



Short communication

# Cathodic pretreatment improves the resistance of boron-doped diamond electrodes to dopamine fouling

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## ABSTRACT

The resistance of cathodically and anodically treated boron-doped diamond electrodes to dopamine fouling was investigated. It was found, using cyclic voltammetry and electrochemical impedance spectroscopy, that the cathodic preparation offers an increased resistance to fouling, in addition to an enhanced electrochemical response.

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## 1. Introduction

Boron-doped diamond (BDD) has attracted increasing attention as a reliable and robust electrode material. This surface has shown its potential in water treatment and ozone generation, and its increased resistance to dopamine (DA) or serotonin foulings [1–3] makes it a promising candidate for bio-analysis [4–7].

Even though the native BDD is hydrogen-terminated, its surface can be modified by adequate pretreatments. Cathodic or anodic pretreatments in acids have been found to regenerate a fouled BDD electrode [8] and to alter the response of BDD, the cathodic one leading to enhanced electrochemical responses [9]. Different preparation procedures for BDD have been found to show different electrochemical responses and to allow for the separation of DA and ascorbic acid oxidation signals [5]. In this communication, the effect of pretreatment on DA fouling has been investigated.

## 2. Experimental

Ferrocenemethanol (FcMeOH), hexaammineruthenium (III) chloride (RuHex), DA, and sulfuric acid (98%) were all obtained from Sigma-Aldrich. Phosphate buffered saline (PBS, pH = 7.4) was obtained

from PAA Laboratories GmbH. Poly-dimethylsiloxane (PDMS) was obtained from Dow Corning, USA. Deionized water was used throughout the experiments. As described elsewhere [1], the boron doped polycrystalline diamond films were grown on p-type (111) silicon wafers (Furuya Metal Co., Japan) using microwave plasma enhanced chemical vapor deposition. Boron-to-carbon (B/C) ratio in the gas phase was here fixed at 0.1%.

Before the electrochemical tests, the BDD surface was ultrasonicated in isopropyl alcohol for 5 min, rinsed successively in isopropyl alcohol and water, and then dried with compressed air. The BDD electrode was delimited by clamping a PDMS gasket (~1 mm thick) featuring a Ø 5 mm hole onto the BDD surface, thus defining a recessed electrode. The electrode was then introduced into a custom-made cell, allowing for electrochemical analysis in few mL of liquid. Eye observation revealed that no leakage between the PDMS and the BDD surface occurred during the experiments. This system was kept assembled for the duration of the pretreatment and electrochemical tests. The setup was completed with an Ag|AgCl, 3 M KCl, reference electrode (Bioanalytical Systems Inc., USA) and a Pt wire as a counter electrode. All the experiments were carried out with an Ivium Powerstat (Ivium, Netherlands) functioning in the 3-electrode mode and run in aerated buffers.

The electrodes were pretreated for 5 min in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The potentials were –3 V and 3 V for the cathodic and anodic pretreatments, respectively. This preparation procedure was carried out before each set of experiments. The charge  $Q_p$  transferred during the pretreatments is shown in Table 1. After the pretreatment, the electrode was rinsed twice with water, and was immediately used. The electrode was not

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**Table 1**

CV characteristics (peak current  $i_p$  and peak separation  $\Delta E_p$ ) obtained in 1 mM RuHex, 1 mM FcMeOH and 1 mM DA (in aerated PBS, scan rate  $100 \text{ mV s}^{-1}$ ) and EIS data (solution resistance  $R_s$  and charge-transfer resistance  $R_{ct}$ ) obtained in 1 mM DA, before and after a 15-minute fouling procedure in 1 mM DA, where applicable. The BDD surfaces were cathodically ( $-3 \text{ V}$ ) and anodically ( $+3 \text{ V}$ ) pretreated. The charge transferred during the pretreatment ( $Q_p$ ) is also reported. The characteristics could not be determined (nd) for the CVs after fouling on the anodically treated surface, as an oxidation peak could not be observed anymore on the CV. The values presented here are averages  $\pm$  standard deviation, for 3 independent measurements. The datasets were compared using double-tailed Student's t-test. The level for significance was  $p < 0.01$  and is indicated by  $^{###}$  (cathodic vs. anodic treatments before fouling) and  $^{**}$  (before vs. after fouling). A non-significant variation is indicated by  $^-$ .

|                | $Q_p/C$             | 1 mM RuHex        |                        | Fouling | 1 mM FcMeOH         |                        | 1 mM DA              |                        |                    |                      |
|----------------|---------------------|-------------------|------------------------|---------|---------------------|------------------------|----------------------|------------------------|--------------------|----------------------|
|                |                     | $i_p/\mu\text{A}$ | $\Delta E_p/m\text{V}$ |         | $i_p/\mu\text{A}$   | $\Delta E_p/m\text{V}$ | $i_p/\mu\text{A}$    | $\Delta E_p/m\text{V}$ | $R_s/\Omega$       | $R_{ct}/k\Omega$     |
| $-3 \text{ V}$ | $-14 \pm 3$         | $26.1 \pm 1.9$    | $78 \pm 3$             | Before  | $21.6 \pm 0.7$      | $73 \pm 3$             | $61.1 \pm 1.8$       | $322 \pm 8$            | $350 \pm 30$       | $6.2 \pm 0.6$        |
|                |                     |                   |                        | After   | $12.4 \pm 1.1^{**}$ | $118 \pm 3^{**}$       | $26 \pm 11^{**}$     | $750 \pm 110^{**}$     | $530 \pm 50^{**}$  | $35 \pm 10^{**}$     |
| $+3 \text{ V}$ | $1.3 \pm 0.1^{###}$ | $26.0 \pm 0.8^-$  | $83 \pm 3^-$           | Before  | $17 \pm 3^-$        | $100 \pm 20^-$         | $39.2 \pm 1.5^{###}$ | $530 \pm 70^{###}$     | $510 \pm 30^{###}$ | $11.0 \pm 1.2^{###}$ |
|                |                     |                   |                        | After   | $4.4 \pm 0.5^{**}$  | $230 \pm 30^{**}$      | nd                   | nd                     | $1180 \pm 50^{**}$ | $75 \pm 9^{**}$      |

left to dry or significantly exposed to the atmosphere after the pretreatment or between the experiments.

The cyclic voltammograms (CV) were performed in PBS (1 mM FcMeOH, 1 mM RuHex or 1 mM DA) at  $100 \text{ mV s}^{-1}$ . The oxidative peak current  $i_p$ , measured as the current difference between the oxidation peak and the extrapolated baseline, and the peak separation  $\Delta E_p$ , the difference of potential between the two redox peaks, were both obtained from each trace. The electrochemical impedance spectroscopy (EIS) scans were performed in 1 mM DA in PBS. The starting potential was  $0.3 \text{ V}$ , the amplitude  $20 \text{ mV}$ . The frequency range was  $1 \text{ MHz}$ – $1 \text{ Hz}$ . The EIS data was analyzed using the built-in facility of the Ivium software.

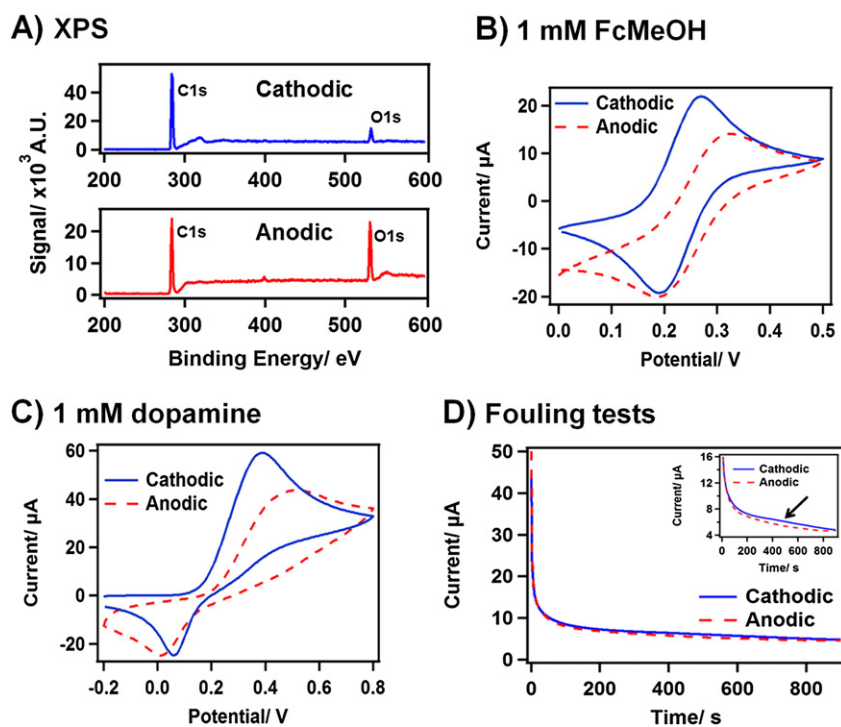
X-ray photoelectron spectroscopy (XPS) analyses were performed on the cathodically and anodically-prepared surfaces with an Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) using an Al  $K\alpha$  source.

### 3. Results and discussion

The XPS data is presented in Fig. 1A. After the cathodic treatment, only a small O1s peak (in comparison to the C1s peak) can be observed.

The relative intensity of this oxygen peak increases after the anodic procedure, thus indicating an increased oxygen content of the surface after this pretreatment.

Initially cyclic voltammograms (CVs) for DA-unfouled electrodes were performed at cathodically and anodically prepared electrodes, for FcMeOH [10] and DA (Fig. 1B, C). The FcMeOH CVs for the anodic treatment show a slightly decreased current in comparison to the cathodic one, even though no significant differences are observed from the CV numerical characteristics ( $p = 0.04$  for  $i_p$  and  $p = 0.1$  for  $\Delta E_p$ ; Table 1). To ensure this observation was not due to variation in the electrode geometry, CVs were carried out in 1 mM RuHex. The results obtained for the two pretreatments were not significantly different, as expected from an outer-sphere redox probe. This establishes that the system geometry is stable during the pretreatments. The fact that the CVs for RuHex, for the two pretreatments, are similar also ensures that there is no noticeable semi-conducting behavior for this electrode [11]. The slightly more sluggish reaction of FcMeOH on the anodically-treated surface could therefore indicate a limited surface-dependence, as reported for instance for ferro/ferricyanide [12]. The electrode



**Fig. 1.** A) XPS spectra obtained for the (top) cathodic and (bottom) anodic preparations. The O1s and C1s peaks are indicated. Typical CVs performed in B) 1 mM FcMeOH and C) 1 mM DA (in aerated PBS, scan rate  $100 \text{ mV s}^{-1}$ ) for the cathodically ( $-3 \text{ V}$ , solid line) and anodically ( $+3 \text{ V}$ , dashed line) pretreated surfaces. D) Typical fouling curves observed in 1 mM DA in aerated PBS for the cathodically ( $-3 \text{ V}$ , solid line) and anodically ( $+3 \text{ V}$ , dashed line) pretreated surfaces. The insert shows a focus of the flat section of the curves emphasizing the slightly higher current observed for the cathodically-treated electrode.

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