^{2+}$ modified electrode in aqueous pH 7 buffer. There is a large difference in peak potential between the oxidative and reductive waves reflecting limitations to charge transport in the thin film.[19,20]

Spectroelectrochemical studies indicate that nearly complete oxidation of the complexes in the film can be affected by potentiostating at voltages more positive than the one-electron oxidation potential; in addition, the process is reversible. However, complete oxidation of the complex in the films is extremely slow ($t_{1/2} \geqslant 15$ min). The implication is that only Ru(II) centers adsorbed near the ITO/TiO_2 interface are readily

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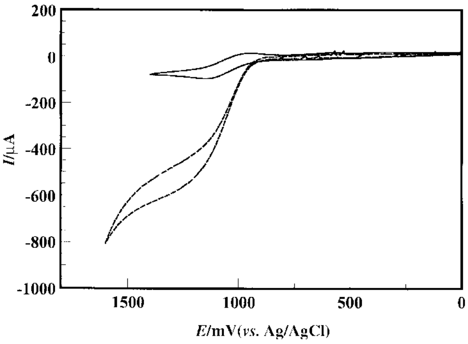

Fig. 1 Cyclic voltammogram of (—) $[Ru(bpppH_2)_3]^{2+}$ modified ITO/TiO_2 electrode in pH 7 buffer solution (0.1 M) and (----) the same modified electrode in the presence of sodium oxalate (0.002 M).

oxidized; oxidation of Ru(II) sites adsorbed away from the interfacial area must be affected by migration of Ru(III) in the TiO_2 thin film or, for films with high complex loading, charge percolation.[8] Cyclic voltammograms obtained following addition of oxalate exhibit a significant increase in current associated with the oxidative wave (Fig. 1). The process is completely irreversible, reflecting the decomposition of the oxidized oxalate. The result illustrates that oxalate is able to permeate the porous TiO_2 film and is oxidized on the cyclic voltammetric time scale [either directly at the electrode surface or by Ru(III) mediated oxidation].

When modified surfaces are potentiostated at > 0.9 V *vs.* Ag/AgCl in stirred solutions containing oxalate (0.02 M), luminescence is observed from all the Ru(II) complex modified electrodes.[21] No emission is observed in the absence of oxalate. The ECL spectrum of $[Ru(bpppH_2)_3]^{2+}$, shown in Fig. 2, is identical to that of the Ru(II) complex in aqueous buffer. The luminescence intensity increases with increasing potential until a maximum is reached at +1.25 V and falls off slightly at potentials above +1.4 V (inset). Thus, luminescence arises from the MLCT excited state of the complexes and the intensity is proportional to the relative steady state concentration of Ru(III) in the films. Whether luminescence arises in these systems from desorbed complex or from complex adsorbed to sites where charge injection is not thermodynamically favorable is not clear.

When the electrode potential is held at a potential positive relative to $E°[Ru(III/II)]$ in a stirred solution containing oxalate, the ECL intensity decreases with time. Both $[(bpy)_2Ru(bpppH_2)]^{2+}$ and $[(bpy)_2Ru(bpdpH_4)]^{2+}$ desorb from the TiO_2 support and dissolve in the buffer solution. Only the complex having three phosphonic acid substituents, $[Ru(bpppH_2)_3]^{2+}$, shows no evidence for desorption from the surface. However, even this complex exhibits a decrease in ECL intensity with time. The decrease in intensity is not related to depletion of oxalate in the solution. We are presently investigating the behavior of the $[Ru(bpppH_2)_3]^{2+}$ complex in greater detail, but preliminary results suggest that the oxidized form of the complex migrates in the film *via* desorption and readsorption processes which lead ultimately to depletion of the complex at the electrode surface.

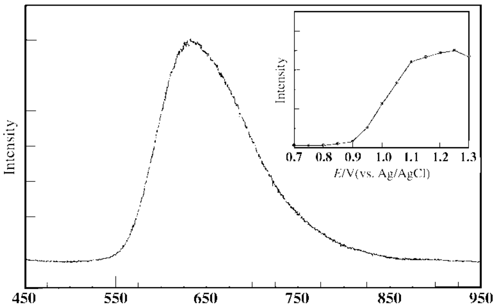

Fig. 2 Dispersed emission from a $[Ru(bpppH_2)_3]^{2+}$ modified ITO/TiO_2 electrode in pH 7 buffer containing sodium oxalate (0.02 M); 5 s exposure. Inset: integrated emission intensity as a function of applied potential.

In summary, ITO optically transparent electrodes modified with a clear ceramic thin film of mesoporous TiO_2 can serve as solid supports for generation of ECL from adsorbed Ru(II) diimine complexes. The Ru(II) complex dyes adsorb *via* interaction of phosphonic acid substituents on the diimine ligands with the surface sites on the TiO_2. Initial results suggest that the stability of the modified surfaces for generation of sustained ECL is dependent on the number of phosphonic acid substituents per chromophore. We are currently exploring covalent attachment of ECL active dyes to these robust, mesoporous thin film electrodes as a potential approach to making sensing devices with improved longevity.

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21 The modified electrode is typically a 1 × 3 cm piece of ITO with the TiO_2 thin film containing the Ru(II) complex covering a 1 × 2 cm area. The electrode is mounted in the sample compartment of a SPEX fluorolog spectrofluorimeter at 45° relative to the emission collection optics. Emission spectra are observed using a spectrograph/CCD with 5–10 s exposure times. ECL is observed by potentiostating the ITO electrode at potentials more positive than 0.9 V in stirred solutions containing oxalate.

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