Solid-state electrogenerated chemiluminescence in sol–gel derived monoliths

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Stable solid-state electrogenerated chemiluminescence has been achieved by trapping the chemiluminescent precursors, ruthenium(II) tris(bipyridine) and tripropylamine, in a porous silicate host matrix prepared by the sol–gel process and exciting them electrochemically *via* an immobilized microelectrode assembly.

The development of new technology and methods for the fabrication of large area emissive panels and displays with low operating voltages is important in the electro-optics industry. Conjugated polymers (*i.e.* the organic semiconductors) have received considerable attention due to the ease at which they can be prepared, processed, and modified.[1–2] To a lesser extent, electrogenerated chemiluminescence[3] (ECL) based materials have also been investigated. These materials hold considerable promise because the ECL can be generated with relatively low voltage bias and with reasonably high efficiency.

To date, several approaches to solid-state ECL have been investigated. Abruna and Bard initially showed in the 1980s that ECL can be observed from electropolymerized films of $Ru(vbpy)_3^{2+}$ (vbpy = 4-vinyl-4′-methyl-2,2′ bipyridyl) on platinum electrodes in acetonitrile *via* sequential oxidation and reduction of the immobilized redox centers.[4] Similar results have also since been observed with chemiluminescence or conjugated polymers prepared from diphenylanthracene and polyphenylenevinylene derivatives.[5,6] More recently, solid-state ECL has been observed from $poly[RuL_3]^{2+}$ (L = vbpy or ester substituted bipyridine) films prepared on interdigitated array electrodes or in a sandwich type arrangement.[7,8] Light emission results from the reaction between RuL_3^{+} and the RuL_3^{3+} states formed *via* independent control of the potentials of the closely spaced electrodes.[7,8] When fixed concentration gradients are established in the film, the system gives rise to ECL in the *absence of solvent*.[7,8] In related work, Rubner and coworkers have also noted solid-state ECL from ruthenium derivatives trapped in an ionic polymer or bound to the polymer framework and sandwiched between two electrodes.[9]

In this work, an entirely different approach has been taken to generate ECL in the absence of solution. Ruthenium(II) tris(bipyridine) [$Ru(bpy)_3^{2+}$] and tripropylamine (TPA) have been encapsulated, along with a microelectrode assembly, in a porous, solid host prepared *via* the sol–gel approach.[10,11] This ECL system was chosen because it allows the luminescence to be generated at a relatively *low* potential bias in an *aqueous* environment.[12,13] The known immunity of the $Ru(bpy)_3^{2+}$–TPA system to water will likely improve the long term stability of the ECL. In this system, emission results when the TPA amine radical formed upon reduction of $Ru(bpy)_3^{3+}$ or *via* direct electrode oxidation reacts with another $Ru(bpy)_3^{2+}$ or additional $Ru(bpy)_3^{3+}$ to form $[Ru(bpy)_3^{2+}]^*$ which then decays to produce orange emission centered at 610 nm.[12,13] The original $Ru(bpy)_3^{2+}$ species is regenerated during the reaction, albeit with consumption of TPA.[12,13] In contrast to previous studies[4–7,9] where the ECL decayed on the timescale of seconds to tens of minutes and often required an inert atmosphere, this approach yields stable emission for over *two hours* under room conditions.

In these experiments, the silica sol was prepared by mixing tetramethoxysilane (Aldrich, 98%) with water and 0.1 M hydrochloric acid followed by rapid stirring for at least 2 h. The hydrolyzed sol was doped with $[Ru(bpy)_3]Cl_2$ (Aldrich) and stirred for 45–90 min. A 2 mL aliquot of the doped sol was pipetted in a silanized glass vial[14] housing the microelectrode assembly.[15] 1 mL of TPA (Aldrich, 99%) in pH 7.0, 0.1 M phosphate buffer was then added to the sol and the resultant solution quickly mixed. The gel was aged for 2–3 days and dried for 1–2 days at a relative humidity of 60–70% by exposing a small hole (*ca.* 2 mm diameter.) in the cap to the atmosphere. Very little shrinkage ($<10\%$) in volume was observed. The solid-state electrochemical cell was placed in a dark box *ca.* 3.5 cm from the photocathode of a Hammamatsu 4632 photomultiplier tube and the data collected with a multichannel scaler (photon counter, EGG Ortec T-914). Either a Pine AFRDE5 bipotentiostat or a BAS 100 potentiostat was used to apply the excitation waveform (linear sweep or potential step).

Fig. 1(a) shows cyclic voltammograms (CVs) of gel-encapsulated $Ru(bpy)_3^{2+}$ at a 13 μm radius Pt ultramicroelectrode acquired at 10 mV s^{-1} (solid line). In the absence of TPA, the voltammograms are steady state in nature and superimposed on a relatively large rising background from solvent oxidation. As the sweep rate is increased (up to 10 V s^{-1}), the

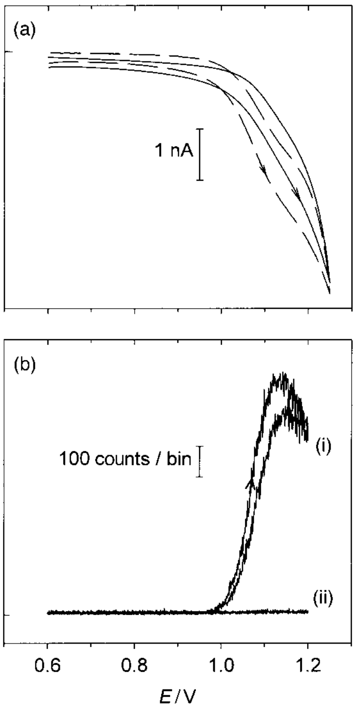

Fig. 1 (a) Cyclic voltammograms of gel-encapsulated $Ru(bpy)_3^{2+}$ (solid line) and gel encapsulated $Ru(bpy)_3^{2+}$ and TPA (dashed line) at a 13 μm radius Pt microdisk electrode. Scan rate: 10 mV s^{-1}. (b) Corresponding intensity–potential curves for gel-encapsulated $Ru(bpy)_3^{2+}$ (i) and gel-encapsulated $Ru(bpy)_3^{2+}$ + TPA (ii). Precursor concentrations in the sol: 10 mM $Ru(bpy)_3^{2+}$ or 10 mM $Ru(bpy)_3^{2+}$ + 10 mM TPA. Bin size = 100 ms.

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voltammograms become more peak shaped in appearance due to the onset of planar diffusion (data not shown).[16,17] A half-wave potential ($E_{1/2}$) of *ca.* 1.1 V was estimated from the voltammograms acquired at 100–1000 mV s^{-1}. This value is consistent with that previously measured for both solution and gel-encapsulated Ru(bpy)$_3^{2+}$.[18] In the presence of TPA, the oxidation current for gel-entrapped Ru(bpy)$_3^{2+}$ increases consistent with the oxidative–reduction mechanism for Ru(bpy)$_3^{2+}$ ECL [Fig. 1(a)], dashed line). The relatively facile nature at which gel-entrapped Ru(bpy)$_3^{2+}$ and TPA can diffuse in the gel and be oxidized at the electrode surface is evident in the shapes of the voltammograms acquired at 10–1000 mV s^{-1} and the resultant luminescence. Although the gel is macroscopically rigid, it is microscopically porous and hydrated.[19,20] Prior work has shown the diffusion coefficients of redox molecules trapped with these solids during the initial stages of drying to be nearly identical to values measured in solution (10^{-6} cm^2 s^{-1}).[19,20]

Corresponding ECL-potential curves for these materials are shown in Fig. 1(b). In the absence of either TPA or Ru(bpy)$_3^{2+}$, no significant ECL emission can be observed at the Pt microdisk electrode. Only when both reagents are present can the ECL be observed. The onset of luminescence is contiguous with the oxidation of gel-encapsulated Ru(bpy)$_3^{2+}$ and TPA and peaks near 1.15 V. It is not fully understood at the present time why the ECL intensity becomes lower as the electrode potential is scanned significantly past $E_{1/2}$, but it may be related to quenching, solvent oxidation products or concentration polarization.

The long term stability of the ECL at the ultramicroelectrode was evaluated by repetitively cycling the electrode potential for >30 min and also by stepping the electrode potential to a near diffusion controlled value for 2 h. The results are shown in Fig. 2. As can be seen, the light intensity is remarkably stable upon repetitive potential cycling at 10 mV s^{-1}. The ECL is typically *ca.* 5–20% lower on the first potential scan relative to subsequent cycles where near constant emission is observed. Fig. 2(b) shows the ECL emission at a 13-μm Pt microdisk electrode following a potential step from 0.6 to 1.15 V. The luminescence increases nearly immediately upon application of the potential step where it then remains at a near constant level for the duration of the experiment. Typically, $<15\%$ drop in intensity is observed over 2 h.

The enhanced stability of the ECL can be attributed not only to the small size of the electrode which results in a decreased consumption of TPA, but also to the steady state or quasi-steady state flux of reagents to the electrode surface.[16,17] For an ultramicroelectrode, the dimensions of the diffusion layer greatly exceed that of the electrode in a relatively short period of time (*e.g.* seconds).[16,17] Because a greater population of TPA molecules are then able to diffuse to the electrode from the increased volume around the electrode, steady state is reached quickly.[16,17] Since the electrode area is very small (10^{-6} cm^2), very little TPA is consumed during the experiment (*i.e.* theoretically calculated to be $\ll 0.01\%$ for a 2 h time period). Similar results were also observed using microband electrodes.

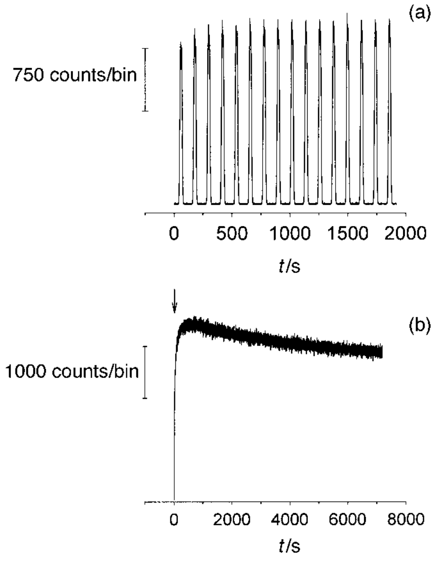

Fig. 2 Intensity–time transients during 16 repetitive potential cycles from 0.6 to 1.2 V at 10 mV s^{-1} (a) and following a potential step from 0.6 to 1.15 V (b) for gel-encapsulated Ru(bpy)$_3^{2+}$ + tripropylamine at a 13-μm radius Pt microdisk electrode. Precursor concentration in the sol: 10 mM Ru(bpy)$_3^{2+}$ + 5 mM tripropylamine. Bin size: 0.2 s (a) and 1 s (b).

In summary, the use of ultramicroelectrodes for the generation of ECL reagents in a solid host results in remarkably stable light emission under room conditions. At a microdisk electrode, the ECL remains at a near constant level upon application of a relatively low potential for time periods in excess of 2 h. One of the most promising aspects of this work is that it provides a relatively simple approach for the generation of light without the use of excess solvent, flowing streams, stringent solution conditions, or inert atmosphere. Different emission wavelengths can likely be achieved through variations in the gel-encapsulated precursor molecules. Likewise, optimization of precursor concentrations, the porosity of the host, and the electrode geometry and size, should result in greater emission intensities. Future work will be directed toward these investigations.

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Notes and references

1 P. L. Burns, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W Gymer, *Nature*, 1992, **356**, 47.
2 Z. Bao, Z. Peng, M. E. Galvin and E. A Chandross, *Chem. Mater*, 1998, **10**, 1201.
3 L. R. Faulkner and A. J. Bard, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1977, vol 10, pp. 1–95.
4 H. D. Abruna and A. J. Bard, *J. Am. Chem. Soc.*, 1982, **104**, 2641.
5 M. M. Richter, F.-R. F. Fan, F. Klavetter, A. J. Heeger and A. J. Bard, *Chem. Phys. Lett.*, 1994, **226**, 115.
6 F.-R. F. Fan, A. Mau and A. J. Bard, *Chem. Phys. Lett.*, 1985, **116**, 400.
7 K. M. Maness, R. H. Terrill, T. J. Meyer, R. W. Murray and R. M Wightman, *J. Am. Chem. Soc.*, 1996, **118**, 10 609.
8 C. M. Elliott, F. Pichot, C. J. Bloom and L. S. Rider, *J. Am. Chem. Soc.*, 1998, **120**, 6781.
9 (a) A. Wu, J. Lee and M. F. Rubner, *Thin Solid Films*, 1998, **327–329**, 663; (b) C. H. Lyons, E. D. Abbas, J.-K. Lee and M. F. Rubner, *J. Am. Chem. Soc*. 1998, **120**, 12100.
10 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328.
11 J. Brinker and G. Scherer, *Sol–Gel Science*, Academic Press, New York, 1989.
12 W.-Y. Lee, *Mikrochim. Acta*, 1997, **127**, 19.
13 J. K. Leland and M. J Powell, *J. Electrochem. Soc.*, 1990, **137**, 3127.
14 The glass vials were silanized with chlorotrimethylsilane.
15 The microelectrode assembly consisted of a working electrode (*i.e.* a Pt microwire sealed in glass) and a reference electrode (silver chloride coated silver wire) sealed in a Nylon cap.
16 C. Amatore, in *Physical Electrochemistry, Principles, Methods, and Applications*, ed. I. Rubinstein, Marcel Dekker, Inc, New York, 1995, pp. 131–208.
17 R. M. Wightman and D. O Wipf, *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1989, vol 15.
18 M. M. Collinson, C. G. Rausch and A. Voigt, *Langmuir*, 1997, **13**, 7245 and references therein.
19 M. M. Collinson, P. Zambrano, H. Wang and J. Taussig, *Langmuir*, 1998, **15**, 662.
20 P. Audebert, P. Griesmar, P. Hapiot and C. Sanchez, *J. Mater. Chem.*, 1992, **2**, 1293.

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