

Detailed analysis of electron transfer properties of azurin adsorbed on graphite electrodes using dc and large amplitude Fourier transformed ac voltammetry

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Supporting Information: Experimental 2nd and 3rd harmonic voltammograms, a table of $E^{0'}$ values derived from harmonic data, experimental and simulated FT dc data, and simulated and experimental power spectra are included here.

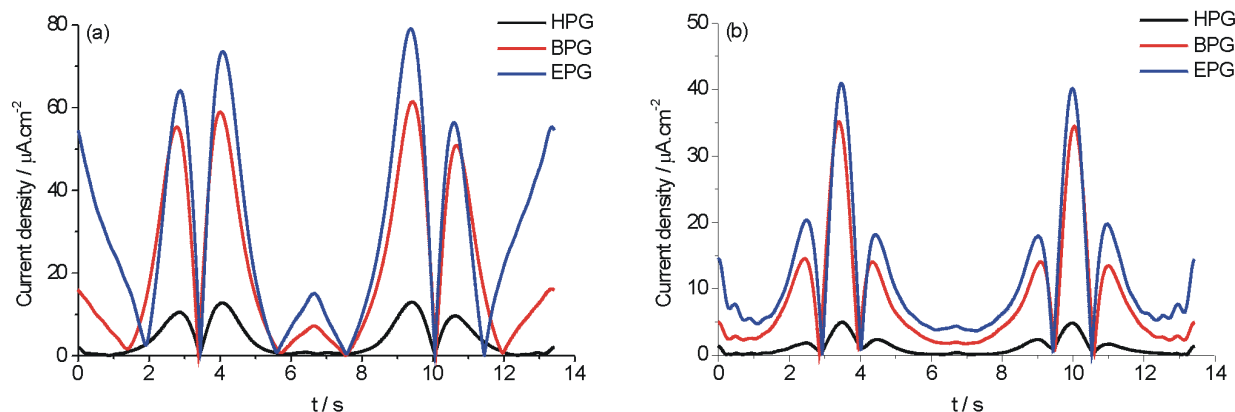


Figure S-1 – The (a) 2nd and (b) 3rd harmonic voltammograms for azurin adsorbed onto HPG (black), BPG (red) and EPG (blue) electrodes. Experimental conditions: $f = 22$ Hz, $\Delta E = 80$ mV, $v = 0.09686$ V.s⁻¹, $E_i = 0.450$ V, $E_s = -0.200$ V.

Table S-1 - $E^{0'}$ values (V vs. SHE) calculated^a from the 1st, 2nd, 3rd and 4th harmonic voltammograms for azurin-modified HPG, BPG & EPG electrodes.

	HPG				BPG				EPG			
f / Hz	1 st	2 nd	3 rd	4 th	1 st	2 nd	3 rd	4 th	1 st	2 nd	3 rd	4 th
10	0.325	0.322	0.317	0.316	0.328	0.327	0.324	0.324	0.325	0.323	0.319	0.318
22	0.326	0.324	0.317	0.316	0.329	0.327	0.324	0.324	0.325	0.323	0.318	0.318
36	-	-	-	-	0.328	0.327	0.324	0.324	0.324	0.323	0.318	0.318
61	-	-	-	-	0.328	0.327	0.323	0.324	0.324	0.323	0.318	0.317
84	-	-	-	-	0.328	0.326	0.323	0.324	0.324	0.322	0.317	0.317
107	-	-	-	-	0.328	0.327	0.324	0.324	0.324	0.322	0.317	0.317
135	-	-	-	-	0.328	0.327	0.324	0.324	0.323	0.322	0.317	0.317

^a As for the dc case, the $E^{0'}$ values were calculated using $(E_p^{ox} + E_p^{red})/2$, however E_p^{ox} and E_p^{red} were measured at the positions of the highest peaks for the 1st and 3rd harmonics, and the position of the minimum between the two largest peaks for the 2nd and 4th harmonics.

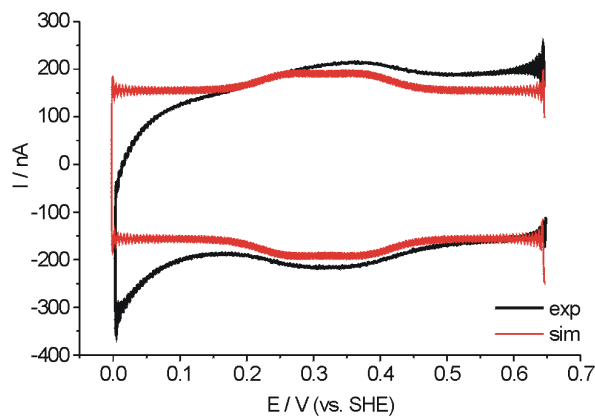


Figure S-2 – Comparison of experimental (black line) and simulated (red line) dc cyclic voltammograms obtained from an ac sine wave experiment for azurin adsorbed onto a BPG electrode. Experimental conditions as per Figure 8, except: $f = 22$ Hz. Simulation parameters: $C_{dl} = 46 \mu\text{F.cm}^{-2}$, $\Gamma_{dc} = 24 \text{ pmoles.cm}^{-2}$, $E^{0'} = 0.318 \text{ V}$, $R_u = 170 \Omega$; $k^{0'} = 1000 \text{ s}^{-1}$, $\alpha = 0.5$.

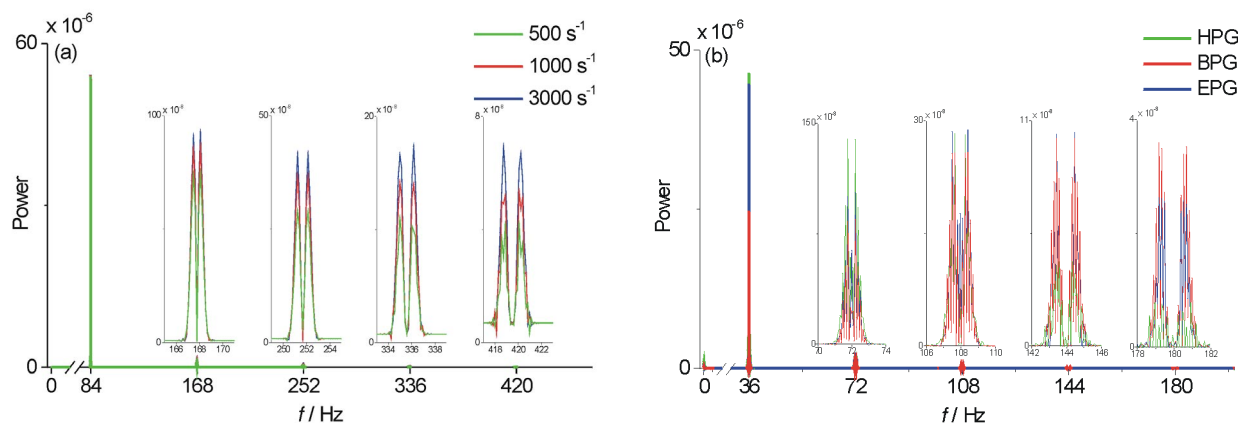


Figure S-3 – Power spectra obtained from (a) simulated total current sine-wave voltammograms having $k^{0'}$ values of 500 (green), 1000 (red) and 3000 s^{-1} (blue), and (b) experimental total current sine-wave voltammograms of azurin adsorbed onto HPG (green), BPG (red) and EPG (blue) electrodes. Simulation parameters: $C_{dl} = 36 \mu\text{F.cm}^{-2}$, $\Gamma = 11 \text{ pmoles.cm}^{-2}$, $E^{0'} = 0.318 \text{ V}$, $R_u = 170 \Omega$, $\alpha = 0.5$. Experimental conditions as per Figure 8.