The Micro-Optical Ring Electrode: Development of a Novel Electrode for Photo electrochemistry

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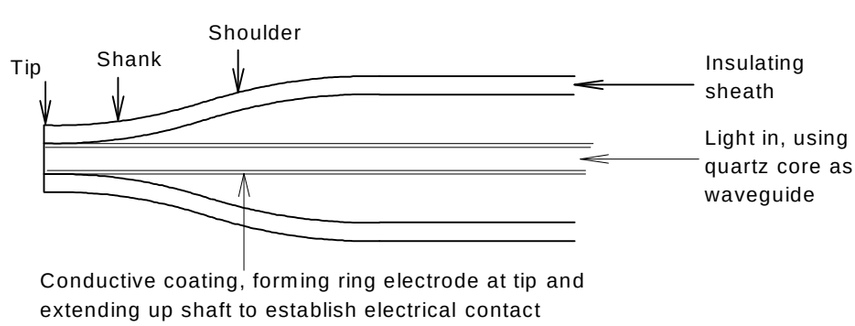
A microelectrode is an electrode with at least one characteristic dimension of less than 50 μm and as such has several advantages as an analytical technique: the small size allows access to hitherto inaccessible media: the correspondingly low current means low analyte consumption and ohmic polarisation and the detection of short-lived species is possible. The aim of this work was to design, build and develop the Micro-Optical Ring Electrode (MORE), a novel device capable of delivering light *via* a fibre optic light guide directly to the region of electrochemical measurement. Based on a ring microelectrode and using the insulating material interior to the ring electrode as a light guide, the MORE can therefore be used to conduct micro electrochemical studies of systems with complex photochemistry.

The MORE employs a thin ring configuration, which offers two additional advantages. (i) The consequent high material flux to the electrode surface facilitates the detection of short lived intermediates generated in the solution phase, and means that surface electron transfer will be rate determining over a wider range than observed on conventional ring electrodes. (ii) All of the extant semi-analytical solutions for the behaviour of ring electrodes in the dark are for thin rings; use of a thin ring MORE therefore precludes the necessity for characterisation of electrode response in the dark, an important consideration when dealing with electrochemically complex systems.

Many users of microelectrodes have experienced electrode failure which derives from two general sources: (i) material failure - one or more of the constituent materials of the electrode assembly has proven to be incompatible with the demands of the experimental environment; (ii) failure of the electrode-body seal, often due to insufficient cleaning of the electrode components during fabrication. Therefore, a novel assembly procedure, involving the deposition of thermally evaporated gold onto an appropriately treated fibre optic, has been developed for the reliable manufacture of MOREs with (ring inner radius)/(ring outer radius) values in excess of 0.999 and ring microelectrodes fabricated in this way demonstrate good agreement between the measured dark electrochemical response and theoretical predictions based on electrode geometry. Further, SEM images of freshly prepared MOREs confirm the presence of a thin ring microelectrode concentric with the fibre optic light guide, with ring thicknesses of less than 10 nm.

Preliminary experiments with photo electrochemically active dyes indicate that we can easily detect electro active species with lifetimes of < 90 μs when using a relatively large MOREs (fibre optic radius = 125 μm, ring thickness = 600 nm) and suggesting the study of $^1O_2$ in aqueous and biological systems (lifetime 4.2 μs) may be feasible with the more recently fabricated thinner microelectrodes.

The MORE has been used to characterise the photo electrochemical behaviour of ruthenium (II) tris bypiridal in the presence of a reducing agent [Fe(III)]. Light on transient experiments have been recorded using increasing concentrations of Fe(III). As expected, a direct correlation has been established between the photocurrent and the concentration of Fe(III) present in solution. A value of the Stern-Volmer constant (K_{st}) for the homogeneous quenching of photo excited $Ru(bipy)_3^{2+}$ by Fe^{3+} has been obtained from electrochemical measurements conducted using the MORE. The value of K_{st} so obtained (1.59 m^3 mol^{-1}) compares favourably with the value of the Stern-Volmer constant for the same reaction obtained from fluorescence measurements (0.9 m^3 mol^{-1}).

Latterly, the spectral dependence of the MORE response has investigated and the resultant photocurrent action spectrum found to correspond to the singlet-to-singlet, metal-to-ligand charge transfer band of the UV-visible spectrum of $Ru(bipy)_3^{2+}$, so demonstrating the potential utility of the MORE as a spectrophotoelectrochemical probe.

A schematic tip cross section of the MORE