**Spectroelectrochemistry on ATR and Integrated Optic Waveguide Elements: Evolving from Monochromatic Studies to True Broad-Band Spectroelectrochemistry**

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Over the last 35 years spectroelectrochemistry has steadily evolved so that most of the electromagnetic spectrum has now been used to monitor solution or interfacial electrochemical events, in real time. Starting with transmission spectroelectrochemistry in the visible wavelength region, using the first optically transparent electrodes (OTE), significant sensitivity enhancements have been sought so as to allow for the characterization of redox events to surface confined molecular species. It has also been a goal to monitor more than one wavelength simultaneously (i.e. it is desirable to be able to do real spectroscopy rather than spectrometry).

Sensitivity enhancements were first obtained using attenuated total reflectance (ATR) elements as the OTE, and sensitivity increased generally not more than 10x of the transmission experiment.[1,2] Visible wavelength spectroelectrochemical sensitivity enhancements then were largely confined to long pathlength spectroelectrochemical cells, until Itoh and Fujishima[3] demonstrated that a channel integrated optic waveguide (IOW) could be overcoated with tin-oxide conductive films, thereby making use of the large number of internal reflections in the IOW, and increasing the sensitivity of the experiment by ca. 200x. Our groups have recently shown that overcoating a step-index IOW with an electroactive indium-tin-oxide layer, EA-IOW, can boost this sensitivity for the redox spectro-electrochemistry of a probe molecule by over 10,000x vs. the transmission experiment.[4,5]

The use of these IOW elements, however, makes it more difficult to couple light into the waveguide, and at first seemed to limit the possibility of ever getting more than one wavelength at a time to be used in the spectroelectrochemical experiment. Mendes, et.al.,[6] then showed that the optical dispersion of the waveguide could be partially compensated in the coupling scheme, and that ca 110 nm of the visible wavelength region could be internally reflected in a conventional IOW, using a combination of grating and prism couplers. Following this it became apparent that it might be possible to couple the entire visible wavelength region into an electroactive waveguide, or ATR element, and that using prism coupling of a collimated white light source, and multichannel (CCD) detection, one could obtain spectral information from ca. 450-900 nm while scanning the potential and changing the redox state of any number of surface-confined molecules and molecular assemblies (Figure 1).[7,8]

This talk will cover our recent development of broad-band electroactive waveguide and ATR elements, and the use of these new spectroelectrochemical tools in the characterization of redox reactions of both simple probe molecules (e.g. methylene blue), heme proteins (cytochrome c), and rod-like aggregate and polymer molecular assemblies, based on disk-shaped monomers (phthalocyanines).[9]

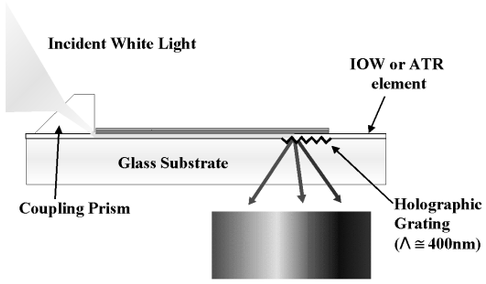


**Fig. 1 – Schematic view of broad-band IOW and ATR technologies, which make possible the full-visible wavelength spectroelectro-chemical characterization of adsorbed dyes and thin film molecular assemblies. Light is prism-coupled into the waveguide element, and outcoupled via an internal grating element, and multichannel detected to provide for a full visible spectrum as the potential of the electrode is scanned or stepped.**

## References

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