Effect of doping level on the biological stability of hydrogenated boron doped diamond electrodes: Electronic supplementary information

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We here present additional data on:

- Fitting of the decrease in oxidative peak current after successive cyclic voltammograms of dopamine
- Interactions between oxidized dopamine and albumin inducing an EC' mechanism

1 Fitting of the decrease in oxidative peak current after successive cyclic voltammograms of dopamine

For the DA experiments, 2 different protocols were used. CVs were initially performed in unstirred solutions, as shown in the main article, but accumulation of oxidised DA on the electrode led to signal distortions (in particular, dramatic oxidative peak shift and apparition of new peaks) after the first scan. Indeed, the BDD or GC electrodes were located at the bottom of the electrochemical cell, and DA oxidation led to sedimentation of dopamine-*o*-quinone films, because of gravity. This effect could be reversed by flushing the cell with a pipette, and was not related to chemical fouling (ie. strong adsorption of spectator species on the electrode surface). For this setup, the first cycle was used for analysis, as no major distortion could be observed. In the second protocol, the solution was magnetically stirred at 1000 RPM to prevent this phenomenon. 10 cycles were performed, and data from the cycles 2 to 10 were used. In particular, the fouling was investigated by calculating the normalized peak current $\frac{I_{ox,n}}{I_{ox,2}}$ where $I_{ox,n}$ is the oxidation peak current from the n-th cycle, $n \in [|2,10|]$. The results for the current ratio were then fitted, using a Levenberg-Marquardt fitting algorithm implemented in the Igor software (Wavemetrics, USA), with an exponential function $f(n) = K_0 + K_1\ exp(-nt/K_2)$ where t is the duration of dopamine oxidation during one cycle. K_0 is the current ratio after an infinite number of cycles and K_2 is the fouling characteristic time, in s.

Successive CVs are shown on Fig.1. These scans were performed in stirred solutions, to avoid accumulation of oxidised dopamine films on the substrate. Magnetic stirring induced a significant amount of noise, which was partially removed by Gaussian filtering. The anodic currents were then measured and the successive values were normalized and fitted with a decreasing exponential. The BDD electrodes were found to have a higher K_0 than the GC. Furthermore, the fouling rate K_2 was also found to be larger on the BDD substrates, thus indicating that these types of material are more resistant to dopamine fouling.

Table 1 Results for the fitting of current ratios in cyclic voltammetry of 1 mM dopamine in PBS, pH = 7.4

	Conditions	K_0 / A.U.	K_2 / s
BDD-0.1%	No albumin	0.88	10.2
	Albumin	0.92	4.1
BDD-1%	No albumin	0.83	15.2
	Albumin	0.93	1.8
BDD-5%	No albumin	0.88	14.8
	Albumin	0.92	1.8
GC-D	No albumin	0.78	3.9
	Albumin	0.87	2.1

In presence of albumin, we see, as expected, that the reverse peak is relatively smaller, as oxidised dopamine as been reduced by the 4% m/v albumin solution. If the current ratios are fitted with a decreasing exponential, we see smaller differences than in the albumin free conditions. In particular, K_0, the ratio after an infinite number of cycles, is close to 90 % for all the electrodes. Additionally, the characteristic time K_2 is about one order of magnitude smaller, thus indicating quicker stabilization of the electrode. Presence of albumin, by regenerating dopamine-*o*-quinone to the non-fouling dopamine, actually protects the electrode from chemical fouling and enhances its stability. This definitely shows that protein and chemical foulings arise from 2 different phenomena, respectively passive adsorption and reaction dependent formation of an inactivating layer.

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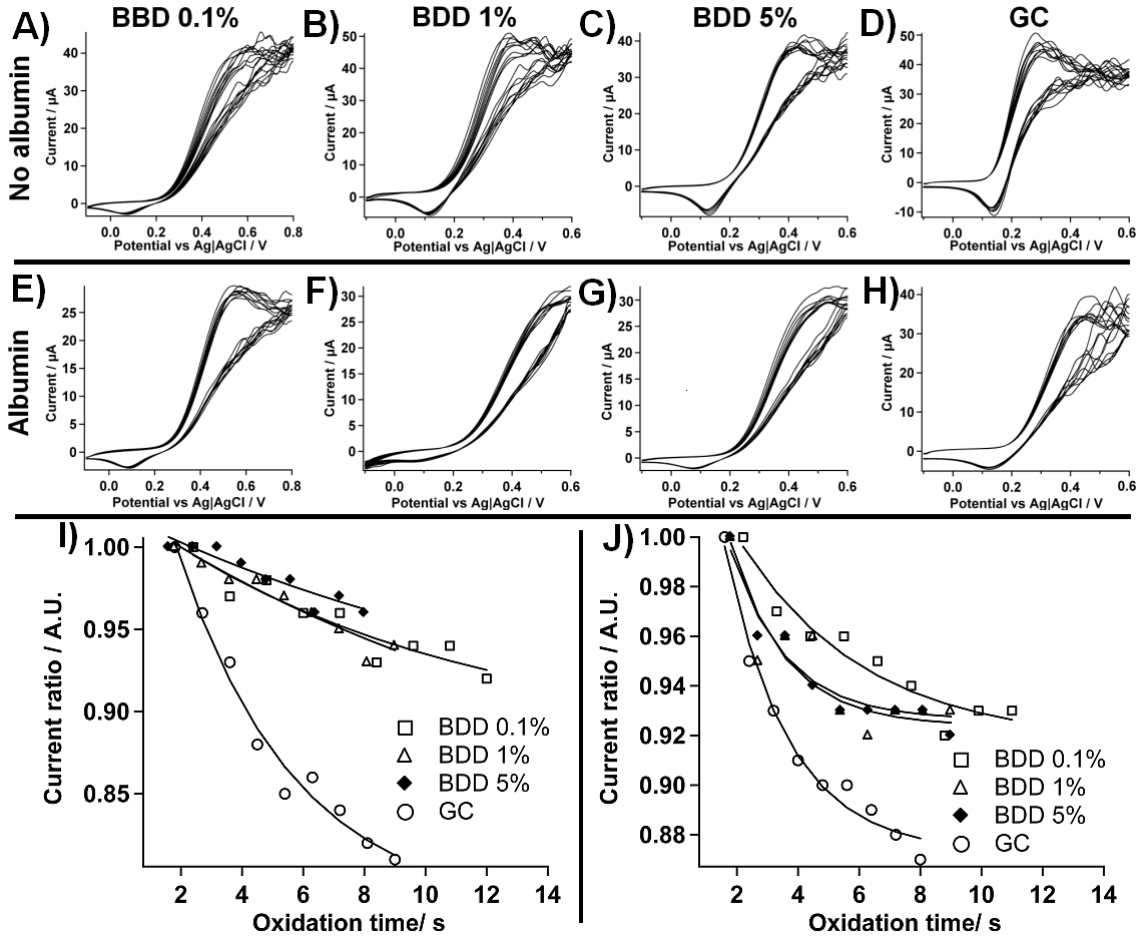

Fig. 1 9 Typical successive cyclic voltammograms (scan rate = 50 mV.s^{-1}) for 1 mM dopamine in PBS, pH = 7.4, performed with A, E) a BDD-0.1% electrode, B, F) a BDD-1% electrode, C, G) a BDD-5% electrode and D, H) a GC electrode, without (A, B, C, D) or with (E, F, G, H) 4% m/v albumin. Exponential fitting of the anodic peak current after 9 successive CV for 1 mM dopamine in PBS, I) without or J) with 4% m/v albumin.

2 Interactions between oxidized dopamine and albumin inducing an EC' mechanism

During an electrochemical reaction, for instance where the specie A is oxidised to B, B can then be regenerated to A by a chemical reaction according to the following scheme, known as an EC' mechanism: [1]

$$A \rightarrow B + e^{-} \ (electrochemical) \quad (1)$$

$$B \rightarrow A \ (chemical) \quad (2)$$

In our case, dopamine, once oxidised to dopamine-*o*-quinone, can be regenerated by the albumin present in the solution, probably through an EC' mechanism involving reduction by the thiol moieties present in albumin.

This is demonstrated by running several CVs, at different scan rates, for 1 mM dopamine in 4 % m/v albumin in PBS. The electrode used was a GC (CH Instruments, Austin, US) polished on 0.05 μm alumina aqueous slurry and sonicated in deionized water. The results (n=1) are shown on Fig.2A
We see that the shape of the i-V curves changes. In particular, as the scan rate decreases, the reverse cathodic peak becomes relatively smaller in comparison to the anodic peak. Fig.2B shows the variations of the ratio $\frac{i_{anodic}}{i_{cathodic}}$ where i_{anodic} and $i_{cathodic}$ are respectively the anodic and cathodic peak currents. These values were fitted with a decreasing exponential. A ratio of 2.19 is expected for infinetly high scan rates, according to this fitting. We can also see that, below ≈150 mV.s^{-1}, the ratio increases as the cathodic peak decreases. This is due to the regeneration of the dopamine, through the reduction of dopamine-*o*-quinone by albumin. This reaction depletes the

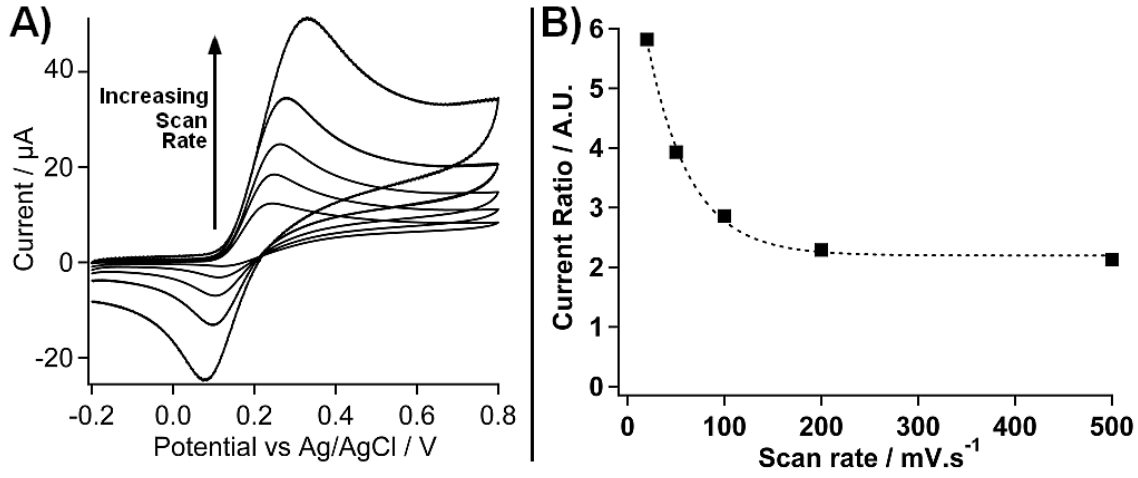

Fig. 2 A) Typical cyclic voltammograms of 1 mM dopamine in PBS, with 4 % albumin, for different scan rates (20, 50, 100, 200 and 500 $mV.s^{-1}$); B) Anodic peak current to cathodic peak current ratio as a function of scan rate (n = 1)

diffusion layer in oxidised species, thus reducing the cathodic current. Furthermore, it appears that this reaction is slow, as the current ratio starts increasing at low (below $\approx$150 $mV.s^{-1}$) scan rates.

References

1 S. Treimer, A. Tang and D. Johnson, *Electroanalysis*, 2002, **14**, 165–171.