Supplementary Information

Electrodeposition of Prussian Blue/Carbon Nanotube Composites at a Liquid-Liquid Interface

Samantha Husmann, a,b Samuel G. Booth, b Aldo J. G. Zarbin* a,b and Robert A. W. Dryfe* a,b

aGrupo de Química de Materiais, Departamento de Química, Universidade Federal do Paraná, CP 19081, 81531-980 Curitiba-PR, Brazil

bSchool of Chemistry, University of Manchester, Oxford Road, M13 9PL Manchester, UK

Figure S1. Cyclic voltammetry of CNTs films in KCl (0.1 mol L$^{-1}$) and K$_3$[Fe(CN)$_6$] (1.0 mmol L$^{-1}$) at pH 5 (a and b) and pH 4 (c and d). Scan rate 50 mV s$^{-1}$. Potential windows (a) –0.3 to 1.1 V; (b) –0.3 to 1.3 V; (c) 0.0 to 1.3 V and (d) –0.2 to 1.3 V.

*e-mail: aldozarbin@ufpr.br; robert.dryfe@manchester.ac.uk
Figure S2. Cyclic voltammetry of the bare water/DCB interface in different potential ranges. Aqueous phase: 0.1 mol L$^{-1}$ LiCl. Scan rate 15 mV s$^{-1}$.

Figure S3. Cyclic voltammetry of the water/DCB interface. Bare interface (a and b) with aqueous phase containing LiCl (0.1 mol L$^{-1}$) and K$_3$[Fe(CN)$_6$] (1.0 mmol L$^{-1}$) at pH 4 (a) and the 50$^{th}$ cycle at different pHs (b). (c) Interface with hollow CNTs (arc discharge) and (d) comparison of the 100$^{th}$ cycle obtained in aqueous solution of LiCl (0.1 mol L$^{-1}$, pH 4) with hollow and iron-filled CNTs assembled at the L/L interface. Scan rate 15 mV s$^{-1}$. 
Figure S4. Cyclic voltammetry of the water/DCB interface. Aqueous phase contains LiCl (0.1 mol L$^{-1}$) and K$_4$[Fe(CN)$_6$] (1.0 mmol L$^{-1}$) in solutions of varying pH. Scan rate 15 mV s$^{-1}$.

Figure S5. Raman spectra at the L/L interface containing assembled CNTs acquired at different times during chronoamperometry at 1.1 V.
Figure S6. Optical images obtained at different heights of the 4-electrode cell after PB deposition on the water/DCB system containing CNTs assembled at the interface. Electrodeposition under polarization of L/L interface at 1.1 V for 30 min with aqueous solution of 1 mmol L\(^{-1}\) K\(_3\)[Fe(CN)]\(_6\) and 0.1 mol L\(^{-1}\) LiCl, pH 3.

Figure S7. Raman spectra of the water/DCB system with CNT/PB assembled at the interface. Aqueous phase: 0.1 mol L\(^{-1}\) LiCl, pH 7.
Figure S8. Raman spectra of the water/DCB system with hollow CNTs assembled at the interface. Aqueous phase: LiCl (0.1 mol L\(^{-1}\)) and K\(_4\)Fe(CN)\(_6\) (1.0 mmol L\(^{-1}\)) pH 4. Projection (a) and spectra (b) of the depth profile obtained from Raman spectra acquired at different heights within the cell; (c) spectra obtained at different times at a fixed applied potential of 1.1 V; (d) spectra of the L/L interface before and after applying 1.1 V across the interface for 2100 s.