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Dopamine Detection on Boron-doped Diamond Electrodes Using Fast Cyclic Voltammetry

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A new method is proposed for the accurate and reproducible detection of dopamine using cyclic voltammetry on boron-doped diamond (BDD) electrode. It is shown that reproducible voltammograms can be obtained when applying a relatively high scan rate ($100\,\mathrm{V\,s^{-1}}$) during the detection measurements. For lower scan rates ($1\,\mathrm{V\,s^{-1}}$), it is proven that electrode fouling occurs due do the deposition of a polymer at the electrode surface arising from the oxidation of aminochrome. Cyclic voltammetry measurements of the $[\mathrm{Fe(CN)_6}]^{3-}/[\mathrm{Fe(CN)_6}]^{4-}$ couple performed before and after dopamine detection on BDD and glassy carbon electrodes have shown that the electrochemical activity of the electrode decreases only at low scan rates for BDD dopamine (DA) detection, which leads to electrode poisoning whereas the activity remains unchanged for higher scan rates. However, on glassy carbon electrodes, the electrochemical activity of the material decreases after DA detection measurements independently of the scan rate applied. Therefore, this study shows that electrode fouling during the detection of dopamine by cyclic voltammetry can be avoided only when using BDD electrode but also only for high applied scan rates.

The development of new technologies for the sensitive and accurate detection of neurotransmitters has attracted much attention recently.[1–4] Dopamine is an essential chemical messenger, which is involved in several senses such as sight, hearing, and touch. Additionally, high levels of dopamine in the brain can lead to Parkinson disease, and for all these reasons, the sensitive and selective in vivo detection of this neurotransmitter is essential in medicine. Several analytical techniques have been proposed, but the use of electrochemical detection seems to be one of the most promising methods.[4–7] Moreover, in order to detect dopamine in vivo, the use of microelectrodes is preferred because besides practical advantages microelectrodes have many other advantages, like low capacitive current, small ohmic drop, superior mass transport (spherical diffusion), and the possibility to work at very high scan rates.[8] Furthermore, the reproducibility of the results often suffers due to electrode poisoning when using conventional electrode materials such as platinum or gold.[3,9] For this reason, the use of boron-doped diamond electrodes was proposed for the in vivo detection of dopamine.[7] This electrode material exhibits outstanding properties such as a wide electrochemical potential window, excellent durability, and a small background current.[10,11] Nevertheless, when electrodes with high surface areas were used, problems related to reproducibility have been reported due to the deposition of a polymeric film at the surface leading to deactivation of the electrode material.[3,9]

In order to solve these problems, in this work, the detection of dopamine using BDD microelectrodes together with fast cyclic voltammetry measurements is presented. Fast scan rates can be applied when using microelectrodes and taking advantage of the exceptional characteristics of boron-doped diamond, a new method is proposed for an accurate and stable detection of dopamine. The influences of dopamine detection measurements on the electrochemical activity of the electrode material and the nature of the electrode material used for this technique are also discussed.

BDD electrodes were prepared using a microwave plasma-assisted chemical vapor deposition (MPCVD) set-up. Acetone was used as a carbon source, and $\mathrm{B(OCH_3)_3}$ as a source of boron. For the microelectrodes, boron-doped diamond was deposited on a tungsten needle ($20\,\mu\mathrm{m}$ in diameter) in an MPCVD chamber at 2.5 kW using high-purity hydrogen as a carrier gas. A portion of the needle was isolated using a glass capillary in order to define the working surface area so that about 1 mm remains uncovered by the capillary.

Figure 1 shows the evolution of cyclic voltammetry measurements for 150 successive scans (only the 2nd, the 5th, the 20th, the 50th, the 100th, and the 150th are displayed)

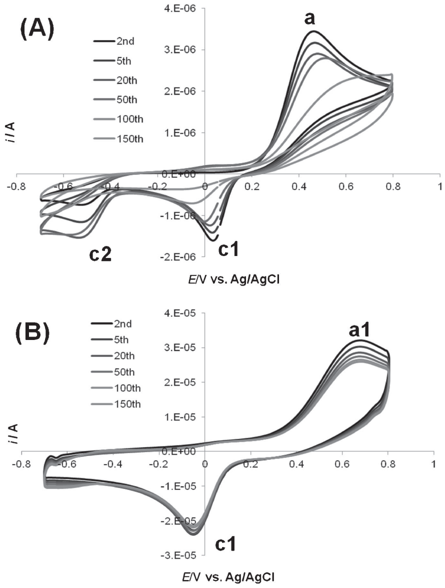

Figure 1. Cyclic voltammograms (150 successive cycles) of 1 mM DA recorded on BDD microelectrode and at different scan rate: (A) 1 and (B) $100\,\mathrm{V\,s^{-1}}$. Support electrolyte: 0.1 M PBS. $T = 23\,°\mathrm{C}$.

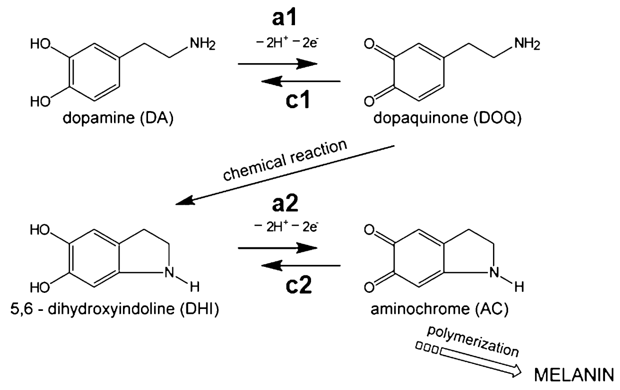

Figure 2. Electrochemical reaction pathways of DA oxidation.

recorded at (A) 1 and (B) $100\,\mathrm{V\,s^{-1}}$ for 1 mM DA solution in 0.1 M phosphate buffered saline (PBS). In Figure 1A, one oxidation peak (**a**) and two reduction peaks (**c1** an **c2**) are observed whereas in Figure 1B, only oxidation peak (**a1**) and reduction peak (**c1**) can be distinguished. The broad peak **a** on Figure 1A probably includes two electrochemical oxidations: dopamine is first oxidized to dopaquinone (DOQ) and after chemical transformation of DOQ to yield 5,6-dihydroxyindoline (DHI), the latter is further oxidized to aminochrome (AC) giving an ECE type mechanism (where E and C denote the electrochemical and the chemical step, respectively).[12] Consequently, the peaks **c1** and **c2** are certainly related to the reductions of DOQ to DA and of AC to DHI respectively as explained in the reaction scheme presented in Figure 2. Two oxidation peaks should be distinguished on Figure 1A, but if the oxidation potentials of DA and DHI are close, overlapping might occur to form the broad peak **a**. However, on Figure 1B, the oxidation peak **a1** should correspond to the oxidation of DA to DOQ only because reduction peak **c2** was not observed.

Moreover, in Figure 1A, an important decrease in current related to the oxidation and reduction peaks can be observed after successive cycles. This is certainly inherent to the formation of a polymer film formed from the electrochemical generation of AC leading to deactivation of the electrode.[3,9] However, this deactivation was not observed when the scan rate applied was higher (Figure 1B). This is probably due to the fact that DOQ is not further transformed to DHI and later AC at high scan rate but is rather reduced to DA and because DHI oxidation is the principal cause of the formation of a polymeric film at the electrode surface, deactivation can be avoided by using high scan rates for the cyclic voltammetry measurements.

Therefore, reproducible electrochemical measurements can be obtained for the accurate detection of dopamine by applying a high scan rate during cyclic voltammetry measurements.

The effect of dopamine detection on the activity of BDD and glassy carbon electrode was studied through cyclic voltammetry measurements performed using the $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ redox couple. Figure 3 shows cyclic voltammetry measurements of the $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ couple (1 mM) performed on BDD electrode at (A) 1 and (B) $100\,\mathrm{V\,s^{-1}}$. In Figures 3A and 3B, cyclic voltammetry measurements performed before and after dopamine detection measurements are displayed: for Figure 3A, 100 cycles at $1\,\mathrm{V\,s^{-1}}$ and for Figure 3B, 1165 cycles at $100\,\mathrm{V\,s^{-1}}$. The number of scans for

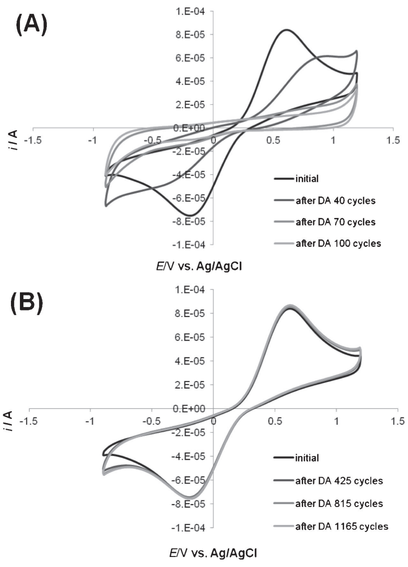

Figure 3. Cyclic voltammograms of $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ couple (1 mM) recorded on BDD electrode (scan rate: $1\,\mathrm{V\,s^{-1}}$). In (A), measurements were performed before and after 100 cycles for 1 mM DA at $1\,\mathrm{V\,s^{-1}}$, and in (B), measurements were performed before and after 1165 cycles for 1 mM DA at $100\,\mathrm{V\,s^{-1}}$. Support electrolyte: 0.1 M PBS. $T = 23$ °C. Electrode area was $0.13\,\mathrm{cm^2}$.

DA detection performed in between the measurements of the $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ couple were chosen in order to obtain the same cumulative voltammetric charge corresponding to DA detection measurements at both scan rates (1 and $100\,\mathrm{V\,s^{-1}}$).

Figure 3A shows clearly that the oxidation and reduction peaks related to the $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ couple disappear completely after performing DA detection measurements proving that the BDD electrode was deactivated due to the formation of a polymeric film at the electrode surface inherent to the low scan rate applied for DA detection. However, Figure 3B shows that DA detection measurements have no influence on the electrochemical activity of the BDD electrode, which proves that the fouling of the electrode can be avoided if the scan rate applied during DA detection is high enough.

The same study was performed using glassy carbon electrode, and the results (Figures 4A and 4B) prove that the electrode is deactivated even when the DA detection measurements were recorded at $100\,\mathrm{V\,s^{-1}}$.

These results prove that electrode fouling can only be avoided by using BDD electrodes together with high scan rates for the DA determination measurements. This is due to the surface inertness of BDD with $\mathrm{sp^3}$ carbon species, while glassy carbon is a composite consisting of amorphous carbon and one or more additional materials.[13] Moreover, it is worthwhile to notice that microelectrodes are preferred for potential in vivo applications due to the possibility of applying very high scan rates.[8]

In summary, here, the influences of the scan rate applied during cyclic voltammetry measurements recorded for dopamine detection, and the nature of the electrode material used were studied. On boron-doped diamond electrodes and at low scan rates, it was shown that dopamine is oxidized to dopaquinone

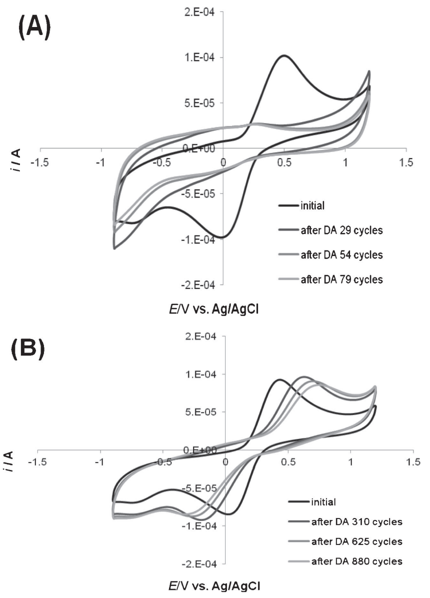

Figure 4. Cyclic voltammograms of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple (1 mM) recorded on glassy carbon electrode (scan rate: $1\,V\,s^{-1}$). In (A), measurements were performed before and after 79 cycles for 1 mM DA at $1\,V\,s^{-1}$, and in (B), measurements were performed before and after 880 cycles for 1 mM DA at $100\,V\,s^{-1}$. Support electrolyte: 0.1 M PBS. $T = 23$ °C. Electrode area was $0.13\,cm^2$.

and later to aminochrome leading to the formation of a polymeric film at the surface of the electrode, which deactivates it. However, if the scan rate is high enough, dopamine is only oxidized to dopaquinone in a way that the polymer film formation can be avoided. Additionally, it was shown that dopamine detection measurements have no influence on the electrochemical activity of the boron-doped diamond electrode only at high scan rates. For lower scan rates, the activity of the diamond film decreases with each set of dopamine detection measurements due to electrode fouling. On other electrode materials such as glassy carbon, the electrochemical activity of the material decreases after cyclic voltammetry measurements performed in the presence of dopamine independently of the scan rate applied due to electrode fouling. Therefore, it was shown that reproducible successive voltammetric scans for dopamine detection can be obtained only on boron-doped diamond electrode and only when the scan rate applied during the cyclic voltammetry measurements is relatively high ($100\,V\,s^{-1}$).

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