COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Investigation of modified basal plane pyrolytic graphite electrodes: definitive evidence for the electrocatalytic properties of the ends of carbon nanotubes†

Craig E. Banks, Ryan R. Moore, Trevor J. Davies and Richard G. Compton*

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, UK OX1 3QZ. E-mail: Richard.Compton@chemistry.ox.ac.uk; Fax: +44 (0)1865 275410; Tel: +44 (0)1865 275413

Received (in Cambridge, UK) 26th May 2004, Accepted 7th June 2004
First published as an Advance Article on the web 15th July 2004

DOI: 10.1039/b406174h

The basis of the electrocatalytic nature of multi-wall carbon nanotubes is suggested to reside in electron transfer from the ends of nanotubes, which structurally resemble the behaviour of edge plane (as opposed to basal plane) graphite, and is demonstrated *via* the comparison of the electrochemical oxidation of epinephrine and the electrochemical reduction of ferricyanide at nanotube-modified electrodes using different types of graphite electrodes and with C_{60}-modified electrodes.

Carbon nanotubes have emerged as a new class of nanomaterials with their electronic, mechanical and chemical properties which have been claimed to be extremely attractive for use as chemical sensors, in particular *via* electrochemical detection;[1–4] Table 1†, although not exhaustive, summarises the prolific use of carbon nanotube-modified electrodes in electrochemistry. Nanotubes are assigned into two classes: single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs). The former are made from a single graphite sheet rolled flawlessly producing a tube diameter of 1–2 nm, while the latter are made of concentric and closed graphite tubules having diameters ranging from 2 to 50 nm.[1–3] Recent studies have shown that nanotube-modified electrodes exhibit attractive electrochemical properties producing ‘electrocatalytic’ effects, namely, enhanced currents with a significant reduction in the overpotential and good signal-to-noise characteristics, in comparison with other carbon based electrode materials, usually glassy carbon.[2,5–8]

Recently we have studied the oxidations of NADH (β-nicotinamide adenine dinucleotide, reduced disodium salt hydrate), epinephrine and norepinephrine using both multi-wall carbon nanotube- and graphite powder-modified basal plane pyrolytic graphite electrodes. Both ‘film’ and abrasive attachment forms of modification were used. Electrocatalytic behaviour of both types of nanotube-modified electrodes was observed with enhanced currents and reduced peak-to-peak separations in the voltammetry in comparison with naked basal plane pyrolytic graphite. However, similar catalytic behaviour was also seen at the graphite powder-modified electrodes, suggesting caution in assigning unique catalytic properties to multi-wall carbon nanotubes.[9]

The open ends of CNTs have been likened to edge planes of highly orientated pyrolytic graphite (hopg) with the tube walls suggested to have properties similar to those of basal planes of hopg electrodes.[10,11] With this in mind, together with the comparison with the graphite powder, we have tried to address the question as to *why* the nanotubes are catalytic, a previously unaddressed issue to the best of our knowledge.

A basal plane pyrolytic graphite (bppg) electrode was prepared for modification as described previously.[9] This was placed into a 1 mM solution of ferricyanide (in 0.1 M KCl) and cyclic voltammograms were recorded over a range of scan rates. C_{60} (99.5+%) was obtained from Lancaster (Morecambe, UK) and used as supplied. 0.0122 g was placed into 1.2 mL of 1,2-dichloroethane. 15 μL was pipetted onto a newly prepared bppg electrode and the organic liquid allowed to volatilise before the voltammetric response was measured in the ferricyanide solution over a range of scan rates. For comparison, a bppg electrode was abrasively modified with C_{60} *via* gentle rubbing of the electrode surface on a fine quality filter paper[9] and was explored *via* cyclic voltammetry in ferricyanide as described above. Fig. 1 shows the comparison of all three electrodes at a scan rate of 100 mV s^{-1}. For the C_{60} abrasively-modified bppg electrode, the peak-to-peak separation is 134 mV (at 100 mV s^{-1}), with a formal potential of 0.16 (±0.1) V (*vs.* SCE) with the peak-to-peak separation increasing with scan rates suggesting quasi-irreversible behaviour. In comparison, the unmodified and C_{60} film-modified electrodes have peak-to-peak separations of 315 mV and 340 mV (*vs.* SCE) respectively. The bare bppg electrode exhibits slow electron transfer as expected,[12] while an apparent paradox arises for the C_{60}-modified bppg electrodes, where the data suggest slow electron transfer at the film-modified electrode but faster electron transfer in the abrasively-modified case; we return to this issue below.

A MWNT-modified[13] electrode was prepared by placing 0.018 g of CNT in 15 mL acetonitrile. This was dispersed, with 10 μL of the suspension pipetted onto a prepared bppg electrode with the carrier liquid allowed to evaporate before use. The MWNTs were used as received since it has been shown that pre-treatment either *via* sonication or acid digestion has no effect on their electrochemical activity.[14] Shown in the ESI are SEM images of MWNT before immobilisation and after modification of a basal plane pyrolytic graphite electrode.† The cyclic voltammetric response was measured in a 1 mM solution of epinephrine (in pH 5 acetate buffer) and is shown in Fig. 2. Oxidation and reduction peaks can be seen at +0.41 (±0.01) V and −0.23 (±0.01) V, respectively (*vs.* SCE) suggesting the nanotubes are ‘electrocatalytic’. In comparison, the bare and C_{60} film-modified bppg electrodes exhibit irreversible oxidation peaks at +0.57 (±0.01) V and +0.64 (±0.01) V respectively suggesting slower electron transfer. In the case of the C_{60} film, the modification of the electrode surface serves to act as inert particles, resulting in a partially blocked electrode surface which appears to slow down the rate of electron transfer.[15,16] Next

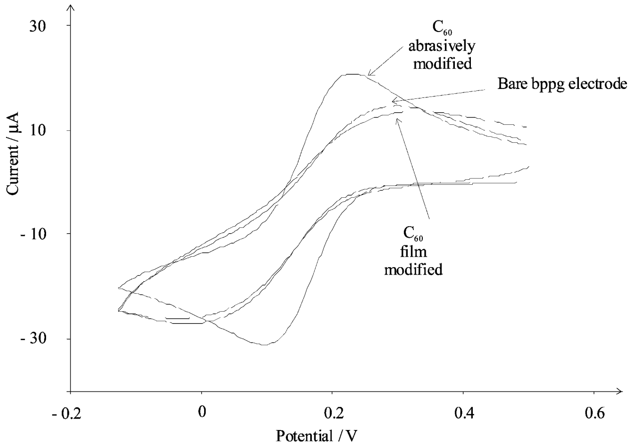

Fig. 1 Cyclic voltammograms of C_{60} abrasively- and film-modified and CNT-modified 4.9 mm (diameter) basal plane pyrolytic graphite electrode for the reduction of ferricyanide (in 0.1 M KCl) at a scan rate of 100 mV s^{-1}. Also shown is the response of the bare bppg electrode.

---

† Electronic supplementary information (ESI) available: the use of CNT-modified electrodes in electrochemistry, and SEM images of MWNTs before immobilisation and after modification of a basal plane pyrolytic graphite electrode. See http://www.rsc.org/suppdata/cc/b4/b406174h/

the response of an edge plane pyrolytic graphite electrode was sought.[17] Cyclic voltammograms run in the epinephrine solution reveal an oxidation peak at +0.38 (±0.01) V which is virtually identical to the oxidation potential observed at the carbon nanotube-modified electrode. The difference in the peak currents for the CNT film-modified case compared to the other electrodes reflects the fact that the nanotube film is potentially 'porous' leading to 'thin layer' behaviour and loss of the diffusional tail seen with the other electrodes.

We next compare the response of the C_{60}- and nanotube-modified film electrodes and the edge and basal pyrolytic graphite electrodes in the electro-reduction of 1 mM ferricyanide (in 0.1 M KCl). As depicted in Fig. 3, the bare and C_{60}-modified electrodes have peak-to-peak separations of 350 mV and 550 mV (at 100 mV s^{-1}) respectively. However, in comparison, the nanotube-modified electrode has a peak-to-peak separation of 58 mV while for the edge plane electrode this is 78 mV suggesting that the electrochemical reaction occurs with a similar rate constant for both. The slight difference in electron transfer rates between the edge plane pyrolytic graphite electrode and carbon nanotube-modified electrodes, may likely reflect slight impurities of basal plane in the edge plane pyrolytic graphite.

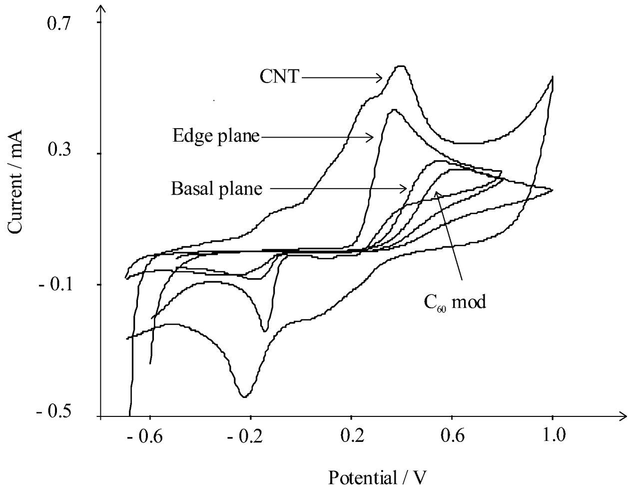

Fig. 2 Cyclic voltammograms for the oxidation of 1 mM epinephrine (in pH 5 buffer) for CNT- and C_{60} film-modified bppg electrodes compared with a bare bppg electrode and an edge plane pyrolytic graphite electrode. All at a scan rate of 100 mV s^{-1}. Note the current for all the CV's except the CNT-modified have been multiplied by a factor of 4 for clarity (see text for details).

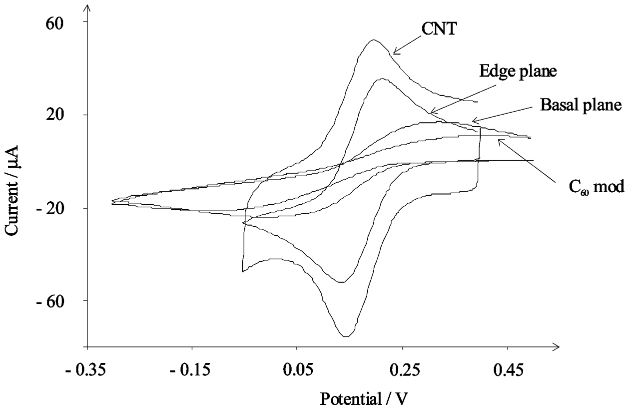

Fig. 3 Cyclic voltammograms for the reduction of 1 mM ferricyanide for CNT- and C_{60} film-modified bppg electrodes. Also shown is the response of a bare bppg electrode and an edge plane pyrolytic graphite electrode. All scans at a rate of 100 mV s^{-1}.

Comparison of the modified and bare electrodes in both the oxidation of epinephrine and the reduction of ferricyanide reveals that there is no significant difference between the use of edge plane pyrolytic graphite electrodes and carbon nanotube-modified graphite electrodes for use as electrocatalysts, at least in the context of the chemical systems studied in this paper, suggesting that the electrocatalytic properties of carbon nanotubes are edge plane like sites which occur at the open ends of the nanotubes.

Returning to Fig. 1, an abrasively C_{60}-modified graphite electrode was shown to be somewhat electrocataytic for the reduction of ferricyanide in comparison with a C_{60} film-modified electrode. It can be inferred that in the preparation of the abrasively-modified electrode, the abrasive nature of the C_{60} crystals serve to 'roughen' the basal plane pyrolytic graphite electrode, introducing edge plane sites and hence the observed electrocatalysis.

If the inference that the 'electrocatalytic' properties of multi-wall nanotubes resides in electron transfer from their ends and that the latter resemble edge plane pyrolytic graphite in behavior is correct, it should be possible to obtain fast electrode kinetics for a variety of substrates (Table 1†) detectable *via* carbon nanotube-modified electrodes by simply using edge plane graphite electrodes. This was examined for the cases of homocysteine, *N*-acetylcysteine, cysteine and glutathione, and for each the electrocatalysis seen at nanotube-modified electrodes was mirrored in the results seen at the edge plane electrode.[18]

CEB and TJD thank the EPSRC for support *via* project studentships.

Notes and references

1 C. N. R. Rao, B. C. Satishkumar, A. Govindaraj and M. Nath, *ChemPhysChem*, 2001, **2**, 78–105.
2 B. S. Sherigara, W. Kutner and F. D'Souza, *Electroanalysis*, 2003, **15**, 753–772.
3 P. M. Ajayan, *Chem. Rev.*, 1999, **99**, 1787–1799.
4 N. Li, J. Wang and M. Li, *Rev. Anal. Chem.*, 2003, **22**, 19–33.
5 H. Luo, Z. Shi, N. Li, Z. Gu and Q. Zhuang, *Anal. Chem.*, 2001, **73**, 915–920.
6 F. H. Wu, G.-C. Zhao and X.-W. Wei, *Electrochem. Commun.*, 2002, **4**, 690–694.
7 M. D. Rubianes and G. A. Rivas, *Electrochem. Commun.*, 2003, **5**, 689–694.
8 J. Wang and M. Musameh, *Anal. Chem.*, 2003, **75**, 2075–2079.
9 R. M. Moore, C. E. Banks and R. G. Compton, *Anal. Chem.*, 2004, **76**, 2677–2682.
10 J. J. Gooding, R. Wibowo, J. Liu, W. Yang, D. Losic, S. Orbons, F. J. Mearns, J. G. Shapter and D. B. Hibbert, *J. Am. Chem. Soc.*, 2003, **125**, 9006–9007.
11 J. M. Nugent, K. S. V. Santhanam, A. Rubio and P. M. Ajayan, *Nano Lett.*, 2001, **1**, 87–91.
12 R. L. McCreery, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1990, **vol. 17**, p. 304.
13 MWCNTs (>95% purity, 10–20 nm diameter, 5–20 µm length) prepared by chemical vapour deposition were obtained commercially from NanoLab (Brighton, MA, USA).
14 N. S. Lawrence, R. P. Deo and J. Wang, *Talanta*, 2004, **63**, 443–449.
15 C. Amatore, J. M. Saveant and D. Tessier, *J. Electroanal. Chem.*, 1983, **147**, 39–51.
16 T. J. Davis, B. A. Brookes and R. G. J. Compton, *Electroanal. Chem.*, 2004, **566**, 193–216.
17 The edge plane pyrolytic graphite was prepared by mounting pyrolytic graphite in epoxy resin with the edge plane exposed, followed by polishing with 0.1 micron alumina paste on soft lapping pads.
18 R. M. Moore, C. E. Banks and R. G. Compton, *Analyst*, 2004, DOI: 10.1039/b406276k.