Nanoelectrodes – New Dimensions of Space and Time in Electroanalysis

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Historically, our understanding of dynamics in electrochemical systems has been limited by the lack of experimental tools with adequate sensitivity. Steady improvements in the fabrication of microelectrodes since the early 1980's have reduced the characteristic dimensions of these ultrasmall probes. This project focuses on the production of nanometer dimensioned electrochemical sensors – nanodes. These small voltammetric probes greatly extend the range of sample environments and experimental timescales that are useful in electrochemical measurements.[1] For example, not only do they promise advances in monitoring target molecule concentrations in biosystems but they can provide information about the chemical reactivity of surfaces through Scanning Electrochemical Microscopy. Images of higher resolution are attained as the size of the scanning tip is reduced.

The principal method used to produce geometrically sharp tips for use in applications such as STM is electrochemical etching. Our approach uses an argon ion laser based micropipette puller to fabricate platinum electrodes of nanometer dimensions. A number of techniques have been implemented to characterize these electrodes. Optical microscopy images provide a rapid and simple method of visualizing the electrode, scanning electron microscopy has also been implemented but the information obtainable from this technique is limited due to charging effects, caused by the non-conducting quartz glass. The most comprehensive and informative technique used is cyclic voltammetry and these results are summarized in this contribution.

The principal application of the nanoelectrodes produced in this work is to measure fast heterogeneous electron transfer rate constants of redox species adsorbed on an electrode surface. Anthraquinone molecules spontaneously adsorb on mercury to form stable monomolecular films. Raman spectroscopy measurements reveal that these molecules adsorb in a parallel orientation at a distance of approximately 4-5 Å from the electrode surface.[2] Hence, the rate of electron transfer is not limited by diffusion processes. Heterogeneous electron transfer rates lie in the range 10^4 to 10^5 s^{-1}. Nanoelectrodes were necessary for these measurements, as the response time of an electrode decreases significantly as the size decreases.[3]

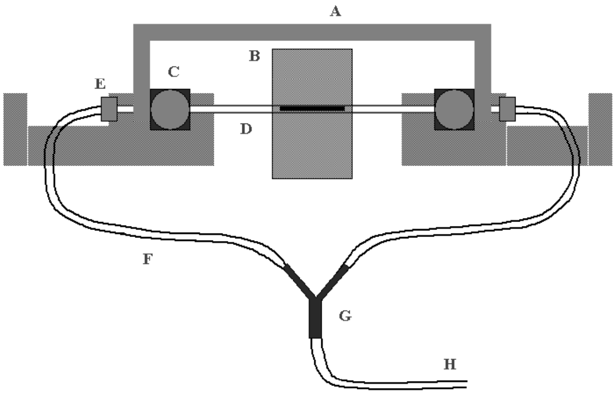

Figure 1. Micropipette puller, (A) metal clamp to prevent the hard pull during the first heating process, (B) laser beam and retro mirror, (C) capillary fixing screws, (D) quartz glass capillary with inserted platinum wire, (E) puller bars, (F) silicon tube connecting to glass capillary to allow its evacuation, (G), Y-connector and (H) silicon tube connection to the vacuum pump.

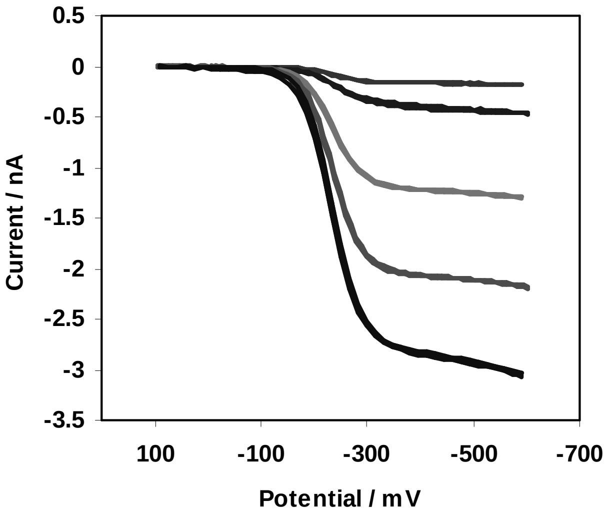

Figure 2. Steady state cyclic voltammetry responses for a range of electrodes produced in 5 mM $[Ru(NH_3)_6]^{3+}$ containing 0.1 M KCl as the supporting electrolyte. The scan rate was 1000 mV s^{-1} and the initial potential was 100 mV. The radius of the electrodes have been calculated, from top to bottom in the illustration as 158, 391, 1170, 1972 and 2741 nm.

References

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[1] Forster, R.J., *Chemical Society Reviews*, **1994**, 289.

[2] Forster, R.J., Keyes, T.E., Farrell, M., O'Hanlon, D., *Langmuir*, **2000**, 16, 9871.

[3] Bard, , A.J., Faulkner, L.R., *Electrochemical Methods:Fundamentals and Applications, Wiley, New York, SecondEdition,* **2001**.