Luminescence Spectroelectrochemistry

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Luminescence spectroscopy is well recognized for improved selectivity and sensitivity relative to absorption spectroscopy. When luminescence spectroscopy is coupled to electrochemistry, luminescence spectroelectrochemistry provides the opportunity to selectively probe the excited state properties of in situ generated chromophores. A versatile long optical path spectroelectrochemical cell suitable for luminescence measurements is described.

Spectroelectrochemical methods provide the opportunity to spectroscopically probe unique chemical species that are generated in situ during redox reactions at electrode surfaces. In many cases electrochemistry yields synthetically inaccessible oxidation states, and therefore spectroelectrochemistry offers new windows for exploring novel chemical pathways.

The major challenge for the development of a spectroelectrochemical method is to design an electrochemical cell that is mutually compatible with the desired spectroscopic technique. Numerous cell designs and optically transparent electrodes (OTEs) for a wide range of spectroscopic techniques are described in the literature, but in general have been developed for a specific application (1-4). An exception to this is the optically transparent thin-layer electrode (OTTLE), which has been routinely used for transmission spectroelectrochemistry (5). The OTTLE cell has been implemented for numerous UV-visible spectroelectrochemical studies under a variety of experimental conditions due to ease of construction, the need for only small sample volumes, and the capability for rapid electrolysis (6).

In contrast to absorption spectroscopy, luminescence spectroscopy has received relatively little use as a general spectroelectrochemical method for investigating solution species even with the inherent sensitivity advantage of luminescence over absorption methods. The primary reason for this trend can be traced to the lack of a versatile spectroelectrochemical cell that satisfies the 90° detection requirement for luminescence measurements and exhibits the positive features of the OTTLE cell. Several reports have been published that use the OTTLE cell for luminescence spectroelectrochemical measurements (7-12). To accommodate detection of the emitted light and the short optical path, the OTTLE cell was placed at 45° relative to the excitation and emission slits. These studies demonstrated the utility of luminescence spectroelectrochemistry, the sensitivity of luminescence over absorption spectroscopy, and the short electrolysis advantage provided by the OTTLE. However, poor signal-to-noise ratios resulting from scattering off the front face of the cell, nonreproducible cell positioning and the short optical path generally offset the positive features. One alternative approach for luminescence spectroelectrochemistry used a cuvette-based configuration with a gold resinate film electrode that permitted detection of the emitted light at 90° (13). Our efforts toward the development of a general spectroelectrochemical cell for luminescence studies have tried to incorporate as many of the advantages of the OTTLE cell while also fulfilling the 90° detection requirement of luminescence spectroscopy (14).

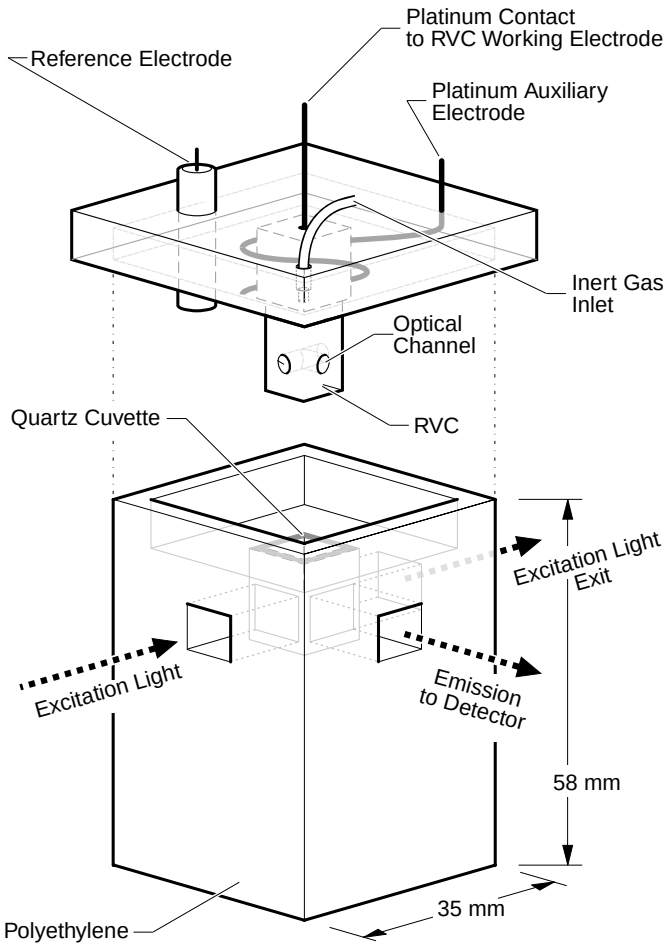
Cell Design

The basic cell and electrode design for luminescence spectroelectrochemistry are shown in ***F1*** (14). This approach addresses the two principal experimental considerations for coupling luminescence spectroscopy with electrochemistry: 1) reproducible excitation and detection of the resultant emission and 2) efficient electrolysis within the optical channels.

The cell body was developed from a solid polyethylene block to resemble, and therefore replace, the cuvette holder in a conventional luminescence spectrophotometer. An upper compartment was first milled into the top of the polyethylene block to house the reference and auxiliary electrodes. A second, lower compartment was then milled into the center of the block for the working electrode. Rectangular openings were cut into each face in line with the lower compartment. A quartz cuvette was inserted into the lower compartment to provide optical windows and a fixed 1 cm opti-

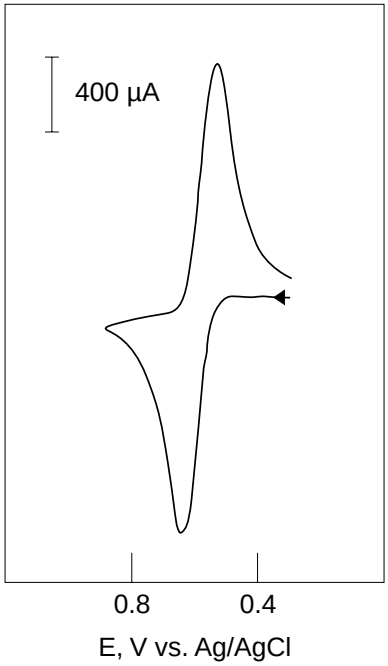
F1

Luminescence spectroelectrochemical cell.



F2

Cyclic voltammogram of 1 mM o-tolidine in 0.5 M CH_3COOH, 1 M $HClO_4$ in the luminescence spectroelectrochemical cell with 2 mm diameter optical channels. Initial potential: +0.4 V vs. Ag/AgCl. Scan rate: 2 mV/s. (Reprinted with permission from reference 14.)



cal path. The windows were positioned to take advantage of the existing optics in an Aminco-Bowman Series 2 spectrophotometer (SLM Instruments, Inc.).

Reticulated vitreous carbon (RVC, 100 pores per inch, Electrosynthesis Co., Inc.) was used as the working electrode. The three-dimensional structure of RVC permits facile fabrication of a working electrode that fits into the lower compartment and extends into the upper compartment. The challenge of incorporating the 90° detection requirement of luminescence spectroscopy within an electrochemical cell is also addressed by drilling optical channels of a tee configuration in line with the windows of the lower compartment. This configuration provides long optical paths for both reproducible excitation and detection of the emission. A diameter of 2 mm was found to afford the optimum tradeoff between electrolysis time and signal-to-noise ratio.

Approximately 2-3 mL of solution is required to completely fill the cell for operation. The solution volume occupied by the RVC working electrode was determined by coulometry of a standard ferricyanide solution to be approximately 0.4 mL. A platinum wire auxiliary electrode, which encircled the working electrode, and a Ag/AgCl reference electrode (BAS MF-2021) were placed in the upper compartment to complete the electrochemical cell. Electrical contact to the working electrode was made with a platinum wire. A cell cover was also machined to support the electrodes and exclude oxygen.

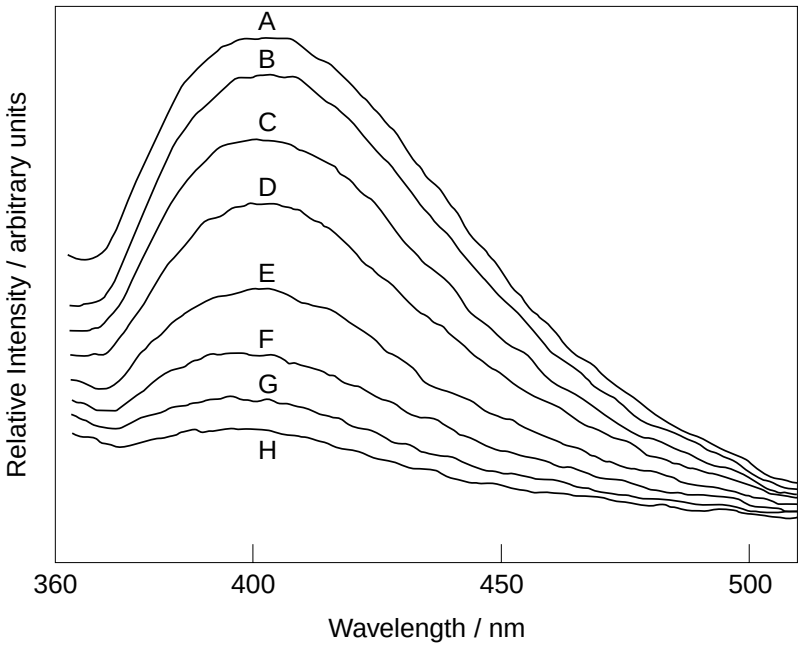
Results and Discussion

From an electrochemical point of view, RVC is inert and displays a wide potential range for electrochemical measurements in aqueous and nonaqueous solutions (15). The porous structure also maintains good communication between the working electrode in the lower sample compartment and the auxiliary and reference electrodes in the upper sample compartment. The porosity of 100 pores per inch RVC is small enough that diffusional mixing from the upper compartment does not occur in the optical channels. Thus, exhaustive electrolysis is achieved in the optical channels within 10-25 mins depending on the optical channel diameter, solvent, electroactive species, analyte concentration and electrolyte. An additional advantage of RVC is that if fouling occurs, the electrode can be easily removed and replaced.

The electrochemical and luminescence capabilities of the spectroelectrochemical cell are easily demonstrated by the *o*-tolidine redox couple. ***F2*** depicts the cyclic voltammogram for the two-electron oxidation of a 1 mM aqueous solution of *o*-tolidine with 0.5 M CH_3COOH and 1 M $HClO_4$ in the luminescence spectroelectrochemical cell. The electrochemical parameters were determined to be $E^{o'}$

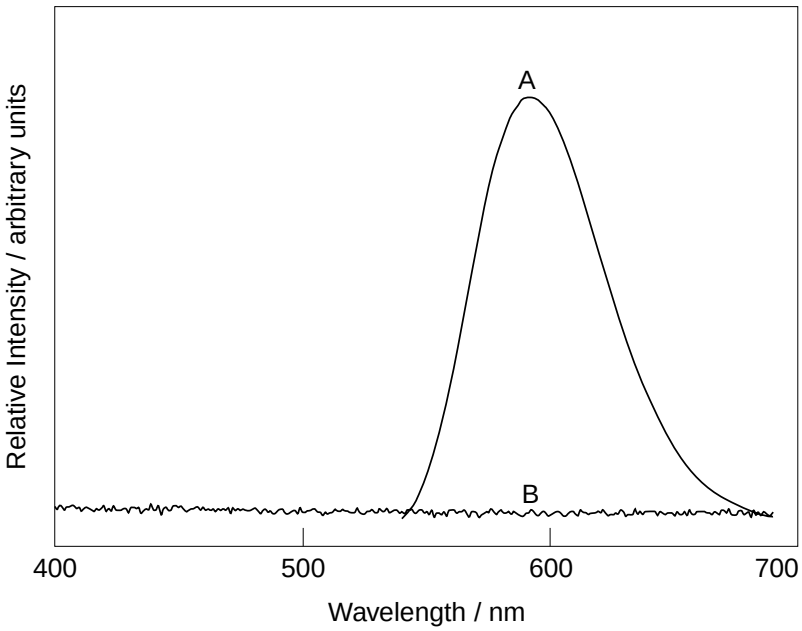
F3

Spectra recorded during a luminescence spectropotentiostatic experiment of 5 µM o-tolidine in 0.5 M CH_3COOH, 1 M $HClO_4$ in the luminescence spectroelectrochemical cell with 2 mm diameter optical channels. Applied potentials in V vs. Ag/AgCl are as follows: (A) +0.405; (B) +0.608; (C) +0.628; (D) +0.637; (E) +0.648; (F) +0.658; (G) +0.670; (H) +0.806. λ_{ex} is 270 nm. (Reprinted with permission from reference 14.)



F4

Uncorrected emission spectra of 0.14 mM (A) $[Re(dmpe)_3]^{2+}$, λ_{ex} = 530 nm; and B) $[Re(dmpe)_3]^{+}$, λ_{ex} = 220 nm in acetonitrile with 0.1 M (n-$Bu)_4NPF_6$ in the luminescence spectroelectrochemical cell. (Reprinted with permission from reference 16.)



= +0.635 V, ΔE_p = 90 mV and i_{pa}/i_{pc} = 1.0, which are in good agreement with literature values (6,13). Furthermore, the spectropotentiostatic oxidation of *o*-tolidine illustrates the stepwise decrease in luminescence intensity following excitation at 270 nm (***F3***). In a manner similar to absorption spectropotentiostatic experiments, $E^{o'}$ and n values can be calculated from the individual spectra with the Nernst equation and equation below, where I_{red}, I_{ox}, and I are the luminescence intensities of the solution under potential conditions that yield the completely reduced form, the completely oxidized form and a mixture of the oxidized and reduced forms, respectively, ϕ is the luminescence quantum efficiency, and b is the optical path length (13).

$$\frac{[Ox]}{[Red]} = \frac{(I_{red} - I)/\phi b}{(I - I_{ox})/\phi b} = \frac{I_{red} - I}{I - I_{ox}}$$

A Nernst plot of the applied potential versus log [Ox]/[Red] yields a straight line with the slope equal to 0.0591/n and the y-intercept equal to $E^{o'}$. The Nernst plot for the data at 405 nm (***F3***) yields $E^{o'}$ = +0.638 V and n = 1.91, which is consistent with the cyclic voltammetry data.

One area where our group has applied luminescence spectroelectrochemistry is in the investigation of the excited state properties of transition metal complexes. Typical photochemical and photophysical studies rely on the synthesis and purification of the complex of interest. Therefore, most photoluminescence studies of transition metal complexes center around easily synthesized electron configurations such as d^3, d^6 or d^{10}. In contrast, the luminescence spectroelectrochemical cell permits the investigation and characterization of synthetically inaccessible oxidation states provided the target oxidation state is electrochemically accessible from a parent complex and is stable in solution.

One example of this is the Re(II) complex, $[Re(dmpe)_3]^{2+}$, where dmpe is 1,2-bis(dimethylphosphino)ethane (16). The parent Re(I) complex, $[Re(dmpe)_3]^{+}$, is easily synthesized and exhibits a reversible one-electron oxidation to Re(II) in acetonitrile. The d^6 Re(I) form is colorless and upon excitation into the UV absorption band shows no luminescence (***F4***). However, oxidation in the luminescence spectroelectrochemical cell to the d^5 Re(II) electron configuration gives a reddish-pink solution with an absorption maximum at 530 nm, which has been assigned as a ligand-to-metal charge-transfer (LMCT) band. Excitation at 530 nm produces an intense emission at 593 nm (***F4***) with a quantum efficiency of 0.066; for comparison, the quantum efficiency of $[Ru(bpy)_3]^{2+}$ in water is 0.042. Consequently, luminescence in conjunction with absorption spectroelectrochemistry has enabled the discovery of a rare example of a highly luminescent transition metal complex with a d^5 electron configuration.

Conclusion

Luminescence spectroelectrochemistry is easily accomplished with the versatile cell design described above. In situ electrochemical generation of stable species coupled to spectroscopic characterization by luminescence and absorption methods clearly opens possibilities for the investigation of the properties of novel excited state species and their reactivity.

Acknowledgments

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