



Surface Characterisation and Functional Properties of Modified Diamond Electrodes

Inga V. Shpilevaya

Chemistry Research Laboratory
Department of Physical and Theoretical Chemistry
St Catherine's College

Trinity Term 2014

A thesis submitted to the board of the Faculty of Physical Sciences
at the University of Oxford in fulfilment of the requirements
for the degree of Doctor of Philosophy

Abstract

In this work, the use of modified diamond as an electrode material with superlative physical and electrochemical properties was investigated in a number of electrochemical applications. The surface chemistry of three differing forms of diamond, namely boron-doped microcrystalline diamond, boron-doped diamond powder and detonation nanodiamond powder was modified utilising such strategies as hydrogen plasma treatment, reactive ion plasma etching along with various chemical treatments. The surface and functional properties of the modified diamond electrodes were studied using a wide spectrum of techniques. The electrochemical activity of these materials was concomitantly investigated in order to expand the knowledge of diamond electrochemistry and to establish an understanding of how the surface chemistry of these materials impacts their electrochemical performance.

In the first study, the nanostructuring strategies of boron-doped diamond surface with platinum nanoparticles were developed. In particular, two types of diamond nanostructures were produced: one consisting of platinum particles located on the top of diamond nanorods, the other with platinum particles located in the bottom of diamond nanopits. For the first time, the experimental evidence proving the mechanism of the diamond nanostructuring process was reported. The electrochemical activity of these nanostructured diamond electrodes with regard to the electrochemical oxidation of glucose and methanol was investigated.

In the second study, the relationship between the surface chemistry of three differing forms of diamond, including microcrystalline boron-doped diamond, boron-doped diamond powder as well as detonation nanodiamond powder, and the electrode fouling in the result of the adsorption processes in methyl viologen and anthraquinonedisulfonate solutions was investigated. The influence of two dissimilar surface terminations: hydrophobic H-terminated and hydrophilic O-terminated on the electrode performance was studied in detail. This work provides a useful insight on the likely reasons for the undesirable adsorption occurrence which may be experienced in many electroanalytical applications that utilise solid and powdered forms of diamond.

The third project extends the discussion on the study of the diamond electrodes, modified with detonation nanodiamond and boron-doped diamond powders and investigates the electrochemical behaviour of these materials. In this work, charge transport within the diamond powder films, partition coefficients of different redox mediators along with heterogeneous electron transfer constants were identified. The chemical modification of these electrodes with platinum nanoparticles along with the mechanism of nucleation and growth of the latter were studied. The enhanced electrode performance with regard to methanol electrooxidation reaction was demonstrated.

The fourth study investigates the preparation of nickel modified boron-doped diamond electrodes and ascertains the relationship between the surface chemistry of the modified diamond and the associated electrocatalytic performance of nickel nanoparticles in hydrogen peroxide and glucose electrooxidation.

The fifth study reports on the development of a novel surface functionalization strategy, based on porphyrin and amide coupling chemistry, which allows the creation of hybrid biomimetic diamond interface that was used as the artificial β -alanine receptor.

Acknowledgements

First, I would like to express my sincere gratitude to Professor John S. Foord, my supervisor, for taking me on as a D.Phil. student in his group and engaging me in this exciting project. His mentorship, scientific expertise, truly critical approach to electrochemical problems along with a great sense of humour were absolutely invaluable throughout these years.

I would like to thank Dr. Geoffrey Nelson, Dr Ashley Shepherd, Dr. Robert Jacobs, Dr. Emina Hadzifejzovic and Dr. Jingping Hu for sharing their profound knowledge and support. Without them, my scientific journey would have stopped with the first applied potential. I am very grateful to the Foord Group students (Sirikarn, Tony, Patrick, Lulu, Seb, Vicky, Johanna and Christos) for their friendship and help in my work. Special thanks to Céline Shepherd, whose cheerful attitude and excellent proof reading skills were of a great help.

It was a special experience for me to work with Dr. Nianjun Yang, Dr Waldemar Smirnov and Prof. Christoph Nebel at the Fraunhofer Institute of Applied Solid State Physics (Freiburg, Germany).

I would like to thank Dr. Maggie Charles and Amanda Jeffries for introducing me to a world of academic writing and for explaining my grammar mistakes. Very special thanks to Dr. Artem Voronov, Dr. Nikita Loik, Victoria Truffaut, Alexey Shokhin and Natalia Vygovskaya, whose friendship and support during these years were truly invaluable.

My research was made possible by Marie Curie Scholarship and the University of Oxford.

Finally, I would like to thank my family for their endless support and patience during these years.

Relevant Publications

Nanostructured diamond decorated with Pt particles: preparation and electrochemistry

I. Shpilevaya, W. Smirnov, S. Hirszt, N. Yang, C. E. Nebel and J. S. Foord, RSC Advances, 2014, 4, 531-537

Electrochemistry of Nanocrystalline and Microcrystalline Diamond

I. Shpilevaya and J. S. Foord, Chapter 15, RSC Nanoscience & Nanotechnology No. 31 Nanodiamond, Edited by Oliver Williams, 2014, 354-384

Electrochemistry of methyl viologen and anthraquinonedisulfonate at diamond and diamond powder electrodes: the influence of surface chemistry

I. Shpilevaya and J. S. Foord, accepted to Electroanalysis

The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

I. Shpilevaya and J. S. Foord, submitted to Electroanalysis

Table of Contents

1	CHAPTER ONE – INTRODUCTION	1
1.1	SYNTHETIC DIAMOND.....	1
1.2	SYNTHETIC DIAMOND IN ELECTROCHEMISTRY	3
1.2.1	<i>Microcrystalline boron-doped diamond.....</i>	<i>6</i>
1.2.2	<i>Nanodiamond powders.....</i>	<i>7</i>
1.3	APPLICATIONS OF DIAMOND ELECTRODES	9
1.4	AIMS AND SCOPE OF THIS THESIS	10
1.5	REFERENCES	12
2	CHAPTER TWO – EXPERIMENTAL THEORY AND TECHNIQUES	16
2.1	X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)	16
2.1.1	<i>XPS Instrumentation</i>	<i>19</i>
2.1.2	<i>XPS Spectral Features</i>	<i>21</i>
2.1.2.1	The main photoelectron line.....	21
2.1.2.2	Auger Peaks	23
2.1.2.3	Shake up satellites	23
2.1.2.4	Other spectral features.....	24
2.1.3	<i>XPS Quantification</i>	<i>25</i>
2.1.4	<i>XPS Experimental Procedure.....</i>	<i>27</i>
2.2	SCANNING ELECTRON MICROSCOPY (SEM).....	27
2.3	RAMAN SPECTROSCOPY	28
2.4	X-RAY DIFFRACTION	30
2.5	ELECTROCHEMICAL METHODS	32
2.5.1	<i>Principles of Electrochemical Theory.....</i>	<i>32</i>
2.5.1.1	Equilibrium Electrochemistry.....	35
2.5.1.2	Non-equilibrium Electrochemistry.....	36
2.5.2	<i>Electrochemical measurements</i>	<i>40</i>

Surface Characterisation and Functional Properties of Modified Diamond Electrodes

2.5.3	<i>Cyclic Voltammetry</i>	41
2.5.4	<i>Chronoamperometry</i>	43
2.5.5	<i>Chronocoulometry</i>	45
2.5.6	<i>Rotating Disk Electrode</i>	45
2.5.7	<i>Electrochemical Impedance Spectroscopy</i>	47
2.6	REFERENCES	50
3	CHAPTER THREE – DECORATED NANOSTRUCTURED DIAMOND ELECTRODES: PREPARATION AND ELECTROCHEMISTRY	52
3.1	INTRODUCTION	52
3.1.1	<i>Unmodified nanostructured diamond</i>	53
3.1.2	<i>Nanostructured diamond modified with catalyst particles</i>	55
3.2	AIMS OF THE PROJECT	56
3.3	EXPERIMENTAL METHODS.....	57
3.3.1	<i>Electrochemical measurements</i>	57
3.3.2	<i>Diamond nanostructuring procedure</i>	58
3.3.3	<i>Morphology and microstructure characterisation</i>	59
3.3.4	<i>Chemicals</i>	60
3.4	RESULTS AND DISCUSSION	60
3.4.1	<i>Morphology and microstructure characterisation</i>	60
3.4.1.1	Pt decorated diamond textured in the form of nanopits	63
3.4.1.2	Pt decorated diamond textured in the form of nanorods	67
3.4.2	<i>X-ray Photoelectron Spectroscopy Study</i>	69
3.4.3	<i>Electrochemical Characterisation</i>	73
3.5	CONCLUDING REMARKS	78
3.6	REFERENCES	79
4	CHAPTER FOUR – ADSORPTION ELECTROCHEMISTRY AT DIAMOND ELECTRODES: THE INFLUENCE OF SURFACE CHEMISTRY	84
4.1	INTRODUCTION	84

Surface Characterisation and Functional Properties of Modified Diamond Electrodes

4.1.1	<i>Adsorption properties of diamond materials</i>	84
4.1.1.1	Background on Detonation Nanodiamond and Boron-doped Diamond Powders	85
4.2	AIMS OF THE PROJECT	86
4.3	EXPERIMENTAL METHODS	88
4.3.1	<i>Electrode Preparation</i>	88
4.3.2	<i>Characterisation</i>	89
4.3.3	<i>Chemicals</i>	91
4.4	RESULTS AND DISCUSSION	92
4.4.1	<i>Morphology and microstructure characterisation</i>	92
4.4.2	<i>XPS characterization of hydrogenated and oxidised diamond electrodes</i>	94
4.4.2.1	Wide scan XPS	94
4.4.2.2	Hydrogen termination and induced surface conductivity	96
4.4.3	<i>Electrochemistry of methyl viologen</i>	100
4.4.3.1	Chronocoulometry study of methyl viologen adsorption	113
4.4.3.2	XPS analysis of adsorbed methyl viologen at diamond electrodes	115
4.4.4	<i>Electrochemistry of anthraquinonedisulfonate</i>	118
4.4.4.1	Chronocoulometry characterisation of 2,6-AQDS adsorption	125
4.4.4.2	XPS characterisation of 2,6-AQDS adsorption	126
4.5	CONCLUDING REMARKS	128
4.6	REFERENCES	129
5	CHAPTER FIVE – DIAMOND POWDER FILMS: ELECTROCHEMICAL PROPERTIES AND APPLICATIONS IN ELECTROCATALYSIS	133
5.1	INTRODUCTION	133
5.1.1	<i>Diamond powders as a highly stable support for electrocatalytic materials</i>	134
5.1.2	<i>Detonation nanodiamond powder</i>	135
5.1.3	<i>Boron-doped diamond powder</i>	137
5.2	AIMS OF THE PROJECT	137
5.3	EXPERIMENTAL METHODS	138
5.3.1	<i>Electrode Preparation</i>	138

5.3.2	<i>Characterisation.....</i>	138
5.4	RESULTS AND DISCUSSION.....	140
5.4.1	<i>XPS characterisation of BDP and DND modified electrodes.....</i>	140
5.4.2	<i>Electrochemical characterisation of BDP and DND modified electrodes</i>	142
5.4.3	<i>Platinum decorated diamond electrodes.....</i>	154
5.4.3.1	Investigation of Pt nucleation and growth on diamond electrodes	155
5.4.3.2	Electrochemical characterisation of platinum decorated diamond electrodes	159
5.5	CONCLUDING REMARKS	163
5.6	REFERENCES	164
6	CHAPTER SIX – THE EFFECT OF THE SURFACE PRE-TREATMENT ON THE ELECTROCHEMICAL BEHAVIOUR OF NICKEL MODIFIED BORON-DOPED DIAMOND ELECTRODES	169
6.1	INTRODUCTION	169
6.2	AIMS OF THE PROJECT	171
6.3	EXPERIMENTAL METHODS	172
6.3.1	<i>Preparation of nickel modified boron-doped diamond electrode</i>	<i>172</i>
6.3.1.1	Preparation of oxygen terminated boron-doped diamond surface	172
6.3.1.2	Preparation of hydrogen terminated boron-doped diamond surface	172
6.3.1.3	Preparation of nickel modified boron-doped diamond electrode	172
6.3.2	<i>Surface characterisation of nickel modified boron-doped diamond electrode</i>	<i>173</i>
6.4	RESULTS AND DISCUSSION.....	174
6.4.1	<i>Morphology and microstructure of nickel modified boron-doped diamond electrodes</i>	<i>174</i>
6.4.1.1	SEM characterisation of nickel modified boron-doped diamond electrodes.....	174
6.4.1.2	XRD characterisation of nickel modified boron-doped diamond electrodes	176
6.4.1.3	XPS characterisation of nickel modified boron-doped diamond electrodes.....	177
6.4.2	<i>Electrochemical characterisation of nickel modified boron-doped diamond electrodes</i>	<i>181</i>
6.4.2.1	Electrochemical oxidation of glucose at nickel modified boron-doped diamond electrodes	186
6.4.2.2	Electrochemical oxidation of hydrogen peroxide at nickel modified boron-doped diamond electrode	188
6.4.2.3	The effects of the surface pre-treatment on the adhesion properties of Ni particles	190

6.5	CONCLUDING REMARKS	191
6.6	REFERENCES	192
 7 CHAPTER SEVEN – CHEMICAL MODIFICATIONS OF DIAMOND SURFACES: PORPHYRIN-DIAMOND		
HYBRID INTERFACES		198
7.1	INTRODUCTION	198
7.1.1	<i>Smart diamond biosensors</i>	<i>198</i>
7.1.2	<i>Chemical functionalisation of diamond surface.....</i>	<i>199</i>
7.2	AIMS OF THE PROJECT	201
7.2.1	<i>Background on the zinc (II) protoporphyrin IX</i>	<i>201</i>
7.3	EXPERIMENTAL SECTION	202
7.3.1	<i>Electrode preparation</i>	<i>202</i>
7.3.1.1	Hydrogen termination of diamond electrodes	202
7.3.1.2	Ethylenediamine covalent functionalisation of polycrystalline boron-doped diamond electrodes	203
7.3.1.3	Ethylenediamine adsorption on polycrystalline boron-doped diamond electrode	203
7.3.1.4	Zinc (II) protoporphyrin IX covalent grafting	203
7.3.1.5	Preparation of Zinc (II) protoporphyrin IX adsorbed onto the ethylenediamine modified boron-doped diamond	204
7.3.2	<i>Characterisation.....</i>	<i>204</i>
7.3.3	<i>Chemicals</i>	<i>205</i>
7.4	RESULTS AND DISCUSSION	205
7.4.1	<i>XPS characterization of hydrogen terminated boron-doped diamond electrode</i>	<i>205</i>
7.4.2	<i>Ethylenediamine covalent functionalisation of diamond electrode.....</i>	<i>206</i>
7.4.2.1	XPS characterisation of amino functionalised diamond electrodes	210
7.4.2.2	Ethylenediamine modification of diamond electrode under base conditions	215
7.4.3	<i>Zinc (II) protoporphyrin IX covalent grafting via amide EDC/NHS coupling reaction.....</i>	<i>216</i>
7.4.4	<i>Electrochemical characterisation of ZnP modified electrodes</i>	<i>224</i>
7.4.4.1	Zinc (II) protoporphyrin-diamond receptor of β -alanine	232
7.5	CONCLUDING REMARKS	234
7.6	REFERENCES	235

List of Figures

FIGURE 1 HISTORICAL DATA FOR THE PERIOD 1988-2014, ILLUSTRATING THE ANNUAL NUMBER OF SCIENTIFIC PUBLICATIONS REGARDING DIAMOND ELECTROCHEMISTRY IN COMPARISON TO SIMILAR DATA FOR GLASSY CARBON. THE DATA FOR GLASSY CARBON WERE DIVIDED BY A FACTOR OF 3.	2
FIGURE 2 CYCLIC VOLTAMMOGRAMS OF WATER ELECTROLYSIS IN 0.5 M H ₂ SO ₄ AT TWO BORON-DOPED POLYCRYSTALLINE FILMS. B: PCD(NRL) WITH 5×10 ¹⁹ [B]·cm ⁻³ AND B: PCD(USU) WITH 5×10 ²⁰ [B] cm ⁻³ ARE COMPARED TO A SINGLE CRYSTAL BORON-DOPED DIAMOND B: (H)SCD WITH 3×10 ²⁰ [B] cm ⁻³ AND WITH AN UNDOPED DIAMOND (H)SCD. DATA FOR Pt, Au AND GLASSY CARBON ARE ALSO PRESENTED. THE PLOTS WERE SHIFTED VERTICALLY FOR THE COMPARISON. REPRODUCED FROM ⁸ ...	4
FIGURE 3 SEM OF MICROCRYSTALLINE BORON-DOPED DIAMOND ELECTRODE	7
FIGURE 4 SCHEMATIC ILLUSTRATION OF DIAMOND POWDER POROUS LAYER ON THE TOP OF DIAMOND ELECTRODE	8
FIGURE 5 SEM OF AS-MILLED BORON-DOPED DIAMOND POWDER.....	9
FIGURE 6 (A) SCHEMATIC PRESENTATION OF THE XPS PROCESS, WHERE PHOTOIONISATION OF AN ATOM BY THE EMISSION OF 1S ELECTRON OCCURS; (B) PRINCIPLE SCHEME OF AN XPS INSTRUMENT, ADAPTED FROM ⁵	17
FIGURE 7 SCHEMATIC PRESENTATION OF AN AUGER PROCESS – RELAXATION OF THE IONIZED ATOM THE EJECTION OF A KL _{2,3} L _{2,3} AUGER ELECTRON, ADAPTED FROM ⁵	19
FIGURE 8 SCHEMATIC PRESENTATION OF XPS APPARATUS EXPERIMENTAL SET-UP, REPRINTED FROM ⁶	20
FIGURE 9 AN EXAMPLE OF A TYPICAL SURVEY SPECTRUM DEMONSTRATING THE APPEARANCE OF XPS AND AUGER PEAKS ABOVE A BACKGROUND OF SCATTERED ELECTRONS, REPRINTED FROM ¹⁰	22
FIGURE 10 A TYPICAL SPIN-ORBIT COUPLING OF Pt 4f SPECTRUM	23
FIGURE 11 π-BOND SHAKE-UP SATELLITE FOR THE C 1s PHOTOELECTRON PEAK IN POLYSTYRENE, REPRINTED FROM ¹¹	24
FIGURE 12 (A) MULTIPLY SPLITTING IN THE Cr 3s LINE; (B) ENERGY PLASMON LOSSES ASSOCIATED WITH 2s LINE OF ALUMINIUM. BOTH FIGURES REPRINTED FROM ¹¹	25
FIGURE 13 (A) THE PRINCIPLE SCHEME OF THE BASIC COMPONENTS OF SEM, ADAPTED FROM ¹⁵ ; (B) A TYPICAL SEM IMAGE OF A MICROCRYSTALLINE BORON-DOPED DIAMOND ELECTRODE	28
FIGURE 14 SCHEMATIC ILLUSTRATION OF RAMAN SCATTERING	29
FIGURE 15 (A) GENERAL RAMAN SPECTRUM OF SINGLE CRYSTAL DIAMOND EXCITED AT ROOM TEMPERATURE AT A WAVELENGTH OF 228.9 NM. THE FIRST, SECOND AND THIRD ORDER RAMAN PEAKS ARE PRESENTED, REPRINTED FROM ¹⁶ ; (B) RAMAN SPECTRA OF BORON-DOPED DIAMOND FILMS AT DIFFERING BORON DOPING CONCENTRATIONS, REPRINTED FROM ¹⁸	30

FIGURE 16 SCHEMATIC ILLUSTRATION OF (A) X-RAY POWDER DIFFRACTOMETER IN Θ - 2Θ ORIENTATION; (B) X-RAY DIFFRACTION ON A CRYSTALLINE SAMPLE, ADAPTED FROM ¹⁹	31
FIGURE 17 SCHEMATIC ILLUSTRATION OF TWO-ELECTRODE ELECTROCHEMICAL CELL, ADAPTED FROM ²²	33
FIGURE 18 HELMHOLTZ DOUBLE LAYER MODEL, ADAPTED FROM ²²	35
FIGURE 19 DEPENDENCE OF THE CURRENT WITH OVERPOTENTIAL FOR (A) LARGE I_0 (REVERSIBLE) AND (B) SMALL I_0 (IRREVERSIBLE). 38	
FIGURE 20 SCHEME OF ELECTRODE REACTION PATHWAY, ADAPTED FROM ²²	39
FIGURE 21 (A) LINEAR POTENTIAL SWEEP DURING CYCLIC VOLTAMMETRY; (B) CYCLIC VOLTAMMOGRAM OBTAINED AT BORON-DOPED DIAMOND ELECTRODE IN 0.1 mM $K_3Fe(CN)_6$ IN 0.1 M KCL AT 0.05 Vs^{-1}	42
FIGURE 22 (A) POTENTIAL-TIME DEPENDENCE OF CHRONOAMPEROMETRIC MEASUREMENT; (B) CHANGE OF CONCENTRATION PROFILES WITH TIME; (C) RESULTING CURRENT-TIME TRANSIENT, ADAPTED FROM ²²	44
FIGURE 23 SCHEME OF ROTATING DISK ELECTRODE	46
FIGURE 24 TYPICAL NYQUIST PLOT OF EIS MEASUREMENT	47
FIGURE 25 A MODEL OF Randles circuit, where R_s is the bulk solution resistance, R_{CT} is the charge transfer resistance, Z_W is the Warburg resistance and C_{DL} is the double layer capacitance	48
FIGURE 26 SCHEMATIC ILLUSTRATION OF UNMODIFIED DIAMOND NANOGRASS AND NANOPORES STRUCTURES; (A) VERTICALLY ALIGNED NANOGRASS, REPRINTED FROM ³³ , (B) NANOPORES IN THE DIAMOND SURFACE, REPRINTED FROM ³⁴	54
FIGURE 27 SCHEMATIC PRESENTATION OF DIAMOND TEXTURING STRATEGIES	57
FIGURE 28 PHOTOGRAPH OF HYDROGEN INDUCTION FURNACE USED FOR CATALYTIC ETCHING OF BORON-DOPED DIAMOND ELECTRODES	59
FIGURE 29 CYCLIC VOLTAMMETRY OF Pt decorated boron-doped diamond in 0.1 M H_2SO_4 recorded at the scan rate of 0.05 Vs^{-1}	61
FIGURE 30 SEM image of (A) polycrystalline boron-doped diamond electrode; (B) Pt nanoparticles deposited on boron-doped diamond electrode	62
FIGURE 31 SEM image of (A) Pt decorated boron-doped diamond that is textured in the form of nanopits; (B) Pt etch pits formed, inset (i) four-sided pyramid with Pt nanoparticle inside, (ii) elongated channel containing Pt nanoparticle, (iii) hexagonal pit with Pt nanoparticle; (C) Pt NPs of Pt_PDE are highlighted in red; (D) Pt nanopits at $[100]$ oriented surface	63
FIGURE 32 SCHEMATIC ILLUSTRATION OF CATALYTIC ETCHING MECHANISM	64
FIGURE 33 DIAMOND Lattice structure view from $[100]$, $[110]$ and $[111]$ planes.....	65

FIGURE 34 (A) SCHEMATIC STRUCTURE OF AN [111] PLANE OCTAHEDRON IN A CUBIC UNIT CELL. THE LATTER IS POSITIONED IN [100], [110] AND [111] ORIENTATIONS; (B) CROSS-SECTIONS THROUGH THE [100], [110] AND [111] PLANES OF THE OCTAHEDRON AND ASSOCIATED GEOMETRIC FORMS WITH THE ANGLES ASSIGNED; (C) POSSIBLE STRUCTURES OF ETCH PITS FROM THE ABOVE VIEW (D) THREE DIMENSIONAL STRUCTURES OF THE ETCH PITS WITH THE SPHERICAL PT NANOPARTICAL INSIDE, ADAPTED FROM ³⁴	66
FIGURE 35 SCHEMATIC ILLUSTRATION OF REACTIVE ION ETCHING MECHANISM.....	67
FIGURE 36 (A) AND (B) SEM IMAGES OF NANORODS TEXTURED PT DECORATED BORON-DOPED DIAMOND THAT WAS ETCHED IN O ₂ PLASMA; (C) THE RODS FORMED; (D) PT NANOPARTICLE ON THE TOP OF THE ROD HIGHLIGHTED IN RED	68
FIGURE 37 C 1s XPS SPECTRA OF (A) PT_BDE, (C) PT_PDE WITH THE INSET OF RAW INTENSITIES OF (- -)PT_BDE AND (-) PT_PDE WITH (II) C 1s PtCx PEAK AND (I) C 1s SP ² DEFECTS OF PT_PDE, (E) PT_RDE; PT 4f XPS SPECTRA OF (B) PT_BDE, (D) PT_PDE, (F) PT_RDE	71
FIGURE 38 CV IN 0.1 M H ₂ SO ₄ OF (A) (-) PT_PDE PRIOR TO STABILITY TESTS, (-) PT_PDE AFTER STABILITY TESTS; (B) (-) PT_RDE PRIOR TO STABILITY TESTS, (-) PT_RDE AFTER STABILITY TESTS. ALL CVs WERE RECORDED AT 0.05 V s ⁻¹	74
FIGURE 39 CALCULATED PLATINUM LOSS (%) FROM (I) PT_RDE, (II) PT_BDE, (III) PT_PDE ELECTRODES	75
FIGURE 40 CYCLIC VOLTAMMOGRAMS OF (A) (-) PT_PDE IN 1 M GLUCOSE, 0.1 M PBS AT 0.05 V s ⁻¹ , (.....) AFTER AQUA REGIA TREATMENT, PT_PDE IN 1 M GLUCOSE, 0.1 M PBS AT 0.05 V s ⁻¹ ; (B) (-) PT_PDE IN 1 M CH ₃ OH, 0.1 M H ₂ SO ₄ AT 0.05 V s ⁻¹ , (.....) PT_PDE AFTER AQUA REGIA TREATMENT IN 1 M CH ₃ OH, 0.1 M H ₂ SO ₄ AT 0.05 V s ⁻¹	77
FIGURE 41 CHEMICAL STRUCTURES OF (A) METHYL VIOLOGEN AND (B) 9,10-ANTHRAQUINONE-2,6-DISULFONIC ACID USED IN THIS WORK	87
FIGURE 42 SEM IMAGE OF (A) BORON-DOPED DIAMOND ELECTRODE; (B) 200 NM LAYER OF BORON-DOPED DIAMOND POWDER; (C) 200 NM LAYER OF DETONATION NANODIAMOND POWDER.....	92
FIGURE 43 RAMAN SPECTRUM OF (A) BORON-DOPED DIAMOND POWDER; (B) DETONATION NANODIAMOND POWDER, REPRINTED FROM ¹⁶	93
FIGURE 44 XPS WIDE SCAN SPECTRA OF (A) HYDROGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE; (B) OXYGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE	96
FIGURE 45 SCHEMATIC ILLUSTRATION OF THE INCREASE IN THE VALANCE BAND ENERGY WHICH IS ACHIEVED THROUGH THE CHANGES OF DIAMOND SURFACE TERMINATION FROM OXYGEN TO HYDROGEN, ADAPTED FROM ⁵⁹	98
FIGURE 46 STRUCTURE OF METHYL VIOLOGEN AT THREE MAIN OXIDATION STATES	100

FIGURE 47 CYCLIC VOLTAMMOGRAM OF 1 mM METHYL VIOLOGEN IN 0.1 M KCL RECORDED AT 0.05 V s ⁻¹ AT (A) HYDROGEN TERMINATED BORON-DOPED DIAMOND; (B) OXYGEN TERMINATED BORON-DOPED DIAMOND.....	101
FIGURE 48 (A) CYCLIC VOLTAMMOGRAMM OF 1 mM MV, 0.1 M KCL RECORDED AT OXYGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE WITH THE SCAN RATES OF 0.02 TO 0.07 Vs ⁻¹ ; (B) CORRESPONDING PLOTS OF PEAK CURRENTS VERSUS SQUARE ROOT OF SCAN RATE.....	103
FIGURE 49 (A) CYCLIC VOLTAMMOGRAMM OF 1 mM MV, 0.1 M KCL RECORDED AT HYDROGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE WITH THE SCAN RATES OF 0.03 TO 0.1 Vs ⁻¹ ; (B) CORRESPONDING PLOTS OF PEAK CURRENTS VERSUS SQUARE ROOT OF SCAN RATE; (C) PLOT OF PEAK CURRENT 3 VERSUS SCAN RATE.....	104
FIGURE 50 CYCLIC VOLTAMMOGRAM IN 1 mM MV, 0.1 M KCL RECORDED AT (A) HBDE (—) INITIAL SCAN, (—) HBDE WAS HELD FOR 30 s, (—) HBDE WAS HELD FOR 60 s; (B) HBDE (—) INITIAL SCAN, (—) OBDE WAS HELD FOR 30 s, (—) HBDE WAS HELD FOR 60 s	106
FIGURE 51 CYCLIC VOLTAMMOGRAMS IN 1 mM MV, 0.1 M KCL RECORDED AT (A) HBDP; (B) OBDP. THE SCANS WERE RECORDED AT 0.05 Vs ⁻¹	108
FIGURE 52 CYCLIC VOLTAMMOGRAMM OF 1 mM MV, 0.1 M KCL RECORDED AT (A) OXYGEN TERMINATED BORON-DOPED DIAMOND POWDER WITH THE SCAN RATES FROM 0.02 TO 0.1 Vs ⁻¹ ; (B) CORRESPONDING PLOTS OF PEAK CURRENTS VERSUS SQUARE ROOT OF SCAN RATE.....	109
FIGURE 53 CYCLIC VOLTAMMOGRAMM OF 1 mM MV, 0.1 M KCL RECORDED AT (A) HYDROGEN TERMINATED BORON-DOPED DIAMOND POWDER WITH THE SCAN RATES FROM 0.02 TO 0.08 Vs ⁻¹ ; (B) CORRESPONDING PLOTS OF PEAK CURRENTS VERSUS SQUARE ROOT OF SCAN RATE; (C) PLOT OF PEAK 3 CURRENTS VERSUS SCAN RATE	110
FIGURE 54 CYCLIC VOLTAMMOGRAMS IN 1 mM MV, 0.1 M KCL RECORDED AT (—) HDND; (---) ODND. THE SCANS WERE RECORDED AT 0.05 Vs ⁻¹	111
FIGURE 55 CYCLIC VOLTAMMOGRAMS AT (—) HBDE IN 1 mM MV, 0.1 M KCL, (---) HBDE AFTER RINSE IN BACKGROUND ELECTROLYTE (0.1 M KCL), THE INSET DISPLAYS A MAGNIFIED MVOADS PEAK REMAINED ON THE HBDE ELECTRODE SURFACE AFTER THE RINSING PROCEDURE	112
FIGURE 56 CHRONOCOULOMETRIC CURVES RECORDED DURING THE POTENTIAL SCANNING FROM -1.0 V TO -0.7 V AT (A) HBDE IN (1) BACKGROUND ELECTROLYTE 0.1 M KCL, (2) AFTER THE RINSING PROCEDURE, (B) ASSOCIATED CHARGE DIFFERENCE AT HBDE; (C) HBDP IN (1) BACKGROUND ELECTROLYTE 0.1 M KCL, (2) AFTER THE RINSING PROCEDURE, (D) ASSOCIATED CHARGE DIFFERENCE AT HBDP; (E) HDND IN (1) BACKGROUND ELECTROLYTE 0.1 M KCL, (2) AFTER THE RINSING PROCEDURE, (B) ASSOCIATED CHARGE DIFFERENCE AT HDND.....	114

FIGURE 57 (A) C 1s XPS REGION AT HBDE; (B) N 1s REGION AT HBDE; (C) C 1s REGION AT HBDP; (D) N 1s REGION AT HBDP; (E) C 1s REGION AT HDND; (F) N 1s REGION AT HDND;	116
FIGURE 58 THE REDOX REACTION OF 2,6-AQDS IN ACIDIC MEDIA	118
FIGURE 59 CYCLIC VOLTAMMOGRAMS OF 1 mM 2,6-AQDS, 0.1 M HNO ₃ RECORDED AT (A) (–) HBDE; (B) HBDE AT THE SCAN RATE FROM 0.02 TO 0.1 Vs ⁻¹ ; (C) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS AT HBDE VS SQUARE ROOT OF THE SCAN RATE; (D) (–) HDND, (–) HDND IN 0.1 M HNO ₃ AFTER THE RINSING PROCEDURE; (E) HDND AT THE SCAN RATES FROM 0.02 TO 0.1 Vs ⁻¹ ; (F) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS VS SQUARE ROOT OF THE SCAN RATE; (G) (–) HBDP, (–) HBDP IN 0.1 M HNO ₃ AFTER THE RINSING PROCEDURE; (B) HBDP AT THE SCAN RATES FROM 0.02 TO 0.1 Vs ⁻¹ ; (C) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS AT HBDP VS SQUARE ROOT OF THE SCAN RATE	119
FIGURE 60 CYCLIC VOLTAMMOGRAMS OF 1 mM 2,6-AQDS, 0.1 M HNO ₃ RECORDED AT (A) (–) OBDE, (–) OBDE IN 0.1 M HNO ₃ AFTER THE RINSING PROCEDURE; (B) OBDE AT THE SCAN RATE FROM 0.02 TO 0.1 Vs ⁻¹ ; (C) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS AT OBDE VS SQUARE ROOT OF THE SCAN RATE; (D) (–) ODND, (–) ODND IN 0.1 M HNO ₃ AFTER THE RINSING PROCEDURE; (E) ODND AT THE SCAN RATES FROM 0.02 TO 0.1 Vs ⁻¹ ; (F) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS VS SQUARE ROOT OF THE SCAN RATE; (G) (–) OBDP, (–) OBDP IN 0.1 M HNO ₃ AFTER THE RINSING PROCEDURE; (B) OBDP AT THE SCAN RATES FROM 0.02 TO 0.1 Vs ⁻¹ ; (C) CORRESPONDING PLOT OF REDUCTION AND OXIDATION PEAK CURRENTS AT OBDP VS SQUARE ROOT OF THE SCAN RATE	123
FIGURE 61 CHRONOCOULOMETRIC CURVES RECORDED DURING POTENTIAL SCANNING FROM 0.6 V TO -0.4 V AT (A) HBDP IN (–) BACKGROUND ELECTROLYTE 0.1 M HNO ₃ , (– –) AFTER THE RINSING PROCEDURE; (B) HDND IN (–) BACKGROUND ELECTROLYTE 0.1 M HNO ₃ , (– –) AFTER THE RINSING PROCEDURE	125
FIGURE 62 (A) C1s XPS SPECTRA OF HBDP; (B) S2p XPS SPECTRA RECORDED AT HBDP; (C) C1s XPS SPECTRA OF HDND; (B) S2p XPS SPECTRA RECORDED AT HDND.....	127
FIGURE 63 ILLUSTRATION OF DETONATION NANODIAMOND PARTICLE STRUCTURE, ADAPTED FROM ²⁷	136
FIGURE 64 (A) SURVEY XPS SPECTRA OF BDE; (B) C 1s XPS REGION OF BDE; (C) O 1s REGION OF BDE; (D) SURVEY XPS SPECTRA OF BDP; (E) C 1s REGION OF BDP; (F) O 1s REGION OF BDP; (G) SURVEY XPS SPECTRA OF DND; (H) C 1s REGION OF DND; (I) O 1s REGION OF DND	141
FIGURE 65 CYCLIC VOLTAMMOGRAMS RECORDED AT (–) PLAIN BDE, (– –) 200 NM DND AND (– – –) 200 NM BDP MODIFIED ELECTRODES IN (A) 0.1 MM IN K ₃ Fe(CN) ₆ , 0.1 M KCL; (B) 0.1 MM IN Ru(NH ₃) ₆ Cl ₃ , 0.1 M KCL; (C) 0.1 MM IN K ₂ IrCl ₆ , 0.1 M KCL; (D) 0.1 MM FcCH ₂ OH, 0.1 M KCL AT A SCAN RATE OF 0.05 Vs ⁻¹	143

FIGURE 66 PEAK CURRENTS THEORETICALLY PREDICTED BY THE RANDLES-ŠEVČÍK EQUATION AND EXPERIMENTALLY RECORDED AT BDE, BDP AND DND ELECTRODES DURING (A) CATHODIC SCAN; (B) ANODIC SCAN AT A SCAN RATE OF 0.05 Vs^{-1}	145
FIGURE 67 CYCLIC VOLTAMMOGRAMS RECORDED AT (–) PLAIN BDE, (– – –) 200 NM DND AND (– – – –) 200 NM BDP MODIFIED ELECTRODES IN (A) 1 mM IN $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCL; (B) 10 mM IN $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCL; (C) 1 mM IN $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, 0.1 M KCL; (D) 10 mM IN $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, 0.1 M KCL; (E) 1 mM IN K_2IrCl_6 , 0.1 M KCL; (F) 10 mM IN K_2IrCl_6 , 0.1 M KCL; (G) 1 mM FcCH_2OH AT A SCAN RATE OF 0.05 Vs^{-1}	148
FIGURE 68 KOUTECKÝ-LEVICH PLOT OF (–) UNMODIFIED BDE; (–) DND MODIFIED BDE IN 1 mM FcCH_2OH DISSOLVED IN 0.1 M KCL, INSET OF LINEAR SWEEP VOLTAMMOGRAM MFROM 0 V TO 0.5 V AT DND MODIFIED ELECTRODE IN 1 mM FcCH_2OH , 0.1 M KCL, REPRINTED FROM REFERENCE ⁴⁷	151
FIGURE 69 (A) SUBTRACTED LSV OF FcCH_2OH AT THE DND MODIFIED ELECTRODE, (B) ASSOCIATED ELECTROLYSIS CHARGE AS A FUNCTION OF DELAY TIME, REPRINTED FROM ⁴⁷	152
FIGURE 70 SEM OF (A) PT DECORATED BDE; (B) PT DECORATED BDP MODIFIED ELECTRODE; (C) PT DECORATED DND MODIFIED ELECTRODE	154
FIGURE 71 DEPOSITION CURRENT OBTAINED FROM 2 mM K_2PtCl_6 DISSOLVED IN 0.5 M H_2SO_4 AT A CONSTANT POTENTIAL OF - 0.2 V AT (– – –) BDE; (– – – –) DND AND (–) BDP ELECTRODE SURFACES.....	155
FIGURE 72 NON-DIMENSIONAL PLOT OF I/I_m VS T/T_m AT -0.1 V OBTAINED AT PT_DND ELECTRODE	158
FIGURE 73 CYCLIC VOLTAMMOGRAMS IN 0.5 M H_2SO_4 RECORDED AT 0.05 Vs^{-1} AT (–) PT_BDE; (– – –) PT_DND AND (– – – –) PT_BDP THAT WERE DEPOSITED AT -0.1 V.....	159
FIGURE 74 CALCULATED PT LOSS (%)AT (1) PT_BDP; (2) PT_DND AND (3) PT_BDE THAT WERE DECORATED AT -0.1 V	161
FIGURE 75 CYCLIC VOLTAMMETRY IN 1 mM CH_3OH , 0.5 M H_2SO_4 RECORDED AT A SCAN RATE OF 0.05 Vs^{-1} AT (–) PT_BDE; (– – –) PT_DND AND (– – – –) PT_BDP ELECTRODES.....	163
FIGURE 76 SEM IMAGE OF (A) MICROCRYSTALLINE BDE; (B) NI NPS DEPOSITED ON OXYGEN TERMINATED BDE; (B) NI NPS DEPOSITED ON HYDROGEN TERMINATED BDE;	174
FIGURE 77 THE COMPARISON OF NI ELECTRODEPOSITION CURRENT TIME-TRANSIENT OBTAINED AT OXIDISED BDE AT -1.3 V WITH SH MODEL: NON-DIMENSIONAL PLOT OF I/I_m VS T/T_m , (–) EXPERIMENTAL CURRENT (– – – –) 3D INSTANTANEOUS NUCLEATION, (– – – –) 3D PROGRESSIVE, (– – – –) 2D INSTANTANEOUS (– – – –) 2D PROGRESSIVE.....	175
FIGURE 78 X-RAY DIFFRACTION PROFILE OF THE NI_HBDE SAMPLE. NICKEL PARTICLES WERE ELECTRODEPOSITED FROM 1 mM $\text{Ni}(\text{NO}_3)_2$ IN 0.1 M ACETATE BUFFER SOLUTION (PH 5) VIA POTENTIOSTATIC METHOD AT A POTENTIAL OF -1.3 V VS Ag/AgCL. THE DIFFRACTION PROFILES INDEXED WITH [HKL] NOTATIONS CORRESPOND TO METAL NI PHASE AND BDE.....	177

FIGURE 79 (A) SURVEY XPS SPECTRA OF HYDROGENATED BORON-DOPED DIAMOND ELECTRODE; (B) A HIGH-RESOLUTION C 1s SPECTRA OF HYDROGEN TERMINATED Ni_HBDE; (C) HIGH-RESOLUTION Ni 2p SPECTRA OF Ni_HBDE; (D) SURVEY XPS SPECTRA OF OXIDISED DIAMOND ELECTRODE; (E) A HIGH-RESOLUTION C 1s SPECTRA OF OXIDISED Ni_OBDE; (F) HIGH-RESOLUTION Ni 2p SPECTRA OF Ni_OBDE	178
FIGURE 80 CYCLIC VOLTAMMOGRAMS RECORDED IN 1 M KOH AT 0.05 Vs ⁻¹ AT (A) (—) Ni_OBDE AND (— · —) Ni_HBDE STRAIGHT AFTER Ni ELECTRODEPOSITION PROCEDURE; (B) AFTER THE ENRICHMENT PROCESS IN 1 M KOH AT 0.05 Vs ⁻¹ AT (—) Ni_OBDE AND (— · —) Ni_HBDE	182
FIGURE 81 SURFACE CONCENTRATION OF Ni(OH) ₂ , COLUMN A: AT (●) Ni_OBDE AFTER Ni ELECTRODEPOSITION AND (■) AT Ni_HBDE AFTER Ni ELECTRODEPOSITION, COLUMN B: (●) Ni_OBDE AFTER THE ENRICHMENT PROCEDURE AND (■) Ni_HBDE AFTER THE ENRICHMENT PROCEDURE	184
FIGURE 82 HIGH RESOLUTION Ni 2p REGION OF THE Ni_HBDE ELECTRODE RECORDED AFTER THE ENRICHMENT PROCEDURE IN 1 M KOH	185
FIGURE 83 CYCLIC VOLTAMMOGRAMS OF 1 mM GLUCOSE ADDITIONS IN 1 M KOH SOLUTION RECORDED AT 0.05 Vs ⁻¹ AT (A) Ni_HBDE; (B) Ni_OBDE, (C) ASSOCIATED CALIBRATION PLOT OF CURRENT DENSITIES VS GLUCOSE CONCENTRATION AT Ni_HBDE; (D) ASSOCIATED CALIBRATION PLOT OF CURRENT DENSITIES VS GLUCOSE CONCENTRATION AT Ni_OBDE.....	186
FIGURE 84 AMPEROMETRIC PLOT OF 1 mM GLUCOSE ADDITIONS RECORDED IN 1 KOH AT (1) Ni_HBDE AND (2) Ni_OBDE	188
FIGURE 85 (A) CYCLIC VOLTAMMETRY RECORDED WITH 0.1 mM H ₂ O ₂ ADDITIONS IN 1 KOH AT Ni_HBDE; (B) CORRESPONDING CALIBRATION PLOT OF PEAK CURRENTS VS H ₂ O ₂ CONCENTRATION; (II) AMPEROMETRIC PLOT OF 0.1 mM H ₂ O ₂ ADDITIONS IN 1 KOH RECORDED AT (1) Ni_HBDE AND (2) Ni_OBDE	189
FIGURE 86 CHEMICAL STRUCTURE OF ZINC (II) PROTOPORPHYRIN IX	201
FIGURE 87 CHEMICAL STRUCTURES OF (A) N-(3-DIMETHYLAMINOPROPYL)-N'-ETHYLCARBODIIMIDE HYDROCHLORIDE (EDC); (B) N-HYDROXYSUCCINIMIDE (NHS)	204
FIGURE 88 XPS WIDE SCAN SPECTRA OF HYDROGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE; (I) ASSOCIATED HIGH-RESOLUTION C 1s REGION.....	206
FIGURE 89 CYCLIC VOLTAMMETOGRAMS OF 1 mM ETHYLENEDIAMINE DISSOLVED IN ANHYDROUS CH ₃ CN, CONTAINING 0.1 M NBu ₄ BF ₄ AT A SCAN RATE OF 0.05 Vs ⁻¹ RECORDED AT HYDROGEN TERMINATED BORON-DOPED DIAMOND	207
FIGURE 90 CYCLIC VOLTAMMOGRAMS OF 1 mM FERROCENEMETHANOL DISSOLVED IN ANHYDROUS CH ₃ CN/DMF, CONTAINING 0.1 M NBu ₄ BF ₄ AT A SCAN RATE OF 0.05 Vs ⁻¹ RECORDED AT (—) HYDROGEN TERMINATED BORON-DOPED DIAMOND PRIOR TO	

EDA GRAFTING ; (–) HBDE POST EDA GRAFTING, (– –) AFTER RINSING OF EDA MODIFIED HBDE WITH 5 ML CH ₃ CN AND 5 ML CH ₂ Cl ₂ SOLUTIONS	208
FIGURE 91 ETHYLENEDIAMINE OXIDATION AT HYDROGEN TERMINATED DIAMOND ELECTRODE	209
FIGURE 92 SURVEY XPS SPECTRA OF (A) EDA THIN FILM ADSORBED ONTO H-TERMINATED BDE; (B) SURFACE OF THE SAME SAMPLE AFTER CH ₂ Cl ₂ /DMF RINSING PROCEDURE	211
FIGURE 93 SURVEY XPS SCAN OF (A) EDA MODIFIED HBDE VIA ELECTROCHEMICAL GRAFTING; (B) SURFACE OF THE SAME SAMPLE AFTER THE WASHING PROCEDURE WITH CH ₂ Cl ₂ ;	212
FIGURE 94 (A) HIGH-RESOLUTION C 1s REGION OF EDA MODIFIED HBDE VIA ELECTROCHEMICAL GRAFTING AFTER THE WASHING PROCEDURE WITH CH ₂ Cl ₂ ; (B) HIGH-RESOLUTION N 1s REGION OF THE SAME SAMPLE; (C) HIGH-RESOLUTION O 1s REGION OF THE SAME SAMPLE	213
FIGURE 95 SCHEMATIC REPRESENTATION OF ZINC (II) PROTOPORPHYRIN IX GRAFTING TO THE EDA MODIFIED BORON-DOPED DIAMOND ELECTRODE VIA AMIDE EDC/NHS COUPLING REACTION.....	216
FIGURE 96 (A) A SURVEY SCAN OF ZNP-EDA MODIFIED HBDE VIA EDC/NHS COUPLING; (B) HIGH-RESOLUTION C 1s REGION OF THE SAME SAMPLE (C) CORRESPONDING HIGH-RESOLUTION N 1s REGION; (D) CORRESPONDING HIGH-RESOLUTION Zn 2p REGION	217
FIGURE 97 (A) A SURVEY SCAN OF ZNP-EDA MODIFIED HBDE VIA EDC/NHS COUPLING AFTER THE WASHING PROCEDURE; (B) HIGH-RESOLUTION C 1s REGION OF THE SAME SAMPLE (C) CORRESPONDING HIGH-RESOLUTION N 1s REGION; (D) CORRESPONDING HIGH-RESOLUTION Zn 2p REGION.....	219
FIGURE 98 (A) A SURVEY SCAN OF ZNP ADSORBED ONTO HBDE; (B) HIGH-RESOLUTION C 1s REGION OF THE SAME SAMPLE (C) HIGH-RESOLUTION N 1s REGION OF THE SAME SAMPLE; (D) HIGH-RESOLUTION Zn 2p REGION OF THE SAME SAMPLE	221
FIGURE 99 SURVEY XPS SPECTRUM OF ZNP ADSORBED ONTO HBDE SAMPLE AFTER THE ULTRASONICATION PROCEDURE IN CH ₂ Cl ₂	222
FIGURE 100 (A) A SURVEY SCAN OF ZNP ADSORBED ONTO THE EDA MODIFIED HBDE; (B) HIGH-RESOLUTION C 1s REGION OF THE SAME SAMPLE (C) HIGH-RESOLUTION N 1s REGION OF THE SAME SAMPLE; (D) HIGH-RESOLUTION Zn 2p REGION OF THE SAME SAMPLE; (E) A SURVEY SCAN OF ZNP ADSORBED ONTO EDA MODIFIED HBDE AFTER THE ULTRASONICATION PROCEDURE IN CH ₂ Cl ₂ /DMF.....	223
FIGURE 101 CV DATA RECORDED AT (–) ZNP COVALENTLY ATTACHED TO THE EDA MODIFIED HBDE IN CH ₃ CN/DMF SOLUTION (4:1 RATIO), CONTAINING 0.1 M NBU ₄ BF ₄ AT A SCAN RATE OF 0.05 V s ⁻¹ IN (A) A REDUCTION REGIME FROM 0 TO -2.5 V; (B) AN OXIDATION REGIME FROM 0 TO +2.5 V; (···) BACKGROUND SCAN	225

FIGURE 102 CV DATA RECORDED DURING THE FIRST SCAN AT (–) ZNP ADSORBED TO THE EDA MODIFIED HBDE IN CH ₃ CN/DMF SOLUTION (4:1 RATIO), CONTAINING 0.1 M NBU ₄ BF ₄ AT A SCAN RATE OF 0.05 VS ⁻¹ IN (A) A REDUCTION REGIME FROM 0 TO -2.5 V; (B) AN OXIDATION REGIME FROM 0 TO +2.5 V	227
FIGURE 103 CYCLIC VOLTAMMOGRAMS OF 0.1 mM FERROCENEMETHANOL DISSOLVED IN ANHYDROUS CH ₃ CN/DMF, CONTAINING 0.1 M NBU ₄ BF ₄ AT A SCAN RATE OF 0.05 VS ⁻¹ RECORDED AT (–) ZNP COVALENTLY ATTACHED TO THE EDA MODIFIED HBDE; (– –) ZNP ADSORBED ONTO THE EDA MODIFIED HBDE	228
FIGURE 104 NYQUIST IMPEDANCE PLOT (–Z''), IMAGINARY PART OF IMPEDANCE VS. Z', REAL PART OF IMPEDANCE) RECORDED FROM (A) ZNP COVALENTLY BINDED TO EDA/HBDE WITH THE INSET OF THE EQUIVALENT Randles Circuit where R _s IS THE SERIES RESISTANCE, CPE IS THE CONSTANT PHASE ELEMENT, R _{CT} IS THE CHARGE TRANSFER RESISTANCE AND W IS THE Warburg IMPEDANCE; (B) ZNP ABSORBED ON THE EDA/HBDE.....	230
FIGURE 105 CYCLIC VOLTAMMOGRAMS OF ZNP COVALENTLY ATTACHED TO THE EDA MODIFIED HBDE IN (–) ANHYDROUS CH ₃ CN/DMF, CONTAINING 0.1 M NBU ₄ BF ₄ AT A SCAN RATE OF 0.05 VS ⁻¹ ; (–) IN THE PRESENCE OF 200 μM OF ALANINE; (–) 400 μM OF ALANINE; (–) 600 μM OF ALANINE; (–) 800 μM OF ALANINE; INSET OF PEAK CURRENT VERSUS ALANINE CONCENTRATION.....	232
FIGURE 106 SCHEMATIC ILLUSTRATION OF POSSIBLE ALANINE BINDING MODE	233

List of Tables

TABLE 1 SOME BASIC PROPERTIES OF DIAMOND (TAKEN FROM ²)	1
TABLE 2 ELECTROCHEMICAL CHARACTERISATION OF PT DECORATED BORON-DOPED DIAMOND ELECTRODE	62
TABLE 3 THE NUMBER OF CARBON BONDS IN A DIAMOND FACE DEPENDING ON THE CRYSTALLOGRAPHIC ORIENTATION, ADAPTED FROM ³⁴	65
TABLE 4 XPS BINDING ENERGIES FOR PT_BDE, PT_PDE AND PT_RDE SAMPLES	72
TABLE 5 FWHM VALUES FOR PT_BDE, PT_PDE AND PT_RDE SAMPLES.....	72
TABLE 6 PT/C ATOMIC RATIOS OF THE DIAMOND NANOSTRUCTURED ELECTRODES BEFORE AND AFTER ATABILITY TESTS*	76
TABLE 7 XPS BINDING ENERGIES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	94
TABLE 8 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	94
TABLE 9 FWHM VALUES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	95
TABLE 10 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT OXYGEN TERMINATED BORON- DOPED DIAMOND ELECTRODE AT 0.05 V s ⁻¹	102
TABLE 11 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT HYDROGEN TERMINATED BORON- DOPED DIAMOND ELECTRODE AT 0.05 V s ⁻¹	102
TABLE 12 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT 0.05 V s ⁻¹ AT HYDROGEN TERMINATED BORON-DOPED DIAMOND POWDER MODIFIED ELECTRODE	108
TABLE 13 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT 0.05 V s ⁻¹ AT OXYGEN TERMINATED BORON-DOPED DIAMOND POWDER MODIFIED ELECTRODE	109
TABLE 14 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT 0.05 V s ⁻¹ AT OXYGEN TERMINATED DETONATION NANODIAMOND POWDER MODIFIED ELECTRODE	111
TABLE 15 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 MM MV, 0.1 M KCL AT 0.05 V s ⁻¹ AT HYDROGEN TERMINATED DETONATION NANODIAMOND POWDER MODIFIED ELECTRODE	111
TABLE 16 MV ⁰ ADSORPTION DATA AT HYDROGEN TERMINATED ELECTRODES	112
TABLE 17 XPS BINDING ENERGIES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	117
TABLE 18 FWHM VALUES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	117

TABLE 19 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	117
TABLE 20 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 mM 2,6-AQDS, 0.1 M HNO ₃ AT 0.05 V s ⁻¹ AT HYDROGEN TERMINATED DIAMOND ELECTRODES	120
TABLE 21 2,6-AQDS ADSORPTION DATA AT HYDROGEN AND OXYGEN TERMINATED ELECTRODES.....	120
TABLE 22 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 mM 2,6-AQDS, 0.1 M HNO ₃ AT 0.05 V s ⁻¹ AT OXYGEN TERMINATED DIAMOND ELECTRODES.....	124
TABLE 23 CHRONOCOULOMETRY DATA RECORDED AT HYDROGEN TERMINATED HBDP AND HDND ELECTRODES.....	125
TABLE 24 XPS BINDING ENERGIES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	126
TABLE 25 FWHM VALUES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	128
TABLE 26 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR HYDROGEN TERMINATED BORON-DOPED DIAMOND, BORON-DOPED DIAMOND POWDER AND DETONATION NANODIAMOND POWDER MODIFIED ELECTRODES.....	128
TABLE 27 XPS BINDING ENERGIES FOR THE BDE, BDP AND DND MODIFIED ELECTRODES	140
TABLE 28 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE BDE, BDP AND DND MODIFIED ELECTRODES	140
TABLE 29 FWHM VALUES FOR THE BDE, BDP AND DND MODIFIED ELECTRODES.....	142
TABLE 30 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 0.1 mM Fe(CN) ₆ ³⁻ , Ru(NH ₃) ₆ ³⁺ , IrCl ₆ ²⁻ AND FcCH ₂ OH SOLUTIONS AT BDP, DND MODIFIED ELECTRODES AND UNMODIFIED B-DOPED DIAMOND ELECTRODE AT A SCAN RATE OF 0.05 Vs ⁻¹	143
TABLE 31 I_p^{OX}/I_p^{RED} RATIO AND PEAK-TO-PEAK SEPARATION DATA ESTIMATED FOR 0.1 mM Fe(CN) ₆ ³⁻ , Ru(NH ₃) ₆ ³⁺ , IrCl ₆ ²⁻ AND FcCH ₂ OH REDOX COUPLES AT BDP, DND MODIFIED ELECTRODES AND UNMODIFIED BORON-DOPED DIAMOND ELECTRODE AT A SCAN RATE OF 0.05 Vs ⁻¹	144
TABLE 32 PERMEABILITIES OF 0.1 mM Fe(CN) ₆ ³⁻ , Ru(NH ₃) ₆ ³⁺ , IrCl ₆ ²⁻ AND FcCH ₂ OH REDOX PROBES THROUGH DND AND BDP MODIFIED ELECTRODES. THE DATA WERE RECORDED AT A SCAN RATE OF 0.05 Vs ⁻¹	146
TABLE 33 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 mM Fe(CN) ₆ ³⁻ , Ru(NH ₃) ₆ ³⁺ , IrCl ₆ ²⁻ AND FcCH ₂ OH REDOX PROBES AT BDP, DND MODIFIED ELECTRODES AND UNMODIFIED B-DOPED DIAMOND ELECTRODE AT A SCAN RATE OF 0.05 Vs ⁻¹	149

Surface Characterisation and Functional Properties of Modified Diamond Electrodes

TABLE 34 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 10 mM $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} AND FcCH_2OH REDOX PROBES AT BDP, DND MODIFIED ELECTRODES AND UNMODIFIED B-DOPED DIAMOND ELECTRODE AT A SCAN RATE OF 0.05 Vs^{-1}	149
TABLE 35 I_p^{OX}/I_p^{RED} RATIO AND PEAK-TO-PEAK SEPARATION DATA ESTIMATED FOR 1 mM AND 10 mM $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} AND FcCH_2OH REDOX PROBES AT BDP, DND MODIFIED ELECTRODES AND UNMODIFIED B-DOPED DIAMOND ELECTRODE AT A SCAN RATE OF 0.05 Vs^{-1}	149
TABLE 36 PERMEABILITIES OF $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} AND FcCH_2OH REDOX MEDIATORS IN THE CONCENTRATION RANGE OF 0.1, 1 AND 10 mM THROUGH DND AND BDP MODIFIED ELECTRODES. THE DATA WERE RECORDED AT A SCAN RATE OF 0.05 Vs^{-1}	150
TABLE 37 KINETIC PARAMETERS OF PLATINUM NUCLEATION ON BDE, DND AND BDP MODIFIED ELECTRODES	159
TABLE 38 ELECTROCHEMICAL CHARACTERISATION OF PLANE BDE, DND AND BDP MODIFIED ELECTRODES AT A PLATINUM LOADING OF 5.05×10^{-5} g	160
TABLE 39 Pt/C ATOMIC RATIOS OF THE DIAMOND ELECTRODES DECORATED WITH Pt PARTICLES AT -0.1 V BEFORE AND AFTER STABILITY TESTS	162
TABLE 40 NICKEL MODIFIED BORON-DOPED DIAMOND ELECTRODE AND THEIR ELECTROANALYTICAL APPLICATIONS	170
TABLE 41 XPS BINDING ENERGIES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	179
TABLE 42 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	179
TABLE 43 FWHM VALUES FOR HYDROGENATED AND OXIDISED BORON-DOPED DIAMOND ELECTRODES	179
TABLE 44 Ni 2p/C 1s RATIOS ESTIMATED FOR THE Ni_HBDE AND Ni_OBDE SAMPLES	180
TABLE 45 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 M KOH AT Ni MODIFIED O- AND H- TERMINATED BORON-DOPED DIAMOND ELECTRODES AT 0.05 V s^{-1}	181
TABLE 46 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN 1 M KOH AFTER THE ENRICHMENT PROCEDURE AT Ni MODIFIED O- AND H- TERMINATED BORON-DOPED DIAMOND ELECTRODES AT 0.05 V s^{-1}	183
TABLE 47 Ni 2p/C 1s OBTAINED PRIOR AND AFTER STABILITY TESTS IN 1 M KOH	190
TABLE 48 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED AT HYDROGEN TERMINATED BORON-DOPED DIAMOND ELECTRODE IN 1 mM ETHYLENEDIAMINE DISSOLVED IN ANHYDROUS CH_3CN , CONTAINING 0.1 M NBU_4BF_4 AT A SCAN RATE OF 0.05 Vs^{-1}	207

TABLE 49 XPS BINDING ENERGIES AND FWHM FOR THE EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED DIAMOND

ELECTRODE	213
-----------------	-----

TABLE 50 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED

DIAMOND ELECTRODE	213
-------------------------	-----

TABLE 51 XPS BINDING ENERGIES AND FWHM FOR THE ZNP-EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED DIAMOND

ELECTRODE	218
-----------------	-----

TABLE 52 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE ZNP-EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED

DIAMOND ELECTRODE	218
-------------------------	-----

TABLE 53 XPS BINDING ENERGIES AND FWHM FOR THE ZNP-EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED DIAMOND

ELECTRODE AFTER THE RINSING PROCEDURE VIA ULTRASONICATION IN $\text{CH}_2\text{Cl}_2/\text{DMF}$	220
--	-----

TABLE 54 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE ZNP-EDA MODIFIED HYDROGEN TERMINATED BORON-DOPED

DIAMOND ELECTRODE AFTER THE RINSING PROCEDURE VIA ULTRASONICATION IN $\text{CH}_2\text{Cl}_2/\text{DMF}$	220
--	-----

TABLE 55 XPS BINDING ENERGIES AND FWHM FOR THE ZNP ADSORBED ON THE HYDROGEN TERMINATED BORON-DOPED DIAMOND

ELECTRODE	222
-----------------	-----

TABLE 56 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE ZNP ADSORBED ON THE HYDROGEN TERMINATED BORON-DOPED

DIAMOND ELECTRODE	222
-------------------------	-----

TABLE 57 XPS BINDING ENERGIES AND FWHM FOR THE ZNP ADSORBED ON THE EDA MODIFIED HBDE

TABLE 58 XPS ELEMENTAL RATIOS AND CHARGING VALUES FOR THE ZNP ADSORBED ON THE EDA MODIFIED HBDE

TABLE 59 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED IN $\text{CH}_3\text{CN}/\text{DMF}$ SOLUTION (4:1 RATIO), CONTAINING 0.1 M

NBU_4BF_4 AT ZNP COVALENTLY ATTACHED TO THE EDA MODIFIED HBDE DURING THE FIRST SCAN AT THE SCAN RATE OF

0.05 V s^{-1}	225
------------------------------	-----

TABLE 60 HETEROGENEOUS ELECTRON TRANSFER CONSTANTS DERIVED FROM IMPEDANCE SPECTROSCOPY AND NICHOLSON MODEL

.....	230
-------	-----

TABLE 61 PEAK POSITION AND CURRENT RESPONSE DATA RECORDED AT HYDROGEN TERMINATED BORON-DOPED DIAMOND

ELECTRODE IN 0.1 mM ETHYLENEDIAMINE DISSOLVED IN ANHYDROUS CH_3CN , CONTAINING 0.1 M NBU_4BF_4 AT A SCAN RATE

OF 0.05 V s^{-1}	232
---------------------------------	-----

List of Abbreviations

AC		Alternating current
AFM		Atomic force microscopy
2,6-AQDS		Anthraquinone-2,6-disulfonate
BEI		Backscattered electron imaging
BDE		Boron-doped diamond electrode
BDP		Boron-doped diamond powder
B.E.		Binding energy
CV		Cyclic voltammetry
CVD		Chemical vapour deposition
CPS		Counts per second
DMF		Dimethylformamide
DMFC		Direct methanol fuel cell
DND		Detonation nanodiamond
EAA		Electrochemical active area
EDA		Ethylenediamine
EDC		N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride
EIS		Electrochemical impedance spectroscopy
ESCA		Electron Spectroscopy for Chemical Analysis
FAT		Fixed analyser transmission
FWHM		Full width at half maximum
fcc		Face centred cubic
GC		Glassy carbon
HOPG		Highly ordered pyrolytic graphite
IMFP		Inelastic mean free path
IR		Infrared
LOD		Limit of detection
MV		Methyl viologen
NHS		N-hydroxysuccinimide
NMR		Nuclear magnetic resonance
NPs		Nanoparticles
OHP		Outer Helmholtz plane
PBS		Phosphate buffered saline
PTFE		Poly(tetrafluoroethylene)
RDE		Rotating disc electrode
R²		Coefficient of determination
SEM		Scanning electron microscopy
SEI		Secondary electron imaging
UHV		Ultra-high vacuum
THF		Tetrahydrofuran
UV-Vis		Ultraviolet-visible
V		Volt
XPS		X-ray photoelectron spectroscopy
XRD		X-ray diffraction
ZnP		Zinc (II) protoporphyrin IX

1 Chapter One – Introduction

1.1 Synthetic Diamond

With the development of Chemical Vapour Deposition (CVD) techniques, the possibility of growing synthetic diamond in the form of thin films under controlled conditions has stimulated intensive research in many areas in order to exploit the excellent properties of this material in a wide range of different applications.¹

Until recently, diamond has been mainly utilized in mechanical drilling, cutting and abrasion areas, where the hardness of the material is of a great advantage. Some of diamond's useful and unique properties can be found in Table 1.

Table 1 Some basic properties of diamond (taken from²)

Properties	Value
Extremely high hardness (Vickers)	Ca. 10000 kp m ⁻²
High thermal conductivity	20 W cm ⁻¹ K ⁻¹ at 300K
Optical transparency (undoped)	λ =2.5 μ m to 230 nm
Large electronic bandgap (undoped)	E_{GAP} =5.5 eV
Young's modulus	1.22 GPa
Density	3.52 g cm ⁻³
Refractive index	2.42 at 546 nm
Melting point	4027 K
Chemically inert surface	Up to 850 K in air Up to 2000 K in vacuum

Among them, the most notable are the high hardness and the excellent thermal conductivity near room temperature. Diamond is highly resistant to abrasion and is extremely rigid, with a Young modulus of 1.22 GPa. Diamond is also transparent to visible and infrared radiation and has a very high refractive index. Moreover, due to advances in chemical vapour deposition (CVD) techniques, diamond can be controllably doped with boron, which results in electrical conductivity characteristic of semiconducting or metallic-like states. The latter is achieved with a boron concentration of typically 10²¹ cm⁻³ or about one boron atom per 1000 carbon atoms.² Since boron-doped diamond surpasses many conventional materials in

mechanical, physical, biological and chemical fields due to its various excellent properties, it has now been established as an electrode with superior performance in many electrochemical applications.

In Figure 1, the annual number of articles concerning diamond electrochemistry is compared to that of a well-established analogue - glassy carbon. Before the mid-1990s, diamond electrode was found to be utilized mainly for a scientific curiosity. However, from 1995, the growth of the interest in diamond electrochemistry is illustrated by a rapid increase in the number of scientific publications. After this point, the diamond activity can be referred to as electrochemistry field of its own, establishing various practical and commercial applications in the area.

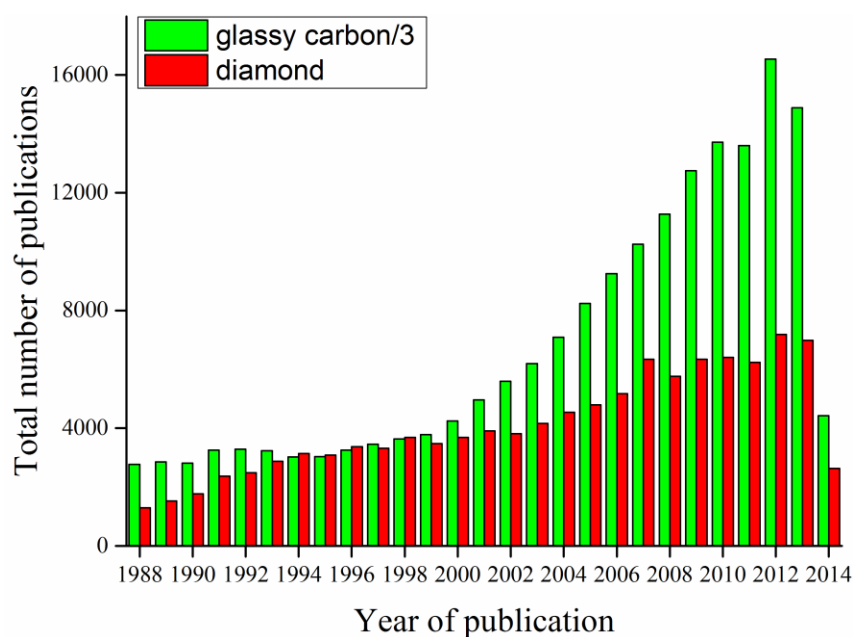


Figure 1 Historical data for the period 1988-2014, illustrating the annual number of scientific publications regarding diamond electrochemistry in comparison to similar data for glassy carbon. The data for glassy carbon were divided by a factor of 3.

1.2 Synthetic Diamond in Electrochemistry

During electrochemical measurement, the electrode should provide a measurable and reproducible response to a particular reaction in a certain potential range. In addition, such a response should not be masked by competing electrochemical reactions or background signals arising from undesirable capacitance in the circuit. The choice of the electrode material is of the utmost importance in electrochemical procedures as it contributes to the reaction of interest.

Depending on the application, the electrodes can vary significantly. They can be metallic and semiconducting, in a solid or liquid state. For example, bulk electrochemical processes employ electrodes which can reach several square metres in area, and which are expected to work for many months, whereas others such as electrochemical biosensor can be less than a square centimetre in area and may be discarded after a single measurement.³

It is evident that the optimal choice of an electrode for a particular application depends on the diverse properties of the material. If the electrode is to be used in hostile environments, the robustness, strength and resistance to corrosion are therefore the most important properties to look for. For example, in many electrochemical measurements an electrode can be poisoned by adsorption of electrically insulating compounds on its surface, which may result in the overall system failure. Thus, an inherent resistance to the electrode fouling is a necessary requirement.⁴

In this context, there are several advantages to boron-doped diamond electrodes as compared to other conventional electrode materials such as glassy carbon and graphitic electrodes that are often employed in many electrochemical applications, where rapid, sensitive, reproducible and easily measurable signal response is the primary requirement.⁴⁻⁶ Firstly, boron-doped diamond electrodes exhibit a relatively low signal-to-background current ratio

due to their smaller double layer capacitance relative to other materials ($\sim 10 \mu\text{F cm}^{-2}$) and a lower density of ionisable and redox active groups on the surface. The minimal presence of these groups on the diamond surface normally results in a significant decrease in the electrochemical data of undesirable distinct background peaks as well as pseudo-capacitive background. Secondly, the chemically inert nature of the diamond surface provides a wide potential window with the width of 3-4 V in aqueous and 5-7.5 V in non-aqueous media.⁷ In aqueous solutions, the potential window is generally defined as a potential range between the onset of hydrogen evolution (rise of current at negative potentials) and oxygen evolution (rise of current at positive potentials) reactions. For example, Figure 2 shows cyclic voltammograms obtained during water electrolysis in 0.5 M H_2SO_4 solution, where in comparison to other conventional electrodes, the electrochemical potential window of diamond electrode is found to be the biggest and the background current - the smallest. It is also interesting to note that the change in the boron doping level makes it possible to control the range of the potential window of the electrode.

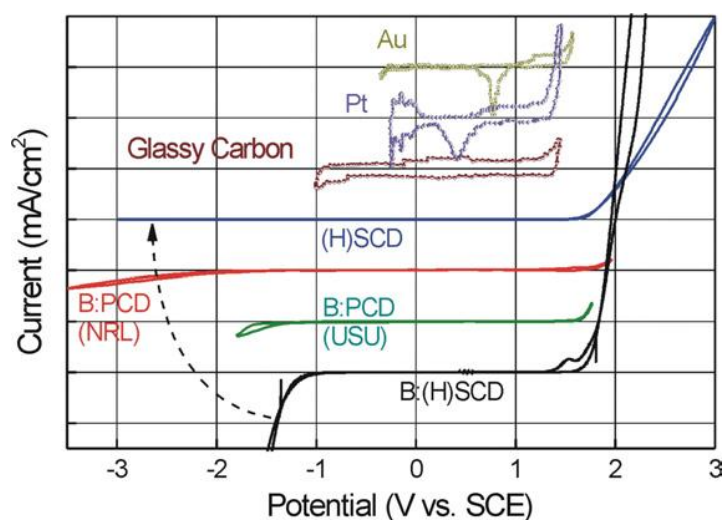


Figure 2 Cyclic voltammograms of water electrolysis in 0.5 M H_2SO_4 at two boron-doped polycrystalline films. B: PCD(NRL) with $5 \times 10^{19} [\text{B}] \cdot \text{cm}^{-3}$ and B: PCD(USU) with $5 \times 10^{20} [\text{B}] \cdot \text{cm}^{-3}$ are compared to a single crystal boron-doped diamond B: (H)SCD with $3 \times 10^{20} [\text{B}] \cdot \text{cm}^{-3}$ and with an undoped diamond (H)SCD. Data for Pt, Au and glassy carbon are also presented. The plots were shifted vertically for the comparison. Reproduced from⁸

Due to the exceptional microstructural stability of the diamond material at high temperatures and high current densities, the latter is also of a great interest in the development of important electroanalytical applications, such as sonoelectroanalysis, where the application of ultrasound in electrochemical system results in the development of cavitation processes, which enhance mass transport to the electrode surface, therefore improving sensitivity and preventing electrode from undesirable adsorption.²

Electrode fouling is a common problem in electrochemistry. The decreased amount of surface groups on the diamond interface results in the weak adsorption of the analyte in many cases and leads to improved resistance to fouling. Another striking characteristic of diamond electrode is the high degree of the reproducibility of electrochemical response that it provides due to the decreased amount of the surface groups. Finally, the long-term responsiveness, robustness along with the optical transparency of diamond in the UV-Vis and IR regions of the electromagnetic spectrum as mentioned above, makes it attractive for spectroelectrochemical applications.

Although natural diamond is an electrical insulator with a bandgap of 5.5 eV at 300 K, its boron-doped form is electrically conductive.² Boron-doping became most prevalent due to chemical vapour deposition (CVD) growth techniques, where boron incorporation was accomplished by the addition of gaseous boron compounds, such as diborane or trimethylborane, to the growth chemistry. It is noteworthy that other types of dopants such as phosphorus⁹, nitrogen¹⁰, hydrogen¹¹ or sulphur¹² have been explored; however, most of the work in diamond electrochemistry is focussed on the boron-doped type materials.

Although boron forms an acceptor level approximately 0.35 eV above the valence band when present at low concentrations ($\sim 10^{17} \text{ cm}^{-3}$), superior conductivity and electrochemical properties are achieved with boron concentrations of 10^{19} - 10^{21} cm^{-3} and carrier mobility of

0.2-0.5 cm² V⁻¹ s⁻¹. When the boron concentration increases, boron centres interact and broaden into an impurity band that moves towards the valence band and thus mediates conduction.

The choice of diamond particularly for electrochemical applications depends on a broad range of factors, including commercial availability, material cost, selection of the appropriate phase purity, microstructure of crystallites comprising the film and electrical and surface conductivity of the material along with its surface chemistry. For the purpose of clarity, the diamond material available can be classified by the grain size - microcrystalline, nanocrystalline and ultrananocrystalline diamond films - and by the crystalline orientation: polycrystalline and monocrystalline films. The following section summarises several important structural properties of diamond materials used in this work and their influence on electrochemistry.

1.2.1 Microcrystalline boron-doped diamond

The majority of research in diamond electrochemistry has been performed on microcrystalline boron-doped diamond (MCD). It is available in the form of large area wafers and as-grown films on large area substrates, with a crystal size of different crystallographic orientation varied in the range of 5 to 50 µm. A typical electron micrograph of MCD is presented in Figure 3. The electrochemical properties of such diamond are mainly influenced by the phase purity, boron concentration and its distribution. These characteristics can be effectively controlled by the choice of the growth conditions, in which low methane-hydrogen ratios in the reactor feedstock results in phase-pure materials with large grain sizes, whilst a higher methane concentration leads to the opposite effect. Boron-doped MCD with relatively low sp² content has found widespread use in electroanalysis, electrosensing, electrosynthesis of organic and inorganic compounds as well as waste water treatment.^{13,14-17}

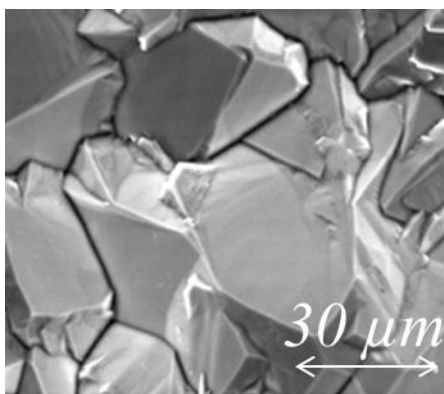


Figure 3 SEM of microcrystalline boron-doped diamond electrode

1.2.2 Nanodiamond powders

The immobilisation of diamond fine powders in the form of porous layers on the diamond electrode is known to result in improved detection of target compounds.¹⁸ In addition, by varying both hydrophobicity and hydrophilicity of the porous layer, adsorption on the electrode surface can be significantly decreased; therefore prolonging the operational life-time of the material.¹⁹

Diamond electrodes are known to be the least susceptible to fouling compared to any other conventional carbon electrode. The wide potential window of boron-doped diamond allows the minimisation of undesirable masking effects that arise from oxygen or hydrogen evolution reactions. However, as previously mentioned, some chemically complicated reactions have imposed the requirement of improved diamond sensitivity. Thus, the ‘porous layer’ approach seems to be especially appealing for the advancement of diamond sensitivity, which can be achieved by creating chemically selective permeable coatings of a high surface area, as schematically presented in Figure 4.

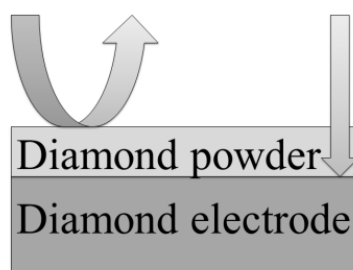


Figure 4 Schematic illustration of diamond powder porous layer on the top of diamond electrode

Two particular modifiers: finely divided diamond powders, namely detonation nanodiamond powder and boron-doped nanocrystalline diamond powder, can be employed in this ‘porous layer’ modification strategy in order to provide enhanced surface area, unique surface chemistry and improved selectivity. These diamond powders differ fundamentally with regard to conductivity.

Detonation nanodiamond (DND) is a carbon based nanomaterial. It is formed, as the name suggests, by the detonation of carbon containing explosive mixtures; where the application of high temperature and high pressure shock waves thereby results in the formation of small quantities of diamond particulates, approximately of 5-10 nm in diameter. The material recently became freely available at low cost and large quantity, mainly from China and Russia. Nanodiamond particles consist of an sp^3 diamond core surrounded by an amorphous shell with a highly functionalised surface.²⁰

Surface chemistry of DND particles strongly depends on production and purification procedure. Commercially obtained DNDs are normally found in a highly oxidized form, containing hydroxyl, carbonyl, carboxyl and lactone surface groups.²¹ Existence of these hydrophilic groups and sp^2 carbon residues result in the strong agglomeration of 100-

1000 nm particles, which are possible to break apart only partially by power ultrasound techniques or ball milling.²²

Recently metallically B-doped diamond nanopowders (BDP) consisting of 100-500 nm nanoparticles have been produced.²³ The material can be fabricated by either milling of boron-doped diamond films²⁴ or by the CVD growth of the conductive layer over the DND surface.²⁵ Initial studies in this work have shown that the two physical forms of BDP and DND are quite different. The latter, as expected, consists of uniformly aggregated nanoparticles, as newly milled boron-doped diamond powder displays a very broad size distribution as shown in Figure 5. By carrying out centrifugation, uniform boron-doped diamond film, with a particle size of approximately 100 nm can be produced.

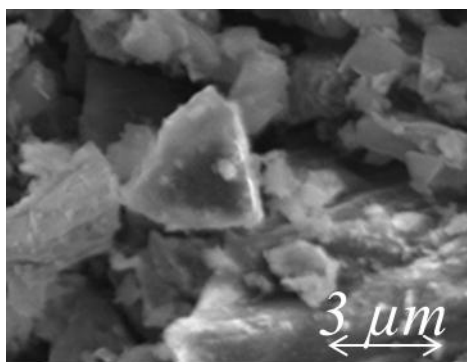


Figure 5 SEM of as-milled boron-doped diamond powder

1.3 Applications of diamond electrodes

In recent years, boron-doped diamond electrodes have been widely employed in a number of distinct electrochemical areas such as electroanalysis,²⁶⁻³⁰ electrosynthesis,^{17,31} electrocatalysis,³²⁻³⁵ energy harvesting^{36,37} and water purification.³⁸⁻⁴⁰ At the moment, the term ‘electrochemistry at boron-doped diamond electrodes’ accounts for more than 2550 publications in SciFinder database.⁴¹ This encompasses the use of diamond in differing

forms, including ultrananocrystalline diamond,⁴² nanocrystalline diamond,⁴³ microcrystalline diamond,⁴⁴ nanowhiskers,⁴⁵ single crystal diamond,⁴⁶ diamond powders⁴⁷ and microfiber arrays.⁴⁸ All of them can be effectively modified by various approaches, including plasma treatment, chemical and electrochemical reactions along with deposition of various materials such as metals and metal oxides.⁴⁹⁻⁵¹

At the moment, a number of excellent reviews discussing the electroanalytical and electrocatalytic aspects of boron-doped diamond electrodes are available. For example, a 2003 review by Marken *et al* gives an in-depth summary on the types of diamond electrodes, their properties and applications in electroanalysis.² The work by Luong *et al* reviews the synthesis, electrochemical properties as well as surface modification procedures developed for diamond electrodes.⁵² More recent reviews by Krueger *et al* and Holt *et al* discuss the modification strategies of detonation nanodiamond powders, their properties and applications.^{53,54} An interesting review on the modification of boron-doped diamond with metal nanoparticles by K. Toghill *et al* is also available for the reader.⁵⁵

1.4 Aims and Scope of this thesis

In the literature discussed above, boron-doped diamond electrodes have shown better electrochemical performance as compared to their conventional analogues. With the growing demand for diamond materials in biochemical and electrochemical fields, this thesis aims to extend and improve electrochemical applications of modified diamond electrodes. During this work, several new structuring and modification strategies of the diamond interfaces were developed, and the relationship between the surface chemistry of the diamond electrode and the electrochemical processes was investigated in detail.

In *Chapter 3*, the nanostructuring technique of diamond with platinum nanoparticles *via* etching in oxygen and hydrogen plasmas was developed. Two types of diamond

nanostructures were produced: the first one consists of platinum particles located on the top of diamond nanorods, the second one has platinum particles in diamond nanopits. The experimental evidence was suggested to prove the mechanism of the diamond nanostructuring. The electrochemical activity of the nanostructured diamond electrodes with regard to the electrochemical oxidation of glucose and methanol was demonstrated.

Chapter 4 investigates the electrochemical behaviour of differing forms of diamond, including microcrystalline boron-doped diamond, boron-doped diamond powder as well as detonation nanodiamond powder with regard to their fouling as a result of the adsorption processes in methyl viologen and anthraquinonedisulfonate solutions. In this work, two types of electrode pre-treatments were employed to produce two dissimilar surface terminations: hydrophobic H-terminated and hydrophilic O-terminated. The relationship between the diamond surface chemistry and the electrode fouling was studied in detail.

Chapter 5 further extends the discussion on the electrochemical behaviour of detonation nanodiamond and boron-doped diamond powders. In particular, charge transport within the diamond powder films, partition coefficients of redox mediators along with heterogeneous electron transfer constants were studied in this chapter. These powder films were further modified with platinum nanoparticles. The kinetics of the nucleation and growth mechanism of platinum nanoparticles were analysed with regard to the nature of the diamond material. The immobilisation of diamond powders has enhanced the electrode performance in methanol electrooxidation reaction by providing uniform morphology, homogeneous catalyst dispersion and improved stability of platinum nanoparticles.

Chapter 6 describes the preparation of nickel modified boron-doped diamond electrodes and investigates the relationship between the surface chemistry of the diamond electrode and the

associated electrocatalytic performance of nickel nanoparticles in glucose and methanol electrooxidation.

Chapter 7 reports on the preparation of hybrid biomimetic diamond interfaces, in particular, on the development of the artificial β -alanine receptor from the zinc protoporphyrin covalently attached to the diamond electrode

1.5 References

- 1 Ristein, J. Diamond surfaces: familiar and amazing. *Appl. Phys. A* **82**, 377-384, doi:10.1007/s00339-005-3363-5 (2006).
- 2 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).
- 3 *Bioinorganic Electrochemistry*. (Springer, 2008).
- 4 Compton, R. G. & Banks, C. E. *Understanding Voltammetry*. (Imperial College Press, 2011).
- 5 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley & Sons, 2001).
- 6 Wang, J. *Analytical Electrochemistry*. (John Wiley & Sons, 2000).
- 7 Yoshimura, M. *et al.* Factors controlling the electrochemical potential window for diamond electrodes in non-aqueous electrolytes. *Diamond and Related Materials* **11**, 67-74, doi:10.1016/s0925-9635(01)00522-2 (2002).
- 8 Nebel, C. E., Rezek, B., Shin, D., Uetsuka, H. & Yang, N. Diamond for bio-sensor applications. *Journal of Physics D-Applied Physics* **40**, 6443-6466, doi:10.1088/0022-3727/40/20/s21 (2007).
- 9 Koizumi, S., Kamo, M., Sato, Y., Ozaki, H. & Inuzuka, T. Growth and characterization of phosphorous doped {111} homoepitaxial diamond thin films. *Applied Physics Letters* **71**, 1065-1067, doi:10.1063/1.119729 (1997).
- 10 Jiang, N. & Ito, T. Electrical properties of surface conductive layers of homoepitaxial diamond films. *Journal of Applied Physics* **85**, 8267-8273, doi:10.1063/1.370668 (1999).
- 11 Gaudin, O., Whitfield, M. D., Foord, J. S. & Jackman, R. B. Deep level transient spectroscopy of CVD diamond: the observation of defect states in hydrogenated films. *Diamond and Related Materials* **10**, 610-614, doi:10.1016/s0925-9635(00)00418-0 (2001).
- 12 Sakaguchi, I. *et al.* Sulfur: A donor dopant for n-type diamond semiconductors. *Physical Review B* **60**, R2139-R2141, doi:10.1103/PhysRevB.60.R2139 (1999).
- 13 Hupert, M. *et al.* Conductive diamond thin-films in electrochemistry. *Diamond and Related Materials* **12**, 1940-1949, doi:10.1016/s0925-9635(03)00260-7 (2003).
- 14 Rodrigo, M. A. *et al.* Oxidation of 4-chlorophenol at boron-doped diamond electrode for wastewater treatment. *Journal of the Electrochemical Society* **148**, D60-D64, doi:10.1149/1.1362545 (2001).
- 15 Saez, C., Rodrigo, M. A. & Canizares, P. Electrosynthesis of ferrates with diamond anodes. *Aiche Journal* **54**, 1600-1607, doi:10.1002/aic.11492 (2008).

- 16 Wadhawan, J. D. *et al.* Emulsion electrosynthesis in the presence of power ultrasound Biphasic Kolbe coupling processes at platinum and boron-doped diamond electrodes. *Journal of Electroanalytical Chemistry* **507**, 135-143, doi:10.1016/s0022-0728(01)00372-2 (2001).
- 17 Griesbach, U., Zollinger, D., Putter, H. & Comninellis, C. Evaluation of boron doped diamond electrodes for organic electrosynthesis on a preparative scale. *J Appl Electrochem* **35**, 1265-1270, doi:10.1007/s10800-005-9038-2 (2005).
- 18 Henstridge, M. C., Dickinson, E. J. F., Aslanoglu, M., Batchelor-McAuley, C. & Compton, R. G. Voltammetric selectivity conferred by the modification of electrodes using conductive porous layers or films: The oxidation of dopamine on glassy carbon electrodes modified with multiwalled carbon nanotubes. *Sensors and Actuators B-Chemical* **145**, 417-427, doi:10.1016/j.snb.2009.12.046 (2010).
- 19 Xiao, L., Wildgoose, G. G. & Compton, R. G. Investigating the voltammetric reduction of methylviologen at gold and carbon based electrode materials. Evidence for a surface bound adsorption mechanism leading to electrode 'protection' using multi-walled carbon nanotubes. *New Journal of Chemistry* **32**, 1628-1633, doi:10.1039/b804842h (2008).
- 20 Mochalin, V. N., Shenderova, O., Ho, D. & Gogotsi, Y. The properties and applications of nanodiamonds. *Nature Nanotechnology* **7**, 11-23, doi:10.1038/nnano.2011.209 (2012).
- 21 Schrand, A. M., Hens, S. A. C. & Shenderova, O. A. Nanodiamond Particles: Properties and Perspectives for Bioapplications. *Critical Reviews in Solid State and Materials Sciences* **34**, 18-74, doi:10.1080/10408430902831987 (2009).
- 22 Krueger, A. *et al.* Deagglomeration and functionalisation of detonation diamond. *Physica Status Solidi a-Applications and Materials Science* **204**, 2881-2887, doi:10.1002/pssa.200776330 (2007).
- 23 Fischer, A. E. & Swain, G. M. Preparation and characterization of boron-doped diamond powder - A possible dimensionally stable electrocatalyst support material. *Journal of the Electrochemical Society* **152**, B369-B375, doi:10.1149/1.1984367 (2005).
- 24 Salazar-Banda, G. R., Eguiluz, K. I. B. & Avaca, L. A. Boron-doped diamond powder as catalyst support for fuel cell applications. *Electrochemistry Communications* **9**, 59-64, doi:10.1016/j.elecom.2006.08.038 (2007).
- 25 Ay, A., Swope, V. M. & Swain, G. M. The physicochemical and electrochemical properties of 100 and 500 nm diameter diamond powders coated with boron-doped nanocrystalline diamond. *Journal of the Electrochemical Society* **155**, B1013-B1022, doi:10.1149/1.2958308 (2008).
- 26 Tenne, R., Patel, K., Hashimoto, K. & Fujishima, A. Efficient electrochemical reduction of nitrate to ammonia using conductive diamond film electrodes. *Journal of Electroanalytical Chemistry* **347**, 409-415, doi:http://dx.doi.org/10.1016/0022-0728(93)80105-Q (1993).
- 27 Stradiotto, N. R., Toghil, K. E., Xiao, L., Moshar, A. & Compton, R. G. The fabrication and characterization of a nickel nanoparticle modified boron-doped diamond electrode for electrocatalysis of primary alcohol oxidation. *Electroanalysis* **21**, 2627-2633, doi:10.1002/elan.200900325 (2009).
- 28 Toghil, K. E., Wildgoose, G. G., Moshar, A., Mulcahy, C. & Compton, R. G. The Fabrication and Characterization of a Bismuth Nanoparticle Modified Boron Doped Diamond Electrode and Its Application to the Simultaneous Determination of Cadmium(II) And Lead(II). *Electroanalysis* **20**, 1731-1737, doi:10.1002/elan.200804277 (2008).

- 29 Dejmekova, H., Scampicchio, M., Zima, J., Barek, J. & Mannino, S. Determination of Total Phenols in Foods by Boron Doped Diamond Electrode. *Electroanalysis* **21**, 1014-1018, doi:10.1002/elan.200804508 (2009).
- 30 Ivandini, T. A., Sato, R., Makide, Y., Fujishima, A. & Einaga, Y. Electroanalytical application of modified diamond electrodes. *Diamond and Related Materials* **13**, 2003-2008, doi:http://dx.doi.org/10.1016/j.diamond.2004.07.004 (2004).
- 31 Fardel, R., Griesbach, U., Pütter, H. & Comninellis, C. Electrosynthesis of trimethylorthoformate on BDD electrodes. *J Appl Electrochem* **36**, 249-253, doi:10.1007/s10800-005-9057-z (2006).
- 32 Harfield, J. C., Toghill, K. E., Batchelor-McAuley, C., Downing, C. & Compton, R. G. Nickel Nanoparticle Modified BDD Electrode Shows an Electrocatalytic Response to Adenine and DNA in Aqueous Alkaline Media. *Electroanalysis* **23**, 931-938, doi:10.1002/elan.201000658 (2011).
- 33 Bian, L. Y., Wang, Y. H., Zang, J. B., Yu, J. K. & Huang, H. Electrodeposition of Pt nanoparticles on undoped nanodiamond powder for methanol oxidation electrocatalysts. *Journal of Electroanalytical Chemistry* **644**, 85-88, doi:10.1016/j.jelechem.2010.04.001.
- 34 Hu, J. P., Lu, X., Foord, J. S. & Wang, Q. Electrochemical deposition of Pt nanoparticles on diamond substrates. *Physica Status Solidi a-Applications and Materials Science* **206**, 2057-2062, doi:10.1002/pssa.200982226 (2009).
- 35 La-Torre-Riveros, L. *et al.* Diamond Nanoparticles as a Support for Pt and PtRu Catalysts for Direct Methanol Fuel Cells. *ACS Appl. Mater. Interfaces* **4**, 1134-1147, doi:10.1021/am2018628 (2012).
- 36 Christy, A. Y. M. T. *et al.* Lithium insertion studies on boron-doped diamond as a possible anode material for lithium batteries. *Ionics* **14**, 157-161, doi:10.1007/s11581-007-0164-1 (2008).
- 37 Ferreira, N. G., Mendonça, L. L., Airoidi, V. J. T. & Rosolen, J. M. Electrochemical intercalation of lithium into boron-doped CVD diamond electrodes grown on carbon fiber cloths. *Diamond and Related Materials* **12**, 596-600, doi:http://dx.doi.org/10.1016/S0925-9635(02)00273-X (2003).
- 38 Zhu, X., Ni, J. & Lai, P. Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes. *Water Research* **43**, 4347-4355, doi:http://dx.doi.org/10.1016/j.watres.2009.06.030 (2009).
- 39 Schmalz, V., Dittmar, T., Haaken, D. & Worch, E. Electrochemical disinfection of biologically treated wastewater from small treatment systems by using boron-doped diamond (BDD) electrodes – Contribution for direct reuse of domestic wastewater. *Water Research* **43**, 5260-5266, doi:http://dx.doi.org/10.1016/j.watres.2009.08.036 (2009).
- 40 Scialdone, O., Randazzo, S., Galia, A. & Silvestri, G. Electrochemical oxidation of organics in water: Role of operative parameters in the absence and in the presence of NaCl. *Water Research* **43**, 2260-2272, doi:http://dx.doi.org/10.1016/j.watres.2009.02.014 (2009).
- 41 SciFinder. (American Chemical Society, 2014).
- 42 Gruen, D. M. Ultrananocrystalline diamond in the laboratory and the cosmos. *Mrs Bulletin* **26**, 771-776 (2001).
- 43 Gruen, D. M. Nanocrystalline diamond films. *Annual Review of Materials Science* **29**, 211-259, doi:10.1146/annurev.matsci.29.1.211 (1999).
- 44 Butler, J. E. & Sumant, A. V. The CVD of nanodiamond materials. *Chemical Vapor Deposition* **14**, 145-160, doi:10.1002/cvde.200700037 (2008).

- 45 Baik, E. S., Baik, Y. J. & Jeon, D. Aligned diamond nanowhiskers. *Journal of Materials Research* **15**, 923-926, doi:10.1557/jmr.2000.0131 (2000).
- 46 Martin, H. B., Argoitia, A., Angus, J. C. & Landau, U. Voltammetry Studies of Single - Crystal and Polycrystalline Diamond Electrodes. *Journal of The Electrochemical Society* **146**, 2959-2964, doi:10.1149/1.1392035 (1999).
- 47 Holt, K. B. Undoped diamond nanoparticles: origins of surface redox chemistry. *Physical Chemistry Chemical Physics* **12**, 2048-2058, doi:10.1039/b920075d (2010).
- 48 Nebel, C. E. *et al.* Diamond nano-wires, a new approach towards next generation electrochemical gene sensor platforms. *Diamond and Related Materials* **18**, 910-917, doi:http://dx.doi.org/10.1016/j.diamond.2008.11.024 (2009).
- 49 Hoffmann, R. *et al.* Electrochemical hydrogen termination of boron-doped diamond. *Applied Physics Letters* **97**, doi:10.1063/1.3476346 (2010).
- 50 Bennett, J. A. & Swain, G. M. Investigating the Nucleation and Growth of Electrodeposited Pt on Polycrystalline Diamond Electrodes. *J. Electrochem. Soc.* **157**, F89-F95, doi:10.1149/1.3430501 (2010).
- 51 Kuo, T. C., McCreery, R. L. & Swain, G. M. Electrochemical modification of boron-doped chemical vapor deposited diamond surfaces with covalently bonded monolayers. *Electrochemical and Solid State Letters* **2**, 288-290, doi:10.1149/1.1390813 (1999).
- 52 Luong, J. H. T., Male, K. B. & Glennon, J. D. Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications. *Analyst* **134**, 1965-1979, doi:10.1039/B910206J (2009).
- 53 Krueger, A. & Lang, D. Functionality is Key: Recent Progress in the Surface Modification of Nanodiamond. *Advanced Functional Materials* **22**, 890-906, doi:10.1002/adfm.201102670 (2012).
- 54 Holt, K. B. Diamond at the nanoscale: applications of diamond nanoparticles from cellular biomarkers to quantum computing. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **365**, 2845-2861, doi:10.1098/rsta.2007.0005 (2007).
- 55 Toghiani, K. E. & Compton, R. G. Metal Nanoparticle Modified Boron Doped Diamond Electrodes for Use in Electroanalysis. *Electroanalysis* **22**, 1947-1956, doi:10.1002/elan.201000072 (2010).

2 Chapter two – Experimental Theory and Techniques

This chapter explains the theoretical background of the techniques employed in this thesis. These include the use of X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Raman Spectroscopy and X-ray Diffraction (XRD) as a means of surface and microstructure characterisation. A special emphasis is given to electrochemical techniques used for investigation and characterisation of diamond materials.

2.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy, also referred as Electron Spectroscopy for Chemical Analysis (ESCA), is a non-destructive surface sensitive spectroscopic technique that allows determination of surface chemical composition of a material as well as chemical and electronic state of the atoms and molecules comprising the surface. XPS allows the analysis of low-energy electrons (in the range of 20-2000 eV) which are ejected from the specimen as a result of the photoemission process. Historically, the study of photoemission processes began in the late 1880s, when German physicist Heinrich Hertz discovered that electrically isolated metal placed under vacuum showed an increased ability to spark if exposed to light.¹ This effect, known as photoelectric effect, later led to the determination of the ratio of Plank's constant over electronic charge, h/e , and the work function, ϕ , an energy required to remove an electron from the Fermi level into vacuum.² In 1905, Albert Einstein explained the photoelectric effect in terms of energy quantisation and showed that it arises from the transfer of energy of photons, $h\nu$, (in the form of light) to the electrons bound within the atoms of a specimen.^{3,4} If this energy of transfer exceeds the energy that binds an electron in an atom of a sample, the induced photoemission from a surface is observed. For the introduction of the

concept of the photon (a quantum of energy with zero rest mass) and the law of the photoelectric effect he was awarded the Nobel Prize in Physics in 1921.

On the basis of these fundamental phenomena, Kai Siegbahn and co-workers in the 1960s constructed an instrument that measured core photoelectron emissions with high energy resolution, so that elemental composition of a surface could be determined. For this contribution to the development of high-resolution electron spectroscopy Kai Siegbahn received the Nobel Prize in Physics in 1981. Further advances in the ultra-high vacuum technologies have now resulted in widespread industrial and scientific use of XPS.

A schematic presentation of photoelectron emission process is displayed in Figure 6 (a). A surface of a sample is irradiated by soft monochromatic X-rays, usually $\text{MgK}\alpha$ (1253 eV) or $\text{AlK}\alpha$ (1486.6 eV) under ultra-high vacuum conditions. The energy of irradiation excites core electrons (K shell or $1s$ electrons in the scheme) which propagate further towards the surface and then are emitted if their kinetic energy is high enough to overcome the work function. As it is shown in Figure 6 (b), the energy of the emitted electrons is then analysed by the electron spectrometer and the final photoelectron spectrum is presented as a plot of intensity versus electron energy.

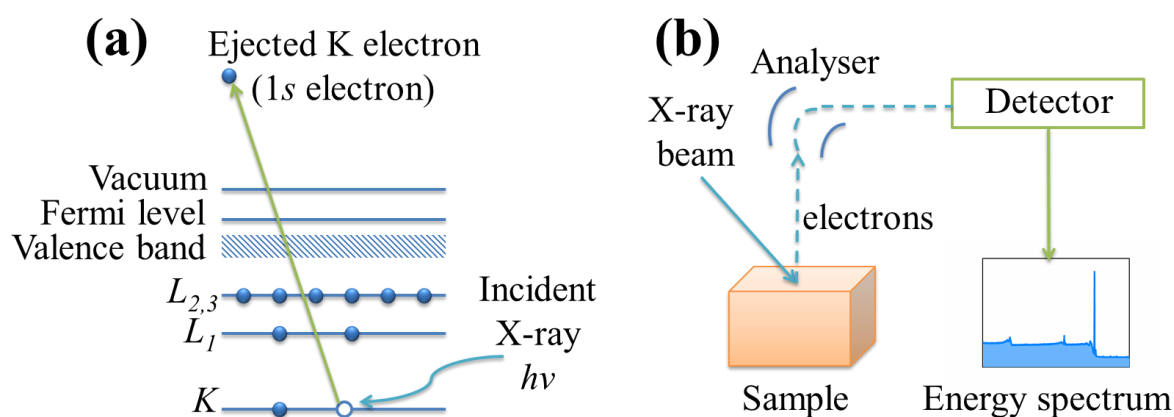


Figure 6 (a) Schematic presentation of the XPS process, where photoionisation of an atom by the emission of $1s$ electron occurs; **(b)** principle scheme of an XPS instrument, adapted from⁵

The kinetic energy, E_K , of the emitted electron, is the experimental quantity measured by the spectrometer. E_K is related to the binding energy, E_B , of the electron through the following equation 2.2.1:

$$E_K = h\nu - E_B - \phi \quad (\text{Equation 2.2.1})$$

Where $h\nu$ is the photon energy, E_B is the binding energy of the core level from which the electron was emitted and ϕ is the spectrometer work function. In contrast to E_K which depends on the photon energy and therefore cannot be considered as intrinsic material property, E_B is unique to each element and may be referred to the ionisation energy of the atom for a specific shell. While X-rays can penetrate into the sample as deep as 1 - 10 μm , the escape depth of the emitted electrons is limited to ~5-10 nm from the surface. Electrons emitted in the bulk below this limit lose energy whilst travelling to the surface and are inelastically scattered, thus contributing to the background of the spectrum.

Apart from the main photoemission process described in Figure 6 (a), some electrons in the XPS are emitted as a result of the Auger effect. As it is shown in Figure 7 (a), when a first electron to depart leaves a hole in the K shell, an electron from a higher level ($L_{2,3}$ in the example) can fall into this hole (Figure 7 (b)). Due to the principle of energy conservation, the energy that was released can result either in generation of radiation known as X-ray fluorescence or in the ejection of another $L_{2,3}$ electron, thus causing a secondary photoemission, as presented in Figure 7 (c). The secondary electron emitted is referred as $KL_{2,3}L_{2,3}$ Auger electron in this case, and is a fingerprint to the material present.

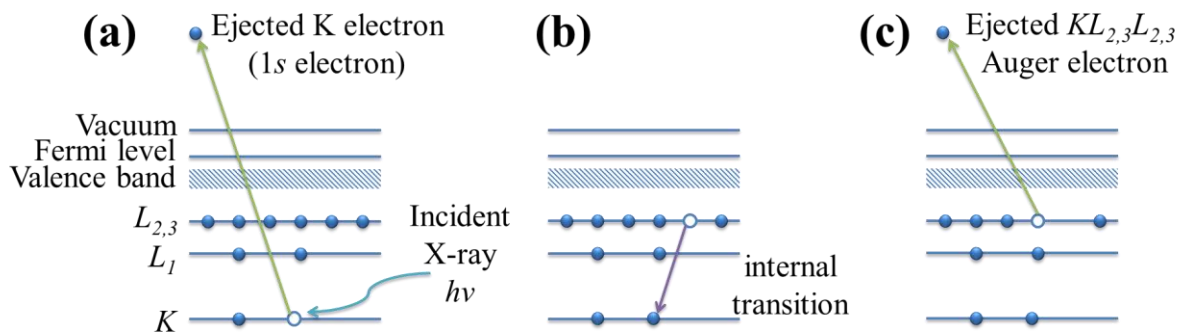


Figure 7 Schematic presentation of an Auger process – relaxation of the ionized atom the ejection of a $KL_{2,3}L_{2,3}$ Auger electron, adapted from⁵

2.1.1 XPS Instrumentation

All XPS measurements in this work were performed using an XPS spectrometer that functions under ultra-high vacuum in the range of $\sim 10^{-9}$ - 10^{-10} Torr. The spectrometer consists of an X-ray source, an electron energy analyser and a detection system, all of which are placed within a vacuum chamber. The schematic presentation of the spectrometer modules is given in Figure 8.

The mounting of a sample into the UHV analysis chamber is achieved through a preparation chamber, which is equipped with a fast entry lock. During the sample mounting, the pressure in the preparation chamber is raised to atmospheric. This is followed by an outgassing procedure until a pressure of 10^{-6} Torr is reached. The sample is transferred from the preparation chamber to the UHV analysis chamber by means of magnetically controlled arms and positioned so that an angle of 45° between the X-ray beam, sample and the detector is preserved. The pressure in the UHV analysis chamber is held below 10^{-9} Torr by means of turbo pumps. This UHV environment is necessary to prevent the formation of adsorbed gas monolayers on the sample surface and to avoid possible scattering of low energy electrons ejected from the sample by residual gas molecules.⁷

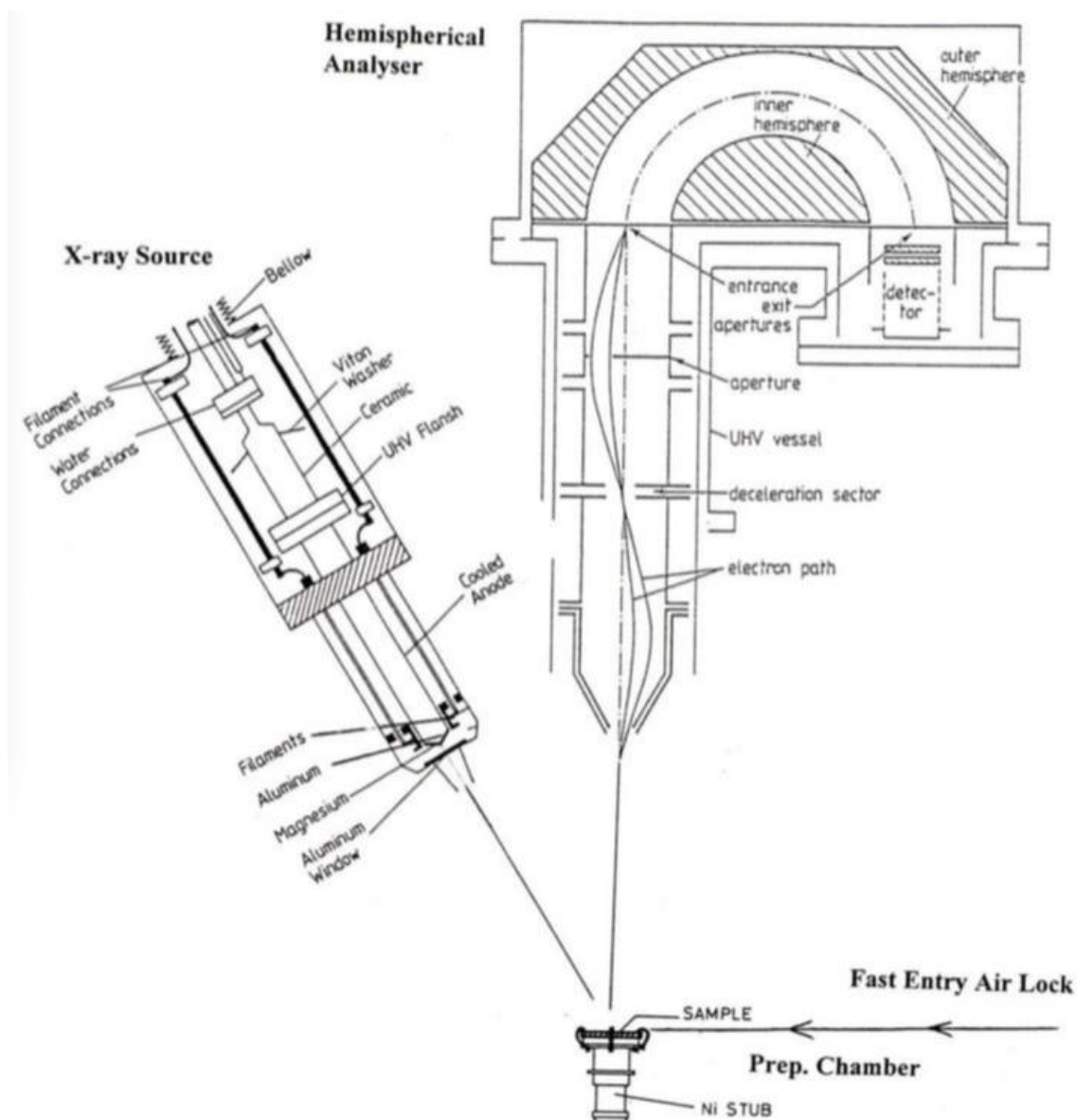


Figure 8 Schematic presentation of XPS apparatus experimental set-up, reprinted from⁶

The X-ray source consists of an X-ray tube that generates X-rays by directing a high energy electronic beam to aluminium or magnesium metallic solid where transitions from $2p$ orbitals to the ionised $1s$ orbital result in $K\alpha$ radiation. The metallic solid is referred as an X-ray anode with the electron source being the cathode.

When the electrons are emitted from the surface, their kinetic energy is generally too big for the analyser to produce sufficiently high resolution, therefore they are retarded.⁷ The latter process is achieved *via* variable electron lenses which adjust the energy of the electrons and focus them on the hemispherical analyser, therefore increasing its resolution. The hemispherical analyser is comprised of two concentric hemispheres with a potential difference applied across them. This potential difference implies that only photoelectrons of a particular energy will be able to pass around the sphere. In all XPS experiments, the hemispherical analyser was operated under a constant potential which corresponds to a fixed analyser transmission (FAT) mode. FAT provides consistent spectral resolution throughout all kinetic energies.⁷ Survey XPS scans were recorded using high pass energy of 50 eV, whereas narrow scans were collected with pass energy of 25 eV in order to achieve a higher resolution. For a narrow region of interest 30 scans were recorded, whilst for a survey region 5 scans were taken. The electrons passed through the hemispherical analyser under the FAT mode further travel to the electron detector equipped with a multi-channel plate electron multiplier. The detector processes the associated current in order to produce corresponding XPS spectrum that will be digitised by the software. All spectra recorded were analysed with CasaXPS software.⁸

2.1.2 XPS Spectral Features

A typical XPS spectrum is displayed as a plot of intensity (usually expressed as counts per second) versus electron binding energy that begins at zero point. A detailed discussion of XPS features will be presented below.

2.1.2.1 The main photoelectron line

Figure 9 presents an example of a typical XPS spectrum consisting of the individual intensive photoelectron peaks and the associated Auger lines arising from de-excitation process that

Chapter Two – Experimental Theory and Techniques

succeeds photoemission. As discussed above, the intense, well-defined and narrow photoemission peaks are due to the electrons emitted from core orbitals without energy loss. Electrons that emerge with random and multiple energy losses contribute to a continuous background at higher binding energies. The most intense photoelectron lines from insulators are generally found to be symmetrical although some asymmetry can arise due to coupling with metal conduction band electrons, inelastic scattering and instrumental response.⁹ The resulting peak width is considered as a function of the natural line width, the width of the X-ray line and the instrumental contribution to the line width.¹⁰

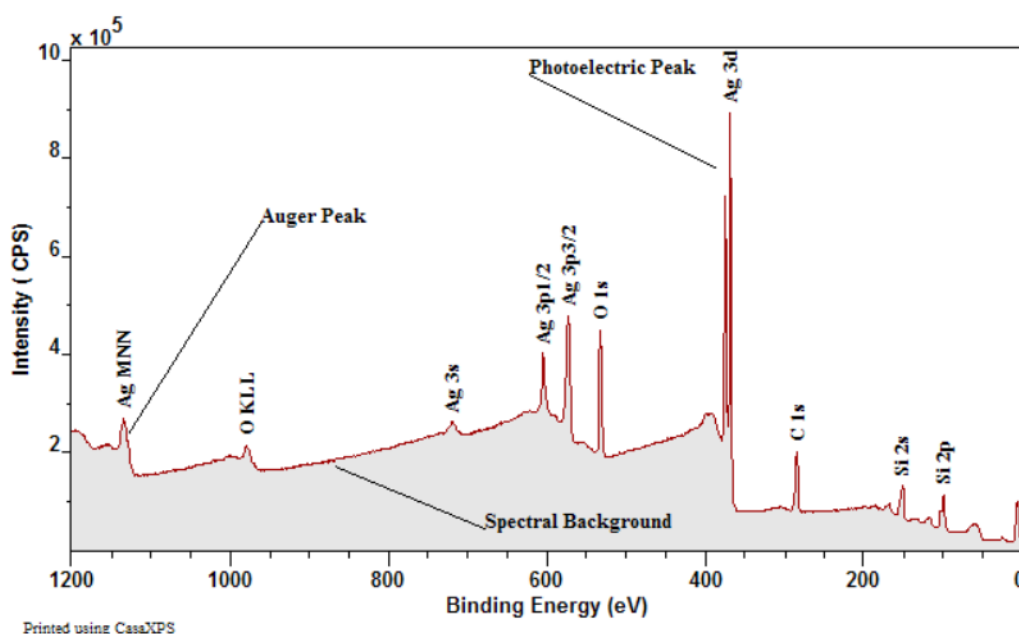


Figure 9 An example of a typical survey spectrum demonstrating the appearance of XPS and Auger peaks above a background of scattered electrons, reprinted from¹⁰

Another source of the XPS peaks is spin-orbit coupling which is illustrated in Figure 10. The p , d and f orbitals become split upon ionisation, resulting in the $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$ states in which the occupying electrons have either the opposite or the same spin respectively.¹¹

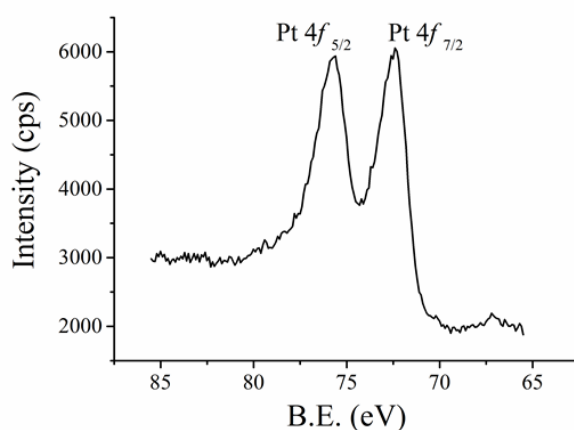


Figure 10 A typical spin-orbit coupling of Pt 4f spectrum

2.1.2.2 Auger Peaks

In Figure 9, Auger lines originating from non-fluorescent relaxation are also present along with the main XPS peaks. The most common are *KLL*, *LMM*, *MNN* and *NOO* series which are notated in terms of initial and final vacancies in the Auger transition. For example, *KLL* series correspond to the initial vacancy in the *K* shell and final double vacancy in the *L* shell. Unlike the photoelectric peaks, the kinetic energy of the Auger lines is independent of the photon energy of the X-ray source.⁵ The photon energy can be altered by changing the X-ray anode material. Such a change in the photon energy will result in the shift of photoelectric peaks, while Auger peaks will be observed at the same energy.

2.1.2.3 Shake up satellites

Apart from the main photoelectron lines described above, shake-up satellites may appear in the spectrum if the outgoing photoemitted electron simultaneously collides with a valence electron and excites it (shakes it up) to a higher energy level. The energy of the emitted photoelectron is therefore reduced, and a satellite structure appears a few electron volts higher than the main peak on a binding energy scale. Shake-up satellites most often have the

intensity of ~5-15% than that of the main line, with separations up to 15 eV from the main line.⁷ A typical example of a shake-up process involving $\pi \rightarrow \pi^*$ transition brought about C 1s line is presented in Figure 11.

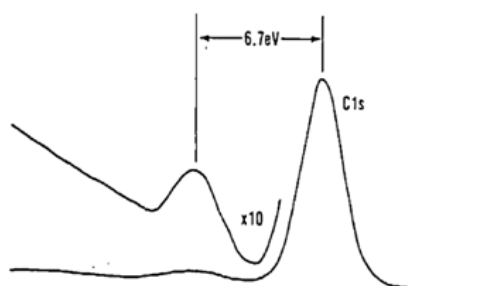


Figure 11 π -bond shake-up satellite for the C 1s photoelectron peak in polystyrene, reprinted from¹¹

2.1.2.4 Other spectral features

Multiplet splitting of a photoelectron peak can take place if atoms comprising the surface have a spin (unpaired electrons). The emission of an electron from a core level leaves an unpaired electron that interacts with other unpaired electrons in the atom and can form an ion with several electronic configurations of different energies. This creates a photoelectron line that is split asymmetrically into components similar to that shown in Figure 12 (a). Multiplet splitting effects can be generally observed in Mn, Cr 3s levels, Co and Ni $2p_{3/2}$ levels.

Plasmon losses occur both in XPS and Auger spectra and are commonly characteristic of clean metal surfaces. When the photoemitted electron excites collective oscillations in the conduction band electrons, it suffers a discrete energy loss or multiple losses as presented in Figure 12 (b).

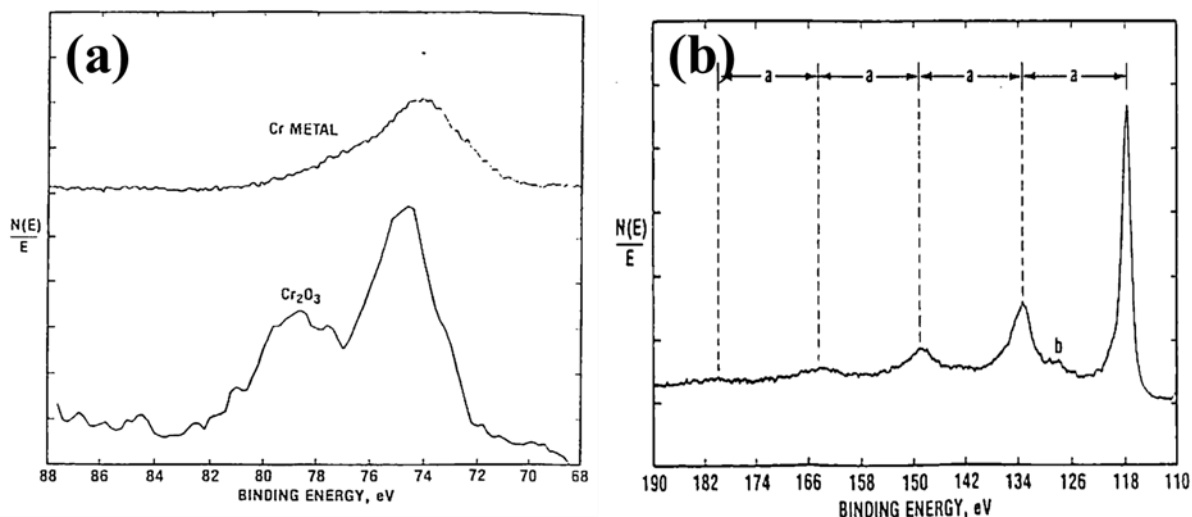


Figure 12 (a) Multiplet splitting in the Cr 3s line; (b) Energy plasmon losses associated with 2s line of aluminium. Both figures reprinted from¹¹

The XPS spectrum can be further complicated by the presence of X-ray satellites and X-ray ghosts that do not possess any analytical use and might be considered as unwanted features because they might occur in the same binding energy range as the main photoemission lines of an element of interest. X-ray satellites appear if unmonochromated radiation is used, and arise from the excitement of characteristic transitions by a minor components, e.g. $AlK\alpha_{3,4}$, $AlK\alpha_{5,6}$ and $AlK\beta$ in case of aluminium cathode.¹¹ X-ray ghosts originate from photoemission of an element other than the X-ray source or sample. For example, a small amount of characteristic X-radiation can be generated as a result of anode misalignment.

2.1.3 XPS Quantification

XPS spectrum quantification comprises the analysis of both peak intensities and peak positions. The former is indicative of how much of the material is present at the surfaces, whereas the latter is characteristic of an element and chemical composition. The peak positions, *i.e.* binding energies of photoelectron peaks, obtained from the XPS data depend extensively on the chemical bonding of the original atom. The change in the binding energy

is also known as a chemical shift. The chemical shift is a valuable source of information as it depends on several important factors such as the oxidation state of the element and electronegativity of neighbouring atoms or ligands. For example, if the oxidation state of the element increases, the chemical shift will also increase; the greater the electronegativity, the greater will be the binding energies of the core electrons. The detailed lists of chemical shifts are available elsewhere in the literature.^{7,11}

Apart from the chemical shifts, full width at half maximum (FWHM) is an important value which provides an insight into chemical state changes and physical influences. Thus, broadening of a peak might suggest: (i) changes in the number of chemical bonds contributing to a peak shape; (ii) a change in the sample condition and (iii) surface charging.¹²

In order to extract quantitative data from an XPS peak, the area under the peak of intensity, I should be determined

The intensity, I , of a photoelectron peak is given by a following equation:⁵

$$I = Jp\sigma K\lambda \quad (\text{Equation 2.2.2})$$

where J is the photon flux, p is the atoms concentration on the surface, σ is the photoionisation cross-section (probability) of photoelectron emission, K is the function of instrument parameters dependent on the transmission function of the spectrometer, detector efficiency and the electron attenuation length and λ is the inelastic mean free path

For a homogeneous material, in order to relate the measured intensity of two components A and B as a part of the atomic concentration, the following equation 2.2.3 can be applied:⁶

$$\frac{[A]}{[B]} = \frac{I_A (\sigma_B \xi_B \lambda_B \eta_B)}{I_B (\sigma_A \xi_A \lambda_A \eta_A)} \approx \frac{I_A S_B}{I_B S_A} \quad (\text{Equation 2.2.3})$$

Where σ is the photoionisation cross section, ξ is the fraction of photoelectron events which occur without intrinsic plasmon excitation, λ is the inelastic mean free path, η is the kinetic energy dependent spectrometer transmission, I is the integrated peak area of interest and S is atomic sensitivity factor. Sensitivity factors are tabulated in literature,¹³ therefore, equation 2.2.3 enables a surface composition of the material to be determined.

2.1.4 XPS Experimental Procedure

X-ray photoelectron spectroscopy spectra were recorded using a hemispherical analyser with Al K α (1486.6 eV) X-ray source at 10 kV anode potential and 10 mA emission current. The survey scans and the high resolution scans were measured at 50 eV with 0.5 eV step and at 20 eV energy passes with 0.1 eV step. The spectra recorded were analysed with CasaXPS software.⁸ The peaks were fitted using a Shirley background with Gaussian-Lorentzian sum functions without restrictions.⁹ The binding energies collected have an error of ± 0.25 eV in accordance with calibration of C 1s peaks.¹¹ The reported and normalised peak areas have an error of $\sim 10\%$.¹²

2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a qualitative imaging technique that is used to produce high-resolution real-time topographic images of the sample surface.¹⁴ Figure 13 (a) presents a principle scheme of a scanning electron microscope. After the sample is placed in a vacuum chamber, a finely focused beam of electrons, of several nanometres in diameter, strike upon the surface by means of an array of lenses. This beam of electrons irradiates the surface of the specimen resulting in either backscattering of incident electrons or the emission of the secondary electrons. The former are the electrons that are deflected back out of the sample, while the latter are due to inelastic interaction of the electron beam with the electric field of an atom in the sample. The differences in the surface composition and its topography

influence the generation, transport and escape of these signals. By processing the intensity and velocity of the electrons emitted and backscattered, an image of the surface of the sample is produced.

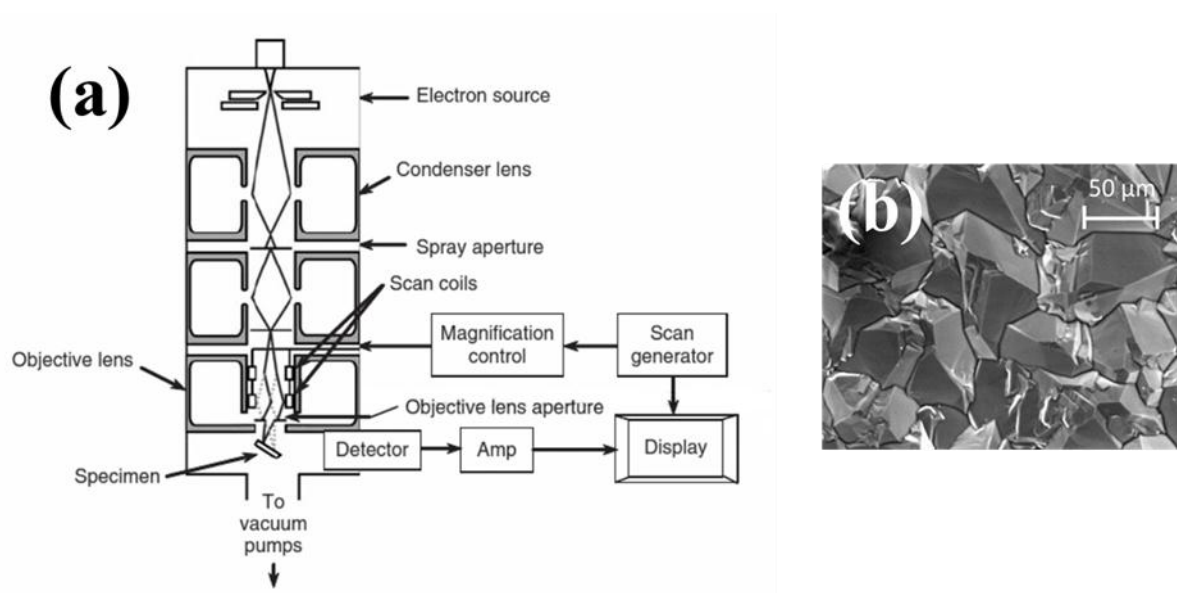


Figure 13 (a) The principle scheme of the basic components of SEM, adapted from¹⁵; (b) a typical SEM image of a microcrystalline boron-doped diamond electrode

The scanning electron microscopy measurement can be performed using two independent operating modes: Secondary Electron Imaging (SEI) mode and Backscattered Electron Imaging (BEI) mode. The analysis in SEI mode yields sample characteristics such as surface topology, phase distributions and crystallinity, while BEI mode can be used in order to provide an information on the chemical composition.¹⁵ A typical SEM image of plain microcrystalline B-doped diamond which is comprised of [111], [100] and [110] diamond grains with an average grain size of 5-50 μm is presented in Figure 13 (b).

2.3 Raman Spectroscopy

Raman Spectroscopy is widely employed non-destructive analytical technique for evaluation of diamond materials. The technique is popular as each carbon morphology possesses a clearly identifiable Raman signature and requires no sample preparation.¹⁶ In Raman

spectroscopy, the changes in atomic states are investigated by analysis of the frequencies present in the radiation scattered by atoms. Atoms in crystals have characteristic vibrational modes that are specific to a chemical bond of an atom and lattice symmetry. If an incident monochromatic light with a frequency of ν_i interacts with the phonons in the crystal of frequency ν_{ph} , it can either activate or de-activate the lattice vibration, therefore causing inelastic scattering of the incident photons to give the anti-Stokes ($\nu_i + \nu_{ph}$) and Raman Stokes ($\nu_i - \nu_{ph}$) lines (Figure 14).¹⁷ At room temperature, Stokes scattering intensity is much stronger than anti-Stokes scattering, and thus is commonly used for the analysis.

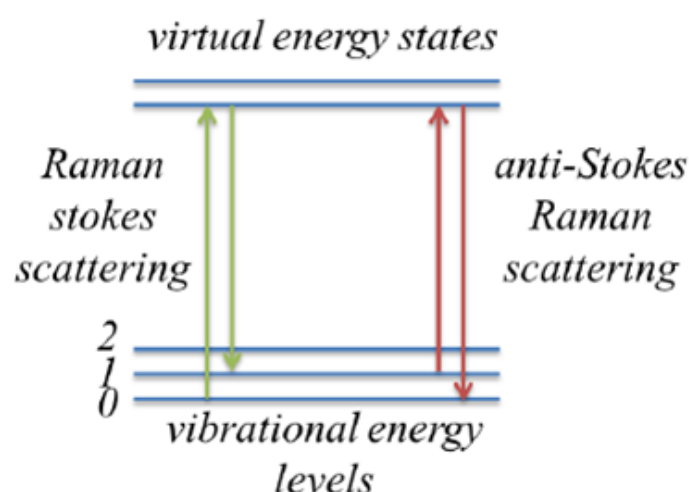


Figure 14 Schematic illustration of Raman Scattering

Depending on the symmetry of a crystal lattice and the resulting availability of vibrational modes, important information regarding the structure of a lattice can be obtained through the Raman measurements. Laser Raman spectroscopy is commonly used for characterisation of diamond and other carbon materials as each of these carbon forms possesses unique Raman features. Figure 15 (a) shows a typical Raman spectrum of a single crystal diamond surface which is dominated by a single first order Raman line at 1332 cm^{-1} that corresponds to the vibration of two interpenetrating face centred cubic (fcc) diamond sublattices.¹⁶ In contrast to a single crystal diamond, in polycrystalline diamond sp^2 graphitic states usually present in

grain boundaries that give rise to the appearance of D band at 1357 cm^{-1} and G band at 1580 cm^{-1} . Therefore, a small ratio of the sp^2 peak intensity to the sp^3 peak intensity detected in the Raman spectrum is indicative of a good diamond quality.

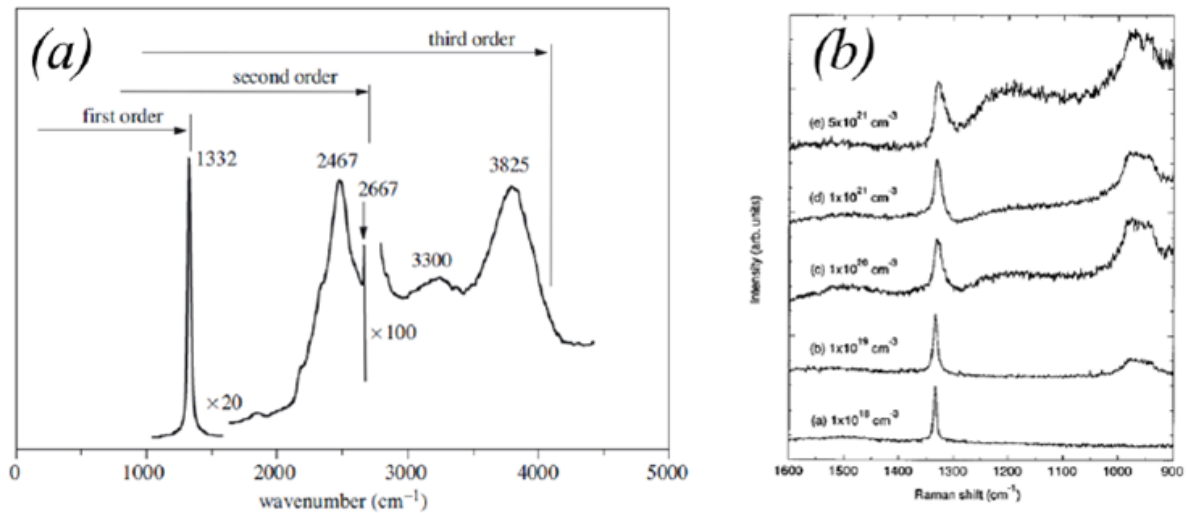


Figure 15 (a) General Raman spectrum of single crystal diamond excited at room temperature at a wavelength of 228.9 nm. The first, second and third order Raman peaks are presented, reprinted from¹⁶; (b) Raman spectra of boron-doped diamond films at differing boron doping concentrations, reprinted from¹⁸.

Characteristic changes to a Raman spectrum of diamond occur in the result of boron doping. Two broad peaks appear at 500 cm^{-1} and 1230 cm^{-1} which intensity increase with the increase of boron concentration, thus making it possible to deduce the boron concentration. At high boron concentration, characteristic single order diamond phonon becomes asymmetric and is shifted to a lower wavenumbers as presented in Figure 15 (b).¹⁸

2.4 X-ray diffraction

X-ray diffraction is a commonly used technique that allows an unknown sample's structure determination, including shape, symmetry and size of the unit cell.

The operating principles of XRD are based on the Bragg's law:¹⁹

$$2d \sin \Theta = n\lambda \quad (\text{Equation 2.2.4})$$

where d is the lattice plane separation, Θ is the glancing angle, n is the reflections order and λ is the wavelength of incident X-rays.

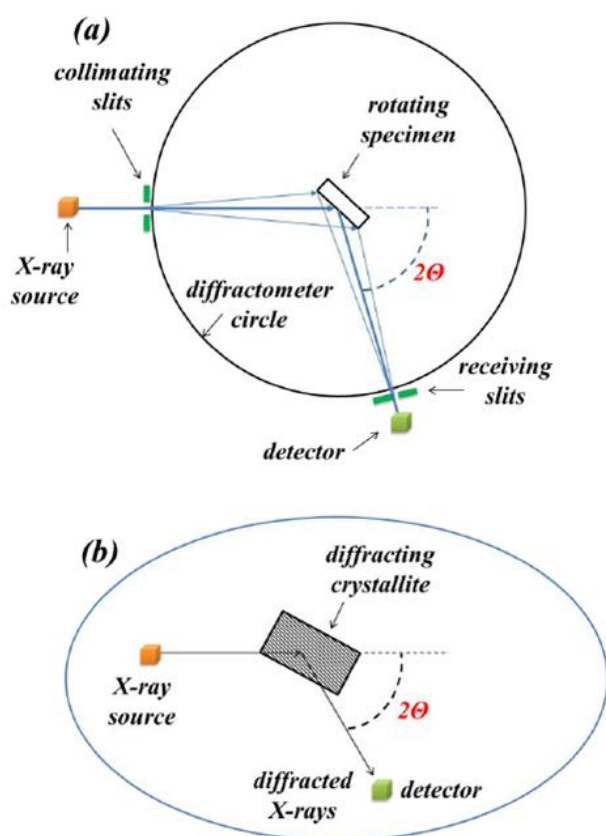


Figure 16 Schematic illustration of (a) X-ray powder diffractometer in Θ - 2Θ orientation; (b) X-ray diffraction on a crystalline sample, adapted from¹⁹.

In an X-ray diffraction experiment (Figure 16), X-rays incident upon the sample, interact with the electron density of the atoms and are scattered to give diffraction patterns. Heavy atoms cause a greater scattering than light atoms. Such a dependence on the number of electrons is expressed in terms of scattering factor, f , of the element.¹⁷ The greater the scattering factor, the greater is the X-rays scattering. For a unit cell, comprised of atoms with

the scattering factor f_i and atom's coordinates $(x_i a, y_i b, z_i c)$, the overall amplitude of a wave diffracted by the (hkl) planes is given by the following equation:¹⁹

$$F_{hkl} = \sum_i f_i e^{j\phi_{hkl}(i)} \text{ and } \phi_{hkl}(i) = 2\pi(hx_i + ky_i + lz_i); j = (-1)^{1/2} \quad (\text{Equation 2.2.5})$$

where F_{hkl} is the structure factor. The observed intensity, I_{hkl} , at the detector is proportional to the square modulus of $|F_{hkl}|^2$.¹⁹

In this thesis, XRD diffraction patterns were recorded using a Philips PANalytical X'pert Pro powder diffractometer with $\text{CuK}\alpha$ monochromatised radiation. The data were analysed by X'Pert Highscore software.

2.5 Electrochemical Methods

This section summarises basic principles underlying electrochemical theory and gives an introduction to main electrochemical techniques that were employed in this thesis in order to modify and investigate electrochemical properties of diamond materials.

2.5.1 Principles of Electrochemical Theory

Electrochemistry studies chemical phenomena associated with charge transfer across an electrode and electrolyte interface. An electrode is a conductor through which charge is carried by electronic movement; electrolyte is a phase through which charge is carried by the transport of ions.

A simple electrochemical measurement requires at least two electrodes to be connected together by conducting paths both through an ionic conductor (electrolyte) and externally (electric wires), so that the charge can be transferred and monitored. As presented in Figure 17, these electrodes comprise an electrochemical cell, which consists of the working electrode - an electrode where the electrochemical reaction of interest is taking place - and a

counter electrode. The latter can operate as a cathode, whilst the working electrode can work as an anode or vice versa.

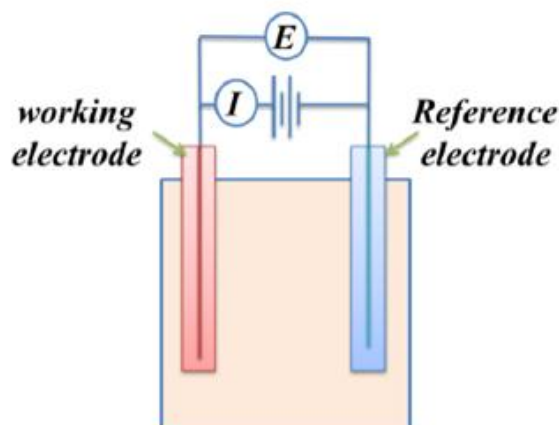


Figure 17 Schematic illustration of two-electrode electrochemical cell, adapted from²²

During the electrochemical measurement, faradaic and non-faradaic processes can take place in the cell. In the former process in accordance with the Faraday's Laws, the quantity of the redox species involved in an electrode reaction is stoichiometrically proportional to the number of charges (electrons) flowing in the circuit. Since the total amount of redox species converted in the electrochemical process is proportional to the amount of charge, the reaction rate, k_j , corresponding to the amount of substance j converted in unit time per unit surface area, A , of the electrode, is proportional to the current density, i :²³

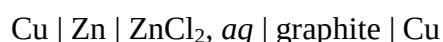
$$k_j = \frac{1}{A} \frac{dv_j}{dt} = v_j \frac{1}{nF} \quad (\text{Equation 2.2.6})$$

where F is the Faraday constant (96487 C mol^{-1}) and v_j is the number of moles converted during the process.

Deviations from the Faraday law are often observed if the charge aside from being involved in the electrochemical process is accumulated in certain parts of circuit, for example due to

reorientation of solvent dipoles, adsorption/desorption and movement of the electrolyte ions at the electrode/electrolyte interface. These processes are also known as non-faradaic.

A typical electrochemical cell can either be employed to produce electrical energy as a result of a spontaneous reaction occurring inside it (i.e. a galvanic cell) or it can consume electricity from an external source to drive a specific reaction (i.e. an electrolytic cell). The schematic sequence of conductors comprising a galvanic cell is presented below:



In this work the main interest is drawn upon the investigation of electrolytic cells. The cathode in such systems is denoted as an electrode where reduction process is taking place, whereas the anode is referred to an electrode where an oxidation process occurs. The cathode is negative relative to the anode, whilst an opposite notation is commonly used in galvanic cells.

The structure of an electrode-solution interface is presented in Figure 18. The inner layer of the interface, also referred to the inner Helmholtz plane, is comprised of adsorbed ions and solvent molecules structured at a distance χ_1 from the electrode surface. The ions which are generally partially solvated, adhere strongly to the electrode surface. An outer Helmholtz plane consists of the fully solvated ions at a distance χ_2 which are attracted by electrostatic interactions. As the charge neutrality should be preserved, the net charge accumulated at the electrode is balanced by a net opposite charge distribution in the solution phase. The latter process occurs through the attraction of charged species and therefore the formation of a diffuse layer.

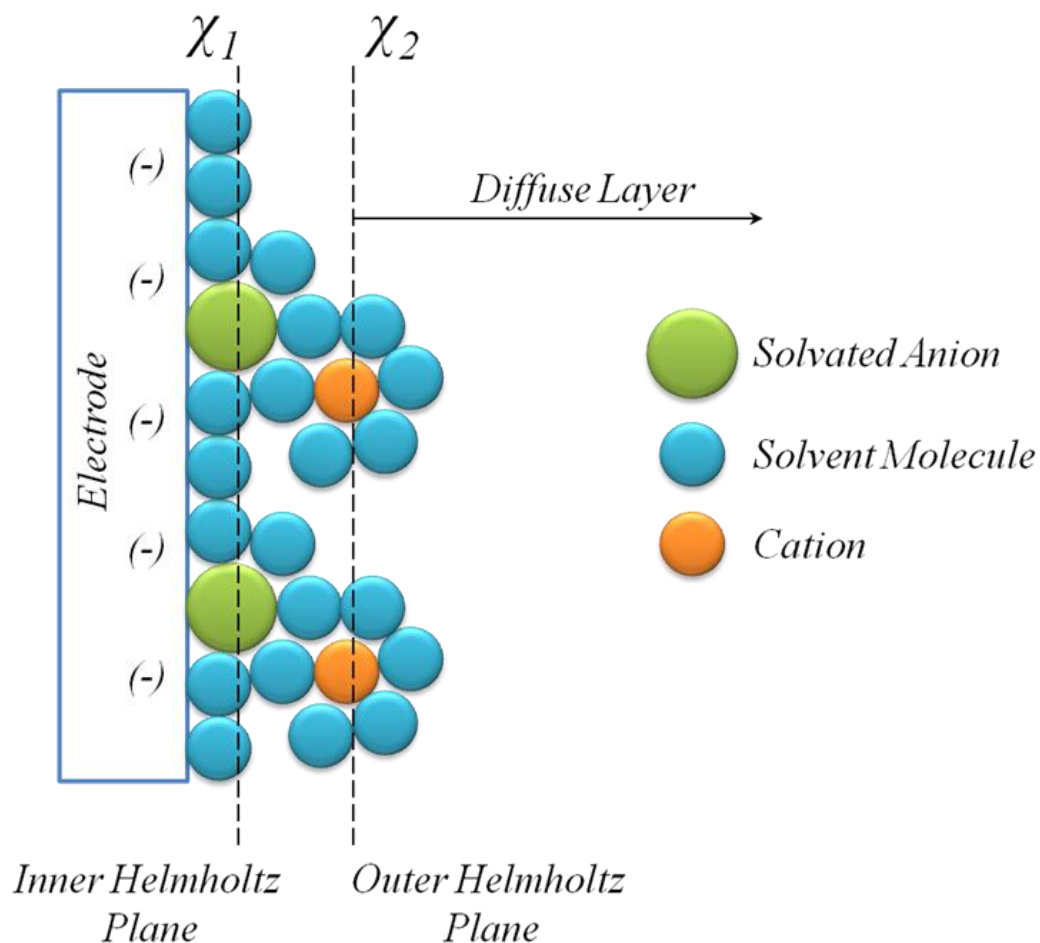


Figure 18 Helmholtz double layer model, adapted from²²

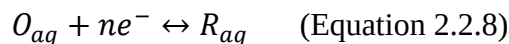
2.5.1.1 Equilibrium Electrochemistry

Equilibrium electrochemical measurements are carried out in the cell under the conditions when no current flows, thus enabling thermodynamic parameters determination. Under these equilibrium conditions, a potential drop across the electrode-solution interface can be expressed by the following equation:

$$\Delta\phi_{e/s} = \phi_e - \phi_s \quad (\text{Equation 2.2.7})$$

where ϕ_e is the potential on the electrode and ϕ_s is the potential in the solution.

For the electrochemical reaction:



The Nernst equation can be used to determine the potential difference established at an electrode at equilibrium:

$$E_{eq} = E_0 + \frac{RT}{nF} \ln \frac{[O]}{[R]} \quad (\text{Equation 2.2.9})$$

where $[O]$ and $[R]$ are the concentrations of the reactants at the electrode surface, E_0 is the standard electrode potential which corresponds to the value of electrode potential that is measured when the activities of the reactants are unity, F is the Faraday constant (96485 C mol⁻¹), n is the number of electrons, R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), T is the Kelvin temperature.

2.5.1.2 Non-equilibrium Electrochemistry

Electrochemical cells can also work under the conditions where a current flows. Under such non-equilibrium conditions, overpotential is needed to drive an electrochemical reaction. The latter is described by following expression:

$$\eta = E - E_{eq} \quad (\text{Equation 2.3.0})$$

Therefore, in order to drive an oxidation process, the electrode potential, E , should be greater than E_{eq} and conversely, for the reduction process to occur, E should be smaller than E_{eq} . In the case of reaction 2.8 under non-equilibrium conditions, the overpotential will cause the reduction of O to R , and the current I will start to flow in the cell. The magnitude of this current is given by:

$$I = AFj = AFk[O] \quad (\text{Equation 2.3.1})$$

Chapter Two – Experimental Theory and Techniques

where A is the electrode area, F is the Faraday constant (96485 C mol^{-1}), j is the flux of O species to the electrode surface and k is the rate constant of the charge transfer reaction. The rate constant can be further described on the basis of the transition state model in the form of Arrhenius equation:²⁴

$$k = Ze^{\frac{-\Delta G^*}{RT}} \quad (\text{Equation 2.3.2})$$

where Z is the frequency factor associated with the rate of collision of the redox species with the electrode surface and ΔG^* is the standard free energy of activation.

The standard free energy of activation depends on the change in the potential difference between the working electrode and the solution. Therefore, the rate constant can be considered as a function of the imposed overpotential described in equation 2.3.0. The rate constant can be quantified by the following expressions:²⁴

$$k_{Red} = k_{red}^0 e^{\frac{-\alpha F \eta}{RT}} \quad (\text{Equation 2.3.3})$$

$$k_{Ox} = k_{ox}^0 e^{\frac{(1-\alpha)F\eta}{RT}} \quad (\text{Equation 2.3.4})$$

where α is the transfer coefficient, the value of which lies in the range of zero to unity ($0 < \alpha < 1$), and k^0 is the standard rate constant.

The transfer coefficient concerns with the sensitivity of the transition state to the changes in the potential difference. If α is close to zero, the transition state (*) resembles the reactant, whilst if α is near unity, the transition state (*) is product like. In case if α is close to 0.5, the transition state lies between the reactant and product.

The overall reaction current in the cell can be expressed as a difference between the oxidation and reduction processes :

$$I = I_a - I_c = nAF(k_{ox}[R]_0 - k_{Red}[O]_0) \quad (\text{Equation 2.3.5})$$

Chapter Two – Experimental Theory and Techniques

In order to introduce the model that will describe the electrode kinetics as a function of the transfer coefficient and the imposed overpotential, the equations 2.3.3 and 2.3.4 are substituted in the equation 2.3.5 to give equation 2.3.6. The resulting expression is known as Butler-Volmer equation:²⁴

$$I = k_{Red}^0 \exp\left[\frac{-\alpha F(E-E_f^0)}{RT}\right] [O]_0 - k_{Ox}^0 \exp\left[\frac{\beta F(E-E_f^0)}{RT}\right] [R]_0 \quad (\text{Equation 2.3.6})$$

$$\text{and } I_0 = nAFk^0 [R]_{bulk}^\alpha [O]_{bulk}^{1-\alpha} \quad (\text{Equation 2.3.7})$$

where I_0 is the exchange current that is associated with the value of the standard rate constant and experimental conditions. Figure 19 illustrates the variation of the net current I as a function of the overpotential for the two limiting scenarios: (a) large I_0 and (b) small I_0 .

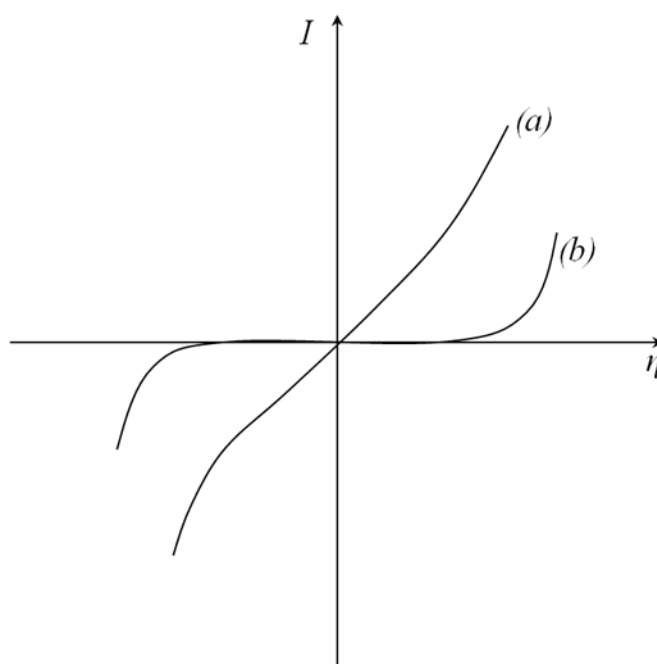


Figure 19 Dependence of the current with overpotential for (a) large I_0 (reversible) and (b) small I_0 (irreversible).

Under the conditions when overpotential is zero, no net current flows for both scenarios (equilibrium conditions). In the case when I_0 is large (a), a small overpotential is required to drive the reaction. Such a reaction is referred to as reversible. Conversely, in order to drive

the process in the scenario (b), a large overpotential should be imposed. The associated reaction is known to be irreversible.

The pathway of electrochemical process can be quite complex, involving a sequence of several steps. As illustrated in Figure 20, these can include: (i) mass transfer from the bulk to the electrode surface by means of such processes as diffusion, migration and convection; (ii) chemical transformations prior electron transfer; (ii) adsorption/desorption processes.²²

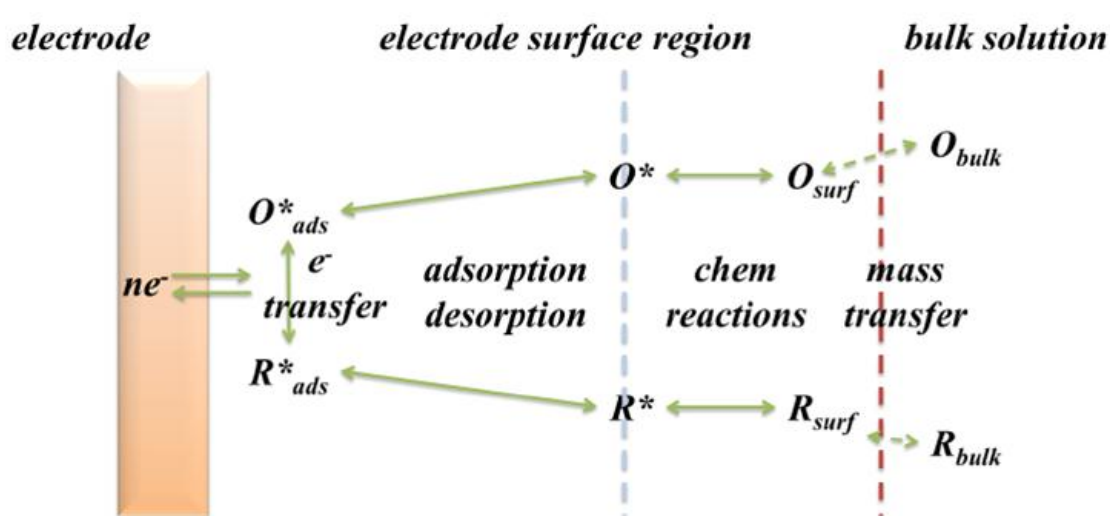


Figure 20 Scheme of electrode reaction pathway, adapted from²²

The rate constant of these reactions is determined by the slowest step in a sequence. A simple reaction pathway generally encompasses the mass transport of redox species to the electrode surface which is followed by the electron transfer across the interface, and the migration of the converted redox species back to the bulk solution. More complex reactions are accompanied by additional chemical transformations or surface processes.

The diffusion phenomenon, which occurs during the mass transfer from the bulk, originates from the concentration gradient. If an uneven concentration distribution exists, the redox

species will diffuse from the area with higher concentration to the area with lower concentration. This process can be described by the first Fick's Law:²⁴

$$j = -D_C \frac{\partial [C]}{\partial x} \quad (\text{Equation 2.3.8})$$

where j is the flux corresponding to the number of moles of species C that pass through unit area in unit time, D_C is the diffusion coefficient of species C and $\frac{\partial [C]}{\partial x}$ is the local concentration gradient at point x .

In order to describe how the concentration of species C varies with time during the diffusion process, the second Fick's Law can be applied:²⁴

$$\frac{\partial [C]}{\partial t} = D_C \frac{\partial^2 [C]}{\partial x^2} \quad (\text{Equation 2.3.9})$$

2.5.2 Electrochemical measurements

In general, electrochemical measurements differ with regard to the type of signal used for the quantification of the charge transfer in the cell and can be principally classified as either potentiometric or potentiostatic.

In potentiometric techniques, if two connected dissimilar electrodes are immersed in the analyte, then the difference between the two interface potentials can be measured under the zero current conditions where equilibrium exists at each electrode surface. The established potential of the cell depends on the standard electrode potentials of the electrochemical couples and on the solution concentrations of the electroactive species. Thus, if the working electrode is made truly selective to the target species, then an accurate electrochemical sensor can be produced. Various types of sensors have been developed to monitor species such as protons, fluoride anions, and calcium and potassium cations; a well-known potentiometric sensor is the pH meter glass electrode. A considerable advantage of such potentiometric

sensors is their cost-effectiveness; however, problems arise due to the lack of the required selectivity, when electroanalytical tasks are more complex.

Potentiostatic or controlled-potential techniques study charge transfer at the electrode/electrolyte interface under dynamic (non-zero current) conditions. In such systems an applied potential to the working electrode drives a charge transfer reaction. As a result, the recorded current can not only provide information on the concentration of the target analyte, but also give an insight into the kinetics and thermodynamics of the electrochemical process.

One of the most versatile approaches in the whole field of potential-controlled measurements is voltammetry. This enables a very sensitive detection (down to picomolar) to be carried out; as well as the distinction of several electroactive species to be made simultaneously providing they react at different potentials. These voltammetric measurements require the use of three electrodes rather than just two as in potentiometry. In this case, a potentiostat is employed to control the current flowing through the working electrode as a function of potential applied between it. Additionally, a reference electrode is connected, through which no current flows.

It is used to provide a stable, solution properties independent value of potential to which the potential of the working electrode can be referred. Finally, a third electrode, known as an auxiliary or counter electrode, provides a balancing counter current to that flowing through the working electrode.

2.5.3 Cyclic Voltammetry

Cyclic voltammetry is one of the most widely employed methodologies in the whole area of voltammetry. In such a system, current flowing through the working electrode is recorded as a function of an applied potential. As presented in Figure 21 (a), the potential of the working electrode is set up to an E_1 value, then it is swept linearly to a potential, E_2 , at which point the

direction of scan is reversed to return to the potential E_1 . The resultant current-potential graph, known as a voltammogram, is a plot of the current signal versus the excitation potential.

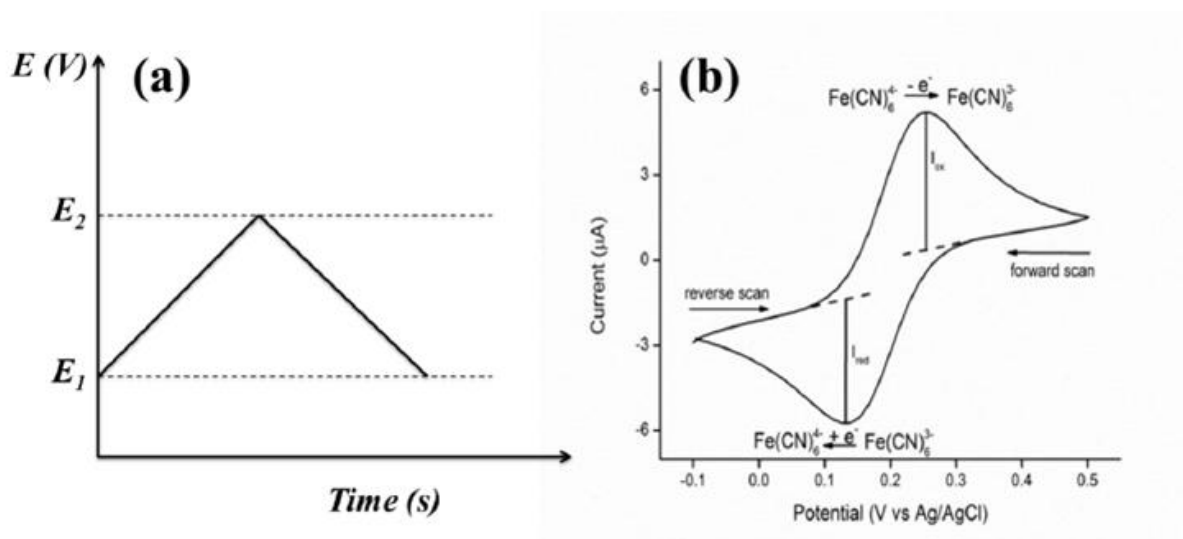


Figure 21 (a) linear potential sweep during cyclic voltammetry; (b) cyclic voltammogram obtained at boron-doped diamond electrode in 0.1 mM $K_3Fe(CN)_6$ in 0.1 M KCl at 0.05 Vs^{-1}

An example of the cyclic voltammetry data obtained from a diamond electrode in 0.1 M $K_3Fe(CN)_6$ solution is illustrated in Figure 21 (b). The ordinate of Figure 21 (b) represents the current flowing through the diamond electrode; the abscissa corresponds to the potential applied to the working electrode versus the Ag/AgCl reference electrode. At the beginning of the experiment, the potential is swept from 0.5 V to 0.1 V. At this time, electrons are supplied to the $Fe(CN)_6^{3-}$ species, giving rise to the reduction peak at 0.13 V. As the potential is swept back from -0.1 V to 0.5 V, an oxidation process takes place (electrons are removed from the species). It is noteworthy that the redox reaction of interest occurs only in the potential region that makes the electron transfer thermodynamically and kinetically favourable. The electron transfer kinetics are presented by the peak-to-peak separation, ΔE_p , of anodic and cathodic processes:

$$\Delta E_p = E_p^a - E_p^c \quad (\text{Equation 2.4.0})$$

If peak separation is below 57 mV, the kinetics are fast and reversible. As the kinetics become slower, the peak-to-peak separation increases, as a greater electrical driving force - overpotential is needed.

The peak current value for the reversible diffusion limited process is described by the Randles- Ševčík equation:²⁴

$$I_p = 0.4463 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A D^{1/2} c v^{1/2} \quad (\text{Equation 2.4.1})$$

where n is the number of electrons, F is the Faraday constant (96485 C mol⁻¹), R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), T is the Kelvin temperature, A is the electrode area, D is the diffusion coefficient, c is the concentration and v is the scan rate.

The voltammetric data allows a fundamental understanding of the electrochemical system; therefore underpinning the production of the electrochemical system related to the sensor. In practical applications, greater sensitivity can be accomplished if pulsed potential waveforms are employed. This has resulted in the development of several alternative voltammetric methods, closely related to the cyclic voltammetry approach described above. There are several excellent books available to the reader which provide an in-depth coverage of the subject.^{22,24,25}

2.5.4 Chronoamperometry

Chronoamperometry is a potential-controlled based technique where the current response is measured as a function of applied potential. The technique involves setting the potential of the working electrode from a value at which no faradaic current flows to a value at which the surface concentration of redox species is zero as illustrated in Figure 22 (a). The potential can

be generated in the form of steps, pulses or waves. If the reaction is carried out at a stationary working electrode under non-stirring conditions, mass transport process is solely controlled by diffusion. Under these conditions, the resulting current-time transient is the function of changing concentration gradient in the vicinity of the electrode surface. This includes a gradual extension of the diffusion layer coupled with the depletion of the reactant, resulting in the decrease of the concentration profile slope with a time (Figure 22 (b)).

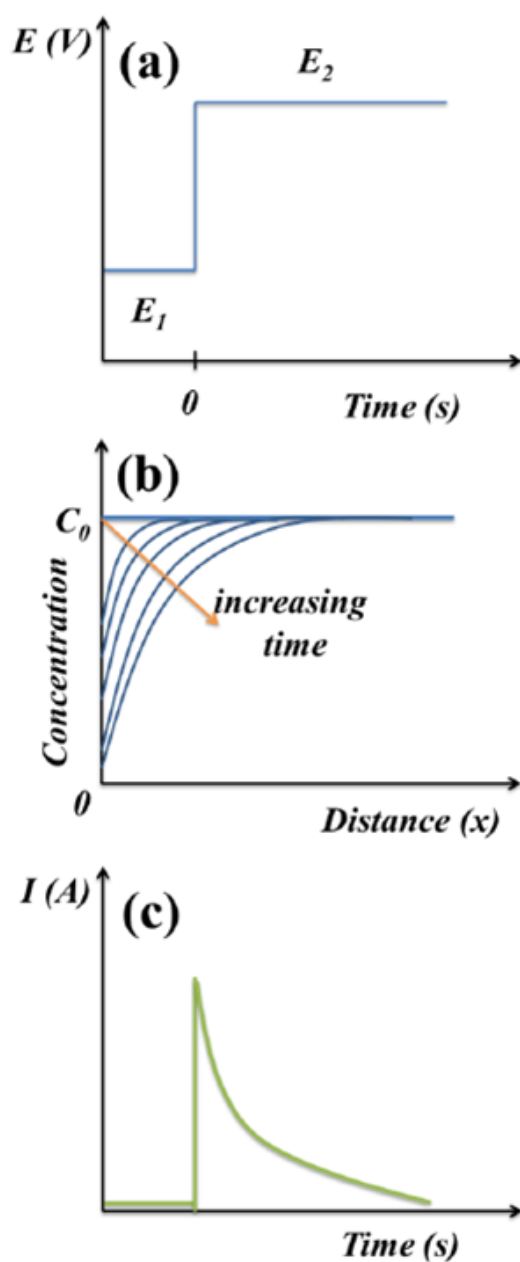


Figure 22 (a) potential-time dependence of chronoamperometric measurement; (b) change of concentration profiles with time; (c) resulting current-time transient, adapted from²²

The associated current recorded at a planar electrode decays with time (Figure 22 (c)). It is described by the Cottrell equation:²²

$$I(t) = \frac{nFAcD^{1/2}}{\pi^{1/2}t^{1/2}} = kt^{-1/2} \quad (\text{Equation 2.4.2})$$

A constant dependency with $t^{-1/2}$ is also known as ‘Cottrell behaviour’. Deviation from Cottrell behaviour generally happens over 100 s due to natural convection.

Electroanalytical applications of chronoamperometry include the measurement of diffusion coefficients of redox species. The techniques can be also applied for electrodeposition studies. The latter will be further discussed in Chapter 5.

2.5.5 Chronocoulometry

Chronocoulometry is another type of potential-controlled technique where the charge is measured as a function of time. This is achieved by integrating the current generated by the potential step. Chronocoulometry is found to be particularly useful for adsorption studies due to possibility to distinguish and separate the charge arising from adsorbed and solution redox species. A resulting charge (Q) versus square root of time ($t^{-1/2}$) transient yields an intercept at $t=0$ that represents the sum of the charge associated with the reaction of the adsorbed molecules double-layer charging.²⁰ The latter can be measured in an identical experiment in the blank solution. If this value is further subtracted from the resulting charge (Q), the adsorption charge can be estimated. This technique was employed in order to investigate the adsorption properties of diamond materials discussed in this thesis.

2.5.6 Rotating Disk Electrode

In a case when an electrochemical experiment should provide an efficient and reproducible mass transport of the redox species, rotating disk electrode can be applied. As presented in

Figure 23, rotating disk electrode consists of vertically aligned motor which is rotated with constant angular velocity, ω , perpendicular to the plain disk surface:

$$\omega = 2\pi f \quad (\text{Equation 2.4.3})$$

where f is the rotation speed (rps).

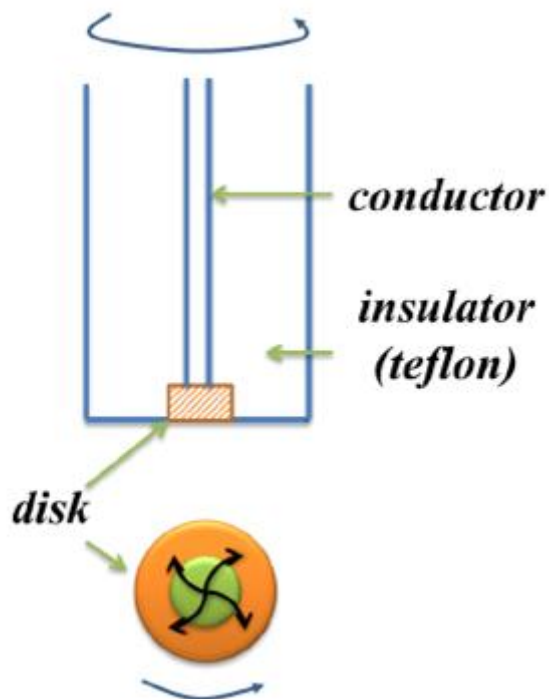


Figure 23 Scheme of rotating disk electrode

Due to this motion, the solution in the adjacent layer develops a radial velocity that transfers it away from the disk centre.²² This solution is then restored by a flow normal to the surface. Thus, rotating disk electrode acts as a pump that brings a fresh fluid from the bulk. The diffusion layer thickness is given by:

$$\delta = 1.61D^{1/3}\omega^{1/2}\nu^{1/6} \quad (\text{Equation 2.4.4})$$

where D is the diffusion coefficient and ν is the kinematic viscosity.

The limiting current for a reversible system depends on the square root of the angular velocity:

$$I_{lim} = nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c \quad (\text{Equation 2.4.5})$$

where n is number of electrons, F is the Faraday constant, A is electrode area, D is diffusion coefficient, ω is angular velocity and ν is the kinematic viscosity.

2.5.7 Electrochemical Impedance Spectroscopy

Electrochemical Impedance spectroscopy (EIS), also known as dielectric spectroscopy, is an electrochemical technique that measures the impedance of a system over a range of frequencies. In an EIS measurement, a small alternating current (AC) is applied to a working electrode which is held at the potential of interest where redox species can be transformed. Due to the presence of the alternating current, a transient state arises at the electrode during each half-period, and the state attained in any half-period changes to the opposite state during the next half-period.²³ These changes are constantly repeated across a range of AC frequencies, and the system is referred as quasisteady (i.e. its average state is time invariant). The data obtained in the measurement can be presented graphically as a Nyquist plot that is shown in Figure 24.

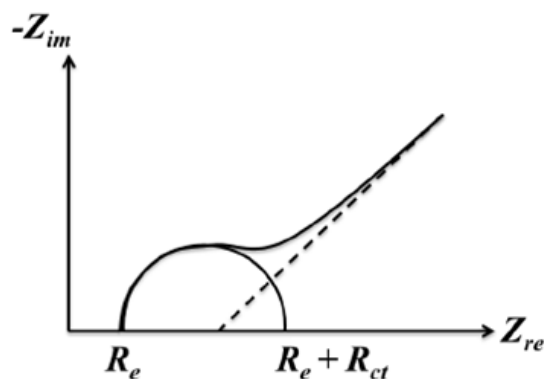


Figure 24 Typical Nyquist plot of EIS measurement

The analysis of the data is accomplished by the design of an equivalent circuit model that is related to the physical components of the electrochemical cell (Figure 25).

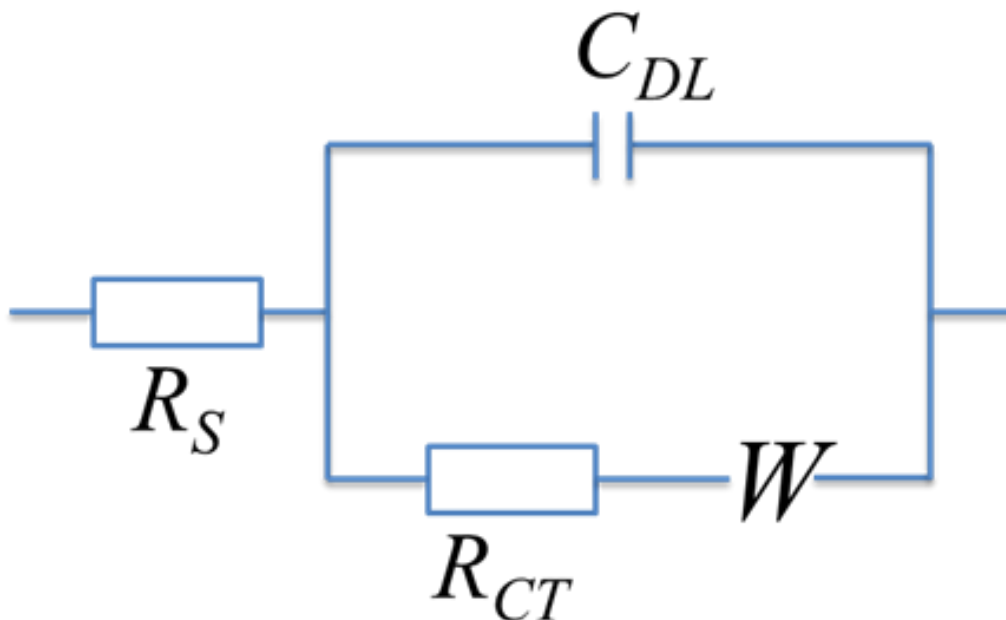


Figure 25 A model of Randles circuit, where R_S is the bulk solution resistance, R_{CT} is the charge transfer resistance, Z_W is the Warburg resistance and C_{DL} is the double layer capacitance

This allows various kinetic and electrical parameters of the redox system to be determined with great precision. At the electrode interface, three layers can be distinguished: (1) the double layer; (2) the diffusion layer and (3) the bulk solution. Due to the application of an alternating current, the alignment of ions and solvated counter ions along the electrode interface takes place, resulting in the formation of the double layer with an associated capacitance, C_{DL} . In the EIS measurement, the charge transfer resistance, R_{CT} , caused by the diffusion of the redox molecule, is influenced by the potential of the redox reaction at the electrode interface as well as the activation barrier formed in the result of electrostatic and steric hindrance.²⁶ R_S is associated with solution resistance, whereas the Warburg impedance,

Chapter Two – Experimental Theory and Techniques

Z_W , describes the difficulty of mass transport of the redox species. The values of C_{DL} and R_{CT} characterise with a high degree of sensitivity the changes in the electrode/solution interface.

2.6 References

- 1 Hertz, H. Ueber einen Einfluss des ultravioletten Lichtes auf die electrische Entladung. *Annalen der Physik* **267**, 983-1000, doi:10.1002/andp.18872670827 (1887).
- 2 Paar, H. *Introduction to Advanced Quantum Physics*. (Wiley, 2010).
- 3 Einstein, A. Motion of suspended particles in stationary liquids required from the molecular kinetic theory of heat. *Ann. Phys. (Weinheim, Ger.)* **17**, 549-560 (1905).
- 4 Einstein, A. Heuristic viewpoint on the production and conversion of light. *Ann. Phys. (Weinheim, Ger.)* **17**, 132-148 (1905).
- 5 Watts, J. F. *An introduction to surface analysis by XPS and AES*. (New York Chichester : Wiley, 2003).
- 6 Briggs, D. & Editor. *Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy*. (Heyden, 1977).
- 7 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 8 <http://www.casaxps.com/>.
- 9 Neal Fairley, A. C. *The Casa cookbook*. (2005).
- 10 Walton, J. *Peak fitting with CasaXPS : a Casa pocket book*. (Knutsford : Acolyte Science 2010).
- 11 C.D. Wagner, W. M. R., L.E. Davis, J.F. Moulder. *Handbook of X-ray photoelectron spectroscopy*. (Perkin-Elmer Corporation, Physical Electronics Division, 1979).
- 12 Huefner, S. *Photoelectron Spectroscopy: Principles and Applications, Second Edition*. (Springer, 1996).
- 13 Wagner, C. D. *et al.* Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *SIA, Surf. Interface Anal.* **3**, 211-225, doi:10.1002/sia.740030506 (1981).
- 14 Adamson, A. W., Gast, A. P. & Editors. *Physical Chemistry of Surfaces, Sixth Edition*. (Wiley, 1997).
- 15 Stokes, D. *Principles and practice of variable pressure/environmental scanning electron microscopy (VP-ESEM) [electronic resource]*. (Chichester, U.K. : Wiley, 2008).
- 16 Praver, S. & Nemanich, R. J. Raman spectroscopy of diamond and doped diamond. *Philos. Trans. R. Soc. London, Ser. A* **362**, 2537-2565, doi:10.1098/rsta.2004.1451 (2004).
- 17 Atkins, P. W. a. *Atkins' physical chemistry*. Tenth edition.. edn, (Oxford : Oxford University Press, 2014).
- 18 Ager, J. W., III, Walukiewicz, W., McCluskey, M., Plano, M. A. & Landstrass, M. I. Fano interference of the Raman phonon in heavily boron-doped diamond films grown by chemical vapor deposition. *Appl. Phys. Lett.* **66**, 616-618, doi:10.1063/1.114031 (1995).
- 19 Hammond, C. *The basics of crystallography and diffraction*. 3rd ed.. edn, (Oxford : International Union of Crystallography/Oxford University Press, 2009).
- 20 Brown, W. *Dynamic light scattering : the method and some applications*. (Oxford : Clarendon Press, 1993).
- 21 Malvern, V. *OmniSIZE software*, <<http://www.malvern.com/en/support/product-support/software/Viscotek-802-OmniSIZE-software-update-v3-0-0-296.aspx>> (
- 22 Wang, J. *Analytical Electrochemistry*. (John Wiley & Sons, 2000).
- 23 Bagotskiĭ, V. S. *Fundamentals of electrochemistry [electronic resource]*. 2nd ed.. edn, (Hoboken, N.J. : Wiley-Interscience, 2006).

Chapter Two – Experimental Theory and Techniques

- 24 Compton, R. G. & Banks, C. E. *Understanding Voltammetry*. (Imperial College Press, 2011).
- 25 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley & Sons, 2001).
- 26 Xu, Q. & Davis, J. J. The Diagnostic Utility of Electrochemical Impedance. *Electroanalysis*, n/a-n/a, doi:10.1002/elan.201400035 (2014).

3 Chapter Three – Decorated nanostructured diamond electrodes: preparation and electrochemistry

3.1 Introduction

This chapter discusses the preparation and characterisation of nanostructured diamond electrodes, decorated with platinum (Pt) particles. The preparation of the nanostructured diamond electrode involves the electrodeposition of Pt nanoparticles on the diamond electrode surface, after which the structure is treated with either an oxygen plasma or an hydrogen plasma. In the former treatment, the Pt particles serve as a hard resist during the oxygen plasma etching of the diamond, yielding structures consisting of Pt particles located on the top of diamond nanorods. In the latter treatment, the Pt catalysed gasification of diamond in the hydrogen plasma occurs, leading to the localisation of the Pt particles in nanopits on the electrode interface. The mechanism of diamond nanostructuring under the hydrogen plasma treatment has been hypothesised in several publications; although no experimental evidence was offered to confirm the hypothesis.¹⁻⁵ The experiments carried out in this chapter provide further insight and clarify the suggested mechanism. The electrochemical activity of the nanostructured diamond electrodes with regard to the electrochemical oxidation of both glucose and methanol is discussed in this chapter. This work demonstrates that the hydrogen plasma treatment provides a viable route for the preparation of Pt decorated electrodes with significantly improved chemical stability.

The production of nanostructured diamond electrodes described in this thesis was carried out in collaboration with the laboratory of Professor Christoph Nebel at the Fraunhofer Institute of Applied Solid State Physics (Freiburg, Germany).

3.1.1 Unmodified nanostructured diamond

Boron-doped diamond has been established as an electrode material with excellent performance in electroanalysis, water purification, electrosynthesis, fuel cells and energy harvesting due to its exceptional chemical stability, wide potential window, low signal-to-background current ratio and variable electrical resistivity controlled by dopant concentration.⁶⁻¹² The modification of boron-doped diamond electrodes (BDEs) with catalyst nanoparticles (NPs) has significantly broadened its electrochemical applications.¹³⁻¹⁷ The preparation of platinum (Pt) decorated BDEs in particular is a subject of significant research in connection with fuel cell technologies and electrochemical sensors.¹⁸⁻²⁰ In order to find an effective preparative route, the electrodeposition of Pt on BDEs has thus been extensively studied.^{15,21,22} A major problem is that the deposited Pt shows poor adhesion to the underlying diamond electrode; it therefore tends to be lost from the electrode during electrochemical applications. A range of methods have been studied to overcome this problem. These have included the ion implantation of Pt and co-deposition of Pt and diamond during CVD growth of the electrode structure.^{23,24} However, all of these methods are problematic. During co-deposition of Pt and diamond, the Pt nanoparticles become buried in the diamond lattice so lose their catalytic activity. Pt ion implantation damages the electrodes and also leads to burial of the Pt, therefore hindering the overall electrochemical performance.

There has also been interest in diamond electrochemistry in the use of nanostructured diamond which has recently become available for electrochemical sensing, DNA sequence technologies, molecular filter applications and energy conversion systems.²⁵⁻³² Nanostructured diamond is available in the form of nanograss, also known as nanorods or nanowires) and nanopits (or nanopores) as presented in Figure 26.

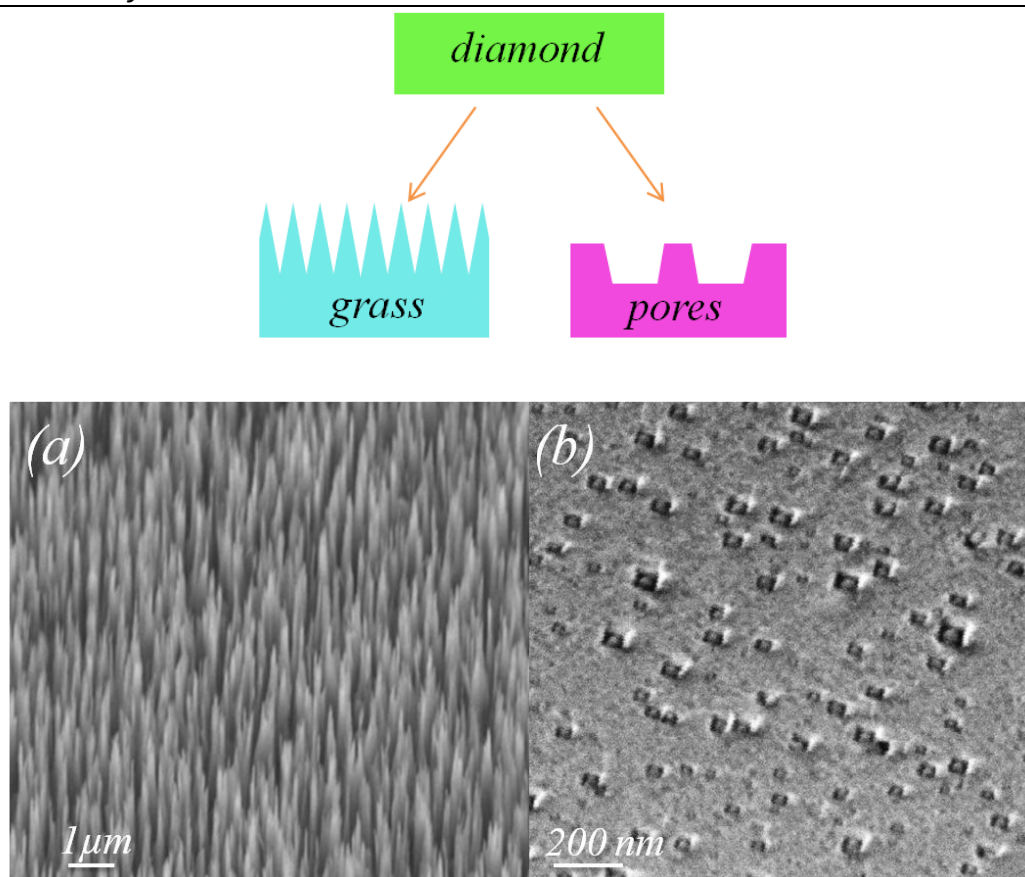


Figure 26 Schematic illustration of unmodified diamond nanograss and nanopores structures; (a) vertically aligned nanograss, reprinted from³³, (b) nanopores in the diamond surface, reprinted from³⁴

When used as electrodes, nanostructured diamond has several advantages over the planar diamond as it provides greater electrode surface area, lower detection limits and an increased signal-to-noise ratio in electrochemical sensing, as well as the possibility to conduct spatially and temporally resolved electrochemical measurements.³⁵ In comparison to a non-modified plain diamond electrode, an enhanced electrochemical detection of glucose,³⁶ dopamine,³⁷ tryptophan,³⁸ catechol³⁹ and diapenem⁴⁰ has been achieved on a non-modified diamond nanograss electrode. Nebel et al have shown that vertically aligned diamond nanowires can also be successfully employed for the sensing of DNA hybridisation in the picomolar (10^{-12} mol L⁻¹) range.⁴¹

The nanostructuring of diamond is technologically challenging due to exceptional hardness and inertness of the material. Several methods based on the hot filament and bias assisted CVD diamond growth were employed to produce nanosculptured surfaces.^{42,43} However, further implementation of these techniques was hindered due to the lack of control over the diamond geometries as well as poor quality of the diamond materials produced.

In contrast to hot filament and bias assisted CVD diamond growth, effective diamond nanostructuring can be achieved by reactive ion etching as it allows precise control over the structure and does not affect the diamond quality. Reactive ion etching process can be described in three main steps:⁴⁴

- (i) an introduction of a plasma resistive mask on a diamond sample;
- (ii) subsequent treatment of the mask modified diamond sample with the reactive ion plasma;
- (iii) chemical removal of the mask. In the etching experiment, a diamond sample is placed in a vacuum chamber which is filled with the gas.

An application of a strong oscillating electric field in the chamber results in the generation of the plasma consisting of reactive ions. These ions interact with the unmasked diamond by means of chemical etching and physical sputtering and etch the diamond material away, whilst the areas covered with the mask remain untouched. Another type of diamond etching is catalytic etching. In this process, the mask deposited onto the diamond sample acts as a catalyst and dissolves the diamond material, forming pores and channels on the surface.

3.1.2 Nanostructured diamond modified with catalyst particles

When such a nanotextured boron-doped diamond is modified with useful electrocatalyst nanoparticles, the range of the compounds probed and the detection limits achieved can be

significantly improved. For example, a strategy based on the preparation of nanostructured diamond modified with catalyst nanoparticles was used for the development of a potential biosensor platform.⁴⁵ In particular, B-doped diamond nanograss, produced by the maskless oxygen plasma etching, was decorated with Ni(OH)₂ particles by electroreduction in order to anchor histidine-tagged peptides.⁴⁵ However, the electroreduction step resulted in the catalyst nanoparticles being deposited everywhere on the nanograss.

3.2 Aims of the project

This work investigates the ways to produce Pt decorated, nanostructured diamond electrodes, which can demonstrate both enhanced Pt catalyst stability whilst also achieving better defined spatial selectivity in the location of the catalyst.

The novel two-step strategy developed during this project commences with the controlled Pt electrodeposition on a planar diamond electrode, which is followed by an etching step, either in an H₂ plasma to produce diamond nanopits with Pt nanocatalyst inside or in an O₂ plasma to produce diamond nanorods with Pt nanocatalyst on top which are schematically presented in Figure 27. In the H₂ plasma etching process, Pt catalyses the graphitisation and subsequent gasification of diamond in the atomic hydrogen rich environment; in the O₂ plasma etching process the deposited Pt particles serve as a hard etch resist.

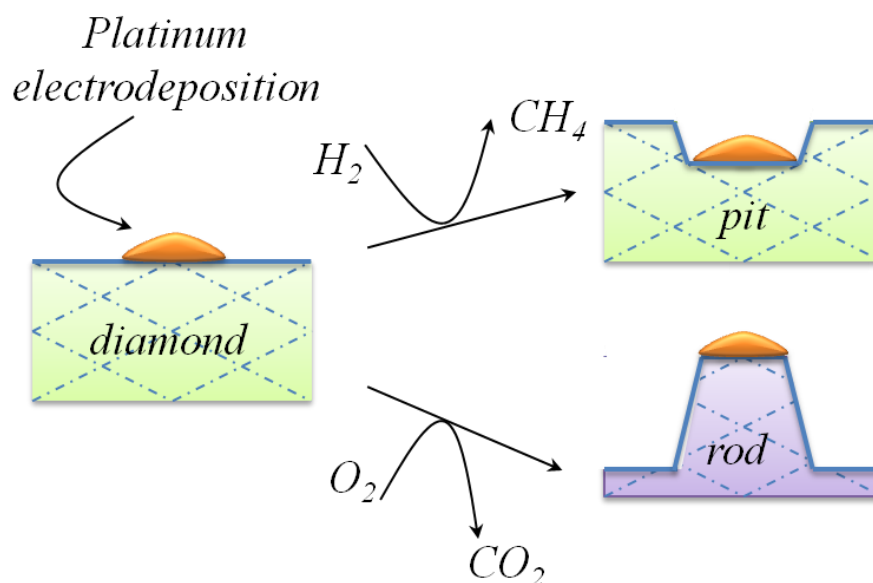


Figure 27 Schematic presentation of diamond texturing strategies

The aim of this project was to systematically study the Pt modified nanostructured electrodes prepared in this way and compare them against Pt modified planar diamond electrodes. In this project the relationship between the geometry of the textured surface and the stability of the nanoparticles was investigated. The application of Pt modified nanostructured diamond for electrochemical oxidation of methanol and glucose was demonstrated.

3.3 Experimental Methods

3.3.1 Electrochemical measurements

Prior to utilisation, plain polycrystalline boron-doped diamond electrodes (from Element Six Co, $10 \times 10 \times 0.6$ mm size, $[B] > 10^{20} \text{ cm}^{-3}$) were cleaned using the following procedure:

- (i) the electrodes were polished for 3 min by $0.3 \mu\text{m}$ alumina powder to remove any physically adsorbed contaminants at the electrode surface;
- (ii) the electrodes were subsequently placed in the distilled water and sonicated in the ultrasonic bath for 10 min to ensure the removal of alumina species;

- (iii) this was followed by a hot *aqua regia* cleaning procedure (60 min, 60°C);
- (iv) the electrodes were then thoroughly rinsed with distilled water and sonicated again in distilled water for 10 min.

A μ -AUTOLAB III electrochemical workstation (Eco-Chemie, Netherlands) was used for all electrochemical measurements. A standard three-electrode configuration was employed with a boron-doped diamond electrode as a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The diamond electrode was incorporated in a PTFE holder, so that a circular area of 0.4 cm^2 was exposed to a working solution. In order to create a reproducible surface termination on the electrode prior to electrodeposition, the latter was conditioned by potential cycling in 0.1 M nitric acid between -1.5 V and 2.5 V, which standardly yields a hydrophilic surface containing a high concentration of oxygen functionalities such as hydroxyl, carbonyl and carboxyl species.

Platinum nanoparticles were electrodeposited from a deaerated 2 mM K_2PtCl_6 in 0.1 M H_2SO_4 solution *via* potentiostatic method at a potential of -0.2 V vs. Ag/AgCl for 100 s. The electrochemical active area (EAA) of the electrodes was estimated from cyclic voltammetry (CV) recorded in 0.1 M H_2SO_4 at a scan rate of 0.05 Vs^{-1} .

3.3.2 Diamond nanostructuring procedure

In order to produce the diamond nanostructures, the protocol that was developed at the Fraunhofer Institute for Applied Solid State Physics was used. This protocol is based on the previous detailed studies of the plasma etching of diamond.^{2,33,46,47}

Diamond structuring in the form of nanopits was achieved *via* catalytic etching in an hydrogen plasma at 900°C for a duration of 90 min in accordance with the method described previously.⁴⁷ The base H_2 pressure in the induction furnace was 500 mbar with a 100 SCCM

H₂ flow rate. The photograph of the apparatus employed for the hydrogen catalytic etching is presented in Figure 28.

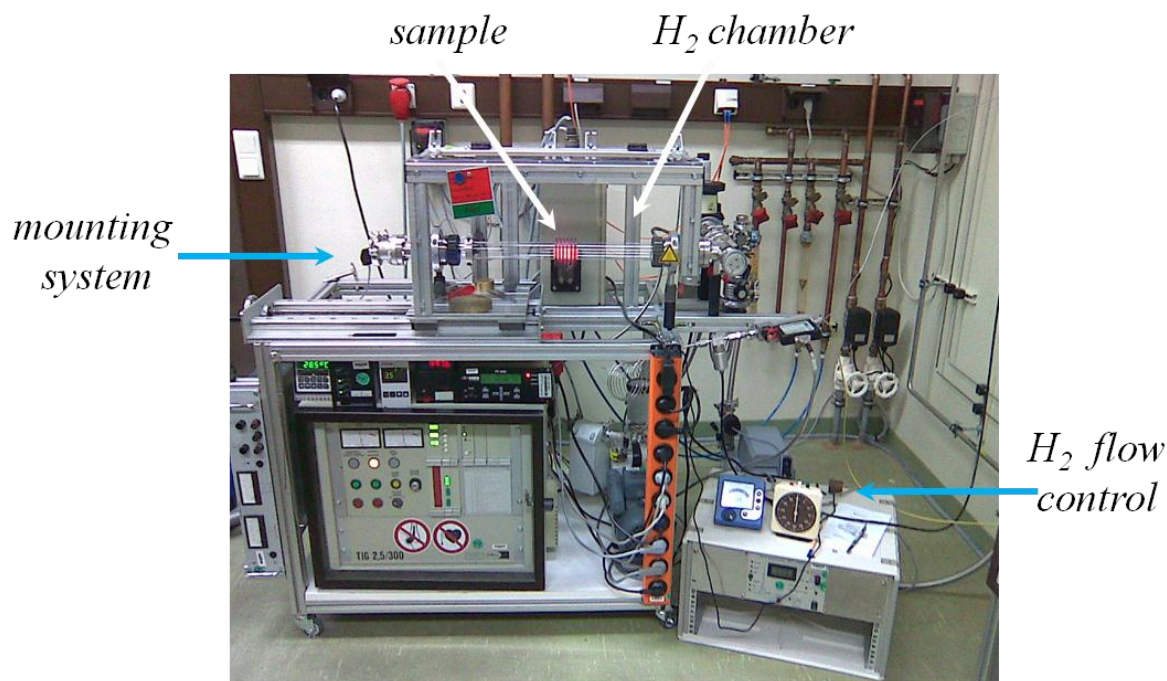


Figure 28 Photograph of hydrogen induction furnace used for catalytic etching of boron-doped diamond electrodes

Diamond structuring in the form of nanorods was performed via oxygen inductive coupled plasma etching in accordance with the method described earlier.⁴⁸ The samples were kept at the temperature of 23°C, a pressure of 5×10^{-2} mbar, oxygen gas flow 20 SCCM and a power of 1000 W for 2 min.

3.3.3 Morphology and microstructure characterisation

A scanning electron microscope with a 20 kV acceleration voltage was used to examine the surface morphology. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a hemispherical analyser and Mg K α (1253.6 eV) X-ray source. The survey scans and the high resolution scans were measured at 50 eV energy pass with 0.5 eV step and at 20 eV energy

pass with 0.1 eV step respectively. The data recorded was analysed by CasaXPS software.⁴⁹

The peaks were fitted using a Shirley background.⁵⁰

3.3.4 Chemicals

All chemicals (from Sigma-Aldrich, UK) were of analytical grade and used without any further purification. Solutions were prepared using ultrapure water (18.2 M Ω ·cm at 23°C, Millipore water systems, UK). The glucose solutions were prepared in 0.1 M phosphate buffered saline. The methanol solutions were made in 0.1 M H₂SO₄.

3.4 Results and discussion

3.4.1 Morphology and microstructure characterisation

The SEM of a typical plain polycrystalline B-doped diamond surface before Pt deposition is presented in Figure 30 (a). It is comprised of [111], [100] and [110] oriented diamond grains in the size range of 5-50 μ m. Spherical, 200-300 nm in diameter Pt nanoparticles were electrodeposited *via* chronoamperometry at a constant potential of -0.2 V. In order to confirm the formation of Pt nanoparticles on the electrode surface, the cyclic voltammetry was carried out in 0.1 M H₂SO₄ between 0.1 V and -0.3 V at the scan rate of 0.05 V s⁻¹ (Figure 29). Several characteristic peaks arising from the electrochemical activity of Pt nanoparticles are presented in Figure 29. In the cathodic regime, the peaks between 0.05 and -0.25 V are associated with the reduction of H⁺ ions and the resulting formation of H₂ adsorbed monolayers on a differing facets of Pt nanoparticles.^{51,52} At the potential below -0.26 V, the hydrogen evolution reaction can be detected. When the potential is reversed in the anodic scan, the oxidation of the adsorbed hydrogen can be observed.

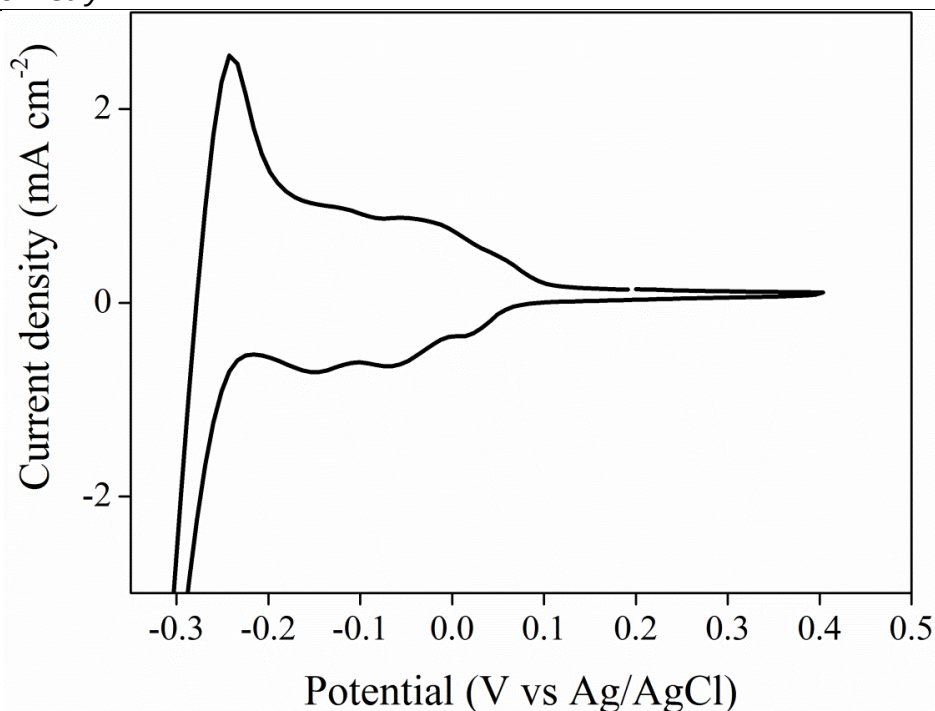


Figure 29 Cyclic voltammetry of Pt decorated boron-doped diamond in 0.1 M H₂SO₄ recorded at the scan rate of 0.05 V s⁻¹.

The hydrogen oxidation charge of 7.5 mC cm⁻² was estimated by integrating the anodic faradic current corresponding to the oxidation of adsorbed hydrogen during the anodic scan. Given that the charge to oxidise a monolayer of hydrogen on the Pt (111) surface is 0.21 mC cm⁻², the electrochemical active platinum area per cm² of the electrode can thus be calculated as 35.9 cm².⁵³ Assuming that the Pt nanoparticles are of a spherical shape, the specific surface area of each particle was derived using the following equation:

$$S = 4n\pi(d/2)^2/m \quad (\text{Equation 3.1})$$

where n is the number of electrons, d is the particle diameter, m is the mass of the whole Pt deposited. The latter is given by:

$$m = \rho V = \frac{4}{3}N\pi(d/2)^3\rho \quad (\text{Equation 3.2})$$

Where N is the number of deposited Pt nanoparticles, ρ is the Pt density (21.45 g cm^{-3}). The electrochemical parameters estimated from cyclic voltammetry are summarised in Table 2.

Table 2 Electrochemical characterisation of Pt decorated boron-doped diamond electrode

Parameter	Value
H-Oxidation Charge (mC cm^{-2})	7.5
Electrochemical Pt active area (cm^2)	35.9
Specific Pt NPs area ($\text{m}^2 \text{ g}^{-1}$)	71.1
Estimated Pt NPs size (nm)	3.9

The SEM image of Pt decorated boron-doped diamond electrode is shown in Figure 30 (b).

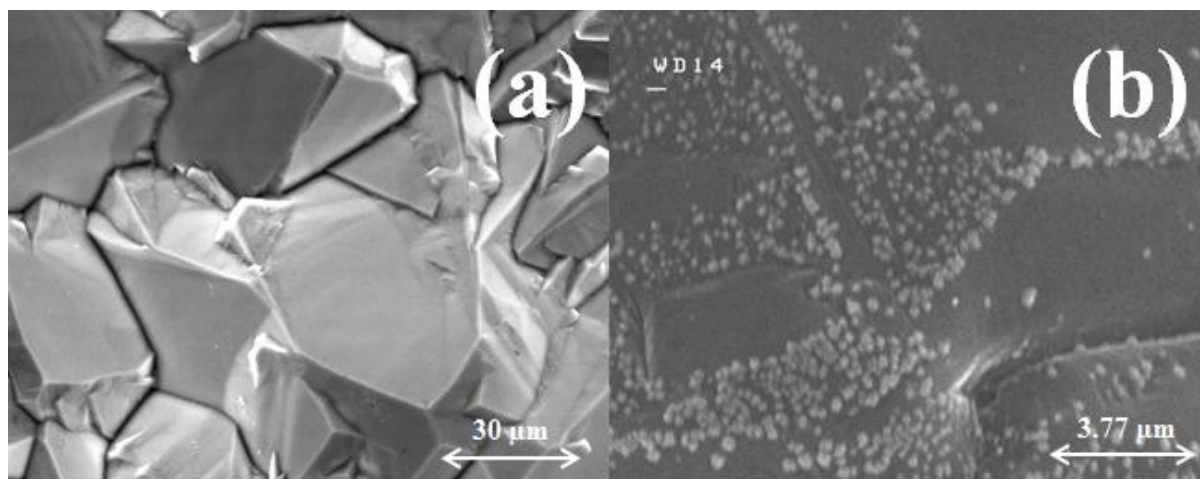


Figure 30 SEM image of (a) polycrystalline boron-doped diamond electrode; (b) Pt nanoparticles deposited on boron-doped diamond electrode

It is interesting to note that during electrodeposition process Pt particles grow preferentially at the edge of diamond grains which is in agreement with the previously reported results.²² Conductive AFM studies⁵⁴⁻⁵⁸ show very heterogenous conductivity across diamond electrode surfaces due to enhanced sp^2 -conductivity of the intercrystalline regions,⁵⁹ the increased number of defects within these regions⁶⁰ and heterogeneity of boron doping⁶¹, all of which could contribute to this observation.

3.4.1.1 Pt decorated diamond textured in the form of nanopits

The Pt decorated plain boron-doped diamond electrode was placed in induction furnace and was etched in an H_2 atmosphere at $900^\circ C$, at a pressure of 500 mbar to produce a Pt decorated nanopits textured surface (Pt_PDE). The SEM image of Pt_PDE diamond electrode is presented in Figure 31 (a). As it can be seen in Figure 31 (b) whilst Pt nanoparticles remain spherically shaped, the pits formed during the etching process have flat sidewall faces, sharply defined edges and certain geometry.

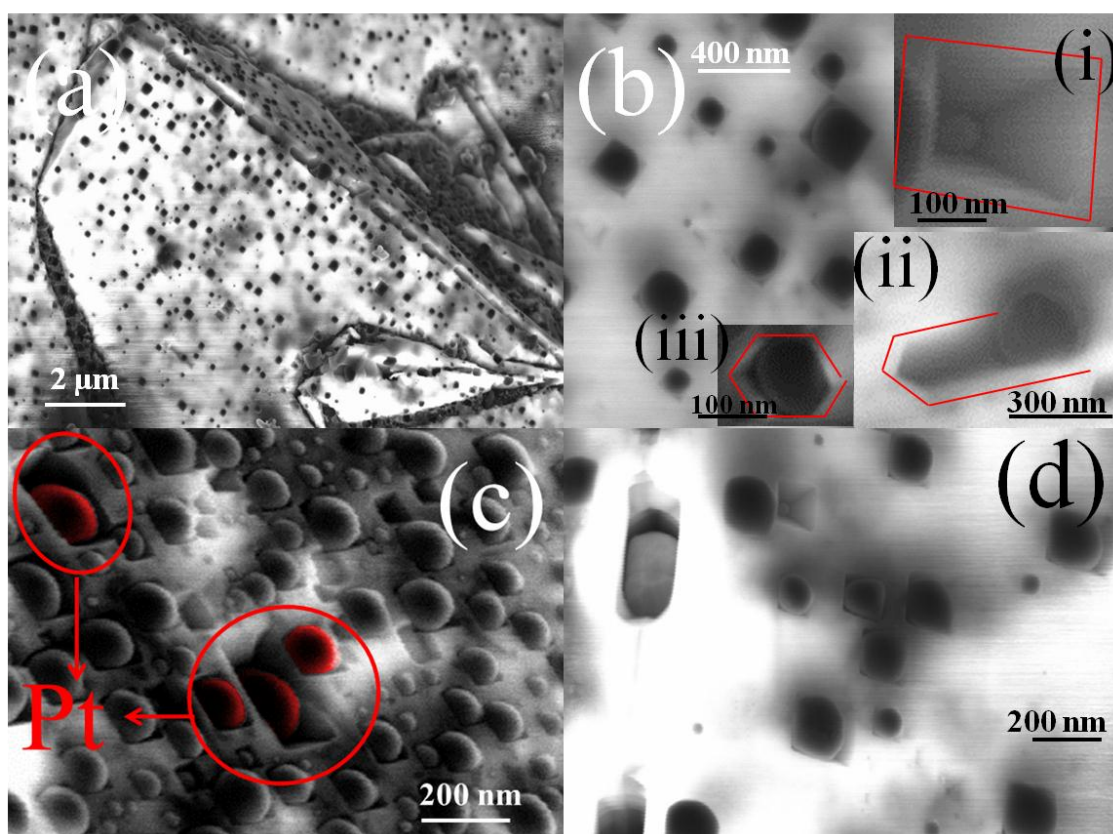


Figure 31 SEM image of (a) Pt decorated boron-doped diamond that is textured in the form of nanopits; (b) Pt etch pits formed, inset (i) four-sided pyramid with Pt nanoparticle inside, (ii) elongated channel containing Pt nanoparticle, (iii) hexagonal pit with Pt nanoparticle; (c) Pt NPs of Pt_PDE are highlighted in red; (d) Pt nanopits at [100] oriented surface

The surface formed includes [100] oriented diamond grains with etch pits in the form of an inverted four-sided pyramid and Pt nanoparticle of ~200-300 nm inside (Figure 31 (b), inset (i), and Figure 31 (c)-(d)). The pore holes in grains with [110] orientation were structured in the form of straight channels (Figure 31 (b), inset (ii)), whereas the etch pits on [111] grains were of hexagonal structure (Figure 31 (b), inset (iii)).⁴⁷ The etch pits tend to be concentrated near the grain boundaries since this is where the Pt is predominantly deposited.

The morphology of the pits depends on the symmetry of the diamond cubic cell in [100], [110] and [111] orientations as well as the etching mechanism. A detailed discussion on the etch pits morphology study can be found in the works of W. Smirnov³⁴, J. Hees, C. Nebel et al⁴⁷ and Sonin³.

In order to understand the geometry of the pits observed in SEM, the etching mechanism should be first considered. The schematic illustration of the etching process is presented in Figure 32.

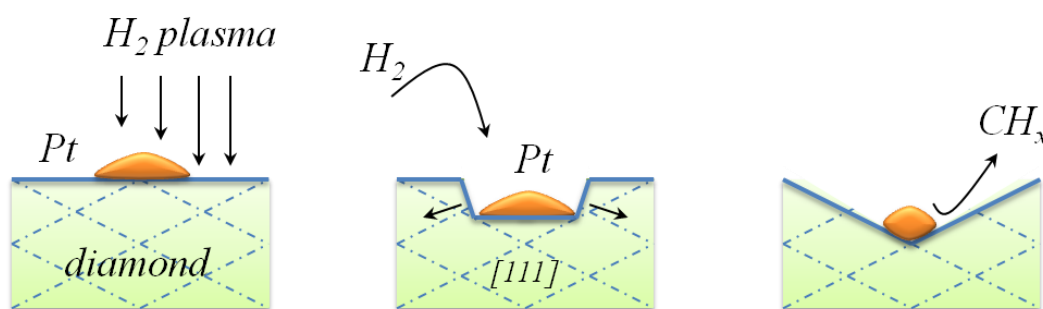


Figure 32 Schematic illustration of catalytic etching mechanism

During the hydrogen plasma etching, the diamond surface below the Pt/diamond interface starts to graphitise due to the formation of amorphous carbon. It is suggested that at 900°C this amorphous carbon can further diffuse into the Pt nanoparticle. Carbon diffusion into Pt

nanoparticle is followed by the precipitation of amorphous carbon at the external Pt/hydrogen interface that is not in contact with diamond surface. At the external Pt interface, hydrogen atoms react with the precipitated amorphous carbon to form methane or CH_x complexes that subsequently evaporate.¹ The process described above allows the Pt particle to move downwards into the forming hole. The rate of the particle movement depends on the density and symmetry of sp³ carbon bonds below the Pt particle, i.e on the diamond crystal orientation. Figure 33 shows the model of sp³ bonded carbon atoms in a face centred cubic diamond cell. The lattice planes with [100], [110] and [111] orientations are highlighted in red. The number of the in plane and out of plane bonds of sp³ carbon atoms in the cell are given in Table 3.³⁴

Table 3 The number of carbon bonds in a diamond face depending on the crystallographic orientation, adapted from³⁴

Plane	In plane bonds	Out of plane bonds (downwards)	Out of plane bonds (upwards)
[100]	0	2	2
[110]	2	1	1
[111]	3	1	0

For the [111] diamond crystallographic orientation, the surface density of carbon atoms is the highest; therefore, the etching rate will be the slowest on such surfaces.

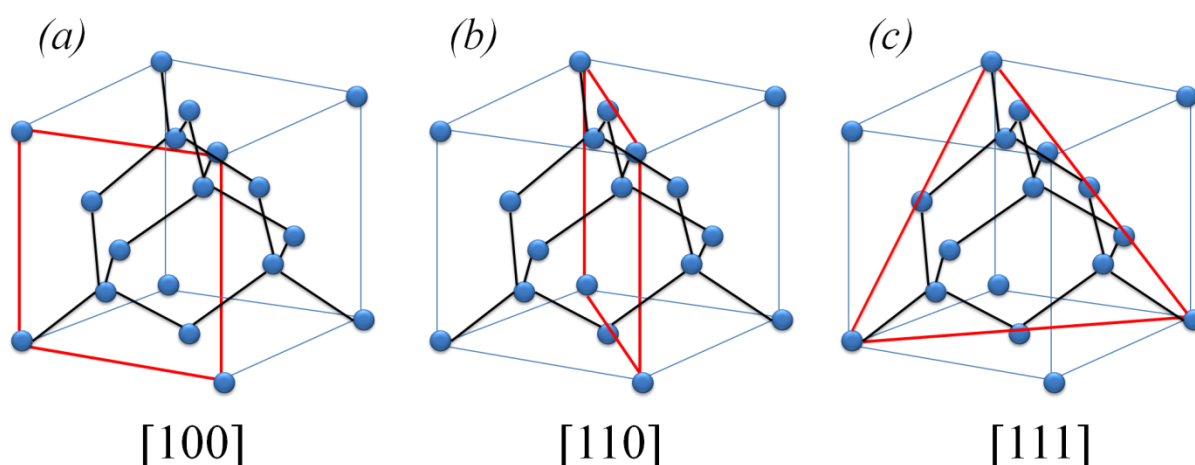


Figure 33 Diamond lattice structure view from [100], [110] and [111] planes

The three dimensional model of the pits structure can be determined by considering a cubic cell of an arbitrary length, a , with the octahedron inside.^{3,34} The latter consists of $[111]$ planes that represent three dimensional diamond structure. Figure 34 (a) illustrates the schematic model of an $[111]$ plane octahedron in a cubic unit cell. The planes of a cubic unit cell are highlighted as they would be visible if the reader looks on the $[100]$, $[110]$ and $[111]$ planes. The associated cross-sections of octahedron are presented in Figure 34 (b). The plain and three dimensional structures of the etch pits are displayed in Figure 34 (c) and (d) respectively.

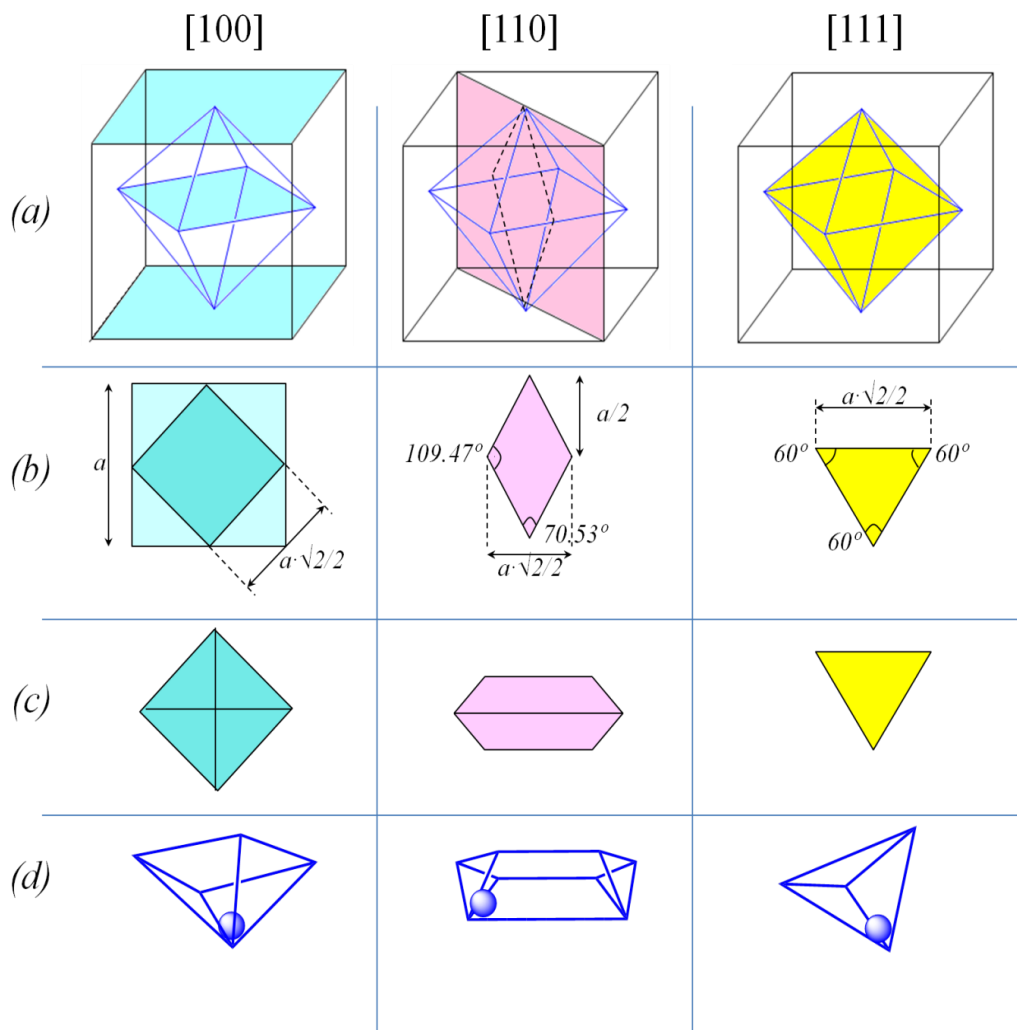


Figure 34 (a) schematic structure of an $[111]$ plane octahedron in a cubic unit cell. The latter is positioned in $[100]$, $[110]$ and $[111]$ orientations; (b) cross-sections through the $[100]$, $[110]$ and $[111]$ planes of the octahedron and

If compared with the SEM image in Figure 31(b), the geometrical structures derived from the considerations above are in a good agreement with the experimental structures of the etch pits in the inset (i), (ii) and (iii), Figure 31(b).

3.4.1.2 Pt decorated diamond textured in the form of nanorods

In order to produce Pt decorated boron-doped diamond textured in the form of nanorods (Pt_RDE), the reactive ion etching was performed in the oxygen plasma at 23°C and a pressure of 5×10^{-2} mbar. The process is schematically illustrated in Figure 35. The platinum particles act as a hard resist. The reactive ion etching occurs by both physical sputtering and ion-enhanced chemical etching,⁶² which in case of O_2 plasmas is achieved through the reaction of the O_2^+ ions with the diamond surface and generation of CO and CO_2 volatile etch products.⁶³⁻⁶⁵

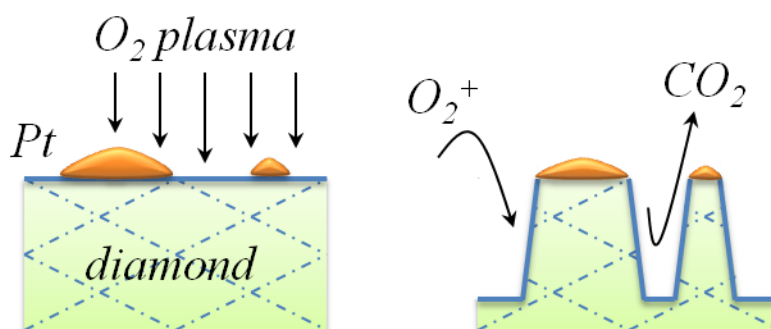


Figure 35 Schematic illustration of reactive ion etching mechanism

The SEM images of the nanorod textured Pt decorated boron-doped diamond formed by O_2 inductive coupled plasma etching of the plain Pt_BDE are shown in Figure 36. The resulting surface is covered by vertically aligned diamond rods of ~ 500 -800 nm height with Pt

nanoparticles approximately 200-400 nm in diameter on top of the rod as shown in a higher resolution image in Figure 36 (c) and (d).

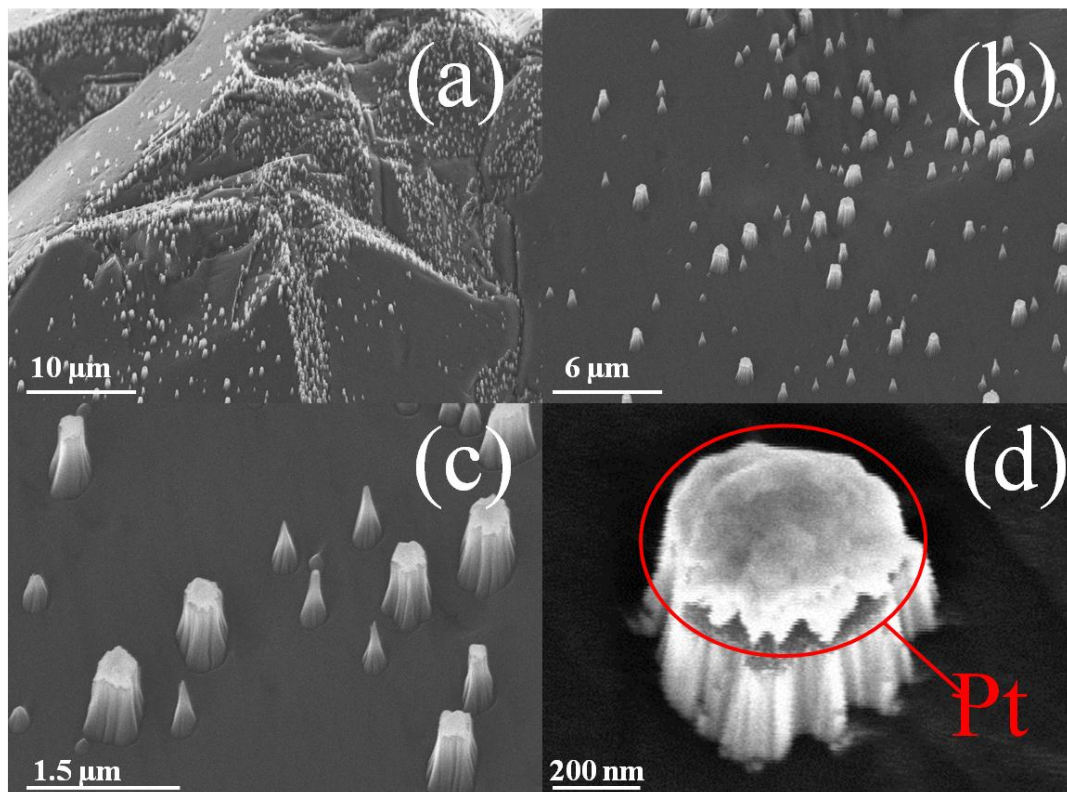


Figure 36 (a) and (b) SEM images of nanorods textured Pt decorated boron-doped diamond that was etched in O₂ plasma; (c) the rods formed; (d) Pt nanoparticle on the top of the rod highlighted in red

As in the case of nanopits, the location of the nanorods is also influenced by the position of the electrodeposited Pt. The rods were mainly observed at the grain boundaries due to the fact that the platinum nanoparticles are located preferably at the grain boundaries (Figure 36 (a)). The minor fraction of rods were formed at the diamond facets. Although this distribution is obviously influenced by the location of the Pt, it is also affected by the nature of the etching process. It was shown previously that for the B-doped diamond the formation of nanorods tends to be especially concentrated along the grain boundaries and areas with increased boron concentration.²⁹ This behaviour was linked to the more intense electron emission from boron

sites in the diamond and the formation of a local electrical field at the vicinity of the boron site. The latter is found to contribute to the formation of the rods in the O₂ plasma etching.²⁹

3.4.2 X-ray Photoelectron Spectroscopy Study

In order to understand the changes in the chemistry of the diamond/platinum interface before and after etching, the samples were analysed using x-ray photoelectron spectroscopy. A typical high-resolution C 1s spectrum of the platinum decorated boron-doped diamond electrode prior to the etching procedure is presented in Figure 37 (a). A C 1s component characteristic of the bulk diamond was positioned at 285.0 eV in each fitting. The peaks at 285.5 eV and 286.6 eV are attributable to C-H_x (x = 2,3) species in polyhydride configurations and hydroxyl surface groups respectively.⁶⁶⁻⁶⁸ The peak at 283.6 eV with the chemical shift of -1.3 eV is generally ascribed to the graphite states involved in π -bonding, which are also known as sp²-defects.⁶⁹ The Pt 4f spectrum of Pt_BDE surface (Figure 37 (b)) presents two well-resolved doublets with the main line of Pt (0) 4f_{7/2} at 72.6 eV and Pt (0) 4f_{5/2} at 76.0 eV respectively; as well as Pt (+4) 4f_{7/2} at 73.7 eV and Pt (+4) 4f_{5/2} at 77.8 eV due to the presence of surface oxide.⁷⁰

The major change in the C 1s spectrum of the Pt_PDE surface after H₂ plasma etching arise from the presence of the peak at 282.7 eV as shown in Figure 37 (c). The raw intensities prior and after etching are compared in Figure 37 (c), inset (i). The chemical shift of -2.3 eV, relative to the bulk diamond at 285.0 eV, is much larger than that of ~-1 – -1.3 eV shift, characteristic of the sp²-defects. The presence of this peak can be explained by the formation of a surface carbide phase PtC_x since the second step of the etching mechanism involves dissolution of the graphitised carbon through the Pt nanoparticle. This observation is also in agreement with the previous XPS data available on Pt-C compounds⁷¹⁻⁷⁵ It is interesting to

note that in comparison to Pt $4f_{7/2}$ peak at 72.6 eV of a plain polycrystalline Pt_BDE, the Pt $4f$ peak of Pt_PDE moves by +0.4 eV after the etching step, as depicted in Figure 37 (d).

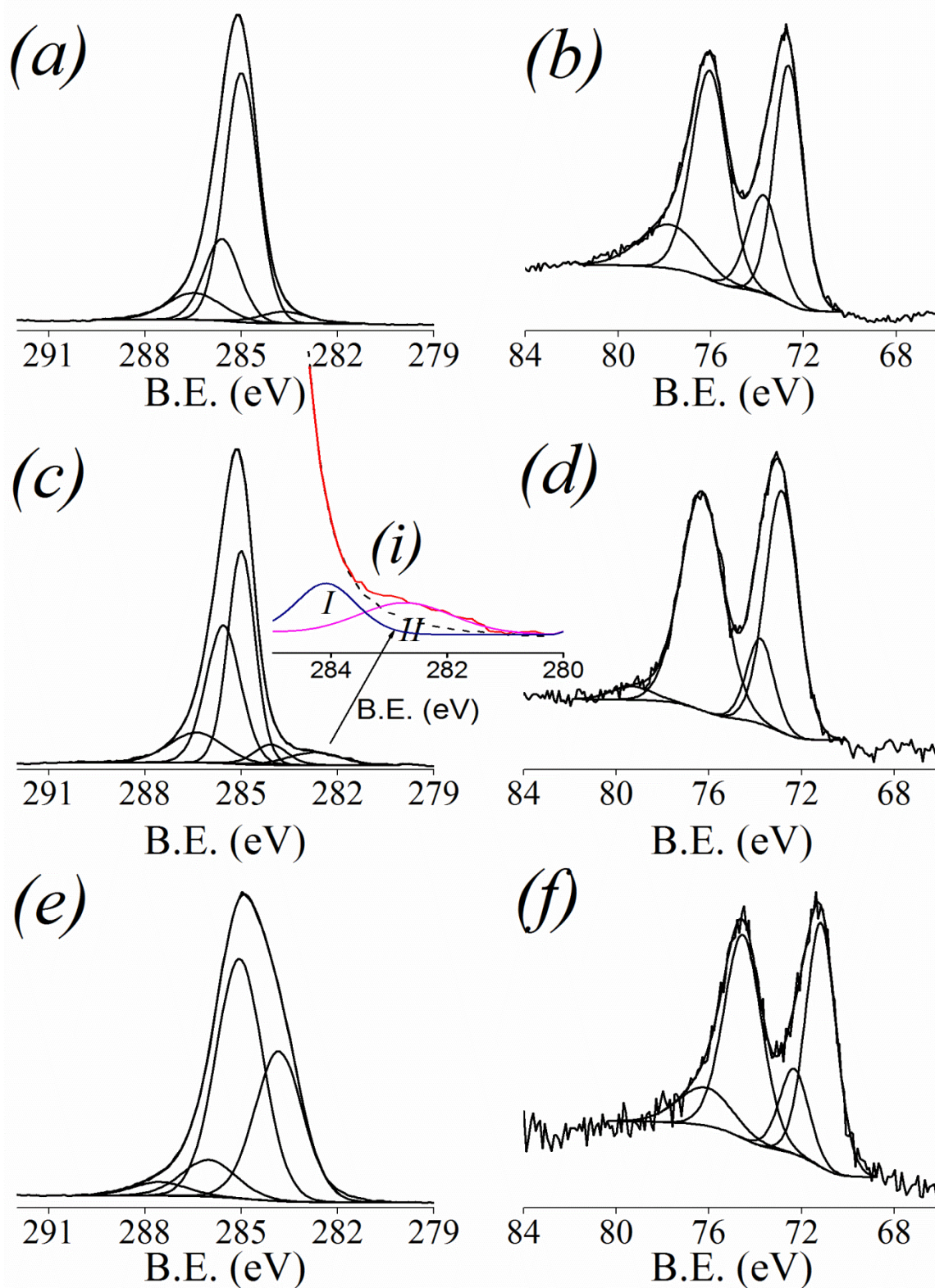


Figure 37 C 1s XPS spectra of (a) Pt_BDE, (c) Pt_PDE with the inset of raw intensities of (---)Pt_BDE and (—) Pt_PDE with (II) C 1s PtCx peak and (I) C 1s sp² defects of Pt_PDE, (e) Pt_RDE; Pt 4f XPS spectra of (b) Pt_BDE, (d) Pt_PDE, (f) Pt_RDE

This charge-shift relationship is associated with a small electron transfer from Pt to C, and supports the carbide phase formation.⁷⁶ A detailed description of XPS binding energies and FWHM can be further obtained in Table 4 and Table 5.

Table 4 XPS binding energies for Pt_BDE, Pt_PDE and Pt_RDE samples

Sample	Binding Energies (eV)								
	C 1s				Pt 4f				
	C-C	C-CHx	-C=O	sp ² def	C-Pt	Pt (0) 4f _{7/2}	Pt (0) 4f _{5/2}	Pt (+4) 4f _{7/2}	Pt (+4) 4f _{5/2}
Pt_BDE	285.0	285.5	286.6	283.6		72.6	76.0	73.7	77.8
Pt_PDE	285.0	285.5	286.5	283.9	282.7	73.0	73.8	76.4	79.4
Pt_RDE	285.0	285.9	287.6	283.8		71.2	72.4	74.7	76.3

Table 5 FWHM values for Pt_BDE, Pt_PDE and Pt_RDE samples

Sample	FWHM (eV)								
	C 1s				Pt 4f				
	C-C	C-CHx	-C=O	sp ² def	C-Pt	Pt (0) 4f _{7/2}	Pt (0) 4f _{5/2}	Pt (+4) 4f _{7/2}	Pt (+4) 4f _{5/2}
Pt_BDE	1.3	1.5	2.0	1.3		1.6	1.8	1.3	3.0
Pt_PDE	1.3	1.4	2.0	1.4	1.5	1.7	1.9	1.6	2.0
Pt_RDE	1.5	2.0	2.0	1.8		1.7	1.8	1.5	2.4

As presented in Figure 37 (e), the C 1s spectrum of the Pt decorated diamond structured in the form of nanorods (Pt_RDE) was found to contain an increased graphitic carbon peak at 283.7 eV, which is in agreement with the graphitisation character of O₂ inductive coupled plasma etching. The Pt 4f peak (Figure 37 (f)) is very similar to that of Pt 4f of Pt_BDE.

The Pt:C ratio deduced from the spectra using the appropriate sensitivity factors^{49,70} showed that 87% of the initially deposited Pt was lost during the reactive ion etching procedure in the oxygen plasma. This is a result of O₂⁺ ions bombardment, compared to the freshly prepared Pt_BDE sample. In contrast, only 20% of Pt was removed from Pt_PDE during catalytic H₂ etching.

An interesting characteristic feature arising from the analysis of the Pt-C compounds XPS spectra is that the Pt 4f peak asymmetry decreases with the increase of the carbon

content.^{72,77-79} The asymmetry of the Pt $4f_{7/2}$ line is given as the ratio of the left half width to the right half width at half maximum of the peak. In the Pt_BDE and Pt_RDE samples, the Pt $4f_{7/2}$ asymmetry was found to be 1.7, whereas in Pt_PDE, etched in H₂ plasma, the peak asymmetry was 1.1. Therefore, such a decrease suggests the increased carbon content in the Pt phase. This decrease in the asymmetry of the Pt $4f_{7/2}$ peak is related either to the possible gain of the s-like electron density once the Pt *d*-band has been completely filled or to the hybridization of the *d*-level of Pt with the *s-p* levels of C, which contributes to the screening of the scattered electrons and therefore to the reduction of the peak asymmetry.⁸⁰

3.4.3 Electrochemical Characterisation

The electrochemical performance and electrocatalytic stability of the nanotextured electrodes were investigated by cyclic voltammetry in 0.1 M H₂SO₄. Figure 38 (a) and (b) display the cyclic voltammograms of Pt_PDE and Pt_RDE electrodes obtained prior and after the stability tests. In the cathodic scan, as exhibited in Figure 38 (a), a peak associated with the hydrogen adsorption onto Pt facets in the potential range from 0 to -0.25 V is observed. It is followed by the onset of the hydrogen evolution reaction below -0.25 V. In the anodic scan, a peak at -0.26 V is related to the hydrogen desorption process. In order to assess the electrocatalytic stability, the electrodes were cycled during 600 times in 0.1 M H₂SO₄. A slight decrease in the electrochemical signal (red line, Figure 38 (a)) suggests that the catalytic activity of Pt nanoparticles in the nanopits etched diamond can be preserved over a long time. Figure 38 (b) shows CV data recorded at Pt nanorods textured electrode. Although the initial CV scan obtained from Pt_RDE was similar to that of Pt_PDE, the cyclic voltammogram recorded after the long-term stability revealed significant losses in electrochemical activity of Pt nanoparticles located on the top of the nanorods.

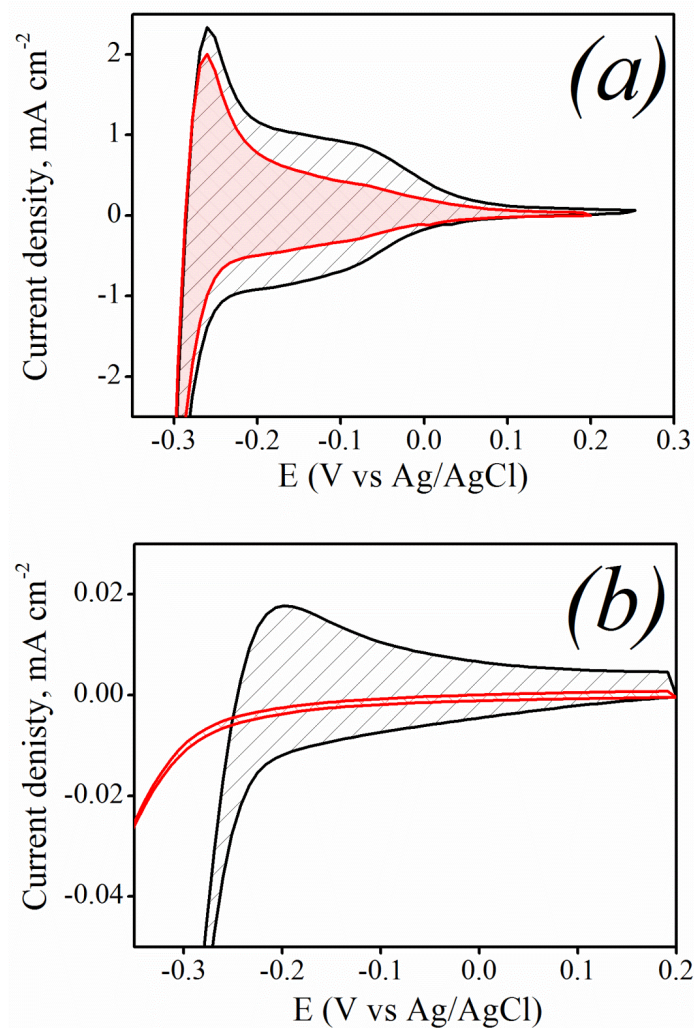


Figure 38 CV in 0.1 M H₂SO₄ of (a) (–) Pt_PDE prior to stability tests, (–) Pt_PDE after stability tests; (b) (–) Pt_RDE prior to stability tests, (–) Pt_RDE after stability tests. All CVs were recorded at 0.05 V s⁻¹.

In accordance with the standard procedure, the electrochemical active area associated with the Pt (EAA) was estimated by integration of the anodic current peak arising from the oxidation of hydrogen adsorbed on Pt, between -0.3 V and 0.1 V.^{81,82}

The EAA decreased as the potential on the electrode was cycled between -0.3 V and 0.1 V, and the calculated Pt loss, normalised to that present at the start of the electrochemical measurements, as a function of the number of cycles, is presented in Figure 39.

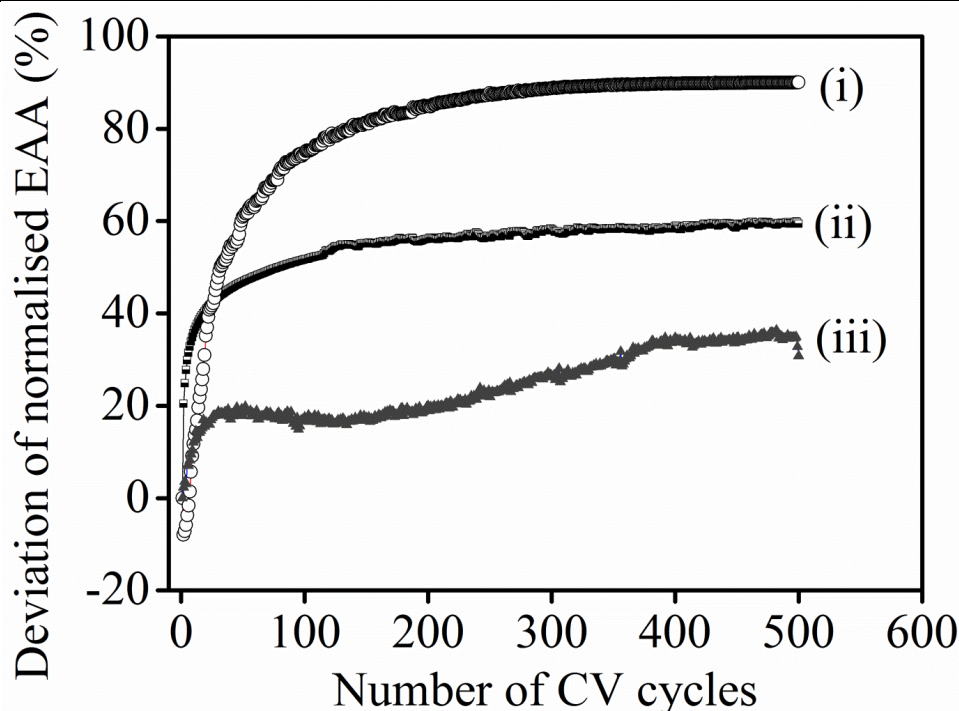


Figure 39 Calculated platinum loss (%) from (i) Pt_RDE, (ii) Pt_BDE, (iii) Pt_PDE electrodes

The loss of electrochemical active area at the Pt_PDE did not exceed more than 35%, whereas 60% and 90% losses were observed at Pt_BDE (Figure 4 (b)) and Pt_RDE (Figure 4 (c)) samples.

It may therefore be concluded that the hydrogen etching treatment presents a straightforward route to enhance the stability of Pt particles on diamond electrodes. This increased stability of the Pt_PDE electrode may be related to the particles being trapped in the diamond pits. However in view of the identified PtC_x phase detected in XPS, it is also possible that the hydrogen plasma treatment, which is carried out at elevated temperatures, enhances the bonding strength at the Pt nanoparticle/diamond interface. The Pt_RDE sample is found to be the least stable, which is perhaps unsurprising given that the Pt nanoparticles are exposed at the top of the pillars. In this type of geometry, the Pt nanoparticles are exposed to the

hydrogen bubbles which are formed during the electrochemical cycling to negative potentials, leading to the physical removal of Pt from the surface.

The areas of the Pt 4f and C 1s peaks displayed in Figure 37 can be used to determine the relative platinum to carbon ratios using the relevant sensitivity factors.⁷⁰ The surface composition measured by XPS prior and after electrochemical cycling in 0.1 M H₂SO₄ is shown in Table 6. The XPS measurements were over the entire active electrode area so determined the total Pt content. It can be seen that 53%, 91% and 30% of Pt remained on Pt_BDE, Pt_PDE and Pt_RDE respectively after the electrochemical experiments, which is in agreement with the stability trend obtained from the decrease of the measured EAA.

Table 6 Pt/C atomic ratios of the diamond nanostructured electrodes before and after atability tests*

Ratios	Pt_BDE		Pt_PDE		Pt_RDE	
	Prior	After	Prior	After	Prior	After
Pt/C ($\times 10^{-2}$)	1.5	0.8	1.2	1.1	0.2	0.06
% Pt retained		53		91		30

***Prior and after stability tests**

This project demonstrated that the hydrogen etching treatment has useful application to improve the stability of the Pt nanoparticles on diamond. This, however, is only of use if the Pt nanoparticles retain their electrocatalytic properties. Therefore, the nanostructured electrodes were tested with regard to the electrochemical oxidation of glucose and methanol. The former was chosen since it is an important step in the detection of glucose using enzyme-free biosensors which often employ Pt nanoparticles.^{83,84} The second was selected since it forms the basis of methanol fuel cells, which again utilise Pt nanoparticles.

Figure 40 (a) shows the cyclic voltammetry wave arising from the electrochemical oxidation and reduction of 1 M glucose at the Pt_PDE electrode. A prominent oxidation wave is seen at 0.6 V and the associated reduction wave occurs at 0.03 V, as expected confirming the Pt

remains electrochemically active in this configuration. This was confirmed since if the Pt on the Pt_PDE electrode is removed by dissolving in *aqua regia* (see Figure 40 (a), red line) no clear redox peaks can be observed when the electrode is exposed to the glucose solution.

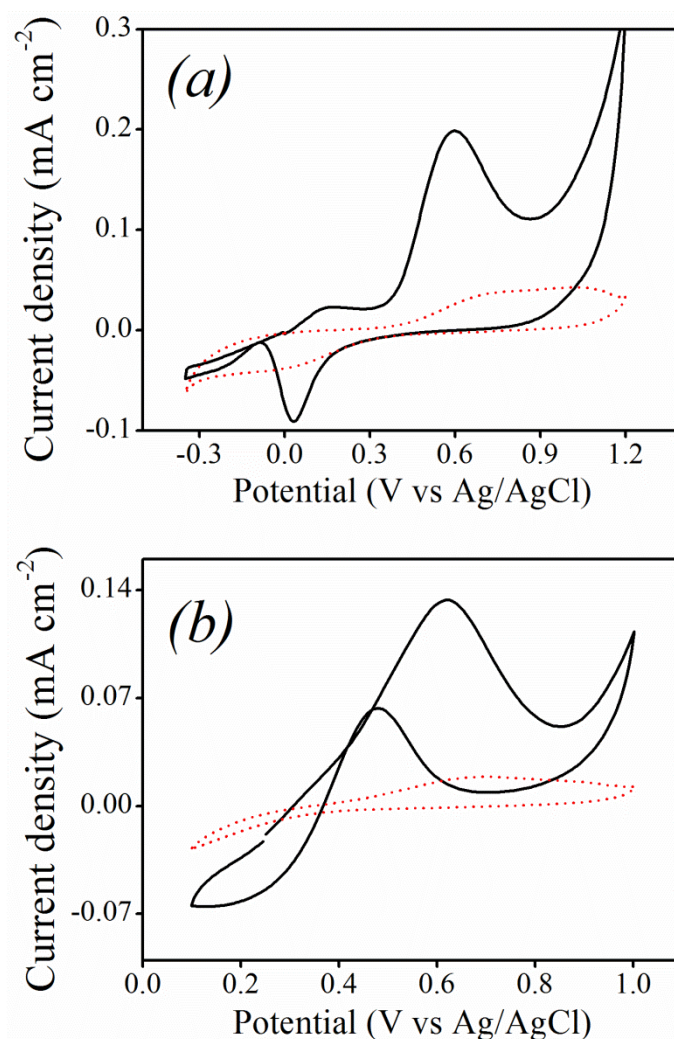


Figure 40 Cyclic voltammograms of (a) (–) Pt_PDE in 1 M glucose, 0.1 M PBS at 0.05Vs⁻¹, (.....) after *aqua regia* treatment, Pt_PDE in 1 M glucose, 0.1 M PBS at 0.05Vs⁻¹; (b) (–) Pt_PDE in 1 M CH₃OH, 0.1 M H₂SO₄ at 0.05 Vs⁻¹, (.....) Pt_PDE after *aqua regia* treatment in 1 M CH₃OH, 0.1 M H₂SO₄ at 0.05 Vs⁻¹

The methanol electrooxidation process was studied by CV in 1 M CH₃OH dissolved in 0.1 M H₂SO₄ solution on the Pt_PDE electrode and data is presented in Figure 40 (b).

The CV recorded is characteristic of a classical methanol oxidation on Pt diamond substrates.⁸⁵ The first peak in the anodic scan represents the increase in methanol oxidation

kinetics which slows at high positive potentials due to the passivation of the Pt. The latter is caused by the adsorption of incompletely oxidised species. A peak is then seen in the cathodic scan at low positive potentials due to the re-oxidation of adsorbed intermediates such as CO_{ads} and the reactivation of the electrode. Again, in order to confirm that the waves observed arise solely from the presence of catalytically active Pt nanoparticles on the Pt_PDE electrode, the Pt was dissolved from the Pt_PDE electrode. The subsequent scan in 1 M CH_3OH , 0.1 M H_2SO_4 solution shows the absence of catalytic activity for methanol electrooxidation.

3.5 Concluding remarks

In Chapter 3, a two-step production process to prepare Pt modified boron-doped diamond, with the Pt present in nanopits or on the top of nanorods, has been demonstrated. The approach involved treating a diamond electrode, with Pt electrodeposited on it, in either O_2 or H_2 plasmas. The mechanism of the diamond nanostructuring in O_2 and H_2 plasmas was discussed in detail in this chapter. The use of X-ray photoelectron spectroscopy has enabled detection of the formation of platinum carbide phase during the catalytic hydrogen plasma etching process which was only hypothesised previously as a part of the etching mechanism. This is the first study of the direct platinum carbide phase detection during the catalytic hydrogen plasma etching.

In this project it was shown that the H_2 plasma treatment yields the electrode structures with the Pt present in nanopits of differing geometry. The principles determining the geometry of the etch pits were discussed in this chapter. It was shown that Pt nanoparticles in etch pits are significantly more stable than Pt simply electrodeposited on planar electrodes, and remain electrochemically active after the plasma treatment over the long-term. This therefore presents a straightforward route for the preparation of Pt-decorated diamond electrodes which

show improved stability over those formed without the plasma treatment. Electrochemical activity has been demonstrated with regard to the enzyme-free oxidation of glucose and the oxidation of methanol.

In contrast to the H₂ plasma etching, it was shown that the O₂ plasma treatment removes a significant amount of the Pt, and the resulting electrode structures readily lose most of the remaining Pt (from on top of the nanorods) when electrochemically cycled.

3.6 References

- 1 Tomita, A. & Tamai, Y. Optical microscopic study on the catalytic hydrogenation of graphite. *The Journal of Physical Chemistry* **78**, 2254-2258, doi:10.1021/j100615a015 (1974).
- 2 Mehedi, H. A. *et al.* Formation of oriented nanostructures in diamond using metallic nanoparticles. *Nanotechnology* **23**, 455302 (2012).
- 3 Sonin, V. M., Chepurov, A. I. & Fedorov, I. I. The action of iron particles at catalyzed hydrogenation of {100} and {110} faces of synthetic diamond. *Diamond and Related Materials* **12**, 1559-1562, doi:http://dx.doi.org/10.1016/S0925-9635(03)00242-5 (2003).
- 4 Konishi, S., Ohashi, T., Sugimoto, W. & Takasu, Y. Effect of the Crystal Plane on the Catalytic Etching Behavior of Diamond Crystallites by Cobalt Nanoparticles. *Chemistry Letters* **35**, 1216-1217 (2006).
- 5 Ohashi, T., Sugimoto, W. & Takasu, Y. Catalytic etching of {100}-oriented diamond coating with Fe, Co, Ni, and Pt nanoparticles under hydrogen. *Diamond and Related Materials* **20**, 1165-1170, doi:10.1016/j.diamond.2011.06.029 (2011).
- 6 Swain, G. M. in *Semiconductors and Semimetals* Vol. Volume 77 (eds E. Nebel Christoph & Ristein Jürgen) 121-148 (Elsevier, 2004).
- 7 Rao, T. N. & Fujishima, A. Recent advances in electrochemistry of diamond. *Diamond Relat. Mater.* **9**, 384-389, doi:10.1016/s0925-9635(99)00234-4 (2000).
- 8 Rao, T. N., Ivandini, T. A., Terashima, C., Sarada, B. V. & Fujishima, A. Applications of bare and modified diamond electrodes in electroanalysis. *New Diamond Front. Carbon Technol.* **13**, 79-88 (2003).
- 9 Panizza, M. & Cerisola, G. Application of diamond electrodes to electrochemical processes. *Electrochimica Acta* **51**, 191-199, doi:http://dx.doi.org/10.1016/j.electacta.2005.04.023 (2005).
- 10 Waldvogel, S. R., Kirste, A. & Mentizi, S. 483-510,, 481 plate (John Wiley & Sons, Inc.).
- 11 Kraft, A. Doped diamond: a compact review on a new, versatile electrode material. *Int. J. Electrochem. Sci.* **2**, 355-385 (2007).
- 12 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).

- 13 Welch, C. & Compton, R. The use of nanoparticles in electroanalysis: a review. *Analytical and Bioanalytical Chemistry* **384**, 601-619, doi:10.1007/s00216-005-0230-3 (2006).
- 14 Burda, C., Chen, X., Narayanan, R. & El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev. (Washington, DC, U. S.)* **105**, 1025-1102, doi:10.1021/cr030063a (2005).
- 15 Hu, J. P., Lu, X., Foord, J. S. & Wang, Q. Electrochemical deposition of Pt nanoparticles on diamond substrates. *Physica Status Solidi a-Applications and Materials Science* **206**, 2057-2062, doi:10.1002/pssa.200982226 (2009).
- 16 Liu, B., Hu, J. & Foord, J. S. Electrochemical detection of DNA hybridization by a zirconia modified diamond electrode. *Electrochemistry Communications* **19**, 46-49, doi:10.1016/j.elecom.2012.03.007 (2012).
- 17 Toghill, K. E. & Compton, R. G. Metal Nanoparticle Modified Boron Doped Diamond Electrodes for Use in Electroanalysis. *Electroanalysis* **22**, 1947-1956, doi:10.1002/elan.201000072 (2010).
- 18 Antolini, E. Carbon supports for low-temperature fuel cell catalysts. *Applied Catalysis B-Environmental* **88**, 1-24, doi:10.1016/j.apcatb.2008.09.030 (2009).
- 19 Hrapovic, S., Liu, Y., Male, K. B. & Luong, J. H. T. Electrochemical Biosensing Platforms Using Platinum Nanoparticles and Carbon Nanotubes. *Analytical Chemistry* **76**, 1083-1088, doi:10.1021/ac035143t (2003).
- 20 Campbell, F. W. & Compton, R. G. The use of nanoparticles in electroanalysis: an updated review. *Analytical and Bioanalytical Chemistry* **396**, 241-259, doi:10.1007/s00216-009-3063-7 (2010).
- 21 González-González, I., Tryk, D. A. & Cabrera, C. R. Polycrystalline boron-doped diamond films as supports for methanol oxidation electrocatalysts. *Diamond and Related Materials* **15**, 275-278, doi:http://dx.doi.org/10.1016/j.diamond.2005.08.037 (2006).
- 22 Bennett, J. A., Show, Y., Wang, S. & Swain, G. M. Pulsed Galvanostatic Deposition of Pt Particles on Microcrystalline and Nanocrystalline Diamond Thin-Film Electrodes: I. Characterization of As-Deposited Metal/Diamond Surfaces. *Journal of The Electrochemical Society* **152**, E184-E192, doi:10.1149/1.1890745 (2005).
- 23 Ivandini, T. A., Sato, R., Makide, Y., Fujishima, A. & Einaga, Y. Pt-implanted boron-doped diamond electrodes and the application for electrochemical detection of hydrogen peroxide. *Diamond and Related Materials* **14**, 2133-2138, doi:http://dx.doi.org/10.1016/j.diamond.2005.08.022 (2005).
- 24 Mitani, S., Teraji, T. & Ito, T. Formation of self-assembled platinum particles on diamond and their embedding in diamond by microwave plasma chemical vapor depositions. *Diamond and Related Materials* **15**, 1544-1549, doi:http://dx.doi.org/10.1016/j.diamond.2005.12.052 (2006).
- 25 Masuda, H. *et al.* Synthesis of Well-Aligned Diamond Nanocylinders. *Advanced Materials* **13**, 247-249, doi:10.1002/1521-4095(200102)13:4<247::aid-adma247>3.0.co;2-h (2001).
- 26 Hausmann, B. J. M. *et al.* Fabrication of diamond nanowires for quantum information processing applications. *Diamond Relat. Mater.* **19**, 621-629, doi:10.1016/j.diamond.2010.01.011 (2010).
- 27 Smirnov, W. *et al.* Diamond-Modified AFM Probes: From Diamond Nanowires to Atomic Force Microscopy-Integrated Boron-Doped Diamond Electrodes. *Anal. Chem. (Washington, DC, U. S.)* **83**, 4936-4941, doi:10.1021/ac200659e (2011).

- 28 Janssen, W. & Gheeraert, E. Dry etching of diamond nanowires using self-organized metal droplet masks. *Diamond Relat. Mater.* **20**, 389-394, doi:10.1016/j.diamond.2011.01.037 (2011).
- 29 Terashima, C. *et al.* Fabrication of Vertically Aligned Diamond Whiskers from Highly Boron-Doped Diamond by Oxygen Plasma Etching. *ACS Appl. Mater. Interfaces* **3**, 177-182, doi:10.1021/am1007722 (2011).
- 30 Yang, Y., Sun, Q., Li, Y.-S., Li, H. & Fu, Z.-W. Nanostructured Diamond-like Carbon Thin Film Electrodes for Lithium-Air Batteries. *J. Electrochem. Soc.* **158**, B1211-B1216, doi:10.1149/1.3623431 (2011).
- 31 Masuda, H. *et al.* Fabrication of a nanostructured diamond honeycomb film. *Adv. Mater. (Weinheim, Ger.)* **12**, 444-447, doi:10.1002/(sici)1521-4095(200003)12:6<444::aid-adma444>3.0.co;2-k (2000).
- 32 Wu, W., Bai, L., Liu, X., Tang, Z. & Gu, Z. Nanograss array boron-doped diamond electrode for enhanced electron transfer from *Shewanella loihica* PV-4. *Electrochemistry Communications* **13**, 872-874, doi:10.1016/j.elecom.2011.05.025 (2011).
- 33 Nebel, C. E. *et al.* Diamond nano-wires, a new approach towards next generation electrochemical gene sensor platforms. *Diamond and Related Materials* **18**, 910-917, doi:10.1016/j.diamond.2008.11.024 (2009).
- 34 Smirnov, W. *Diamond diversity from micro- and nanostructuring to multifunctional tools and devices* PhD thesis, (2012).
- 35 Hees, J. *et al.* Nanocrystalline Diamond Nanoelectrode Arrays and Ensembles. *ACS Nano* **5**, 3339-3346, doi:10.1021/nn2005409 (2011).
- 36 Luo, D., Wu, L. & Zhi, J. Fabrication of Boron-Doped Diamond Nanorod Forest Electrodes and Their Application in Nonenzymatic Amperometric Glucose Biosensing. *ACS Nano* **3**, 2121-2128, doi:10.1021/nn9003154 (2009).
- 37 Wei, M., Terashima, C., Lv, M., Fujishima, A. & Gu, Z.-Z. Boron-doped diamond nanograss array for electrochemical sensors. *Chem. Commun. (Cambridge, U. K.)*, 3624-3626, doi:10.1039/b903284c (2009).
- 38 Szunerits, S., Coffinier, Y., Galopin, E., Brenner, J. & Boukherroub, R. Preparation of boron-doped diamond nanowires and their application for sensitive electrochemical detection of tryptophan. *Electrochemistry Communications* **12**, 438-441, doi:10.1016/j.elecom.2010.01.014 (2010).
- 39 Lv, M. *et al.* Electrochemical detection of catechol based on as-grown and nanograss array boron-doped diamond electrodes. *Electroanalysis* **22**, 199-203, doi:10.1002/elan.200900296 (2010).
- 40 Zhong, P., Luo, D., Ren, Y. & Zhi, J. Electrochemical detection of biapenem by a boron-doped diamond nanorod electrode. *Huaxue Yanjiu Yu Yingyong* **23**, 1246-1249 (2011).
- 41 Yang, N., Uetsuka, H. & Nebel, C. E. Biofunctionalization of vertically aligned diamond nanowires. *Adv. Funct. Mater.* **19**, 887-893, doi:10.1002/adfm.200801392 (2009).
- 42 Yang, Q., Chen, W., Xiao, C., Hirose, A. & Sammynaiken, R. Simultaneous growth of well-aligned diamond and graphitic carbon nanostructures through graphite etching. *Diamond Relat. Mater.* **14**, 1683-1687, doi:10.1016/j.diamond.2005.06.009 (2005).
- 43 Chih, Y. K. *et al.* Nano-scale diamond tips: Synthesis in the CH₄/N₂/H₂ plasma. *Diamond Relat. Mater.* **15**, 1246-1249, doi:10.1016/j.diamond.2005.09.037 (2006).
- 44 Sugawara, M. *Plasma Etching: Fundamentals and Applications*. (Oxford Univ Press, 1998).

- 45 Subramanian, P. *et al.* Diamond nanowires decorated with metallic nanoparticles: A novel electrical interface for the immobilization of histidinylated biomolecules. *Electrochimica Acta*, doi:http://dx.doi.org/10.1016/j.electacta.2012.11.010.
- 46 Kriele, A. *et al.* Formation of nano-pores in nano-crystalline diamond films. *Chemical Physics Letters* **507**, 253-259, doi:10.1016/j.cplett.2011.03.089 (2011).
- 47 Smirnov, W. *et al.* Anisotropic etching of diamond by molten Ni particles. *Applied Physics Letters* **97**, doi:073117
10.1063/1.3480602 (2010).
- 48 Yang, N., Uetsuka, H., Osawa, E. & Nebel, C. E. Vertically Aligned Nanowires from Boron-Doped Diamond. *Nano Letters* **8**, 3572-3576, doi:10.1021/nl801136h (2008).
- 49 <http://www.casaxps.com/>.
- 50 Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Physical Review B* **5**, 4709-4714 (1972).
- 51 Furuya, N. & Koide, S. Hydrogen adsorption on platinum single-crystal surfaces. *Surf. Sci.* **220**, 18-28, doi:10.1016/0039-6028(89)90460-3 (1989).
- 52 Yamamoto, K., Kolb, D. M., Koetz, R. & Lehmpfuhl, G. Hydrogen adsorption and oxide formation on platinum single crystal electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **96**, 233-239, doi:10.1016/s0022-0728(79)80380-0 (1978).
- 53 Tamizhmani, G., Dodelet, J. P. & Guay, D. Crystallite size effects of carbon-supported platinum on oxygen reduction in liquid acids. *J. Electrochem. Soc.* **143**, 18-23, doi:10.1149/1.1836381 (1996).
- 54 Deslouis, C. *et al.* Electrochemical behavior of (111) B-doped polycrystalline diamond: morphology/surface conductivity/activity assessed by EIS and CS-AFM. *Diamond Relat. Mater.* **20**, 1-10, doi:10.1016/j.diamond.2010.10.005 (2011).
- 55 Wang, S., Swope, V. M., Butler, J. E., Feygelson, T. & Swain, G. M. The structural and electrochemical properties of boron-doped nanocrystalline diamond thin-film electrodes grown from Ar-rich and H₂-rich source gases. *Diamond and Related Materials* **18**, 669-677, doi:http://dx.doi.org/10.1016/j.diamond.2008.11.033 (2009).
- 56 Wang, S. & Swain, G. M. Spatially Heterogeneous Electrical and Electrochemical Properties of Hydrogen-Terminated Boron-Doped Nanocrystalline Diamond Thin Film Deposited from an Argon-Rich CH₄/H₂/Ar/B₂H₆ Source Gas Mixture. *The Journal of Physical Chemistry C* **111**, 3986-3995, doi:10.1021/jp0669557 (2007).
- 57 Wilson, N. R., Clewes, S. L., Newton, M. E., Unwin, P. R. & Macpherson, J. V. Impact of Grain-Dependent Boron Uptake on the Electrochemical and Electrical Properties of Polycrystalline Boron Doped Diamond Electrodes. *The Journal of Physical Chemistry B* **110**, 5639-5646, doi:10.1021/jp0547616 (2006).
- 58 Holt, K. B., Bard, A. J., Show, Y. & Swain, G. M. Scanning Electrochemical Microscopy and Conductive Probe Atomic Force Microscopy Studies of Hydrogen-Terminated Boron-Doped Diamond Electrodes with Different Doping Levels. *The Journal of Physical Chemistry B* **108**, 15117-15127, doi:10.1021/jp048222x (2004).
- 59 Butler, J. E. & Sumant, A. V. The CVD of nanodiamond materials. *Chemical Vapor Deposition* **14**, 145-160, doi:10.1002/cvde.200700037 (2008).
- 60 Gruen, D. M. Nanocrystalline diamond films. *Annual Review of Materials Science* **29**, 211-259, doi:10.1146/annurev.matsci.29.1.211 (1999).
- 61 Patten, H. V., Lai, S. C. S., Macpherson, J. V. & Unwin, P. R. Active Sites for Outer-Sphere, Inner-Sphere, and Complex Multistage Electrochemical Reactions at Polycrystalline Boron-Doped Diamond Electrodes (pBDD) Revealed with Scanning Electrochemical Cell Microscopy (SECCM). *Anal. Chem. (Washington, DC, U. S.)* **84**, 5427-5432, doi:10.1021/ac3010555 (2012).

- 62 Steinbruechel, C., Lehmann, H. W. & Frick, K. Mechanism of dry etching of silicon dioxide. A case of direct reactive ion etching. *J. Electrochem. Soc.* **132**, 180-186, doi:10.1149/1.2113757 (1985).
- 63 Williams, K. R. & Muller, R. S. Etch rates for micromachining processing. *J. Microelectromech. Syst.* **5**, 256-269, doi:10.1109/84.546406 (1996).
- 64 Leech, P. W., Reeves, G. K. & Holland, A. Reactive ion etching of diamond in CF₄, O₂, O₂ and Ar-based mixtures. *Journal of Materials Science* **36**, 3453-3459, doi:10.1023/a:1017964129419 (2001).
- 65 Teii, K., Hori, M. & Goto, T. Codeposition on diamond film surface during reactive ion etching in SF₆ and O₂ plasmas. *J. Vac. Sci. Technol., A* **18**, 2779-2784, doi:10.1116/1.1316098 (2000).
- 66 Taki, Y. & Takai, O. XPS structural characterization of hydrogenated amorphous carbon thin films prepared by shielded arc ion plating. *Thin Solid Films* **316**, 45-50, doi:http://dx.doi.org/10.1016/S0040-6090(98)00386-1 (1998).
- 67 Ley, L., Graupner, R., Cui, J. B. & Ristein, J. Electronic properties of single crystalline diamond surfaces. *Carbon* **37**, 793-799, doi:10.1016/s0008-6223(98)00273-5 (1999).
- 68 Ferro, S., Dal Colle, M. & De Battisti, A. Chemical surface characterization of electrochemically and thermally oxidized boron-doped diamond film electrodes. *Carbon* **43**, 1191-1203, doi:http://dx.doi.org/10.1016/j.carbon.2004.12.012 (2005).
- 69 Goeting, C. H., Marken, F., Gutierrez-Sosa, A., Compton, R. G. & Foord, J. S. Electrochemically induced surface modifications of boron-doped diamond electrodes: an X-ray photoelectron spectroscopy study. *Diamond and Related Materials* **9**, 390-396 (2000).
- 70 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 71 Clifton, P. H. & Evans, S. XPS STUDIES OF DIAMOND TRANSITION-METAL INTERFACES. *Industrial Diamond Review* **55**, 26-31 (1995).
- 72 Delrue, J. P., Pireaux, J. J., Caudano, R., Robert, T. & Hecq, A. X-ray photoelectron spectroscopy of sputtered platinum thin films containing large amounts of carbon. *Journal of Vacuum Science and Technology* **19**, 257-259 (1981).
- 73 Gaowei, M. *et al.* Annealing dependence of diamond-metal Schottky barrier heights probed by hard x-ray photoelectron spectroscopy. *Applied Physics Letters* **100**, 201606 (2012).
- 74 Lewin, E. *et al.* Carbide and nanocomposite thin films in the Ti–Pt–C system. *Thin Solid Films* **518**, 5104-5109, doi:10.1016/j.tsf.2010.03.017 (2010).
- 75 Kvon, R. I., Koscheev, S. V. & Boronin, A. I. XPS study of carbon species at the surface of platinum single crystal planes. *Journal of Molecular Catalysis A: Chemical* **158**, 297-300, doi:10.1016/s1381-1169(00)00094-7 (2000).
- 76 Ramqvist, L., Hamrin, K., Johansson, G., Fahlman, A. & Nordling, C. Charge transfer in transition metal carbides and related compounds studied by ESCA. *Journal of Physics and Chemistry of Solids* **30**, 1835-1847, doi:10.1016/0022-3697(69)90252-2 (1969).
- 77 Wertheim, G. K. & Walker, L. R. Many-body effects in transition metals: role of the density of states. *Journal of Physics F: Metal Physics* **6**, 2297 (1976).
- 78 Shevchik, N. J. & Bloch, D. XPS d bands and core levels of Pt-Ni alloys. *Journal of Physics F: Metal Physics* **7**, 543 (1977).
- 79 Yafet, Y. & Wertheim, G. K. Many-body effects in X-ray photoemission from the noble metals. *Journal of Physics F: Metal Physics* **7**, 357 (1977).

- 80 Watson, R. E. & Perlman, M. L. PHOTOELECTRON-SPECTROSCOPY OF SOLIDS. *Physica Scripta* **21**, 527-534, doi:10.1088/0031-8949/21/3-4/047 (1980).
- 81 Feltham, A. M. & Spiro, M. Platinized platinum electrodes. *Chemical Reviews* **71**, 177-193, doi:10.1021/cr60270a002 (1971).
- 82 Pozio, A., De Francesco, M., Cemmi, A., Cardellini, F. & Giorgi, L. Comparison of high surface Pt/C catalysts by cyclic voltammetry. *Journal of Power Sources* **105**, 13-19, doi:http://dx.doi.org/10.1016/S0378-7753(01)00921-1 (2002).
- 83 Lu, J., Do, I., Drzal, L. T., Worden, R. M. & Lee, I. Nanometal-Decorated Exfoliated Graphite Nanoplatelet Based Glucose Biosensors with High Sensitivity and Fast Response. *ACS Nano* **2**, 1825-1832, doi:10.1021/nn800244k (2008).
- 84 Rong, L.-Q., Yang, C., Qian, Q.-Y. & Xia, X.-H. Study of the nonenzymatic glucose sensor based on highly dispersed Pt nanoparticles supported on carbon nanotubes. *Talanta* **72**, 819-824, doi:10.1016/j.talanta.2006.12.037 (2007).
- 85 Salazar-Banda, G. R., Suffredini, H. B., Calegaro, M. L., Tanimoto, S. T. & Avaca, L. A. Sol-gel-modified boron-doped diamond surfaces for methanol and ethanol electro-oxidation in acid medium. *Journal of Power Sources* **162**, 9-20, doi:http://dx.doi.org/10.1016/j.jpowsour.2006.06.045 (2006).

4 Chapter Four – Adsorption electrochemistry at diamond electrodes: the influence of surface chemistry

4.1 Introduction

This chapter investigates the electrochemical behaviour of differing forms of diamond, including microcrystalline boron-doped diamond, boron-doped diamond powder as well as detonation nanodiamond powder with regard to their fouling as a result of the adsorption processes in methyl viologen and anthraquinonedisulfonate solutions. In this work, two types of electrode pre-treatments were employed to produce two dissimilar surface terminations: hydrophobic H-terminated and hydrophilic O-terminated. In the case of methyl viologen, it was found that the reduced neutral molecule adsorbed on all three electrodes if they were hydrogen terminated, but not if they were oxygen terminated. For anthraquinonedisulfonate, no adsorption was found on the solid diamond electrode, although significant adsorption was identified on the powder electrodes, provided they were hydrogen terminated. The reasons underlying these observations are discussed in terms of hydrophobic and coulombic interactions and the electrode morphology. This work provides information into the likely occurrence of adsorption and concomitant electrode fouling, which may be experienced in electrochemical applications using solid and powdered forms of diamond.

4.1.1 Adsorption properties of diamond materials

Boron-doped diamond has attracted interest in a number of distinct electrochemical fields in recent years. The areas include electroanalysis, electrosynthesis, water purification, fuel cells and energy harvesting.¹⁻⁸ For these particular applications there are several notable advantages to boron-doped diamond electrode (BDE) as compared to other conventional electrode materials. These encompass exceptional chemical stability in aqueous and non-

aqueous environments, good biocompatibility and attractive electrochemical properties such as wide potential window, low signal-to-background current ratio and, more importantly, resistance to electrode fouling.⁹⁻¹²

Apart from the use of solid diamond electrodes, there has been increasing interest in the use of conductive boron-doped diamond powders and insulating detonation nanodiamond powders in areas such as fuel cell electrochemistry and in electrochemical sensing applications, where enhanced surface area could be advantageous.¹³⁻¹⁸

4.1.1.1 Background on Detonation Nanodiamond and Boron-doped Diamond Powders

Detonation Nanodiamond (DND) is a carbon based nanomaterial which is produced *via* the detonation process of carbon containing explosive compounds, where the application of high temperature and high pressure shock waves result in the formation of small quantities of diamond particles, approximately 5-10 nm in diameter. The particle consists of an sp^3 diamond core surrounded by an amorphous sp^2 shell with a highly functionalised surface containing hydroxyl, carbonyl, carboxyl and lactone surface groups.^{19,20}

Although DND is undoped and therefore insulating in a dry state, it is capable of producing an effective electrochemical response in solution due to the surface chemistry of DND particles. Further discussion of this exciting phenomenon is available in Chapter 5.

In contrast to the detonation nanodiamond, boron-doped diamond powders are boron-doped, and thus are conductive both in a dry state as well as in solutions. Conductive boron-doped diamond powders (BDP) can be produced by milling plain boron-doped diamond films²¹ or by the CVD growth of the conductive layer over the DND particles.¹⁵ The material is generally comprised of ~100 – 500 nm particles of irregular shape. Depending on the

production technique, the surface chemistry of BDP typically tends to be similar to that of plain polycrystalline boron-doped diamond.

The morphology and the size of both DND and BDP powders play an important role in their physical and chemical properties.^{22,23} The size control of these powders is required to produce high surface area electrodes as well as to achieve desirable electrochemical activity.

4.2 Aims of the project

One of the significant features that make diamond material so attractive in many electrochemical applications is its inert and stable surface chemistry. In contrast to other conventional carbon and metal based electrodes, boron-doped diamond has been generally reported to exhibit significant resistance to electrode fouling, which is of particular advantage in electroanalytical applications, where adsorption to the electrode is a frequent reason for electrode failure.^{24,25} However, contrary to the widespread belief that adsorption at boron-doped diamond electrodes is negligible, in recent studies BDE was found to be surprisingly efficient in adsorbing large organic compounds.²⁶⁻²⁸

For example, an interesting study by Compton *et. al.* shows that quinizarin strongly adsorbs to the electrode surface, dependent on the pre-exposure of the electrode to organic solvents.²⁹

Another report on the electrochemical studies of surface-bound processes at diamond electrodes was published by Swain *et. al.*²⁴ Chronocoulometry and cyclic voltammetry were employed to investigate the electrochemistry of anthraquinone-2,6-disulfonate (2,6-AQDS) which was chosen as a model compound. Although no attention was given to the surface chemistry of the electrodes, the authors concluded that both diamond electrode and glassy carbon (GC) were less susceptible to fouling as compared to highly oriented pyrolytic graphite (HOPG) and GC electrode. In the latter case, it was suggested that 2,6-AQDS

physisorbs on various defect sites of HOPG electrodes and approximately forms a more than a monolayer on the surface, 40% of which can be removed by the rinsing procedure.

It is thus obvious that the adsorption processes on boron-doped diamond electrodes can play a key role in controlling electrochemical performance in systems where electrode fouling is at risk of occurring. At present, little is known about how the surface termination of diamond controls the tendency for adsorption to take place and how this may vary between solid diamond and diamond powder electrodes. During the past few years, versatile methods of diamond surface chemical modification have been established.³⁰⁻³⁴ The ability to prepare several stable diamond surface terminations, among which H-termination and O-termination are the most commonly used, allows variation in important surface properties such as hydrophobicity and conductivity.³⁵ These differing surface terminations are also expected to play a role in controlling the extent of electrode fouling.

In order to examine how the tendency for adsorption to occur varies with the nature and surface termination of the diamond materials used, the electrochemistry of methyl viologen dichloride hydrate (MV) and 9,10-anthraquinone-2,6-disulfonic acid disodium salt (2,6-AQDS), which are known to adsorb strongly on Pt, Hg, Au and GC electrodes,³⁶⁻⁴⁰ was studied in this work at two widely used surface modifications of diamond: hydrophobic H-terminated and hydrophilic O-terminated. The chemical structures of the molecules used in this work are presented in Figure 41.

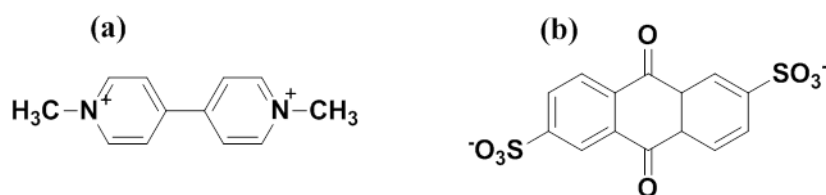


Figure 41 Chemical structures of (a) methyl viologen and (b) 9,10-anthraquinone-2,6-disulfonic acid used in this work

In this chapter, diamond powders as well as solid microcrystalline diamond electrodes were investigated, including detonation nanodiamond and milled boron-doped material. This work shows that the H-terminated diamond surface exhibits significantly stronger adsorption characteristics than the O-terminated surface, with the greatest extent of adsorption being observed at the DND electrode interface.

4.3 Experimental Methods

4.3.1 Electrode Preparation

Microcrystalline boron-doped diamond electrode (BDE) was used as a working electrode in all experiments (from Element Six Co, 10×10×0.6 mm size, [B] ~ 10²⁰ cm⁻³). BDP was produced by the milling of CVD boron-doped diamond ([B] ~ 10²⁰ cm⁻³). Detonation nanodiamond powder (DND) with a particle size of 4 nm was purchased from Yorkshire Bioscience. The preparation of 200 nm thin film BDP and DND powder film electrodes was carried out *via* drop coating of 0.08 mg BDP or DND in 60 µL aliquot of absolute ethanol onto BDE surface. The samples were dried overnight at 23°C.

Hydrogen plasma modification of diamond is known to provide hydrogen-terminated, defect free, clean and hydrophobic surfaces. In this work, the hydrogen termination of BDE, BDP and DND modified electrodes was produced by a previous method, using microwave hydrogen plasma treatment at 1.5 kW microwave power, an H₂ gas flow of 200 sccm, 60 mbar pressure and at a temperature of 600°C during 60 minutes.⁴¹ The sample was allowed to cool down in the hydrogen plasma by switching off the heating element and gradually reducing the microwave power until the plasma extinguished. The sample was cooled to a room temperature under a hydrogen flow. It was further confirmed by XPS that

the microwave hydrogen plasma treatment results in an electrode surface being largely free of adsorbed oxygen functionalities, hydrocarbons, and sp^2 species.

In order to produce an oxidised surface, as-prepared both powder and bare electrodes were treated by potential cycling *via* cyclic voltammetry in 0.1 M nitric acid between -1.5 V and +1.5 V. This procedure standardly results in the formation of a hydrophilic surface containing a high concentration of oxygen functionalities.^{42,43}

4.3.2 Characterisation

A scanning electron microscope (SEM, Hitachi S530) with a 20 kV acceleration voltage was used to examine the surface morphology. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a hemispherical analyser and Al $K\alpha$ (1486.6 eV) X-ray source. The survey scans and the high resolution scans were measured at 50 eV pass energy with 0.5 eV step and at 20 eV pass energy with 0.1 eV step respectively. The spectra recorded were analysed with CasaXPS software.⁴⁴ The peaks were fitted using Shirley background.⁴⁵ Raman spectra were recorded using Raman microscope spectrometer (Renishaw inVia) with a 514 nm argon laser.

The electrical conductance of as-received DND and BDP was measured from the ohmic resistance of the samples placed between the two metal plates.

The electrical conductance, σ , is described by the following equation:

$$\sigma = \frac{l}{RA} \quad (\text{Equation 4.1.1})$$

where R is the measured ohmic resistance (Ω), l is the thickness of the powder layer (cm), A is the cross-sectional area of the sample (cm^2).

Electrochemical measurements were performed using a μ -AUTOLAB III electrochemical workstation (Eco-Chemie, Netherlands) at 23°C. A standard three-electrode configuration comprising the BDE as a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode was employed in the study. The working electrode was incorporated in a PTFE holder, so that a circular area of 0.4 cm² was exposed to a working solution. Cyclic voltammetry (CV) was employed to characterise electrochemical behaviour of the electrodes in 1 mM anthraquinone-2,6-disulfonate (2,6-AQDS), 0.1 M HNO₃ and 1 mM methyl viologen (MV), 0.1 M KCl in the scan rate range of 0.02-0.1 V s⁻¹. The surface coverage of the adsorbed analyte formed on the electrode surface after the CV measurements was estimated from a charge obtained at an area under the CV peak, as shown in equation 4.1.2:⁴⁶

$$Q = nFA\Gamma \quad (\text{Equation 4.1.2})$$

where n is the number of electrons involved in the redox process, F is the Faraday constant (96485 C mol⁻¹), A is the diamond electrode area (0.4 cm²), Γ is the surface concentration of the analyte.

As a comparison, chronocoulometry was also carried out during potential scanning of the electrode in the presence and absence of analyte using the methodology described previously.²⁴ Chronocoulometry measures the charge that has been transferred across the electrode/electrolyte interface when the potential of the electrode is scanned from a value where no current is flowing to a value where a faradaic current flows. The charge detected provides quantitative information on the surface coverage of the adsorbed molecules. The charge measured is described by the following equation 4.1.3:⁴⁷

$$Q_{total} = Q_{faradaic} + Q_{dl} + Q_{ads} = \frac{2nFA\sqrt{DC\sqrt{t}}}{\pi} + Q_{dl} + Q_{ads} \quad (\text{Equation 4.1.3})$$

where n is the number of electrons transferred, F is the Faraday constant, A is the electrode area, D is the diffusion coefficient of redox species, C is the concentration. Q_{faradaic} in the equation 4.1.3 describes the faradaic charge that correlates with semi-infinite linear diffusion controlled electrolysis.²⁴ The second term is the double layer charging, and the third corresponds to the adsorbed analyte. The double layer charging, Q_{dl} was first determined by carrying out chronocoulometry only in the presence of background electrolyte. Subsequent cyclic voltammetry measurements in the presence of analyte and rinsing procedure were then followed by chronocoulometry again in order to estimate the amount of the analyte adsorbed to the electrode surface after the electrode rinsing. By plotting the measured charge in each experiment against $t^{1/2}$ and estimating the difference between the intercepts at $t = 0$ of Q_{total} after the rinsing procedure and Q_{dl} plots, the amount of charge, Q_{ads} , required to instantaneously oxidise the adsorbed analyte left at the electrode was obtained. Surface coverage values can be further estimated by equating Q_{ads} to the term $nFA\Gamma$ as in equation 4.1.2.

4.3.3 Chemicals

All chemicals (from Sigma-Aldrich, UK) were of analytical grade and used without any further purification. Solutions (1 mM) of methyl viologen dichloride hydrate (MV^{2+}) and 9,10-anthraquinone-2,6-disulfonic acid disodium salt (2,6-AQDS) were prepared in 0.1 M KCl and 0.1 M HNO_3 respectively using ultrapure water (18 M Ω cm at 23°C, Millipore water systems, UK). All solutions were deaerated by passing N_2 gas for 20 min prior to experiment.

4.4 Results and Discussion

4.4.1 Morphology and microstructure characterisation

The SEM of a typical plain microcrystalline B-doped diamond electrode (BDE) used in this work is presented in Figure 42 (a). It is comprised of [111], [100] and [110] oriented diamond grains of ~5-50 μm size range. The SEM of as received boron-doped diamond powder (BDP) is shown in Figure 42 (b). BDP is formed of irregular particles with sharp edges of 100 nm – 5 μm size. The SEM image of a dried film of detonation nanodiamond powder (DND) is displayed in Figure 42 (c). It consists of agglomerated ~10-100 nm densely packed spherical particles. Some cracks are visible in the powder film due to the solvent evaporation during the drop-coating procedure.

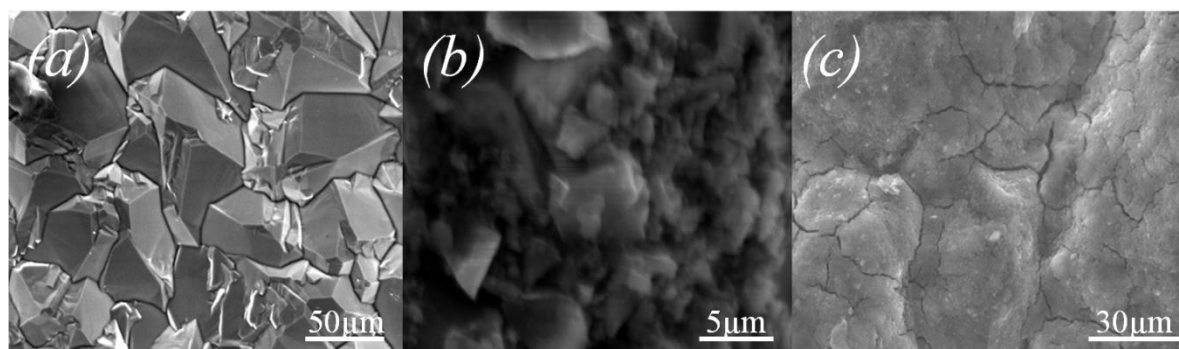


Figure 42 SEM image of (a) boron-doped diamond electrode; (b) 200 nm layer of boron-doped diamond powder; (c) 200 nm layer of detonation nanodiamond powder.

The electrical conductance of dry BDP was measured as described in Section 4.3.2, using a sample of 1×1×0.1 cm dimension. The value of $1.8 \Omega^{-1} \text{cm}^{-1}$ was estimated in a good agreement with the results reported previously,^{14,15,17,48} indicative of a boron doping of $\sim 10^{20} \text{cm}^{-3}$.⁴⁹ Further studies of B-doping and morphology were carried out by Raman

spectroscopy. The Raman spectrum of the BDP film is presented in Figure 43 (a).

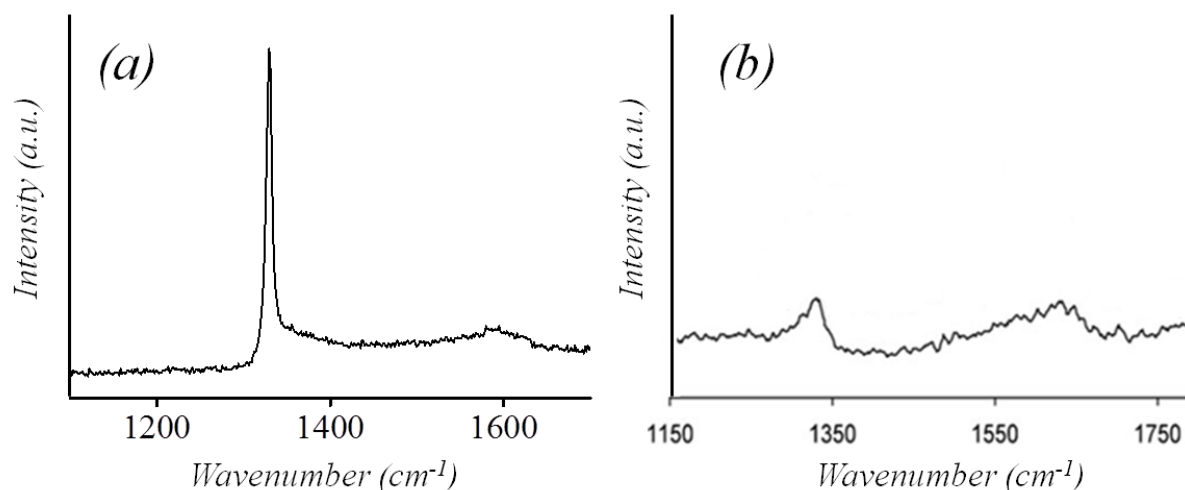


Figure 43 Raman spectrum of (a) Boron-doped diamond powder; (b) Detonation nanodiamond powder, reprinted from¹⁶

It is characteristic of a good quality diamond with the single first-order phonon at 1330 cm⁻¹. The peak detected at 1580 cm⁻¹ is ascribed to the sp²-bonded carbon. Since the argon laser is almost 100 times more sensitive to sp² carbon,⁵⁰ the small ratio of the sp² peak intensity to the sp³ intensity suggests that the BDP is of a high phase purity. With the position of the first-order phonon at 1330 cm⁻¹, no Fano-type line shape is observed; however the asymmetry in the first-order phonon is still present which is in a good agreement with the suggested boron concentration of ~10²⁰ cm⁻³.⁵¹ Thus, in accordance with the conductance measured and Raman data obtained, the boron concentration of BDP is consistent with 10²⁰ cm⁻³ values.

The Raman spectrum of the DND sample was identical to those measured and described in detail previously.¹⁶ As shown in Figure 43 (b), characteristic sp³ peak for DND is detected at 1325 cm⁻¹ which is lower than that of bulk diamond at 1330 cm⁻¹. This feature is attributable to the phonon confinement effect predicted for nanoparticles of this size.¹⁶ A broad asymmetric band at 1620 cm⁻¹ is assigned to sp² defects on the DND surface.⁵² A shoulder at ~1590 cm⁻¹ suggests the presence of G band, whereas no D band at ~1350 cm⁻¹ was

detected.¹⁶ The conductance of the dry DND powder was found to be much lower than the BDP, about $3 \cdot 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ as expected due to the absence of doping. However, despite this lower conductance in the dry state, as we observe below DND is capable of producing an active electrode in solution.^{16,17,53} This feature will be discussed in detail in Chapter 5.

4.4.2 XPS characterization of hydrogenated and oxidised diamond electrodes

4.4.2.1 Wide scan XPS

After the hydrogen plasma treatment and before carrying out electrochemical measurements, the diamond samples were analysed by XPS in order to evaluate the initial chemical state of the surface. Figure 44 (a) displays a typical survey scan of H-terminated diamond electrode (HBDE) which is representative of the initial hydrogenated diamond surface used throughout this work. The associated atomic concentrations, binding energies and FWHM values can be found in Table 7, Table 8 and Table 9. The C 1s photoemission peak at 285 eV as well as characteristic C KVV and C KLL Auger peaks at 980 eV and 1000 eV confirm the elemental purity of the hydrogenated diamond sample.⁵⁴ A minor O 1s component at 532 eV binding energy is also present in the spectrum, mainly due to adsorbed water vapour. Assuming the uniformity of oxygen species distribution, the relative signal areas were converted to relative atomic concentrations using standard XPS sensitivity factors.⁴⁴ The O 1s elemental concentration within the XPS sampling depth is estimated at around 3.4%.

Table 7 XPS binding energies for hydrogenated and oxidised boron-doped diamond electrodes

Sample	Binding energies (eV)						
	C 1s					O 1s	
	Csp ³	C-CHx	C=O	sp ² def	O-C	O=C	H ₂ O
HBDE	285.0	285.8	286.5	283.4	n/a	533.7	530.1
OBDE	285.0	285.8	287.4	282.2	532.4	534.7	530.0

Table 8 XPS elemental ratios and charging values for hydrogenated and oxidised boron-doped diamond electrodes

Sample	Elemental concentrations (%)	Charging (eV)
	O 1s	Relative to C 1s (285.0 eV)

Chapter Four – Adsorption electrochemistry at diamond electrodes: the influence of surface chemistry

HBDE	3.4	8.0
OBDE	12.1	8.4

Table 9 FWHM values for hydrogenated and oxidised boron-doped diamond electrodes

Sample	FWHM (eV)						
	C 1s					O 1s	
	Csp ³	C-CHx	C=O	sp ² def	O-C-	O=C	H ₂ O
HBDE	1.2	1.1	2.0	1.5	n/a	2.3	4.2
OBDE	1.8	1.4	2.1	1.6	2.1	2.0	1.8

In order to produce an oxidised diamond surface, the electrodes were conditioned in 0.1 M nitric acid by potential cycling (40 scans) between -1.5 V and + 2.5 V as described in section 2. A wide XPS scan of an oxidised boron-doped diamond electrode used in this work is presented in Figure 44 (b). The C 1s component at 285 eV with characteristic C KVV and C KLL Auger peaks at 980 eV and 1000 eV and a distinct O 1s peak at 532 eV are observed in the spectrum. The minor lines from silicon Si 2s and Si 2p core levels are related to a possible SiO₂ contamination from glassware. As presented in Table 8, the O 1s/C 1s ratio within the XPS sampling depth is calculated to be at 12.1% which is almost 4 times greater than that of hydrogenated boron-doped diamond.

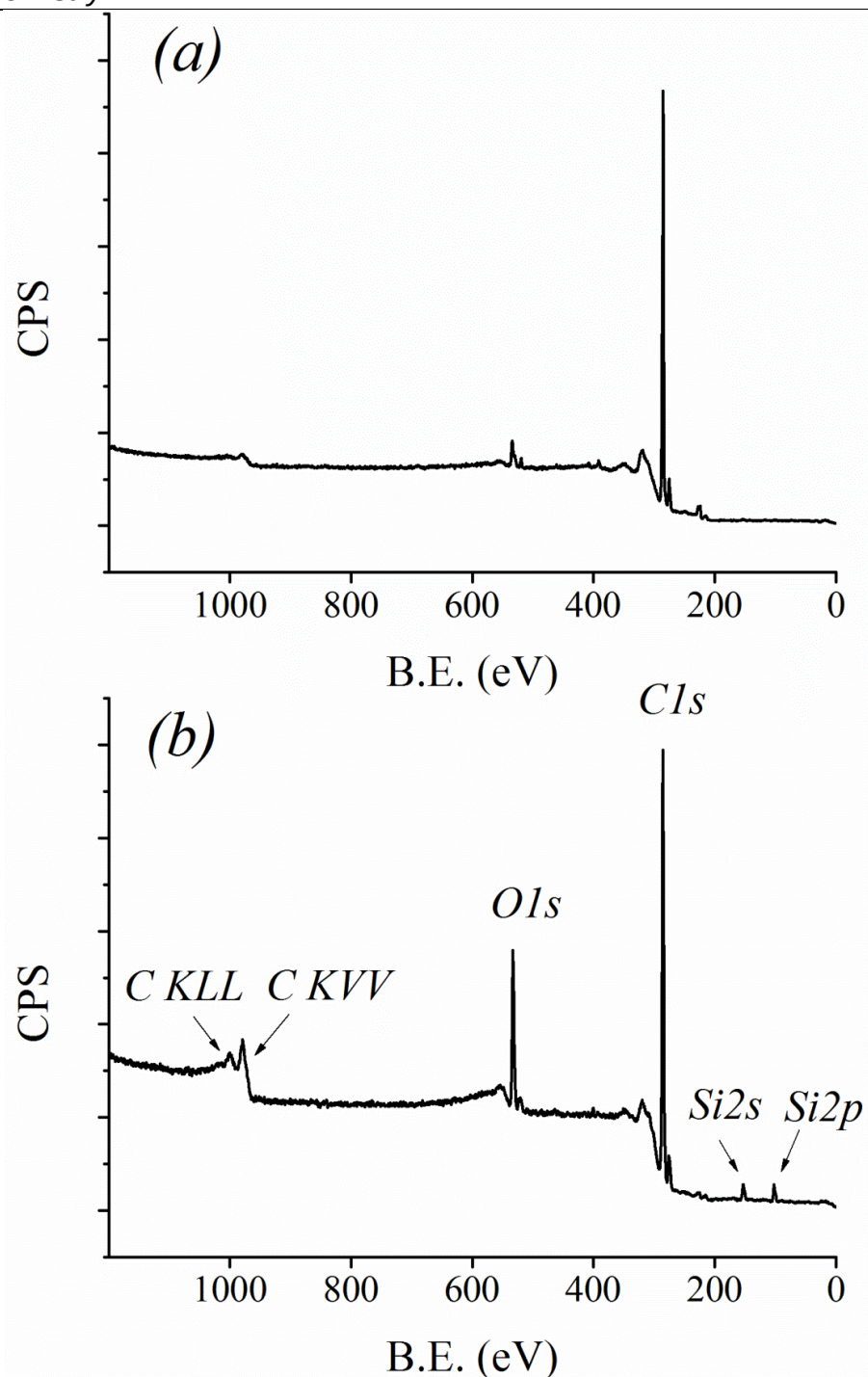


Figure 44 XPS wide scan spectra of (a) hydrogen terminated boron-doped diamond electrode; (b) oxygen terminated boron-doped diamond electrode

4.4.2.2 Hydrogen termination and induced surface conductivity

As it will be shown in the following sections, hydrogen plasma treatment introduces significant changes to the electrochemical performance of the diamond electrodes. In order to

understand the underlying principles of this effect, characteristic surface-induced conductivity resulting from the hydrogen plasma treatment will be discussed below.

Undoped, high quality diamond with a band gap of 5.5 eV is known to be one of the best insulators with a resistivity of more than $10^{11} \Omega \text{ cm}$. In 1989, Landstrass and Ravi showed that if undoped CVD diamond was terminated with a chemically bound hydrogen in the result of a hydrogen plasma treatment, a pronounced conductivity was detected when a sample was exposed to air.⁵⁵ The surface conductivity disappeared if a diamond sample was annealed. In order to explain the effect observed, it was suggested that at elevated temperatures (above 800°C) hydrogen atoms diffuse into the diamond lattice generating additional acceptor states with the positive hole carrier densities (up to 10^{13} cm^{-2}), and therefore introducing a p-type conductivity which is confined to a narrow near-surface region.

This reversible transformation of undoped diamond from insulating to metallic state has attracted a widespread attention and caused a lot of controversy. Chakrapani *et. al.* reported that a surface conductivity also occurs at undoped hydrogen terminated diamond/liquid interface, originating from the migration of carries from diamond into the liquid.⁵⁶ Two electrochemical models were suggested to describe the phenomenon,^{57,58} according to which electrolyte layers adsorbed on the diamond surface react with the hydrogen layer, causing the creation of holes. However, these layers were found to be ill-defined as it was difficult to describe the electrochemical basis of the phenomenon.⁵⁹

For the migration or tunnelling of the electrons from the solid into the electrolyte to be possible, the empty electronic states should be present in the liquid. These empty states can be filled if no substantial energy barrier exists between the solid/liquid interfaces. In semiconductors, the valence band filled with electrons is considered to be the main electron

source in the tunnelling process.⁵⁹ As most of the semiconductors have a valence-band maximum lower than associated electrochemical levels, surface dipole layers are required to tune this process. Therefore, by changing the termination of the diamond surface from oxygen to hydrogen, it is possible to shift the valence-band maximum to a higher level as displayed in Figure 45.

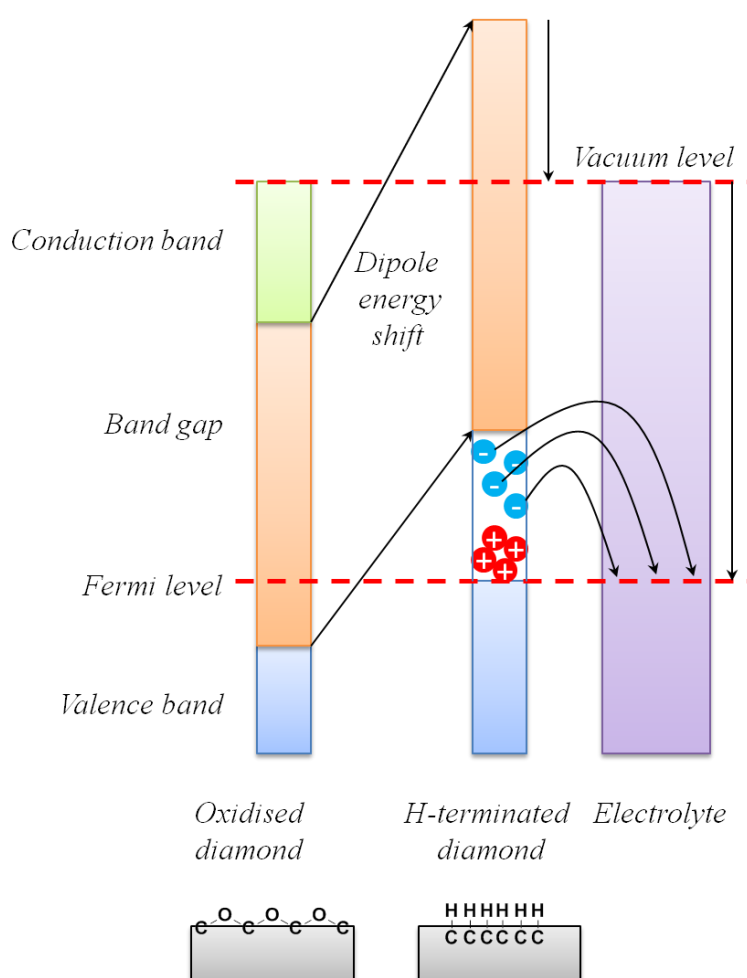


Figure 45 Schematic illustration of the increase in the valence band energy which is achieved through the changes of diamond surface termination from oxygen to hydrogen, adapted from⁵⁹

As further illustrated in Figure 45, for this tunnelling to be possible, the energy level of the valence-band maximum of the diamond surface should be greater than the chemical potential of the electrolyte. As hydrogen termination results in the formation of a C–H surface dipole layer with a negative charge concentrated on the carbon atom ($C^{\delta-}$) and a positive charge on

the hydrogen atom ($H^{\delta+}$), this dipole generates electrostatic potential, perpendicular to the surface over a distance of the order of the C–H bond length (1.1 Å), and shifts all energy levels of diamond up to 1.6 eV with regard to the chemical potential of an electrolyte. The latter results in the ‘negative electron affinity’ which is caused by the conduction band states of the diamond being above the vacuum level of the electrolyte. Therefore, it is energetically favourable for the electrons from the diamond valence band to tunnel into the empty electronic states of the electrolyte until a thermodynamic equilibrium between the Fermi level of diamond and electrochemical potential of the electrolyte is established.

Boron-doped diamond is also known to show surface induced conductivity upon hydrogenation.⁶⁰⁻⁶² It was shown that hydrogen termination of a boron-doped diamond results in the formation of additional hole carriers in the surface as compared to oxidised boron-doped diamond, and the carrier density was found to be independent of a boron doping concentration.

A general trend to arise from these studies is that the change in the surface termination introduces significant changes to the electrochemical behaviour of the diamond electrodes. For example, $Fe(CN)_6^{3-/4-}$ redox couples are found to be very sensitive to the surface chemistry of a diamond electrode as the electron transfer kinetics can change by several orders of magnitude with regard to the electrode termination.

In the following sections, the extent to which the changes in the surface chemistry of the boron-doped diamond electrodes influence the associated electrode performance as well as the electrode fouling will be investigated using electrochemical techniques and high-resolution X-ray photoelectron spectroscopy.

The diagram illustrates the three redox states of methylviologen (MV):

- Top structure (MV²⁺):** The fully oxidized state, consisting of two 4-vinylpyridinium rings connected by a double bond. Each nitrogen atom is positively charged and bonded to a methyl group (H₃C- and -CH₃).
- Middle structure (MV^{•+}):** The radical cation state, formed by the loss of one electron (-e⁻) from the oxidized state. It features a double bond between the two rings, which are now in a quinonoid configuration. The left nitrogen is double-bonded to the ring and carries a positive charge, while the right nitrogen is single-bonded and carries a radical cation (•+).
- Bottom structure (MV^{•-}):** The radical anion state, formed by the gain of one electron (+e⁻) from the radical cation state. It also features a double bond between the rings in a quinonoid configuration. The left nitrogen is single-bonded and carries a radical anion (•-), while the right nitrogen is double-bonded to the ring and carries a negative charge.

Vertical double-headed arrows with $-e^-$ and $+e^-$ indicate the reversible electron transfer between these states.

The cyclic voltammetric behaviour of 1 mM methylviologen in 0.1 M KCl, scanned at 0.05 Vs⁻¹ from 0 to -1.4 V at hydrogenated and oxidised boron doped diamond electrodes is compared in Figure 47. The associated peak positions and current responses (i.e. current normalised by electrode area) are summarised in Table 10 and Table 11.

$$\text{MV}^{2+} + \text{e}^- \leftrightarrow \text{MV}^{\bullet+} \text{ (peak 1) (Equation 4.1.4)}$$
$$\text{MV}^{\cdot+} + \text{e}^- \leftrightarrow \text{MV}^0 \text{ (peak 2)} \quad (\text{Equation 4.1.5})$$

As the potential sweep is extended to the oxidation regime, two peaks 2' and 1' at -0.99 V and -0.65 V respectively appear due to the following reactions:⁶³

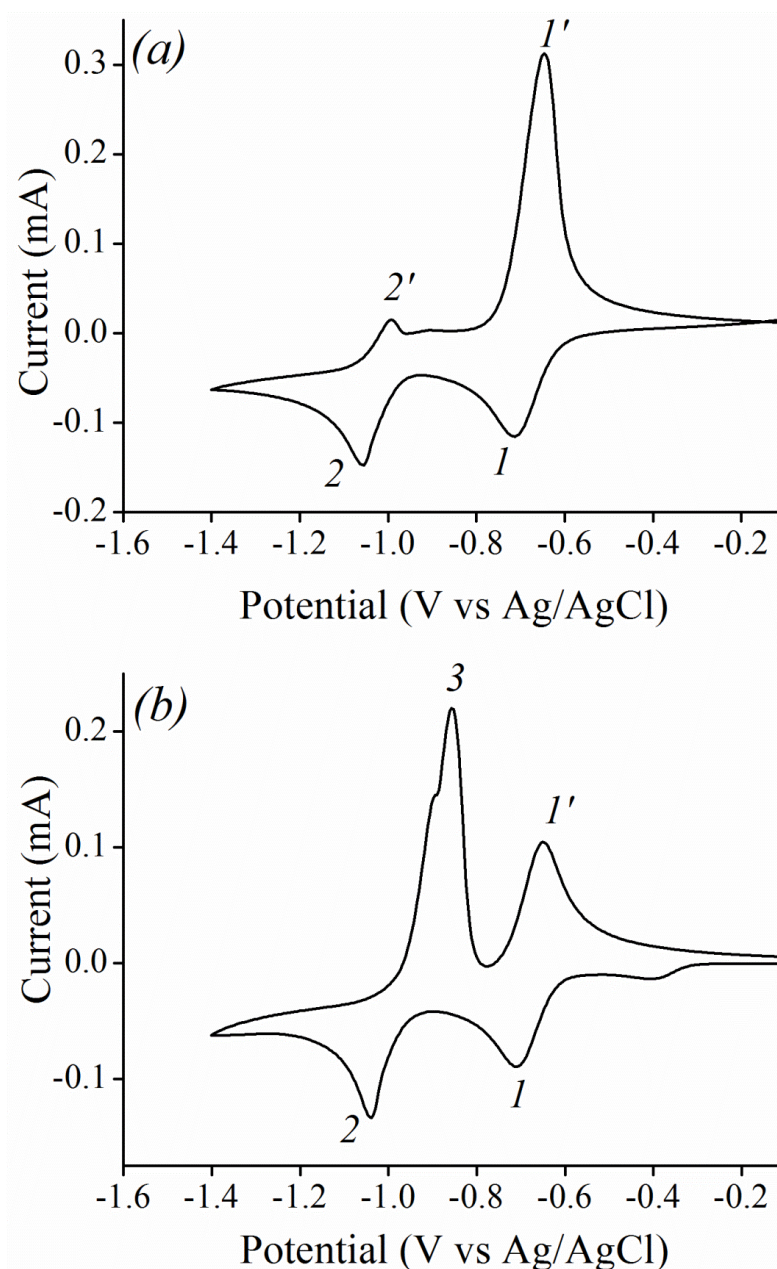
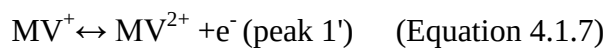
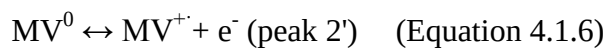


Figure 47 Cyclic voltammogram of 1 mM methyl viologen in 0.1 M KCl recorded at 0.05 V s⁻¹ at (a) hydrogen terminated boron-doped diamond; (b) oxygen terminated boron-doped diamond

Chapter Four – Adsorption electrochemistry at diamond electrodes: the influence of surface chemistry

Table 10 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at oxygen terminated boron-doped diamond electrode at 0.05 V s⁻¹

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.71	-9.44×10 ⁻⁵	-2.36×10 ⁻⁴
2	-1.05	-9.59×10 ⁻⁵	-2.39×10 ⁻⁴
2'	-0.99	2.94×10 ⁻⁵	7.35×10 ⁻⁴
1'	-0.65	3.08×10 ⁻⁴	7.70×10 ⁻³

Table 11 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at hydrogen terminated boron-doped diamond electrode at 0.05 V s⁻¹

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.71	-6.59×10 ⁻⁵	-1.64×10 ⁻⁴
2	-1.04	-8.52×10 ⁻⁵	-2.13×10 ⁻⁴
3	-0.85	2.32×10 ⁻⁴	5.80×10 ⁻⁴
1'	-0.65	1.06×10 ⁻⁴	2.65×10 ⁻⁴

The peak-to-peak separation, $\Delta E_{MV^{2+}/MV^{\cdot+}}$, for the curve recorded at OBDE is 66 mV at 0.05 Vs⁻¹. The apparent electron transfer rate constant for the MV²⁺/MV^{·+} redox process (without double layer or IR effects correction), k_{app}^0 , was determined in accordance with the theoretical model of Nicholson:⁶⁴

$$k_{app}^0 = \psi \left(\pi \frac{nF\nu}{RT} D_0 \right)^{1/2} / \gamma \quad (\text{Equation 4.1.8})$$

where ψ is dimensionless charge transfer parameter related to ΔE_p . ψ value that corresponds to a specific ΔE_p value is tabulated in reference ⁶⁴. n is the number of electrons transferred, F is the Faraday constant, ν is the scan rate, R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), T is the Kelvin temperature, D_0 is the diffusion coefficient of MV²⁺ (6.56×10⁻⁶ cm² s⁻¹) and $\gamma = \left(\frac{D_{ox}}{D_{red}} \right)^{1/2}$ is assumed to equal unity.^{64,65}

An application of Equation 4.9 gives the k_{app}^0 value of 2.6×10⁻² cm s⁻¹ ($\psi=4$) which is in agreement with previously reported.^{12,25}

As presented in Figure 48, at OBDE, the peak currents for both redox processes were found to increase linearly with the square root of scan rate (from 0.02 to 0.1 V s^{-1} , $R^2 = 0.9958$), thus suggesting a diffusion control reaction at the interface.

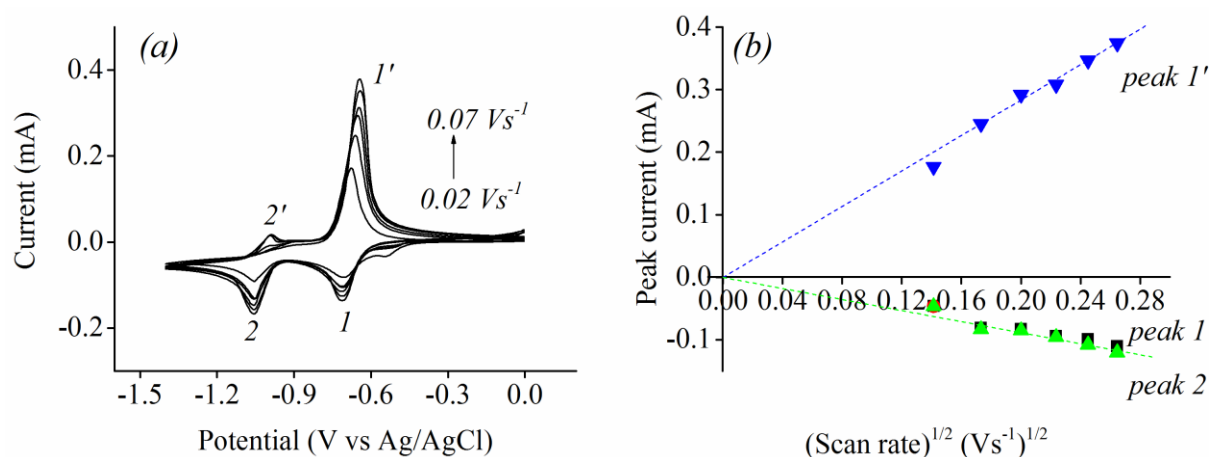


Figure 48 (a) Cyclic voltammogram of 1 mM MV, 0.1 M KCl recorded at oxygen terminated boron-doped diamond electrode with the scan rates of 0.02 to 0.07 Vs^{-1} ; (b) corresponding plots of peak currents versus square root of scan rate

At hydrogen terminated BDE (HBDE) (Figure 49 (a)), two cathodic peaks at -0.71 V and -1.04 V vs Ag/AgCl correspond to the reduction of MV^{2+} and $\text{MV}^{\cdot+}$ as in equation (4.1.4) and (4.1.5). The $\text{MV}^{2+}/\text{MV}^{\cdot+}$ redox reaction was found to be diffusion controlled as verified by the constancy of I_p vs $v^{1/2}$ values (v from 0.03 to 0.1 V s^{-1} , $R^2 = 0.9897$) (as presented in Figure 49 (b)). For the cyclic voltammogram obtained at HBDE, $\Delta E_{\text{MV}^{2+}/\text{MV}^{\cdot+}}$ is reduced to 58 mV at 0.05 Vs^{-1} with $k_{\text{app}}^0 = 0.13 \text{ cm s}^{-1}$ ($\psi = 21$), thus suggesting a faster electron transfer on an H-terminated surface.

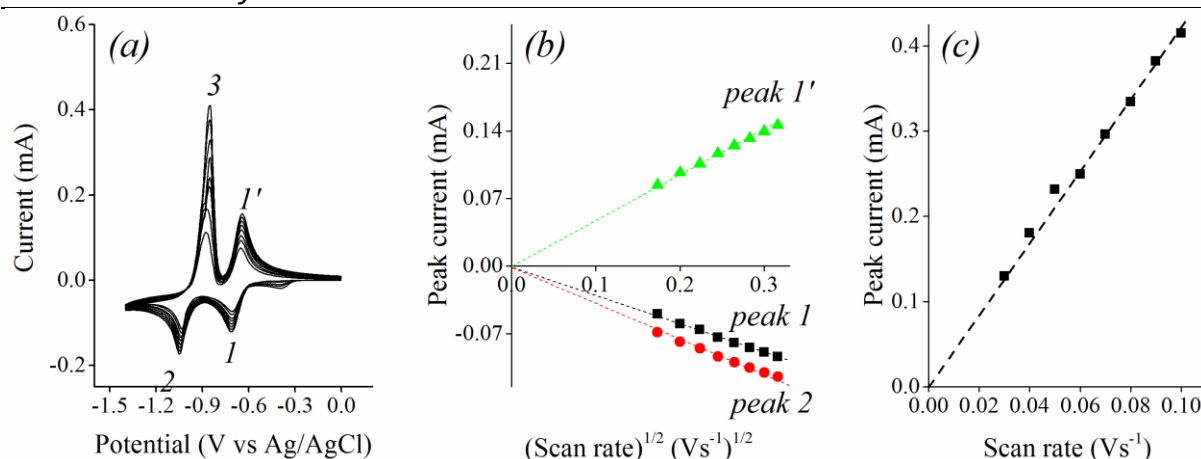
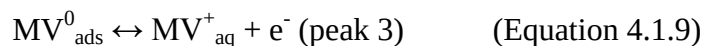


Figure 49 (a) Cyclic voltammogram of 1 mM MV, 0.1 M KCl recorded at hydrogen terminated boron-doped diamond electrode with the scan rates of 0.03 to 0.1 Vs⁻¹; (b) corresponding plots of peak currents versus square root of scan rate; (c) plot of peak current 3 versus scan rate

In the anodic scan, an important difference induced by the hydrogen termination of the diamond electrode is observed in the appearance of peak 3 at -0.85 V, uncharacteristic of O-terminated BDE. Peak 3 solely arises from the surface bound process as it was shown in the recent studies of methyl viologen reduction at carbon based electrodes by Compton et al.³⁹



The I_p^{OX} values of peak 3 increase linearly with the scan rate from 0.03 to 0.1 Vs⁻¹, thus indicating the occurrence of adsorption controlled process (Figure 49 (c)).⁶⁶ The amount of MV_{ads}^0 formed in the first scan on the H-terminated diamond electrode was estimated from the charge corresponding to the peak area under the oxidation peak 3, as shown in equation 4.1.9. Thus, 11 nmol cm⁻² of MV_{ads}^0 was found to form on the HBDE surface after the first scan. The monolayer coverage of methyl viologen is known to be 0.2 or 0.4 nmol cm⁻² depending on vertical or flat orientation of the molecule.⁶⁷ Therefore it can be concluded that many monolayers are adsorbed on the HBDE electrode when in solution, driven by the π - π interactions between adjacent MV_{ads}^0 molecules.⁶⁷

In order to investigate the formation of MV^0_{ads} on the H-terminated BDE further, cyclic voltammetry was performed in the conditions, where the sweep potential was held at -1.3 V for 30 and 60 s before reversing the direction of the scan (Figure 50 (a)).³⁹

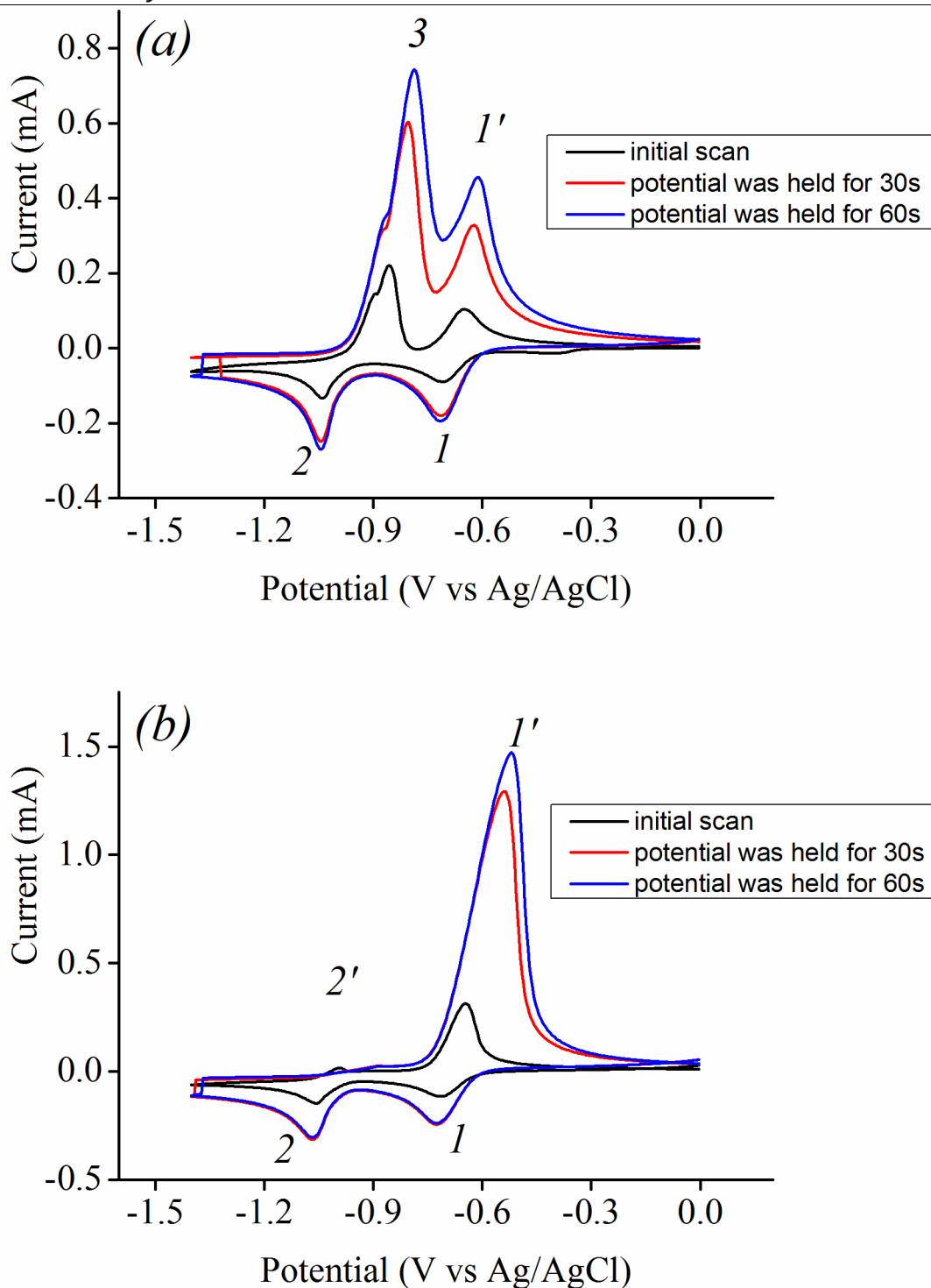


Figure 50 Cyclic voltammogram in 1 mM MV, 0.1 M KCl recorded at (a) HBDE (—) initial scan, (—) HBDE was held for 30 s, (—) HBDE was held for 60 s; (b) HBDE (—) initial scan, (—) OBDE was held for 30 s, (—) HBDE was held for 60 s

As shown in Figure 50 (a), the treatment results in the consecutive enlargement of peak 3, whilst peak 1 and 2 increase insignificantly, therefore indicating that peak 3 is the only surface bound process that occurs in the system. It should be noted that under the same

conditions at O-terminated BDE (Figure 50 (b)), peak 3 is not observed, thus confirming that the surface bound process is characteristic only of H-terminated diamond and may lead to a suggestion that MV^0_{ads} does not adsorb at hydrophilic diamond surfaces. The adsorption at HBDE is most likely to arise from the hydrophobic interaction between the hydrophobic hydrogen-terminated diamond surface and hydrophobic and low polar MV^0_{ads} . Such a tendency was previously assigned to a favourable accumulation of hydrophobic compounds by H-terminated diamond surface in order to decrease the overall hydrated surface.⁶⁶

Another interesting feature, characteristic only of O-terminated BDE during -1.3 V treatment is the disappearance of peak 2' ($MV^{\cdot+}$) which takes place after reversing the direction of a scan (Figure 50 (b)). The same effect was reported previously and is due to the following reaction:⁶⁸



This process is supported by the observation that MV^0 does not adsorb at O-terminated BDE and is thus available to react with MV^{2+} species.

Figure 51 displays the cyclic voltammograms of 1 mM methylviologen in 0.1 M KCl recorded at hydrogenated and oxygen terminated boron doped diamond powder electrodes. The associated peak positions and current response can be found in Table 12 and

Table 13. In the cathodic scan, reduction peaks are similar for both HBDE and OBDE surfaces and comparable to those seen at H- and O-terminated BDEs. $\Delta E_{MV^{2+}/MV^{\cdot+}}$ at OBDE is 62 mV at 0.05 V s^{-1} and k^0_{app} is $5.7 \times 10^{-2} \text{ cm s}^{-1}$ ($\psi=9$). The peak currents were found to vary linearly with the square root of scan rate from 0.02 to 0.1 V s^{-1} , suggesting the presence of diffusion controlled process at the interface (Figure 52). Similar to O-terminated diamond electrode, peak 2' (Figure 51 (b)) characteristic of $MV^0 \leftrightarrow MV^+ + e^-$ process does not appear at OBDE surface due to the influence of the chemical reaction (Equation 4.2.0).⁶⁸

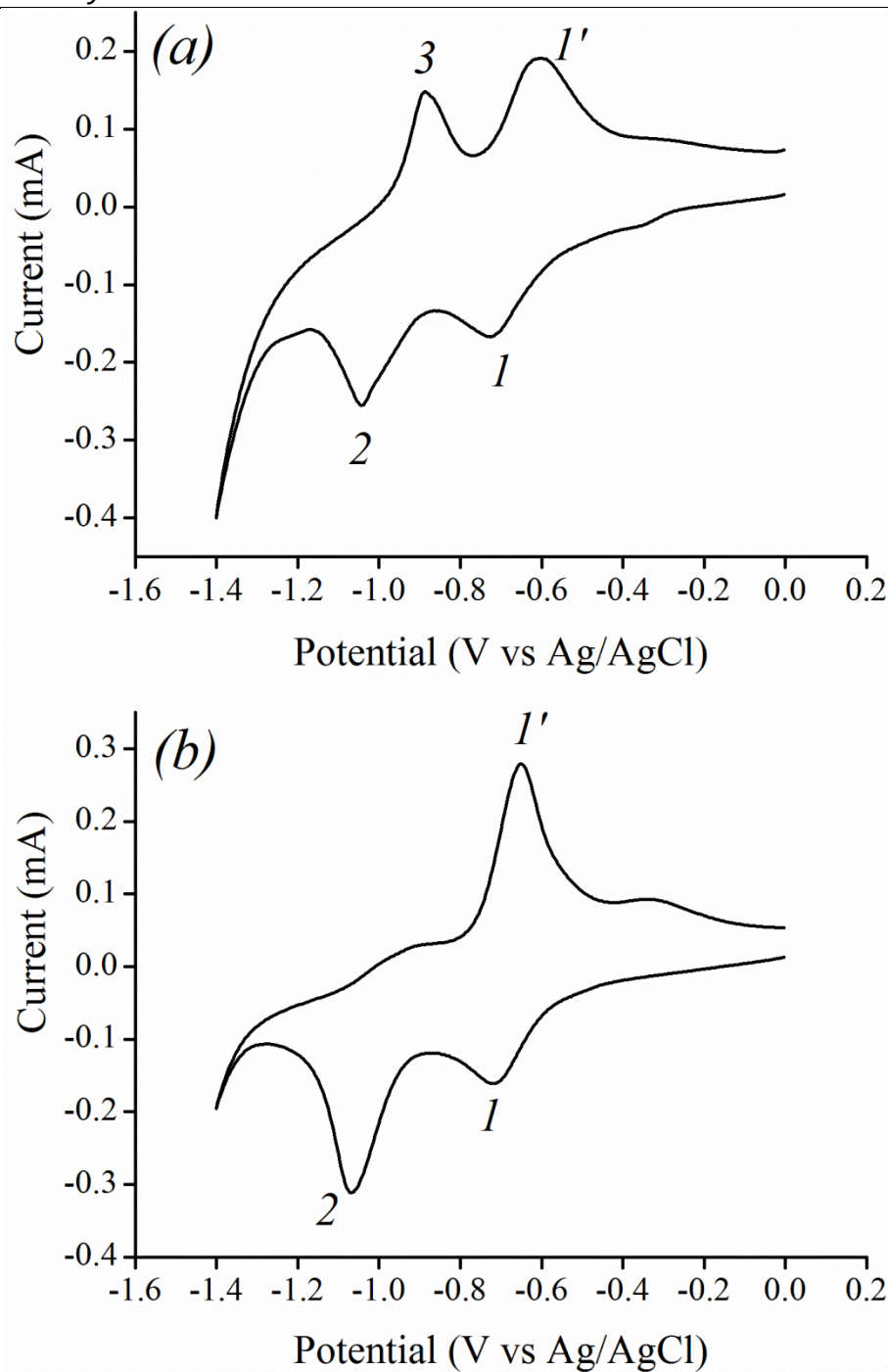


Figure 51 Cyclic voltammograms in 1 mM MV, 0.1 M KCl recorded at (a) HBDP; (b) OBDP. The scans were recorded at 0.05 Vs⁻¹

Table 12 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at 0.05 V s⁻¹ at hydrogen terminated boron-doped diamond powder modified electrode

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.71	-6.76×10^{-5}	-1.69×10^{-4}
2	-1.04	-1.04×10^{-4}	-2.60×10^{-4}
3	-0.89	1.22×10^{-4}	3.05×10^{-4}
1'	-0.60	1.24×10^{-4}	3.10×10^{-4}

Table 13 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at 0.05 V s⁻¹ at oxygen terminated boron-doped diamond powder modified electrode

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.71	-7.95×10 ⁻⁵	-1.98×10 ⁻⁴
2	-1.07	-1.99×10 ⁻⁴	-4.98×10 ⁻⁴
1'	-0.65	2.23×10 ⁻⁴	5.78×10 ⁻⁴

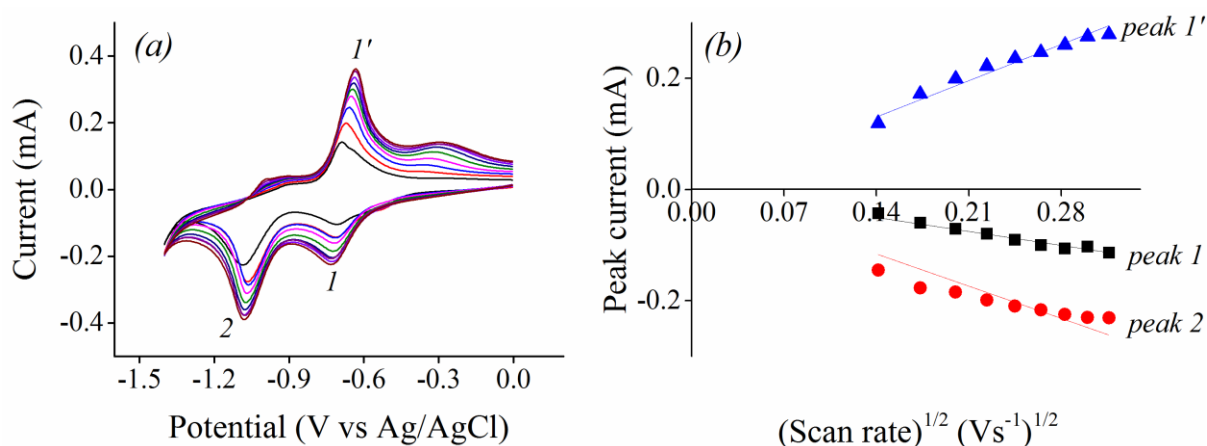


Figure 52 Cyclic voltammogram of 1 mM MV, 0.1 M KCl recorded at (a) oxygen terminated boron-doped diamond powder with the scan rates from 0.02 to 0.1 V s⁻¹; (b) corresponding plots of peak currents versus square root of scan rate

At HBDP, $\Delta E_{MV^{2+}/MV^{\cdot+}}$ is 116 mV with $k_{app}^0 = 2.5 \times 10^{-3} \text{ cm s}^{-1}$ ($\psi=0.39$). In the anodic scan, the peak at -0.89 V corresponding to MV_{ads}^0 is again characteristic only of H-terminated BDP and is not detectable at O-terminated BDP. As shown in Figure 53 (c), peak 3 is found to vary linearly with the scan rate from 0.02 to 0.08 V s⁻¹, therefore confirming the occurrence of the adsorption process.

The surface coverage of MV_{ads}^0 in the first scan is estimated at 7 nmol cm⁻² at HBDP (Table 16). Despite the significant increase in the surface roughness which occurs by coating the plane BDE electrode with BDP, the amount of MV_{ads}^0 adsorbed is thus surprisingly smaller than at the plane BDE electrode. This shows that the tendency to form thick multilayer MV_{ads}^0 phases must be quite sensitive to the diamond surface morphology.

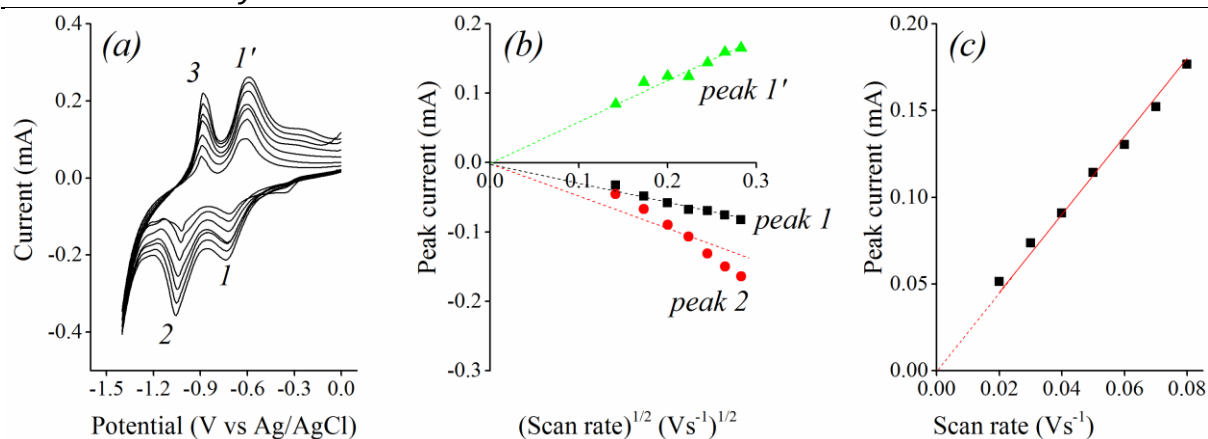


Figure 53 Cyclic voltammogram of 1 mM MV, 0.1 M KCl recorded at (a) hydrogen terminated boron-doped diamond powder with the scan rates from 0.02 to 0.08 Vs⁻¹; (b) corresponding plots of peak currents versus square root of scan rate; (c) plot of peak 3 currents versus scan rate

Figure 54 compares the cyclic voltammograms of 1 mM methylviologen recorded at the oxygen terminated DND powder modified electrode (dash dot, red line) and hydrogen terminated DND electrode (black line). The related peak positions and current responses are presented in

Table 14 and Table 15. The electrochemical behaviour of methylviologen at ODND electrode is similar to that of OBDE. $\Delta E_{MV^{2+}/MV^{+}}$ at ODND is 83 mV and k_{app}^0 is $6.4 \times 10^{-3} \text{ cm s}^{-1}$ ($\psi=1$). At HDND, $\Delta E_{MV^{2+}/MV^{+}}$ is 78 mV with $k_{app}^0 = 8.9 \times 10^{-3} \text{ cm s}^{-1}$ ($\psi=1.4$). In the anodic process at HDND, again there is an evidence that the adsorption of MV^0 is favoured by the H termination of the electrode as witnessed by the shift in the oxidation peak current from -0.98 V to -0.89 V as the termination is changed from O-terminated to H-terminated, although the difference in the electrochemical traces for the two surface terminations are not as big as for the other electrodes investigated. The surface coverage of MV_{ads}^0 in the first scan is estimated to be less than 5 nmol cm^{-2} at HDND (Table 16).

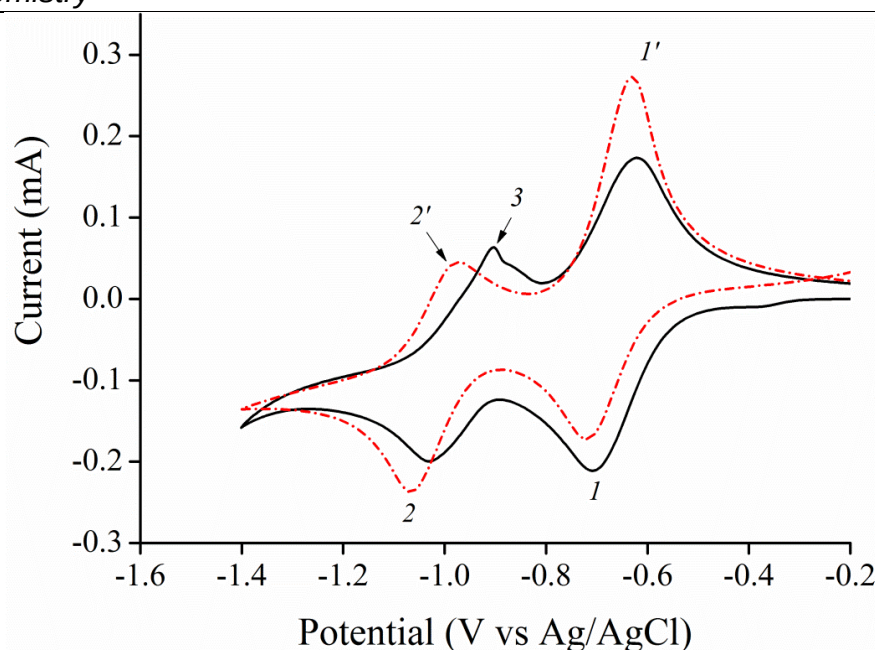


Figure 54 Cyclic voltammograms in 1 mM MV, 0.1 M KCl recorded at (–) HDND; (– –) ODND. The scans were recorded at 0.05 Vs⁻¹

Table 14 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at 0.05 V s⁻¹ at oxygen terminated detonation nanodiamond powder modified electrode

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.71	-1.29×10 ⁻⁴	-3.22×10 ⁻⁴
2	-1.06	-1.33×10 ⁻⁴	-3.33×10 ⁻⁴
2'	-0.99	8.49×10 ⁻⁵	2.12×10 ⁻⁴
1'	-0.63	2.64×10 ⁻⁴	6.60×10 ⁻⁴

Table 15 Peak position and current response data recorded in 1 mM MV, 0.1 M KCl at 0.05 V s⁻¹ at hydrogen terminated detonation nanodiamond powder modified electrode

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-0.70	-1.39×10 ⁻⁴	-3.48×10 ⁻⁴
2	-1.03	-7.17×10 ⁻⁵	-1.79×10 ⁻⁴
3	-0.89	7.95×10 ⁻⁵	1.98×10 ⁻⁴
1'	-0.62	1.55×10 ⁻⁴	3.88×10 ⁻⁴

In order to assess the stability and persistence of the adsorbed MV⁰ at H-terminated diamond, the effects of electrode rinsing were investigated. Freshly prepared electrodes were held in 1 mM methylviologen for 60 s at -1.3 V to accumulate MV⁰_{ads} at the electrode surface. The electrodes were then removed from the cell and rinsed four times with 5 ml of water.

Afterwards, the cyclic voltammetry was performed as described earlier in a blank solution of 0.1 M KCl (no methylviologen). The data recorded are presented in Figure 55.

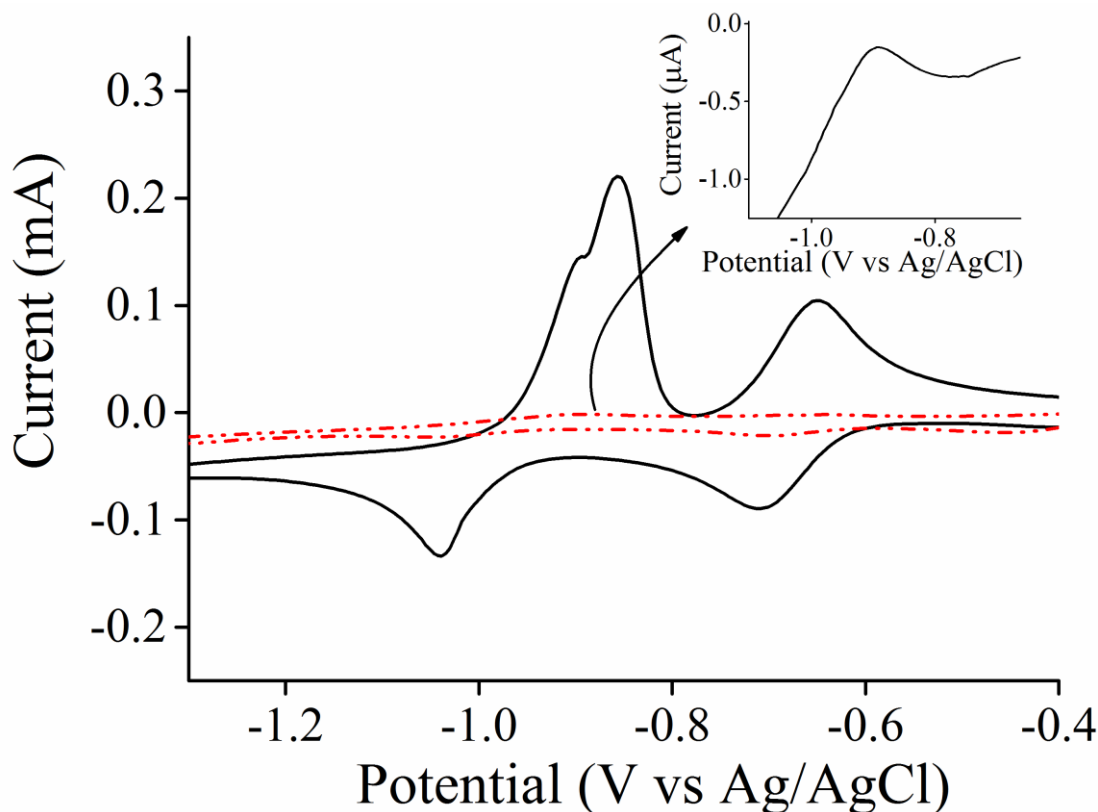


Figure 55 Cyclic voltammograms at (–) HBDE in 1 mM MV, 0.1 M KCl, (– · – ·) HBDE after rinse in background electrolyte (0.1 M KCl), the inset displays a magnified MV_{0ads} peak remained on the HBDE electrode surface after the rinsing procedure

Table 16 MV⁰ adsorption data at hydrogen terminated electrodes

Electrode	CV MV ⁰ _{ads} peak area (C)		CV Γ data (nmol cm ⁻²)		CC Γ data (nmol cm ⁻²)	XPS data
	in solution	after rinse	in solution	after rinse	after rinse	N 1s/C 1s ratio (×10 ⁻³)
HBDE	4.2×10 ⁻⁴	4.6×10 ⁻⁶	10.8	0.1	0.09	2.4
HBDP	2.7×10 ⁻⁴	1.3×10 ⁻⁵	7	0.4	0.25	6.9
HDND	1.8×10 ⁻⁴	4.5×10 ⁻⁵	5	1.2	1.17	8.7

The amount of MV⁰_{ads} left on the electrode surface was estimated from the area under the oxidation peak 3 as in equation 4.1.9. The data are summarised in Table 16. The greatest amount of MV⁰_{ads} (1.2 nmol cm⁻²) is found on the HDND electrode with three times less (0.4 nmol cm⁻²) at the HBDP electrode, and negligible amounts at the HBDE surface. This

most likely arises since at the HDND and HBDP electrodes the MV_{ads}^0 species become trapped within the powder layer and therefore are not easily removed by flowing water over the external surface.

4.4.3.1 Chronocoulometry study of methyl viologen adsorption

In further experiments, chronocoulometric (CC) measurements were used in a similar way to examine the adsorption properties of MV_{ads}^0 at H-terminated electrodes: in the presence and absence of the analyte by scanning the electrode from -1.0 V to -0.7 V over 5 s. Figure 56 presents chronocoulometric $Q-t^{1/2}$ curves of the oxidation of 1 mM methylviologen at the HBDE, HBDP and HDND electrodes. Q_{dl} (red line 1) was obtained in the background electrolyte (0.1 M KCl). The as-prepared electrodes were then exposed to 1 mM methylviologen for 60 s at -1.3 V as described in CV measurements. The treatment was followed by the rinsing procedure (four times with 5 mL of water). The subsequent chronocoulometric measurement in background electrolyte provides the value of $Q_{after\ rinse}$ (black line 2). The difference between the intercepts ($t = 0$) of $Q_{after\ rinse}$ and Q_{dl} with the ordinate is the charge which is required to oxidise instantaneously an adsorbed layer of MV_{ads}^0 (Figure 56 (b-f)). The intercepts with the ordinate were estimated from the data points between 1 to 1.5 s time period. The surface coverage values obtained from chronocoulometry are compared in Table 16. After the rinsing procedure, the surface coverage of MV_{ads}^0 was found to be 1.17 nmol cm^{-2} at HDND, 0.25 nmol cm^{-2} at HBDP and 0.09 nmol cm^{-2} at HBDE respectively. These are in a good agreement with the values estimated by CV.

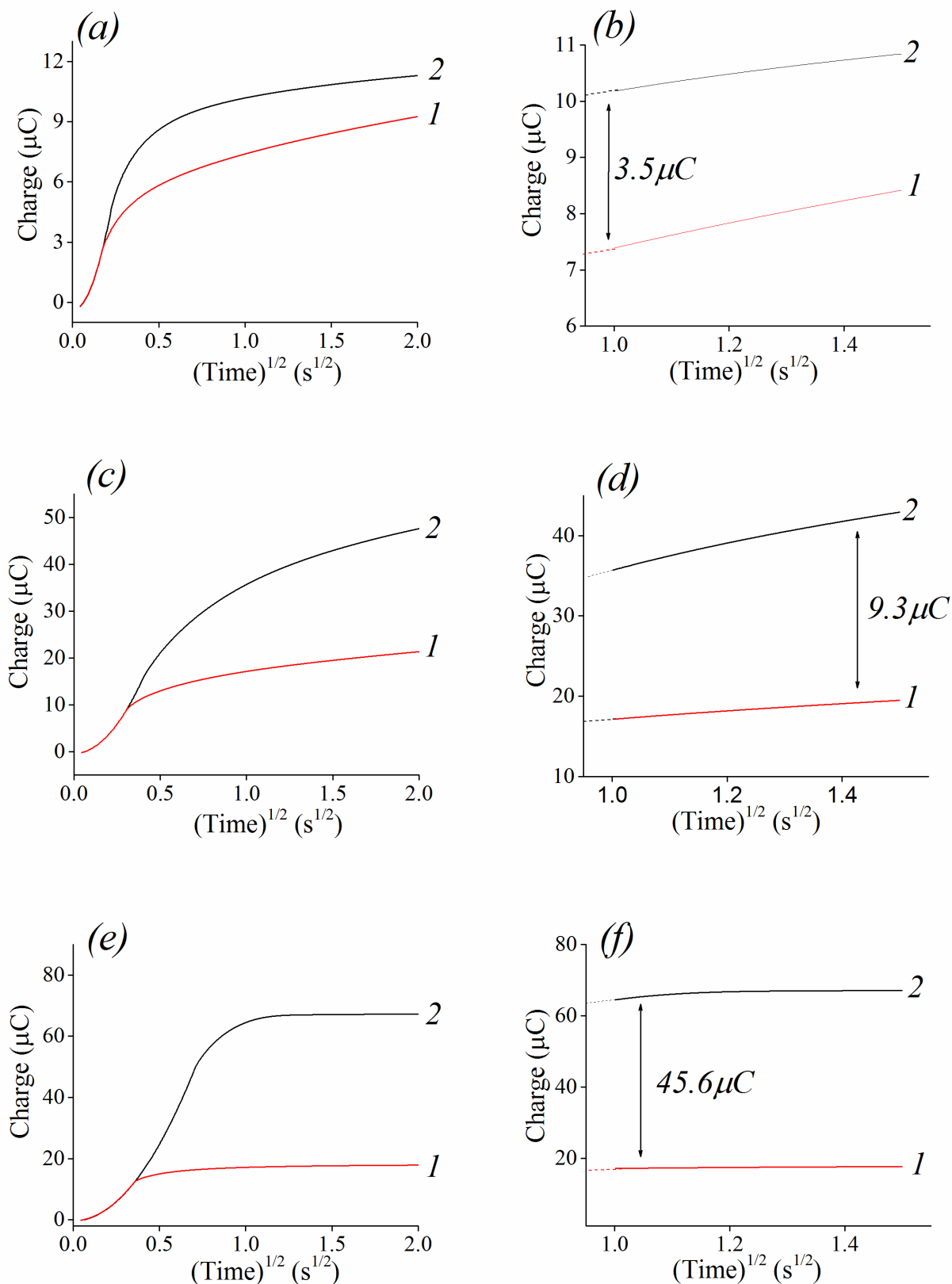


Figure 56 Chronocoulometric curves recorded during the potential scanning from -1.0 V to -0.7 V at (a) HBDE in (1) background electrolyte 0.1 M KCl, (2) after the rinsing procedure, (b) associated charge difference at HBDE; (c) HBDEP in (1) background electrolyte 0.1 M KCl, (2) after the rinsing procedure, (d) associated charge difference at HBDEP; (e) HDND in (1) background electrolyte 0.1 M KCl, (2) after the rinsing procedure, (f) associated charge difference at HDND

An additional series of XPS experiments were performed in order to understand the changes in the surface chemistry of the diamond after the exposure to methyl viologen. Again, freshly prepared electrodes were held in 1 mM methylviologen solution for 60 s at -1.3 V before being removed from the cell and rinsed four times with 5 ml of water. The XPS data recorded are shown in Figure 57, with associated peak parameters and elemental ratios in Table 17, Table 18 and Table 19. The high resolution C 1s spectra of HBDE are presented in Figure 57 (a). A C 1s component characteristic of the bulk diamond was positioned at 285.0 eV. The peaks at 285.7 eV and 287.3 eV correspond to C-H_x (x = 2,3) species in polyhydride configurations and carboxyl surface groups respectively.⁶⁹⁻⁷¹ The peak at 283.4 eV is ascribed to the graphitic type states involved in π -bonding, such as associated with sp² defects.⁷² The N 1s spectral region is shown in Figure 57 (b). An N 1s component located at 400.5 eV confirms the presence of neutral MV⁰ species which is in agreement with the CV data described above. The C 1s spectra of HBDP were found to be similar to that of HBDE (Figure 57 (c)). Figure 57 (d) displays the N 1s spectral region of HBDP. The N 1s binding energy of 399.9 eV is also consistent with typical values of N bonded in neutral state in carbon polymeric materials.⁷³ The C 1s region of HDND (Figure 57 (e)) is characterised by a slight change in the peak shape at a higher binding energies due to stronger photoelectron signals from C-CH_x and COOH species. The N 1s component of HDND is presented in Figure 57 (f). A well resolved singlet at 399.8 eV confirms the presence of MV⁰_{ads}.

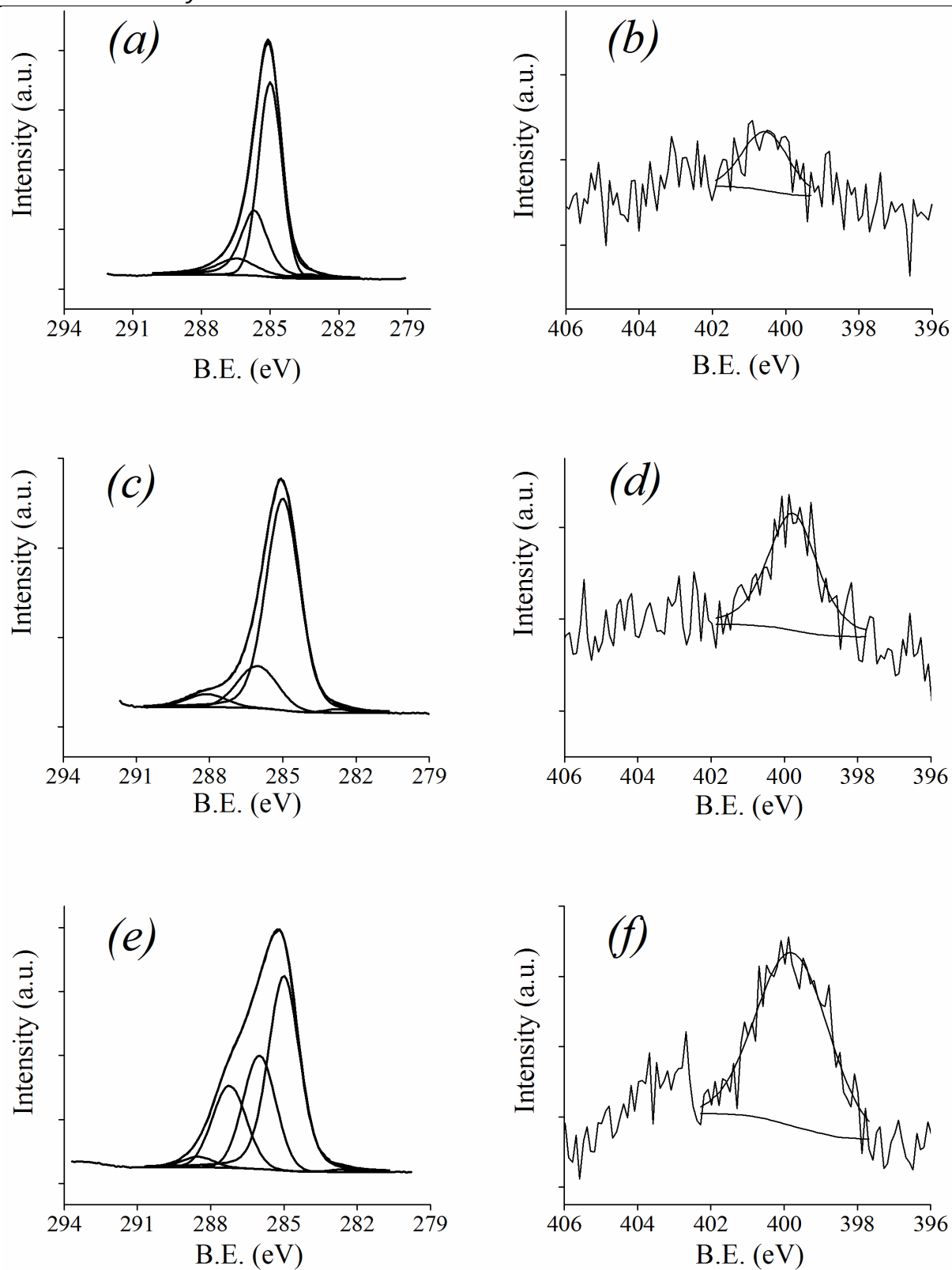


Figure 57 (a) C 1s XPS region at HBDE; (b) N 1s region at HBDE; (c) C 1s region at HBDP; (d) N 1s region at HBDP; (e) C 1s region at HDND; (f) N 1s region at HDND;

Table 17 XPS binding energies for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	Binding energies (eV)					N 1s
	C 1s					
	Csp ³	C-CHx	C=O	COOH	sp ² def	
HBDE	285.0	285.7	286.5	n/a	283.4	400.5
HBDP	285.0	286	n/a	288.1	282.7	399.9
HDND	285.0	286.0	287.2	288.5	282.6	399.8

Table 18 FWHM values for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	FWHM (eV)					N 1s
	C 1s					
	Csp ³	C-CHx	C=O	COOH	sp ² def	
HBDE	1.2	1.4	1.5	n/a	2	1.5
HBDP	1.6	1.9	n/a	1.9	1.2	1.6
HDND	1.5	1.6	1.6	1.5	1	2.3

Table 19 XPS elemental ratios and charging values for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	N 1s/C 1s ratios (×10 ⁻³)	Charging (eV)
		Relative to C 1s (285.0 eV)
HBDE	2.4	5.8
HBDP	6.9	11.3
HDND	8.7	11.3

The N:C ratios deduced from the spectra using the appropriate sensitivity factors⁴⁴ are shown in Table 19. Again, the same qualitative trend as seen in the electrochemical studies can be noted, with the amount of MV⁰ adsorbed being greatest on HDND and significantly smaller on HBDE. The amount of MV⁰ adsorbed on the latter surface is clearly very small and the surface concentration in nmol cm⁻² can be calculated under these circumstances using the following equation:⁷³

$$\frac{I_A}{I_B} = \frac{n_A S_A}{P_A \int_0^\infty D_B S_B e^{-x/\lambda_B} dx} = \frac{n_A S_A}{P_A D_B S_B \lambda_B} \quad (\text{Equation 4.2.1})$$

where A – adsorbed species, B – uniform solid surface, n_A is the number density of the adsorbed species A , λ_B is the inelastic mean free path of emitted photoelectrons from the bulk diamond through the overlayer of adsorbed species A , P_A is their transmission probability

through the adsorbed layer A , $S_{A,B}$ are the surface sensitivity factors which are estimated by dividing the conventional bulk factors⁷⁴ by appropriate value of inelastic mean free path,⁴¹ D_B is the atomic density of atoms in the bulk solid and x is the distance below the solid surface.⁷³ Diamond is the main source of carbon at these low MV^0_{ads} coverages, for which an inelastic mean free path (appropriate to Al K α C 1s electrons) of 1.7 nm can be used, along with a density of carbon atoms of 1.8×10^{23} .⁴¹ P_A is assumed to equal unity given the low concentration of MV^0 . The use of these factors in the equation 4.2.1 gives the surface coverage of 0.1 nmol cm^{-2} at HBDE electrode which is consistent with a surface concentration well below a monolayer as observed in the electrochemical studies. A similar analysis for HBDP and HDND yielded surface concentrations of 0.3 and 0.5 nmol cm^{-2} respectively, indicative of monolayer coverage, although there is probably some errors in using such an analysis for these more morphologically complex interfaces.

4.4.4 Electrochemistry of anthraquinonedisulfonate

In acidic media, the redox transformation of anthraquinonedisulfonate is described by the following reaction:

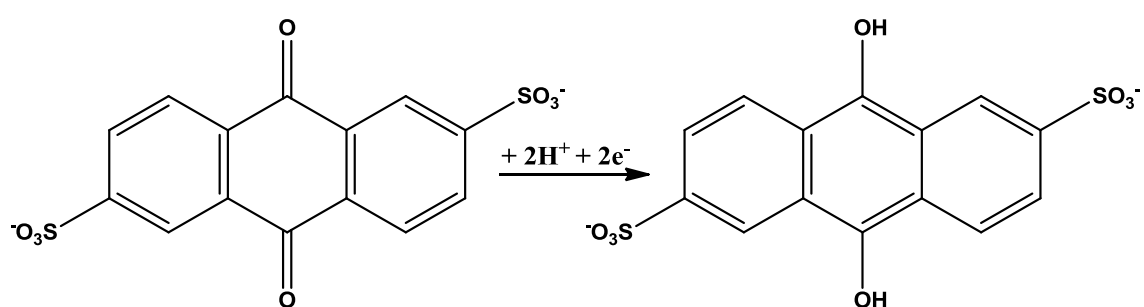


Figure 58 The redox reaction of 2,6-AQDS in acidic media

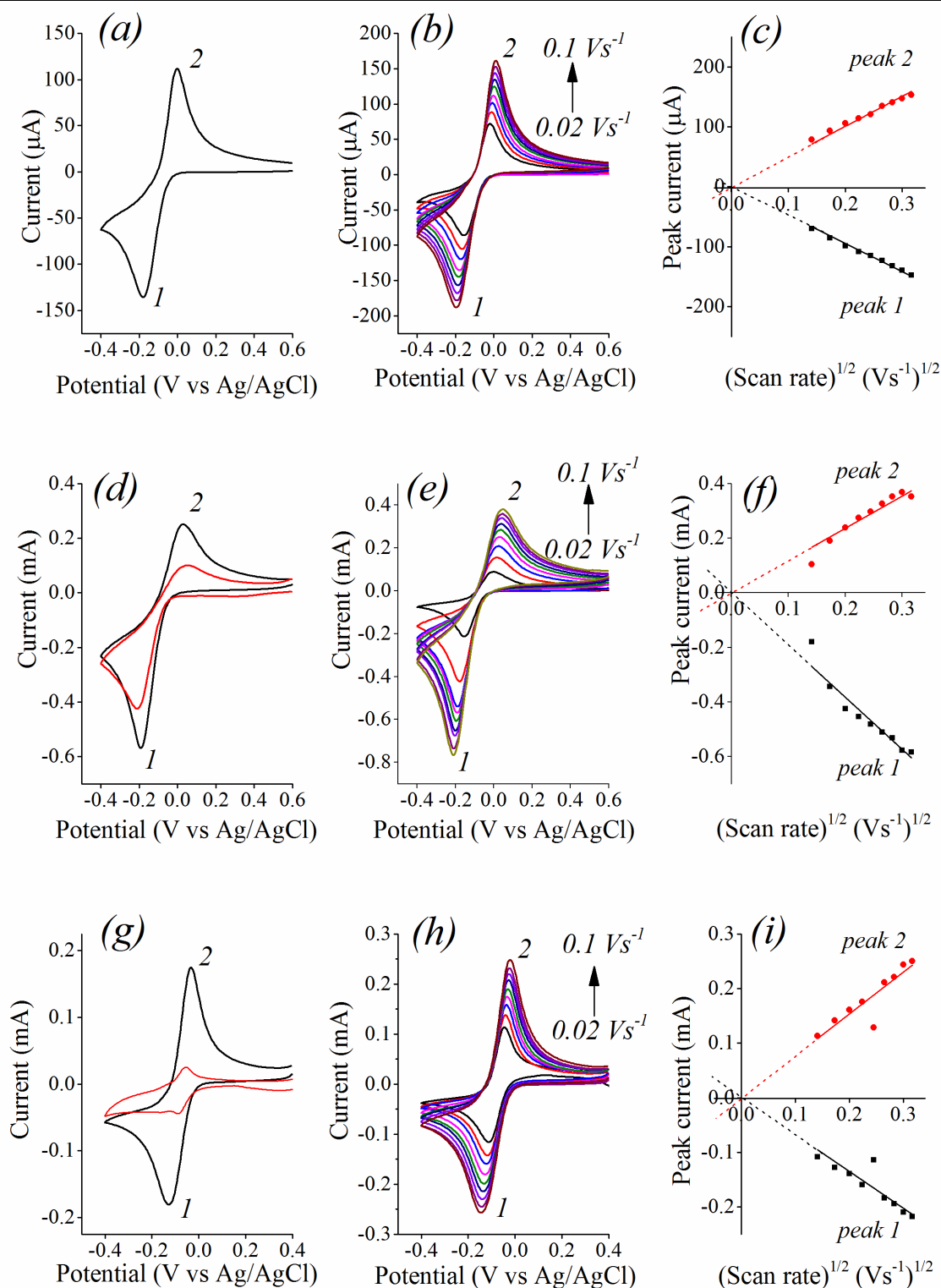


Figure 59 Cyclic voltammograms of 1 mM 2,6-AQDS, 0.1 M HNO₃ recorded at (a) (–) HBDE; (b) HBDE at the scan rate from 0.02 to 0.1 V s⁻¹; (c) corresponding plot of reduction and oxidation peak currents at HBDE vs square root of the scan rate; (d) (–) HDND, (–) HDND in 0.1 M HNO₃ after the rinsing procedure; (e) HDND at the scan rates from 0.02 to 0.1 V s⁻¹; (f) corresponding plot of reduction and oxidation peak currents vs square root of the scan rate; (g) (–) HBDP, (–) HBDP in 0.1 M HNO₃ after the rinsing procedure; (h) HBDP at the scan rates from 0.02 to 0.1 V s⁻¹; (i) corresponding plot of reduction and oxidation peak currents at HBDP vs square root of the scan rate

Figure 59 shows CV curves of 1 mM 2,6-AQDS dissolved in 0.1 M HNO₃ recorded at a H-terminated diamond electrodes. The associated peak positions and current responses are summarised in Table 20.

Table 20 Peak position and current response data recorded in 1 mM 2,6-AQDS, 0.1 M HNO₃ at 0.05 V s⁻¹ at hydrogen terminated diamond electrodes

Electrode	Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
HBDE	1	-0.176	-1.07×10 ⁻⁴	-2.68×10 ⁻⁴
	2	-0.005	1.16×10 ⁻⁴	2.90×10 ⁻⁴
HDND	1	-0.186	-4.49×10 ⁻⁴	-1.12×10 ⁻³
	2	0.024	2.84×10 ⁻⁴	7.10×10 ⁻⁴
HBDP	1	-0.123	-1.56×10 ⁻⁴	-3.90×10 ⁻⁴
	2	-0.035	1.83×10 ⁻⁴	4.58×10 ⁻⁴

At HBDE (Figure 59 (a)), a typical quasi-reversible CV response is observed with a peak separation $\Delta E_p = 171$ mV, corresponding to a k_{app}^0 of 8.9×10^{-4} cm s⁻¹ as estimated by the Nicholson method described in Section 4.4.3. The diffusion coefficient of 5×10^{-6} cm² s⁻¹ was used in the calculations.²⁴ Consistent with this picture, the peak currents are close to those estimated from the transport limited, two electron transfer, irreversible electrochemical reaction.⁴⁶ As presented in Table 21, from the integration of the CV data, 4.4 nmol cm⁻² of dihydroxyanthracene was formed during the cathodic scan, and 4.4 nmol cm⁻² of the corresponding anthraquinone were re-formed in solution during the first anodic scan.

Table 21 2,6-AQDS adsorption data at hydrogen and oxygen terminated electrodes

Electrode	CV Γ data in solution (nmol cm ⁻²)		CV Γ data after rinse (nmol cm ⁻²)	
	Red	Ox	Red	Ox
HBDE	4.4	4.4	0	0
HBDP	6.5	6.4	0.8	0.8
HDND	18	15	11	6
OBDE	n/a	0.2	0	0
ODBP	2.2	2.6	0	0
ODND	2.3	2.9	0	0

The I_p^{OX} and I_p^{RED} (Figure 59 (c)) seem to increase linearly with the (scan rate)^{1/2} between 0.02 and 0.1 V s⁻¹, confirming the occurrence of diffusion controlled process.

Dramatic differences are seen at the HDND electrode. An interesting feature observed from the CV curve at HDND electrode (Figure 59 (d)) is that the reduction of 1 mM 2,6-AQDS occurs with a peak height 4 times greater than that of HBDE electrode. This significant increase in peak current must be indicative of pre-concentration effects of the analyte at the electrode surface, thus giving rise to enhanced currents. To prove this, the electrode was removed from the 2,6-AQDS solution, rinsed and studied in background electrolyte. Voltammetric peaks of an amplitude similar to those seen in the 2,6-AQDS solution are observed, showing that a significant amount of 2,6-AQDS must be adsorbed in the DND layer. By contrast, if this experiment was repeated at the HBDE electrode, negligible signal responses were seen in the background electrolyte. Clearly, the high surface-area-to-volume ratio of the hydrogenated DND powders tend to accumulate a high amount of the analyte. Therefore a deviation from linearity of I_p^{OX} and I_p^{RED} with the $(\text{scan rate})^{1/2}$ between 0.02 and 0.1 V s^{-1} in 1 mM 2,6-AQDS solution is observed in Figure 59 (f). As presented in Table 21, the highest amount of 18 nmol cm^{-2} of dihydroxyanthracene and 15 nmol cm^{-2} of anthraquinone were formed at HDND electrode. The subsequent scan in the background electrolyte after the rinsing procedure shows reduction and oxidation peaks corresponding to the transfer of 11 nmol cm^{-2} dihydroxyanthracene to the background electrolyte.

Although adsorption seems to be dominating the voltammetric response, it is notable that the voltammetric peak profiles do not show the classical symmetric adsorption voltammetric response characterised by $\Delta E_p = 0$ which can be expected.⁴⁶ Rather the profiles are somewhat characteristic of diffusional voltammetry and look quite similar whether the voltammetry is carried out in the redox solution or in the background electrolyte. A likely explanation is that when immersed in the 2,6-AQDS solution, the redox molecule becomes adsorbed on the high surface HDND particles, so is not efficiently removed when the electrode is rinsed. However, when transferred to fresh background electrolyte, the 2,6-AQDS slowly dissolves as a result

of the large concentration gradient, thus giving rise to voltammetric curves which look quite similar to those recorded in the redox solution itself.

The cyclic voltammetric curve for the HBDP electrode is presented in Figure 59 (g). Again, the simple diffusional model in the plots of peak current versus (scan rate)^{1/2} are observed (Figure 59 (i)). The scan in the supporting electrolyte after the rinsing procedure clearly shows that the transfer of the analyte to the background solution takes place, although not to the extent seen for the HDND electrode. From the CV recorded (red line, Figure 59 (i)) in the background electrolyte, a transfer of 0.8 nmol cm⁻² of dihydroxyanthracene was detected at the HBDP surface. This is about 13 times smaller than seen at the HDND electrode (as compared in Table 2), and is likely to be associated with the lower electrode surface area of the HBDP powder layer.

The electrochemical behaviour of oxidised electrodes presented in Figure 60 differs significantly from that of hydrogen treated electrodes. An oxidised OBDE (Figure 60 (a)) is found to be largely inactive with the oxidation peak current at 0.32 V being almost twenty times smaller than that of H-terminated BDE surface.³⁰ The reduction process was not observed at OBDE during cathodic scan since it is lost in the background arising from hydrogen evolution, in part as a result of the higher overpotentials which seem to be associated with the OBDE electrode. This is attributable to the fact that 2,6-AQDS carries a negative charge and is thus repelled from the diamond surface due to the negative charge of the oxygen functionalities present. As displayed in Figure 60 (d), the introduction of electrically conducting OBDP film results in some restoration of the redox currents comparable to that of observed at HBDP.

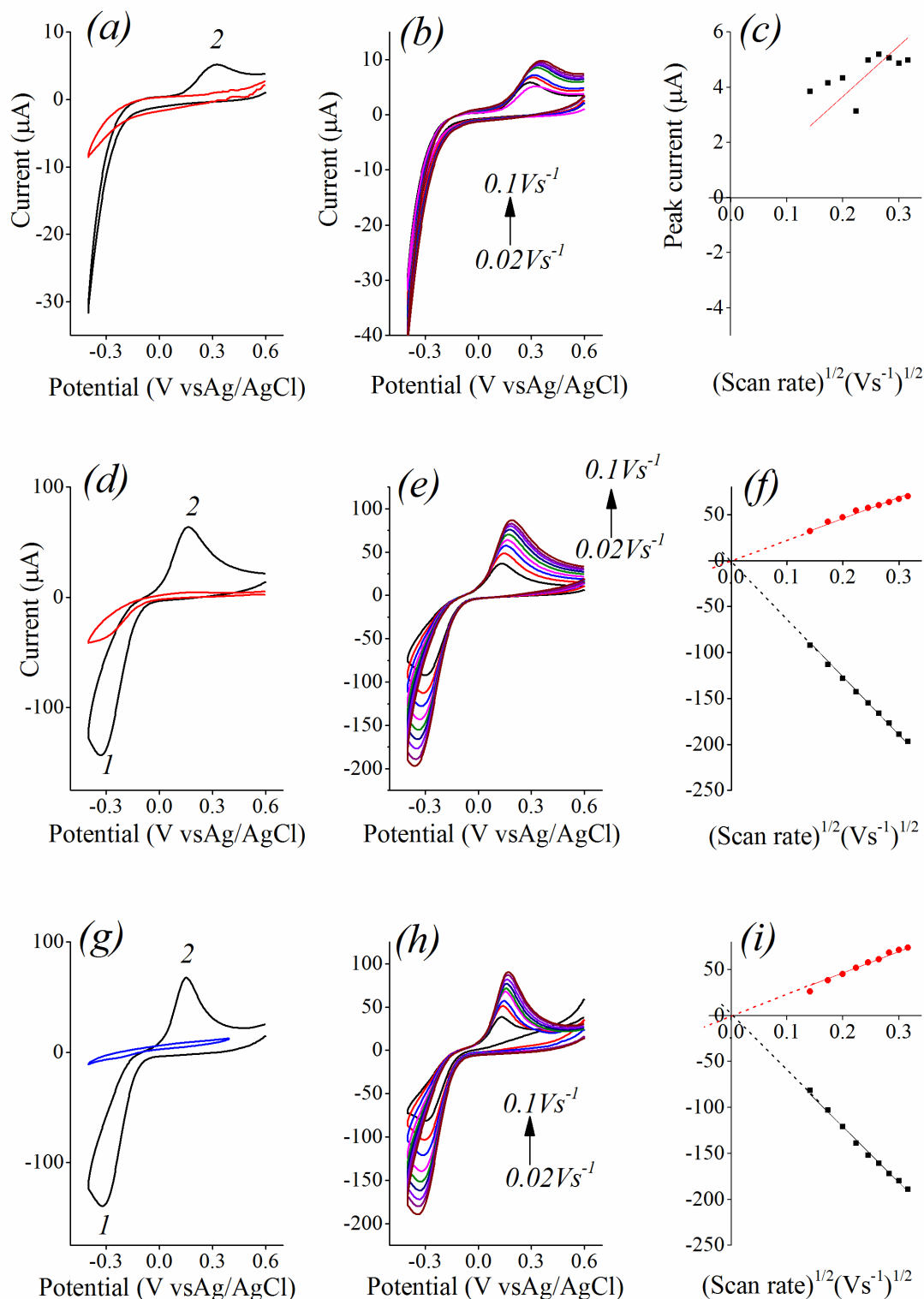


Figure 60 Cyclic voltammograms of 1 mM 2,6-AQDS, 0.1 M HNO₃ recorded at (a) (–) OBDE, (–) OBDE in 0.1 M HNO₃ after the rinsing procedure; (b) OBDE at the scan rate from 0.02 to 0.1 V s⁻¹; (c) corresponding plot of reduction and oxidation peak currents at OBDE vs square root of the scan rate; (d) (–) ODND, (–) ODND in 0.1 M HNO₃ after the rinsing procedure; (e) ODND at the scan rates from 0.02 to 0.1 V s⁻¹; (f) corresponding plot of reduction and oxidation peak currents vs square root of the scan rate; (g) (–) OBDP, (–) OBDP in 0.1 M HNO₃ after the rinsing procedure; (h) OBDP at the scan rates from 0.02 to 0.1 V s⁻¹; (i) corresponding plot of reduction and oxidation peak currents at OBDP vs square root of the scan rate

Table 22 Peak position and current response data recorded in 1 mM 2,6-AQDS, 0.1 M HNO₃ at 0.05 V s⁻¹ at oxygen terminated diamond electrodes

Electrode	Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
OBDE	1	n/a	n/a	n/a
	2	0.307	2.98×10 ⁻⁶	7.45×10 ⁻⁶
ODND	1	-0.327	-1.43×10 ⁻⁴	-3.58×10 ⁻⁴
	2	0.161	5.33×10 ⁻⁵	1.33×10 ⁻⁴
OBDP	1	-0.317	-1.39×10 ⁻⁴	-3.48×10 ⁻⁴
	2	0.151	5.62×10 ⁻⁵	1.41×10 ⁻⁴

The reaction kinetics are however much slower; at OBDP a large peak separation with $\Delta E_p = 469$ mV is seen, therefore suggesting slower electron transfer rates as compared to HBDP. Another difference is the ratio of cathodic and anodic peak currents at OBDP which is greater than unity; whereas $I_p^{\text{RED}}/I_p^{\text{OX}} \sim 1$ was observed at HBDP. The former effect, characteristic of oxidised BDP, can be related to the occurrence of chemical processes associated with the reduced forms of 2,6-AQDS which can form, leading to molecular aggregation, thus removing dihydroxy AQDS for subsequent oxidation during the anodic scan.⁷⁵⁻⁷⁷ It is notable that this does not occur on the hydrogenated electrodes to such an extent as a result of the adsorption process noted above. The electrochemical response at the ODND electrode (Figure 60 (g)) is similar to that of OBDP with the ΔE_p value of 493 mV and $I_p^{\text{RED}}/I_p^{\text{OX}}$ ratio greater than unity.

A major difference between the hydrogenated and oxidised diamond electrodes concerns the extent to which adsorption takes place. Whereas significant amounts of electrolyte were adsorbed on the former electrodes as discussed above, no evidence for adsorption was seen at the oxidised electrodes. This is after exposure to 2,6-AQDS, the ODND or OBDP electrodes were rinsed and then immersed in background electrolyte no voltammetric responses were observed as shown in Figure 60 (a, d and g), red line.

4.4.4.1 Chronocoulometry characterisation of 2,6-AQDS adsorption

As a comparison to the electrochemical behaviour observed in CV experiments, further chronocoulometric studies were performed. The electrode potential was scanned from 0.6 V to -0.4 V in the presence and absence of 2,6-AQDS. The results are summarised in

Table 23 Chronocoulometry data recorded at hydrogen terminated HBDP and HDND electrodes. The values obtained at H-terminated electrodes are in a good agreement with the cyclic voltammetry discussed above. Zero adsorption was detected at oxygen terminated electrodes, thus confirming that adsorption does not take place at hydrophilic, O-terminated surfaces mainly due to repulsion forces.

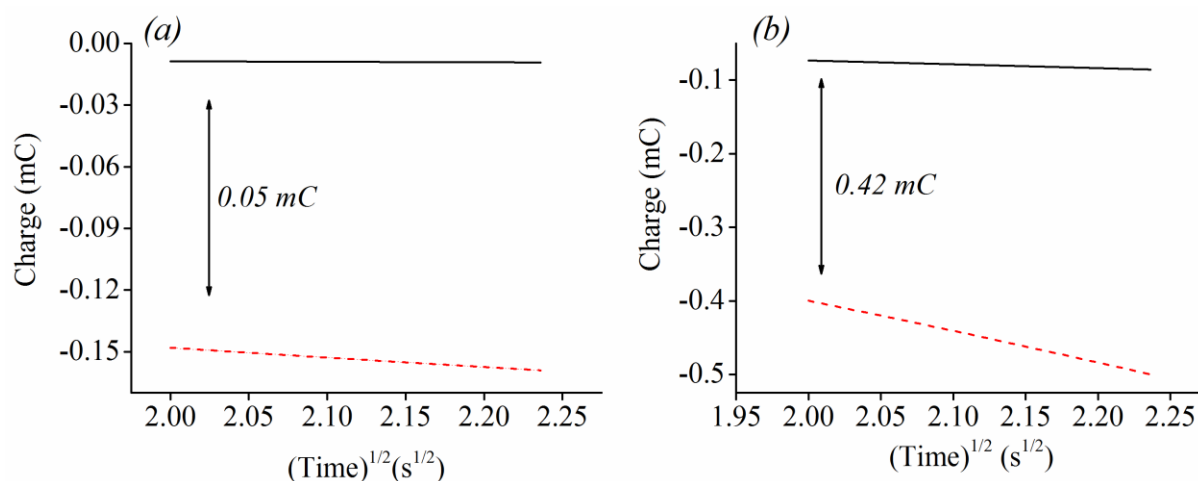


Figure 61 Chronocoulometric curves recorded during potential scanning from 0.6 V to -0.4 V at (a) HBDP in (–) background electrolyte 0.1 M HNO₃, (– –) after the rinsing procedure; (b) HDND in (–) background electrolyte 0.1 M HNO₃, (– –) after the rinsing procedure

Table 23 Chronocoulometry data recorded at hydrogen terminated HBDP and HDND electrodes

Electrode	Charge difference ($\times 10^{-4}$ C)	CC Γ data after rinse (nmol cm ⁻²)
HBDP	0.51	0.7
HDND	4.2	5.5

In further experiments, an additional series of XPS measurements were performed in order to understand the changes in the surface chemistry induced by the exposure of hydrogenated diamond electrodes to 2,6-AQDS solution. The data are presented in Figure 62 with associated peak parameters and elemental ratios in Table 24,

Table 25, and Table 26. As expected, the XPS results for the HBDE electrode were typical of a clean hydrogen terminated, boron-doped diamond confirming zero adsorption on the electrode. The C 1s higher energy resolution scan recorded at H-terminated BDP electrode is shown in Figure 62 (a). A C 1s component at 285.0 eV is ascribed to the bulk diamond with the chemical shifts at 285.7 eV and 287.0 eV related to C-H_x (x = 2,3) species in polyhydride configurations and carbonyl surface groups respectively.⁶⁹⁻⁷¹ The peak at 283.4 eV is characteristic of sp²-defects.⁷² An S 2p spectral region of HBDE is presented in Figure 62 (b). A well-defined S 2p component at 169.4 eV binding energy arises from -SO₃⁻ groups of 2,6-AQDS adsorbed on the HBDE surface.⁷³ Typically for the HDND modified electrode, the C 1s region contains strong photoelectron signals arising from C-CH_x and oxidised carbon species at 286 and 288.3 eV respectively (Figure 62 (c)). Figure 62 (d) displays the S 2p spectral region of the HDND electrode. A well-resolved S 2p singlet at 169.2 eV confirms the presence of -SO₃⁻ groups of 2,6-AQDS confined to the electrode surface. The S:C ratios derived from the XPS spectra are summarised in Table 26. The XPS analysis confirms significant adsorption of 2,6-AQDS on the HDND electrode, with a less contamination found on the HBDE electrode.

Table 24 XPS binding energies for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	Binding energies (eV)					S 2p
	C 1s					
	Csp ³	C-CHx	C=O	COOH	sp ² def	
HBDP	285.0	285.7	286.4	n/a	283.7	169.4

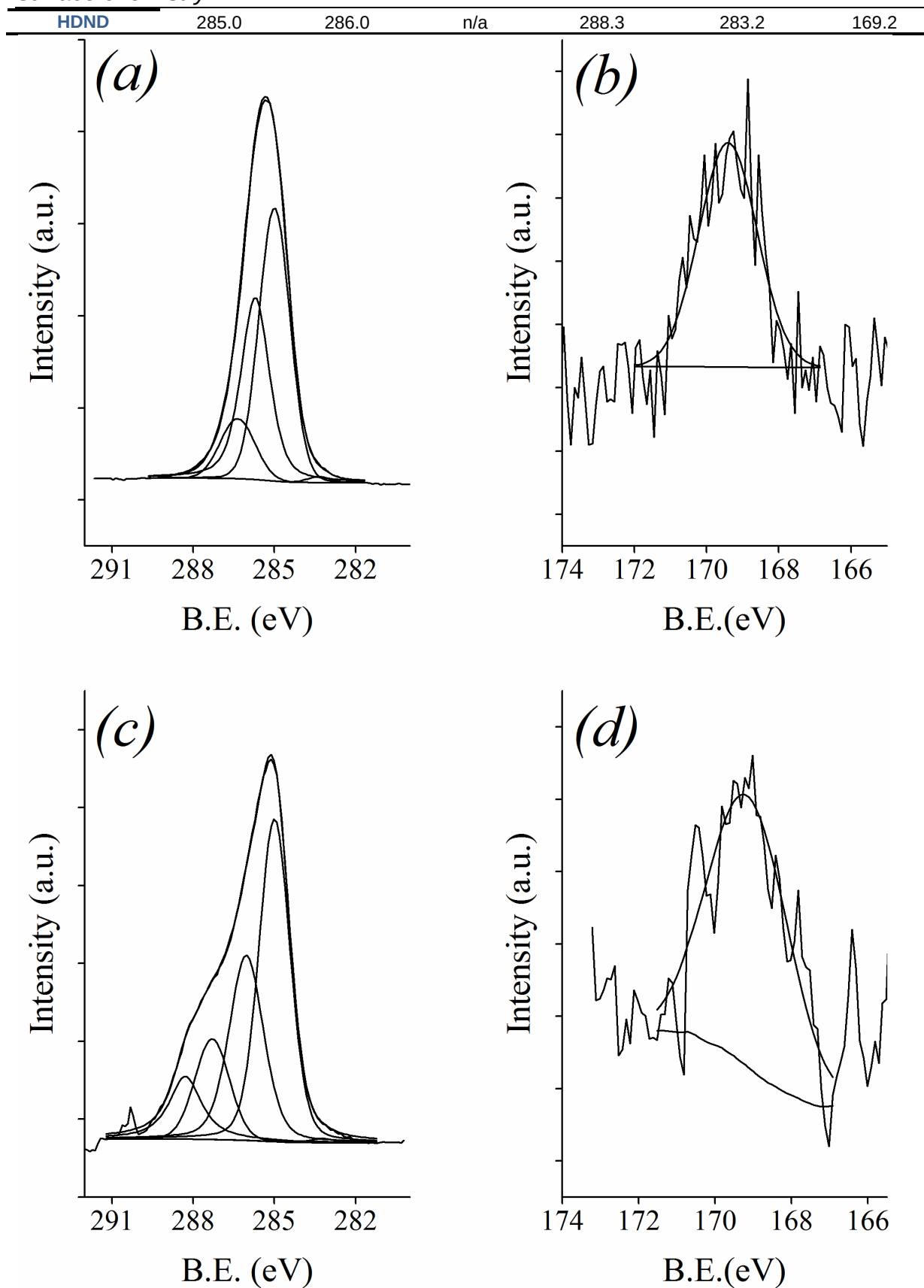


Figure 62 (a) $C1s$ XPS spectra of HBDP; (b) $S2p$ XPS spectra recorded at HBDP; (c) $C1s$ XPS spectra of HDND; (d) $S2p$ XPS spectra recorded at HDND

Table 25 FWHM values for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	FWHM (eV)					S 2p
	C 1s					
	Csp ³	C-CHx	C=O	COOH	sp ² def	
HBDP	1.4	1.2	1.5	n/a	1	1.9
HDND	1.4	1.5	n/a	1.5	1	2.4

Table 26 XPS elemental ratios and charging values for hydrogen terminated boron-doped diamond, boron-doped diamond powder and detonation nanodiamond powder modified electrodes

Sample	S 2p/C 1s ratios (×10 ⁻³)	Charging (eV)
		Relative to C 1s (285.0 eV)
HBDP	1.5	10.34
HDND	6.1	10.78

4.5 Concluding remarks

The electrochemical behaviour of methyl viologen and anthraquinonedisulfonate has been studied at plain microcrystalline boron-doped diamond electrodes, boron-doped diamond powders and detonation nanodiamond powders with differing surface pre-treatments. The hydrogenated surface studied is known to be characterised by hydrophobic properties, with C^{δ-}-H^{δ+} polar bonds. In contrast, the oxygenated surface investigated has hydrophilic character with the opposite bond polarity.

The electrochemistry observed is found to be extremely sensitive to the chemical termination of the diamond surface. In the methyl viologen study, at hydrogen treated plain microcrystalline diamond electrode, methyl viologen oxidation results in the formation of MV⁰_{ads} species which strongly adsorb to the H-terminated electrode surface, whilst at the oxidised analogue this process does not take place. The formation of MV⁰_{ads} was found to be a function of diamond surface morphology as the amount of species detected varies depending on the electrode surface; the H-terminated DND and BDP electrodes show a greater tendency to adsorb methyl viologen than as-grown microcrystalline electrode studied.

Similar results are seen in the 2,6-AQDS study, with no adsorption being observed on the microcrystalline H- and O- terminated diamond electrodes. However, significant adsorption is seen on the H-terminated DND and BDP electrodes, but not on the O-terminated powder electrodes.

Overall therefore the trend would appear to be that the tendency for adsorption to take place is increased if the electrode is H-terminated. Both of the redox couples studied possess hydrophobic ring moieties, along with polar functional groups, so one explanation is that the interaction of the former with the diamond surface dominates the observations. In addition, 2,6-AQDS carries a net negative charge so repulsion is expected with the negatively charged oxygen functionalities on the oxidised surface, while it may be attracted to the positively charged adsorbed to $H^{\delta+}$ of $C^{\delta-}-H^{\delta+}$ bonds.

With regard to morphology, a pronounced trend is seen with methyl viologen and 2,6-AQDS in that the rough powder diamond materials show a much larger tendency to exhibit adsorption.

Overall, it can be concluded that the studies confirm that adsorption and electrode fouling on diamond electrodes does indeed occur, but that it is sensitive to the form and termination of the electrode, and can apparently be minimised by the use of O-terminated electrode structures.

4.6 References

- 1 Swain, G. M. in *Semiconductors and Semimetals* Vol. Volume 77 (eds E. Nebel Christoph & Ristein Jürgen) 121-148 (Elsevier, 2004).
- 2 Rao, T. N. & Fujishima, A. Recent advances in electrochemistry of diamond. *Diamond Relat. Mater.* **9**, 384-389, doi:10.1016/s0925-9635(99)00234-4 (2000).
- 3 Rao, T. N., Ivandini, T. A., Terashima, C., Sarada, B. V. & Fujishima, A. Applications of bare and modified diamond electrodes in electroanalysis. *New Diamond Front. Carbon Technol.* **13**, 79-88 (2003).

- 4 Panizza, M. & Cerisola, G. Application of diamond electrodes to electrochemical processes. *Electrochimica Acta* **51**, 191-199, doi:http://dx.doi.org/10.1016/j.electacta.2005.04.023 (2005).
- 5 Waldvogel, S. R., Kirste, A. & Mentizi, S. 483-510,, 481 plate (John Wiley & Sons, Inc.).
- 6 Kraft, A. Doped diamond: a compact review on a new, versatile electrode material. *Int. J. Electrochem. Sci.* **2**, 355-385 (2007).
- 7 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).
- 8 Hartl, A. *et al.* Protein-modified nanocrystalline diamond thin films for biosensor applications. *Nature Materials* **3**, 736-742, doi:10.1038/nmat1204 (2004).
- 9 Freitas, R. A., Jr. *Nanomedicine, Volume IIA: Biocompatibility*. (Landes Bioscience, 2003).
- 10 Pleskov, Y. V., Sakharova, A. Y., Krotova, M. D., Builov, L. L. & Spitsyn, B. V. Photoelectrochemical properties of semiconductor diamond. *J. Electroanal. Chem. Interfacial Electrochem.* **228**, 19-27 (1987).
- 11 Martin, H. B., Argoitia, A., Angus, J. C. & Landau, U. Voltammetry studies of single-crystal and polycrystalline diamond electrodes. *Journal of the Electrochemical Society* **146**, 2959-2964, doi:10.1149/1.1392035 (1999).
- 12 Alehashem, S., Chambers, F., Strojek, J. W., Swain, G. M. & Ramesham, R. Cyclic Voltammetric Studies of Charge Transfer Reactions at Highly Boron-Doped Polycrystalline Diamond Thin-Film Electrodes. *Anal. Chem.* **67**, 2812-2821, doi:10.1021/ac00113a014 (1995).
- 13 Sasaki, I., Swope, V. M., Ay, A., Kim, D. Y. & Swain, G. M. Microstructural Stability of Electrically Conducting Diamond Powder as Probed Using Electrochemical Methods and In Situ Raman Spectroscopy. *J. Electrochem. Soc.* **158**, B1446-B1452, doi:10.1149/2.087111jes (2011).
- 14 Fischer, A. E. & Swain, G. M. Preparation and characterization of boron-doped diamond powder - A possible dimensionally stable electrocatalyst support material. *Journal of the Electrochemical Society* **152**, B369-B375, doi:10.1149/1.1984367 (2005).
- 15 Ay, A., Swope, V. M. & Swain, G. M. The physicochemical and electrochemical properties of 100 and 500 nm diameter diamond powders coated with boron-doped nanocrystalline diamond. *Journal of the Electrochemical Society* **155**, B1013-B1022, doi:10.1149/1.2958308 (2008).
- 16 Holt, K. B. *et al.* Redox properties of undoped 5 nm diamond nanoparticles. *Physical Chemistry Chemical Physics* **10**, 303-310, doi:10.1039/b711049a (2008).
- 17 Holt, K. B. Undoped diamond nanoparticles: origins of surface redox chemistry. *Physical Chemistry Chemical Physics* **12**, 2048-2058, doi:10.1039/b920075d (2010).
- 18 Bian, L. Y., Wang, Y. H., Zang, J. B., Yu, J. K. & Huang, H. Electrodeposition of Pt nanoparticles on undoped nanodiamond powder for methanol oxidation electrocatalysts. *Journal of Electroanalytical Chemistry* **644**, 85-88, doi:10.1016/j.jelechem.2010.04.001.
- 19 Schrand, A. M., Hens, S. A. C. & Shenderova, O. A. Nanodiamond Particles: Properties and Perspectives for Bioapplications. *Critical Reviews in Solid State and Materials Sciences* **34**, 18-74, doi:10.1080/10408430902831987 (2009).

- 20 Mochalin, V. N., Shenderova, O., Ho, D. & Gogotsi, Y. The properties and applications of nanodiamonds. *Nature Nanotechnology* **7**, 11-23, doi:10.1038/nnano.2011.209 (2012).
- 21 Salazar-Banda, G. R., Eguiluz, K. I. B. & Avaca, L. A. Boron-doped diamond powder as catalyst support for fuel cell applications. *Electrochemistry Communications* **9**, 59-64, doi:10.1016/j.elecom.2006.08.038 (2007).
- 22 Williams, O. A. *et al.* Size-Dependent Reactivity of Diamond Nanoparticles. *ACS Nano* **4**, 4824-4830, doi:10.1021/nn100748k (2010).
- 23 Kulakova, I. I. Surface chemistry of nanodiamonds. *Phys. Solid State* **46**, 636-643, doi:10.1134/1.1711440 (2004).
- 24 Xu, J. S., Chen, Q. Y. & Swain, G. M. Anthraquinonedisulfonate electrochemistry: A comparison of glassy carbon, hydrogenated glassy carbon, highly oriented pyrolytic graphite, and diamond electrodes. *Analytical Chemistry* **70**, 3146-3154, doi:10.1021/ac9800661 (1998).
- 25 Granger, M. C. *et al.* Standard Electrochemical Behavior of High-Quality, Boron-Doped Polycrystalline Diamond Thin-Film Electrodes. *Analytical Chemistry* **72**, 3793-3804, doi:10.1021/ac0000675 (2000).
- 26 Garguilo, J. M., Davis, B. A., Buddie, M., Kock, F. A. M. & Nemanich, R. J. Fibrinogen adsorption onto microwave plasma chemical vapor deposited diamond films. *Diamond Relat. Mater.* **13**, 595-599, doi:10.1016/j.diamond.2003.10.008 (2004).
- 27 Hoffmann, R. *et al.* Adsorption of cytochrome c on diamond. *Physica Status Solidi a-Applications and Materials Science* **207**, 2073-2077, doi:10.1002/pssa.201000043 (2010).
- 28 Steinmueller-Nethl, D. *et al.* Strong binding of bioactive BMP-2 to nanocrystalline diamond by physisorption. *Biomaterials* **27**, 4547-4556, doi:10.1016/j.biomaterials.2006.04.036 (2006).
- 29 Dimov, I. B., Batchelor-McAuley, C., Aldous, L. & Compton, R. G. The adsorption of quinizarin on boron-doped diamond. *Phys. Chem. Chem. Phys.* **14**, 2375-2380, doi:10.1039/c2cp23380k (2012).
- 30 Nebel, C. E., Rezek, B., Shin, D. & Watanabe, H. Surface electronic properties of H-terminated diamond in contact with adsorbates and electrolytes. *Physica Status Solidi a-Applications and Materials Science* **203**, 3273-3298, doi:10.1002/pssa.200671401 (2006).
- 31 Krueger, A. & Lang, D. Functionality is Key: Recent Progress in the Surface Modification of Nanodiamond. *Advanced Functional Materials* **22**, 890-906, doi:10.1002/adfm.201102670 (2012).
- 32 Zhang, G.-J. *et al.* DNA Micropatterning on Polycrystalline Diamond via One-Step Direct Amination. *Langmuir* **22**, 3728-3734, doi:10.1021/la050883d (2006).
- 33 Takahashi, K., Tanga, M., Takai, O. & Okamura, H. DNA preservation using diamond chips. *Diamond and Related Materials* **12**, 572-576, doi:10.1016/s0925-9635(03)00070-0 (2003).
- 34 Kuo, T. C., McCreery, R. L. & Swain, G. M. Electrochemical modification of boron-doped chemical vapor deposited diamond surfaces with covalently bonded monolayers. *Electrochemical and Solid State Letters* **2**, 288-290, doi:10.1149/1.1390813 (1999).
- 35 Sussman, R. S. in *Wiley Series in Materials for Electronic and Optoelectronic Applications* (ed Professor Safa Kasap Dr. Peter Capper) 571 (John Wiley & Sons Ltd, 2009).

- 36 McDermott, M. T., Kneten, K. & McCreery, R. L. ANTHRAQUINONEDISULFONATE ADSORPTION, ELECTRON-TRANSFER KINETICS, AND CAPACITANCE ON ORDERED GRAPHITE-ELECTRODES - THE IMPORTANT ROLE OF SURFACE-DEFECTS. *Journal of Physical Chemistry* **96**, 3124-3130, doi:10.1021/j100186a063 (1992).
- 37 He, P., Crooks, R. M. & Faulkner, L. R. Adsorption and electrode reactions of disulfonated anthraquinones at mercury electrodes. *The Journal of Physical Chemistry* **94**, 1135-1141, doi:10.1021/j100366a023 (1990).
- 38 Anson, F. C. & Epstein, B. Chronocoulometric study of the adsorption of anthraquinone monosulfonate on mercury. *J. Electrochem. Soc.* **115**, 1155-1158, doi:10.1149/1.2410928 (1968).
- 39 Xiao, L., Wildgoose, G. G. & Compton, R. G. Investigating the voltammetric reduction of methylviologen at gold and carbon based electrode materials. Evidence for a surface bound adsorption mechanism leading to electrode 'protection' using multi-walled carbon nanotubes. *New Journal of Chemistry* **32**, 1628-1633, doi:10.1039/b804842h (2008).
- 40 Engelman, E. E. & Evans, D. H. SODIUM ALKYL SULFATE INDUCED DEPOSITION OF METHYL VIOLOGEN CATION RADICAL ON GLASSY-CARBON SURFACES. *Langmuir* **8**, 1637-1644, doi:10.1021/la00042a024 (1992).
- 41 Wang, H., Griffiths, J.-P., Egdell, R. G., Moloney, M. G. & Foord, J. S. Chemical Functionalization of Diamond Surfaces by Reaction with Diaryl Carbenes. *Langmuir* **24**, 862-868, doi:10.1021/la702701p (2008).
- 42 Granger, M. C. & Swain, G. M. The influence of surface interactions on the reversibility of ferri/ferrocyanide at boron-doped diamond thin-film electrodes. *J. Electrochem. Soc.* **146**, 4551-4558, doi:10.1149/1.1392673 (1999).
- 43 Goeting, C. H., Marken, F., Gutierrez-Sosa, A., Compton, R. G. & Foord, J. S. Boron-doped diamond electrodes: Growth, surface characterisation and sono-electrochemical applications. *New Diamond and Frontier Carbon Technology* **9**, 207-228 (1999).
- 44 <http://www.casaxps.com/>.
- 45 Shirley, D. A. High-resolution x-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B* **[3]5**, 4709-4714 (1972).
- 46 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley & Sons, 2001).
- 47 Anson, F. C. Innovations in the study of adsorbed reactants by chronocoulometry. *Anal. Chem.* **38**, 54-57, doi:10.1021/ac60233a014 (1966).
- 48 Zang, J. B., Wang, Y. H., Huang, H. & Tang, W. Electrochemical behavior of high-pressure synthetic boron doped diamond powder electrodes. *Electrochimica Acta* **52**, 4398-4402, doi:10.1016/j.electacta.2006.12.028 (2007).
- 49 Werner, M. *et al.* The Relationship between Resistivity and Boron Doping Concentration of Single and Polycrystalline Diamond. *physica status solidi (a)* **154**, 385-393, doi:10.1002/pssa.2211540127 (1996).
- 50 Correa, E. J., Wu, Y., Wen, J.-G., Chandrasekharan, R. & Shannon, M. A. Electrical conduction in undoped ultrananocrystalline diamond thin films and its dependence on chemical composition and crystalline structure. *Journal of Applied Physics* **102**, 113706 (2007).
- 51 Locher, R. *et al.* Optical and electrical characterization of boron-doped diamond films. *Diamond and Related Materials* **4**, 678-683, doi:http://dx.doi.org/10.1016/0925-9635(94)05297-2 (1995).

- 52 Praver, S. *et al.* The Raman spectrum of nanocrystalline diamond. *Chem. Phys. Lett.* **332**, 93-97, doi:10.1016/s0009-2614(00)01236-7 (2000).
- 53 Holt, K. B., Caruana, D. J. & Millan-Barrios, E. J. Electrochemistry of Undoped Diamond Nanoparticles: Accessing Surface Redox States. *Journal of the American Chemical Society* **131**, 11272-+, doi:10.1021/ja902216n (2009).
- 54 Mizokawa, Y., Miyasato, T., Nakamura, S., Geib, K. M. & Wilmsen, C. W. The C KLL first - derivative x - ray photoelectron spectroscopy spectra as a fingerprint of the carbon state and the characterization of diamondlike carbon films. *Journal of Vacuum Science & Technology A* **5**, 2809-2813, doi:doi:http://dx.doi.org/10.1116/1.574312 (1987).
- 55 Landstrass, M. I. & Ravi, K. V. RESISTIVITY OF CHEMICAL VAPOR-DEPOSITED DIAMOND FILMS. *Applied Physics Letters* **55**, 975-977, doi:10.1063/1.101694 (1989).
- 56 Chakrapani, V. *et al.* Charge Transfer Equilibria Between Diamond and an Aqueous Oxygen Electrochemical Redox Couple. *Science* **318**, 1424-1430, doi:10.1126/science.1148841 (2007).
- 57 Maier, F., Riedel, M., Mantel, B., Ristein, J. & Ley, L. Origin of surface conductivity in diamond. *Physical Review Letters* **85**, 3472-3475, doi:10.1103/PhysRevLett.85.3472 (2000).
- 58 Gi, R. S. *et al.* Formation mechanism of p-type surface conductive layer on deposited diamond films. *Jpn. J. Appl. Phys., Part 1* **34**, 5550-5555, doi:10.1143/jjap.34.5550 (1995).
- 59 Nebel, C. E. Surface-Conducting Diamond. *Science* **318**, 1391-1392, doi:10.1126/science.1151314 (2007).
- 60 Takeuchi, D., Yamanaka, S., Watanabe, H., Okushi, H. & Kajimura, K. Spatial uniformity of Schottky contacts between aluminum and hydrogenated homoepitaxial diamond films. *Appl. Surf. Sci.* **159-160**, 572-577, doi:10.1016/s0169-4332(00)00103-3 (2000).
- 61 Hayashi, K. *et al.* Investigation of the effect of hydrogen on electrical and optical properties in chemical vapor deposited on homoepitaxial diamond films. *J. Appl. Phys.* **81**, 744-753, doi:10.1063/1.364299 (1997).
- 62 Masai, S. *et al.* Effects of hydrogenation on electrical properties of B-doped homoepitaxial diamond. *New Diamond Front. Carbon Technol.* **9**, 115-117 (1999).
- 63 Bird, C. L. & Kuhn, A. T. ELECTROCHEMISTRY OF THE VIOLOGENS. *Chemical Society Reviews* **10**, 49-82, doi:10.1039/cs9811000049 (1981).
- 64 Nicholson, R. S. Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. *Anal. Chem.* **37**, 1351-1355, doi:10.1021/ac60230a016 (1965).
- 65 Kaifer, A. E. & Bard, A. J. Micellar effects on the reductive electrochemistry of methylviologen. *J. Phys. Chem.* **89**, 4876-4880, doi:10.1021/j100268a044 (1985).
- 66 Hees, J., Hoffmann, R., Yang, N. & Nebel, C. E. Diamond Nanoelectrode Arrays for the Detection of Surface Sensitive Adsorption. *Chemistry – A European Journal* **19**, 11287-11292, doi:10.1002/chem.201301763 (2013).
- 67 Kobayashi, K., Fujisaki, F., Yoshimine, T. & Niki, K. An analysis of the voltammetric adsorption waves of methyl viologen. *Bull. Chem. Soc. Jpn.* **59**, 3715-3722, doi:10.1246/bcsj.59.3715 (1986).
- 68 Bruinink, J., Kregting, C. G. A. & Ponjee, J. J. Modified viologens with improved electrochemical properties for display applications. *J. Electrochem. Soc.* **124**, 1854-1858, doi:10.1149/1.2133175 (1977).

- 69 Taki, Y. & Takai, O. XPS structural characterization of hydrogenated amorphous carbon thin films prepared by shielded arc ion plating. *Thin Solid Films* **316**, 45-50, doi:http://dx.doi.org/10.1016/S0040-6090(98)00386-1 (1998).
- 70 Ley, L., Graupner, R., Cui, J. B. & Ristein, J. Electronic properties of single crystalline diamond surfaces. *Carbon* **37**, 793-799, doi:10.1016/s0008-6223(98)00273-5 (1999).
- 71 Ferro, S., Dal Colle, M. & De Battisti, A. Chemical surface characterization of electrochemically and thermally oxidized boron-doped diamond film electrodes. *Carbon* **43**, 1191-1203, doi:http://dx.doi.org/10.1016/j.carbon.2004.12.012 (2005).
- 72 Goeting, C. H., Marken, F., Osborn, A. R., Compton, R. G. & Foord, J. S. Surface Modification of Chemical Vapor Deposited Diamond Induced by Power Ultrasound. *Electrochemical and Solid State Letters* **4**, E29-E31, doi:10.1149/1.1377488 (2001).
- 73 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 74 Wagner, C. D. *et al.* Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *SIA, Surf. Interface Anal.* **3**, 211-225, doi:10.1002/sia.740030506 (1981).
- 75 Tang, Y., Wu, Y. & Wang, Z. Spectroelectrochemistry for Electroreduction of p-Benzoquinone in Unbuffered Aqueous Solution. *Journal of The Electrochemical Society* **148**, E133-E138, doi:10.1149/1.1353575 (2001).
- 76 Forster, R. J. & O'Kelly, J. P. Protonation reactions of anthraquinone-2,7-disulphonic acid in solution and within monolayers. *Journal of Electroanalytical Chemistry* **498**, 127-135, doi:http://dx.doi.org/10.1016/S0022-0728(00)00331-4 (2001).
- 77 Quan, M., Sanchez, D., Wasylkiw, M. F. & Smith, D. K. Voltammetry of Quinones in Unbuffered Aqueous Solution: Reassessing the Roles of Proton Transfer and Hydrogen Bonding in the Aqueous Electrochemistry of Quinones. *J. Am. Chem. Soc.* **129**, 12847-12856, doi:10.1021/ja0743083 (2007).

5 Chapter five – Diamond powder films: electrochemical properties and applications in electrocatalysis

5.1 Introduction

Chapter 5 further discusses the electrochemical behaviour of boron-doped diamond electrodes modified with (a) boron-doped diamond powder and (b) detonation nanodiamond powder, and explores the application of such electrodes as electrocatalyst support for platinum nanoparticles. In this work, the permselective properties of boron-doped diamond powder films along with detonation nanodiamond powder films were systematically investigated. In the concentrated solutions of standard redox mediators with a concentration range of 1-10 mM, the presence of fine diamond powders on the electrode surface has little influence on the electrochemical behaviour observed. In contrast, in diluted solutions of standard redox probes, diamond powder modified electrodes were found to exhibit a distinct impact on the electrochemical properties recorded, causing a well-defined amplification of current responses in solutions of neutral (ferrocenemethanol) and positively charged redox mediators ($\text{Ru}(\text{NH}_3)_6^{3+}$), whilst no significant difference was detected with negatively charged $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{2-} -redox probes. The amplification of current responses observed with neutral and positively charged redox probes is attributable to the partitioning of the latter within the powder film. The reasons underlying these effects are further discussed in terms of electrostatic interactions and powder films morphology. Partition coefficients, film permeabilities and associated diffusion coefficients of redox probes within the powder films were estimated in this chapter.

In further studies, the powder modified electrodes were decorated with platinum nanoparticles, and the kinetics of nucleation and growth of platinum nanoparticles on the three diamond substrates was assessed. Platinum decorated boron-doped diamond powder

modified electrode was found to be the most efficient in methanol electrooxidation as compared to platinum modified plane boron-doped diamond and detonation nanodiamond powder modified electrodes. The work in Chapter 5 demonstrates that the modification of boron-doped diamond powders with platinum nanoparticles provides an effective route for the creation of highly stable and electrocatalytically active platinum-diamond interface.

5.1.1 Diamond powders as a highly stable support for electrocatalytic materials

Fuel cells are attracting an increasing attention as an efficient energy converting device due to the necessity to prevent environmental pollution whilst meeting the growing energy demand. Fuel cells can be utilized in automotive transport, in devices of portable power generation and in personal electronics. They can operate at low temperatures and pressures, can be fuelled by sustainable supplies, and in the case of hydrogen fuel cells, emit zero CO₂.¹ However, the widespread commercialization of fuel cells is limited by the cost, performance and stability of catalysts employed in such devices.² Therefore, the development of cost-effective catalytic systems with a greater electroactive area, smaller particle size, and higher stability are vital for a widespread implementation of fuel cells.³⁻⁵

In many fuel cells, platinum and platinum alloy catalysts deposited on porous carbon materials such as carbon black and graphite are used as an electrode system.⁶⁻⁸ The performance of these electrodes is limited by the stability of the sp²-bonded carbon support. Such supports were found to be susceptible to considerable corrosion and microstructural degradation in fuel cell operating environments along with catalytic activity loss through catalyst detachment.^{5,9}

An exceptionally stable alternative to sp²-carbon supports has emerged with the development of synthetic diamond that is now available at affordable price due to new gas and plasma phase deposition techniques.^{10,11} In comparison to sp²-carbon materials, diamond electrodes

in a boron-doped form exhibit exceptional chemical stability and wide potential window along with low signal-to-background current ratio.¹²

At the moment, the preparation of platinum modified boron-doped diamond electrodes is a subject of significant research in connection with fuel cell technologies. Platinum modified boron-doped diamond electrodes have been extensively studied for methanol and ethanol electrooxidation along with oxygen reduction and hydrogen oxidation reactions – processes which are essential in fuel cells.¹³⁻¹⁶ A range of methods has been studied in order to find an effective route for the preparation of platinum decorated boron-doped diamond electrodes. These include electrochemical deposition *via* cyclic voltammetry, galvanostatic techniques, potentiostatic step methods, ion implantation of Pt and co-deposition of Pt during CVD diamond growth.^{13,17-19} As many of these deposition methods result in poor adhesion of Pt nanoparticles, the development of stable platinum/diamond interface is of particular importance.

There has also been interest in the use of diamond in the form of finely divided powders: detonation nanodiamond powder (DND) and B-doped diamond powder (BDP) which have recently become available for electrocatalytic applications, electrochemical sensing and energy conversion.²⁰⁻²³ There are several advantages over the planar synthetic diamond as powders provide a porosity that is necessary for fuel cell electrode system, increased surface area and a possibility to conduct spatially and temporally resolved electrochemical measurements.^{21,24-26}

5.1.2 Detonation nanodiamond powder

Detonation nanodiamond powder is a nanocarbon material which is produced by the detonation of carbon explosives such as trinitrotoluene, hexogen or octogen under the application of shock waves.²⁷ During this process, the short time explosion with a negative

oxygen balance and a fast cooling rates ($3000\text{--}4000\text{ K min}^{-1}$) result in the formation of detonation diamond crystallites of approximately 3-5 nm size. Apart from the diamond crystallites, other graphitic forms are found after the detonation process, and several cleaning procedures such as treatments with gaseous ozone and nitric acid are usually employed to dissolve sp^2 carbon and metallic impurities.²⁷ Detonation nanodiamond was first synthesised in the USSR under a cloak of secrecy, and its high volume production began in the late 1980s.²⁸

Commercially available detonation nanodiamond is typically comprised of 98% of diamond in a form of 3-10 nm particles and a minor amount of sp^2 carbon allotrope.²⁷ The diamond particle itself has an sp^3 diamond core that is surrounded by an amorphous carbon shell with a highly functionalised surface mainly consisting of hydroxyl, carbonyl, carboxylic and lactone surface groups (Figure 63).²⁹

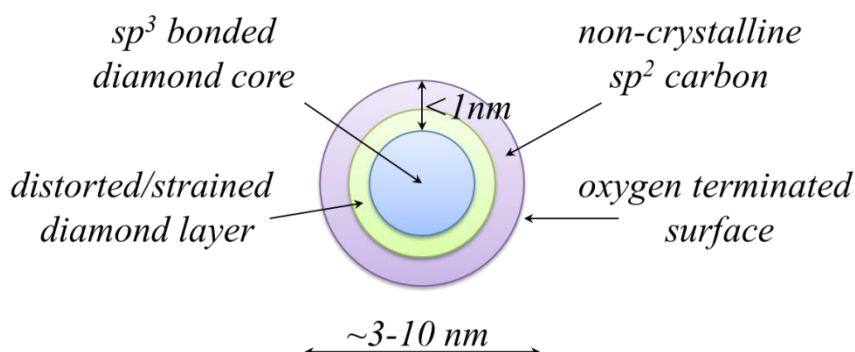


Figure 63 Illustration of detonation nanodiamond particle structure, adapted from²⁷

Recently, detonation nanodiamond powders have attracted attention in several electrochemical applications.²⁷ The detailed work by K. Holt *et al.* revealed that undoped and insulating in a dry state DND is capable of producing an effective electrochemical response in solution due to its surface chemistry.³⁰⁻³² It was observed that the electrochemical response

in solutions of standard redox couples such as $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ arose not only from the redox mediator, but also from the DND layer itself.^{30,33} The origin of this phenomenon was related to the electrochemical activity of unsaturated surface groups, in particular, to surface alcohol and unsaturated ketone/quinone groups.³⁰⁻³² It was proposed that the underlying electrode is responsible for the reduction/oxidation of the redox probe. However, when this reduced/oxidised form of the redox probe diffuses within the DND surface, it becomes spontaneously oxidized or reduced by the redox active surface groups (ketone/quinone groups) of the DND powder itself, thus giving the rise to the amplified currents.³³

5.1.3 Boron-doped diamond powder

As opposed to detonation nanodiamond powder, boron-doped diamond powder (BDP) is conductive both in a dry state and in solutions. The anticipated advantages to boron-doped diamond powders over conventional carbon supports include improved stability, higher surface electrode area along with enhanced electrode performance.

The material can be fabricated by mechanical grinding of plain boron-doped diamond films. Another approach involves CVD growth of the conductive layer over the DND particles.^{21,34} The stock BDP material consists of ~100 nm-50 μm particles of irregular shape. A more uniform particle size distribution can be achieved through the application of centrifugation step. As it will be discussed below, the surface chemistry of BDP typically is similar to that of a plain polycrystalline boron-doped diamond.

5.2 Aims of the project

Although some electrochemical studies of diamond powders and platinum and platinum-ruthenium decorated diamond films have been reported,^{14,21,35} a comparative analysis of the

electrochemical properties of DND and BDP films as well as their platinum decorated forms has not been performed. In this chapter, a comparative investigation of electrochemical properties of powder diamond films as well as their characteristics as carbon support for platinum electrocatalyst will be presented. The mechanism of nucleation and growth of the platinum nanoparticles on the diamond substrates will be discussed.

5.3 Experimental Methods

5.3.1 Electrode Preparation

Microcrystalline boron-doped diamond electrode (BDE) was used as a working electrode in all experiments (Element Six Co, 10×10×0.6 mm size, [B] ~ 10²⁰ cm⁻³). Boron-doped diamond powder (BDP) was produced by the milling of CVD boron-doped diamond ([B] ~ 10²⁰ cm⁻³). Detonation nanodiamond powder (DND) with a particle size of 4 nm was purchased from Yorkshire Bioscience.

The preparation of 200 nm BDP and DND powder films was carried out *via* drop coating of 0.08 mg BDP or DND dissolved in 60 µL aliquot of absolute ethanol onto the BDE surface. The samples were dried overnight at 23°C.

5.3.2 Characterisation

A scanning electron microscope (SEM, Hitachi S530) with a 20 kV acceleration voltage was used to examine the surface morphology. X-ray photoelectron spectroscopy (XPS) spectra were recorded using a hemispherical analyser and Al K α (1486.6 eV) X-ray source. The survey scans and the high resolution scans were measured at 50 eV pass energy with 0.5 eV step and at 20 eV pass energy with 0.1 eV step respectively. The spectra recorded were analysed using CasaXPS software.³⁶ The peaks were fitted using Shirley background.³⁷

Electrochemical measurements were performed using a μ -AUTOLAB III electrochemical workstation (Eco-Chemie, Netherlands) at 23°C. A standard three-electrode configuration comprising the BDE as a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode was employed in the study. The working electrode was incorporated in a PTFE holder, so that a circular area of 0.4 cm^2 was exposed to a working solution. Cyclic voltammetry (CV) was employed to characterise electrochemical behaviour of the powder modified electrodes in hexaamineruthenium (III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), ferrocenemethanol (FcCH_2OH), and potassium hexachloroiridate (IV) (K_2IrCl_6) dissolved in 0.1 M KCl with 0.1 mM, 1 mM and 10 mM concentrations at the scan rate of 0.05 V s^{-1} .

Prior to platinum electrodeposition, the electrodes were cleaned in *aqua regia* as described in Chapter 3. The electrodes were then treated by potential cycling in 0.1 M nitric acid between -1.5 V and +1.5 V, which standardly yields a hydrophilic surface containing a high concentration of oxygen functionalities.

Platinum nanoparticles were electrodeposited from a deaerated 2 mM K_2PtCl_6 dissolved in 0.1 M H_2SO_4 via potentiostatic method during 100 s. A series of deposition potentials of -0.05, -0.1, -0.2 and -0.25 V vs. Ag/AgCl were used in order to investigate the influence of the deposition potential on the particles morphology. The electrochemical active area (EAA) of Pt modified boron-doped diamond electrodes was estimated from cyclic voltammetry (CV) recorded in 0.1 M H_2SO_4 at a scan rate of 0.05 V s^{-1} .

All chemicals (from Sigma-Aldrich, UK) were of analytical grade and used without any further purification. Solutions were prepared using ultrapure water ($18.2\text{ M}\Omega\cdot\text{cm}$ at 293 K, Millipore water systems, UK)

5.4 Results and Discussion

5.4.1 XPS characterisation of BDP and DND modified electrodes

Prior to electrochemical characterisation, the surface composition of the boron-doped diamond electrode along with the DND and BDP modified electrodes was analysed using X-ray Photoelectron spectroscopy. Figure 64 (a) shows a typical survey scan of unmodified boron-doped diamond electrode. For the BDE surface, the main features detected are the C 1s photoemission line at 285 eV along with the O 1s component at 532 eV. The O 1s elemental concentration within the XPS sampling depth is estimated at around 8%. A high resolution C 1s spectral region is presented in Figure 64 (b). The photoelectron signal at 285.0 eV is assigned to the sp^3 bulk diamond. The peak at 285.6 eV and 287.2 are attributable to the C-H_x (x = 2,3) species in polyhydride configurations and carbonyl surface groups respectively.³⁸ The peak at 283.7 eV is characteristic of sp^2 defects.³⁸ The associated atomic concentrations, binding energies and FWHM values can be found in Table 27, Table 8 and Table 9.

Table 27 XPS binding energies for the BDE, BDP and DND modified electrodes

Sample	Binding energies (eV)								
	C 1s						O 1s		
	Csp ³	C-CH _x	C=O	COOH	esters	sp ² def	O-C	O=C	H ₂ O
BDE	285.0	285.6	287.2	n/a	n/a	283.7	n/a	532.6	530.5
BDP	285.0	285.7	287.1	n/a	n/a	283.8	532.8	531.7	530.0
DND	285.0	n/a	287.0	288.0	288.9	283.1	532.7	531.7	530.0

Table 28 XPS elemental ratios and charging values for the BDE, BDP and DND modified electrodes

Sample	Elemental concentrations (%)	Charging (eV)
	O 1s	Relative to C 1s (285.0 eV)
BDE	8	6.1
BDP	18	6.9
DND	25	9.8

The high resolution O 1s region, associated with the BDE surface, is shown in Figure 64 (c). The O 1s signal was fitted with two peaks at 532.6 eV and 530.5 eV respectively that arise from the presence of carbonyl surface groups and a minor presence of water molecules on the surface.³⁹

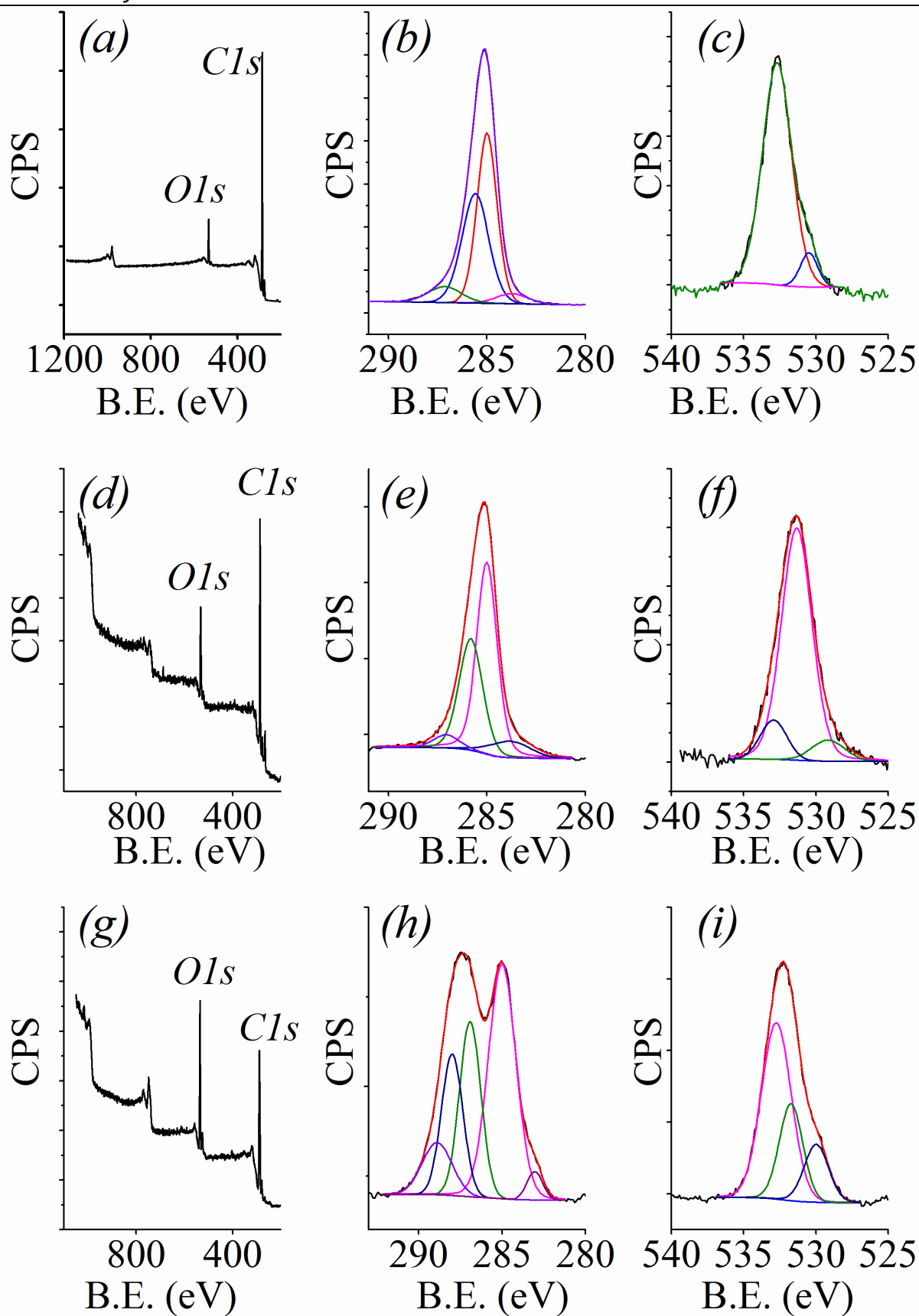


Figure 64 (a) survey XPS spectra of BDE; (b) C 1s XPS region of BDE; (c) O 1s region of BDE; (d) survey XPS spectra of BDP; (e) C 1s region of BDP; (f) O 1s region of BDP; (g) survey XPS spectra of DND; (h) C 1s region of DND; (i) O 1s region of DND

Table 29 FWHM values for the BDE, BDP and DND modified electrodes

Sample	FWHM (eV)								
	C 1s						O 1s		
	Csp ³	C-CHx	C=O	COOH	esters	sp ² def	O-C-	O=C	H ₂ O
BDE	1.2	1.6	2.2	n/a	n/a	1.9	n/a	2.4	1.7
BDP	1.2	1.4	1.5	n/a	n/a	2.4	2.7	2.4	2.0
DND	1.9	n/a	1.5	1.5	2.1	1.1	2.4	1.9	1.9

As presented in Figure 64 (d), the survey scan at the BDP surface is found to be similar to that of the BDE sample, with a increase in the O 1s elemental concentration up to 17% (Table 8). The high resolution C 1s region of the BDP sample is shown in Figure 64 (e). The C 1s signal was deconvoluted with four constituent peaks. The peak at 285 eV corresponds to the bulk diamond environment; the peak at 285.7 eV is assigned to carbon in polyhydride configurations.³⁸ The peak at 287.1 eV is related to the carbonyl containing moieties, and the peak at 283.8 is characteristic of sp² defects.⁴⁰ The high resolution O 1s region was found to be similar to that of the BDE surface, with the small features arising from the presence of C-OH and C=O species (Figure 64 (f)).³⁹

Dramatic differences are seen at the DND electrode. The O 1s elemental concentration is increased up to 25%. The changes in the high resolution C 1s area arise from the presence of strong signals at 287 eV, 288 eV and 288.9 eV characteristic of highly oxidized moieties such as carbonyl, carboxyl and carbonate ester groups (-C(O)-O-C(O)-) respectively (Figure 64 (h)).⁴¹ The associated high resolution O 1s region is presented in Figure 64 (i). The O 1s components, located at 532.7 eV, 531.7 eV and 530 eV binding energy, are characteristic of highly oxidized carbonyl, carboxyl and carbonate ester species which is in agreement with the C 1s data described above.^{38,41}

5.4.2 Electrochemical characterisation of BDP and DND modified electrodes

Typical cyclic voltammograms of 0.1 mM Fe(CN)₆³⁻, Ru(NH₃)₆³⁺, IrCl₆²⁻ and FcCH₂OH redox couples at BDP, DND modified electrodes and unmodified boron-doped diamond

electrode are presented in Figure 65. The associated peak positions and current responses are summarised in Table 30.

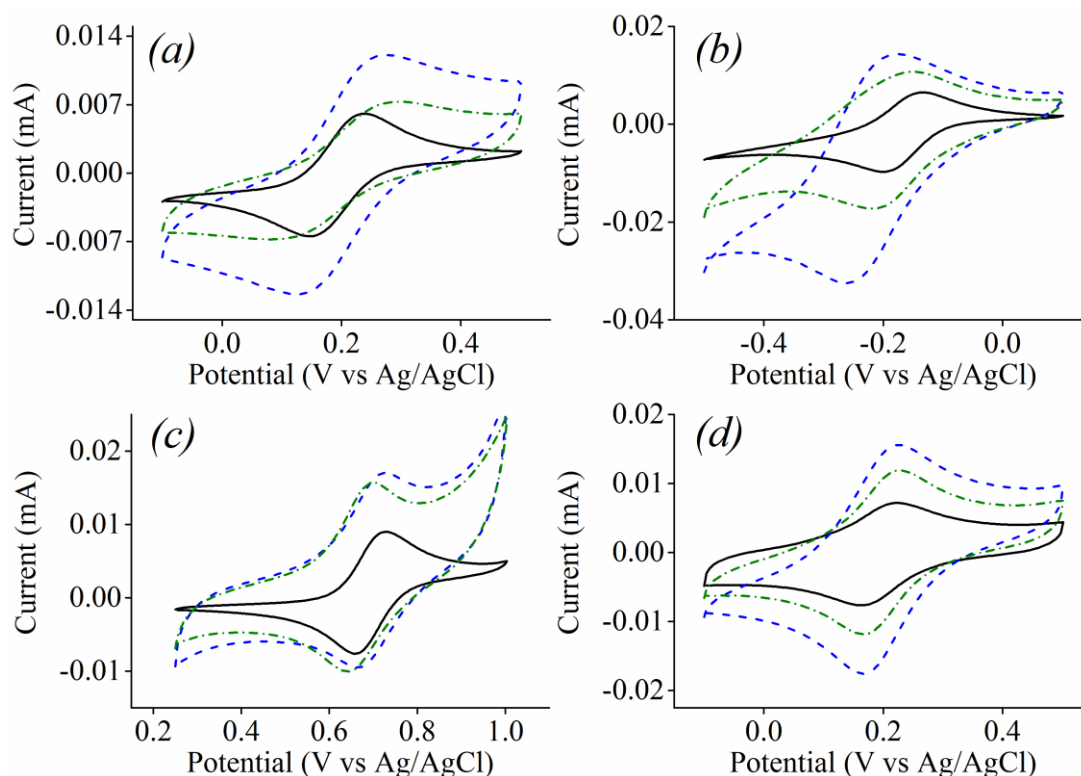


Figure 65 Cyclic voltammograms recorded at (-) plain BDE, (- - -) 200 nm DND and (· · ·) 200 nm BDP modified electrodes in (a) 0.1 mM in $K_3Fe(CN)_6$, 0.1 M KCl; (b) 0.1 mM in $Ru(NH_3)_6Cl_3$, 0.1 M KCl; (c) 0.1 mM in K_2IrCl_6 , 0.1 M KCl; (d) 0.1 mM $FcCH_2OH$, 0.1 M KCl at a scan rate of 0.05 Vs^{-1}

Table 30 Peak position and current response data recorded in 0.1 mM $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$, $IrCl_6^{2-}$ and $FcCH_2OH$ solutions at BDP, DND modified electrodes and unmodified B-doped diamond electrode at a scan rate of 0.05 Vs^{-1}

Sample		0.1 mM $Fe(CN)_6^{3-}$				
	$E(I_p^{Red})\text{ (V)}$	$I_p^{Red}\text{ (A)}$	$i_p^{Red}\text{ (A cm}^{-2}\text{)}$	$E(I_p^{Ox})\text{ (V)}$	$I_p^{Ox}\text{ (A)}$	$i_p^{Ox}\text{ (A cm}^{-2}\text{)}$
BDE	0.151	-5.65×10^{-6}	-1.41×10^{-5}	0.234	6.13×10^{-6}	1.53×10^{-5}
BDP	0.123	-4.15×10^{-6}	-7.88×10^{-6}	0.275	4.84×10^{-6}	9.6×10^{-6}
DND	0.143	-7.83×10^{-6}	-1.95×10^{-5}	0.254	7.54×10^{-6}	1.18×10^{-5}
0.1 mM $Ru(NH_3)_6^{3+}$						
BDE	-0.195	-7.43×10^{-6}	-1.86×10^{-5}	-0.137	7.71×10^{-6}	1.92×10^{-5}
BDP	-0.203	-9.51×10^{-6}	-2.37×10^{-5}	-0.166	1.09×10^{-5}	2.72×10^{-5}
DND	-0.249	-1.58×10^{-5}	-3.95×10^{-5}	-0.199	1.97×10^{-5}	4.93×10^{-5}
0.1 mM $IrCl_6^{2-}$						
BDE	0.622	-8.67×10^{-6}	-2.17×10^{-5}	0.724	7.26×10^{-6}	1.81×10^{-5}
BDP	0.650	-9.79×10^{-6}	-2.43×10^{-5}	0.691	7.57×10^{-6}	1.79×10^{-5}
DND	0.674	-8.49×10^{-6}	-2.12×10^{-5}	0.711	6.32×10^{-6}	1.28×10^{-5}
0.1 mM $FcCH_2OH$						
BDE	0.168	-5.17×10^{-6}	-1.29×10^{-5}	0.217	5.01×10^{-6}	1.25×10^{-5}
BDP	0.172	-8.79×10^{-6}	-2.20×10^{-5}	0.221	8.27×10^{-6}	2.07×10^{-5}
DND	0.172	-1.39×10^{-5}	-3.48×10^{-5}	0.217	1.32×10^{-5}	1.32×10^{-5}

Chapter five – Diamond powder films: electrochemical properties and applications in electrocatalysis

Table 31 I_p^{Ox}/I_p^{Red} ratio and peak-to-peak separation data estimated for 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH redox couples at BDP, DND modified electrodes and unmodified boron-doped diamond electrode at a scan rate of 0.05 V s^{-1}

Sample	0.1 mM $\text{Fe}(\text{CN})_6^{3-}$		0.1 mM IrCl_6^{2-}	
	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)
BDE	0.92	83	1.19	102
BDP	0.82	152	1.37	41
DND	1.04	111	1.34	37
Sample	0.1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$		0.1 mM FcCH_2OH	
	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)
BDE	0.96	58	1.03	49
BDP	0.87	37	1.06	49
DND	0.80	50	1.05	45

It can be clearly seen from Figure 65 that the introduction of BDP and DND powder films results in the discernable amplification of redox signals when compared to the plain unmodified microcrystalline BDE. At the DND modified electrode, the oxidation and reduction currents in $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$ and FcCH_2OH solutions are found to be $2 \mu\text{A}$ and $8 \mu\text{A}$, $8 \mu\text{A}$ and $12 \mu\text{A}$, $9 \mu\text{A}$ and $8 \mu\text{A}$ respectively bigger if compared to those seen at the unmodified boron-doped diamond electrode. However, no significant changes in the current response were detected with the IrCl_6^{2-} redox mediator. At the BDP modified electrode, an enhancement of the oxidative and reductive currents by $2 \mu\text{A}$ and $3 \mu\text{A}$, $1 \mu\text{A}$ and $0.3 \mu\text{A}$, $3 \mu\text{A}$ and $3 \mu\text{A}$ in $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH solutions respectively can be observed, whereas voltammetric peaks of an amplitude similar to that of BDE are seen in the $\text{Fe}(\text{CN})_6^{3-}$ solution. Small peak shifts are also found on both DND and BDP modified surfaces as compared to unmodified microcrystalline boron-doped diamond electrode (Table 31).

The differences observed in the peak-to-peak separations and the peak currents are likely to arise from the changes in electron transfer kinetics as well as mass transfer characteristics that occur upon the introduction of the BDP and DND films on the electrode surface. An additional mechanism that can explain the observations above concerns electrostatic interactions between the negatively charged surface groups of the DND and BDP powders

and negatively, positively charged or neutral redox probes. In particular, electrostatic repulsion between the IrCl_6^{2-} or $\text{Fe}(\text{CN})_6^{3-}$ redox mediators and negatively charged surface groups of the diamond powders may contribute to the effect observed above, whereas attraction forces can operate with the positively charged redox probes.

In order to quantify these effects further and eliminate possible electrostatic interactions which may contribute to the electrochemical response in diluted solutions, the peak current responses of neutral FcCH_2OH redox mediator were analysed in accordance with the Randles-Ševčík equation:⁴²

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \quad (\text{Equation 5.1.1})$$

where I_p is the peak current, α is the transfer coefficient, n is the number of electrons, A is the electrode area, C is the bulk concentration, D is the diffusion coefficient ($7.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and ν is the scan rate (0.05 V s^{-1}).⁴³ The results are summarised in Figure 66.

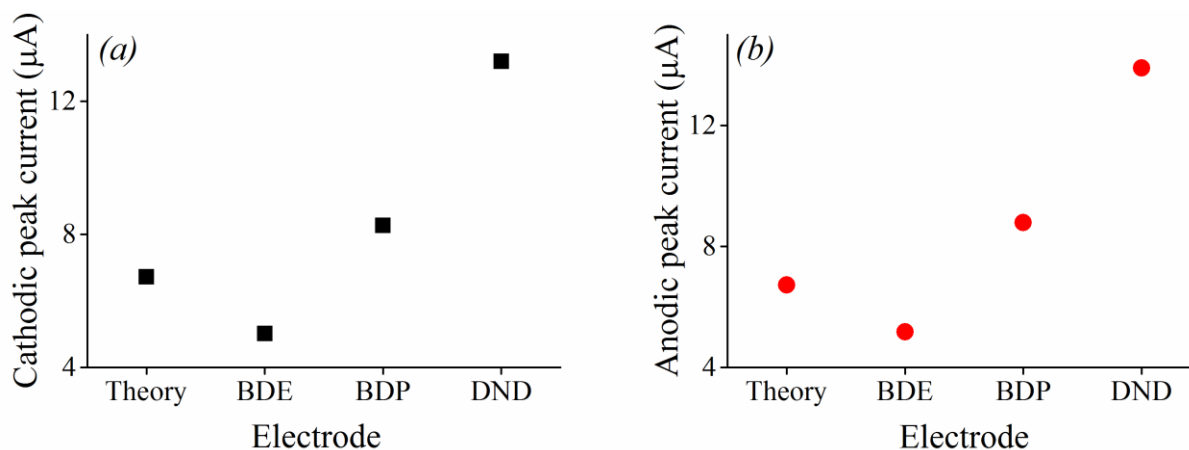


Figure 66 Peak currents theoretically predicted by the Randles-Ševčík equation and experimentally recorded at BDE, BDP and DND electrodes during (a) cathodic scan; (b) anodic scan at a scan rate of 0.05 Vs^{-1}

For the unmodified microcrystalline boron-doped diamond electrode, the current response is found to be below than that predicted by the Randles-Ševčík equation. This is commonly

related to the roughness and spatially heterogeneous electrochemical activity of the diamond surface.⁴⁴ In contrast, the peak current responses recorded at the BDP and DND modified electrodes exceed the predicted values. This partially can be attributable to the increased roughness of the powder modified boron-doped diamond electrode, but clearly could also have additional origins such as thin layer diffusional effects.

In further analysis, the cyclic voltammetry data were assessed in terms of permeability.⁴⁵ The permeability, P , of the redox probe through the diamond powder film is described by the following equation:⁴⁶

$$P = \frac{I_{p(FILM)}}{I_{p(unmodified\ BDE)}} \times 100\% \quad (\text{Equation 5.1.2})$$

where $I_{p(FILM)}$ and $I_{p(unmodified\ BDE)}$ are the peak currents recorded at the powder modified electrode and unmodified microcrystalline boron-doped diamond electrode respectively. If the film exhibits a blocking effect, the P values below 100% are observed, whereas if a presence of the film results in the enhancement of redox currents, the P values above 100% are detected. The permeabilities obtained at the BDP and DND modified electrodes are summarised in Table 32.

Table 32 Permeabilities of 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH redox probes through DND and BDP modified electrodes. The data were recorded at a scan rate of 0.05 Vs^{-1}

Redox mediator	P through DND modified electrode (%)		P through BDP modified electrode (%)	
	Reduction scan	Oxidation scan	Reduction scan	Oxidation scan
$\text{Fe}(\text{CN})_6^{3-}$	139	123	73	79
$\text{Ru}(\text{NH}_3)_6^{3+}$	213	256	128	141
IrCl_6^{2-}	98	87	113	104
FcCH_2OH	269	263	170	165

The results above show that the tendency to exhibit amplified current responses must be quite sensitive to the diamond surface morphology. Apart from the case with IrCl_6^{2-} redox probe, a general trend arising from the cyclic voltammetry studies is that the peak currents at DND

modified electrode are bigger than that of observed at the BDP sample. This significant increase in the peak currents at the DND modified electrode are likely to stem from pre-concentration effects of the analyte at the high surface area-to-volume ratio of the DND electrode. In addition, previously reported feedback mechanism observed at the DND powder can contribute as well.^{30,33}

Cyclic voltammetry studies in 0.1 mM $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH redox couples were also carried out at different scan rates from 0.02 to 0.1 V s^{-1} . As expected, significant deviations from linearity of the peak currents with the square root of the scan rate were observed, thus suggesting the occurrence of other processes rather than simple diffusion controlled reaction at the interface.

In further experiments, the cyclic voltammetry in 1 mM and 10 mM solutions of $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH redox mediators was carried out at BDP, DND modified electrodes and plain boron-doped diamond electrode, as shown in Figure 67. The associated peak positions and current responses are summarised in Table 33 and Table 34.

It can be seen from Figure 67 that at a high concentrations of the redox species, the diffusional electrochemistry prevails at the BDP and DND films, and the current responses are very similar to that seen at unmodified BDE. Consistent with this picture, the peak currents were found to be close to those calculated from Randles-Ševčík analysis. This is in contrast to the situation when the cyclic voltammetry was performed in diluted solution of redox mediators, where the significant amplification of redox signals was detected at DND and BDP modified electrodes.

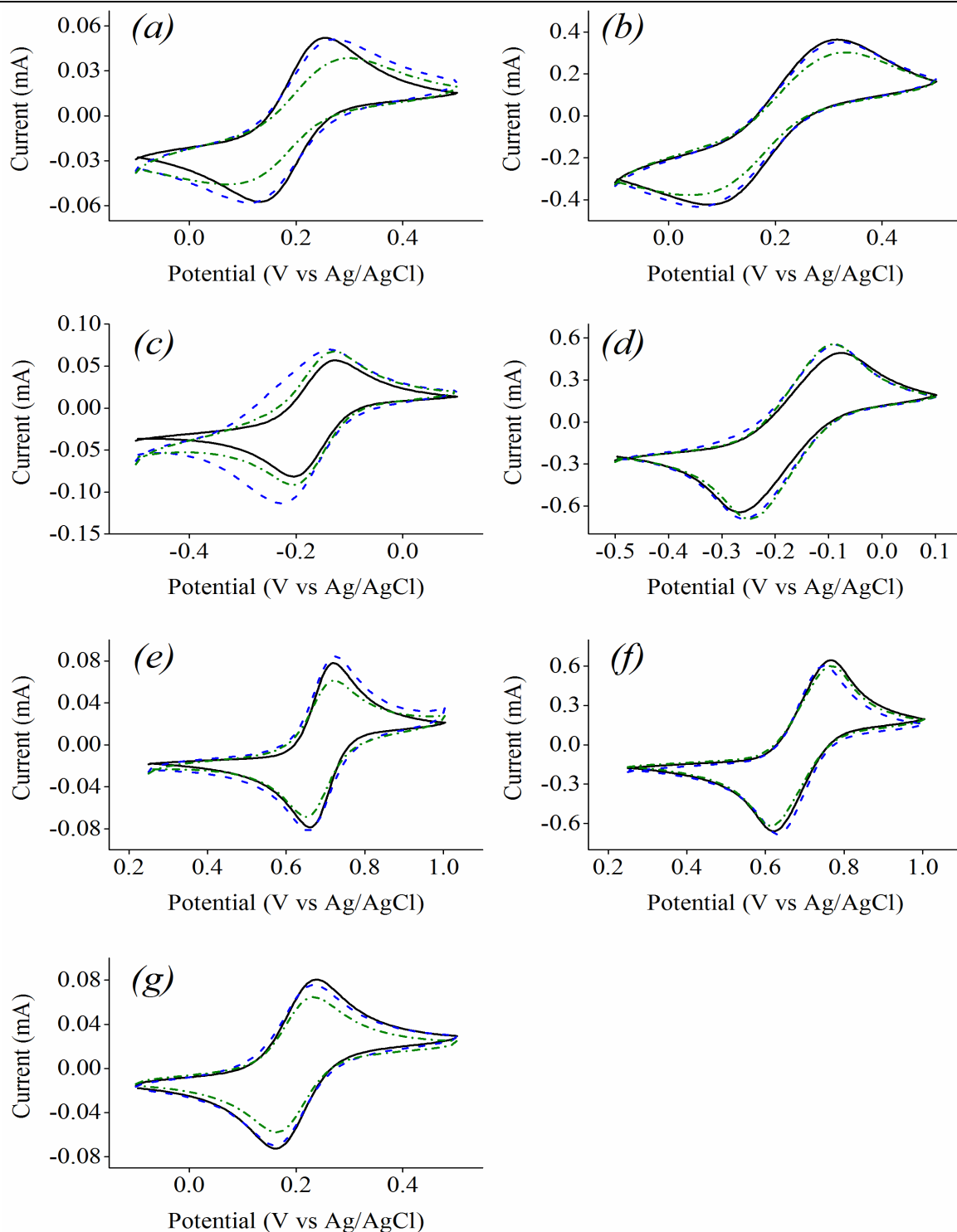


Figure 67 Cyclic voltammograms recorded at (-) plain BDE, (- - -) 200 nm DND and (- · - ·) 200 nm BDP modified electrodes in (a) 1 mM in K₃Fe(CN)₆, 0.1 M KCl; (b) 10 mM in K₃Fe(CN)₆, 0.1 M KCl; (c) 1 mM in Ru(NH₃)₆Cl₃, 0.1 M KCl; (d) 10 mM in Ru(NH₃)₆Cl₃, 0.1 M KCl; (e) 1 mM in K₂IrCl₆, 0.1 M KCl; (f) 10 mM in K₂IrCl₆, 0.1 M KCl; (g) 1 mM FcCH₂OH at a scan rate of 0.05 V s⁻¹

Chapter five – Diamond powder films: electrochemical properties and applications in electrocatalysis

Table 33 Peak position and current response data recorded in 1 mM Fe(CN)₆³⁻, Ru(NH₃)₆³⁺, IrCl₆²⁻ and FcCH₂OH redox probes at BDP, DND modified electrodes and unmodified B-doped diamond electrode at a scan rate of 0.05 Vs⁻¹

Sample	1 mM Fe(CN) ₆ ³⁻					
	$E(I_p^{Red})$ (V)	I_p^{Red} (A)	i_p^{Red} (A cm ⁻²)	$E(I_p^{Ox})$ (V)	I_p^{Ox} (A)	i_p^{Ox} (A cm ⁻²)
BDE	0.143	-4.76×10 ⁻⁵	-1.19×10 ⁻⁴	0.250	5.46×10 ⁻⁵	1.37×10 ⁻⁴
BDP	0.102	-2.27×10 ⁻⁵	-5.68×10 ⁻⁵	0.279	3.14×10 ⁻⁵	7.85×10 ⁻⁵
DND	0.127	-4.08×10 ⁻⁵	-1.02×10 ⁻⁴	0.258	4.57×10 ⁻⁵	1.14×10 ⁻⁴
	1 mM Ru(NH ₃) ₆ ³⁺					
BDE	-0.199	-7.17×10 ⁻⁵	-1.79×10 ⁻⁴	-0.129	6.31×10 ⁻⁵	1.58×10 ⁻⁴
BDP	-0.199	-6.71×10 ⁻⁵	-1.68×10 ⁻⁴	-0.133	6.44×10 ⁻⁵	1.61×10 ⁻⁴
DND	-0.220	-9.33×10 ⁻⁵	-2.33×10 ⁻⁴	-0.146	7.52×10 ⁻⁵	1.88×10 ⁻⁴
	1 mM IrCl ₆ ²⁻					
BDE	0.662	-8.13×10 ⁻⁵	-2.03×10 ⁻⁴	0.720	7.67×10 ⁻⁵	1.92×10 ⁻⁴
BDP	0.654	-6.65×10 ⁻⁵	-1.66×10 ⁻⁴	0.720	5.57×10 ⁻⁵	1.39×10 ⁻⁴
DND	0.658	-8.09×10 ⁻⁵	-2.02×10 ⁻⁴	0.720	7.48×10 ⁻⁵	1.87×10 ⁻⁴
	1 mM FcCH ₂ OH					
BDE	0.164	-7.37×10 ⁻⁵	-1.84×10 ⁻⁴	0.234	7.07×10 ⁻⁵	1.77×10 ⁻⁴
BDP	0.168	-5.79×10 ⁻⁵	-1.45×10 ⁻⁴	0.230	5.62×10 ⁻⁵	1.41×10 ⁻⁴
DND	0.164	-6.86×10 ⁻⁵	-1.72×10 ⁻⁴	0.230	6.56×10 ⁻⁵	1.64×10 ⁻⁴

Table 34 Peak position and current response data recorded in 10 mM Fe(CN)₆³⁻, Ru(NH₃)₆³⁺, IrCl₆²⁻ and FcCH₂OH redox probes at BDP, DND modified electrodes and unmodified B-doped diamond electrode at a scan rate of 0.05 Vs⁻¹

Sample	10 mM Fe(CN) ₆ ³⁻					
	$E(I_p^{Red})$ (V)	I_p^{Red} (A)	i_p^{Red} (A cm ⁻²)	$E(I_p^{Ox})$ (V)	I_p^{Ox} (A)	i_p^{Ox} (A cm ⁻²)
BDE	0.10	-2.51×10 ⁻⁴	-6.28×10 ⁻⁴	0.296	3.29×10 ⁻⁴	8.23×10 ⁻⁴
BDP	0.085	-1.85×10 ⁻⁴	-4.63×10 ⁻⁴	0.308	2.25×10 ⁻⁴	5.63×10 ⁻⁴
DND	0.077	-2.09×10 ⁻⁴	-5.23×10 ⁻⁴	0.300	2.96×10 ⁻⁴	7.40×10 ⁻⁴
	10 mM Ru(NH ₃) ₆ ³⁺					
BDE	0.10	-5.55×10 ⁻⁴	-1.39×10 ⁻³	-0.088	4.49×10 ⁻⁴	1.12×10 ⁻³
BDP	0.085	-6.12×10 ⁻⁴	-1.53×10 ⁻³	-0.096	5.29×10 ⁻⁴	1.32×10 ⁻³
DND	0.077	-6.03×10 ⁻⁴	-1.51×10 ⁻³	-0.092	5.10×10 ⁻⁴	1.28×10 ⁻³
	10 mM IrCl ₆ ²⁻					
BDE	0.625	-6.62×10 ⁻⁴	-1.66×10 ⁻³	0.761	6.04×10 ⁻⁴	1.51×10 ⁻³
BDP	0.617	-6.12×10 ⁻⁴	-1.53×10 ⁻³	0.765	5.54×10 ⁻⁴	1.39×10 ⁻³
DND	0.637	-6.60×10 ⁻⁴	-1.65×10 ⁻³	0.744	5.97×10 ⁻⁴	1.49×10 ⁻³

Table 35 I_p^{Ox}/I_p^{Red} ratio and peak-to-peak separation data estimated for 1 mM and 10 mM Fe(CN)₆³⁻, Ru(NH₃)₆³⁺, IrCl₆²⁻ and FcCH₂OH redox probes at BDP, DND modified electrodes and unmodified B-doped diamond electrode at a scan rate of 0.05 Vs⁻¹

Sample	1 mM Fe(CN) ₆ ³⁻		10 mM Fe(CN) ₆ ³⁻	
	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)	I_p^{Ox}/I_p^{Red} (A)	ΔE_{pp} (mV)
1				
BDE	0.87	107	0.76	196
BDP	0.72	177	0.82	223
DND	0.89	131	0.71	223
	1 mM Ru(NH ₃) ₆ ³⁺		10 mM Ru(NH ₃) ₆ ³⁺	
BDE	1.14	70	1.24	188
BDP	1.04	66	1.16	181
DND	1.24	74	1.18	169
	1 mM IrCl ₆ ²⁻		10 mM IrCl ₆ ²⁻	
BDE	1.06	58	1.10	136
BDP	1.19	66	1.10	148
DND	1.08	62	1.11	107
	1 mM FcCH ₂ OH			
BDE	1.04	70		
BDP	1.03	62		
DND	1.05	66		

The permeabilities obtained at the BDP and DND modified electrodes in 1 mM and 10 mM solutions of redox probes are summarised in Table 36.

Table 36 Permeabilities of $\text{Fe}(\text{CN})_6^{3-}$, $\text{Ru}(\text{NH}_3)_6^{3+}$, IrCl_6^{2-} and FcCH_2OH redox mediators in the concentration range of 0.1, 1 and 10 mM through DND and BDP modified electrodes. The data were recorded at a scan rate of 0.05 Vs^{-1}

Redox mediator	P through DND modified electrode (%)		P through BDP modified electrode (%)	
	Reduction scan	Oxidation scan	Reduction scan	Oxidation scan
1 mM solution:				
$\text{Fe}(\text{CN})_6^{3-}$	86	84	48	58
$\text{Ru}(\text{NH}_3)_6^{3+}$	130	119	94	102
IrCl_6^{2-}	100	98	82	73
FcCH_2OH	93	93	79	79
10 mM solution:				
$\text{Fe}(\text{CN})_6^{3-}$	83	90	74	68
$\text{Ru}(\text{NH}_3)_6^{3+}$	109	114	110	118
IrCl_6^{2-}	100	99	92	92

As it can be seen from Table 36, although a slight amplification of the peak currents detected at the DND surface with $\text{Ru}(\text{NH}_3)_6^{3+}$ are likely to be related to electrostatic attractions between the positively charged redox probe and negatively charged surface groups of the latter electrode, permeabilities close to 100% are detected. It can be further suggested that at the concentration range of 1 mM and 10 mM of redox solutions the amplification of the redox currents in cyclic voltammetry becomes invisible due to the overall high current densities. This is in contrast to a different picture seen in the diluted solutions, where permeabilities were largely increased.

A useful insight can be further obtained from consideration of a charge transport within the diamond powder film under controlled hydrodynamic conditions. Hydrodynamic voltammetry was carried out at boron-doped diamond rotating disk electrode covered with a 200 nm DND film in 1 mM solution of redox probes. In accordance with the Levich equation, the limiting current at an unmodified RDE electrode, I_L , is related to the rotation rate, w , through the following expression:⁴²

$$I_L = 0.62nFAC_s D_s^{2/3} \nu^{-1/6} w^{1/2} \quad (\text{Equation 5.1.3})$$

where n is the number of electrons involved in the redox process, F is the Faraday constant, A is the electrode area, C_s is the concentration of redox mediator in the bulk solution, D_s is the diffusion coefficient of redox mediator in the bulk solution, ν is the kinematic viscosity of the solution and w is the rotation speed of the rotating disk electrode.

If the RDE is covered by a porous thin DND layer, the limiting current is characterised by the inverse Levich equation:⁴²

$$\frac{1}{i_L} = \frac{d}{nFAD_{app}C_s} + \frac{1}{0.62nFAC_sD_s^{2/3}\nu^{-1/6}w^{1/2}} \quad (\text{Equation 5.1.4})$$

where D_{app} is the apparent diffusion coefficient of the redox mediators within the DND film.

The apparent diffusion coefficient equals to $\alpha D_{s,DND}$, where α is the partition coefficient of redox species through the DND layer and $D_{s,DND}$ describes the true diffusion coefficient of redox mediator in the DND film.

A typical RDE data in 1 mM FcCH₂OH dissolved in 0.1 M KCl recorded at unmodified microcrystalline BDE and DND modified electrode is presented in Figure 68.

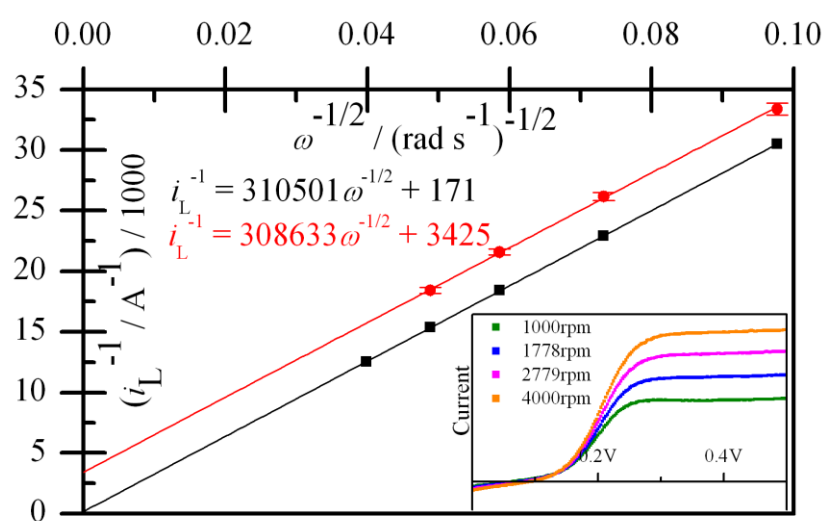


Figure 68 Koutecký-Levich plot of (-) unmodified BDE; (-) DND modified BDE in 1 mM FcCH₂OH dissolved in 0.1 M KCl, inset of linear sweep voltammogram mfrom 0 V to 0.5 V at DND modified electrode in 1 mM FcCH₂OH, 0.1 M KCl, reprinted from reference⁴⁷

The application of Equation 5.1.3 gives the value of $D_s = 6.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ which is lower than $7.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ reported previously.⁴³ This observation is in agreement with the fact that the actual geometrical area of microcrystalline boron-doped diamond electrode is greater than its active area due to the roughness of the electrode and spatially heterogeneous electrochemical activity. The apparent diffusion coefficient, D_{app} , was found to be $0.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This is much smaller than that of D_s , thus suggesting that some of the FcCH_2OH species are trapped within the DND layer due to its extensive porosity.

In further experiments, the partition coefficient, α , of FcCH_2OH redox probe was measured *via* coulometric assay using linear sweep voltammetry (LSV) as presented in Figure 69.

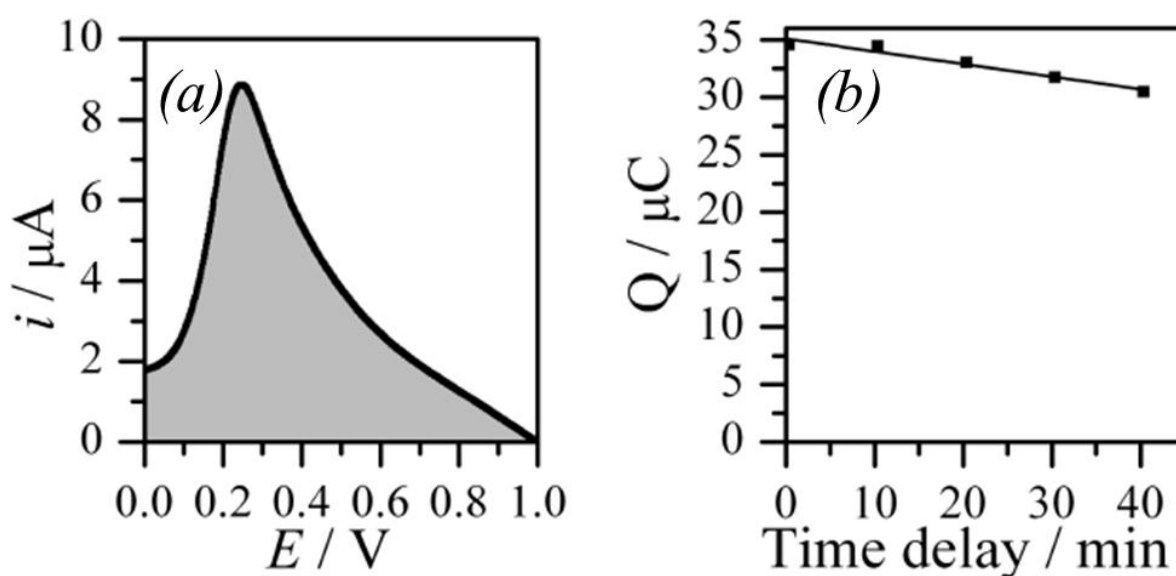


Figure 69 (a) subtracted LSV of FcCH_2OH at the DND modified electrode, (b) associated electrolysis charge as a function of delay time, reprinted from⁴⁷

In order to estimate the amount of FcCH_2OH partitioned within the DND film, the DND electrode was immersed into a 1 mM solution of FcCH_2OH for six hours to achieve equilibration and was subsequently transferred into background electrolyte (0.1 M KCl). This was followed by the linear sweep voltammetry measurement (Figure 69 (a)), in which the

forward peak current after the subtraction of the background scan was integrated and then divided by the scan rate to give the electrolysis charge, Q_0 . The latter is related to α by the following expression:⁴³

$$\alpha = Q_0 / nFV_{FILM}C_s \quad (\text{Equation 5.1.5})$$

where n is the number of electrons passed, F is the Faraday constant, V_{FILM} is the volume of the DND film ($3.9 \times 10^{-12} \text{ m}^3$), C_s is the bulk solution concentration of the FcCH₂OH redox probe.

This measurement was repeated in a range of delay times of 10-40 min (Figure 69 (b)), between transferring the DND modified electrode into background electrolyte and measuring the LSV. As presented in Figure 69 (b), the electrolysis charge recorded with the LSV experiments decreased proportionally with the delay time due to the diffusion of the FcCH₂OH redox probe away from the DND film into the background electrolyte.

The use of the factors in Equation 5.5 gives the α value of 93 for FcCH₂OH redox probe.

The diffusion coefficient within the DND film can be further estimated through the following equation:

$$D_{s,FILM} = D_{app} / \alpha \quad (\text{Equation 5.1.6})$$

The value of $D_{s,FILM} = 0.01 \text{ cm}^2 \text{ s}^{-1}$ was estimated for the FcCH₂OH species. The fact that the true diffusion coefficient within the DND film is found to be smaller than that of in the bulk suggests that the introduction of the DND film on the electrode surface results in the occurrence of pre-concentration effects of the analyte within the film.

5.4.3 Platinum decorated diamond electrodes

Platinum nanoparticles were electrodeposited on unmodified microcrystalline BDE as well as BDP and DND modified electrodes *via* chronoamperometry in accordance with the protocol described in Section 5.3.1. A typical SEM image of a Pt modified microcrystalline BDE (Pt_BDE) is presented in Figure 70 (a).

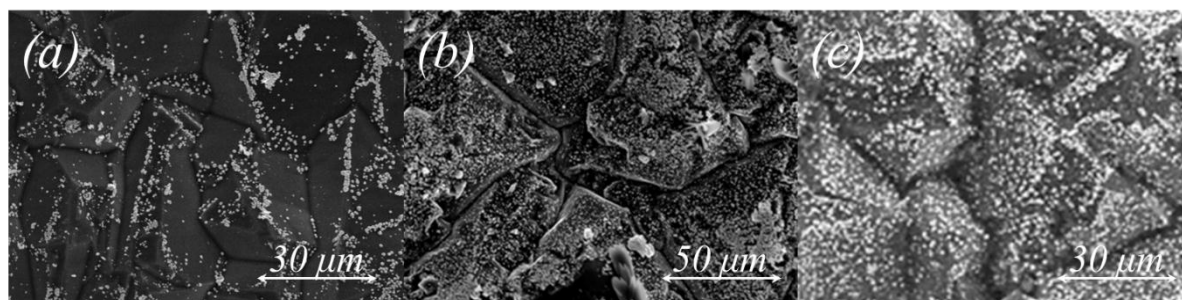


Figure 70 SEM of (a) Pt decorated BDE; (b) Pt decorated BDP modified electrode; (c) Pt decorated DND modified electrode

As expected, Pt particles were found to grow preferentially at the edge of the diamond grains which is in agreement with previously reported behaviour.⁴⁸ This preferential growth of Pt nanoparticles on the edge of the diamond grains is attributable to heterogeneous conductivity across diamond electrode surfaces due to enhanced sp^2 -conductivity of the intercrystalline regions,⁴⁹ the increased number of defects within these regions⁵⁰ along with heterogeneity of B-doping.⁵¹ The analysis of SEM data in Figure 70 (a) shows that electrodeposition on the unmodified microcrystalline BDE results in the formation of spherical Pt particles of 300-400 nm in size with the cluster coverage of approximately $0.6 \times 10^8 \text{ cm}^{-2}$. The SEMs of Pt decorated BDP (Pt_BDP) and DND (Pt_DND) modified electrodes are presented in Figure 70 (b) and (c) respectively. In contrast to the picture observed at unmodified microcrystalline BDE in Figure 70 (a), where a distinct segregation of Pt particles occurs, it can be clearly seen that on the BDP (Figure 70(b)) and DND (Figure 70 (c)) modified electrodes Pt dispersion is significantly improved with quite uniform distribution and cluster coverage of $\sim 32 \times 10^8 \text{ cm}^{-2}$ and $\sim 26 \times 10^8 \text{ cm}^{-2}$ respectively. This is likely to result from the increased

surface roughness of the electrode along with some changes in the surface chemistry induced by the introduction of BDP and DND powders enriched with sp^2 defects.²⁶

5.4.3.1 Investigation of Pt nucleation and growth on diamond electrodes

In order to further investigate the effects observed above, the nucleation and growth mechanism of Pt nanoparticles on the three differing types of diamond was analysed. Figure 71 shows typical platinum deposition currents recorded at a constant potential of -0.1 V from 2 mM K_2PtCl_6 dissolved in 0.5 M H_2SO_4 .

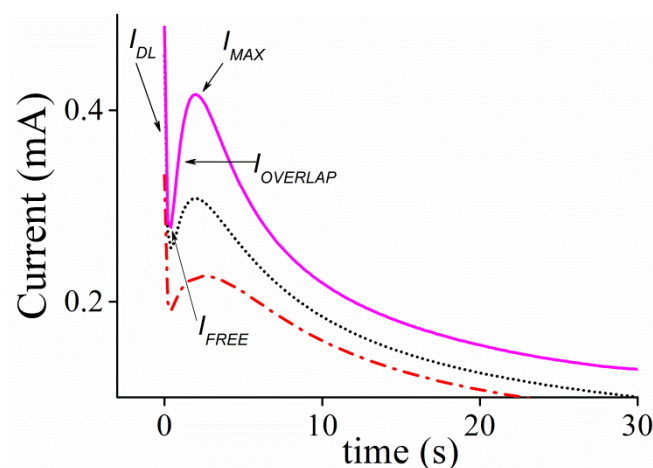


Figure 71 Deposition current obtained from 2 mM K_2PtCl_6 dissolved in 0.5 M H_2SO_4 at a constant potential of -0.2 V at (---) BDE; (....) DND and (—) BDP electrode surfaces

At the beginning of the deposition process (Figure 71), a rapid current drop, I_{DL} , which is attributable to the double layer charging, can be observed. This is followed by the initiation of the nucleation process at the minimum current. The rising part of the curve at the point of I_{FREE} represents the growth of independent nuclei which is controlled by hemi-spherical diffusion. The I_{FREE} current increases until the hemi-spherical diffusion zones start to interact with each other, thus giving rise to the deposition current with overlapping effects, $I_{OVERLAP}$. When this overlap becomes significant, hemi-spherical mass transfer is changed to linear

mass transfer. This switch in the diffusion regime is characterised by the maximum current, I_{MAX} . As soon as the I_{MAX} is reached, the growth of the Pt cluster is controlled by the linear diffusion, and the deposition current constantly decreases.^{52,53}

An interesting feature characteristic of platinum electrodeposition on the unmodified BDE surface is that it starts at lower currents as compared to the DND and BDP modified electrodes (Figure 71). This is likely to arise from the increased number of sp^2 defects on the DND and BDP powders which can act as additional source of the nucleation sites.

The mass of Pt deposited onto the electrode surface was obtained from the charge, Q_{Pt} , recorded during the reaction:⁴²

$$m(Pt) = Q_{Pt}nM/F \quad (\text{Equation 5.1.7})$$

where n is the number of electrons transferred, M is the atomic weight of Pt ($195.09 \text{ g mol}^{-1}$), F is the Faraday constant. This corresponds to a platinum loading of $5.05 \times 10^{-5} \text{ g}$, which was identical in all deposition experiments.

The mechanism of platinum formation was analysed via two classical nucleation and growth models:⁵⁴ (1) ‘Scharifker and Hills’ (SH model)⁵⁵ in order to identify the nucleation mechanism; and (2) ‘Scharifker and Mostany’ (SM model)⁵⁶ to estimate the number density of active sites on the electrode surface along with the nucleation rate.

The number of nuclei, N , on the electrode surface is described by the following equation:^{45, 46}

$$N(t) = N_0(1 - \exp(-At)) \quad (\text{Equation 5.1.8})$$

where N_0 is the maximum number of active sites, A is the rate of conversion of an active site into a nucleus.

‘Instantaneous’ and ‘progressive’ nucleation are considered to be the limits of this expression for a relatively large A and infinitely small A . Instantaneous nucleation corresponds to the extreme situation of a fast nucleation on a relatively small number of active sites ($N \approx N_0$), assuming that all these sites are converted to nuclei instantaneously. In contrast, progressive nucleation is characterised by a slow nucleation on a relatively large number of active sites ($N \approx AN_0t$), where the number of nuclei, N , is a function of time, t .

The theoretical relationship for the determination of the nucleation mechanism in the SH model is given by the following equations.⁵⁵

$$\frac{I}{I_m} = \frac{t}{t_m} \exp \left[-\frac{1}{2} \left(\frac{t^2 - t_m^2}{t_m^2} \right) \right] \quad \text{2D instantaneous} \quad (\text{Equation 5.1.9})$$

$$\frac{I}{I_m} = \left(\frac{t}{t_m} \right)^2 \exp \left[-\frac{2}{3} \left(\frac{t^3 - t_m^3}{t_m^3} \right) \right] \quad \text{2D progressive} \quad (\text{Equation 5.2.0})$$

$$\left(\frac{I}{I_m} \right)^2 = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad \text{3D instantaneous} \quad (\text{Equation 5.2.1})$$

$$\left(\frac{I}{I_m} \right)^2 = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2 \quad \text{3D progressive} \quad (\text{Equation 5.2.2})$$

Using the equations above, the I/I_m term can be expressed as a function of t/t_m , where I_m and t_m are experimental values of maximum current with associated time. The resulting non-dimensional curves were further compared with the experimental transients in order to determine whether the nucleation mechanism has progressive or instantaneous character (Figure 72).

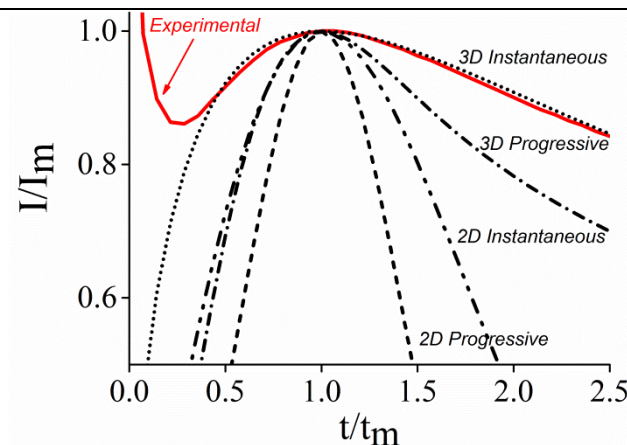


Figure 72 Non-dimensional plot of I/I_m vs t/t_m at -0.1 V obtained at Pt_DND electrode

For all the surfaces, the experimental non-dimensional current-time transients match 3D instantaneous nucleation curve as shown in Figure 72. An effective instantaneous character of the nucleation process determined on three diamond surfaces indicates that all platinum clusters formed are almost of the same age, similar shape and grow at a similar rate.

SM model was employed in order to estimate the nucleation rate, A , and the number density of active sites, N . A general expression of the potentiostatic current transient in SM theory is given by the following expression:⁵⁶

$$I(t) = nFc \left(\frac{D}{\pi t} \right)^{1/2} \left(1 - \exp \left\{ - (2\pi)^{3/2} D \left(\frac{cM}{\rho} \right)^{1/2} \frac{N_0}{A} \left[t - (1 - e^{-At})/A \right] \right\} \right) \quad (\text{Equation 5.2.3})$$

where n is the number of electrons transferred, c is the bulk concentration, D is the diffusion coefficient, M is the Pt molar mass and ρ is the density of Pt. The nucleation rate, A , and the number density of active sites, N_0 , were calculated from the first order derivative of equation 5.2.3⁵⁶ by the Newton method using Wolfram Mathematica 7 Software.⁵⁷ The resulting A and N_0 are summarised in Table 37.

Table 37 Kinetic parameters of platinum nucleation on BDE, DND and BDP modified electrodes

Parameter	Deposition potential of -0.05 V			Deposition potential of -0.1 V		
	BDE	DND	BDP	BDE	DND	BDP
N_0 (cm ⁻²)	1.0×10^7	1.2×10^7	3.5×10^7	2.5×10^7	3.8×10^7	2.2×10^8
A (s ⁻¹)	6.6×10^2	6.4×10^2	6.1×10^2	7.8×10^3	4.8×10^3	3.5×10^3
	Deposition potential of -0.2 V			Deposition potential of -0.25 V		
N_0 (cm ⁻²)	4.4×10^7	5.0×10^7	1.0×10^8	1.0×10^7	1.3×10^7	1.8×10^8
A (s ⁻¹)	4.9×10^3	4.5×10^3	4.1×10^3	3.1×10^3	1.9×10^3	1.2×10^3

As presented in Table 37, the introduction of conducting BDP powder results in improved number of active sites which is an order of magnitude greater than that seen at the plane BDE and DND modified electrodes. This improved number of nucleation sites at the BDP surface concomitantly contributes to the enhanced dispersion of Pt particles seen in SEM (Figure 70 (b)). Despite the significant increase in the surface roughness that arises from the coating of the plane BDE with DND, the amount of active nucleation sites at the DND surface is quite similar to that of estimated at the unmodified BDE electrode. This shows that the tendency to form Pt nuclei on the electrode surface must be quite sensitive to the diamond surface morphology.

5.4.3.2 Electrochemical characterisation of platinum decorated diamond electrodes

Following the platinum deposition procedure described in Section 5.3.2, cyclic voltammetry was performed in 0.5 M H₂SO₄ in order to compare the electrochemical properties of Pt deposited on the plane microcrystalline BDE, DND and BDP modified electrodes (Figure 73).

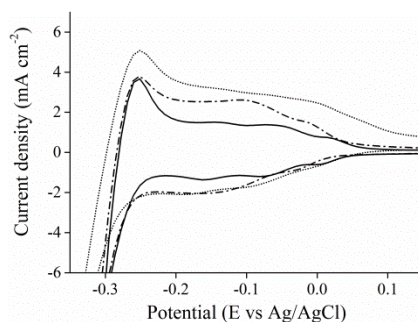


Figure 73 Cyclic voltammograms in 0.5 M H₂SO₄ recorded at 0.05 Vs⁻¹ at (—) Pt_{BDE}; (---) Pt_{DND} and (....) Pt_{BDP} that were deposited at -0.1 V

In the cathodic scan in Figure 73, the cyclic voltammograms correspond to formation of hydrogen molecules due to the reduction process of H^+ ions results in the adsorption of H_2 monolayers on the surface of Pt nanoparticles of differing crystallographic orientation.⁵⁸ In the anodic scan, this process is reversed, and the distinct peak appears at -0.25 V vs Ag/AgCl in the result of the hydrogen oxidation. The peaks recorded at BDP and DND modified electrodes are 1.6 and 0.4 $mA\ cm^{-2}$ larger than that of recorded at unmodified plane Pt_BDE.

In accordance with the standard electrochemical method, based on the integration of the anodic peak arising from the oxidation of hydrogen adsorbed on platinum between the -0.3 V and 0.1 V, the electrochemical active area of the electrodes (EAA), specific platinum surface area along with platinum particle size were estimated as described in detail in Chapter 3. The results are summarized in Table 38.

Table 38 Electrochemical characterisation of plane BDE, DND and BDP modified electrodes at a platinum loading of 5.05×10^{-5} g

Parameter	Deposition potential of -0.05 V			Deposition potential of -0.1 V		
	<i>BDE</i>	<i>DND</i>	<i>BDP</i>	<i>BDE</i>	<i>DND</i>	<i>BDP</i>
H-oxidation charge ($mC\ cm^{-2}$)	8.5	12.2	13.4	10.1	15.1	19.8
EAA (cm^2)*	40.5	58.3	63.7	48	72.1	93.4
Specific Pt NPs area ($m^2\ g^{-1}$)	80.1	115.4	126.1	95	142.8	186.7
Estimated Pt NPs size (nm)	3.5	2.4	2.2	2.9	2.0	2.0
	Deposition potential of -0.2 V			Deposition potential of -0.25 V		
H-oxidation charge ($mC\ cm^{-2}$)	9.7	10.1	11	7.3	8.8	10.2
EAA (cm^2)	46	48.3	52.2	34.6	41.8	48.5
Specific Pt NPs area ($m^2\ g^{-1}$)	91.1	95.6	103.3	68.6	82.7	96
Estimated Pt NPs size (nm)	3.1	2.9	2.7	4.1	3.4	2.9

*electrochemical active area per cm^2 of the substrate

The electrochemical active area of Pt deposited onto the plane boron-doped diamond electrode is around $48\ cm^2$, whereas at both DND and BDP modified electrodes these values are significantly improved with $EAA=72\ cm^2$ at DND and $EAA=93\ cm^2$ at BDP decorated at -0.1 V. The associated specific platinum surface area at the BDP modified electrode at -0.1 V is close to the values typically obtained at conventional highly dispersed electrocatalyst materials.⁵⁹ The platinum particle size estimated from cyclic voltammetry

(Table 38) is much smaller than that of observed in SEM. The likely explanation is that the visual inspection of the SEM images tends to highlight the larger particles; therefore, a highly dispersed nature of the platinum nanoparticles cannot be straightforwardly deduced from the SEM studies.²⁶ In addition, AFM investigations indicate that the platinum particles detected in SEM are often found in the form of agglomerates of much smaller crystals which contribute to the improved surface area observed in cyclic voltammetry studies.²⁶

In order to assess the persistence and stability of platinum particles on the plane microcrystalline BDE, DND and BDP modified electrodes, the effects of electrode performance during long-term cyclic voltammetry scans in 0.5 M H₂SO₄ were investigated. The estimated Pt loss (%), normalised to the EAA present at the start of the electrochemical measurements, as a function of the number of cycles, is presented in Figure 74.

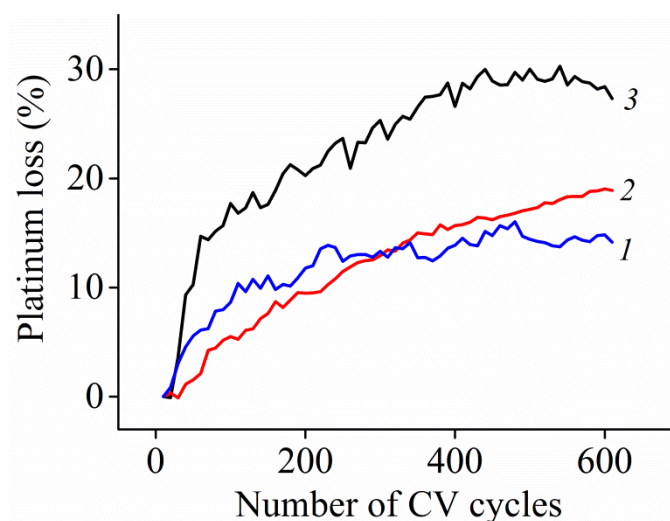


Figure 74 calculated Pt loss (%) at (1) Pt_BDP; (2) Pt_DND and (3) Pt_BDE that were decorated at -0.1 V

It can be seen that at unmodified Pt_BDE electrode the electrochemical active area decreased by 30 % as the potential on the electrode was scanned between -0.3 V and 0.1 V, whereas the

loss of EAA at the Pt_DND and Pt_BDP electrodes did not exceed more than 12% and 19% respectively.

In further experiments, the surface composition of the electrodes decorated at -0.1 V prior and after electrochemical cycling in 0.5 M H₂SO₄ was characterised by XPS. The data are shown in Table 39.

Table 39 Pt/C atomic ratios of the diamond electrodes decorated with Pt particles at -0.1 V before and after stability tests

Ratios	Pt_BDE		Pt_DND		Pt_BDP	
	Prior	After	Prior	After	Prior	After
Pt/C ($\times 10^{-2}$)	2.1	0.9	2.2	1.6	2.3	1.9
% Pt retained		43		72		82
*Prior and after stability tests						

As presented in Table 39, 82%, 72% and 43% of Pt retained on the Pt_BDP, Pt_DND and Pt_BDE respectively after the electrochemical scans, which is in agreement with the stability trend obtained from the decrease of the measured EAA, as shown in Figure 74.

Therefore, it can be suggested that the modification of the diamond electrode with conductive boron-doped diamond powders as well as detonation nanodiamond powders has a useful application in improving the stability of the Pt nanoparticles deposited on diamond.

A useful insight can be further obtained from the investigation of the electrochemical oxidation of methanol since such system forms the basis of methanol fuel cells that employ Pt nanoparticles as electrocatalyst material.³⁵

The methanol electrooxidation process was studied by cyclic voltammetry in 1 M CH₃OH, 0.5 M H₂SO₄ solution at three electrodes as presented in Figure 75.

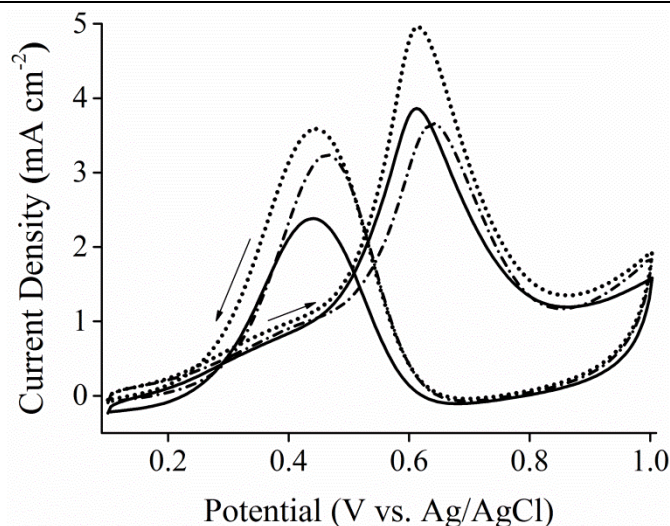


Figure 75 Cyclic voltammetry in 1 mM CH₃OH, 0.5 M H₂SO₄ recorded at a scan rate of 0.05 Vs⁻¹ at (–) Pt_BDE; (– · –) Pt_DND and (····) Pt_BDP electrodes

In Figure 75, the peak in the forward scan is characteristic of methanol oxidation process; in the reverse scan, a peak at lower positive potentials arises from the oxidation of adsorbed intermediates such as CO_{ads} and the reactivation of the electrode.

The electrocatalytic efficiency of the methanol oxidation is commonly characterised by the two main parameters: (1) the magnitude of the peak current I_f in the forward scan, a higher value of which corresponds to a greater catalytic activity of methanol oxidation, and (2) the ratio of the forward scan to the reverse scan, I_f/I_r , the higher the ratio of which the more complete oxidation process takes place at the electrode.² The I_f value recorded at Pt_BDP electrode is found to be 30% enhanced as compared to the Pt_DND and Pt_BDE samples. The I_f/I_r ratio of 1.4 is estimated for the Pt_BDP which is also greater than that of observed at Pt_BDE and Pt_DND, thus suggesting the lower poisoning of Pt/BDP.

5.5 Concluding remarks

In Chapter 5, the electrochemical studies of two differing types of finely divided diamond material, namely boron-doped diamond powder and detonation nanodiamond powder have

been discussed. It was observed in this work that at high concentrations of standard redox mediators, the diffusional electrochemistry at the films prepared from each of the two powders prevails, and the electrochemical behaviour of the films is found to be quite similar to that seen at unmodified microcrystalline boron-doped diamond electrode. However, significant differences arise at low concentrations, where the powder modified electrodes have shown amplified currents that are likely to be attributable to the pre-concentration effects within the powder film.

Platinum decorated diamond electrodes have become of great interest in many useful electrochemical applications such as fuel cells and electrochemical sensors. In Chapter 5, it was demonstrated that the electrochemical properties of such electrodes can be significantly improved upon modification of the latter with conductive boron-doped diamond powder. The improvement in electrochemical performance is likely to be related to the microscopic roughening of the electrode surface and resulting enhanced dispersion of platinum particles. The investigation of nucleation and growth of platinum nanoparticles on the three differing forms of diamond have also shown that the BDP surface provides the highest number of nucleation sites, thus contributing to the better dispersion seen in SEM.

The electrocatalytic activity of Pt_BDP modified electrode with respect to the oxidation of methanol was found to be the largest when compared to Pt_BDE and Pt_DND modified substrates. Finally, it was shown that Pt nanoparticles electrodeposited on the BDP modified diamond provides a highly stable platinum/diamond interface in long term.

5.6 References

- 1 Service, R. F. Bringing fuel cells down to Earth. *Science* **285**, 682-+, doi:10.1126/science.285.5428.682 (1999).
- 2 Liu, H. *et al.* A review of anode catalysis in the direct methanol fuel cell. *Journal of Power Sources* **155**, 95-110, doi:http://dx.doi.org/10.1016/j.jpowsour.2006.01.030 (2006).

- 3 Steele, B. C. H. & Heinzl, A. Materials for fuel-cell technologies. *Nature* **414**, 345-352 (2001).
- 4 Borup, R. *et al.* Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chemical Reviews* **107**, 3904-3951, doi:10.1021/cr050182l (2007).
- 5 Shao, Y., Yin, G. & Gao, Y. Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell. *Journal of Power Sources* **171**, 558-566, doi:10.1016/j.jpowsour.2007.07.004 (2007).
- 6 Wang, J. *et al.* Effect of carbon black support corrosion on the durability of Pt/C catalyst. *Journal of Power Sources* **171**, 331-339, doi:10.1016/j.jpowsour.2007.06.084 (2007).
- 7 Hoogers, G. *Fuel Cell Technology Handbook*. (2003).
- 8 Shao, Y., Liu, J., Wang, Y. & Lin, Y. Novel catalyst support materials for PEM fuel cells: current status and future prospects. *Journal of Materials Chemistry* **19**, 46-59, doi:10.1039/b808370c (2009).
- 9 Shao, Y., Yin, G., Wang, Z. & Gao, Y. Proton exchange membrane fuel cell from low temperature to high temperature: Material challenges. *Journal of Power Sources* **167**, 235-242, doi:10.1016/j.jpowsour.2007.02.065 (2007).
- 10 Butler, J. E. & Windischmann, H. Developments in CVD-diamond synthesis during the past decade. *MRS Bull.* **23**, 22-27 (1998).
- 11 Sauer, R. Synthetic diamond. Basic research and applications. *Cryst. Res. Technol.* **34**, 227-241, doi:10.1002/(sici)1521-4079(199902)34:2<227::aid-cratt227>3.0.co;2-y (1999).
- 12 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).
- 13 Montilla, F., Morallon, E., Duo, I., Comninellis, C. & Vazquez, J. L. Platinum particles deposited on synthetic boron-doped diamond surfaces. Application to methanol oxidation. *Electrochimica Acta* **48**, 3891-3897, doi:10.1016/s0013-4686(03)00526-7 (2003).
- 14 Salazar-Banda, G. R., Suffredini, H. B., Calegaro, M. L., Tanimoto, S. T. & Avaca, L. A. Sol-gel-modified boron-doped diamond surfaces for methanol and ethanol electro-oxidation in acid medium. *Journal of Power Sources* **162**, 9-20, doi:10.1016/j.jpowsour.2006.06.045 (2006).
- 15 Toghill, K. E., Xiao, L., Stradiotto, N. R. & Compton, R. G. The Determination of Methanol Using an Electrolytically Fabricated Nickel Microparticle Modified Boron Doped Diamond Electrode. *Electroanalysis* **22**, 491-500, doi:10.1002/elan.200900523 (2010).
- 16 Stradiotto, N. R., Toghill, K. E., Xiao, L., Moshar, A. & Compton, R. G. The fabrication and characterization of a nickel nanoparticle modified boron-doped diamond electrode for electrocatalysis of primary alcohol oxidation. *Electroanalysis* **21**, 2627-2633, doi:10.1002/elan.200900325 (2009).
- 17 Mitani, S., Teraji, T. & Ito, T. Formation of self-assembled platinum particles on diamond and their embedding in diamond by microwave plasma chemical vapor depositions. *Diamond and Related Materials* **15**, 1544-1549, doi:http://dx.doi.org/10.1016/j.diamond.2005.12.052 (2006).
- 18 González-González, I., Tryk, D. A. & Cabrera, C. R. Polycrystalline boron-doped diamond films as supports for methanol oxidation electrocatalysts. *Diamond and Related Materials* **15**, 275-278, doi:http://dx.doi.org/10.1016/j.diamond.2005.08.037 (2006).

- 19 Wang, J. & Swain, G. M. Fabrication and Evaluation of Platinum/Diamond Composite Electrodes for Electrocatalysis: Preliminary Studies of the Oxygen-Reduction Reaction. *Journal of The Electrochemical Society* **150**, E24-E32, doi:10.1149/1.1524612 (2003).
- 20 Fischer, A. E. & Swain, G. M. Preparation and characterization of boron-doped diamond powder - A possible dimensionally stable electrocatalyst support material. *Journal of the Electrochemical Society* **152**, B369-B375, doi:10.1149/1.1984367 (2005).
- 21 Salazar-Banda, G. R., Eguiluz, K. I. B. & Avaca, L. A. Boron-doped diamond powder as catalyst support for fuel cell applications. *Electrochemistry Communications* **9**, 59-64, doi:10.1016/j.elecom.2006.08.038 (2007).
- 22 Spataru, N., Zhang, X., Spataru, T., Tryk, D. A. & Fujishima, A. Platinum electrodeposition on conductive diamond powder and its application to methanol oxidation in acidic media. *J. Electrochem. Soc.* **155**, B264-B269, doi:10.1149/1.2830857 (2008).
- 23 Zang, J. B., Wang, Y. H., Huang, H. & Tang, W. Electrochemical behavior of high-pressure synthetic boron doped diamond powder electrodes. *Electrochimica Acta* **52**, 4398-4402, doi:10.1016/j.electacta.2006.12.028 (2007).
- 24 Bian, L. Y., Wang, Y. H., Zang, J. B., Yu, J. K. & Huang, H. Electrodeposition of Pt nanoparticles on undoped nanodiamond powder for methanol oxidation electrocatalysts. *Journal of Electroanalytical Chemistry* **644**, 85-88, doi:10.1016/j.jelechem.2010.04.001.
- 25 Schrand, A. M., Hens, S. A. C. & Shenderova, O. A. Nanodiamond Particles: Properties and Perspectives for Bioapplications. *Critical Reviews in Solid State and Materials Sciences* **34**, 18-74, doi:10.1080/10408430902831987 (2009).
- 26 Hu, J., Lu, X. & Foord, J. S. Nanodiamond pretreatment for the modification of diamond electrodes by platinum nanoparticles. *Electrochemistry Communications* **12**, 676-679, doi:10.1016/j.elecom.2010.03.004 (2010).
- 27 Holt, K. B. Diamond at the nanoscale: applications of diamond nanoparticles from cellular biomarkers to quantum computing. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **365**, 2845-2861, doi:10.1098/rsta.2007.0005 (2007).
- 28 Dolmatov, V. Y. Detonation synthesis ultradispersed diamonds: properties and applications. *Russ. Chem. Rev.* **70**, 607-626, doi:10.1070/RC2001v070n07ABEH000665 (2001).
- 29 Mochalin, V. N., Shenderova, O., Ho, D. & Gogotsi, Y. The properties and applications of nanodiamonds. *Nature Nanotechnology* **7**, 11-23, doi:10.1038/nnano.2011.209 (2012).
- 30 Holt, K. B., Caruana, D. J. & Millan-Barrios, E. J. Electrochemistry of Undoped Diamond Nanoparticles: Accessing Surface Redox States. *Journal of the American Chemical Society* **131**, 11272-+, doi:10.1021/ja902216n (2009).
- 31 Holt, K. B. *et al.* Redox properties of undoped 5 nm diamond nanoparticles. *Physical Chemistry Chemical Physics* **10**, 303-310, doi:10.1039/b711049a (2008).
- 32 Scholz, J., McQuillan, A. J. & Holt, K. B. Redox transformations at nanodiamond surfaces revealed by in situ infrared spectroscopy. *Chemical Communications* **47**, 12140-12142, doi:10.1039/c1cc14961j (2011).
- 33 Holt, K. B. Undoped diamond nanoparticles: origins of surface redox chemistry. *Physical Chemistry Chemical Physics* **12**, 2048-2058, doi:10.1039/b920075d (2010).
- 34 Ay, A., Swope, V. M. & Swain, G. M. The physicochemical and electrochemical properties of 100 and 500 nm diameter diamond powders coated with boron-doped

- nanocrystalline diamond. *Journal of the Electrochemical Society* **155**, B1013-B1022, doi:10.1149/1.2958308 (2008).
- 35 La-Torre-Riveros, L. *et al.* Diamond Nanoparticles as a Support for Pt and PtRu Catalysts for Direct Methanol Fuel Cells. *ACS Appl. Mater. Interfaces* **4**, 1134-1147, doi:10.1021/am2018628 (2012).
- 36 <http://www.casaxps.com/>.
- 37 Shirley, D. A. High-resolution x-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B* **[3]5**, 4709-4714 (1972).
- 38 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 39 Briggs, D. & Editor. *Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy*. (Heyden, 1977).
- 40 Goeting, C. H., Marken, F., Osborn, A. R., Compton, R. G. & Foord, J. S. Surface Modification of Chemical Vapor Deposited Diamond Induced by Power Ultrasound. *Electrochemical and Solid State Letters* **4**, E29-E31, doi:10.1149/1.1377488 (2001).
- 41 Shenderova, O. *et al.* Hydroxylated Detonation Nanodiamond: FTIR, XPS, and NMR Studies. *The Journal of Physical Chemistry C* **115**, 19005-19011, doi:10.1021/jp205389m (2011).
- 42 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley & Sons, 2001).
- 43 Miao, W., Ding, Z. & Bard, A. J. Solution Viscosity Effects on the Heterogeneous Electron Transfer Kinetics of Ferrocenemethanol in Dimethyl Sulfoxide–Water Mixtures. *The Journal of Physical Chemistry B* **106**, 1392-1398, doi:10.1021/jp013451u (2002).
- 44 Holt, K. B., Bard, A. J., Show, Y. & Swain, G. M. Scanning Electrochemical Microscopy and Conductive Probe Atomic Force Microscopy Studies of Hydrogen-Terminated Boron-Doped Diamond Electrodes with Different Doping Levels. *The Journal of Physical Chemistry B* **108**, 15117-15127, doi:10.1021/jp048222x (2004).
- 45 Sawangphruk, M. & Foord, J. S. Permselective properties of polystyrene opal films at diamond electrode surfaces. *Physical Chemistry Chemical Physics* **12**, 7856-7864, doi:10.1039/B926005F (2010).
- 46 Olivia, H., Sarada, B. V., Shin, D., Rao, T. N. & Fujishima, A. Selective amperometric detection of dopamine using OPPy-modified diamond microsensor system. *Analyst* **127**, 1572-1575, doi:10.1039/B208729D (2002).
- 47 Griffiths, R. A. *Electronic and physical properties of nanodiamond films*, University of Oxford, (2010).
- 48 Bennett, J. A., Show, Y., Wang, S. & Swain, G. M. Pulsed Galvanostatic Deposition of Pt Particles on Microcrystalline and Nanocrystalline Diamond Thin-Film Electrodes: I. Characterization of As-Deposited Metal/Diamond Surfaces. *Journal of The Electrochemical Society* **152**, E184-E192, doi:10.1149/1.1890745 (2005).
- 49 Butler, J. E. & Sumant, A. V. The CVD of nanodiamond materials. *Chemical Vapor Deposition* **14**, 145-160, doi:10.1002/cvde.200700037 (2008).
- 50 Gruen, D. M. Nanocrystalline diamond films. *Annual Review of Materials Science* **29**, 211-259, doi:10.1146/annurev.matsci.29.1.211 (1999).
- 51 Patten, H. V., Lai, S. C. S., Macpherson, J. V. & Unwin, P. R. Active Sites for Outer-Sphere, Inner-Sphere, and Complex Multistage Electrochemical Reactions at Polycrystalline Boron-Doped Diamond Electrodes (pBDD) Revealed with Scanning Electrochemical Cell Microscopy (SECCM). *Anal. Chem. (Washington, DC, U. S.)* **84**, 5427-5432, doi:10.1021/ac3010555 (2012).

- 52 Paunovic, M. & Schlesinger, M. *Fundamentals of electrochemical deposition*. 2nd edn, (Hoboken, N.J. : Wiley-Interscience 2006).
- 53 Budevski, E., Staikov, G. & Lorenz, W. J. *Electrochemical phase formation and growth : an introduction to the initial stages of metal deposition*. (Weinheim ; Cambridge : VCH 1996).
- 54 Scharifker, B. R., Mostany, J., Palomar-Pardave, M. & Gonzalez, I. On the theory of the potentiostatic current transient for diffusion-controlled three-dimensional electrocrystallization processes. *Journal of the Electrochemical Society* **146**, 1005-1012 (1999).
- 55 Scharifker, B. & Hills, G. THEORETICAL AND EXPERIMENTAL STUDIES OF MULTIPLE NUCLEATION. *Electrochimica Acta* **28**, 879-889 (1983).
- 56 Scharifker, B. R. & Mostany, J. Three-dimensional nucleation with diffusion controlled growth. Part I. Number density of active sites and nucleation rates per site. *J. Electroanal. Chem. Interfacial Electrochem.* **177**, 13 (1984).
- 57 Wolfram Mathematica 7, <<http://www.wolfram.com/mathematica/>> (
- 58 Yamamoto, K., Kolb, D. M., Koetz, R. & Lehmpfuhl, G. Hydrogen adsorption and oxide formation on platinum single crystal electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **96**, 233-239, doi:10.1016/s0022-0728(79)80380-0 (1978).
- 59 Antolini, E. Carbon supports for low-temperature fuel cell catalysts. *Applied Catalysis B-Environmental* **88**, 1-24, doi:10.1016/j.apcatb.2008.09.030 (2009).

6 Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

This chapter discusses the effects of the surface pre-treatments on the electrocatalytic activity and adhesion of nickel particles on the boron-doped diamond electrode surface. The preparation of nickel modified diamond electrode involves the electrodeposition of Ni nanoparticles on two dissimilar diamond electrode surfaces: hydrophobic H-terminated and hydrophilic O-terminated. The use of nickel modified boron-doped diamond electrode for the electroanalysis of hydrogen peroxide and glucose was investigated. It was shown that a nickel modified hydrogen terminated boron-doped diamond provides an improved electrochemical performance and stability as compared to nickel modified oxygen terminated boron-doped diamond electrode. The reasons underlying these observations are discussed in terms of electronic properties of the two dissimilar diamond surface pre-treatments.

6.1 Introduction

With the progress of Chemical Vapour Deposition techniques, boron-doped diamond has become widely available in different forms and variety of doping levels. The properties of boron-doped diamond electrode including excellent chemical stability, wide potential window and low signal-to-background current ratio make it exceptionally attractive in many electrochemical applications such as wastewater treatment, electrosynthesis, fuel cells and energy harvesting.¹⁻⁷

Recently, the decoration of boron-doped diamond electrodes (BDEs) with catalyst metal nanoparticles (NPs) to modify the electrode activity has been examined, resulting in a considerable diversity of possible electrochemical applications.⁸⁻¹² The preparation of nickel (Ni) modified boron-doped diamond electrode in particular is a subject of increasing interest

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

in connection with water splitting technologies and electrochemical sensing such as enzyme-free detection of glucose,^{13,14} methanol¹⁵, adenine and DNA¹⁶ along with primary alcohols.¹⁷

The summary of some electroanalytical applications that employ nickel modified boron-doped diamond electrodes is given in Table 40.

Table 40 Nickel modified boron-doped diamond electrode and their electroanalytical applications

Electrode modification	Analyte	Reference
Nickel (drop coated on BDE)	Glucose	18
Nickel (electrodeposited)	Glucose	13
Nickel (implanted)	Glucose	19
Nickel (electrodeposited)	Ethanol and Glycerol	17
Nickel (electrodeposited)	Methanol	15
Nickel (implanted)	Tetracyclines	20
Nickel (ultrasound assisted electrodeposition)	L-alanine	21
Nickel (electrodeposited)	Adenine and DNA	16

As shown in Table 40, several preparative routes to nickel immobilisation on the diamond electrode surface have been developed, including ion implantation, drop coating and evaporation as well as electrochemical deposition.^{15-17,19-22} Among them, the direct formation of nickel particles *via* electrodeposition is found to be the most advantageous as it yields highly dispersed particles on the surface without causing any damage to the electrode surface.¹⁴

Apart from the modification of the boron-doped diamond electrode with catalyst particles mentioned above, the electrode surface itself can be terminated with oxygen or hydrogen functionalities. Oxygen termination can be produced by electrochemical oxidation, oxygen plasma treatment, ultrasonic treatment as well as ozone oxidation along with chemical oxidation in the presence of mineral acid mixtures such as *aqua regia* or *piranha* solution.²³⁻

²⁶ Electrochemical oxidation is an effective straightforward technique that results in the electrode surface being terminated with different oxygen functional groups such as hydroxyl, carbonyl as well as carboxyl, which are responsible for the hydrophilic properties of the

diamond surface.^{14,16,17,19,22,27} A full termination of the diamond electrode with hydrogen atoms can be achieved mainly by the hydrogen plasma treatment which gives rise to hydrophobic properties of the electrode surface.²⁸

Oxygen termination leads to an insulating character of the diamond surface with positive electron affinity, whereas hydrogen termination gives rise to negative electron affinity and surface induced conductivity.^{29,30} Despite very dissimilar surface properties of H- and O-terminated diamond, only a few recent reports have investigated the influence of the diamond surface chemistry on the electrochemical performance of the electrode.³¹⁻³³

It is interesting to note that all previous electrochemical studies of nickel modified boron-doped diamond electrodes were performed on electrochemically cleaned and therefore oxidised diamond electrode. At present, little is known about how the diamond surface pre-treatment influences the electrochemical performance of Ni modified diamond electrodes.

6.2 Aims of the project

The work in this chapter explores in detail how the surface chemistry of diamond electrode affects the chemical properties of Ni modified boron-doped diamond electrode. The methods employed commence with controlled formation of either hydrophobic H-terminated or hydrophilic O-terminated surface at a boron-doped diamond electrode, which is followed by the nickel electrodeposition. In the former process, microwave hydrogen plasma was used to prepare a hydrogen terminated boron-doped diamond; in the latter process the electrochemical oxidation was used to produce a highly oxidised diamond surface.

The electrodes prepared in this way were systematically studied, and the differences in electrocatalytic activity and adherence of nickel particles to the H- and O-terminated diamond surface were investigated. The application of the hydrogen plasma pre-treatment for the

improved electrochemical detection of glucose and hydrogen peroxide at the Ni modified H-terminated boron-doped diamond was demonstrated in this work.

6.3 Experimental methods

6.3.1 Preparation of nickel modified boron-doped diamond electrode

6.3.1.1 Preparation of oxygen terminated boron-doped diamond surface

As it was previously described in Chapter 4, in order to produce an oxidised diamond surface, BDE was conditioned by potential cycling in 0.1 M nitric acid between -1.5 V and + 2.5 V, which results in a hydrophilic surface containing a high concentration of oxygen functionalities such as hydroxyl, carbonyl and carboxylic acid groups.^{34,35}

6.3.1.2 Preparation of hydrogen terminated boron-doped diamond surface

A hydrogen terminated boron-doped diamond surface was produced as described in Chapter 4 by microwave hydrogen plasma treatment at 1.5 kW microwave power, 60 mbar pressure and at a temperature of 600°C during 60 minutes.³⁶ The sample was cooled down in the hydrogen plasma by switching of the heating element and gradually reducing the microwave power until the plasma extinguished. The sample was cooled to a room temperature under hydrogen flow. This treatment yields a surface being largely free of adsorbed oxygen functionalities, hydrocarbons and sp² species.

6.3.1.3 Preparation of nickel modified boron-doped diamond electrode

Electrochemical measurements were performed with a μ -AUTOLAB III electrochemical workstation (Eco-Chemie, Netherlands) at 23°C. A standard three-electrode configuration consisting of a boron-doped microcrystalline diamond electrode (BDE from Element Six Co, 10×10×0.6 mm size, boron doping concentration of $\sim 10^{20}$ cm⁻³) as a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode was used. The boron-doped diamond electrode was mounted in a PTFE holder, so that a circular area of 0.4 cm² was exposed to a

solution. Nickel particles were electrodeposited from deaerated 1 mM $\text{Ni}(\text{NO}_3)_2$ in 0.1 M acetate buffer solution (pH 5). During the electrodeposition procedure, 400 mC were passed using chronoamperometry at a potential of -1.3 V vs Ag/AgCl for 600s. In accordance with the method reported previously, nickel particles formed on the electrode surface were subsequently enriched with $\text{Ni}(\text{OH})_2$ by cyclic voltammetry in 1 M KOH, H_2O solution during 500 scans at a scan rate of 0.05 V s^{-1} .^{13,16,17,22,37} Cyclic voltammetry and chronoamperometry were employed to investigate the electrochemical detection of 0.1 mM hydrogen peroxide and 1 mM glucose solutions.

All chemicals (purchased from Sigma-Aldrich, UK) were of analytical grade and used without any further purification. Solutions were prepared using ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$ at 293 K, Millipore water systems, UK).

6.3.2 Surface characterisation of nickel modified boron-doped diamond electrode

The surface morphology was examined with a scanning electron microscope at a 20 kV acceleration voltage. X-ray photoelectron spectroscopy (XPS) spectra were collected using a hemispherical analyser and Al $\text{K}\alpha$ (1486.6 eV) X-ray source. The survey scans and the high resolution scans were recorded at 50 eV with 0.5 eV step and at 20 eV energy passes with 0.1 eV step respectively. The associated data were analysed by CasaXPS software.³⁸ The peaks were fitted using a Shirley background.³⁹ High resolution X-ray diffraction (XRD) measurements were performed using a Philips Xpert Diffractometer with monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

6.4 Results and Discussion

6.4.1 Morphology and microstructure of nickel modified boron-doped diamond electrodes

6.4.1.1 SEM characterisation of nickel modified boron-doped diamond electrodes

A typical SEM image of a microcrystalline boron-doped diamond (BDE) electrode surface prior to Ni electrodeposition is presented in Figure 76 (a). It consists of diamond grains with [111] and [110] crystallographic orientation with an average grain size of 5-50 μm . The hydrogen and oxygen terminations of the boron-doped diamond electrode were produced as described in Sections 6.3.1.1 and 6.3.1.2. In the following experiments, Ni nanoparticles were electrodeposited on the BDE via chronoamperometry at a constant potential of -1.3 V vs Ag/AgCl from 1 mM $\text{Ni}(\text{NO}_3)_2$ solution in 0.1 M acetate buffer (pH 5). The formation of metal Ni particles is described by the following equation:^{40,41}



The SEM images of Ni decorated oxygen terminated boron-doped diamond electrode (further denoted as Ni_OBDE) and Ni modified hydrogen terminated boron-doped diamond electrode (Ni_HBDE) are shown in Figure 76 (b) and Figure 76 (c) respectively.

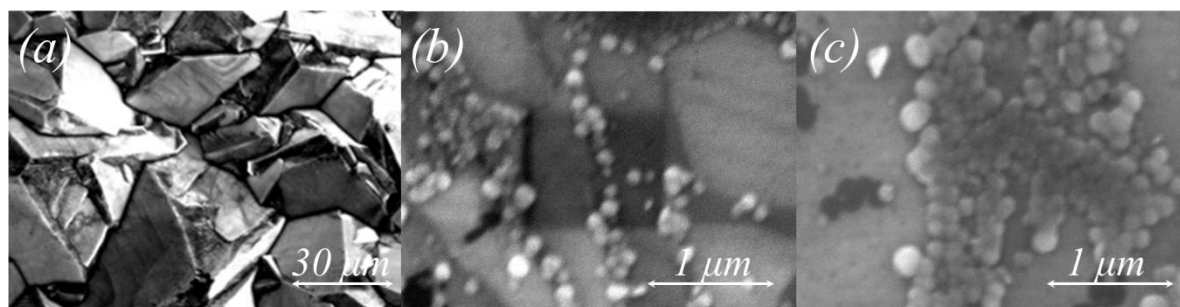


Figure 76 SEM image of (a) microcrystalline BDE; (b) Ni NPs deposited on oxygen terminated BDE; (b) Ni NPs deposited on hydrogen terminated BDE;

It can be seen from Figure 76 (b and c) that hemispherical Ni particles of an average size of 200-300 nm are distributed with some preferential location at the edge of diamond grains. This is in agreement with the previously observed behaviour that was related to the presence of heterogeneous conductivity across diamond electrode surface in the result of enhanced sp^2 -conductivity of the intercrystalline regions²⁴ and heterogeneity of boron doping.⁴²⁻⁴⁷

The analysis of the SEM images suggests the presence of approximately 2.1×10^6 particles per cm^{-2} on the oxidised and 2.3×10^6 particles per cm^{-2} on hydrogenated diamond surfaces. This corresponds to the presence of $22 \mu g cm^{-2}$ and $24 \mu g cm^{-2}$ of nickel on the oxidised and hydrogenated diamond surfaces respectively.

The electrodeposition currents were used to simulate the mechanism of Ni particles formation on oxidised and hydrogenated diamond surfaces. Ni electrodeposition currents were analysed by ‘Scharifker and Hills’ (SH) nucleation model as described in detail in Chapter 5.⁴⁸ Analogous to the analysis presented in Chapter 5, the nucleation mechanism (progressive or instantaneous) was determined by comparison of the experimental curves with the theoretical as presented in Figure 77.

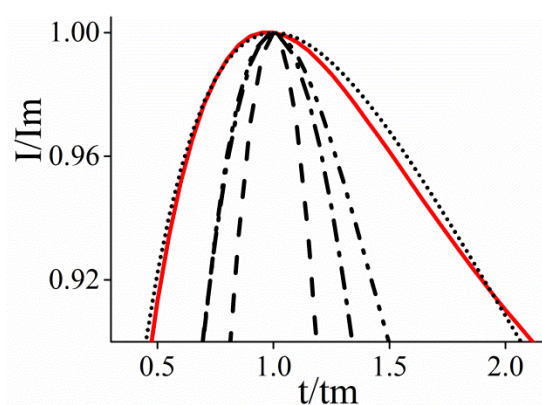


Figure 77 The comparison of Ni electrodeposition current time-transient obtained at oxidised BDE at -1.3 V with SH model: non-dimensional plot of I/I_m vs t/t_m , (—) experimental current (....) 3D Instantaneous nucleation, (- · - ·) 3D Progressive, (- - -) 2D Instantaneous (—) 2D Progressive

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

For both oxidised and hydrogenated diamond surfaces, the experimental non-dimensional current-time transients matched closely to the 3D instantaneous nucleation curve as presented in Figure 77. Thus, it can be suggested that Ni particles on both surfaces should grow with a similar rate and of a similar size due to the distinct instantaneous character of the nucleation process. The number of Ni nuclei formed on both oxidised and hydrogenated diamond surfaces during electrodeposition were estimated by SH model using the following equation:⁴⁸

$$Im = 0.6382nFDc(kN)^{1/2} \quad (\text{Equation 6.1.2})$$

where Im is the maximum current observed during electrodeposition, n is the number of electrons, F is the Faraday constant (96485 C mol^{-1}), k is empirical constant that is expressed by $k=(8\pi cM/\rho)^{1/2}$, D is the diffusion coefficient of Ni ions, N is the number of nuclei on the electrode surface.

The application of the equation above gives the number of Ni nuclei of 3.1×10^6 nuclei per cm^{-2} on the oxygen terminated diamond surface along with 4.3×10^6 nuclei per cm^{-2} estimated at the hydrogen terminated diamond surface. These estimations are in a good agreement with the SEM data discussed above. Although the number of Ni nuclei calculated for both surfaces are of the same order of magnitude, slightly higher number of nuclei was predicted for the hydrogen terminated surface. This higher number of nuclei estimated for the hydrogen terminated surface is likely to be related to the surface conductivity of an H-terminated diamond electrode induced by the transfer doping mechanism.^{28,49}

6.4.1.2 XRD characterisation of nickel modified boron-doped diamond electrodes

In further experiments, the XRD patterns were recorded at 23°C in the 10° - 90° 2θ range using $\text{CuK}\alpha$ radiation as described in Section 6.3.2. The associated 2θ profile of the

Ni_HBDE sample is displayed in Figure 78. The reflections of Ni particles at $44.5^{\circ}2\theta$ and $51.9^{\circ}2\theta$ degrees clearly reveal the presence of metal phase with [111] and [100] orientations respectively.⁵⁰ The dominant diffraction peaks at $43.9^{\circ}2\theta$ and $75.3^{\circ}2\theta$ degrees correspond to [111] and [220] diamond grains.⁵¹ It is noteworthy that the XRD data were found to be identical for both hydrogenated and oxidised samples. This suggests that Ni particles produced by electrodeposition on both surfaces are of a similar form and exist mainly in metallic state, independently of the diamond surface chemistry.

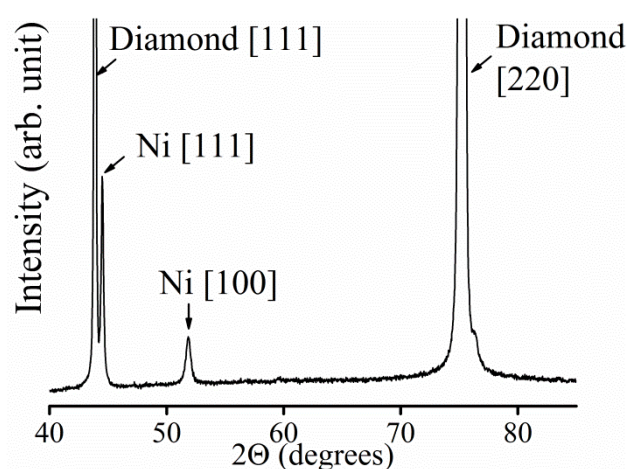


Figure 78 X-ray diffraction profile of the Ni_HBDE sample. Nickel particles were electrodeposited from 1 mM $\text{Ni}(\text{NO}_3)_2$ in 0.1 M acetate buffer solution (pH 5) via potentiostatic method at a potential of -1.3 V vs Ag/AgCl. The diffraction profiles indexed with [hkl] notations correspond to metal Ni phase and BDE

6.4.1.3 XPS characterisation of nickel modified boron-doped diamond electrodes

A useful insight into the chemical state of the nickel/diamond interface can be further obtained by an XPS analysis. A typical wide scan spectrum of the hydrogen terminated diamond electrode prior to Ni electrodeposition is presented in Figure 79 (a). The C 1s photoemission line at 285 eV along with a small O 1s signal at 532 eV and the characteristic C KLL Auger line at 980 eV verify the elemental purity of the HBDE surface. The O 1s/C 1s ratio within the XPS sampling depth was found to be at around 4%, which is in agreement with the generally observed O 1s/C 1s levels recorded at hydrogen terminated diamond surfaces.⁵²

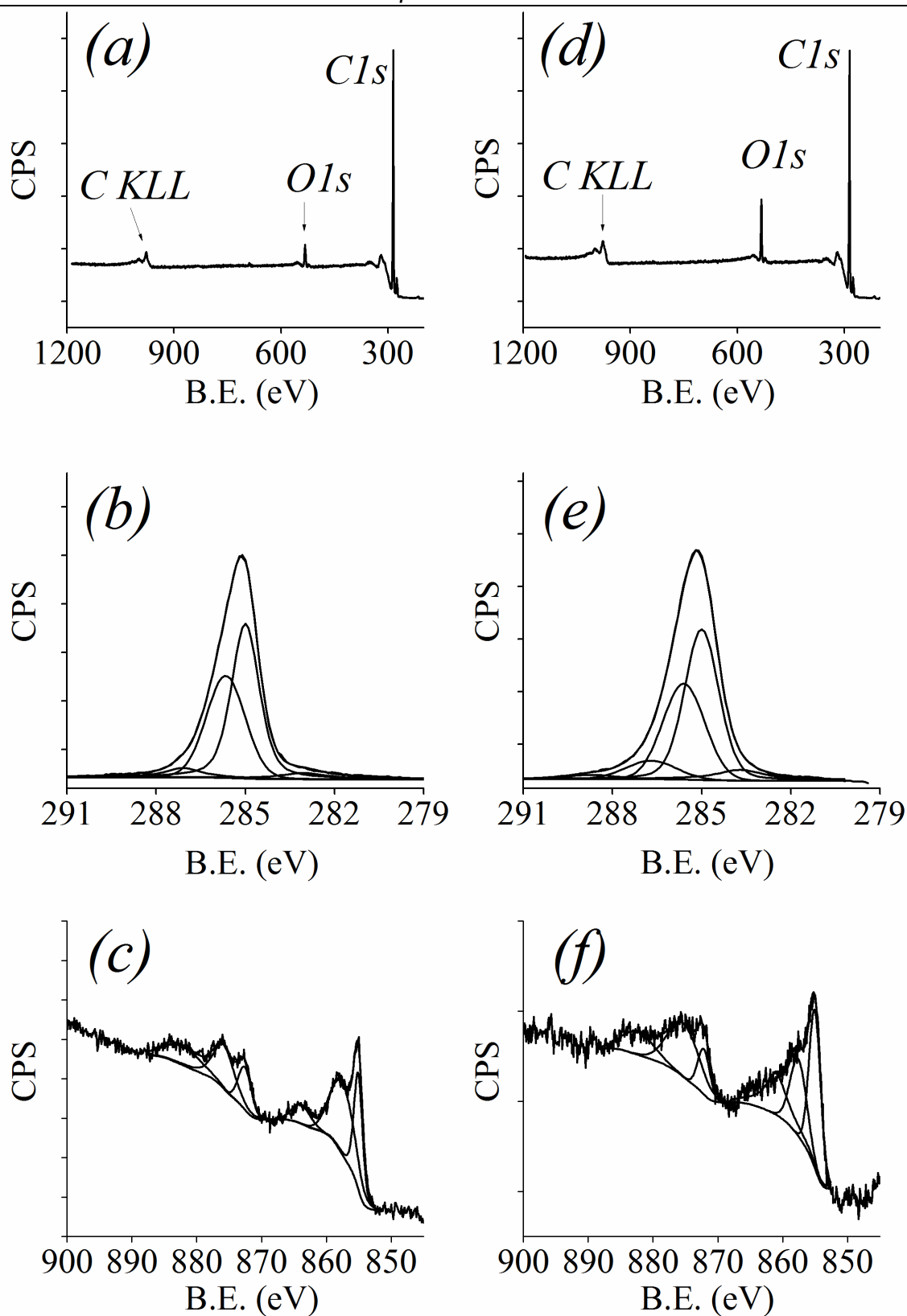


Figure 79 (a) survey XPS spectra of hydrogenated boron-doped diamond electrode; (b) a high-resolution C 1s spectra of hydrogen terminated Ni_HBDE; (c) high-resolution Ni 2p spectra of Ni_HBDE; (d) survey XPS spectra of oxidised diamond electrode; (e) a high-resolution C 1s spectra of oxidised Ni_OBDE; (f) high-resolution Ni 2p spectra of Ni_OBDE

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

The high-resolution scan of the C 1s region of H-terminated diamond electrode in Figure 79 (b) shows a peak at 285 eV that corresponds to the bulk diamond along with the peaks at 285.7 eV and 287.1 eV that are attributable to C-H_x (x = 2,3) species in polyhydride configurations and carbonyl surface groups respectively.⁵³⁻⁵⁵ A small peak at 283.3 eV with the chemical shift of -1.3 eV is characteristic of the graphitic states involved in π -bonding, such as sp²-defects.²⁵ The associated atomic concentrations, binding energies and FWHM values can be found in Table 7, Table 8 and Table 43.

Table 41 XPS binding energies for hydrogenated and oxidised boron-doped diamond electrodes

Sample	Binding energies (eV)							
	C 1s						Ni 2p	
	Csp ³	C-CH _x	C=O	C-OH	COOH	sp ² def	Ni (+2) 2p _{3/2}	Ni (+2) 2p _{1/2}
Ni_HBDE	285.0	285.7	287.1	n/a	n/a	283.1	855.1	872.5
Ni_OBDE	285.0	285.6	n/a	286.7	288.7	282.2	855.1	872.3

Table 42 XPS elemental ratios and charging values for hydrogenated and oxidised boron-doped diamond electrodes

Sample	Elemental concentrations (%)	Charging (eV)
	O 1s	Relative to C 1s (285.0 eV)
Ni_HBDE	4	5.3
Ni_OBDE	13	6.2

Table 43 FWHM values for hydrogenated and oxidised boron-doped diamond electrodes

Sample	FWHM (eV)							
	C 1s						Ni 2p	
	Csp ³	C-CH _x	C=O	C-OH	COOH	sp ² def	Ni (+2) 2p _{3/2}	Ni (+2) 2p _{1/2}
Ni_HBDE	1.1	1.5	1.2	n/a	n/a	2.0	1.6	2.3
Ni_OBDE	1.4	1.7	n/a	2.0	2.1	2.0	2.2	2.3

The Ni 2p high resolution spectra recorded at hydrogen terminated boron-doped diamond electrode straight after Ni electrodeposition is presented in Figure 79 (c). The Ni 2p component presents two well-resolved doublet with a Ni (+2) 2p_{3/2} line at 855.1 eV and Ni (+2) 2p_{1/2} line at 872.5 eV.⁵⁶ In the Ni 2p spectrum the principal line is accompanied by an evident shoulder at 858.1 eV attributable to the presence of NiO phase^{57,58} which is formed on particle surface due to the spontaneous oxidation of metallic Ni when exposed to air and

water.^{42,59,60} The prominent satellite band with characteristic maximum at a higher binding energy of 864.4 eV originates from charge transfer multielectron transitions.^{58,61}

A wide XPS scan obtained from the oxygen terminated boron-doped diamond electrode is presented in Figure 79 (d). The C 1s line at 285 eV along with C KLL Auger series at 980 eV and pronounced O 1s peak at 532 eV can be observed in the spectrum. The O 1s/C 1s ratio within the XPS sampling depth was estimated at around 13% which is more than 4 times greater than that estimated at hydrogen terminated diamond. The high-resolution scan of C 1s region obtained from oxygen terminated diamond surface is presented in Figure 79 (e). The associated atomic concentrations, binding energies and FWHM values are summarised in Table 7, Table 8 and Table 43. As compared to the C 1s spectral region of Ni_HBDE, the main differences arise from the presence of more intense signals at 286.7 and 288.7 eV attributable to the presence of hydroxyl groups and carboxyl compounds respectively.⁵⁶

High resolution Ni 2p spectra recorded straight after Ni electrodeposition on the oxygen terminated boron-doped diamond electrode is presented in Figure 79 (f). The Ni 2p component shows characteristic Ni (+2) 2p_{3/2} line at 855.1 eV, with the transitions at 857.7 eV that arise from the presence of NiO surface structures. A satellite peak at 861.6 eV is associated with the multielectron excitations.^{32, 57}

Table 44 Ni 2p/C 1s ratios estimated for the Ni_HBDE and Ni_OBDE samples

Sample	Ni 2p/C 1s ratio ($\times 10^{-2}$)
Ni_HBDE	3.4
Ni_OBDE	3.6

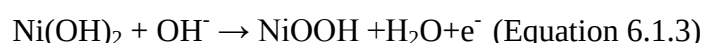
From the XPS analysis discussed above it can be concluded that the Ni 2p spectra of the freshly deposited Ni particles at HBDE and OBDE samples are found to be quite similar. The Ni 2p/C 1s ratio within the XPS sampling depth is estimated at around 3.4×10^{-2} and 3.6×10^{-2} at hydrogenated and oxidised electrodes respectively (Table 44). This confirms that the

amount and the surface coverage of Ni particles produced by electrodeposition technique on both electrodes are rather similar.

6.4.2 Electrochemical characterisation of nickel modified boron-doped diamond electrodes

In further studies, cyclic voltammetry was used to characterise Ni decorated H- and O-terminated boron-doped diamond electrodes. Figure 80 compares cyclic voltammograms obtained in 1 M KOH at 0.05 V s^{-1} straight after Ni electrodeposition on the hydrogen and oxygen terminated diamond electrodes. The associated peak positions and current responses are presented in Table 10.

When metal nickel particles are in contact with 1 M KOH solution, their surface becomes spontaneously covered with the adlayer of Ni(OH)_2 .^{42,62} In the anodic scan of Ni_HBDE (dash dot red line, Figure 80 (a)), as the potential is swept in a positive direction, the appearance of a peak at 0.38 V vs Ag/AgCl corresponds to the consecutive electrooxidation of Ni(OH)_2 (Ni^{2+}) to NiOOH (Ni^{3+}). The process can be described by the following reaction:



In the reduction scan, the peak observed at 0.34 V vs Ag/AgCl (Figure 80 (a)) is characterised by the reverse process of nickel oxyhydroxide reduction to nickel hydroxide.

Table 45 Peak position and current response data recorded in 1 M KOH at Ni modified O- and H- terminated boron-doped diamond electrodes at 0.05 V s^{-1}

Peak	Peak Position (V)	Current (A)	Current Response (A cm^{-2})
at Ni_HBDE:			
oxidation scan	0.38	3.7×10^{-4}	9.2×10^{-4}
reduction scan	0.34	-2.6×10^{-4}	-6.6×10^{-4}
at Ni_OBDE			
oxidation scan	0.41	8.4×10^{-5}	2.1×10^{-4}
reduction scan	0.35	-7.2×10^{-5}	-1.8×10^{-4}

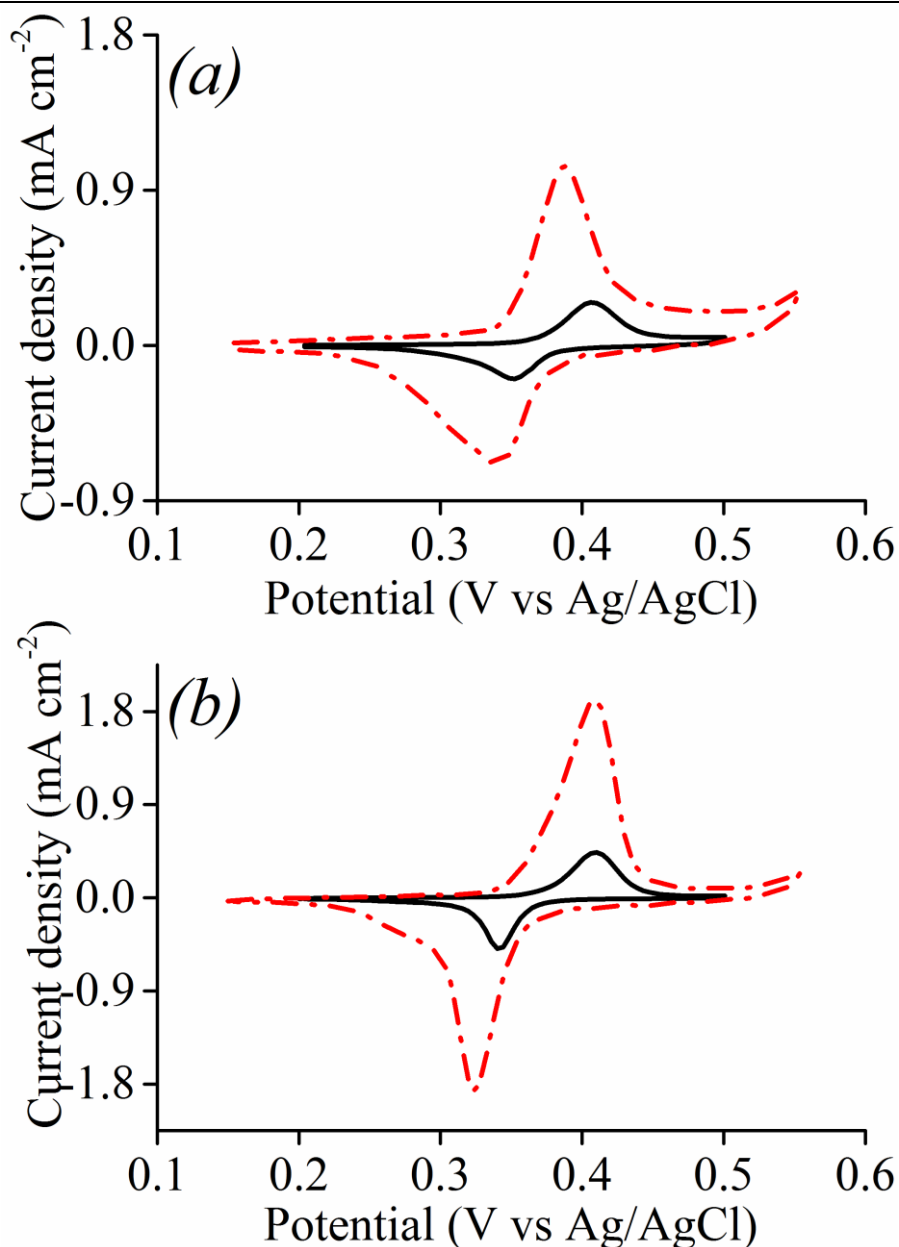


Figure 80 Cyclic voltammograms recorded in 1 M KOH at 0.05 Vs⁻¹ at (a) (-) Ni_OBDE and (- -) Ni_HBDE straight after Ni electrodeposition procedure; (b) after the enrichment process in 1 M KOH at 0.05 Vs⁻¹ at (-) Ni_OBDE and (- -) Ni_HBDE

Although a physical state of nickel particles after electrodeposition appeared to be unaffected by the termination of the diamond electrode surface, dramatic differences in voltammetric behaviour can be observed, with the Ni_HBDE sample producing current densities four times bigger than that recorded at the Ni_OBDE. The peak-to-peak separation, ΔE_p , of the

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

Ni(II)/Ni(III) redox couple at the Ni decorated hydrogen terminated boron-doped diamond electrode is found to be 46 mV, whereas $\Delta E_p = 55$ mV was estimated for the Ni_OBDE sample, which suggests a decrease in heterogeneous electron transfer rates at Ni_OBDE surfaces.

In further experiments, in order to enrich the electrodes with electrocatalytically active Ni(OH)₂ layers, Ni_HBDE and Ni_OBDE were conditioned by potential cycling for 500 cycles in 1 M KOH solution until a stable response was obtained (Figure 80 (b)).^{13,17,22}

Table 46 Peak position and current response data recorded in 1 M KOH after the enrichment procedure at Ni modified O- and H- terminated boron-doped diamond electrodes at 0.05 V s⁻¹

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
Ni_HBDE:			
oxidation scan	0.40	7.2×10^{-4}	1.8×10^{-3}
reduction scan	0.33	-6.8×10^{-4}	-1.7×10^{-3}
Ni_OBDE			
oxidation scan	0.41	1.6×10^{-4}	4×10^{-4}
reduction scan	0.34	-1.6×10^{-4}	-4×10^{-4}

Again, a similar trend as seen in electrochemical studies straight after nickel electrodeposition process can be observed, with the current densities being dramatically increased at the Ni_HBDE surface and much smaller currents at the Ni_OBDE.

The amount of nickel hydroxide formed on the diamond surface prior and after the enrichment procedure was estimated from a charge obtained at an area under the reduction scan, as shown in the equation below:

$$Q_{red} = nFA\Gamma \quad (\text{Equation 6.1.4})$$

where n is the number of electrons involved in the redox process, F is the Faraday constant (96485 C mol⁻¹), A is the diamond electrode area (0.4 cm²), Γ is the surface concentration of Ni(OH)₂ (mol cm⁻²).

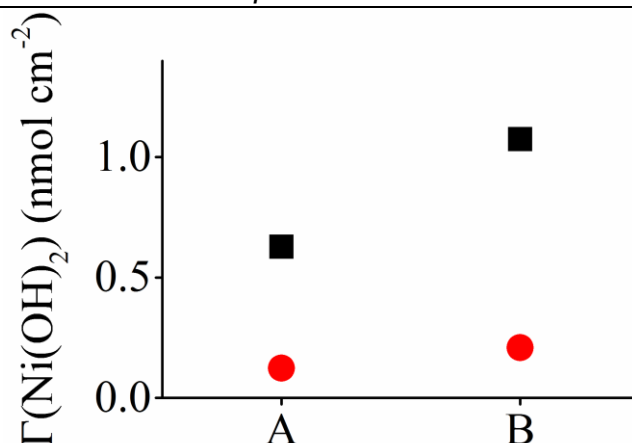


Figure 81 Surface concentration of Ni(OH)₂, column A: at (●) Ni_OBDE after Ni electrodeposition and (■) at Ni_HBDE after Ni electrodeposition, column B: (●) Ni_OBDE after the enrichment procedure and (■) Ni_HBDE after the enrichment procedure

The use of the equation above suggests that prior to the enrichment procedure, 0.6 nmol cm⁻² and 0.12 nmol cm⁻² of Ni(OH)₂ are formed on the Ni_HBDE and Ni_OBDE electrodes respectively (column A, Figure 81). After the enrichment procedure, the amount of 1.1 nmol cm⁻² and 0.2 nmol cm⁻² of Ni(OH)₂ were estimated on hydrogenated and oxidised surfaces (column B, Figure 81). The monolayer coverage of Ni(OH)₂ is known to be 1.06 nmol cm⁻².⁶³ This suggests a presence of Ni(OH)₂ monolayer at the Ni_HBDE substrate and a less than a monolayer at Ni_OBDE.

An additional series of XPS experiments were performed in order to estimate the changes in the Ni/diamond interface that were induced by the long-term potential cycling in 1 mM KOH. The high resolution Ni 2p spectral region of Ni_HBDE sample is presented in Figure 82. A well-resolved doublet with characteristic Ni (+2) 2p_{3/2} signal at 857.3 eV and Ni (+2) 2p_{1/2} line at 875.1 eV can be observed.⁵⁶ The distinct peaks at 863.3 eV and 881.5 eV correspond to the satellite bands respectively.⁵⁷ The peak-to-peak separation of 17.8 eV between the Ni (+2) 2p_{3/2} and Ni (+2) 2p_{1/2} lines along with the absence of multielectron transitions in the N 2p spectra are consistent with the presence of a uniform Ni(OH)₂ phase.⁵⁷ This is in

contrast to the situation observed straight after electrodeposition process (Figure 79 (c)), where characteristic peaks attributable to the presence of NiO phases were detected.

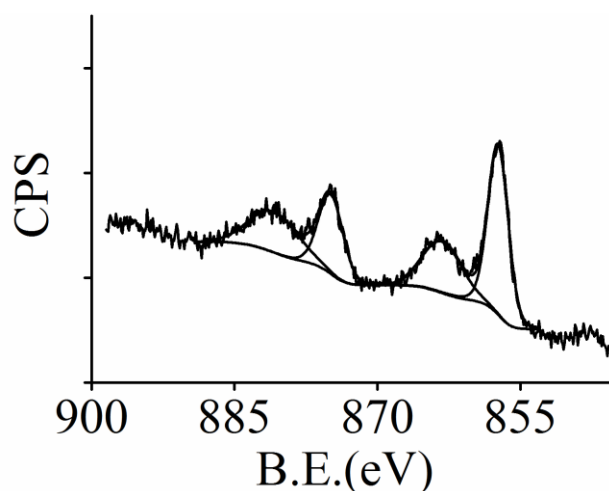


Figure 82 High resolution Ni 2p region of the Ni_HBDE electrode recorded after the enrichment procedure in 1 M KOH

An important difference arising from the electrochemical studies of Ni_HBDE and Ni_OBDE electrodes is that, despite the fact that the amount and the physical state of the Ni particles initially electrodeposited on the H- and O- terminated diamond electrodes were almost identical, the surface concentration of Ni(OH)₂ formed at Ni_HBDE electrode is dramatically bigger if compared to the Ni_OBDE. This is likely to arise from the differences in electrochemical reactivity of Ni particles that subsequently depend on the chemical termination of the diamond electrode. The H-terminated diamond surface is likely to be more electron donating than the O-terminated interface, as a result of the differing dipoles of the chemical bonds terminating the surface, with the increased electron density associated with the Ni particles on the H-terminated diamond leading to enhanced ease of oxidation.

The observations above are supported by the study of Fujishima et al.⁶⁴ In their work, the electrochemical investigations of the surface pre-treatments on the copper/diamond interface showed that electrochemical cathodic pre-treatment (which corresponds to the partial H-termination of the diamond electrode) results in the current responses being dramatically

increased as opposed to the partially oxidised diamond surface.⁶⁴ This feature was related to the differences in chemical structures of H- and O- terminated diamond surfaces.

6.4.2.1 Electrochemical oxidation of glucose at nickel modified boron-doped diamond electrodes

A non-enzymatic determination of glucose at nickel modified boron-doped diamond electrode has been a subject of significant research in connection with the development of electrochemical sensors.¹⁴ In this context, electrochemical behaviour of Ni nanoparticles deposited on the two differing diamond surfaces in glucose solution was studied.

In the first sets of experiments, cyclic voltammetry was carried out at the Ni modified hydrogen terminated boron-doped diamond electrode, where ten scans were recorded from 1 mM to 10 mM, with 1 mM glucose increment (Figure 83 (a)). The choice of the glucose concentration range was based on the fact that an average blood sugar levels in humans are known to vary between 3 mM and 8 mM.¹³

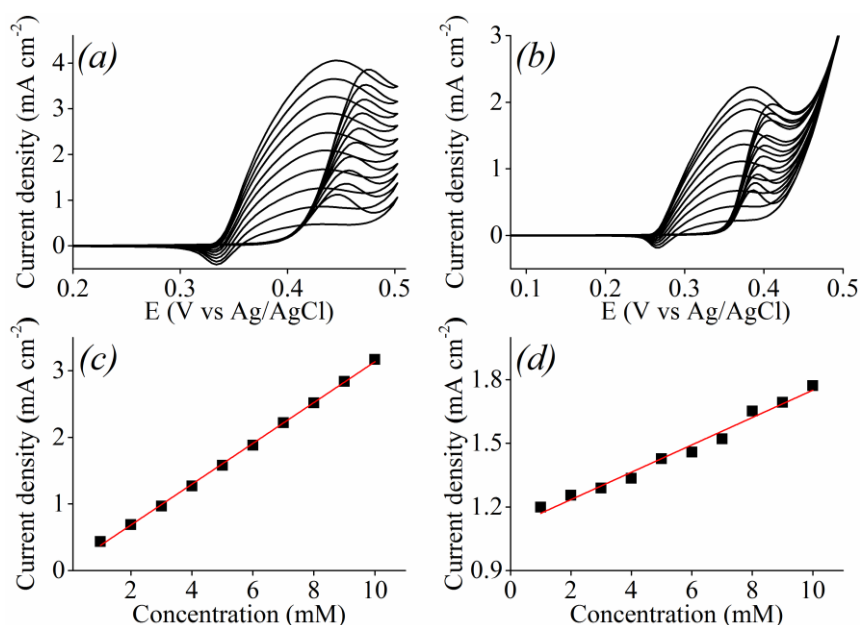
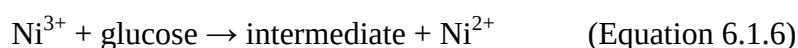


Figure 83 Cyclic voltammograms of 1 mM glucose additions in 1 M KOH solution recorded at 0.05 Vs⁻¹ at (a) Ni_HBDE; (b) Ni_OBDE, (c) associated calibration plot of current densities vs glucose concentration at Ni_HBDE; (d) associated calibration plot of current densities vs glucose concentration at Ni_OBDE

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

The electrocatalytic effect of Ni(II)/Ni(III) redox couple arises from the presence of unpaired d-electrons or empty d-orbitals of the oxidized form of Ni(III) that are available for the bond formation with adsorbed species and intermediates.^{14,65} The mechanism of the glucose oxidation can be described by the following reactions:^{42,66}



where oxidised products such as gluconolactones, methanoates and gluconic acid can be formed in the result of the reaction.⁶⁷⁻⁷¹

As it can be seen from Figure 83 (a), the oxidation peak current of electroactive Ni(II)/Ni(III) redox couple at hydrogen terminated surface increases gradually with each glucose addition, and a peak potential shifts towards positive values upon addition of the glucose aliquot. The peak currents were found to increase linearly with the increase of the glucose concentration from 1 mM to 10 mM, with a correlation coefficient of 0.9989 and the slope of 0.12 mA mM cm⁻². The limit of detection (LOD) estimated using the 3σ/slope ratio is 33 μM.

The changes in the electrocatalytic activity of the nickel modified electrode induced by the oxygen termination are presented in Figure 83 (b). Although the electrochemical behaviour is similar to that observed at Ni_HBDE, approximately 50% smaller current densities were recorded at the Ni_OBDE sample. This is consistent with the surface concentration of Ni(OH)₂ at Ni_OBDE substrate being several times lower than that of detected at Ni_HBDE.

The peak currents at Ni_OBDE showed a linear increase in the concentration range from 1 mM to 10 mM (Figure 83 (d)). A similar analysis for the Ni_OBDE electrode yields the

slope value of $0.03 \text{ mA mM cm}^{-2}$ and the LOD using the $3\sigma/\text{slope}$ of $140 \text{ }\mu\text{M}$. The major difference observed between the hydrogenated and oxidised nickel modified boron-doped diamond electrodes concerns the LOD value which is found to be almost 4 times smaller at the Ni_HDBE sample.

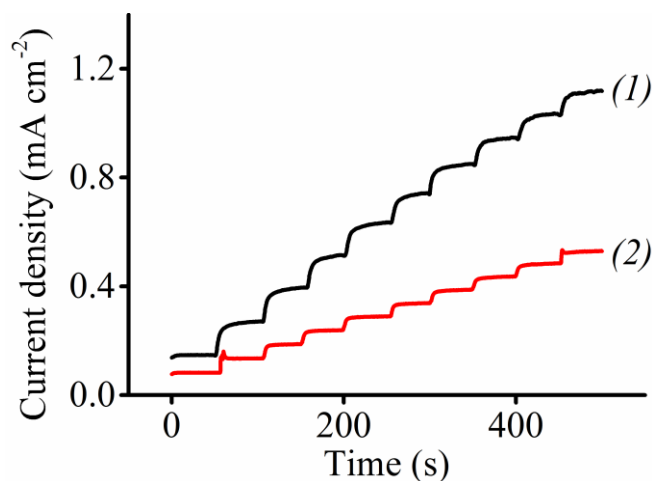


Figure 84 Amperometric plot of 1 mM glucose additions recorded in 1 KOH at (1) Ni_HBDE and (2) Ni_OBDE

The amperometric response of Ni_HBDE and Ni_OBDE electrodes to the 1 mM glucose additions in 1 M KOH is compared in Figure 84. At both samples, the injection of 1 mM glucose aliquot gives rise to the distinct amplification of the current density which is found to be the largest at the Ni_HBDE sample. This confirms that hydrogen pre-treatment can be effectively used for the enhancement of the detection limits at boron-doped diamond electrodes.

6.4.2.2 Electrochemical oxidation of hydrogen peroxide at nickel modified boron-doped diamond electrode

In further studies, Ni_HBDE and Ni_OBDE substrates were tested with regard to the electrochemical oxidation of hydrogen peroxide.

Figure 85 (a) shows ten consecutive cyclic voltammetry scans in 1 M KOH recorded at Ni_HBDE in the presence of H₂O₂ in the concentration range 0.1 mM to 1 mM, with 0.1 mM increment.

The mechanism of the H₂O₂ electrooxidation can be described by the following reactions:

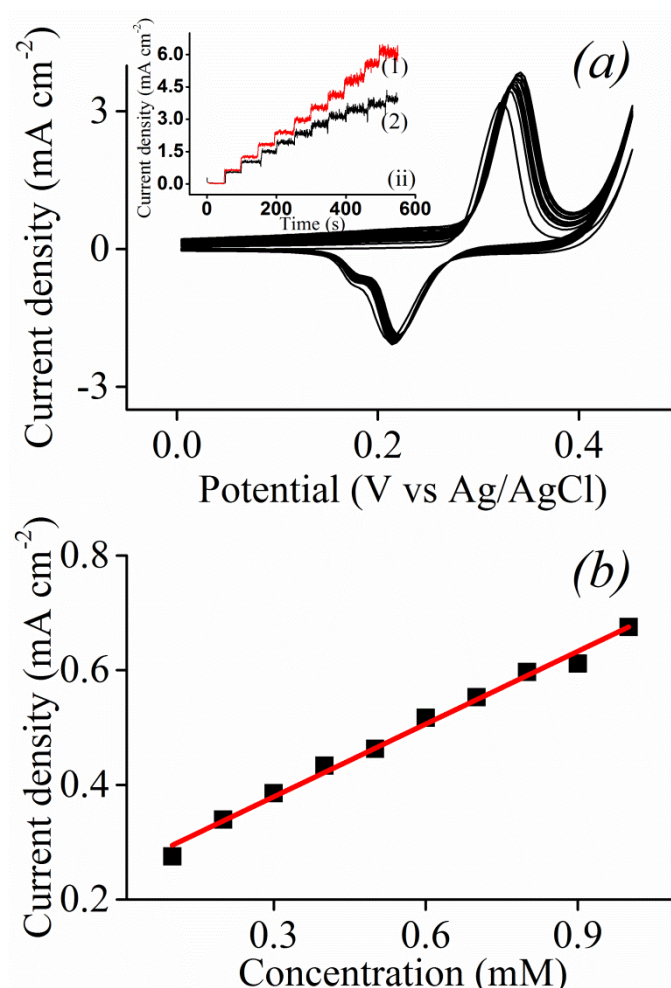
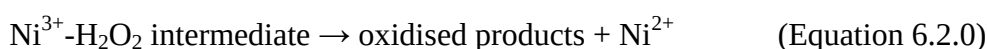


Figure 85 (a) Cyclic voltammetry recorded with 0.1 mM H₂O₂ additions in 1 M KOH at Ni_HBDE; (b) corresponding calibration plot of peak currents vs H₂O₂ concentration; (ii) amperometric plot of 0.1 mM H₂O₂ additions in 1 M KOH recorded at (1) Ni_HBDE and (2) Ni_OBDE

Chapter six – The effect of the surface pre-treatment on the electrochemical behaviour of nickel modified boron-doped diamond electrodes

As it can be seen from Figure 85 (b), consecutive additions of hydrogen peroxide aliquots results in the enhancement of current responses of Ni(II)/Ni(III) redox couple. The anodic peak heights were found to increase linearly with the increase of the H₂O₂ concentration. The sensitivity value of 0.19 mA mM cm⁻² and LOD of 64 µM were estimated for the Ni_HBDE substrate, while the sensitivity of 0.16 mA mM cm⁻² and LOD of 0.1 mM were found at the Ni_OBDE.

6.4.2.3 The effects of the surface pre-treatment on the adhesion properties of Ni particles

In order to assess the stability and adhesion of Ni particles on the differently pre-treated diamond electrodes, the Ni_HBDE and Ni_OBDE substrates were exposed to a constant potential of -1.7 V in 1 M KOH solution for 6 hours *via* chronoamperometry. The decrease in the Ni surface concentration prior and after stability test in 1 M KOH was monitored by XPS. The data are summarised in Table 47.

Table 47 Ni 2p/C 1s obtained prior and after stability tests in 1 M KOH

XPS Ratios	Ni_HBDE		Ni_OBDE	
	<i>Prior</i>	<i>After</i>	<i>Prior</i>	<i>After</i>
Ni 2p/C 1s (×10 ⁻²)	3.4	3.2	3.6	2.7
% Ni retained		95		66
<i>*prior and after stability tests</i>				

As it can be seen from Table 47, approximately 95% of Ni signal remained on Ni_HBDE surface, whereas only 66% of Ni signal was detected at the Ni_OBDE substrate. In the case of oxygen terminated diamond electrode, the data above implicitly suggest that the adhesion properties of nickel particles, fully covered by the Ni(OH)₂ adlayers, are affected by the coulombic interactions between the negatively charged surfaces functionalities on the OBDE electrode and negatively charged nickel clusters in the solution.

6.5 Concluding remarks

In this work, the effects of the diamond surface pre-treatment on the electrochemical properties of nickel particles deposited on the boron-doped diamond electrodes were investigated. Prior to nickel electrodeposition, the preparation approach involves treating diamond electrode in microwave hydrogen plasma to produce hydrogen terminated hydrophobic surface and electrochemical cycling in 0.1 M nitric acid which yields oxygen terminated hydrophilic surface. It was shown that independently of the surface pre-treatment, nickel particles electrodeposited on both hydrogen and oxygen terminated boron-doped diamond electrodes are of a similar physical state, form and size.

In contrast, the electrochemical properties of nickel particles were found to differ dramatically with regard to the surface termination of the diamond electrode. On the hydrogen terminated diamond electrode, nickel particles showed much greater chemical reactivity than that observed at the oxygen terminated diamond electrode. Nickel modified hydrogen terminated diamond electrode has demonstrated much greater electrocatalytic activity with regard to the enzyme-free oxidation of glucose and hydrogen peroxide as compared to the activity observed at nickel modified oxygen terminated diamond electrode. It was also found that hydrogen plasma treated diamond surface yields superior adhesion of Ni particles to the diamond surface, whereas oxygen terminated diamond surface provides less adhesion to nickel particles due to high levels of oxidation of the surface. Hydrogen plasma treatment therefore presents a straightforward route for the preparation of stable Ni modified boron-doped diamond electrodes which show improved electrochemical activity over those formed without the plasma treatment.

It can be concluded that electrochemical properties of nickel modified diamond electrodes can be strongly influenced by the surface chemistry of the diamond electrode.

6.6 References

- 1 Swain, G. M. in *Semiconductors and Semimetals* Vol. Volume 77 (eds E. Nebel Christoph & Ristein Jürgen) 121-148 (Elsevier, 2004).
- 2 Rao, T. N. & Fujishima, A. Recent advances in electrochemistry of diamond. *Diamond Relat. Mater.* **9**, 384-389, doi:10.1016/s0925-9635(99)00234-4 (2000).
- 3 Rao, T. N., Ivandini, T. A., Terashima, C., Sarada, B. V. & Fujishima, A. Applications of bare and modified diamond electrodes in electroanalysis. *New Diamond Front. Carbon Technol.* **13**, 79-88 (2003).
- 4 Panizza, M. & Cerisola, G. Application of diamond electrodes to electrochemical processes. *Electrochimica Acta* **51**, 191-199, doi:http://dx.doi.org/10.1016/j.electacta.2005.04.023 (2005).
- 5 Waldvogel, S. R., Kirste, A. & Mentizi, S. 483-510,, 481 plate (John Wiley & Sons, Inc.).
- 6 Kraft, A. Doped diamond: a compact review on a new, versatile electrode material. *Int. J. Electrochem. Sci.* **2**, 355-385 (2007).
- 7 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).
- 8 Welch, C. & Compton, R. The use of nanoparticles in electroanalysis: a review. *Analytical and Bioanalytical Chemistry* **384**, 601-619, doi:10.1007/s00216-005-0230-3 (2006).
- 9 Burda, C., Chen, X., Narayanan, R. & El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev. (Washington, DC, U. S.)* **105**, 1025-1102, doi:10.1021/cr030063a (2005).
- 10 Hu, J. P., Lu, X., Foord, J. S. & Wang, Q. Electrochemical deposition of Pt nanoparticles on diamond substrates. *Physica Status Solidi a-Applications and Materials Science* **206**, 2057-2062, doi:10.1002/pssa.200982226 (2009).
- 11 Liu, B., Hu, J. & Foord, J. S. Electrochemical detection of DNA hybridization by a zirconia modified diamond electrode. *Electrochemistry Communications* **19**, 46-49, doi:10.1016/j.elecom.2012.03.007 (2012).
- 12 Toghiani, K. E. & Compton, R. G. Metal Nanoparticle Modified Boron Doped Diamond Electrodes for Use in Electroanalysis. *Electroanalysis* **22**, 1947-1956, doi:10.1002/elan.201000072 (2010).
- 13 Toghiani, K. E., Xiao, L., Phillips, M. A. & Compton, R. G. The non-enzymatic determination of glucose using an electrolytically fabricated nickel microparticle modified boron-doped diamond electrode or nickel foil electrode. *Sens. Actuators, B* **147**, 642-652, doi:10.1016/j.snb.2010.03.091 (2010).
- 14 Hutton, L. A. *et al.* Electrodeposition of Nickel Hydroxide Nanoparticles on Boron-Doped Diamond Electrodes for Oxidative Electrocatalysis. *The Journal of Physical Chemistry C* **115**, 1649-1658, doi:10.1021/jp109526b (2010).
- 15 Toghiani, K. E., Xiao, L., Stradiotto, N. R. & Compton, R. G. The determination of methanol using an electrolytically fabricated nickel microparticle modified boron doped diamond electrode. *Electroanalysis* **22**, 491-500, doi:10.1002/elan.200900523 (2010).
- 16 Harfield, J. C., Toghiani, K. E., Batchelor-McAuley, C., Downing, C. & Compton, R. G. Nickel Nanoparticle Modified BDD Electrode Shows an Electrocatalytic Response to Adenine and DNA in Aqueous Alkaline Media. *Electroanalysis* **23**, 931-938, doi:10.1002/elan.201000658 (2011).

- 17 Stradiotto, N. R., Toghil, K. E., Xiao, L., Moshar, A. & Compton, R. G. The fabrication and characterization of a nickel nanoparticle modified boron-doped diamond electrode for electrocatalysis of primary alcohol oxidation. *Electroanalysis* **21**, 2627-2633, doi:10.1002/elan.200900325 (2009).
- 18 Uchikado, R., Rao, T. N., Tryk, D. A. & Fujishima, A. Metal-modified diamond electrode as an electrochemical detector for glucose. *Chem. Lett.*, 144-145, doi:10.1246/cl.2001.144 (2001).
- 19 Ivandini, T. A., Sato, R., Makide, Y., Fujishima, A. & Einaga, Y. Electroanalytical application of modified diamond electrodes. *Diamond and Related Materials* **13**, 2003-2008, doi:http://dx.doi.org/10.1016/j.diamond.2004.07.004 (2004).
- 20 Tretepvijit, S. *et al.* Use of nickel implanted boron-doped diamond thin film electrode coupled to HPLC system for the determination of tetracyclines. *Talanta* **68**, 1329-1335, doi:10.1016/j.talanta.2005.07.047 (2006).
- 21 Dai, W., Li, M., Li, H. & Yang, B. Amperometric biosensor based on nanoporous nickel/boron-doped diamond film for electroanalysis of l-alanine. *Sensors and Actuators B: Chemical* **201**, 31-36, doi:http://dx.doi.org/10.1016/j.snb.2014.05.005 (2014).
- 22 Toghil, K. E., Xiao, L., Stradiotto, N. R. & Compton, R. G. The Determination of Methanol Using an Electrolytically Fabricated Nickel Microparticle Modified Boron Doped Diamond Electrode. *Electroanalysis* **22**, 491-500, doi:10.1002/elan.200900523 (2010).
- 23 Krueger, A. & Lang, D. Functionality is Key: Recent Progress in the Surface Modification of Nanodiamond. *Advanced Functional Materials* **22**, 890-906, doi:10.1002/adfm.201102670 (2012).
- 24 Butler, J. E. & Sumant, A. V. The CVD of nanodiamond materials. *Chemical Vapor Deposition* **14**, 145-160, doi:10.1002/cvde.200700037 (2008).
- 25 Goeting, C. H., Marken, F., Osborn, A. R., Compton, R. G. & Foord, J. S. Surface Modification of Chemical Vapor Deposited Diamond Induced by Power Ultrasound. *Electrochemical and Solid State Letters* **4**, E29-E31, doi:10.1149/1.1377488 (2001).
- 26 Foord, J. & Opperman, D. in *Diamond Electronics - Fundamentals to Applications* Vol. 956 *Materials Research Society Symposium Proceedings* (eds P. Bergonzo, R. Gat, R. B. Jackman, & C. E. Nebel) 97-103 (2007).
- 27 Notsu, H., Tatsuma, T. & Fujishima, A. 218-237 (Elsevier B.V.).
- 28 Nebel, C. E., Rezek, B., Shin, D. & Watanabe, H. Surface electronic properties of H-terminated diamond in contact with adsorbates and electrolytes. *Physica Status Solidi a-Applications and Materials Science* **203**, 3273-3298, doi:10.1002/pssa.200671401 (2006).
- 29 Maier, F., Riedel, M., Mantel, B., Ristein, J. & Ley, L. Origin of surface conductivity in diamond. *Physical Review Letters* **85**, 3472-3475, doi:10.1103/PhysRevLett.85.3472 (2000).
- 30 Nebel, C. E. & Ristein, J. *Thin-Film Diamond II*. [In: *Semicond. Semimetals*, 2004; 77]. (Academic Press, 2004).
- 31 Hoffmann, R. *et al.* Electrochemical hydrogen termination of boron-doped diamond. *Applied Physics Letters* **97**, doi:10.1063/1.3476346 (2010).
- 32 Jiang, Y. *et al.* Investigation on Electrochemically Cathodic Polarization of Boron-Doped Diamond Electrodes and Its Influence on Lead Ions Analysis. *Journal of The Electrochemical Society* **161**, H410-H415, doi:10.1149/2.106406jes (2014).
- 33 Spătaru, T. *et al.* Effect of the chemical termination of conductive diamond substrate on the resistance to carbon monoxide-poisoning during methanol oxidation of

- platinum particles. *Journal of Power Sources* **261**, 86-92, doi:http://dx.doi.org/10.1016/j.jpowsour.2014.03.044 (2014).
- 34 Granger, M. C. & Swain, G. M. The influence of surface interactions on the reversibility of ferri/ferrocyanide at boron-doped diamond thin-film electrodes. *J. Electrochem. Soc.* **146**, 4551-4558, doi:10.1149/1.1392673 (1999).
- 35 Goeting, C. H., Marken, F., Gutierrez-Sosa, A., Compton, R. G. & Foord, J. S. Boron-doped diamond electrodes: Growth, surface characterisation and sono-electrochemical applications. *New Diamond and Frontier Carbon Technology* **9**, 207-228 (1999).
- 36 Wang, H., Griffiths, J.-P., Egdell, R. G., Moloney, M. G. & Foord, J. S. Chemical Functionalization of Diamond Surfaces by Reaction with Diaryl Carbenes. *Langmuir* **24**, 862-868, doi:10.1021/la702701p (2008).
- 37 Toghiani, K. E. & Compton, R. G. Electrochemical non-enzymatic glucose sensors: a perspective and an evaluation. *Int. J. Electrochem. Sci.* **5**, 1246-1301 (2010).
- 38 <http://www.casaxps.com/>.
- 39 Shirley, D. A. High-resolution x-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B* **[3]5**, 4709-4714 (1972).
- 40 Arvia, A. J. & Posadas, D. 211-421 (Dekker).
- 41 Sasaki, K. Y. & Talbot, J. B. Electrodeposition of iron-group metals and binary alloys from sulfate baths. I. Experimental study. *J. Electrochem. Soc.* **145**, 981-990, doi:10.1149/1.1838375 (1998).
- 42 Fleischmann, M., Korinek, K. & Pletcher, D. Kinetics and mechanism of the oxidation of amines and alcohols at oxide-covered nickel, silver, copper, and cobalt electrodes. *J. Chem. Soc., Perkin Trans. 2*, 1396-1403 (1972).
- 43 Deslouis, C. *et al.* Electrochemical behavior of (111) B-doped polycrystalline diamond: morphology/surface conductivity/activity assessed by EIS and CS-AFM. *Diamond Relat. Mater.* **20**, 1-10, doi:10.1016/j.diamond.2010.10.005 (2011).
- 44 Wang, S., Swope, V. M., Butler, J. E., Feygelson, T. & Swain, G. M. The structural and electrochemical properties of boron-doped nanocrystalline diamond thin-film electrodes grown from Ar-rich and H₂-rich source gases. *Diamond and Related Materials* **18**, 669-677, doi:http://dx.doi.org/10.1016/j.diamond.2008.11.033 (2009).
- 45 Wang, S. & Swain, G. M. Spatially Heterogeneous Electrical and Electrochemical Properties of Hydrogen-Terminated Boron-Doped Nanocrystalline Diamond Thin Film Deposited from an Argon-Rich CH₄/H₂/Ar/B₂H₆ Source Gas Mixture. *The Journal of Physical Chemistry C* **111**, 3986-3995, doi:10.1021/jp0669557 (2007).
- 46 Wilson, N. R., Clewes, S. L., Newton, M. E., Unwin, P. R. & Macpherson, J. V. Impact of Grain-Dependent Boron Uptake on the Electrochemical and Electrical Properties of Polycrystalline Boron Doped Diamond Electrodes. *The Journal of Physical Chemistry B* **110**, 5639-5646, doi:10.1021/jp0547616 (2006).
- 47 Holt, K. B., Bard, A. J., Show, Y. & Swain, G. M. Scanning Electrochemical Microscopy and Conductive Probe Atomic Force Microscopy Studies of Hydrogen-Terminated Boron-Doped Diamond Electrodes with Different Doping Levels. *The Journal of Physical Chemistry B* **108**, 15117-15127, doi:10.1021/jp048222x (2004).
- 48 Scharifker, B. & Hills, G. Theoretical and experimental studies of multiple nucleation. *Electrochimica Acta* **28**, 879-889, doi:http://dx.doi.org/10.1016/0013-4686(83)85163-9 (1983).
- 49 Landstrass, M. I. & Ravi, K. V. RESISTIVITY OF CHEMICAL VAPOR-DEPOSITED DIAMOND FILMS. *Applied Physics Letters* **55**, 975-977, doi:10.1063/1.101694 (1989).
- 50 Swanson, H. E. & Tatge, E. Standard x-ray diffraction powder patterns. *Natl. Bur. Stand. Circ. (U. S.)* **539**, 95 pp. (1953).

- 51 Swanson, H. E. & Fuyat, R. K. Standard x-ray diffraction powder patterns. *Natl. Bur. Stand. Circ. (U. S.)* **539**, 65 pp. (1953).
- 52 Strobel, P., Riedel, M., Ristein, J. & Ley, L. Surface transfer doping of diamond. *Nature (London, U. K.)* **430**, 439-441, doi:10.1038/nature02751 (2004).
- 53 Taki, Y. & Takai, O. XPS structural characterization of hydrogenated amorphous carbon thin films prepared by shielded arc ion plating. *Thin Solid Films* **316**, 45-50, doi:http://dx.doi.org/10.1016/S0040-6090(98)00386-1 (1998).
- 54 Ley, L., Graupner, R., Cui, J. B. & Ristein, J. Electronic properties of single crystalline diamond surfaces. *Carbon* **37**, 793-799, doi:10.1016/s0008-6223(98)00273-5 (1999).
- 55 Ferro, S., Dal Colle, M. & De Battisti, A. Chemical surface characterization of electrochemically and thermally oxidized boron-doped diamond film electrodes. *Carbon* **43**, 1191-1203, doi:http://dx.doi.org/10.1016/j.carbon.2004.12.012 (2005).
- 56 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 57 Grosvenor, A. P., Biesinger, M. C., Smart, R. S. C. & McIntyre, N. S. New interpretations of XPS spectra of nickel metal and oxides. *Surf. Sci.* **600**, 1771-1779, doi:10.1016/j.susc.2006.01.041 (2006).
- 58 McIntyre, N. S. & Cook, M. G. X-ray photoelectron studies on some oxides and hydroxides of cobalt, nickel, and copper. *Anal. Chem.* **47**, 2208-2213, doi:10.1021/ac60363a034 (1975).
- 59 Piontelli, R. Electrochemistry of metallic single crystals. *Electrochim. Metal.* **1**, 5-74 (1966).
- 60 Wang, K., Chottiner, G. S., Scherson, D. A. & Reid, M. The nickel (111)/alkaline electrolyte interface. *Proc. - Electrochem. Soc.* **90-4**, 35-43 (1990).
- 61 Ekstig, B., Kallne, E., Noreland, E. & Manne, R. Electron interaction in transition metal x-ray emission spectra. *Phys. Scr.* **2**, 38-44, doi:10.1088/0031-8949/2/1-2/007 (1970).
- 62 Weininger, J. L. & Breiter, M. W. Effect of crystal structure on the anodic oxidation of nickel. *J. Electrochem. Soc.* **110**, 484-490, doi:10.1149/1.2425798 (1963).
- 63 Bode, H., Dehmelt, K. & Witte, J. Nickel hydroxide electrodes. I. Nickel(II) hydroxide hydrate. *Electrochim. Acta* **11**, 1079-1087 (1966).
- 64 Ohta, N., Nakabayashi, S. & Fujishima, A. Surface transition kinetics on synthetic metallic diamond. *Chem. Lett.*, 1147-1148, doi:10.1246/cl.1999.1147 (1999).
- 65 Cox, P. & Pletcher, D. Electrosynthesis at oxide coated electrodes. Part 1. The kinetics of ethanol oxidation at spinel electrodes in aqueous base. *J. Appl. Electrochem.* **20**, 549-554, doi:10.1007/bf01008862 (1990).
- 66 Ojani, R., Raoof, J.-B. & Salmany-Afagh, P. Electrocatalytic oxidation of some carbohydrates by poly(1-naphthylamine)/nickel modified carbon paste electrode. *J. Electroanal. Chem.* **571**, 1-8, doi:10.1016/j.jelechem.2004.03.032 (2004).
- 67 Tominaga, M. *et al.* Electrocatalytic oxidation of glucose at gold–silver alloy, silver and gold nanoparticles in an alkaline solution. *Journal of Electroanalytical Chemistry* **590**, 37-46, doi:http://dx.doi.org/10.1016/j.jelechem.2006.02.018 (2006).
- 68 Tominaga, M., Shimazoe, T., Nagashima, M. & Taniguchi, I. Electrocatalytic oxidation of glucose at gold nanoparticle-modified carbon electrodes in alkaline and neutral solutions. *Electrochemistry Communications* **7**, 189-193, doi:http://dx.doi.org/10.1016/j.elecom.2004.12.006 (2005).
- 69 Zhao, C., Shao, C., Li, M. & Jiao, K. Flow-injection analysis of glucose without enzyme based on electrocatalytic oxidation of glucose at a nickel electrode. *Talanta* **71**, 1769-1773, doi:http://dx.doi.org/10.1016/j.talanta.2006.08.013 (2007).

- 70 Mho, S.-i. & Johnson, D. C. Electrocatalytic response of carbohydrates at copper-alloy electrodes. *Journal of Electroanalytical Chemistry* **500**, 524-532, doi:http://dx.doi.org/10.1016/S0022-0728(00)00277-1 (2001).
- 71 Danaee, I., Jafarian, M., Forouzandeh, F. & Gopal, F. Kinetic studies of glucose electrocatalytic oxidation on GC/Ni electrode. *International Journal of Chemical Kinetics* **44**, 712-721, doi:10.1002/kin.20721 (2012).

7 Chapter seven – Chemical modifications of diamond surfaces: porphyrin-diamond hybrid interfaces

7.1 Introduction

In Chapter 7, a novel surface functionalization strategy of the boron-doped diamond interface using porphyrin and amide coupling chemistry was developed. The use of this strategy allows creation of hybrid biomimetic diamond interface that was successfully employed as the artificial β -alanine receptor.

7.1.1 Smart diamond biosensors

In recent years, advances in the fields of smart bioelectronics, sensors and biotechnology have developed the need for novel and stable biochip interfaces. Currently, silicon is the major constitutive material used in the biochip production.¹ The main drawback of silicon is its interaction with biological medium which may result in high levels of noise if interfaced with electronics. In this context, diamond is an attractive choice since it is biocompatible and conductive when doped. It exhibits exceptional chemical stability and corrosion resistance along with attractive electrochemical properties such as wide potential window, low signal-to-background current ratio and resistance to interface fouling, as discussed elsewhere in this thesis.

A fundamental requirement of biosensors is a selective and stable response to the target compound in the presence of co-interfering species. Various electrochemical approaches allow characterisation of compounds on the basis of half-wave potential of the redox reaction, or rather subtle features such as the rate of the diffusion to the electrode surface, which can be complicated by the presence of chemically similar species. This situation is generally resolved if external techniques are employed. For instance, chemically similar compounds

can be separated using chromatographic systems, or a selective membrane can be introduced in which only the target species can permeate the membrane and reach the electrode surface.

‘Molecular recognition’ strategy, which enables measurement of electrochemical signals derived only from the target compounds, can be suggested as a sophisticated alternative to the separation techniques, such as chromatography and membrane filtration. This can be achieved by chemical functionalization of electrode surface, so it only recognises the target compound.

7.1.2 Chemical functionalisation of diamond surface

Recently, versatile methods of diamond surface chemical functionalisation have been developed. These include hydrogen termination of the diamond surface which is typically generated in the CVD reactor on account of the growth process. Hydrogen terminated diamond surface is found to be very stable in the atmospheric moisture at room temperatures, although a very slow oxidation takes place if it is exposed to the air in the long term.

If the hydrogenated diamond has been lastingly exposed to air, changes in the surface termination occur. The oxygen groups formed at the diamond surface during this exposure include carbonyl and ether groups, along with hydroxyl groups which are found to prevail if the surface was exposed to the ambient atmosphere.² Diamond oxidization can be also produced by oxygen plasma treatment, anodic electrochemical oxidation, ultrasonic treatment, ozone oxidation or wet chemistry in the presence of mineral acids mixtures such as *aqua regia* or *piranha* solutions.²⁻⁷

In 1998, Ohtani et al. published the work on chlorination and subsequent grafting of quaternary pyridinium salts on the CVD diamond surface.⁸ Chlorine termination can be also obtained either by plasma, photochemical or thermal decomposition of chlorine containing

gases.⁹ Today, chlorine termination is generally used as an intermediate step towards more complex diamond functionalizations.¹⁰

Fluorine termination can be achieved by the exposure of diamond electrode to fluorine radicals; CF₄ and C₄F₈ plasmas, atomic and molecular fluorine beams as well as chemical treatment in anhydrous HF.^{10,11,12} Surface fluorination results in significant extension of potential window of diamond electrode up to 5 V; thus allowing the electrochemical detection of various compounds in the widest potential range.¹³ Due to the imposed hydrophobicity, the controllable adsorption of bioactive compounds can be achieved at the fluorinated electrodes.

Another important modification can be achieved by amination of the diamond surface. NH₂-terminated diamond surfaces are of particular interest because they allow various bioactive compounds to be covalently bonded to the diamond electrodes. Approaches, including the exposure of the H- or Cl- terminated diamond to NH₃ gas under UV irradiation, plasma treatment with ammonia along with photochemical functionalization and the reaction of diamond with amines under weak base conditions have been applied to achieve NH₂ termination.¹⁴⁻¹⁶

In addition to the covalent modifications of the diamond surface described above, various organic compounds with important biological functions can be further immobilised on the chemically modified diamond surfaces. For example, diamond sensors with covalently attached DNA and enzymes have been developed.^{17,18}

In this context, modification of the diamond surface with covalently attached metalloporphyrins represents an important step in the development of hybrid biomimetic diamond interfaces. Until present, only one report on the covalent attachment of cobalt porphyrin to the azide-functionalised boron-doped diamond electrode has been published.¹⁹

7.2 Aims of the project

This chapter explores the covalent attachment of zinc (II) protoporphyrin IX (ZnP) to the diamond surface. In order to produce porphyrin-diamond hybrid interface, the controlled covalent amination of the diamond electrode was followed by the covalent functionalization of ZnP to the amine modified diamond. In order to introduce covalently bonded NH_2 groups to the diamond interface, ethylenediamine electrochemical oxidation was employed.²⁰ The covalent bonding of the ZnP molecules was achieved through the NH_2 - groups of the diamond surface *via* EDC/NHS amide coupling agent.

7.2.1 Background on the zinc (II) protoporphyrin IX

Zinc (II) protoporphyrin IX is a natural compound found in red blood cells.²¹ Four pyrrole nuclei are linked in an alpha positions by methine groups to form a macrocyclic structure where the 18π out of 22π electrons are delocalised to form an aromatic structure in accordance with Hückel's rule (Figure 86).^{22,23}

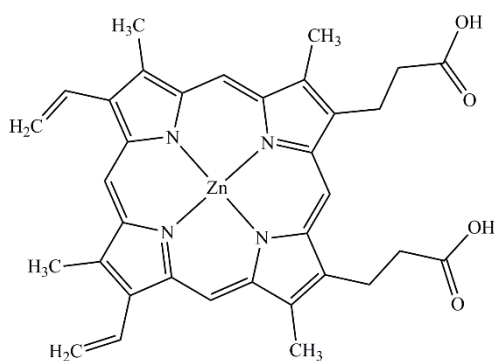


Figure 86 Chemical structure of zinc (II) protoporphyrin IX

For the design of hybrid biomimetic diamond interfaces, zinc (II) protoporphyrin IX is of a great interest due to its critical roles in biological processes such as heme biosynthesis.²¹ ZnP has various binding sites such as the hydrophobic binding pocket, lewis-acidic site (Zn), and electrostatic-recognition sites (COO^- groups). As a result, ZnP may act as a binder for a

variety of ligands dependent on the size, charge and polarity of the guest compound.²⁴⁻²⁶ Due to its ability to bind both amines and amino acids, as confirmed by NMR and UV-Vis spectroscopies, ZnP was tested as an artificial peptide receptor in solutions.²⁵⁻²⁸ It was also shown that zinc porphyrins form 1:1 complexes with imidazoles and pyridine.^{29,30}

Therefore, this work investigates the applicability of ZnP covalently attached to the NH₂-modified boron-doped diamond electrode for the sensing of beta-alanine – a neurotransmitter and neuromodulator that was recently shown to be related to the pain sensing.³¹

7.3 Experimental Section

7.3.1 Electrode preparation

Polycrystalline boron-doped diamond electrode (BDE) was used as a working electrode in all experiments (from Element Six Co, 10×10×0.6 mm size, [B] ~ 10²⁰ cm⁻³). Prior to use, the BDEs were polished with alumina powder (particle size 0.3 μm). The electrodes were further cleaned by ultrasonication in water and acetone. This was followed by a three hour treatment in *aqua regia* solution which was prepared by mixing nitric and hydrochloric acid in a 1:3 ratio. The electrodes were then thoroughly rinsed and ultrasonicated in water and acetone solutions.

7.3.1.1 Hydrogen termination of diamond electrodes

In this work, the hydrogen termination of polycrystalline boron-doped diamond electrode was produced following the method developed previously *via* microwave hydrogen plasma treatment.³² The MWCVD reactor was operated at 1.5 kW microwave power, an H₂ gas flow of 200 sccm, 60 mbar pressure and at a temperature of 600°C for 60 minutes. The sample was allowed to cool down in the hydrogen plasma by switching off the heating element and gradually reducing the microwave power until the plasma extinguished. At this point, the

microwave power supply was turned off, and the sample was cooled to a room temperature under a hydrogen flow. A wide XPS scan confirmed that the microwave hydrogen plasma treatment results in an electrode surface being largely free of adsorbed oxygen functionalities, hydrocarbons and sp^2 species.

7.3.1.2 Ethylenediamine covalent functionalisation of polycrystalline boron-doped diamond electrodes

Prior to electrochemical modifications, boron-doped diamond electrodes (BDE) were rinsed three times with anhydrous CH_3CN solution and dried under nitrogen flow. In order to functionalise the diamond surface with ethylenediamine, an hydrogen terminated polycrystalline boron-doped diamond electrode was treated by potential cycling between 0.2 V and 1.5 V during three scans via cyclic voltammetry in 1 mM ethylenediamine dissolved in anhydrous CH_3CN , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 V s^{-1} .²⁰

7.3.1.3 Ethylenediamine adsorption on polycrystalline boron-doped diamond electrode

NH_2 - covalently modified electrodes were compared against the electrodes modified by adsorption. In order to prepare the electrode with ethylenediamine absorbed on its surface, an hydrogen terminated polycrystalline boron-doped diamond electrode (HBDE) was placed in 1 mM ethylenediamine dissolved in anhydrous CH_3CN solution for twelve hours.

7.3.1.4 Zinc (II) protoporphyrin IX covalent grafting

In order to covalently attach zinc (II) protoporphyrin IX (ZnP) molecules to the surface of an amino modified diamond electrode, an amide coupling reaction/s using N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) was employed.³³ Prior to this treatment, 0.1 mM zinc (II) protoporphyrin IX was dissolved in anhydrous acetonitrile and N, N-dimethylformamide

solution (4:1 ratio).³⁴ This was followed by the addition of 3.2 µg of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride.³⁵ The ZnP and EDC were allowed to react for 20 min, stirring in a nitrogen atmosphere. At this point, 4.6 µg of N-hydroxysuccinimide (NHS) was added to the mixture. The amino modified boron-doped diamond electrode was then placed in this solution and left stirring in a nitrogen atmosphere for twelve hours to complete the reaction.

For reference, the chemical structures of N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-Hydroxysuccinimide (NHS) are given in Figure 87.

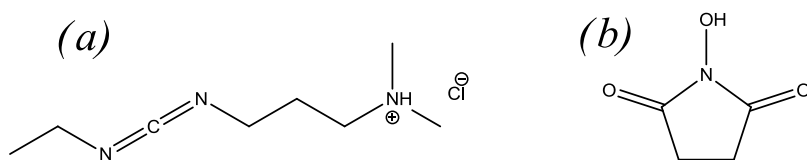


Figure 87 Chemical structures of (a) N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC); (b) N-Hydroxysuccinimide (NHS)

7.3.1.5 Preparation of Zinc (II) protoporphyrin IX adsorbed onto the ethylenediamine modified boron-doped diamond

For comparison, BDE modified with physically absorbed ZnP was also prepared. In this case, freshly prepared ethylenediamine modified boron-doped diamond was placed in 0.1 mM zinc (II) protoporphyrin IX dissolved in anhydrous acetonitrile and N, N-dimethylformamide solution (4:1 ratio) and left for twelve hours in solution under a nitrogen atmosphere.

7.3.2 Characterisation

X-ray photoelectron spectroscopy (XPS) spectra were recorded using a hemispherical analyser and Al K α (1486.6 eV) X-ray source. The survey scans and the high resolution scans were measured at 50 eV pass energy with 0.5 eV step and at 20 eV pass energy with 0.1 eV step respectively. The spectra recorded were analysed with CasaXPS software.³⁶ The peaks

were fitted using Shirley background.³⁷ The binding energies were referenced to the C 1s sp^3 peak positioned at 285.0 eV.

Electrochemical measurements were performed using a μ -AUTOLAB III electrochemical workstation (Eco-Chemie, Netherlands) at 23°C. A standard three-electrode configuration comprising of the BDE as a working electrode, an Ag/AgCl reference electrode and a Pt counter electrode was employed in the study. The working electrode was mounted in a PTFE holder, so that a circular area of 0.4 cm² was exposed to a working solution.

The electrochemical characterisation of modified diamond electrodes was carried out using cyclic voltammetry under a nitrogen atmosphere in anhydrous acetonitrile/DMF solution (4:1 ratio), containing 0.1 M NBu₄BF₄.

7.3.3 Chemicals

Tetrabutylammonium tetrafluoroborate (NBu₄BF₄), ethylenediamine (EDA), N-hydroxysuccinimide (NHS), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), zinc (II) protoporphyrin IX, acetonitrile (CH₃CN, anhydrous), tetrahydrofuran (THF, anhydrous) and dichloromethane (CH₂Cl₂, anhydrous) were used as-received from Sigma Aldrich, UK. N, N-dimethylformamide (anhydrous) was purchased from Rathburn Chemicals, UK. Prior to electrochemical measurements, all solutions were deaerated by passing N₂ gas for 10 min.

7.4 Results and discussion

7.4.1 XPS characterization of hydrogen terminated boron-doped diamond electrode

After the hydrogen plasma treatment and before performing any chemical modifications on the diamond electrode, the samples were characterised by XPS in order to establish the initial chemical environment at the diamond surface. A typical survey scan of a hydrogen terminated diamond surface used throughout this work is presented in Figure 88.

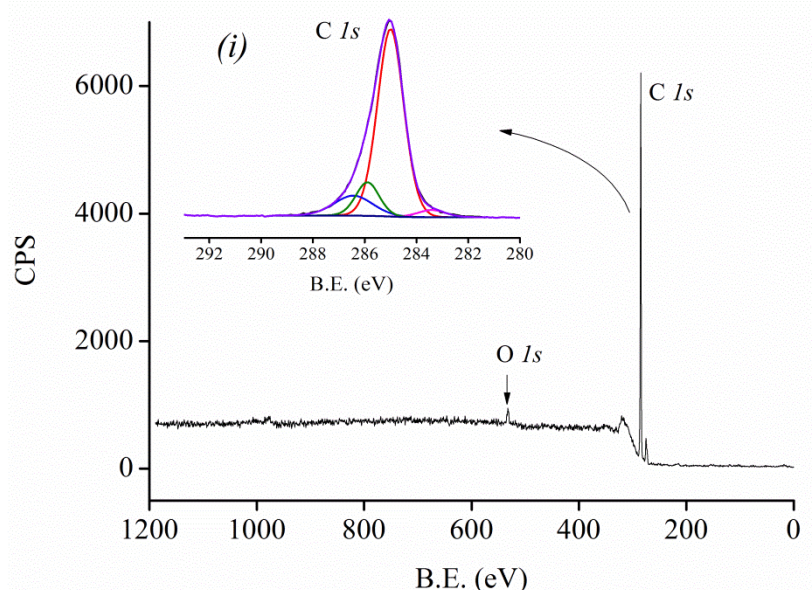


Figure 88 XPS wide scan spectra of hydrogen terminated boron-doped diamond electrode; (i) associated high-resolution C 1s region

The main C 1s photoemission line at 285 eV along with characteristic C KVV and C KLL Auger series at 980 eV and 1000 eV confirm that the substrate is well hydrogenated and is free of any metal contamination. The oxygen content is negligible, with a O 1s/C 1s ratio being less than 3%. A high-resolution C 1s spectra (Figure 88 (i)) was deconvoluted into four photoelectron peaks, with each peak exhibiting contributions from differing C 1s chemical bonding: the main signal at 285.0 eV is characteristic of C sp^3 bulk diamond and the two minor peaks at 285.7 eV and 286.4 eV correspond to C-H_x (x = 2,3) species in polyhydride configurations and C-O surface groups respectively.³⁸⁻⁴⁰ A small peak towards a lower binding energy at 283.4 eV is attributable to the graphitic type states involved in π -bonding, such as those associated with sp^2 defects.⁴

7.4.2 Ethylenediamine covalent functionalisation of diamond electrode

Electrochemical oxidation of ethylenediamine on boron-doped diamond electrode presents a straightforward route for a covalent introduction of NH₂ groups to the electrode surface.⁴¹

This section investigates the nature of these NH_2 bonded species *via* cyclic voltammetry and XPS.

The cyclic voltammetric curves of 1 mM ethylenediamine dissolved in anhydrous CH_3CN , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 V s^{-1} from 0.2 to 1.4 V at hydrogen terminated boron-doped diamond electrode are presented in Figure 89. The associated peak position and current response (i.e. current normalised by electrode area) are summarised in Table 48.

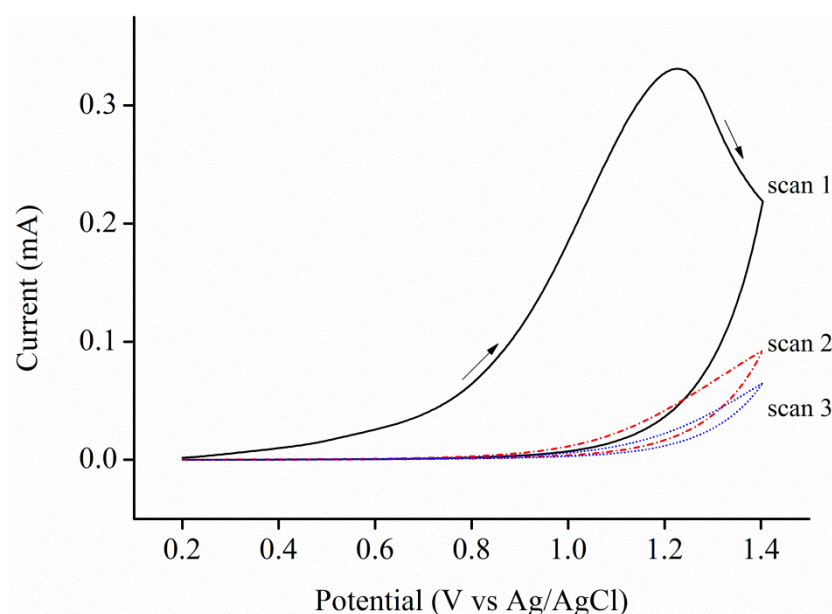


Figure 89 Cyclic voltammograms of 1 mM ethylenediamine dissolved in anhydrous CH_3CN , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 Vs^{-1} recorded at hydrogen terminated boron-doped diamond

Table 48 Peak position and current response data recorded at hydrogen terminated boron-doped diamond electrode in 1 mM ethylenediamine dissolved in anhydrous CH_3CN , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 Vs^{-1}

Scan	Peak Position (V)	Current (A)	Current Response (A cm^{-2})
1	1.2	1.47×10^{-4}	3.67×10^{-4}

The first scan in Figure 89 shows an irreversible peak at 1.2 V vs Ag/AgCl which represents the ethylenediamine grafting process to the diamond surface. No cathodic peak is detected in the reverse scan, thus suggesting that the first electron transfer process involves a chemical

reaction. In the subsequent scans, the current response diminishes with the peak current being lost by the second scan. Similar results have been obtained for other carbon electrode materials such as glassy carbon, and this is believed to be due to the passivation of the electrode in the result of ethylenediamine attachment to the electrode surface.^{42,43}

The effect of the passivation of the electrode surface is further illustrated in Figure 90, where the cyclic voltammetry was carried out prior and post EDA grafting in 1 mM ferrocenemethanol dissolved in CH₃CN/DMF solution, containing 0.1 M NBu₄BF₄.

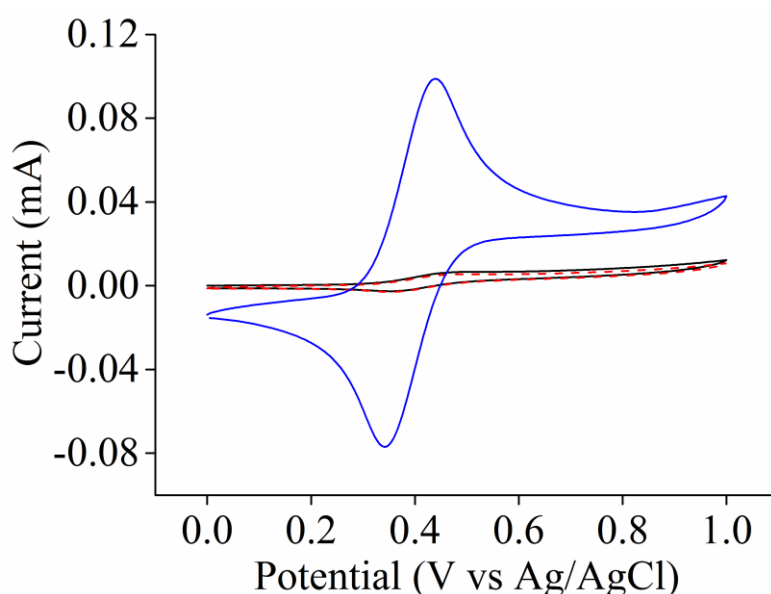


Figure 90 Cyclic voltammograms of 1 mM ferrocenemethanol dissolved in anhydrous CH₃CN/DMF, containing 0.1 M NBu₄BF₄ at a scan rate of 0.05 Vs⁻¹ recorded at (–) hydrogen terminated boron-doped diamond prior to EDA grafting ; (–) HBDE post EDA grafting, (– –) after rinsing of EDA modified HBDE with 5 mL CH₃CN and 5 mL CH₂Cl₂ solutions

The first scan in Figure 90 (blue line) shows a well-defined redox reaction of ferrocenemethanol at a clean, hydrogen-terminated boron-doped diamond electrode. The electrode was then modified with 1 mM ethylenediamine as described in the previous section (Figure 89). The subsequent CV scan in 1 mM ferrocenemethanol (black line, Figure 90) shows no current response to the redox couple, which suggests that the electrode is blocked by the ethylenediamine chains on its surface. The rinsing procedure with 5 mL of CH₃CN and

5 mL CH₂Cl₂ has no effect on the electrochemical activity of the EDA modified HBDE (red dash line, Figure 90), thus confirming that the EDA layer was not removed.

The number of electrons, n , involved in the electrochemical oxidation of EDA was estimated using Equation 7.1. The latter describes a peak current for the transport limited n -electron transfer irreversible reaction:⁴⁴

$$I_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} A C D^{1/2} \nu^{1/2} \quad (\text{Equation 7.1})$$

where I_p is the peak current (A), α is the transfer coefficient, n_a is the number of electrons involved in the rate determining step (equals unity in aprotic solvents),⁴¹ A is the electrode area (cm²), C is the bulk concentration (mol cm⁻³), D is the diffusion coefficient (1.4×10⁻⁷ cm² s⁻¹)^{45,46} and ν is the scan rate (V s⁻¹). The value of $n = 2.1$ was obtained which is in a good agreement with the results previously reported for carbon electrodes.⁴¹ This two-electron oxidation process is suggested to be caused by the occurrence of two monoelectron transfers to each amino group.⁴¹ The cation radical species formed in the result of this process then attack C-H bonds of the diamond surface, allowing the subsequent immobilization of EDA molecules through C-N bonds. Therefore, the most likely pathway of the ethylenediamine electrografting on the hydrogen terminated diamond electrode can be described by the following reaction, seen in Figure 91:

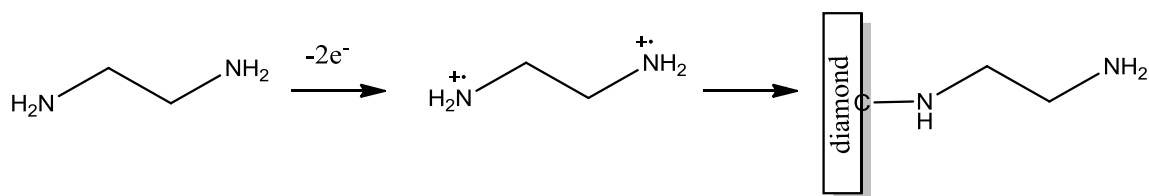


Figure 91 Ethylenediamine oxidation at hydrogen terminated diamond electrode

The amount of ethylenediamine molecules grafted in the first scan on the H-terminated diamond electrode was estimated from the charge, Q , corresponding to the area under the oxidation peak in accordance with Equation 7.2:

$$Q = nFA\Gamma \quad (\text{Equation 7.2})$$

where n is the number of electrons involved in the redox process, F is the Faraday constant (96485 C mol^{-1}), A is the diamond electrode area (0.4 cm^2), Γ is the surface concentration of the analyte. The value of $Q = 4.84 \times 10^{-4} \text{ C}$ was obtained from the area under the oxidation peak. Therefore, 5.7 nmol cm^{-2} of EDA was found to form on the HBDE surface after the first scan. The monolayer coverage of ethylenediamine is around 0.5 nmol cm^{-2} .⁴⁷ Therefore it can be concluded that several monolayers are formed on the HBDE electrode which causes the passivation of the electrode driven by the formation of polyethylenimine chains on the electrode surface.

7.4.2.1 XPS characterisation of amino functionalised diamond electrodes

XPS experiments were carried out in order to compare the electrochemical modification route, which allows covalent grafting of ethylenediamine to the diamond surface, to a simpler physical adsorption route. XPS experiments were used to investigate the chemical changes at the two types of EDA modified diamond surfaces:

1. Ethylenediamine thin film physically adsorbed on the H-terminated diamond electrode
2. Ethylenediamine deposited *via* electrochemical oxidation route on the H-terminated diamond electrode

The preparation of a thin ethylenediamine film adsorbed on the hydrogen terminated diamond surface was carried out by placing the HBDE into 1 mM ethylenediamine dissolved in

anhydrous CH_3CN solution for twelve hours. The associated XPS survey scan is presented in Figure 92 (a).

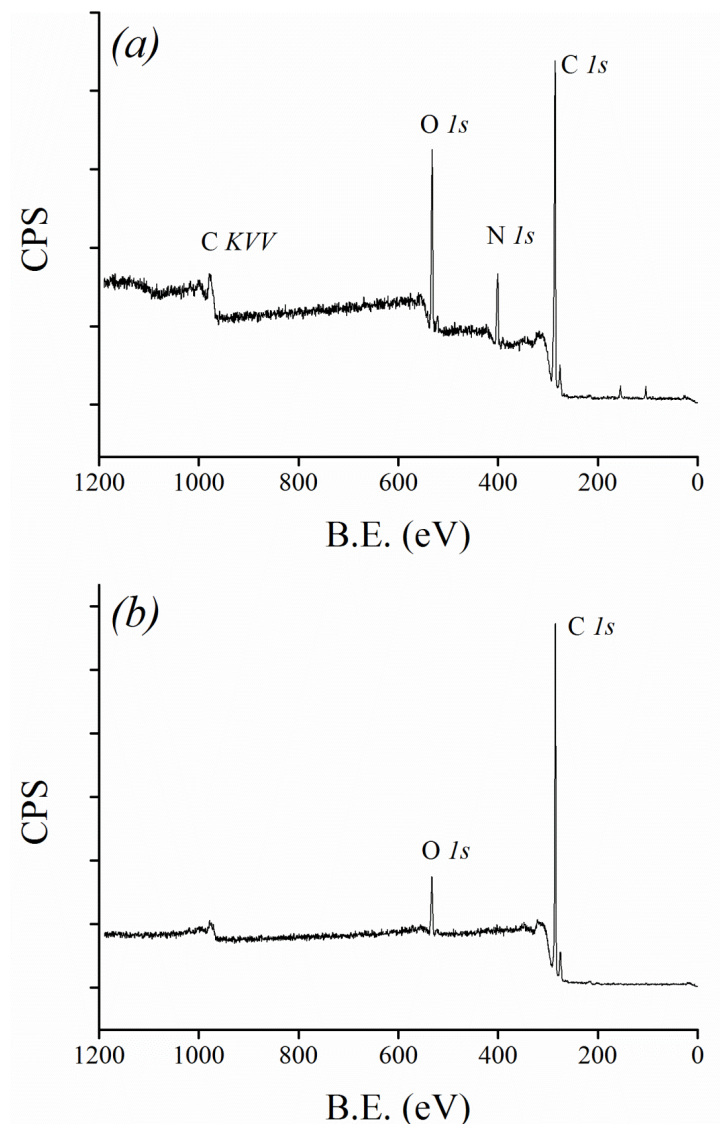


Figure 92 Survey XPS spectra of (a) EDA thin film adsorbed onto H-terminated BDE; (b) surface of the same sample after $\text{CH}_2\text{Cl}_2/\text{DMF}$ rinsing procedure

The survey spectrum in Figure 92 (a) has a characteristic $\text{C } 1s$ photoemission peak at 285 eV and $\text{N } 1s$ line at 400.5 eV along with C KVV and C KLL Auger peaks at 980 eV and 1000 eV respectively. An $\text{O } 1s$ signal at 532 eV is likely to arise from H_2O adsorption from the atmospheric moisture. Two lines from silicon $\text{Si } 2s$ and $\text{Si } 2p$ core levels at 103.8 eV and

154.3 eV are related to a minor SiO₂ contamination from glassware. An application of the standard XPS sensitivity factors suggests a O 1s/C 1s ratio of 13.4% and N 1s/C 1s ratio of 11.2%.³⁶

An important feature of the EDA film adsorbed on the diamond surface is that it is easily removed if subsequently rinsed with CH₂Cl₂ and DMF solutions. As presented in Figure 92 (b), no nitrogen signal was detected during the survey scan of the rinsed electrode. Therefore, it can be concluded that no NH₂-containing species have become covalently attached to the diamond electrode.

In further experiments, cyclic voltammetry at the H-terminated BDE was performed in the conditions, where the potential of the electrode was swept from 0.2 V to 1.4 V in 1 mM EDA, dissolved in CH₃CN, so the electrografting reaction can be completed. The electrode was then removed from the cell and cleaned by ultrasonication in CH₂Cl₂/DMF solution during 30 min. The following XPS spectra of the as-prepared sample and a sample cleaned in CH₂Cl₂/DMF are presented in Figure 93 (a) and (b) respectively.

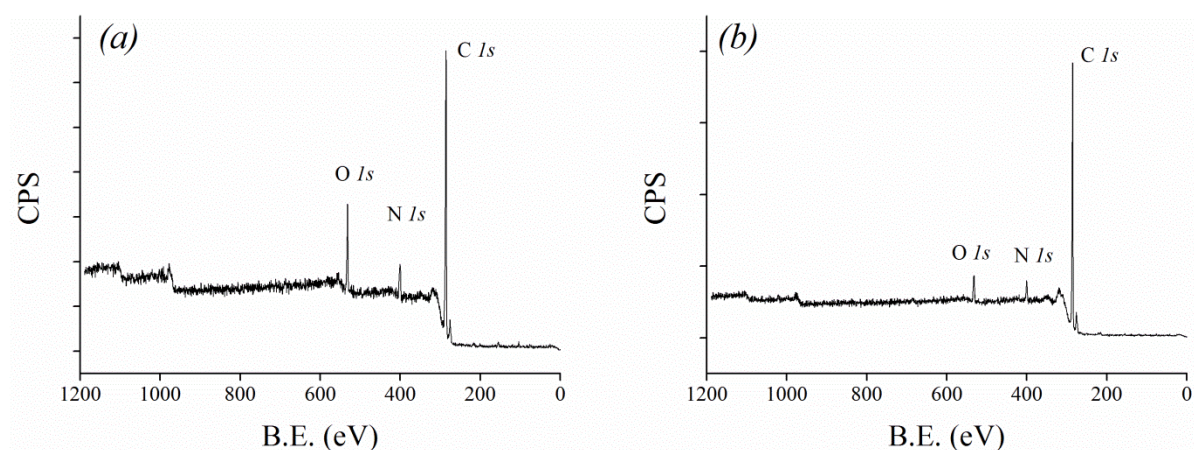


Figure 93 Survey XPS scan of (a) EDA modified HBDE via electrochemical grafting; (b) surface of the same sample after the washing procedure with CH₂Cl₂;

From Figure 93 (b) it can be seen that significant differences to electrochemically grafted EDA layers occur when the latter is washed and ultrasonicated in CH₂Cl₂/DMF solution.

Although N 1s signal decreases after the washing procedure, a significant amount of nitrogen now persists on the diamond surface and could not be easily removed by CH₂Cl₂/DMF rinsing. This is in contrast to the situation when the EDA film was physically adsorbed onto HBDE. In the latter case, all the ethylenediamine moieties were easily removed from the sample (Figure 92 (b)).

A useful insight can be further obtained from consideration of the high-resolution XPS spectra of the C 1s, N 1s and O 1s regions of EDA covalently attached to the HBDE after the washing treatment. Associated peak parameters and elemental ratios are summarised in Table 49 and Table 50.

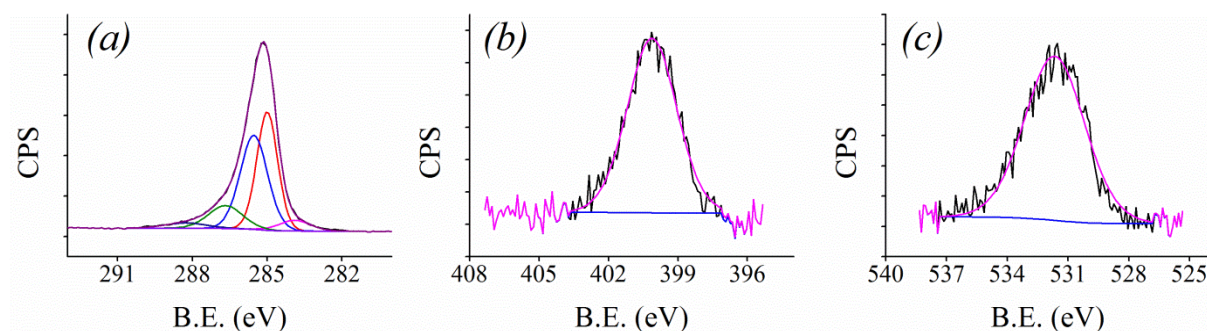


Figure 94 (a) high-resolution C 1s region of EDA modified HBDE via electrochemical grafting after the washing procedure with CH₂Cl₂; (b) high-resolution N 1s region of the same sample; (c) high-resolution O 1s region of the same sample

Table 49 XPS binding energies and FWHM for the EDA modified hydrogen terminated boron-doped diamond electrode

Sample	Binding energies (eV)						
HBDE electrochemically modified with EDA	C 1s					N 1s	O 1s
	Csp ³	C-N	C-O	COOH	sp ² def		
	285.0	285.8	286.6	288.7	283.6	400.1	531.7
	FWHM						
	C 1s					N 1s	O 1s
	1.03	1.55	1.41	1.98	1.47	2.5	3.4

Table 50 XPS elemental ratios and charging values for the EDA modified hydrogen terminated boron-doped diamond electrode

Sample	N 1s/C 1s ratio (%)	O 1s/C 1s ratio (%)	Charging (eV)
EDA/HBDE	4.5	3.9	Relative to C 1s (285.0 eV) 11.6

In the high-resolution C 1s spectra of the EDA modified HBDE (Figure 94 (a)) a different picture is seen if compared to C 1s spectra of HBDE in Figure 88 (i). The photoelectron signal at 285.0 eV is due to the sp³ bulk diamond. The major change in the C 1s spectra of the EDA modified HBDE arise from the significant increase in the intensity of the second component at 285.8 eV which can be related to the presence of C-N functionalities.^{48,49} This C-N binding energy is also consistent with typical values of C bonded in polyethyleneimine materials.⁵⁰ The peaks at 286.6 eV and 288.3 eV correspond to hydroxyl and carboxyl surface groups respectively.⁴⁹ The peak at 283.6 eV is associated with sp² defects.⁴ The N 1s spectral region shows a peak at 400.1 eV that arises from NHx-C species (Figure 94 (b)). This binding energy is consistent with reported values for surface-bound ethylenediamine groups.⁵¹ The O 1s spectral region of EDA modified HBDE is presented in Figure 94 (c). The peak at 531.5 eV is likely to arise both from C-O and COOH species formed as a result of the anodic treatment of the electrode and atmospheric moisture adsorbed on the electrode surface.

The extent of the electrochemical grafting reaction can be quantified by estimating the grafting density of ethylenediamine species attached to the H-terminated boron-doped diamond electrode. If the monolayer of ethylenediamine species (component A) is grafted to a uniform and homogeneous diamond (component B), the surface concentration in nmol cm⁻² can be determined using the following equation:⁴⁹

$$\frac{I_A}{I_B} = \frac{n_A S_A}{P_A \int_0^\infty D_B S_B e^{-x/\lambda_B} dx} = \frac{n_A S_A}{P_A D_B S_B \lambda_B} \quad (\text{Equation 7.3})$$

where D_B is the carbon density in the bulk, λ_B is the inelastic mean free path (IMFP) of emitted photoelectrons from the bulk diamond, P_A is the transmission probability through the grafter overlayer A, n_A is the number density of the grafted species A, $S_{A,B}$ are the surface sensitivity factors which are estimated by dividing the conventional bulk factors⁵² by the appropriate value of inelastic mean free path,³² and x is the distance below the solid surface.⁴⁹

For this estimate, an inelastic mean free path (appropriate to Al K α C 1s electrons) of 1.7 nm will be used, along with a density of carbon atoms of $1.8 \times 10^{23} \text{ cm}^{-3}$. P_A will be assumed to equal unity for this calculation. The use of these factors in the Equation 7.3 gives a rough estimate of the surface coverage of 2.3 nmol cm^{-2} at HBDE electrode which is in a good agreement with a surface concentration derived from the electrochemical studies.

The electrochemical data and XPS analysis discussed above confirm that ethylenediamine can be covalently attached to the hydrogen terminated boron-doped diamond electrode *via* the electrografting procedure.

7.4.2.2 Ethylenediamine modification of diamond electrode under base conditions

In order to comprehensively investigate the ethylenediamine attachment to the diamond surface, another grafting strategy was also explored in this work. This includes the spontaneous reaction of protonated primary amines -NH_3^+ with hydrogen terminated diamond in aqueous alkaline solutions ($\text{pH} > 10$).^{16,53,54} Although the mechanism of the bonding is still under investigation, it has been suggested that a lone pair of amine -NH_3^+ group can react with an hydrogenated diamond surface.⁵⁴

A protocol reported in references^{53,54} was reproduced to test this strategy. A freshly prepared H-terminated BDE was placed into 1 M ethylenediamine dissolved in 0.1 M PBS ($\text{pH} 10.3$) and left for 20 hours. The changes to the surface of the diamond sample prior and after modification were monitored by cyclic voltammetry with standard redox couples and XPS. No post modification changes were detected in CV experiments with redox couple mediators. XPS analysis also did not show any N 1s photoelectron signals after 20 hours treatment, therefore suggesting that this amination strategy was not successful. Since it is not expected for the amines to react with the diamond surface under mild base conditions, possibly some unusual and yet unrealised feature is needed to drive this reaction.

7.4.3 Zinc (II) protoporphyrin IX covalent grafting via amide EDC/NHS coupling reaction

In accordance with the procedure described in experimental Section 7.3.1.4, the EDA modified electrode was placed in 0.1 mM Zinc (II) protoporphyrin IX dissolved in CH₃CN/DMF (4:1 ratio) containing EDC/NHS amide coupling agent and left stirring for 12 hours.

The scheme of Zinc (II) protoporphyrin IX grafting to the EDA covalently attached at the boron-doped diamond electrode *via* amide EDC/NHS coupling reaction is presented in Figure 95.⁵⁵

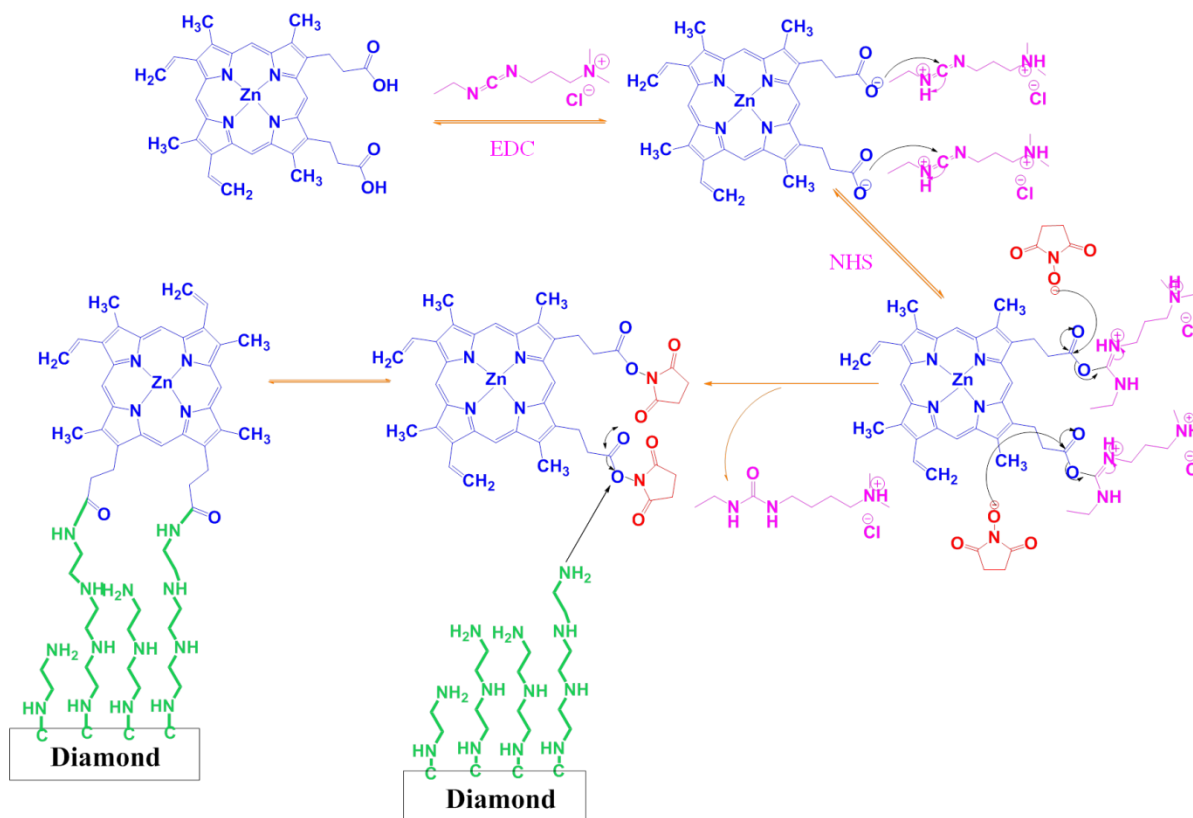


Figure 95 Schematic representation of Zinc (II) protoporphyrin IX grafting to the EDA modified boron-doped diamond electrode *via* amide EDC/NHS coupling reaction

In order to investigate the nature of ZnP grafted species, the surface composition of the modified electrode was studied using XPS. Figure 96 (a) presents a survey scan of ZnP

immobilized onto the EDA modified boron-doped diamond electrode. The main photoelectron features are the C *1s* peak at 285 eV along with the N *1s* peak at 400.2 eV, O *1s* at 532 eV and Zn *2p* signal that is splitted into Zn *2p*_{3/2} at 1020.6 eV and Zn *2p*_{1/2} at 1043.4 eV.

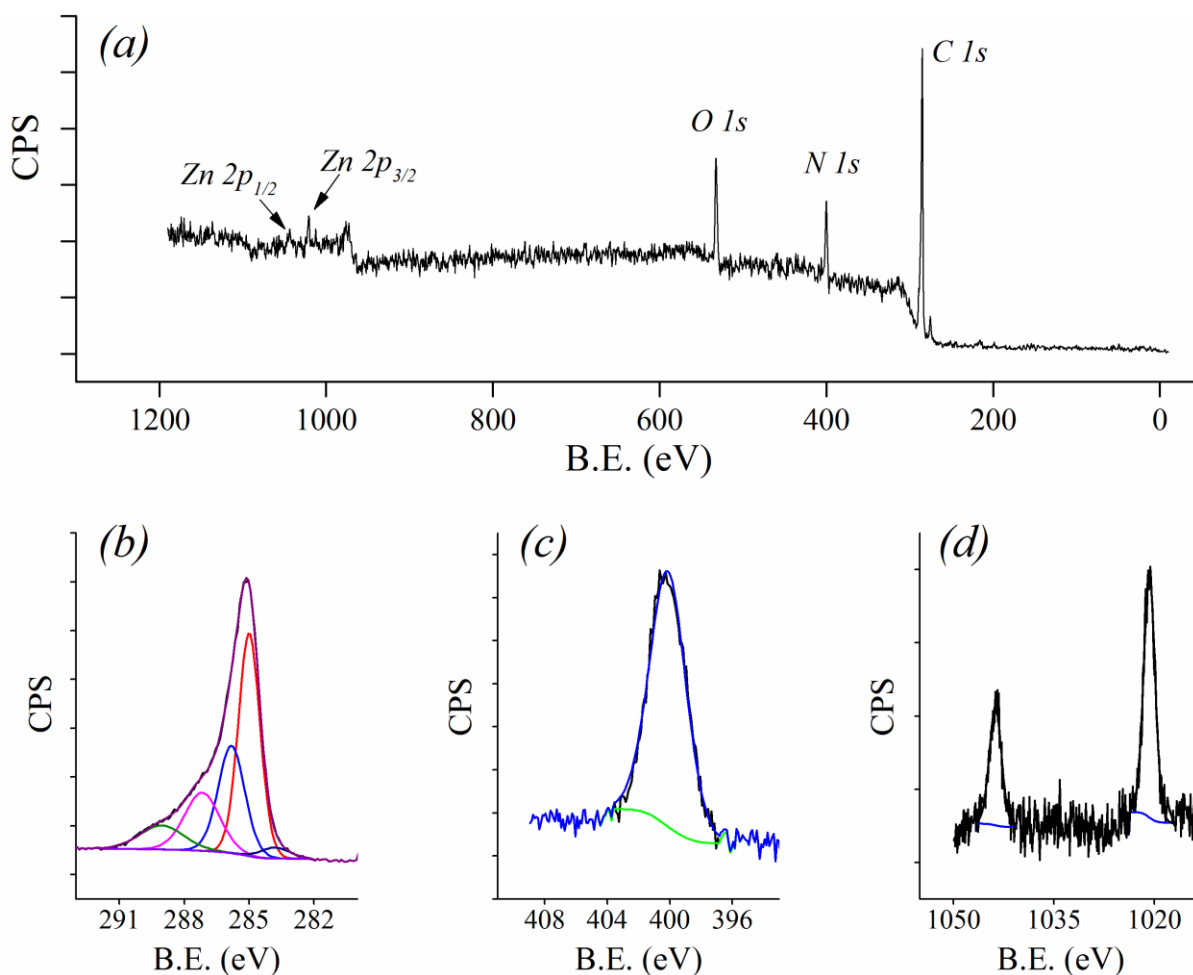


Figure 96 (a) a survey scan of ZnP-EDA modified HBDE via EDC/NHS coupling; (b) high-resolution C *1s* region of the same sample (c) corresponding high-resolution N *1s* region; (d) corresponding high-resolution Zn *2p* region

A high-resolution C *1s* spectral region of ZnP-EDA modified HBDE via EDC/NHS coupling is shown in Figure 96 (b). The C *1s* peak was deconvoluted into five constituent peaks. The associated peak parameters and elemental ratios are given in Table 51 and Table 52. The C *1s* peak that is characteristic of the bulk diamond was positioned at 285.0 eV. The peak at 285.9 eV was assigned to C-N chemical environments.⁴⁹ A strong peak detected at 287.1 eV

corresponds to carbonyl component arising from -C(=O)-NH- functional groups.⁵⁶⁻⁵⁸ This is in contrast to the C 1s peak of unmodified hydrogen-terminated boron-doped diamond electrode (Figure 88 (i)) and ethylenediamine modified HBDE (Figure 94 (a)), where no C=O component was recorded from the electrode surface. A weaker peak at 289.0 eV is associated with -COOH groups which are likely to arise from partially reacted ZnP species, and a small feature at 283.8 eV is characteristic of sp²-defects.⁴⁹ Figure 96 (c) displays the N 1s spectral region of the ZnP-EDA modified HBDE electrode. A well-resolved N 1s component at 400.1 eV binding energy is consistent with the typical values of nitrogen bonded in neutral state of NHx-C groups.⁵⁹ The Zn 2p spectra of ZnP-EDA modified HBDE in Figure 96 (d) presents two well-resolved doublets with Zn 2p_{3/2} signal at 1020.7 eV and Zn 2p_{1/2} at 1043.7 eV.⁴⁸ The peak-to-peak separation ($\Delta B.E._p = B.E._{Zn\ 2p_{1/2}} - B.E._{Zn\ 2p_{3/2}}$) of 23.0 eV is characteristic of a neutral zinc state.⁴⁸ Thus, taking into account ZnP coupling mechanism (Figure 95) and the previous XPS data available on the -C(=O)-NH- compounds,⁵⁸ it can be concluded that the appearance of a dominant signal from carbonyl component is consistent with the existence of peptide bonds. This confirms that ZnP species have become covalently attached to the EDA modified diamond surface.

Table 51 XPS binding energies and FWHM for the ZnP-EDA modified hydrogen terminated boron-doped diamond electrode

Sample	Binding energies (eV)								
ZnP-EDA modified HBDE	C 1s				N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}	
	Csp ³	C-N	C=O	COOH	sp ² def				
	285.0	285.9	287.1	289.0	283.8	400.1	532.6	1020.7	1043.7
	FWHM (eV)								
	C 1s				N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}	
	1.17	1.44	1.90	2.39	1.56	2.70	2.84	1.99	2.10

Table 52 XPS elemental ratios and charging values for the ZnP-EDA modified hydrogen terminated boron-doped diamond electrode

Sample	Zn 2p/C 1s ratio (%)	N 1s/C 1s ratio (%)	O 1s/C 1s ratio (%)	Charging (eV)
ZnP-EDA HBDE	0.45	11.27	9.8	Relative to C 1s (285.0 eV) 10.06

In order to prove the covalent attachment of ZnP species, the ZnP-EDA modified HBDE electrode was thoroughly rinsed by CH₂Cl₂, DMF and THF solutions. This was followed by

ultrasonication in $\text{CH}_2\text{Cl}_2/\text{DMF}$ solution for 1 hour. The XPS data collected after this treatment is presented in Figure 97. The associated binding energies and FWHM values are given in Table 53.

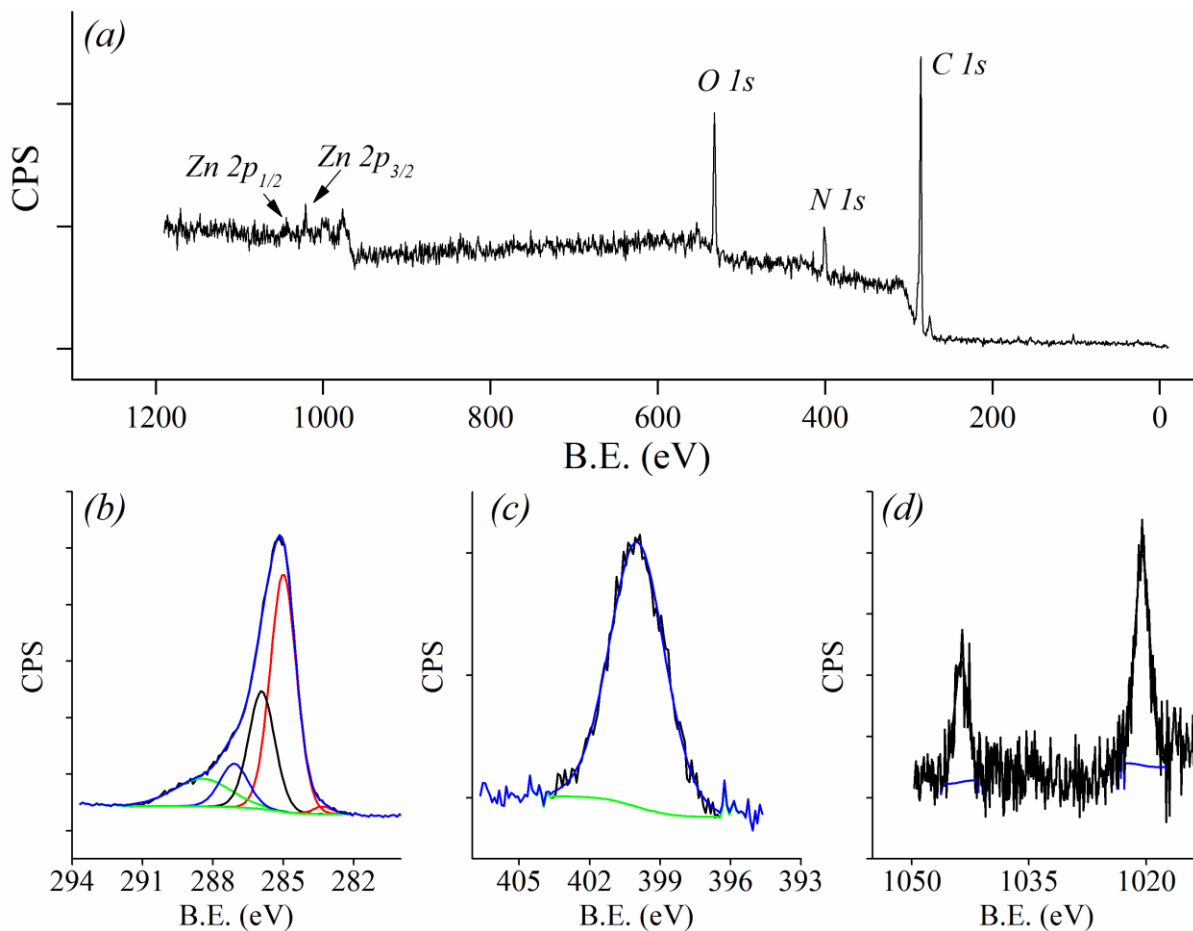


Figure 97 (a) a survey scan of ZnP-EDA modified HBDE via EDC/NHS coupling after the washing procedure; (b) high-resolution C 1s region of the same sample (c) corresponding high-resolution N 1s region; (d) corresponding high-resolution Zn 2p region

It can be seen from Figure 97 (a) that the washing procedure produces very little change to the XPS spectra of the ZnP-EDA modified electrode. A significant amount of Zn 2p and N 1s remained on the diamond surface and cannot be washed off by extensive solvent rinsing or prolonged sonication. The Zn 2p/C 1s and N 1s/C 1s ratios deduced from the spectra by applying appropriate sensitivity factors³⁶ are presented in Table 54. A value of 0.3% is calculated for the Zn coverage and 9.46% for the N coverage at the ZnP-EDA modified

Chapter seven – Chemical modifications of diamond surfaces: porphyrin-diamond hybrid interfaces

HBDE after the rinsing treatment, compared to a value of 0.45% for the Zn coverage along with 11.3% for the N coverage at the ZnP-EDA modified HBDE surface with EDC/NHS coupling agent. This shows that ZnP molecules were likely to be covalently attached to the EDA modified HBDE electrode.

Table 53 XPS binding energies and FWHM for the ZnP-EDA modified hydrogen terminated boron-doped diamond electrode after the rinsing procedure via ultrasonication in CH₂Cl₂/DMF

Sample	Binding energies (eV)									
	C 1s					N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}	
ZnP-EDA modified HBDE	Csp ³	C-N	C=O	COOH	sp ² def					
	285.0	285.9	287.1	288.7	283.3	399.9	532.2	1020.5	1043.7	
	FWHM (eV)									
	C 1s					N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}	
	1.31	1.30	1.41	2.85	0.92	2.76	2.60	2.28	2.06	

Table 54 XPS elemental ratios and charging values for the ZnP-EDA modified hydrogen terminated boron-doped diamond electrode after the rinsing procedure via ultrasonication in CH₂Cl₂/DMF

Sample	Zn 2p/C 1s ratio (%)	N 1s/C 1s ratio (%)	O 1s/C 1s ratio (%)	Charging (eV)
ZnP-EDA HBDE	0.30	9.5	12.6	Relative to C 1s (285.0 eV) 10.3

As a comparison, a surface composition of two samples: (1) Zinc (II) protoporphyrin IX (ZnP) adsorbed on HBDE surface; and (2) ZnP adsorbed onto the EDA modified HBDE without EDC/NHS coupling agent were comprehensively analysed by XPS.

The survey XPS spectra of ZnP adsorbed onto the clean HBDE surface (Figure 98 (a)) has the characteristic C 1s peak at 285 eV binding energy, N 1s at 398.2 eV along with O 1s core line at 532.5 eV. The photoemission peak at 1020.5 eV corresponds to Zn 2p_{3/2} signal, and the peak at 1043.2 eV is assigned to Zn 2p_{1/2}. A high-resolution C 1s region in (Figure 98 (b)) was resolved into four constituent peaks. The peak at 285.0 eV was referred to carbon in the bulk diamond. A strong peak at 285.5 eV is attributable to carbon bonded in polyhydride configurations (-CH_x, x≥2).⁴⁹ The peak at 288.6 eV is due the COOH species present on

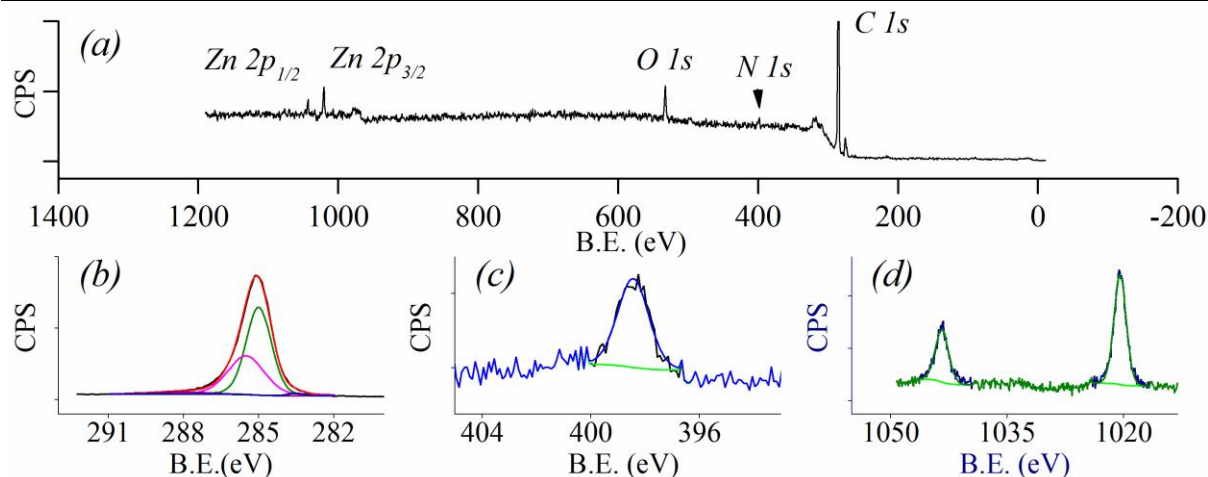


Figure 98 (a) a survey scan of ZnP adsorbed onto HBDE; (b) high-resolution C 1s region of the same sample (c) high-resolution N 1s region of the same sample; (d) high-resolution Zn 2p region of the same sample

the electrode surface.⁴⁹ The peak at 283.5 eV corresponds to sp² defects.⁴⁹ As expected, no signal arising from the presence of carbonyl groups was detected at this sample. This is in contrast to the situation when ZnP species were covalently attached to the EDA modified HBDE via peptide bond formation. In the latter case, a dominant signal from -C(=O)-NH- chemical environment was observed at 287.1 eV (Figure 97 (b)). The N 1s spectral region in Figure 98 (c) shows a single peak at 398.4 eV binding energy which arises from pyrrole rings of adsorbed ZnP species.⁶⁰ The N 1s peak is 1.9 eV lower than that detected at ZnP/EDA modified HBDE (Figure 97 (c)). This again confirms the different nature of N 1s transitions at ZnP adsorbed onto HBDE and ZnP covalently grafted to the EDA modified HBDE. A high-resolution Zn 2p spectral region associated with ZnP adsorbed onto HBDE surface is presented in Figure 98 (d). The Zn 2p_{3/2} and Zn 2p_{1/2} photoelectron peaks at 1020.5 eV and 1043.4 eV arise from the two spin orbit states of Zn. The final elemental Zn 2p/C 1s ratio estimated with appropriate sensitivity factors is approximately 0.59% (Table 56). A slightly higher Zn 2p/C 1s ratio than that of observed at ZnP-EDA HBDE indicates the tendency to form multilayer ZnP phases during the adsorption process. The decrease in the N 1s/C 1s ratio (the latter is around 1.24%) is consistent with the absence of EDA layer on the electrode surface as compared to the ZnP-EDA modified HBDE.

Chapter seven – Chemical modifications of diamond surfaces: porphyrin-diamond hybrid interfaces

Table 55 XPS binding energies and FWHM for the ZnP adsorbed on the hydrogen terminated boron-doped diamond electrode

Sample	Binding energies (eV)								
	C 1s					N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}
	Csp ³	-CHx	C=O	COOH	sp ² def				
	285.0	285.5	n/a	288.6	283.5	398.4	532.5	1020.5	1043.4
ZnP adsorbed on HBDE	FWHMv(eV)								
	C 1s					N 1s	O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}
	1.20	1.44	n/a	2.51	0.87	1.34	2.56	1.85	2.01

Table 56 XPS elemental ratios and charging values for the ZnP adsorbed on the hydrogen terminated boron-doped diamond electrode

Sample	Zn 2p/C 1s ratio (%)	N 1s/C 1s ratio (%)	O 1s/C 1s ratio (%)	Charging (eV)
ZnP-EDA HBDE	0.59	1.24	6.0	Relative to C 1s (285.0 eV) 10.7

In the following experiment, the ZnP adsorbed onto HBDE sample was thoroughly rinsed by CH₂Cl₂, DMF and THF solutions and ultrasonicated in CH₂Cl₂/DMF solution for 1 hour as described in the preceding section. The XPS data collected after this treatment (Figure 99) showed that the survey scan was restored to a state which is very similar to that of initial HBDE surface, thus confirming that the adsorbed ZnP species were effectively dissolved away.

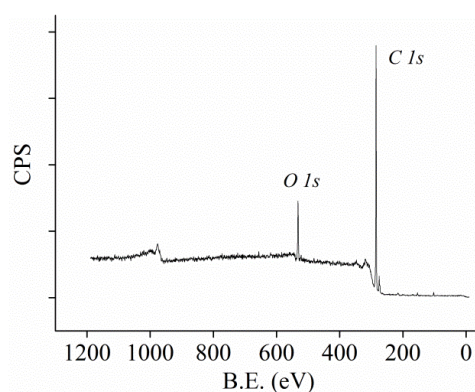


Figure 99 Survey XPS spectrum of ZnP adsorbed onto HBDE sample after the ultrasonication procedure in CH₂Cl₂

A useful insight can be further obtained by the XPS analysis of ZnP species physically adsorbed onto the ethylenediamine modified HBDE without EDC/NHS linker. The resulting survey scan is presented in Figure 100 (a).

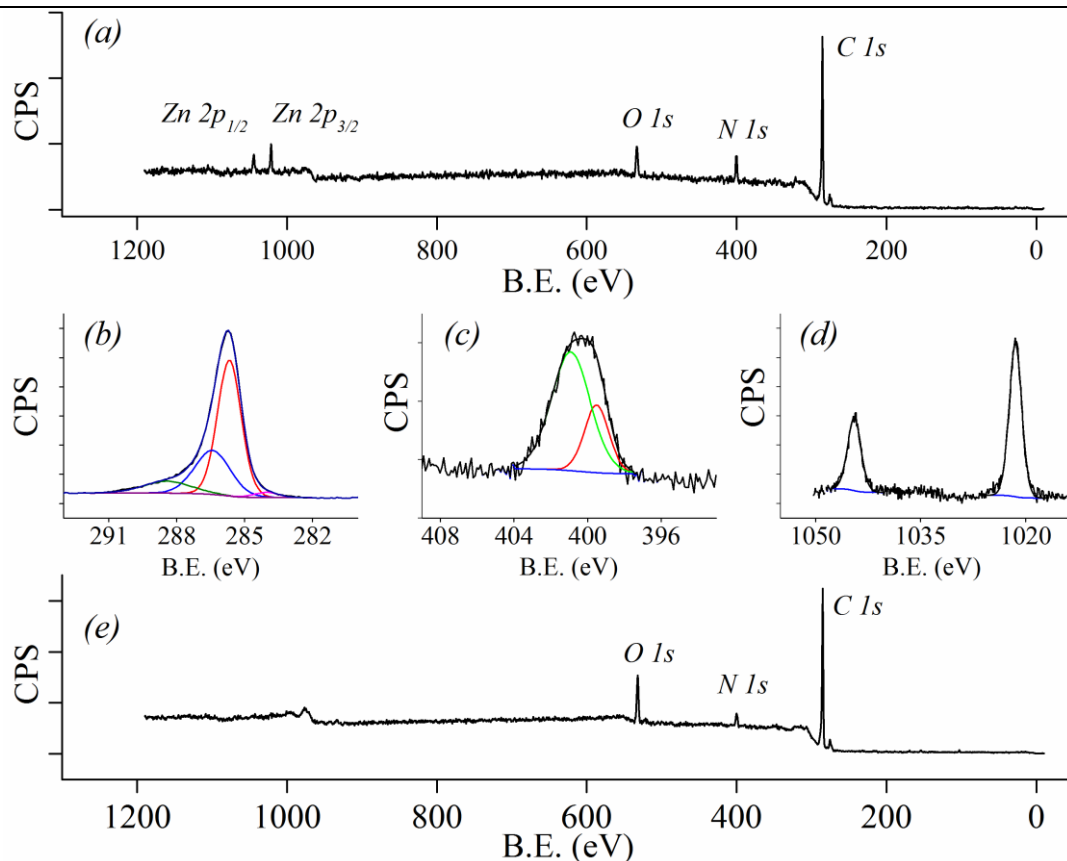


Figure 100 (a) a survey scan of ZnP adsorbed onto the EDA modified HBDE; (b) high-resolution C 1s region of the same sample (c) high-resolution N 1s region of the same sample; (d) high-resolution Zn 2p region of the same sample; (e) a survey scan of ZnP adsorbed onto EDA modified HBDE after the ultrasonication procedure in $\text{CH}_2\text{Cl}_2/\text{DMF}$

The main photoemission features include the C 1s signal at 285.0 eV, N 1s at 400.7 eV, O 1s peak at 533.2 eV along with Zn $2p_{3/2}$ signal at 1021.5 eV and Zn $2p_{1/2}$ at 1044.2. A high-resolution C 1s region in Figure 100 (b) was deconvoluted into four constituent peaks, with the peak at 285.0 eV having contribution from sp^3 carbon in the bulk diamond (Table 57). A strong peak at 285.9 eV is referred to carbon bonded in C-N configurations due to the EDA grafting reaction.⁴⁹ The peak at 288.6 eV is characteristic of the COOH groups, and a small feature at 283.9 eV corresponds to sp^2 defects.⁴⁹ Again, no carbonyl signal was found in the C 1s region, thus providing the necessary evidence that the EDC/NHS amide coupling agent is essential for the $-\text{C}(=\text{O})-\text{NH}-$ formation described above. The analysis of the N 1s photoelectron signal (Figure 100 (c)) suggests a contribution from two types of nitrogen species: the first signal at 398.8 eV arises from N atoms in pyrrole rings of ZnP moieties; the

second at 400.9 eV is attributable to NH₂ groups of EDA layer.⁴⁹ A high-resolution Zn 2p spectral region (Figure 100 (d)) contains a well-resolved doublet with Zn 2p_{3/2} line at 1021.5 eV and Zn 2p_{1/2} at 1044.2 eV. The XPS elemental ratios are given in Table 57.

In the subsequent experiment, the ZnP adsorbed onto the EDA/HBDE surface was rinsed in CH₂Cl₂, DMF and THF solutions and ultrasonicated in CH₂Cl₂/DMF for 1 hour. The XPS data recorded after this treatment is presented in Figure 100 (e). The absence of the Zn 2p signal and a significant decrease in the N 1s signal confirms the effective removal of ZnP molecules that were physically adsorbed on the EDA/HBDE surface.

Table 57 XPS binding energies and FWHM for the ZnP adsorbed on the EDA modified HBDE

Sample		Binding energies (eV)								
ZnP adsorbed on HBDE	C 1s					N 1s		O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}
	Csp ³	C-N	C=O	COOH	sp ² def	-N=p*	NH ₂			
	285.0	285.9	n/a	288.1	283.5	398.8	400.2	532.5	1021.5	1044.2
	FWHM (eV)									
	C 1s					N 1s		O 1s	Zn 2p _{3/2}	Zn 2p _{1/2}
	1.23	1.84	n/a	2.51	0.87	1.56	2.47	2.81	2.01	2.43
-N=p* - N atoms in pyrrole rings										

Table 58 XPS elemental ratios and charging values for the ZnP adsorbed on the EDA modified HBDE

Sample	Zn 2p/C 1s ratio (%)	N 1s/C 1s ratio (%)	O 1s/C 1s ratio (%)	Charging (eV)
ZnP-EDA HBDE	0.89	8.2	8.5	Relative to C 1s (285.0 eV) 9.1

Therefore, the XPS surface characterisation described above shows clearly that ZnP can be covalently attached to the ethylenediamine modified boron-doped diamond electrode *via* EDC/NHS amide coupling agent.

7.4.4 Electrochemical characterisation of ZnP modified electrodes

The cyclic voltammetric behaviour of ZnP covalently attached to the EDA modified HBDE surface *via* EDC/NHS amide coupling is presented in Figure 101. Cyclic voltammetry was performed in anhydrous CH₃CN/DMF solution (4:1 ratio), containing 0.1 M NBu₄BF₄ at a scan rate of 0.05 V s⁻¹. The associated peak positions and current responses (i.e. current

normalised by electrode area) are summarised in Table 59. Although no electrochemical data are available on the ZnP species covalently attached to the diamond surface, it can be expected to observe the ring based electrochemistry according to previous studies of zinc (II) protoporphyrin IX in solutions.⁶¹ As presented in Figure 101, ZnP covalent attachment to the EDA/HBDE results in restoration of electrochemical activity of the surface. This is in contrast to the situation when the electrode surface was blocked with the EDA layer, and no electrochemical activity was detected (Figure 90).

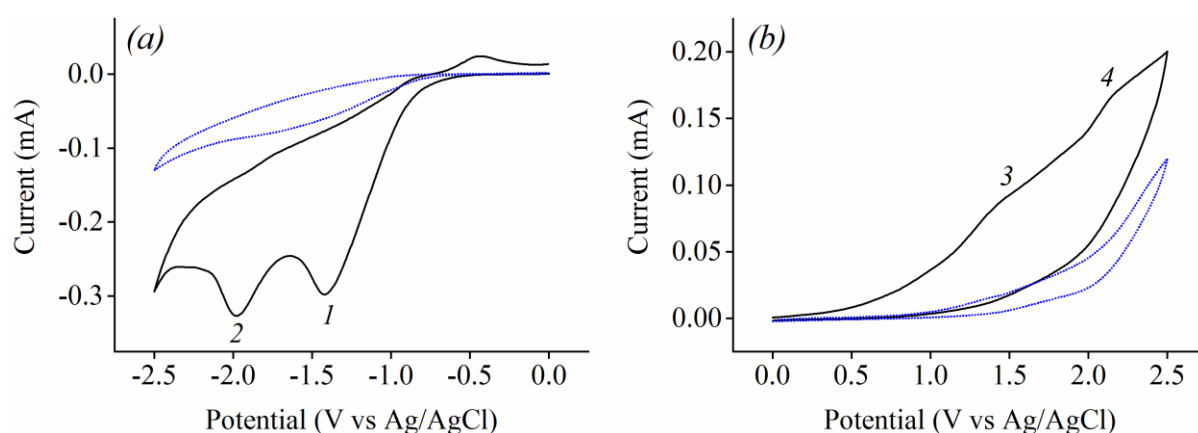


Figure 101 CV data recorded at (–) ZnP covalently attached to the EDA modified HBDE in CH₃CN/DMF solution (4:1 ratio), containing 0.1 M NBu₄BF₄ at a scan rate of 0.05 Vs⁻¹ in (a) a reduction regime from 0 to -2.5 V; (b) an oxidation regime from 0 to +2.5 V; (···) background scan

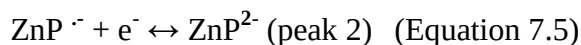
Table 59 Peak position and current response data recorded in CH₃CN/DMF solution (4:1 ratio), containing 0.1 M NBu₄BF₄ at ZnP covalently attached to the EDA modified HBDE during the first scan at the scan rate of 0.05 V s⁻¹

Peak	Peak Position (V)	Current (A)	Current Response (A cm ⁻²)
1	-1.42	-1.13×10 ⁻⁴	-2.83×10 ⁻⁴
2	-1.97	-7.33×10 ⁻⁵	-1.88×10 ⁻⁴
3	1.43	5.6×10 ⁻⁶	1.4×10 ⁻⁵
4	2.15	8.2×10 ⁻⁶	2.1×10 ⁻⁵

In the reduction regime (Figure 101 (a)), the peak 1 at -1.39 V vs Ag/AgCl corresponds to the formation of anion radical ZnP^{•-} due to the following reaction:⁶²



The second reduction peak 2 at -1.97 V arises from the formation of Zn porphyrin dianion at the electrode surface:⁶²



The overall reduction process is found to be irreversible since no oxidation waves coupled to the reduction peaks 1 and 2 were detected.

Figure 101 (b) shows an oxidation reaction for the freshly prepared ZnP covalently attached to the EDA modified HBDE surface. The presence of peak 3 and 4 at 1.43 V and 2.15 V respectively correspond to the formation of porphyrin cation radical and dication, as in the following scheme:⁶³



Again, no reduction peaks were detected in the reverse scan, thus suggesting the occurrence of the irreversible process.

The surface coverage of ZnP covalently attached to the EDA modified HBDE was estimated from the charge associated with the peak area under the reduction peak 1 in the first scan between -1.2 V and -1.6 V, in accordance with equation (NN). Thus, 5.2 nmol cm⁻² of ZnP was found to be immobilised on the EDA modified HBDE surface. The estimated surface coverage approximately is attributable to the bilayer presence with a monolayer of ZnP moieties standing on the electrode surface with the ring oriented perpendicular to the substrate and the second layer being attached due to π -stacking and hydrophobic effects.⁶⁴

The electrochemical behaviour of ZnP species physically adsorbed on the EDA modified HBDE without EDC/NHS coupling agent (Figure 102) differs significantly from that of ZnP covalently bonded to the EDA/HBDE. In the reduction scan (Figure 102 (a)), a ZnP adsorbed onto EDA/HBDE shows only one distinct peak at -1.43 V, likely due to the overlap between

the first and the second reduction steps of the ring system.⁶⁵ In the oxidation regime, a single peak related to the processes in Equation 7.6 and Equation 7.6 can be observed.

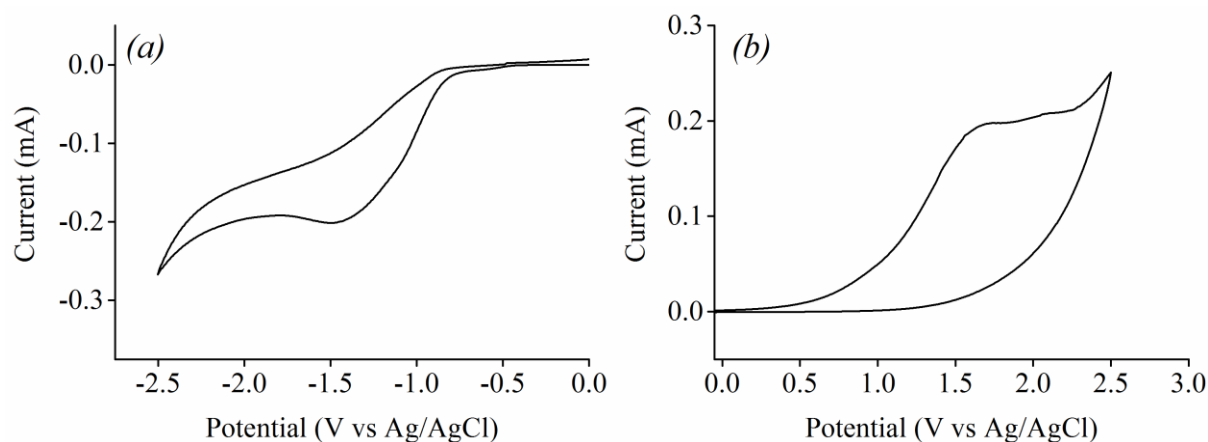


Figure 102 CV data recorded during the first scan at (–) ZnP adsorbed to the EDA modified HBDE in CH₃CN/DMF solution (4:1 ratio), containing 0.1 M NBu₄BF₄ at a scan rate of 0.05 Vs⁻¹ in (a) a reduction regime from 0 to -2.5 V; (b) an oxidation regime from 0 to +2.5 V

Another interesting feature, characteristic of ZnP physically adsorbed on the EDA/HBDE, is the reduction current response which is almost 30% smaller than that observed at ZnP covalently grafted to the EDA/HBDE surface. The electrochemical properties of the two surfaces are likely to be dependant on the morphology and structural integrity of the adsorbed and covalently bonded ZnP species.

In further experiments, ferrocenemethanol redox probe was chosen to investigate quantitatively the kinetics of the heterogeneous electron transfer at ZnP covalently attached and ZnP adsorbed onto EDA modified HBDE surface. Ferrocenemethanol redox mediator presents a convenient and electrochemically reversible, one electron transfer, outer sphere redox mediator.^{66,67}

Figure 103 shows cyclic voltammograms recorded at ZnP covalently attached and ZnP adsorbed onto EDA modified HBDE electrodes in 0.1 mM ferrocenemethanol, dissolved in anhydrous CH₃CN/DMF, containing 0.1 M NBu₄BF₄. It can be seen from Figure 103 that electrochemical performance was restored for both samples in contrast to the behaviour

observed at EDA modified HBDE, where the electrode was blocked due to the ethylenediamine presence (Figure 90). With the ZnP covalently attached to the EDA/HBDE surface, the oxidation peak current of ferrocenemethanol occurs at 0.398 V and the reduction peak current at 0.345 V. The peak currents recorded at ZnP covalently attached to the EDA/HBDE surface are greater than that of observed at ZnP adsorbed to the EDA/HBDE surface. The associated peak-to-peak separation, $\Delta E_{FcCH_2OH^+/FcCH_2OH^0}$, at ZnP covalently attached to the EDA/HBDE sample is 63 mV, whereas the $\Delta E_{FcCH_2OH^+/FcCH_2OH^0} = 81$ mV was estimated for the ZnP adsorbed on the EDA/HBDE.

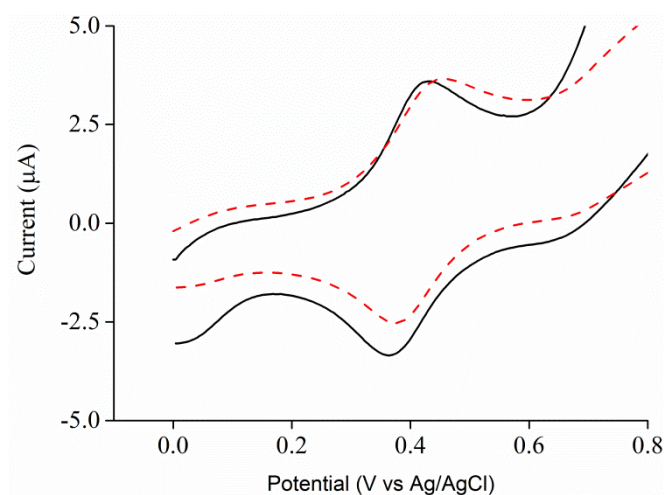


Figure 103 Cyclic voltammograms of 0.1 mM ferrocenemethanol dissolved in anhydrous CH_3CN/DMF , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 Vs^{-1} recorded at (–) ZnP covalently attached to the EDA modified HBDE; (– –) ZnP adsorbed onto the EDA modified HBDE

The electron transfer at a thin layer modified electrodes is known to occur *via* three possible pathways: (1) by tunnelling the electrons through the ZnP-EDA layer; (2) by permeation of the redox species into the ZnP-EDA layer which is followed by the diffusion in the layer and electron transfer at the HBDE electrode (membrane model) and (3) by the diffusion of the redox compound to pinhole or defect sites and electron transfer at the electrode surface (pinhole model).⁶⁸ Two approaches were undertaken in order to investigate how the electron

transfer rate constant of the $\text{FcCH}_2\text{OH}^+/\text{FcCH}_2\text{OH}^0$ redox process is influenced by the two differing films: ZnP covalently bonded to EDA/HBDE and ZnP adsorbed onto EDA/HBDE.

The first one estimates the apparent electron transfer rate constant of the $\text{FcCH}_2\text{OH}^+/\text{FcCH}_2\text{OH}^0$ redox reaction (without double layer or IR effects correction), k_{app}^0 , in accordance with the theoretical model of Nicholson⁶⁹ as described in Chapter 4. The diffusion coefficient of $2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was used in the calculations.⁷⁰

The value of $k_{\text{app}}^0 = 8.5 \times 10^{-2} \text{ cm s}^{-1}$ was estimated for the ZnP covalently attached to the EDA/HBDE surface. In contrast, the ZnP adsorbed on the EDA/HBDE shows slower electron transfer kinetics with the value of $k_{\text{app}}^0 = 1.2 \times 10^{-2} \text{ cm s}^{-1}$.

Further experiments for both electrodes were performed *via* impedance spectroscopy in 0.1 mM ferrocenemethanol dissolved in anhydrous $\text{CH}_3\text{CN}/\text{DMF}$, containing 0.1 M NBu_4BF_4 . The data recorded were fitted to the *Randles equivalent circuit* as shown in Figure 104. The latter consists of an uncompensated series resistance, R_S , which is connected to a constant phase element, CPE , in parallel with a charge transfer resistance, R_{CT} , and a Warburg impedance, Z_W , in series as presented in Figure 104 (a). The fitted data are summarised in Figure 98.

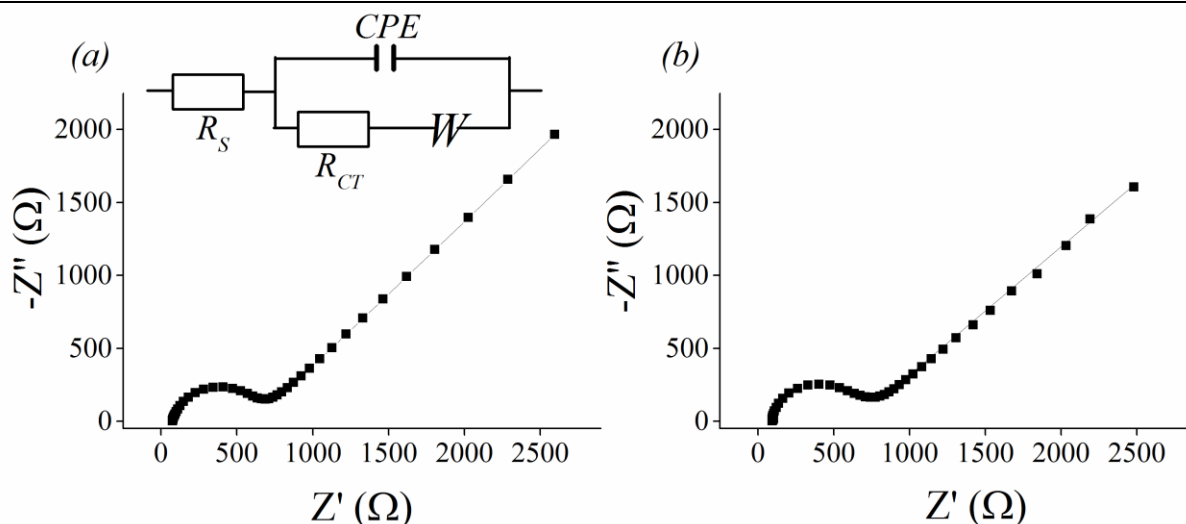


Figure 104 Nyquist impedance plot ($-Z''$, imaginary part of impedance vs. Z' , real part of impedance) recorded from (a) ZnP covalently binded to EDA/HBDE with the inset of the equivalent Randles circuit where R_s is the series resistance, CPE is the constant phase element, R_{CT} is the charge transfer resistance and W is the Warburg impedance; (b) ZnP adsorbed on the EDA/HBDE

Table 60 Heterogeneous electron transfer constants derived from impedance spectroscopy and Nicholson model

Sample	Impedance spectroscopy					Nicholson model	
	$R_s (\Omega)$	$C_p (\mu F)$	n in CPE	$R_{CT} (\Omega)$	$k^0 (\text{cm s}^{-1})$	$\Delta E_p (\text{mV})$	$k^0 (\text{cm s}^{-1})$
ZnP coval. binded to EDA/HBDE	76.0	1.2	0.94	564	1.2×10^{-2}	63	8.5×10^{-2}
ZnP adsorbed on EDA/HBDE	94.0	1.5	0.82	633	1.0×10^{-2}	81	1.2×10^{-2}

The analysis of the data gives a capacitance of $1.2 \mu F$ at ZnP covalently attached to the EDA/HBDE sample and a capacitance of $1.5 \mu F$ at ZnP adsorbed to the EDA/HBDE. The measured capacitance here is generally considered as the space charge capacitance at the electrode interface, as the double layer capacitance is normally of an order of magnitude larger.⁷¹ The differences observed above are likely to be related to the differences in the structural integrity (such as coverage, ZnP orientation and order) of the two differing ZnP layers.

Another useful insight can be obtained from the n parameter of the constant phase element that can be derived as a result of the fitting procedure. The n parameter describes the deviation of the constant phase element from the ideal capacitor ($n=1$) due to the surface

impurities as well as inhomogeneous distribution of local electroactive regions at the interface. The value of $n=0.94$ was obtained at ZnP covalently attached to the EDA/HBDE surface, whereas $n=0.82$ was estimated at the ZnP adsorbed at the EDA/HBDE. Therefore it can be suggested that ZnP covalently attached to the EDA/HBDE exhibits more uniform electroactivity at the interface than that of ZnP adsorbed to the EDA/HBDE.

The electron transfer rate given in Equation 7.8 was derived from the standard current-potential equation for the electrochemical reaction under the conditions of kinetic control:⁴⁴

$$k^0 = \frac{RT}{(n^2 F^2 c_{ox}^{\alpha} c_{red}^{\beta} R_{CT})} \quad (\text{Equation 7.8})$$

where R is the universal gas constant, T is the Kelvin temperature, n is the number of electrons transferred during the redox reaction, F is the Faraday constant, $c_{ox/red}$ is the concentration of the redox species, α, β are the transfer coefficients and R_{CT} is the charge transfer resistance.

The application of Equation 7.8 gives the value of $k^0=1.2 \times 10^{-2} \text{ cm s}^{-1}$ at ZnP covalently attached to the EDA/HBDE surface and $k^0=1.0 \times 10^{-2} \text{ cm s}^{-1}$ at the ZnP adsorbed at the EDA/HBDE. Again, the same quantitative trend as in CV measurements is observed, with the k^0 being the largest at the ZnP covalently attached to the EDA/HBDE.

Since both the Nicholson and impedance spectroscopy methods described above predict the k^0 values of an order of $10^{-2} \text{ cm s}^{-1}$, which are much larger than the rate constant estimated by considering only the tunnelling process ($k_{tunneling}^0 \sim 10^{-7} \text{ cm s}^{-1}$),⁷² it can be suggested that the defects sites can also contribute to the electron transfer process to the $\text{FcCH}_2\text{OH}^+/\text{FcCH}_2\text{OH}^0$ probe. The electron transfer *via* the membrane model was eliminated here, as the soaking experiments did not reveal any changes in cyclic voltammetry after the electrodes were exposed to ferrocenemethanol solution over 1 hour.

7.4.4.1 Zinc (II) protoporphyrin-diamond receptor of β -alanine

In order to explore the electrochemical application of Zn protoporphyrin-diamond interfaces further, the binding of β -alanine to a freshly prepared ZnP covalently attached to the EDA/HBDE surface was investigated by cyclic voltammetry. The alanine aliquots (200-800 μ M range) were added under stirring before the CV scan was carried out at each concentration. The CV data are presented in Figure 105. The peak positions and current responses are summarised in Table 61.

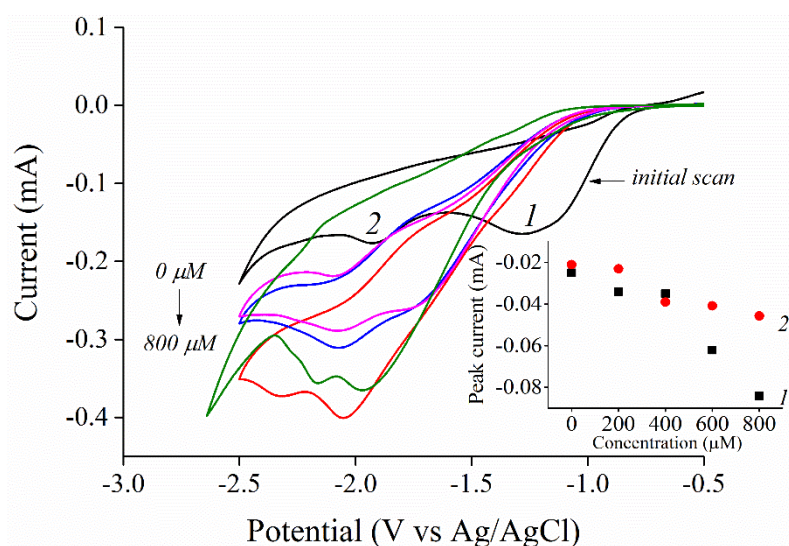


Figure 105 Cyclic voltammograms of ZnP covalently attached to the EDA modified HBDE in (–) anhydrous $\text{CH}_3\text{CN}/\text{DMF}$, containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 Vs^{-1} ; (–) in the presence of 200 μM of alanine; (–) 400 μM of alanine; (–) 600 μM of alanine; (–) 800 μM of alanine; inset of peak current versus alanine concentration

Table 61 Peak position and current response data recorded at hydrogen terminated boron-doped diamond electrode in 0.1 mM ethylenediamine dissolved in anhydrous CH_3CN , containing 0.1 M NBu_4BF_4 at a scan rate of 0.05 Vs^{-1}

Scan	Position of peak 1 (V)	Peak current 1 (A)	Current response of peak 1 (A cm^{-2})	Position of peak 2 (V)	Peak current 2 (A)	Current response of peak 2 (A cm^{-2})
1	-1.30	-2.5×10^{-5}	-6.25×10^{-5}	-1.90	-2.1×10^{-5}	-5.25×10^{-5}
2	-1.70	-3.4×10^{-5}	-7.13×10^{-5}	-2.02	-2.3×10^{-5}	-5.75×10^{-5}
3	-1.75	-3.5×10^{-5}	-8.75×10^{-5}	-2.08	-3.9×10^{-5}	-9.75×10^{-5}
4	-1.96	-6.2×10^{-5}	-1.55×10^{-4}	-2.16	-4.1×10^{-5}	-1.03×10^{-4}
5	-2.05	-8.4×10^{-5}	-2.10×10^{-4}	-2.33	-4.6×10^{-5}	-1.15×10^{-4}

In the first scan, prior to alanine addition, the reduction peak 1 and 2 at -1.3 V and at -1.9 V respectively correspond to the formation of the anion radical and dianion species as described earlier in Equation 7.4 and Equation 7.5. When $200\text{ }\mu\text{M}$ of alanine has been added, the peak 1 and 2 shift to -1.7 V and -2.0 V respectively, with the peak current density being significantly increased (inset of Figure 105). Similar trends have been obtained in the following scans as the concentration of alanine was increased (Table 61).

Hence the reduction potentials of ZnP covalently attached to EDA/HBDE surface are shifted to significantly lower values in the presence of alanine aliquots, it can be suggested that the axial bonding of alanine takes place, as the presence of a hydrophobic binding pocket and a Lewis acidic site (Zn) in the porphyrin system makes the ligation of the amino acid favourable (Figure 106).^{73,74}

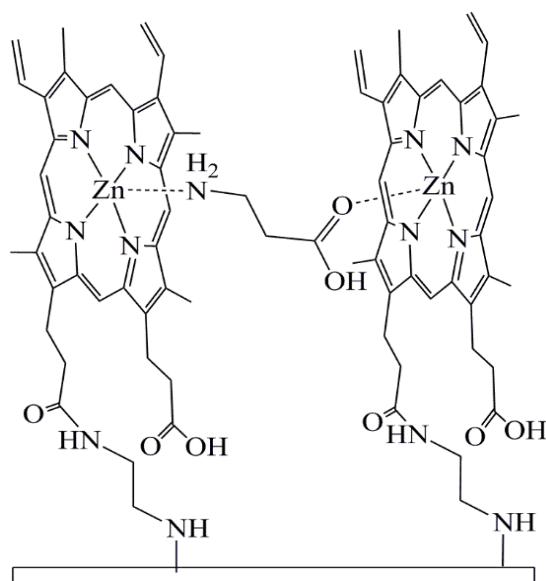


Figure 106 Schematic illustration of possible alanine binding mode

The increase in the current responses observed upon addition of the alanine aliquots is also consistent with the changes in charge transfer properties caused by the alanine binding. This behaviour is analogous with the previous studies by Hecht *et al.*,⁷³ where the addition of

imidazole to a Fe protoporphyrin immobilised on a gold electrode resulted in significant current enhancement.

7.5 Concluding remarks

For the first time, Chapter 7 investigated the creation of biomimetic diamond hybrid interface *via* covalent attachment of zinc (II) protoporphyrin IX to the ethylenediamine modified boron-doped diamond electrode. A new electrochemical route to covalently modify the diamond surface with NH₂ groups prior to covalent binding of the porphyrin complex has been developed. As confirmed *via* XPS study, this method was found to be more successful than a previously reported scheme involving the reaction of diamond with amines under base conditions.

Both covalent attachment and physical adsorption of the Zinc (II) protoporphyrin IX complexes to the ethylenediamine modified hydrogen terminated surface were found to be successful. However, significant variations in stability and electrochemical behaviour were observed depending on the preparation route. It has been demonstrated using XPS that a stable ZnP layer can be immobilized in the result of the covalent attachment *via* EDC/NHS amide coupling agent. In this case, the formation of peptide bonds between the COOH groups of the ZnP species and NH₂ moieties of the EDA modified boron-doped diamond was detected by XPS.

The solvent washing and subsequent ultrasonication procedure in CH₂Cl₂, DMF and THF solutions was found to introduce little changes to the ZnP covalently attached to the EDA/HBDE surface, whereas ZnP adsorbed to the EDA/HBDE was easily washed off as a result of the same procedure.

The electrochemical behaviour of ZnP covalently attached to the EDA/HBDE was compared to ZnP attached *via* a physical adsorption method. The electron transfer rate constant was

derived both via the Nicholson method and impedance spectroscopy. The rate constant observed with FcCH_2OH , an outer-sphere electron transfer mediator, is likely to be dependent upon the structural integrity of the ZnP film. The lower rate constant on ZnP adsorbed on the EDA/HBDE sample is consistent with a lower order of the porphyrin structural units on the diamond surface. This demonstrates the superior merits of ZnP covalently attached to the EDA/HBDE in electrochemical applications. Changes in the electrochemical response upon addition of β -alanine down to micromolar concentration ranges were observed, thus suggesting the ligation process that occurs in the system.

In summary, this investigation demonstrates a successful preparation of covalently attached zinc protoporphyrin-diamond receptors for β -alanine.

7.6 References

- 1 Kasemo, B. Biological surface science. *Surface Science* **500**, 656-677, doi:http://dx.doi.org/10.1016/S0039-6028(01)01809-X (2002).
- 2 Goeting, C. H., Marken, F., Gutierrez-Sosa, A., Compton, R. G. & Foord, J. S. Electrochemically induced surface modifications of boron-doped diamond electrodes: an X-ray photoelectron spectroscopy study. *Diamond and Related Materials* **9**, 390-396 (2000).
- 3 Goeting, C. H., Marken, F., Gutierrez-Sosa, A., Compton, R. G. & Foord, J. S. Boron-doped diamond electrodes: Growth, surface characterisation and sono-electrochemical applications. *New Diamond and Frontier Carbon Technology* **9**, 207-228 (1999).
- 4 Goeting, C. H., Marken, F., Osborn, A. R., Compton, R. G. & Foord, J. S. Surface Modification of Chemical Vapor Deposited Diamond Induced by Power Ultrasound. *Electrochemical and Solid State Letters* **4**, E29-E31, doi:10.1149/1.1377488 (2001).
- 5 Compton, R. G., Foord, J. S. & Marken, F. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* **15**, 1349-1363, doi:10.1002/elan.200302830 (2003).
- 6 Kulisch, W. *et al.* Investigation of the UV/O₃ treatment of ultrananocrystalline diamond films. *Surface and Interface Analysis* **42**, 1152-1155, doi:10.1002/sia.3264 (2010).
- 7 Ghodbane, S. *et al.* HREELS Investigation of the Surfaces of Nanocrystalline Diamond Films Oxidized by Different Processes. *Langmuir* **26**, 18798-18805, doi:10.1021/la1032652 (2010).
- 8 Ohtani, B. *et al.* Surface functionalization of doped CVD diamond via covalent bond. An XPS study on the formation of surface-bound quaternary pyridinium salt. *Chem. Lett.*, 953-954, doi:10.1246/cl.1998.953 (1998).
- 9 Sotowa, K.-I., Amamoto, T., Sobana, A., Kusakabe, K. & Imato, T. Effect of treatment temperature on the amination of chlorinated diamond. *Diamond and*

- Related Materials* **13**, 145-150, doi:http://dx.doi.org/10.1016/j.diamond.2003.10.029 (2004).
- 10 Krueger, A. & Lang, D. Functionality is Key: Recent Progress in the Surface Modification of Nanodiamond. *Advanced Functional Materials* **22**, 890-906, doi:10.1002/adfm.201102670 (2012).
 - 11 Smentkowski, V. S., Yates, J. T., Chen, X. J. & Goddard, W. A. Fluorination of diamond - C4F9I and CF3I photochemistry on diamond(100). *Surface Science* **370**, 209-231, doi:10.1016/s0039-6028(96)00894-1 (1997).
 - 12 Freedman, A. & Stinespring, C. D. FLUORINATION OF DIAMOND (100) BY ATOMIC AND MOLECULAR-BEAMS. *Applied Physics Letters* **57**, 1194-1196, doi:10.1063/1.104097 (1990).
 - 13 Ferro, S. & De Battisti, A. The 5-V window of polarizability of fluorinated diamond electrodes in aqueous solutions. *Analytical Chemistry* **75**, 7040-7042, doi:10.1021/ac034717r (2003).
 - 14 Koch, H. *et al.* Plasma amination of ultrananocrystalline diamond/amorphous carbon composite films for the attachment of biomolecules. *Diamond Relat. Mater.* **20**, 254-258, doi:10.1016/j.diamond.2010.12.010 (2011).
 - 15 Zhang, G.-J. *et al.* DNA Micropatterning on Polycrystalline Diamond via One-Step Direct Amination. *Langmuir* **22**, 3728-3734, doi:10.1021/la050883d (2006).
 - 16 Bongrain, A. *et al.* High Sensitivity of Diamond Resonant Microcantilevers for Direct Detection in Liquids As Probed by Molecular Electrostatic Surface Interactions. *Langmuir* **27**, 12226-12234, doi:10.1021/la2013649 (2011).
 - 17 Bijmens, N. *et al.* Synthetic diamond films as a platform material for label-free protein sensors. *Physica Status Solidi a-Applications and Materials Science* **206**, 520-526, doi:10.1002/pssa.200880485 (2009).
 - 18 Huang, H. *et al.* Ultrananocrystalline Diamond Thin Films Functionalized with Therapeutically Active Collagen Networks. *The Journal of Physical Chemistry B* **113**, 2966-2971, doi:10.1021/jp9004086 (2009).
 - 19 Yao, S. A. *et al.* Covalent Attachment of Catalyst Molecules to Conductive Diamond: CO₂ Reduction Using "Smart" Electrodes. *J. Am. Chem. Soc.* **134**, 15632-15635, doi:10.1021/ja304783j (2012).
 - 20 Jarrar, H., Rolland, M., Downard, A. J. & Cretin, M. Glucose biosensor at ethylenediamine modified carbon electrode. *Sens. Lett.* **9**, 2368-2370, doi:10.1166/sl.2011.1772 (2011).
 - 21 Labbé, R. F., Vreman, H. J. & Stevenson, D. K. Zinc Protoporphyrin: A Metabolite with a Mission. *Clinical Chemistry* **45**, 2060-2072 (1999).
 - 22 Zhu, Y. & Silverman, R. B. Electronic Effects of Peripheral Substituents at Porphyrin Meso Positions. *J. Org. Chem.* **72**, 233-239, doi:10.1021/jo061951j (2007).
 - 23 *International Union of Pure and Applied Chemistry Gold Book.*
 - 24 Buchler, J. W. 157-231 (Elsevier).
 - 25 Mizutani, T., Wada, K. & Kitagawa, S. Molecular Recognition of Amines and Amino Esters by Zinc Porphyrin Receptors: Binding Mechanisms and Solvent Effects. *J. Org. Chem.* **65**, 6097-6106, doi:10.1021/jo000557x (2000).
 - 26 Mizutani, T., Wada, K. & Kitagawa, S. Porphyrin Receptors for Amines, Amino Acids, and Oligopeptides in Water. *J. Am. Chem. Soc.* **121**, 11425-11431, doi:10.1021/ja9922126 (1999).
 - 27 Imai, H., Munakata, H., Uemori, Y. & Sakura, N. Chiral Recognition of Amino Acids and Dipeptides by a Water-Soluble Zinc Porphyrin. *Inorg. Chem.* **43**, 1211-1213, doi:10.1021/ic0302837 (2004).

- 28 Tanasova, M. *et al.* An Unusual Conformation of α -Haloamides Due to Cooperative Binding with Zincated Porphyrins. *Eur. J. Org. Chem.*, 4242-4253, S4242/4241-S4242/4106, doi:10.1002/ejoc.200900089 (2009).
- 29 Nappa, M. & Valentine, J. S. The influence of axial ligands on metalloporphyrin visible absorption spectra. Complexes of tetraphenylporphinatozinc. *J. Am. Chem. Soc.* **100**, 5075-5080, doi:10.1021/ja00484a027 (1978).
- 30 Miller, J. R. & Dorough, G. D. Pyridinate complexes of some metallo-derivatives of tetraphenylporphine and tetraphenylchlorine. *J. Am. Chem. Soc.* **74**, 3977-3981 (1952).
- 31 Shinohara, T. *et al.* Identification of a G Protein-coupled Receptor Specifically Responsive to β -Alanine. *Journal of Biological Chemistry* **279**, 23559-23564, doi:10.1074/jbc.M314240200 (2004).
- 32 Wang, H., Griffiths, J.-P., Egdell, R. G., Moloney, M. G. & Foord, J. S. Chemical Functionalization of Diamond Surfaces by Reaction with Diaryl Carbenes. *Langmuir* **24**, 862-868, doi:10.1021/la702701p (2008).
- 33 Bedel-Cloutour, C. H., Maneta-Peyret, L., Pereyre, M. & Bezian, J.-H. Synthesis of a monoclonal antibody-indium-111-porphyrin conjugate. *Journal of Immunological Methods* **144**, 35-41, doi:http://dx.doi.org/10.1016/0022-1759(91)90227-7 (1991).
- 34 Hirano, C. & Imae, T. Electrochemical properties of protoporphyrin IX zinc(II) films. *Journal of Colloid and Interface Science* **280**, 478-483, doi:http://dx.doi.org/10.1016/j.jcis.2004.08.027 (2004).
- 35 Jiang, K. *et al.* Protein immobilization on carbon nanotubes via a two-step process of diimide-activated amidation. *Journal of Materials Chemistry* **14**, 37-39, doi:10.1039/b310359e (2004).
- 36 <http://www.casaxps.com/>.
- 37 Shirley, D. A. High-resolution x-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B* **[3]5**, 4709-4714 (1972).
- 38 Taki, Y. & Takai, O. XPS structural characterization of hydrogenated amorphous carbon thin films prepared by shielded arc ion plating. *Thin Solid Films* **316**, 45-50, doi:http://dx.doi.org/10.1016/S0040-6090(98)00386-1 (1998).
- 39 Ley, L., Graupner, R., Cui, J. B. & Ristein, J. Electronic properties of single crystalline diamond surfaces. *Carbon* **37**, 793-799, doi:10.1016/s0008-6223(98)00273-5 (1999).
- 40 Ferro, S., Dal Colle, M. & De Battisti, A. Chemical surface characterization of electrochemically and thermally oxidized boron-doped diamond film electrodes. *Carbon* **43**, 1191-1203, doi:http://dx.doi.org/10.1016/j.carbon.2004.12.012 (2005).
- 41 Barbier, B., Pinson, J., Desarmot, G. & Sanchez, M. Electrochemical bonding of amines to carbon fiber surfaces toward improved carbon-epoxy composites. *J. Electrochem. Soc.* **137**, 1757-1764, doi:10.1149/1.2086794 (1990).
- 42 Barnes, K. K. & Mann, C. K. Electrochemical oxidation of primary aliphatic amines. *J. Org. Chem.* **32**, 1474-1479, doi:10.1021/jo01280a037 (1967).
- 43 Deinhammer, R. S., Ho, M., Anderegg, J. W. & Porter, M. D. Electrochemical oxidation of amine-containing compounds: a route to the surface modification of glassy carbon electrodes. *Langmuir* **10**, 1306-1313, doi:10.1021/la00016a054 (1994).
- 44 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley & Sons, 2001).
- 45 Gubskaya, A. V. & Kusalik, P. G. Molecular Dynamics Simulation Study of Ethylene Glycol, Ethylenediamine, and 2-Aminoethanol. 1. The Local Structure in Pure Liquids. *The Journal of Physical Chemistry A* **108**, 7151-7164, doi:10.1021/jp0489222 (2004).

- 46 Munir, A. *et al.* Detailed Electrochemistry of the Environmental Toxin Ethylene Diamine. *Journal of The Electrochemical Society* **161**, H370-H374, doi:10.1149/2.044406jes (2014).
- 47 Cruickshank, A. C., Tan, E. S. Q., Brooksby, P. A. & Downard, A. J. Are redox probes a useful indicator of film stability? An electrochemical, AFM and XPS study of electrografted amine films on carbon. *Electrochem. Commun.* **9**, 1456-1462, doi:10.1016/j.elecom.2007.02.004 (2007).
- 48 C.D. Wagner, W. M. R., L.E. Davis, J.F. Moulder. *Handbook of X-ray photoelectron spectroscopy*. (Perkin-Elmer Corporation, Physical Electronics Division, 1979).
- 49 Briggs, D., Seah, M. P. & Editors. *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*. (John Wiley and Sons, 1983).
- 50 Beamson, G. & Briggs, D. High-resolution monochromated x-ray photoelectron spectroscopy of organic polymers: a comparison between solid-state data for organic polymers and gas-phase data for small molecules. *Mol. Phys.* **76**, 919-936, doi:10.1080/00268979200101761 (1992).
- 51 Lindquist, J. M., Ziegler, J. P. & Hemminger, J. C. Photoelectron spectroscopy studies of the hydrogenation of cyanogen on platinum(111): comparison with hydrogen cyanide and ethylenediamine. *Surf. Sci.* **210**, 27-45, doi:10.1016/0039-6028(89)90101-5 (1989).
- 52 Wagner, C. D. *et al.* Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *SIA, Surf. Interface Anal.* **3**, 211-225, doi:10.1002/sia.740030506 (1981).
- 53 Agnes, C. *et al.* Local bio-sensitization of nanocrystalline Boron Doped Diamond surfaces with biotin using electrospeotting. *Sens. Lett.* **7**, 872-879, doi:10.1166/sl.2009.1165 (2009).
- 54 Omnes, F. J., Agnes, C., Ruffinatto, S. & Mailley, P. Functionalization of sp³ hybridized carbon, silicon, and/or germanium surfaces for the preparations of biochips. FR2947544A1 (2011).
- 55 Fischer, M. J. E. Amine coupling through EDC/NHS: a practical approach. *Methods Mol. Biol. (Totowa, NJ, U. S.)* **627**, 55-73, doi:10.1007/978-1-60761-670-2_3 (2010).
- 56 Tidwell, C. D. *et al.* Static time-of-flight secondary ion mass spectrometry and x-ray photoelectron spectroscopy characterization of adsorbed albumin and fibronectin films. *Surf. Interface Anal.* **31**, 724-733, doi:10.1002/sia.1101 (2001).
- 57 Ithurbide, A., Frateur, I., Galtayries, A. & Marcus, P. XPS and flow-cell EQCM study of albumin adsorption on passivated chromium surfaces: Influence of potential and pH. *Electrochim. Acta* **53**, 1336-1345, doi:10.1016/j.electacta.2007.04.109 (2007).
- 58 Wagner, C. D. NIST X-ray Photoelectron Spectroscopy (XPS) database. 62 pp. (Natl. Inst. Stand. Technol., 1991).
- 59 Briggs, D. & Editor. *Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy*. (Heyden, 1977).
- 60 Spadavecchia, J., Methivier, C., Landoulsi, J. & Pradier, C.-M. Interaction of ZnII Porphyrin with TiO₂ Nanoparticles: From Mechanism to Synthesis of Hybrid Nanomaterials. *ChemPhysChem* **14**, 2462-2469, doi:10.1002/cphc.201300193 (2013).
- 61 Kadish, K. M., Smith, K. M., Guiland, R. & Editors. *The Porphyrin Handbook: Volume 16 / Phthalocyanines: Spectroscopic and Electrochemical Characterization*. (Academic Press, 2003).
- 62 Lin, C.-I., Fang, M.-Y. & Cheng, S.-H. Substituent and axial ligand effects on the electrochemistry of zinc porphyrins. *J. Electroanal. Chem.* **531**, 155-162, doi:10.1016/S0022-0728(02)01056-2 (2002).

- 63 Kadish, K. M. & Rhodes, R. K. Reactions of metalloporphyrin π radicals. 2. Thin-layer spectroelectrochemistry of zinc tetraphenylporphyrin cation radicals and dications in the presence of nitrogenous bases. *Inorg. Chem.* **20**, 2961-2966, doi:10.1021/ic50223a041 (1981).
- 64 Knoblen, W., Crego-Calama, M. & Brongersma, S. H. Comparison of nitric oxide binding to different pure and mixed protoporphyrin IX monolayers. *Sensors and Actuators B: Chemical* **166–167**, 349-356, doi:http://dx.doi.org/10.1016/j.snb.2012.02.068 (2012).
- 65 Kadish, K. M. *et al.* Influence of Electronic and Structural Effects on the Oxidative Behavior of Nickel Porphyrins. *Inorg. Chem.* **41**, 6673-6687, doi:10.1021/ic0200702 (2002).
- 66 Connelly, N. G. & Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev. (Washington, D. C.)* **96**, 877-910, doi:10.1021/CR940053X (1996).
- 67 Carney, M. J., Lesniak, J. S., Likar, M. D. & Pladziewicz, J. R. Ferrocene derivatives as metalloprotein redox probes: electron-transfer reactions of ferrocene and ferricenium ion derivatives with cytochrome c. *J. Am. Chem. Soc.* **106**, 2565-2569, doi:10.1021/ja00321a013 (1984).
- 68 Porter, M. D., Bright, T. B., Allara, D. L. & Chidsey, C. E. D. Spontaneously organized molecular assemblies. 4. Structural characterization of n-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy, and electrochemistry. *Journal of the American Chemical Society* **109**, 3559-3568, doi:10.1021/ja00246a011 (1987).
- 69 Nicholson, R. S. Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. *Anal. Chem.* **37**, 1351-1355, doi:10.1021/ac60230a016 (1965).
- 70 Tsierkezos, N. Cyclic Voltammetric Studies of Ferrocene in Nonaqueous Solvents in the Temperature Range from 248.15 to 298.15 K. *J Solution Chem* **36**, 289-302, doi:10.1007/s10953-006-9119-9 (2007).
- 71 Morrison, S. R. *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*. (Plenum Press, 1980).
- 72 Cannes, C., Kanoufi, F. & Bard, A. J. Cyclic voltammetry and scanning electrochemical microscopy of ferrocenemethanol at monolayer and bilayer-modified gold electrodes. *Journal of Electroanalytical Chemistry* **547**, 83-91, doi:http://dx.doi.org/10.1016/S0022-0728(03)00192-X (2003).
- 73 Das, A., Trammell, S. A. & Hecht, M. H. Electrochemical and ligand binding studies of a de novo heme protein. *Biophys. Chem.* **123**, 102-112, doi:10.1016/j.bpc.2006.04.011 (2006).
- 74 Kadish, K. M. & Van, C. E. Electrochemistry of porphyrins and related macrocycles. *J. Solid State Electrochem.* **7**, 254-258, doi:10.1007/s10008-002-0306-3 (2003).