

Nanocomposite Oxygen Reduction Electrocatalysts formed using Bioderived Reducing Agents

*Lee Johnson, Wim Thielemans and Darren A. Walsh**

School of Chemistry and Faculty of Engineering, The University of Nottingham,
Nottingham, NG7 2RD, UK

Figure S1 shows an SEM image of the surface of the cellulose/Ag nanocomposite-modified GC electrode used in the electrochemical measurements. The film was reasonably smooth but showed nanoparticulate features buried within the film.

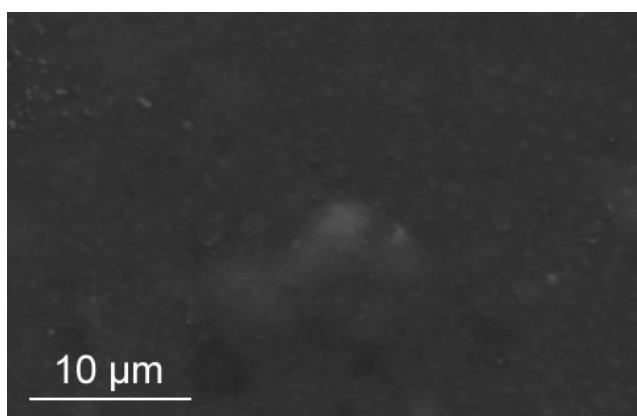


Figure S1 SEM image of the cellulose/Ag nanocomposite modified GC surface prepared by drop coating the reaction product obtained from heating a mixture of 211 mg AgNO₃ and 5 ml of 0.29 % wt. cellulose suspension to 80 °C for 2 hours.

To investigate the stability of cellulose nanofibrils in alkaline solutions, X-ray diffraction patterns of cellulose were compared before and after storing the nanofibrils in 0.1 M NaOH for 4 hours (Figure S2). No degradation of the crystal structure was observed within this time period, indicating that cellulose nanofibrils are suitable for use in alkaline media for extended periods of time.

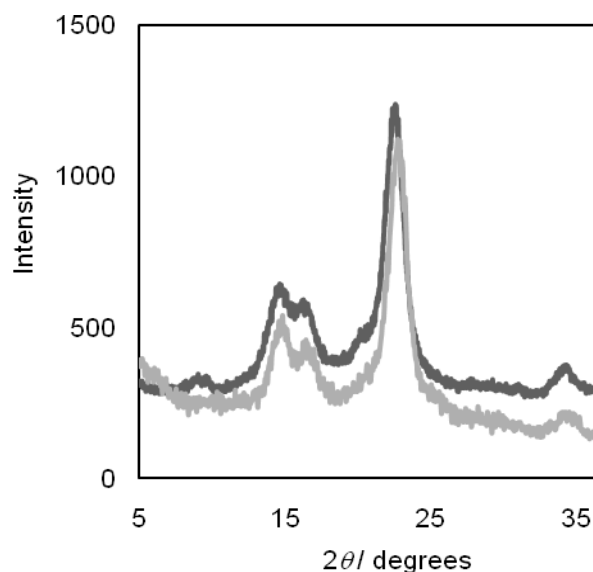


Figure S2 X-ray diffraction pattern of crystalline cellulose nanofibrils before (dark line) and after (light line) storage in a 0.1 M NaOH solution for 4 hours.

Rotating ring disk electrode (RRDE) voltammetry was used to confirm that the 4-electron reduction of O_2 occurred at the cellulose/Ag composite electrode in alkaline media (Figure S3A). The negligible ring current at all potentials demonstrates that the 4-electron reduction of oxygen was dominant at this surface. Furthermore, the stoichiometric number of electrons (n) can be determined from the voltammograms obtained using the RRDE by:

$$n = \frac{4}{1 + \left(\frac{i_R}{i_D} \times N \right)} \quad (1)$$

where i_R is the current at the ring, i_D is the current at the disk and N is the collection efficiency of the ring in the RRDE assembly (0.2). This clearly shows that the 4-electron reduction of O_2 was dominant at all potentials studied.

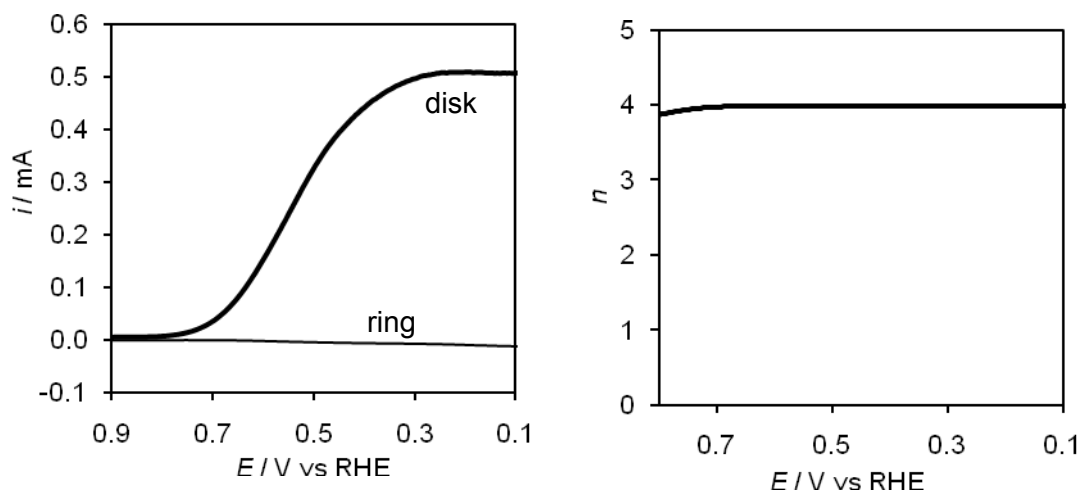


Figure S3. (A) Rotating ring-disk electrode polarisation curves obtained at a cellulose/Ag-modified glassy carbon disk/platinum ring assembly in O_2 -saturated 0.1 M NaOH. The potential of the disk was swept from 0.9 V to 0.1 V and the ring potential was maintained at 1.2 V to detect peroxide. (B) Plot of n versus E calculated from the experimental RRDE data.