Functionalization of Multi Walled Carbon Nanotubes with Pyrene-based Groups for Enhanced Oxygen Reduction by Laccase

Fabien Giroud [a], Shelley D. Minteer [a,b]
[a] Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, United States
[b] Department of Materials Science and Engineering, University of Utah, Utah 84112, United States

Multi copper oxidases are enzymes that can reduce oxygen. This property makes them suitable enzyme for their use on the biocathode in biofuel cells. Fungal laccase, a MCO, is a very attractive candidate at the cathode due to its ability to reduce O_2 directly to water via a 4 electron process. Moreover, laccases are known to be able to undergo direct electron transfer (DET) from the current collector material to the active center of the enzyme where oxygen is reduced in a four electrons process avoiding the use of small redox mediator (potentially toxic and not stable). To achieve DET at the electrode, the enzyme has to be orientated specifically and has to be in close proximity of the electrode. With its natural substrates, i.e. phenolic compounds, electrons enter in the enzyme *via* the T1 copper site and are tunneled to the T2/T3 copper center.

Many strategies are used to immobilize laccase at the cathode [1-4]. However, the random immobilization of the enzyme often results in low current densities which can decrease in the overall performances of the biofuel cell. An elegant approach first developed by Blandford et al. [5], due to its structure, anthracene can fit in the hydrophobic pocket of laccase in close vicinity to the T1 copper and acts as an electron relay to shuttle electron directly from the conductive material to the copper atom. Since then, different research groups have been adapted this technique with gold surfaces [6], carbon nanotubes (either ends or the walls) [7, 8].

Here, we report a new strategy to functionalize carbon nanotube (CNT) walls using pyrene groups modified by anthracene groups. Pyrene groups, themselves, have been reported to improve DET of laccase (thus orientation). A further modification of the pyrene with an anthracene group show an increase in catalytic current compared to the regular pyrene-based CNTs. Different pyrene moieties are examined in this study. Finally, the resulting electrodes are assembled with different anodes in complete glucose/oxygen biofuel cells.

References

[1] E. Nazaruk, A. Michota, J. Bukowska, S. Shleev, L. Gorton,R. Bilewicz, JBIC Journal of Biological Inorganic Chemistry, 12 (2006) 335-344.
[2] U.B. Jensen, M. Vagin, O. Koroleva, D.S. Sutherland, F. Besenbacher,E.E. Ferapontova, Journal of Electroanalytical Chemistry, 667 (2012) 11-18.
[3] C. Vaz-Dominguez, S. Campuzano, O. Rüdiger, M. Pita, M. Gorbacheva, S. Shleev, V.M. Fernandez,A.L. De Lacey, Biosensors and Bioelectronics, 24 (2008) 531-537.
[4] A. Zebda, C. Gondran, A. Le Goff, M. Holzinger, P. Cinquin,S. Cosnier, Nature Communications, 2 (2011) 370.
[5] C.F. Blanford, R.S. Heath,F.A. Armstrong, Chemical Communications, (2007) 1710.
[6] M.S. Thorum, C.A. Anderson, J.J. Hatch, A.S. Campbell, N.M. Marshall, S.C. Zimmerman, Y. Lu,A.A. Gewirth, The Journal of Physical Chemistry Letters, 1 (2010) 2251-2254.
[7] M.T. Meredith, M. Minson, D. Hickey, K. Artyushkova, D.T. Glatzhofer,S.D. Minteer, ACS Catalysis, 1 (2011) 1683-1690.
[8] K. Stolarczyk, M. Sepelowska, D. Lyp, K. Żelechowska, J.F. Biernat, J. Rogalski, K.D. Farmer, K.N. Roberts,R. Bilewicz, Bioelectrochemistry, 87 (2012) 154-163.