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Quinone electrochemistry for the comparative assessment of sp^2 surface content of boron doped diamond electrodes

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ABSTRACT

Surface coverage measurements of electroactive quinone groups present on sp^2 carbon sites, are used to inform on the sp^2 surface content of boron doped diamond (BDD) electrodes. Laser micromachining of an electrode surface is used to systematically increase the amount of sp^2 carbon present by increasing the area machined. A linear relationship between quinone surface coverage and surface area lasered is determined ($R^2 = 0.9999$). This approach can also be used for comparative assessment of electrodes containing different amounts of surface sp^2 carbon.

1. Introduction

Polycrystalline boron doped diamond (BDD) has emerged as a popular material for the electrochemist in recent years [1,2] due to its intriguing electroanalytical properties compared to more conventional electrode materials including: extended solvent window (SW), low background currents, high chemical inertness and mechanical robustness, as well as increased resistance to fouling. For this reason, BDD electrodes have found use in a wide range of applications, such as electroanalysis [3], biosensing [4], wastewater processing [5] and spectroelectrochemistry [6]. Many of these properties arise from the sp^3 bonded carbon structure. However, achieving a pure sp^3 material during diamond synthesis especially in combination with high boron dopant levels is challenging and almost impossible for nano- and smaller sized grain material [7,8]. Increasing sp^2 content has disadvantages e.g. increased background current, reduced SW, increased susceptibility to corrosion etc., but can also be advantageous [9] e.g. enhanced electrocatalytic properties [10], provision of pH active functional groups [11]. Thus for each electrochemical application sp^2 surface presence needs to be carefully considered, and controlled, if possible.

Raman spectroscopy is widely used to assess sp^2 content in BDD electrodes [12], often by comparing the ratio of the sp^3 ($1332\ cm^{-1}$) peak to the G ($1580\ cm^{-1}$) peak [13]. This method is however qualitative [14], works best when comparing electrodes of the same dopant density and samples only a small area per measurement (~μm^2 – tens of μm^2 depending on magnification) which is especially problematic when sp^2 content is spatially heterogeneous [15]. Often neglected is the fact Raman also penetrates up to several microns [16] into the surface, returning information over this depth range, which is non-ideal for the electrochemist, who cares only about sp^2 surface content. It is therefore imperative that *surface sensitive* characterisation methods are employed when assessing BDD material quality for *electrochemical* applications. To this end photoelectron spectroscopy has been explored [17], but the method is relatively expensive, time-consuming and requires trained operators. It is also difficult to resolve the sp^2 and sp^3 signatures [18], and peak deconvolution is required, leading to variations in peak assignments throughout the literature [19,20].

In contrast electrochemistry represents a low cost, rapid characterisation technique providing information about charge transfer processes occurring at the electrode-solution interface. The presence of sp^2 carbon at the electrode surface has been shown previously to modify the SW and capacitance (C) of BDD electrodes [2,21] and result in surface bound quinone groups, which show a pH dependent redox signature when suitably activated [11]. However, to date, no attempt has been made to correlate these observations with sp^2 surface content. In this communication, we demonstrate the use of the quinone redox signature to provide information on BDD sp^2 surface coverage. Direct comparisons with SW and C are also made.

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2. Materials and methods

2.1. Materials

All solutions were prepared from Milli-Q water (Millipore Corp.), resistivity 18.2 MΩ cm at 25 °C. Four different BDD electrodes, numbered 1–4, were grown under different microwave chemical vapour deposition (CVD) conditions, in order to deliberately vary the sp^2 content of the electrodes. Electrodes 1–3 (Element Six, UK) contained ca. 3×10^{20} boron atoms cm^{-3}, and were grown thick (ca. 250–500 μm) so that they could be removed from the growth substrate and polished to ~ nm roughness. Due to the thickness of the material, large grain sizes of μm's to tens of μm's result. Electrode 1 was used as the baseline material for all laser machining studies and was expected to contain minimal sp^2 carbon (Diafilm EA grade material) [21]. Electrode 4 (Advanced Diamond Technologies Inc., USA) was ultrananocrystalline (UNC) BDD, 2 μm thick (1.6×10^{21} boron atoms cm^{-3}) [21]. The surface was left as-grown (surface roughness 9.3 ± 0.4 nm) with the electrode still attached to its niobium growth substrate.

C and SW measurements were run in 0.1 M potassium nitrate (KNO$_3$, Fisher Scientific). For quinone surface coverage (Γ) measurements, a pH 2 Carmody buffer was prepared [22], with solution pH measured using a pH meter (SevenEasy, Mettler Toledo).

2.2. Electrode preparation

Electrode 1 was laser machined using a 532 nm Nd:YAG nanosecond laser micromachiner (A-532 system, Oxford Lasers Ltd). Laser machining of BDD is known to result in sp^2 formation on the surface [23]. To systematically increase sp^2 content, six squares ($n = 3$ for each i.e. 18 squares in total) of increasing size (length dimension 200 μm increasing to 700 μm) were machined into 18 individual electrodes of uniform geometric diameter, as shown in Fig. 1a. Identical laser parameters were employed (1000 Hz/0.195 W with a machining speed of 0.3 mm s^{-1}) optimised to maximise sp^2 production [24]. Once machined, the electrodes were acid treated in boiling concentrated H$_2$SO$_4$ (98%) saturated with KNO$_3$ to oxygen-terminate the surface and remove any loosely contacted sp^2 introduced during machining [11]. To provide a reliable ohmic contact, Ti (10 nm)/Au (300 nm) was sputtered (MiniLab 060 Platform, Moorfield Nanotechnology Ltd.) onto the back face of Electrodes 1–3 and top face of Electrode 4, and annealed at 400 °C for 5 h [21].

For comparative electrode measurements (vide infra), all electrodes were acid treated in the same way prior to experiment. This involved running cyclic voltammetry (CV) experiments in 0.1 M H$_2$SO$_4$, at 0.1 V s^{-1}, from 0 V to −2 V and then 2 V, before returning to 0 V for 20 cycles.

2.3. Electrochemical setup

All electrochemical measurements were performed using a platinum counter and a saturated calomel reference electrode (SCE), using a potentiostat (CHI760C, CH Instruments, USA). A Faraday cage was used to reduce electrical noise. The BDD electrodes were mounted onto a Ti/Au sputtered glass slide, using silver epoxy (RS Components Ltd.). To restrict the electrode area, Kapton tape (RS Components Ltd.) was laser machined to create 1 mm diameter holes and positioned on the electrodes accordingly (for all electrodes in Figs. 1a and 3a). All potentials are quoted versus SCE, with all experiments conducted at room temperature (25 ± 2 °C). SW values are calculated using a current density threshold of ±0.4 mA cm^{-2} [21]. Analysis of the quinone CV data was carried out after baseline correction and smoothing (Origin Pro software) [25]. The baseline correction involved subtracting a linear baseline from the raw data (from +0.25 V to +0.62 V) whilst the current signal was smoothed using a ten point adjacent averaging procedure [25,26].

2.4. White light laser interferometry (WLI)

A Bruker ContourGT (Bruker Nano Inc., USA) was used to record WLI profiles. 3D rendering of interferometry data was performed and the increase in electrode area after machining calculated using Gwyddion 2.42.

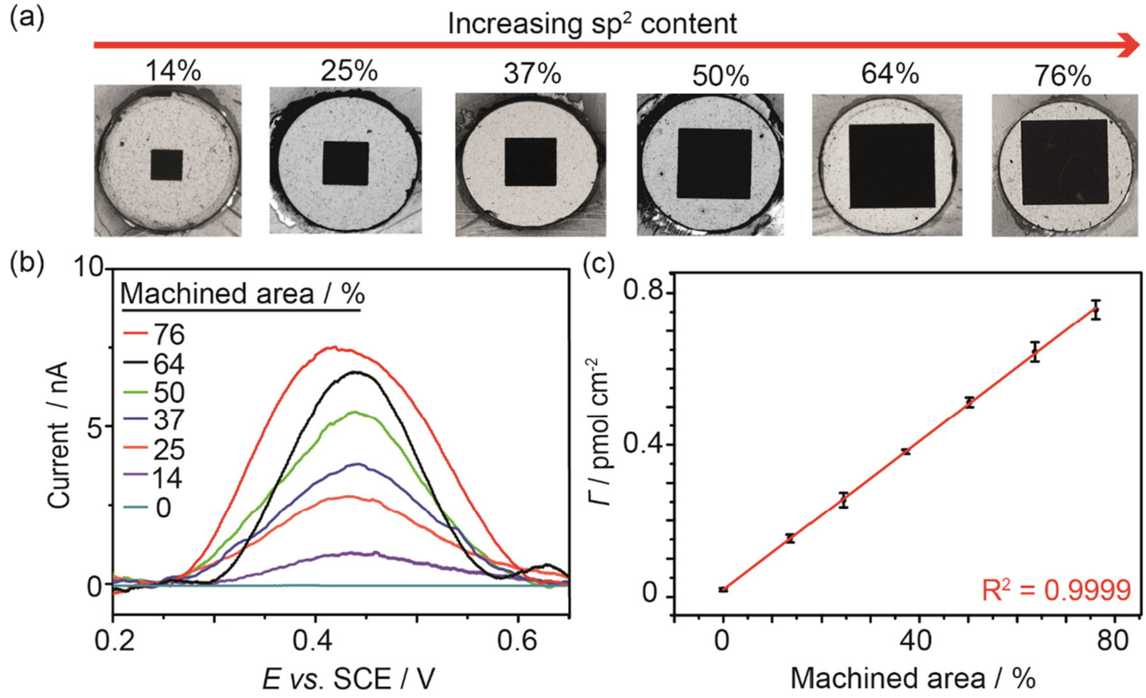

Fig. 1. (a) Optical images of the squares of increasing size (side length: left to right) 200, 300, 400, 500, 600 to 700 μm, laser machined into BDD; (b) Representative quinone oxidation peaks for the six machined electrodes and a blank, in pH 2 buffer, at a scan rate of 0.1 V s^{-1}. (c) Plot of machined surface area (%) versus Γ.