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Improving the Function of Dopamine Electrodes with Novel Carbon Materials

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***Abstract*— For therapeutic purposes, an accurate measurement of dopamine level *in situ* would be highly desirable. A novel strategy for the selective determination of dopamine concentration based on the diamond-like carbon (DLC) electrode is presented in this abstract. The developed DLC electrode is able to detect 10 µM dopamine and has improved sensitivity compared to platinum. Compared to carbon fiber electrodes, the DLC electrode is more stable because the background current is much lower.**

I. Introduction

Neurotransmitters, such as dopamine, provide the communication link between neurons. Abnormal dopamine transmission has been associated to several neurological disorders, e.g. Parkinson's disease, schizophrenia, and Huntington's disease [1]. For therapeutic purposes, an accurate measurement of dopamine level *in situ* would be highly desirable.

The primary challenge is that the concentration of dopamine in the extracellular fluid is low (0.01 – 1 µM) [2], [3], while the concentrations of the main detection interferers, such as ascorbic acid, are several orders of magnitude higher and that the interferers undergo oxidation within the same potential window as dopamine. Secondly, the released dopamine is rapidly cleared from the extracellular space. Therefore, the sensor must be sensitive, selective and fast. The third challenge is stability, which is confronted by the adsorption of oxidation products leading to the fouling of the electrode. We aim to solve these problems with novel carbon materials.

II. Materials and Methods

Prior to deposition, platinum wires were cleaned by using organic solvents, followed by argon ion beam sputtering. A 20 nm thick layer of titanium was deposited to enhance the diamond-like carbon (DLC) layer adhesion. DLC was deposited using a cathodic arc deposition. The capacitor bank of 2.6 mF capacitance was discharged yielding a current pulse with a frequency of 1 Hz, a maximum current of about 3 kA and a half width of 150 µs. An accumulation of about 1.4×10^{15} atoms/cm^2 during each pulse was obtained. The sample holder was rotated with the rotation axis perpendicular to the direction of the plasma plume.

The DLC coating was characterized with scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and X-ray reflectivity. The electrochemical performance of the electrodes was evaluated with cyclic voltammetry in 0.15 M H_2SO_4. The ability to detect dopamine was assessed with cyclic voltammetry in nitrogen purged phosphate buffered saline with 5 nM – 100 µM dopamine. The performance was compared to

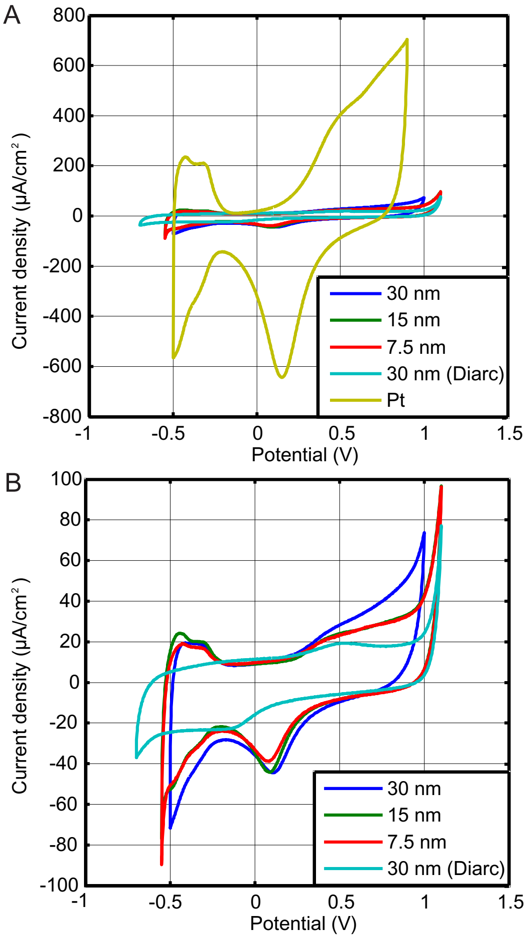

Fig. 1. (A) The electrochemical performance of the DLC electrodes in H_2SO_4 compared to pure platinum electrodes. (B) A closer view of the electrochemical performance of the DLC electrodes in H_2SO_4. The thickness of the DLC coating is indicated in the label.

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TABLE I

Peak potentials (E_{pc}) and peak currents compared to background (ΔI_{pc}) of 10 µM or 100 µM dopamine concentrations.

Sample	E_{pc}	10 µM ΔI_{pc}	100 µM ΔI_{pc}
Pt	230 mV	-	46 µA/cm^2
7.5 nm DLC	410 mV	4 µA/cm^2	50 µA/cm^2
15 nm DLC	800 mV	11 µA/cm^2	76 µA/cm^2
30 nm DLC	540 mV	7 µA/cm^2	78 µA/cm^2

three types of commercial electrodes: DLC (Diarc technology, Finland), boron doped diamond (BDD, Windsor Scientific, UK) and carbon fiber microelectrode (World Precision Instruments, FL, USA).

III. Results and Discussion

A. Characterization of DLC

The DLC coating had highly (>80%) sp3 bonded thermally stable hydrogen-free structure (Raman spectroscopy and X-ray reflectivity). The structure of the coating was amorphous and the thickness of the coating was uniform (transmission electron microscopy).

B. Electrochemical Performance of DLC electrodes

Fig. 1 demonstrates the electrochemical performance of different DLC electrodes in H_2SO_4. The reduction peak of platinum can be seen in the homemade DLC coatings. A possible explanation for this is the weak adhesion of titanium on the platinum surface. The weak platinum-titanium interface is caused by the presence of remnants of water vapor in the coating process. Water is trapped in the coatings, and results in formation of titanium oxide at the interface between the metals. This amorphous layer was observed with transmission electron microscopy. Commercial DLC coatings, however, have a more solid coverage and stronger adhesion to the substrate. Thus, the reduction peak of platinum cannot be seen.

C. Dopamine Detection

Commercial DLC electrodes were unable to detect dopamine. The homemade electrodes with a 7.5 − 30 nm thick DLC coating on a 20 nm thick titanium coating on a platinum wire have potential in dopamine detection. The DLC electrode detects 10 µM dopamine (Fig. 2). The results indicate that the DLC electrode is more sensitive in dopamine detection than the platinum electrode, which can only detect 100 µM dopamine. Furthermore, the DLC electrode provides a slightly stronger signal than the platinum electrode. Moreover, the maximum oxidation potential is 410 − 800 mV on the DLC electrode and 230 mV on the platinum electrode. This verifies that the detection of dopamine occurs on the DLC surface and not on the platinum background. The numerical results are presented at Table I.

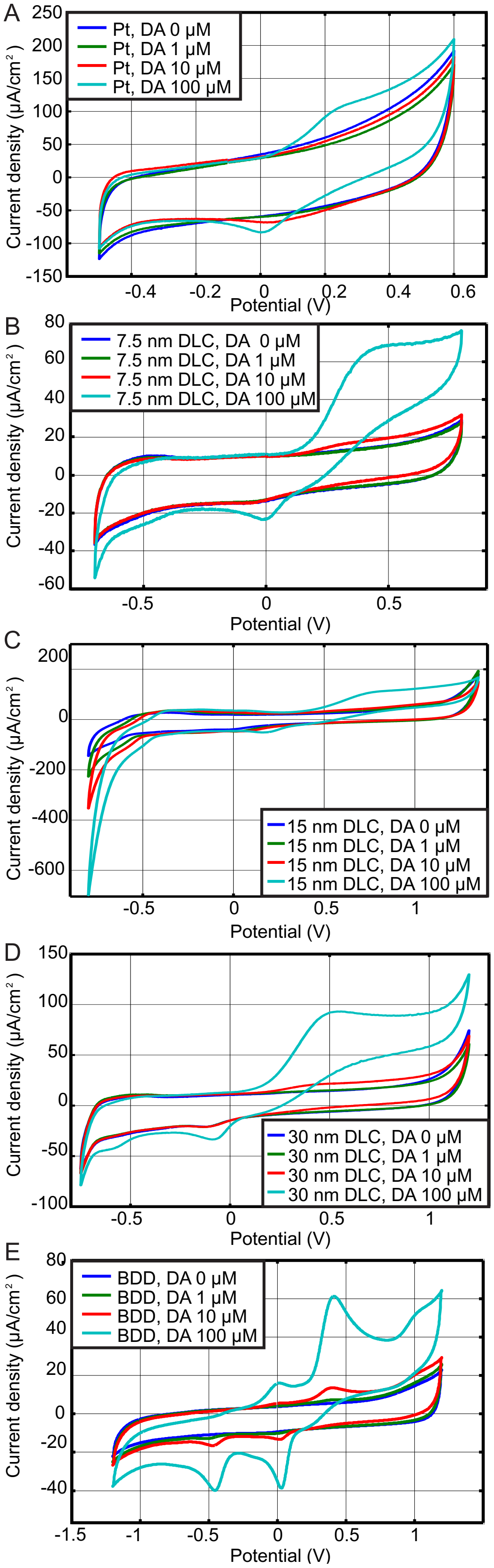

Fig. 2. Detection of dopamine using (A) a platinum electrode, an electrode with (B) 7.5 nm, (C) 15 nm or (D) 30 nm thick DLC-coating and (E) a BDD electrode. The concentration of the dopamine is indicated in the label.

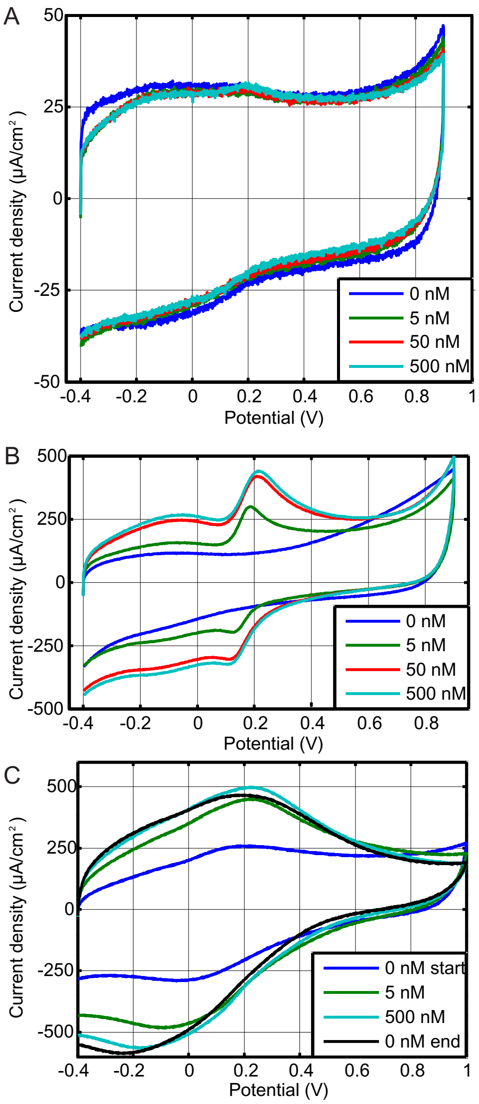

Fig. 3. The detection of dopanine using (A) untreated, (B) base treated and (C) fouled carbon fiber electrodes. The concentration of the dopamine is indicated in the label.

BDD electrode is able to detect 1 μM dopamine (Fig. 2 C). The current density of DLC electrodes and BDD electrodes is approximately in the same range. Thus, DLC and BDD appear to be chemically alike.

Commercial 10 μm carbon fiber electrodes were not able to detect dopamine unless pretreated in base (10 min, 150 mM NaCl, NaOH, pH 9 – 9.5, Fig. 3 A, B). This pretreatment significantly improved the performance of the carbon fiber electrodes. A drawback of these electrodes is that significant electrode fouling occurs in repeated use, even with pretreatment. Fig. 3 C shows less distinct peaks and increased peak separation ΔE_p, which indicates slower electron transfer kinetics.

Importantly, the scale of the current density of carbon fiber electrodes is significantly different compared to DLC electrodes. Whereas the current density of the 7.5 nm DLC electrodes is <80 μA/cm^2, the current density of the carbon fiber electrodes reaches 500 μA/cm^2. The DLC coating is more stable compared to solutions containing one carbon allotrope.

An improved sensitivity of the DLC electrode compared to platinum electrode was demonstrated here. Future work should include evaluation of the selectivity of the electrode, i.e. peak separation of dopamine from ascorbic acid and uric acid.

The long term aim is to develop 2-dimensional tailored surfaces suitable for area-array electrodes. For this aim, DLC has some advantages compared to BDD and carbon fibers. Chemical vapor deposition, used for BDD coating, requires high temperatures (>800°C), which limits the choice of substrate material. In contrast, the cathodic arc deposition, used for DLC coating, can be performed at room temperature. Carbon fibers, being fibers, are only suitable for traditional wire electrodes and cannot be applied for area-array approaches. Furthermore, it has been shown that patterned DLC coating improves the biocompatibility of silicon surfaces [4], [5], [6]. Therefore, DLC is an attractive material for area-array surfaces.

IV. CONCLUSION

A novel strategy for the selective detection of dopamine based on the DLC electrode has been presented in this abstract. The developed DLC electrode is able to detect 10 μM dopamine and has improved sensitivity compared to platinum. Compared to carbon fiber electrodes, the DLC electrode is more stable as the background current is much lower. The BDD electrode detects dopamine in the similar current density range and is more sensitive than the DLC electrode. However, the applicability of the BDD is limited because of the high-temperature requiring fabrication process. This novel strategy for the selective detection of dopamine based on the DLC electrode has certain advantages compared to BDD electrodes and carbon fiber electrodes although the sensitivity needs to be further improved.

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