ACCUMULATION AND REACTIVITY OF THE REDOX PROTEIN CYTOCHROME C IN MESOPOROUS FILMS OF TIO_2 PHYTATE

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The formation of nanofilm deposits of TiO_2 nanoparticle phytates based on the 'directed assembly' methodology [1] is demonstrated. Alternant exposure of a tin-doped indium oxide (ITO) electrode surface to aqueous solutions of TiO_2 nanoparticles (3-4 % in HNO_3, ca. 6 nm diameter) and phytic acid (40 mM, at pH 3) causes layer-by-layer growth of a three dimensional mesoporous structure.

Cytochrome *c* in aqueous phosphate buffer (pH 7) is readily accumulated into the mesoporous TiO_2 phytate film predominantly due to electrostatic binding of the positively charged protein to the negatively charged interfacial phytic acid. Voltammetric data for the reversible reduction and re-oxidation of cytochrome *c* suggest strong adsorption and 'ideal' thin film behaviour over a wide range of conditions. Voltammetric data is analysed quantitatively based on the model of a finite diffusion zone. For a TiO_2 phytate modified electrode immersed in aqueous 0.1 M phosphate buffer (pH 7), strong accumulation (a three orders of magnitude increase in concentration) of cytochrome *c*, an apparent standard rate constant for electron transfer, $k_{0\text{apparent}}$ = 3 x 10^{-8} m s^{-1}, and an effective diffusion coefficient for cytochrome *c* within the mesoporous structure, $D_{\text{effective}}$ = 2 x 10^{-14} m^2 s^{-1}, are obtained. The redox processes within the nanoporous membrane, which are insensitive to impurities and strongly affected by the electrolyte concentration in the aqueous buffer solution, are proposed to be dominated by electron 'hopping' between adjacent cytochrome *c* molecules.

References

[1] K.J. McKenzie, F. Marken, M. Hyde, R.G. Compton, *New J. Chem*., 26 (2002) 625.

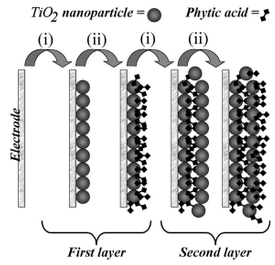

Fig. 1. Schematic Description of the 'Directed Assembly' Deposition Process.

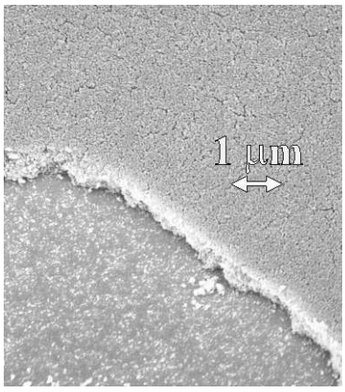

Fig. 2. FEGSEM image of the TiO_2 phytate Membrane Deposit.

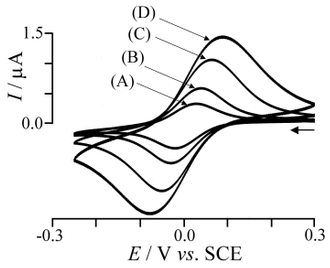

Fig. 3. Cyclic voltammograms (3rd scan, scan rate (A) 1, (B) 2, (C) 5, (D) 10 mV s^{-1}) obtained for the reduction of 0.05 mM cytochrome c in 0.1 M aqueous phosphate buffer (pH 7) at a TiO_2 phytate film modified ITO electrode (30 layer deposit).