Diamond & Related Materials 74 (2017) 182–190

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Porous boron-doped diamond/CNT electrode as electrochemical sensor for flow-injection analysis applications

Bruna C. Lourencao [a,*], Romario A. Pinheiro [b], Tiago A. Silva [a], Evaldo J. Corat [b], Orlando Fatibello-Filho [a]

[a] Department of Chemistry, Federal University of São Carlos, Rod. Washington Luís km 235, São Carlos CEP 13560-970, SP, Brazil
[b] National Institute for Space Research, Avenida dos Astronautas 1758, São José dos Campos CEP 12227-010, SP, Brazil

ARTICLE INFO

Article history:
Received 4 January 2017
Received in revised form 17 February 2017
Accepted 3 March 2017
Available online 15 March 2017

Keywords:
Boron-doped diamond
Carbon nanotubes
Porous electrodes
Flow-injection analysis (FIA)
Paracetamol
Adrenaline

ABSTRACT

Porous boron-doped diamond (p-BDD) electrodes were prepared and explored as a potential electrochemical sensor for applications in flow-injection analysis (FIA) coupled to amperometric detection systems. Porous BDD films were grown by Hot Filament Chemical Vapor Deposition (HFCVD) over oxygen plasma functionalized carbon nanotubes and, morphological and chemical characterizations of the obtained composite material were carried out by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) and Raman spectroscopy. The analytical performance of the designed p-BDD electrode under FIA conditions was investigated using two model electroactive analytes, epinephrine (EP, an important neurotransmitter) and acetaminophen (AC, a commonly consumed analgesic). All experimental parameters, such as applied potential, flow-rate and injection volume for both analytes were optimized. Under the best experimental conditions, the analytical curves for EP and AC were linear from 0.60 to 30.0 μmol L^{-1} (EP) and from 0.80 to 70.0 μmol L^{-1} (AC), with detection limits of 0.50 μmol L^{-1} and 0.70 μmol L^{-1} for EP and AC, respectively. Measurement precision was demonstrated from a number of amperometric measurements performed for successive injections of standard AC and EP solutions. In addition, the applicability of the developed FIA procedure was reported for the AC and EP determination in human serum fluid.

1. Introduction

Among the different morphological forms of boron-doped diamond (BDD) reported in literature, three-dimensional models are commonly reported. For instance, it is possible to encounter reports on: diamond powders coated with nanocrystalline BDD [1]; BDD nanorod forest prepared on silicon nanowires [2]; BDD coated "black silicon" [3]; and the BDD nanograss array [4]. All of them have shown interesting electrochemical properties and, therefore, may be useful as electrochemical sensor for applications in electroanalytical chemistry [4–9].

According to the reported in literature many different procedures [7,10–14] create these various types of porous BDD (p-BDD) surfaces. Therefore, strategies focusing on fabricating BDD electrodes with large surface area have been emerging recently. This porous material developed is a promising electrode for electroanalysis improving the selectivity, sensitivity and reproducibility in comparison with flat electrodes previously studied [15]. However, some methods as nanowires fabrication, for example, present complex and very long synthesis steps [16].

Kato et al. introduced a new concept to produce nanostructured diamond electrodes known as "diamond foam". These electrodes were obtained by deposition of boron doped diamond on silicon sphere as template [17]. Zhuang et al. reported a simple approach to fabricate porous diamond with three-dimensionally interconnected pores. Their new approach combined the deposition of diamond on β-SiC with a chemical selective etching of the β-SiC phase [18]. Hébert et al. presented a BDD/porous polypyrrole composite prepared by chemical vapour deposition (CVD) method [14]. Shi et al. proposed an etching method in which the BDD grains were etched by atomic hydrogen with metal as nanocatalyst to synthesizing a highly porous electrode [10]. Kondo et al. also developed a technique based on two thermal treatments to obtain porous BDD. It consists in a graphitization procedure using argon atmosphere at 1000 °C, followed by an oxidation step in order to remove graphitic components in ambient atmosphere at around 425 °C [13]. In general, the porous BDD as electrodic material has shown improved selectivity, higher sensitivity [3,19] or higher surface area [6] when compared to conventional flat BDD electrode (f-BDD).

A porous conductive diamond thin film was designed by Sun et al. [12] using Hot Filament Chemical Vapor Deposition (HFCVD) technique and a Ti substrate. Studies using cyclic voltammetry revealed that the new proposed material presented stable electrochemical response and

---

[*] Corresponding author.
E-mail address: brunalourencao@gmail.com (B.C. Lourencao).

http://dx.doi.org/10.1016/j.diamond.2017.03.006
0925-9635/© 2017 Elsevier B.V. All rights reserved.

a wide working potential window. In another case, Shi et al. [10] prepared a p-BDD by catalytic etching under hydrogen–argon plasma. The electrochemical behaviour, as studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), showed higher specific capacitance when compared with a pristine BDD electrode.

Zanin et al. [6] also innovated in p-BDD films production by carrying out diamond deposition on top of vertically aligned carbon nanotubes (VACNT) by CVD. The deposition of BDD films over CNTs based substrates is a growing field of research since it seeks to combine the electrochemical features of BDD (e.g. wide potential window, low and stable background current, lower adsorption effects and robustness) and of CNTs (high surface area and electrocatalytic properties). Therefore, applying this method various porous 3D microstructures emerged depending on areal density and the VACNT length. Then, Lourencao et al. [5] explored the electrochemical performance of this p-BDD for use as an electrochemical sensor, in which was seen that the electrode characterization using two redox probes and dopamine, acetaminophen and epinephrine as biomolecules proved good electrochemical response of such porous material when compared to a f-BDD electrode. Therefore, the proposed sensor showed faster electron transfer rate than f-BDD electrode. Besides that, the magnitude of analytical signal improved for all analytes studied. Pinheiro et al. [20] improved diamond deposition on carbon nanotubes (CNTs) to be quite similar to pristine CNT morphology, presenting large surface area and capacitance.

Flow injection analysis (FIA) in analytical chemistry procedures presents several advantages, such as, low cost of apparatus; high sampling frequency; setup automation; reagents and samples reduced consumption and, therefore, the reduced waste generation. The FIA coupled with amperometric detection is sensitive and presents some improvements when compared to voltammetric methods. The much smaller contact time between sample and redox products with the electrode reduces surface contamination compared to the stationary electrochemical cell system. In addition, the presence of capacitive current is negligible, which makes it easier to detect target compounds in low concentrations [21,22]. Besides, its routine analysis does not require sample pretreatment [21].

Thus, in this study the analytical performance of a p-BDD electrode as electrochemical sensor in a FIA setup with amperometric detection is reported. The electrodes are alike the ones produced by Pinheiro et al. [20]. We developed rapid and simple methods to quantify two biomolecules of well-known redox behaviour, epinephrine (EP) and acetaminophen (AC). We also applied the proposed method in the analysis of synthetic serum samples. For the best of our knowledge, this is the first time that a p-BDD material is explored as FIA electrochemical sensor.

2. Material and methods

2.1. Reagents, standards and solutions

All solutions were prepared with ultrapure water (resistivity not less than 18 MΩ cm) obtained with a Millipore Milli–Q system and all the reagents used were of analytical grade.

The stock solutions of 1.0×10^{-2} mol L^{-1} EP and AC (Sigma-Aldrich) were prepared in supporting electrolyte solution, protected from light and prepared daily before use. For all experiments, a 0.2 mol L^{-1} phosphate buffer (pH 7.0) solution as the supporting electrolyte and carrier solution, was used.

Regarding analysis of the two compounds in real biological human serum samples, specific licenses from the Ethics Committee of our University and from ANVISA (Health Surveillance Brazilian Federal Agency) must to be obtained. Nevertheless, a synthetic substitute simulating very well human serum was prepared. The synthetic human serum sample was prepared as described by Parham and Zargar [23] containing the following chemical species: tyrosine, arginine, histidine, phenylalanine, NaCl, glycine, tryptophan, serine, lysine, water, alanine, $NaHCO_3$, and aspartic acid. This solution was used immediately after its preparation.

Afterward, this synthetic sample was spiked with two different known concentrations of EP or AC. Appropriate aliquots of these spiked samples were diluted with the 0.2 mol L^{-1} phosphate buffer (pH 7.0) solution and the final solutions were injected in the FIA system. Thus, the concentration of each analyte was determined by interpolation on the respective analytical curve.

2.2. Apparatus

A potentiostat/galvanostat μAutolab type III (Ecochemie) controlled with the GPES software (version 4.9) was used for the cyclic voltammetric and amperometric measurements.

For the cyclic voltammetric assays, it was used a three-electrode electrochemical glass cell (20 mL total capacity), containing a Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode, a Pt counter electrode and the p-BDD working electrode (exposed area of 0.3 cm^2). Amperometric measurements on flow conditions were carried out using a FIA system coupled to electrochemical detector, which was a homemade three-electrode wall-jet electrochemical cell. A complete description about the design of this electrochemical detection system could be consulted in our previous work [24]. Regarding the electrodes, a stainless-steel tube was used as counter electrode, along with a miniaturized Ag/AgCl (3.0 mol L^{-1} KCl) as reference electrode [24] and the working electrode was the p-BDD electrode.

2.3. Synthesis and characterization of porous BDD material

CNTs were grown on titanium substrates and oxidized at 800 °C for 5 min. This titanium oxide layer formed a diffusion barrier for Fe nanocatalysts. CNTs deposition by floating catalysts [25] took place at atmospheric pressure in tubular thermal CVD reactor. An initial growth step was the uniform catalyst deposition on samples. For such, a saturated solution of ferrocene in hexane was dripped at 0.2 mL min^{-1} into a 200 °C chamber to evaporate and then an argon flow (200 sccm) drew it to the reaction zone at 650 °C, during 5 min. The second step was an additional growth step in which, camphor solution in hexane (200 g L^{-1}) dripping at the same rate as in first step was used and its vapour was drawn into the reaction zone at 800 °C, during 10 min. This camphor solution in hexane proved to be excellent carbon source for CNT growth.

CNT samples functionalization and seeding were necessary for efficient BDD growth. As grown nanotubes were hydrophobic and functionalization was essential to promote hydrophilicity. Oxygen plasma in a pulsed DC plasma reactor (at 0.08 Torr and 700 V during 2 min) exposed CNT samples to polar oxygen groups [26], which generates superhydrophilic CNT films. These polar groups grafted on CNT surface confer a positive electrostatic charge to the substrate that ideally attracts the negatively charged nanodiamond particles (ND) for seeding.

ND with 98% purity (International Technology Centre - ITC) had an initial particle size of 4–5 nm. KCl solution based on Liu et al. [27] was used to disperse the ND particles reaching a primary ND dispersion of 750 mg/L concentration in deionized water. The supernatant was then diluted with an aqueous 1.0×10^{-2} mol L^{-1} KCl solution 10 times. This low ND concentration was necessary to prevent CNT saturation with nanodiamond particles (ND). The zeta potential of ND is around −40 mV when in solution containing dispersant dissolved in deionized water [27,28]. The negative charge attributed to carboxylic acid groups present on the ND surface [29] assures Electrostatic Self Assembly (ESA) onto polar groups on CNT surface. An efficient seeding should cover the CNTs individually, keeping their morphology and their large surface area.

The BDD films were grown by Hot Filament Chemical Vapor Deposition (HFCVD). The gas mixture contained 1.0% of CH_4 in H_2, at a 100 sccm flow rate and a 50 Torr reactor pressure. The BDD growth