Oxidation of guanosine 5'-monophosphate on the carboxyl terminated boron doped diamond electrode

Gustavo S. Garbellini[1] (PQ)*, Carolina V. Uliana[1] (PG), Hideko Yamanaka[1] (PQ), Luis A. Avaca (PQ)[2].
***garbellini@iq.unesp.br**

[1] São Paulo State University – UNESP – Institute of Chemistry of Araraquara – Brazil.
[2] São Paulo University – USP – Institute of Chemistry of São Carlos – Brazil.

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Introduction

The boron-doped diamond (BDD) electrode presents wide potential window, low capacitive background currents and good compatibility with biological materials[1]. The synthesized BDD films are hydrophobic and the surface terminations are mainly C–H functions. This surface is sensitive to anodic polarization in aqueous media and allows partial derivatization of C–H terminations into carbonyl, carboxyl and hydroxyl functions[2].

For bioelectroanalysis, BDD electrochemical oxidation leads to enlargement of the electrochemical window in aqueous media especially in oxidation case[2]. This allows the electrochemical determination of highly positive oxidation species such as purine (guanine and adenine) and pyrimidine (cytosine and tymine) bases within DNA structures. DNA consists of two antiparallel chains formed by nucleotide monomeric units. Each nucleotide consists of a phosphate group, a sugar called deoxyribose and four different nitrogenous bases. For example, it has the guanosine 5'-monophosphate (GMP)

The aim of this work is to evaluate the influence of carboxyl terminated BDD surface[1] on the GMP oxidation in aqueous solutions. The study will allow applying this surface modification for immobilization of DNA probes on the BDD electrode surface.

Results and Discussion

The electrochemical experiments were carried out in a three-electrode-arrangement using a one-compartment glass cell. The BDD films have boron content of 8000 ppm order. The reference electrode was the Ag/AgCl (3.0 mol L^{-1} KCl) and the counter one was a 1 cm^2 Pt foil. Electrochemical measurements were performed using a PGSTAT 30 Autolab potentiostat. At first, cyclic voltammograms of the $K_4Fe(CN)_6$ solution (Figure 1) were obtained on the H-terminated BDD surface (the electrode received a pre-treatment at +3.0 and –3.0 V during 5 and 30 s respectively in a 0.5 mol L^{-1} H_2SO_4 solution) and on the carboxyl terminated BDD surface (+3.0 V for 60 min in a 1 mol L^{-1} H_2SO_4 solution). The kinetics and voltammetric response of the $Fe(CN)_6^{4-/3-}$ redox couple was greatly affected by the carboxyl groups on the BDD surface.

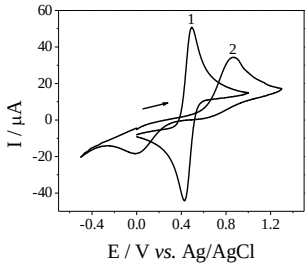

Figure 1. Cyclic voltammograms (50 mV s^{-1}) for 1.0 x 10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ in 0.5 mol L^{-1} H_2SO_4 solution on the hydrogen (1) and carboxyl (2) terminated BDD surface.

Since this carboxyl group can be used for biomolecules immobilization[1], such as DNA, the response of GMP was evaluated on the surface (Figure 2).

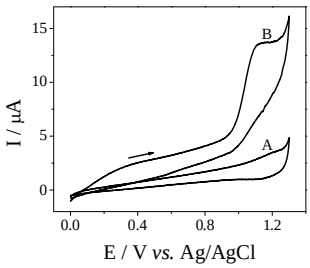

Figure 2. Cyclic voltammograms (50 mV s^{-1}) for (A) 0.1 mol L^{-1} phosphate buffer solution (pH 7) and (B) buffer + 1.4 x 10^{-3} mol L^{-1} GMP on the carboxyl terminated BDD surface.

An irreversible oxidation process for GMP with satisfactory voltammetric shape and intense response was observed. The effect of pH (2 to 12) on the GMP data was investigated in 0.1 mol L^{-1} BR buffer solutions and GMP voltammograms were more appropriate at 6 and 7 pH values.

Conclusions

The carboxyl terminated BDD surface allows the obtainment of satisfactory responses for GMP and it can be applied for immobilization of DNA probes on electrode surface.

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