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Graphene Ring Nanoelectrodes: Application as a Photoelectrochemical Sensor

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We report on the fabrication and characterisation of the first Graphene Ring Nanoelectrode (GRiN), **Figure 1**. Graphene was prepared from exfoliated graphite oxide (GO). GO was dip coated from suspension onto fibre optics and the resultant GO layers were converted to graphene by a two step hydrazine thermal, reduction process. The behaviour of the so-formed graphene ring nanoelectrodes was studied using ferricyanide and ruthenium hexamine as a probe redox system and electrode thicknesses assessed using well established electrochemical methods in conjunction with lateral force microscopy measurements. Ring thicknesses in the range 6-70 nm were obtained corresponding to ring inner to outer radius ratios in excess of 0.999, so allowing use of asymptotic analytical solutions derived for very thin ring microelectrodes in data analysis. The resultant nanoelectrodes are highly reliable (response invariant over >3000 scans), the nanoring design allowing for efficient utilisation of electrochemically active edge sites and the associated nanoamp scale currents neatly obviating issues relating to the high resistivity of undoped graphene.

Compared to conventional microelectrodes, the nanometer scale architecture of the GRiNs leads to enhanced rates of mass transport (due to spatially adjacent edge effects) and electron transfer rates (due to a more rapid potential drop within the diffuse double layer)[1, 2]. Study of these phenomena provides molecular level insight into the breakdown of the electroneutrality approximation at the nanoelectrodes surface and allows for fundamental studies of application areas such as nanomaterial fabrication, new energy generation and storage systems and novel nanosensors. Two-dimensional materials offer the possibility of a new paradigm in nanoelectrode design, material thickness being exploited to produce electrodes with characteristic dimensions on the nm/sub-nm scale. Graphene is the most attractive 2D material in this context, because of both its ease of fabrication and the high electrochemical activities of carbon based materials[3, 4, 5, 6].

The ring nanoelectrode is built around an optical fibre that allows for the delivery of light to the region of measurement. As such, it is capable of interrogating the electrochemistry of systems with complex photochemistries and possesses advantages associated with nanoelectrodes (it allows access to hitherto inaccessible media, the low current allows for a low analyte consumption, it renders possible the detection of short-lived species). Since redox chemistry is the basis of the GRiN's function, photocurrents generated should allow for simultaneous spectro and electrochemically derived selectivity and sensitivity for the target analyte. We further report the use of graphene nanoelectrodes to measure electron transfer rate constants for the $Fe(CN)_6^{4/3-}$ and $Ru(NH_3)_6^{3/2+}$ couples, finding that these are an order of magnitude larger than those obtained using macroelectrodes. The electrodes themselves exhibit specific capacitances >2 orders of magnitude greater than those reported for equivalent macro/ microelectrodes, a result that has profound implications for supercapacitor design. Thus, the availability of easy-to-fabricate GRiNs greatly expands the scope of both nanoelectrode and graphene-based electrochemical devices.

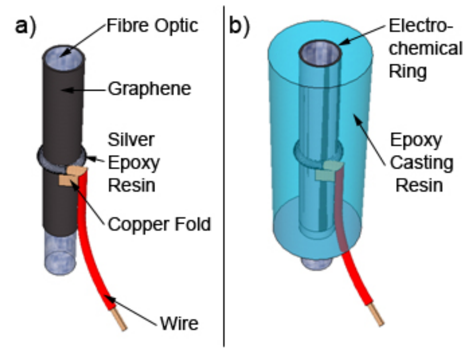

Figure 1: Construction of the GRIN. **a)** Attachment of electrical connector to the fibre optic mounted, graphene layer; **b)** casting of the assembly in epoxy resin.

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