

Surface chemical and particle modification of diamond electrodes



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Abstract

Boron-doped diamond electrodes (BDDs) offer a range of advantageous properties for electrochemical sensing. They are normally used with a chemical surface termination comprised of oxygen species, but hydrogen terminations are also stable. A hydrogen surface termination offers different hydrophobicity, band alignments and surface conductivity of the BDD-electrolyte interface. The broad aim of this thesis is therefore to establish the influence of surface termination on the electrochemical sensing properties of BDDs. The work also encompasses the properties of BDD electrodes decorated with metal, metal hydroxide and two types of carbon black particles that introduce additional chemical functionality. The structural and chemical properties of the prepared BDD interfaces are examined with a range of experimental techniques including SEM, AFM and XPS. This information is then related to electrochemical performance as measured using cyclic voltammetry and other dynamic electrochemical methods.

The first study explores the use of gold nanoparticles on BDD for mercury sensing. BDD decoration was achieved by either electrochemical deposition or by drop coating pre-formed nanoparticles onto hydrogen- and oxygen-terminated BDDs. Although the deposition methods affected characteristics such as morphology and dispersion of the gold nanoparticles on the BDDs, the BDD surface termination was of greater importance than the deposition method for the purposes of mercury sensing. In particular, the gold nanoparticles from either deposition method were in the best electrical communication with the underlying electrode when the BDD had a hydrogen-terminated surface, on which the gold nanoparticles were also notably more stable, making the hydrogen-terminated, gold-decorated BDD the electrode of choice for mercury sensing.

The second study examines commercial BDD electrodes functionalised with electrodeposited nickel hydroxide for the electrochemical oxidation of glucose. The results were significantly affected by variability in the BDDs used. In general, nickel hydroxide on hydrogen-terminated BDDs had consistently larger glucose oxidation currents in accordance with the increased surface conductivity and the better electrical contact of hydrogen-terminated BDDs. However, the nickel hydroxide-decorated, oxygen-terminated BDD had more stable and reproducible oxidation currents in the glucose concentration range of 0.1-1.3 mM.

The third and fourth studies investigate the role of surface termination in the modification of BDDs by carbon black. Acetylene carbon black and Monarch 430 carbon black, which differ in their chemical composition and physical structure, were used to investigate the electro-oxidation of acetaminophen and hydroquinone. The electrochemical properties of the electrodes depended on both the BDD surface termination and the carbon black. The detection limit for acetaminophen was 100 nM for hydrogen-terminated BDDs and dropped to a state-of-the-art 10 nM when modified by carbon black. A similar performance was not obtained with oxygen-terminated BDDs even in the presence of carbon black. With regards to hydroquinone, hydrogen-terminated BDDs displayed a competitive detection limit of 0.5 μ M that was not improved by carbon black decoration. In contrast, oxygen-terminated BDDs were largely inactive to the electro-oxidation of hydroquinone, although some activity could be observed with carbon black modification.

The thesis concludes with a discussion of key results and suggests future research topics.

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Abbreviations

The following table contains the most common abbreviations used in this thesis.

Ac	acetaminophen
ACB	acetylene carbon black
AFM	atomic force microscopy
BDD	boron-doped diamond
BDDH	hydrogen-terminated, boron-doped diamond
BDDO	oxygen-terminated, boron-doped diamond
CB	Monarch 430 carbon black
CNT	carbon nanotubes
CV	cyclic voltammetry
CV-AuNPs	gold nanoparticles deposited by cyclic voltammetry
DC	drop-cast
DC-AuNPs	drop-cast gold nanoparticles
DPV	differential pulse voltammetry
HQ	hydroquinone
LSV	linear sweep voltammetry
NP	nanoparticle
PB	sodium phosphate buffer
PbUPD	lead underpotential deposition
RSF	relative sensitivity factor
SEM	scanning electron microscopy
SWV	square wave voltammetry
UHV	ultra-high vacuum
XPS	x-ray photoelectron spectroscopy

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Chapter 1

Introduction

Carbon is an element found in a variety of allotropes, many of which are chemically stable, highly conducting and available at fairly low costs.[1, 2] These properties have made carbon-based materials highly desirable for use in various branches of chemistry and materials engineering including, but not limited to, aerospace structures, lubrication, drug delivery in medicine, and chemical sensing.[3] The more commonly used carbon allotropes are amorphous carbon, graphite and diamond, of which the latter is of growing interest as an electrode material. Diamond is sp^3 hybridised and takes a face-centred cubic structure with a lattice parameter of 3.57 Å[4] and is shown schematically in Fig. 1.1. This chapter discusses the historical development of synthetic diamond, the chemical doping and surface termination used to obtain diamond with specific properties, and how doped diamond is used in electrochemistry. The chapter then discusses the modification of the diamond surface with small particles to alter the electrochemical performance of the diamond electrode. The types of particle modification presented include modification with metals, metal oxides as well as other carbon allotropes. The chapter ends with a brief outline of the remaining chapters in this thesis.

1.1 Synthetic diamond

The high thermal conductivity and extreme hardness of diamond have been known for at least 2,000 years;[6] the latter characteristic has been exploited by engravers for millenia and,

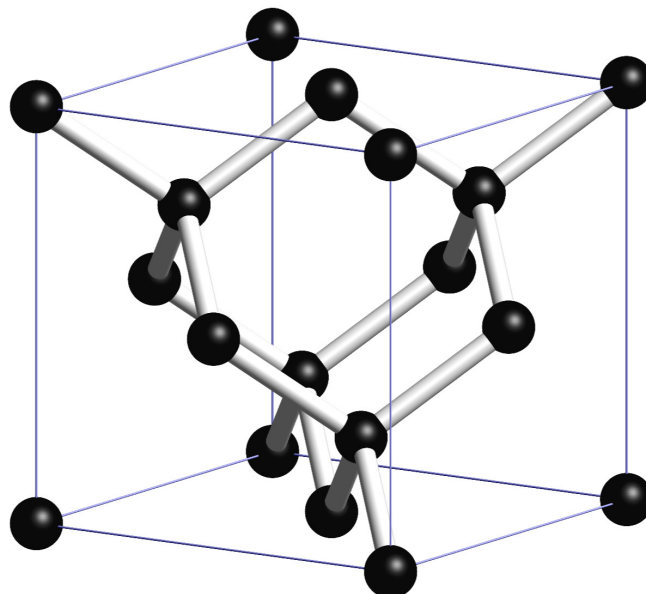


Figure 1.1: The face-centred cubic crystal structure of diamond. The black balls represent carbon atoms, the white rods are bonds. The blue lines are all equivalent to the lattice parameter. Adapted from [4, 5].

in more modern times, has made diamond useful in drilling.[6, 7] After Lavoisier reported diamond to be a form of carbon in 1772,[8] synthesising artificial diamond became an active area of research. One of the earliest claims of successfully synthesised artificial diamond was published by J. B. Hannay in 1879, but although his idea of using heat and pressure to convert common carbon sources such as naphtha, lamp-black and paraffin into diamond [9] was scientifically sound, the actual execution was beyond the scope of 19th century laboratory equipment.¹[10] It was not until nearly a hundred years later that the first artificial diamond was successfully synthesised.[10] Synthetic diamond has since become readily available, primarily due to the development of chemical vapour deposition techniques.[11, 12]

CVD diamond is made at high temperatures and low pressures by reacting simple ingredients such as methane and hydrogen, where the methane is the carbon source and hydrogen is the carrier gas.[13–15] Schematics of common microwave CVD reactors are shown in Fig. 1.2. The hydrogen carrier gas, which prevents surface reconstruction after the growth process has completed, is the largest component of the gas mixture used during the CVD growth process.[15, 16] Even during the growth process, the dangling carbon bonds must be

¹Most of Hannay’s reaction tubes, not to mention his furnace, exploded. He remarked on the difficulty in reproducing his experiments himself.

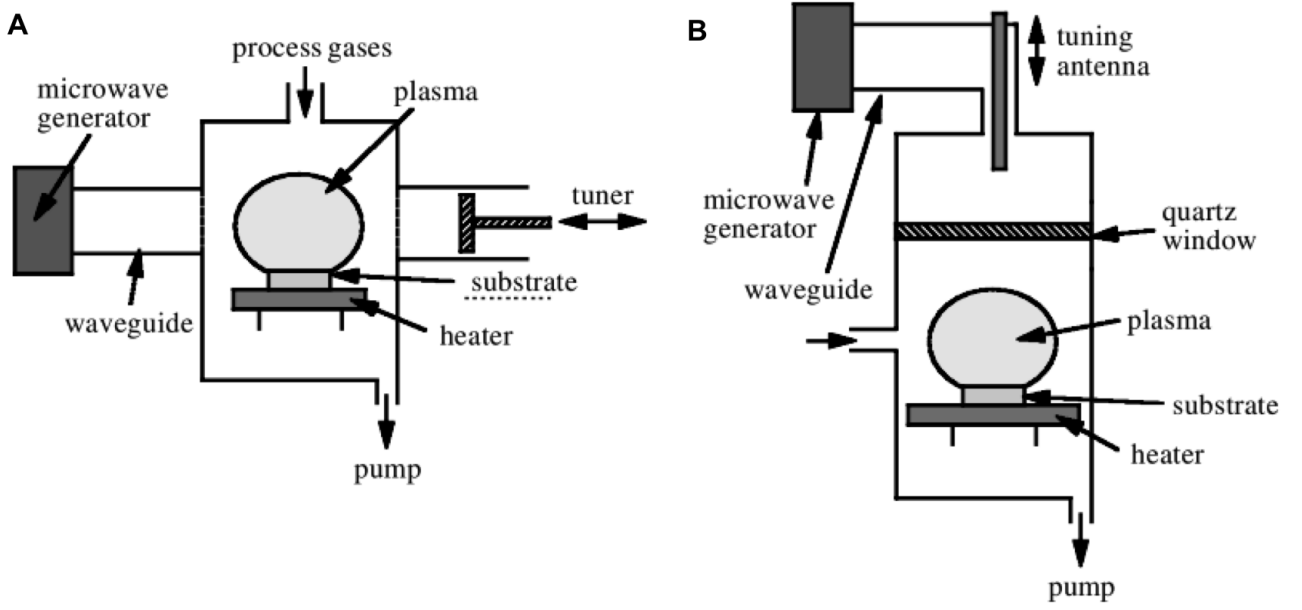


Figure 1.2: Schematics of common CVD reactors. A) A NIRIM-type reactor and B) an ASTEX-type reactor. From [14]

hydrogen-terminated to sterically hinder the bond saturation that would otherwise cause the growing diamond surface to revert to the graphitic structure.[15–17] Other elements — such as boron, nitrogen or phosphorus — can also be included in the gaseous mixture to dope the diamond and thereby change the electronic properties of the diamond.[12] Diamond, by itself, is an insulator with a bandgap of 5.5 eV.[16, 18] Doping the diamond with boron, which is usually done by including B_2H_6 at a few ppm into the CVD reaction mixture,[14] introduces an acceptor level with a charge carrier activation energy of 0.37 eV above the diamond valence band.[19] Doping the diamond with nitrogen or phosphorus introduces donor levels 1.6 and 0.6 eV below the diamond conduction band, respectively, which results in n-type conductivity.[12]

Most CVD diamond films are polycrystalline with faceted edges and grain sizes ranging from a few nanometers to hundreds of micrometers.[14] A typical SEM of a polycrystalline, boron-doped diamond (BDD) is shown in Fig. 1.3.

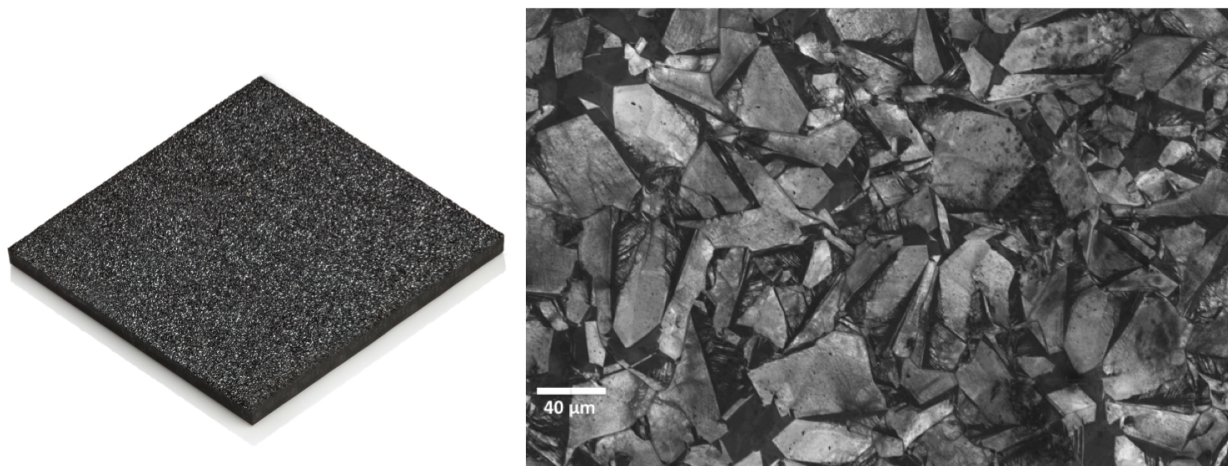


Figure 1.3: A black boron-doped diamond wafer (1 cm^2) grown by microwave plasma CVD from Element 6 (right) and a typical SEM image of the as-grown BDD surface (left).

1.1.1 Boron-doped diamond for electrochemistry

BDD is the most commonly used form of conducting diamond.[19, 20] During BDD synthesis, doping levels need to be carefully controlled since properties of BDD are highly sensitive to doping levels; doping levels of $10^{17} - 10^{18}\text{ cm}^{-3}$ results in p-type semiconducting BDD while higher doping levels ($10^{20} - 10^{21}\text{ cm}^{-3}$) results in metal-like conductivity.[19, 20] The colour of the diamond gives the approximate doping level: blue diamond contains enough boron to make the electrode a semi-conductor while black diamond has sufficient boron content to make the electrode metal-like.[21] Inclusion of non-diamond carbon in the diamond can also contribute to a black colour.[21] Fig. 1.3 shows a metal-like BDD used in electrochemistry and Fig. 1.4 shows the variation in conductivity with boron concentration over a range of temperatures. Boron distribution in the BDD samples is not homogeneous; in addition to aggregating along grain boundaries, boron uptake varies with the crystal orientation of the grain with higher uptake in (111) than (100) grains.[23] This can result in some grains having higher conductivity and different electrochemical responses than others.[24]

BDD is, by now, a well-established electrode material [21] due to its excellent electrochemical properties such as a wide potential window, low background current, low capacitance and chemical stability even in corrosive environments.[18, 25–30] The wide potential window, 3.2 V in aqueous media,[31] allows for the study of electrochemical processes that

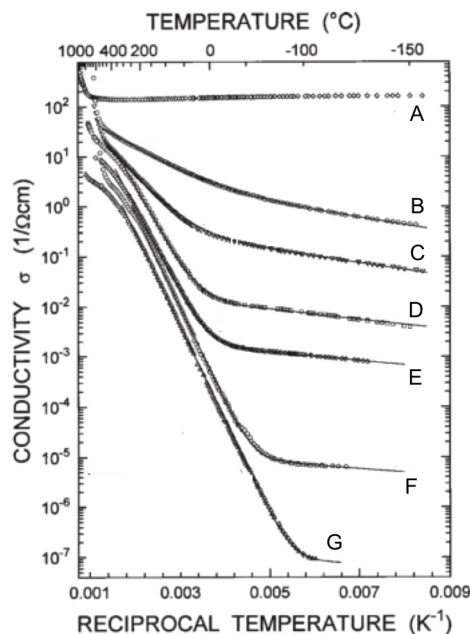


Figure 1.4: The conductivity variation with temperature for BDDs with a boron concentration of A) $3 \times 10^{20} \text{ cm}^{-3}$ B) $1.2 \times 10^{20} \text{ cm}^{-3}$ C) $4 - 5 \times 10^{19} \text{ cm}^{-3}$ D) $1.2 \times 10^{19} \text{ cm}^{-3}$ E) $3 - 9 \times 10^{18} \text{ cm}^{-3}$ G) $7 - 15 \times 10^{17} \text{ cm}^{-3}$. From [22]

is not possible with other, more conventional electrodes such as platinum or glassy carbon. The low capacitive background current of BDD enhances the signal-to-noise ratio of the electrochemical current, which improves the limit of detection of analytes, while the chemical stability makes BDD resistant to fouling. These properties make BDD an excellent electrode choice for electroanalysis.[18] There are several reviews of BDD electrochemistry in the literature, covering topics ranging from synthesis procedures, electrochemical properties and analytical applications.[32–36]

1.2 Surface chemistry of synthetic diamond

In addition to the wide potential window, low background current and chemical stability that make BDD an excellent electrode material, diamond can also be given stable surface terminations. Changes in the surface termination of diamond affect changes in the electronic properties that can be desirable for tuning the behaviour of diamond.[16, 17, 25, 33, 37] Most commonly, the diamond surface is either oxygen-terminated or hydrogen-terminated, though other species can be chemically adsorbed onto the surface.[17] This thesis concerns itself only

with oxygen- and hydrogen-terminated surfaces of BDD.

1.2.1 Hydrogen-terminated diamond

In 1989, Landstrass and Ravi reported the conductivity of both natural and undoped CVD diamonds after exposure to hydrogen plasma.[38] Since then, the conductivity of hydrogen-terminated diamonds has been corroborated by other groups and extensively reviewed.[17, 37, 39]

Several mechanisms have been proposed to explain the induced surface conductivity in hydrogen-terminated diamond. The original mechanism proposed assumed that hydrogen is incorporated into the diamond during plasma treatment and therefore electrically neutralizes deep donors in the diamond sample.[38] Other researchers agreed with this proposed mechanism [40, 41] until the surface conductivity was shown to be lost even without attacking the bulk diamond.[42] The next proposed mechanism relied on acceptor-like surface states.[43, 44] This theory relied on electrons being transferred from the bulk diamond to acceptor-like surface states in the hydrogenated surface that would be lost after oxidation. The location of the acceptor states was investigated further, but rather than corroborating the proposed mechanism, the results showed unrealistically high hole densities or a Fermi level that was too close to the valence band maximum.[45–47] Instead, the surface conductivity was found to depend on, and vary with, the atmospheric environment in which the hydrogen-terminated diamond is stored.[48–51] Maier, who probed the conductivity of the hydrogen-terminated diamond both before and after exposing the diamond to air, showed that hydrogen-termination alone is not sufficient to induce surface conductivity.[48] Instead, hydrogen terminating the surface lowers the ionization energy and permits the formation of a physisorbed, atmospheric layer that causes the surface conductivity.[17, 39] The surface conductivity of diamond arises from an electrochemical-like process in which electrons are transferred from the diamond valence band, which oxidises the diamond, to an oxidative species in the physisorbed layer.[50, 52] This process, called “surface transfer doping” and shown schematically in Fig. 1.5, has been corroborated by theoretical studies investigating the electron transfer between the diamond and a physisorbed layer made of dif-

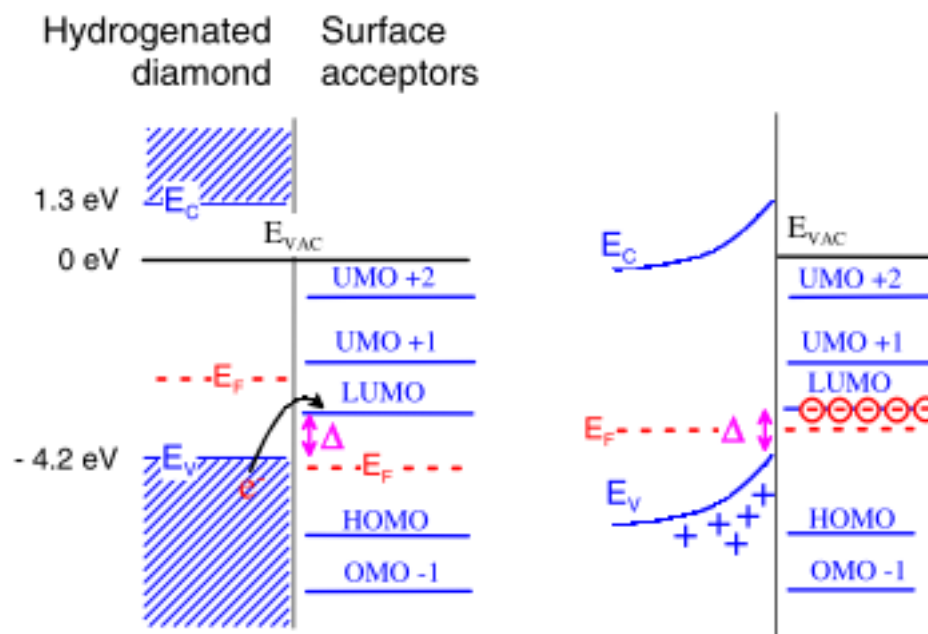


Figure 1.5: Surface transfer doping of hydrogen-terminated BDD. The energy diagram on the left shows the diamond and surface acceptor states before the charge exchange occurs and the right-hand diagram shows the energy levels of the diamond-acceptor system at equilibrium after the transfer doping has occurred. In both cases, OMO refers to occupied molecular orbitals and UMO to unoccupied molecular orbitals. From [52]

ferent oxidative species.[17] Larsson's calculations showed that neither a physisorbed layer consisting of only water nor an oxygen-terminated surface resulted in measurable charge transfer.[17] Chakrapani *et al.* showed that charge transfer similar to that which occurs between the hydrogen-terminated diamond surface and the physisorbed atmospheric layer also occurs at the solid/liquid interface between a hydrogen-terminated diamond electrode and an electrolyte.[53, 54]

The use of hydrogen as the carrier gas during diamond CVD growth causes as-grown diamond to have a hydrogen-terminated surface.[16] Fig. 1.6 shows the expected structure of the hydrogen-terminated diamond (111) and (100) surfaces. For the (111) surface, reconstruction to the (2×1) surface is an effect of temperature annealing or hydrogen desorption,[55] while reconstruction to the (2×1) (100) face is an energetically favourable transition from the sterically repulsive (1×1) (100) dihydride surface.[56, 57] While the hydrogen-terminated surface has been reported to be stable in air for months,[58] using the hydrogen-terminated BDD for electrochemistry or exposing them to oxidising species such as nitric acid reoxidises

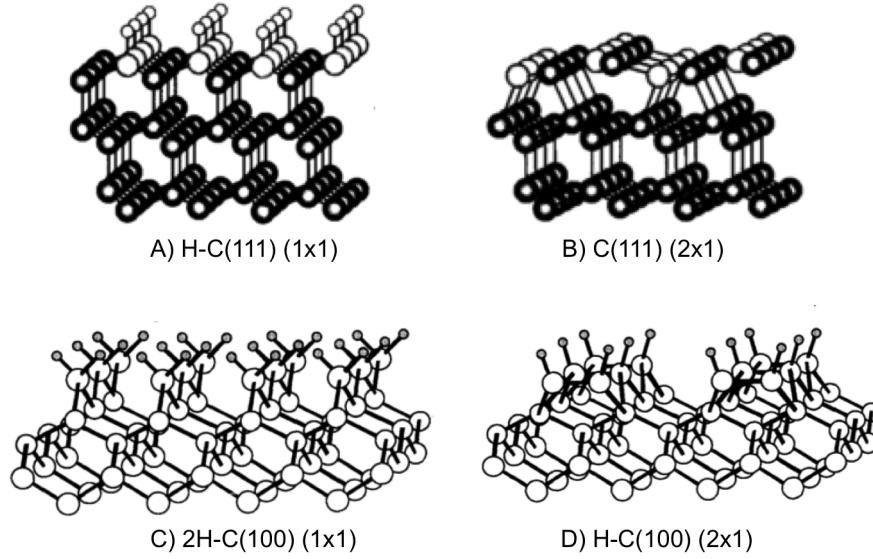


Figure 1.6: Schematic of the hydrogen-terminated diamond (111) surface (A) and the reconstruction to the π -bonded C(111) surface (B). The large spheres indicate C atoms and the small spheres H atoms.[55] The dihydride diamond (100) surface (C) is sterically unfavourable and tends to reconstruct to the (2×1) (100) surface (D).[56]

the surface. The hydrogen-termination can be regenerated by fresh exposure to hydrogen plasma or by electrochemical methods.[59]

In addition to the induced surface conductivity, hydrogen-terminated diamond has a nonpolar, hydrophobic nature.[19, 60–62]

1.2.2 Oxygen-terminated diamond

Oxygen-terminated diamond differs from hydrogen-terminated diamond in several key aspects. First, oxygen-termination does not result in surface conductivity.[63] Second, while the hydrogenated surface tends to gradually reoxidise in air,[25] the oxygen-termination is more stable.[63] Finally, unlike the hydrogen-terminated diamond, oxygen-terminated diamond is hydrophilic [60, 64] and has a negative surface charge.[65]

Given the differences between the hydrogenated and oxygenated diamond, several methods have been developed to change the hydrogen termination to an oxygen termination. Two of the most commonly used methods are oxygen plasma treatment and strong, oxidising acid.[24] Each of these methods has its own advantages and disadvantages. Oxygen plasma treatment results in an oxygen-terminated surface in a matter of minutes but re-

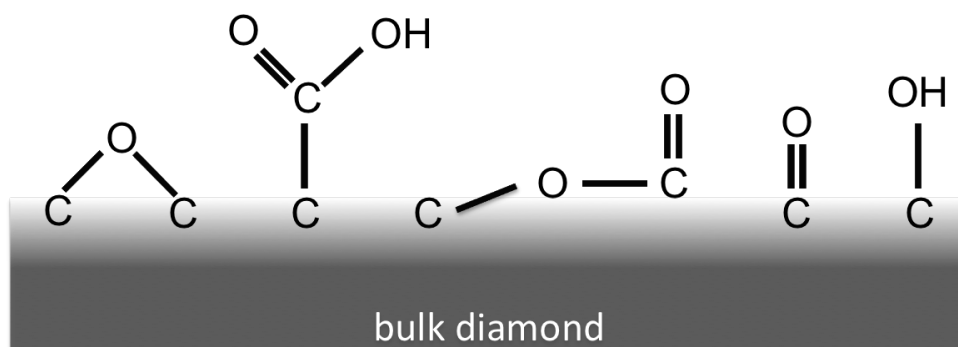


Figure 1.7: A schematic of the different oxygen groups that are likely to form on diamond. The dark gray represents bulk diamond, light gray shows the surface region with representative C atoms indicated to show bonding to different oxygen-containing functional groups. Bond lengths and orientation are not to scale.

quires expensive, specialized equipment. Moreover, overexposing the diamond to oxygen plasma can damage the diamond by pitting and etching.[66] On the other hand, treating the diamond with strong acid is easily done with common laboratory equipment but requires a processing time of several hours.[67] During oxygenation, oxygen attaches to the surface by either single or double bonds.[66] Both ether and carbonyl functional groups are common on the diamond surface,[68] but carboxylic, hydroxy- and lactone-like terminations are also possible.[68–70] The terminal oxygen groups that can form on the diamond surface are shown schematically in Fig. 1.7. According to Navas *et al.*, acid treatment results primarily in ether and hydroxyl oxygen species.[67] An oxygen to carbon ratio of 0.18 as measured by x-ray photoelectron spectroscopy indicates an oxygen-terminated surface.[66]

1.2.3 Effect of surface termination on diamond electrochemistry

Overall, the surface termination of BDD can significantly affect the electrochemical performance of the electrode, especially with regards to surface wettability, surface bond polarity that affect electrostatic interactions between the electrode and the electrolyte, and electron transfer kinetics.[21] This thesis directly compares the performance of hydrogen-terminated and oxygen-terminated BDD for a number of sensing applications.

1.3 Surface decoration of boron-doped diamond electrodes and their applications

Pleskov *et al.* pioneered the use of doped diamond in electrochemistry.[71] Since then, BDDs have been used in a plethora of electrochemical applications ranging from electroanalysis,[18, 29, 32, 34, 72, 73] water purification,[12, 74–77] and energy conversion and storage.[78] In addition to tuning the behaviour of BDD electrodes by changing their surface termination, BDDs can be decorated with catalytic particles that enhance their performance by acting as an active catalytic surface supported on BDD, or by increasing the electrode sensitivity to the analyte. This section gives an overview of the types of particles that have been used to modify the surface of BDD electrodes and their intended uses.

1.3.1 BDD surface modification with metals and metal oxides

Modifying an electrode surface with metal or metal oxide particles affects both the electroactive surface area of the electrode as well as the sensitivity and selectivity of the electrode towards a particular analyte.[79, 80] Toghiani [80] and Nelson and Foord [81] have reviewed the use of different metals and metal oxides on BDD for electroanalysis. Some of the most commonly-used metals to modify BDD include silver, gold, platinum and nickel, and the resulting electrode ensembles can be used for hydrogen peroxide evolution, detection of heavy metals, biosensing and alcohol oxidation.[80, 81]

Two important factors to consider when decorating the BDD with metal or metal oxide particles are 1) the environment in which the electrode will be used, and 2) the sensitivity of the metal or metal oxide towards the analyte or chemical process of interest.[81, 82] For example, when selecting a metal to be used for alcohol oxidation, it is important to consider the possibility that the metal particles become fouled by the products of the oxidation process. Additionally, many metals dissolve in acid, and so it may be better to consider alternative metals or metal oxides if the electrode is to be used in acidic media.

When a suitable metal or metal oxide has been selected for use, the next consideration is the method by which the particles are deposited onto the electrode surface. The behaviour

of the metal particles is intrinsically linked to their size and geometry — parameters that, in turn, are affected by their preparation and deposition method.[80, 81, 83] Particle size is of particular importance since nanoparticles often exhibit properties not present in the bulk material.[80, 81, 83] Of the various electrochemical deposition techniques that have been used, potentiostatic deposition from a solution of the metal salt is one of the most common.[81] Unfortunately, this technique has certain drawbacks, including large particle size and poor adhesion to the underlying substrate.[81] An alternative deposition method involves the formation of colloidal particles by wet chemistry followed by deposition of the particles onto the electrode surface by physical means such as drop casting or spin coating.[80] This method allows for size selection of the particles before deposition but suffers from heterogeneous dispersion of the particles over the electrode surface. The distribution of nanoparticles over the BDD surface is particularly important in the electrochemical use of the decorated electrode; the spacing of the nanoparticles strongly affects the diffusional processes at the electrode/electrolyte interface.[80] If the nanoparticles are situated close together on the BDD surface, the diffusion layers at each particle overlap with that of neighbouring particles and overall linear diffusion results. On the other hand, nanoparticles that are widely spaced do not have overlapping diffusion layers, which results in three-dimensional diffusion.[80, 81]

1.3.2 BDD surface modification with carbon particles

Many of the metals used to decorate BDD electrodes tend to be either toxic, like lead and cadmium, or expensive, like gold and platinum. Therefore, the modification of BDD surfaces with cheap, non-toxic materials such as carbon is of increasing interest for the improved performance of BDD electrodes. Nanocarbons in particular are becoming more widely used as electrode modifiers. Decorating electrodes with conducting nanocarbons results in the formation of porous, conducting films on the electrode surface that improve the sensitivity of electrodes [84] — an effect that has been particularly exploited in biosensing applications.[85] The properties of commonly used nanocarbons, such as carbon nanotubes, nanodiamond and carbon blacks, have been reviewed in great detail elsewhere.[31, 65, 86]

Carbon nanotubes, which consist of rolled-up graphite sheets,[87] are promising electrode modifiers due to their high electrical conductivity, chemical stability and mechanical strength.[88] Carbon nanotubes have been used successfully in many electrochemical applications including chlorine sensing, DNA electroanalysis and oxygen reduction.[85, 89–91] However, they also suffer from drawbacks such as poor solubility and a tendency to tangle that can make carbon nanotubes difficult to work with.[86] Further modification of the carbon nanotubes themselves is often required prior to their use as electrode modifiers.

Nanodiamonds retain the properties of macroscopic diamond [92] but increase the electroactive surface area when used as an electrode modifier.[31] Structurally, nanodiamonds are made of sp^3 cores with surface shells of delocalised π systems [92, 93] that can be modified or functionalised with relative ease.[94–96] Additionally, nanodiamonds are the most biocompatible of nanocarbons.[97] To date, nanodiamonds have been used in the sensing of biomolecules such as glucose [98] and tryptophan,[99] as well as the detection of hydrogen peroxide.[94] Yang *et al.* [31] provides a recent review of the field of nanoscale diamond electrochemistry.

Unlike carbon nanotubes and nanodiamond, carbon black is a mixture of sp^3 and sp^2 carbon. The conductivity of carbon black varies with the sp^2 to sp^3 ratio [100] while other characteristics, such as oxygen content, density and porosity, depend on the starting material and synthesis method.[101–103] While carbon black has only recently been used as an electrode modifier for electrochemical sensing, it has already been used in the detection of a range of biomolecules, including DNA, bisphenol A and tryptophan.[104–107]

1.4 Aims and scope of this thesis

BDD modification by both explicit surface termination and particle decoration has been studied by other groups. However, few researchers have directly compared the performance of particle-decorated, explicitly surface terminated diamond even though promising results have been obtained by each type of modification. This thesis directly compares the performance of oxygen- and hydrogen-terminated BDDs decorated with metal, metal oxide and carbon

particles with the aim of establishing the extent to which surface termination affects

1. the electrochemical behaviour of the BDD,
2. the interaction between the underlying BDD and particles used to modify the BDD surface, and
3. the overall performance of the particle-decorated, surface-terminated BDD as an electrochemical sensor.

This thesis also aims to determine if the electrochemical characteristics of the hydrogen-terminated BDD can be reproduced with a carbon-black-decorated, oxygen-terminated BDD.

Chapter 2 explains the electrochemical principles and techniques used in this thesis, together with the operating principles of x-ray photoelectron spectroscopy. Brief descriptions of atomic force and scanning electron microscopy are also given.

Chapter 3 explores gold nanoparticles deposited onto hydrogen- and oxygen-terminated BDDs by both cyclic voltammetry and drop-casting. The aim of this chapter is to determine how both the gold nanoparticle deposition method and the BDD surface termination affect the overall performance of the decorated electrode in the oxidation of mercury. The extent to which physical characteristics of the nanoparticles, including morphology and distribution over the underlying BDD surface, are affected by both the deposition method and the BDD surface termination was investigated by x-ray photoelectron spectroscopy, microscopy and lead underpotential deposition. The variations in electrochemical behaviour of the modified electrodes were measured by cyclic voltammetry while the ability of the gold particles to detect mercury was measured by square-wave voltammetry.

Chapter 4 studies the use of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox couple supported on hydrogen- and oxygen-terminated BDD for glucose sensing. This chapter builds on the work previously reported by Toghill [108] and Hutton [109] by extending the use of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ on oxygen-terminated BDD for glucose sensing to hydrogen-terminated BDD. Three different nickel loadings were used in this study. The particle size and distribution of each loading were determined by scanning electron microscopy. X-ray photoelectron spectroscopy was used to calculate the relative ratios of metallic nickel to nickel hydroxide for each loading and to

probe how this ratio differed between the hydrogen- and oxygen-terminated BDD. Glucose oxidation with the nickel hydroxide-modified, surface-terminated BDDs was investigated by both cyclic voltammetry and amperometry to determine the sensitivity and reliability of each electrode.

Chapter 5 investigates the use of two different types of carbon black on both hydrogen- and oxygen-terminated BDD for acetaminophen sensing. This chapter has three aims: 1) to determine the differences in the ability of hydrogen- and oxygen-terminated BDD to electrooxidise acetaminophen; 2) to investigate if and how BDD surface modification with carbon blacks affects the performance of the BDD electrode in acetaminophen oxidation; and 3) to evaluate the possibility of using an oxygen-terminated, carbon black-modified BDD in place of explicitly hydrogen-terminated BDD in electrochemical applications. This chapter used x-ray photoelectron spectroscopy to measure changes in surface oxygen content between both the clean and carbon black-decorated explicitly surface-terminated BDDs. Randles-Sevcik type experiments were used to calculate the change in electroactive surface area of the BDDs with carbon black decoration and to detect any changes in diffusional behaviour. Detection limits of acetaminophen with each electrode was determined by differential pulse voltammetry.

Chapter 6 continues the investigation presented in chapter 5 by studying the use of carbon-black-decorated, explicitly surface-terminated BDDs for the electrooxidation of another small organic molecule, hydroquinone. The aims of this chapter are to establish if the conclusions from chapter 5 can be generalised for other organic molecules and to determine if the carbon-black-decorated oxygen-terminated BDD can mimic the electrochemical behaviour and activity of the hydrogen-terminated BDD.

Chapter 7 presents a brief summary of key results and conclusions together with a discussion of future work.

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Chapter 2

Experimental theory and techniques

This thesis relies on the application of experimental techniques that have already been developed and, by now, are well established in the literature. This chapter, therefore, aims to explain the theory behind the techniques to the level of detail at which they were used and, where appropriate, to provide some insight into the broader applications of these techniques.

Electrochemistry will be presented first, together with the specific electrochemical techniques that are necessary for later chapters. Since electrochemistry comprises the bulk of the work in this thesis, it is proportionally presented here followed by the thesis' secondary technique: x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are presented briefly at the end of the chapter.

2.1 Electrochemistry

Electrochemistry is the study of charge transfer between an electrode and an electrolyte. This charge transfer results in the oxidation and/or reduction of one or more chemical species in the electrolytic solution. The potential at which the charge transfer occurs varies with both the particular species being oxidized or reduced and the material of the electrode. If both the oxidation and the reduction processes occur, the potential difference between the processes provides information about the reaction kinetics. Numerous electrochemical methods have been designed to quantitatively measure the parameters affected by, or in control of, the electron transfer process. This section provides a brief overview of electrochemistry and of

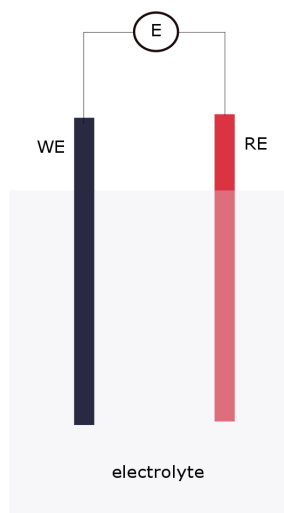


Figure 2.1: The simplest functioning electrochemical cell consists of a working electrode (WE), a reference electrode (RE), and the electrolyte. Adapted from [1].

the methods used in this thesis.

2.1.1 Electrochemical cells

Electrochemistry is heterogeneous; electrons are transferred from the solution-phase electrolyte to the solid electrode or vice-versa, and this transfer is driven by the energy difference between the electrode and the electrolyte.[1] Even if the electrode is in perfect conducting contact with the electrolyte, there is no way to measure the local potential difference. A second electrode is therefore needed to make a measurement. For the measurement to be meaningful, this second electrode, called the reference electrode, must have a stable potential in the electrolyte. This gives a readable measurement

$$\Delta\phi = (\phi_{\text{WE}} - \phi_{\text{aq}}) - (\phi_{\text{ref}} - \phi_{\text{aq}}), \quad (2.1)$$

where the first term is the difference in potential, ϕ between the electrode of interest, called the working electrode (WE), and the electrolyte, and the second term is the potential difference between the reference electrode and the solution. The two electrodes and the electrolyte make up an electrochemical cell. The main issue with the two-electrode cell shown in Fig. 2.1 is that there is a potential difference between the electrode and the solution at both the

working and the reference electrodes and the potential drop between the two electrodes is distributed in a complex, unknown gradient. Furthermore, if a current is flowing, the ability to measure the potential depends on the stability of the reference electrode. Therefore a third electrode, called the counter electrode (CE), is often included in electrochemical cells. The counter electrode changes in polarity to be the opposite of that of the working electrode, making the current flow between the counter electrode and the working electrode rather than through the reference electrode. This makes the potential between the counter and reference electrodes steady, and all potentials are reported relative to the reference electrode.

2.1.2 Principles of electrochemistry

This section describes the principles of electrochemical theory. The difference in current contributions from faradaic and non-faradaic processes are explained first, followed by the structure of the electrode-solution interface. Mass transport is then discussed for both equilibrium and dynamic electrochemistry.

Faradaic and non-faradaic processes

The current flowing under an applied potential arises from many sources. These sources are categorized into faradaic and non-faradaic processes in the electrochemical cell. Faradaic processes are processes for which the number of electrons flowing in the circuit is proportional to the stoichiometry of the reaction.

$$Q = Fnq, \tag{2.2}$$

where Q is the total charge flowing in the cell, F is Faraday's constant, equal to the charge magnitude of one mole of electrons ($96485.3 \text{ C mol}^{-1}$), n is the number of moles of product, and q is the number of electrons involved in the reaction. For example, in the oxidation of Fe^{2+} to Fe^{3+} , there is only one electron being transferred ($q = 1$). Taking the derivative of

Eq. 2.2 with respect to time, gives the current

$$I = \frac{dQ}{dt} = Fq \frac{dn}{dt}. \quad (2.3)$$

For faradaic processes, the current (I) is directly proportional to the change in product concentration with respect to time. However, other processes that are not directly related to the formation of product can also contribute to the current. Since these currents deviate from the faradaic behaviour delineated in Eq. 2.2 and 2.3, they are called non-faradaic processes. The resulting current is called “non-faradaic current” or “capacitative current.” Examples include solvent dipole reorientation, movement of electrolyte ions and double-layer charging.[2, 3] During electrochemical measurements, these currents tend to be short lived.

Electrode-solution interface

A three-electrode cell is typically used to make meaningful measurements even though the chemistry of interest occurs at the interface of the working electrode and the electrolyte. This section discusses the nature of that interface.

In the absence of applied potentials or currents, and prior to any charge flow, the interface between the working electrode and electrolyte is that of a mixed solution and a solid, as shown in Fig. 2.2A. Depending on the nature of the electrolyte and electrode, a separation of charge may occur over time—a separation that inevitably occurs in the presence of an applied voltage, current or induced charge transfer. This results in the formation of a double layer, as shown in Fig. 2.2B. If the ions lose their solvation at the inner Helmholtz plane (IHP), they adsorb onto the electrode surface. Solvent molecules close to the electrode surface and any adsorbed ions make up what is alternatively called the compact, Helmholtz or Stern layer.

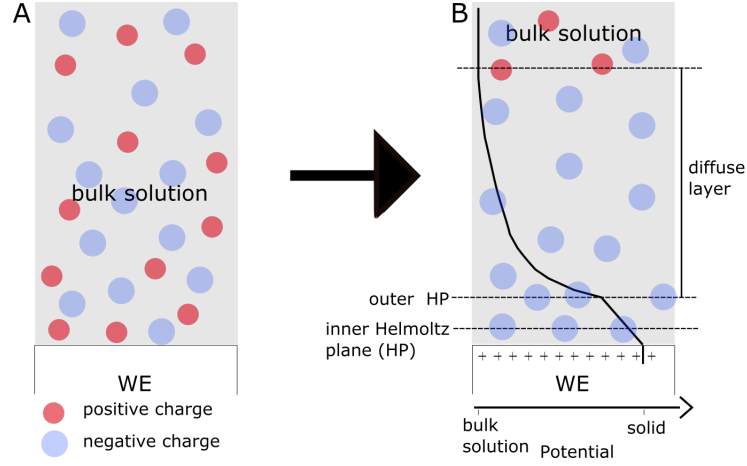


Figure 2.2: The double layer (solvent molecules and solvation shells not shown. Not to scale.)

Equilibrium electrochemistry

Electrochemistry involves the transfer of an electron between the solid electrode and the aqueous electroactive species, A:



where A is an electroactive species of oxidation state x in the electrolyte, the n number of electrons (e^{-}) come from the solid working electrode and B is the product of the reduction reaction with oxidation state $x - n$. At equilibrium, the rate at which A is reduced equals the rate of oxidation of B, which results in zero current flow, a negligible change in the concentration of the redox species and a potential drop across the electrode-solution interface.

The potential drop is quantified by the Nernst equation,^[4]

$$\phi_s - \phi_{aq} = \frac{\Delta\mu^0}{nF} + \frac{RT}{nF} \ln \left(\frac{\alpha_A}{\alpha_B} \right), \quad (2.5)$$

where ϕ_s and ϕ_{aq} are the electrical potentials of the solid electrode and the aqueous electrolyte, respectively, $\Delta\mu^0$ is the difference between the standard chemical potentials of A and B, n is the number of electrons involved in the redox process, F is Faraday's constant, R is the universal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$), T is the temperature and α_A and α_B

are the activities of A and B, respectively.¹ As discussed in section 2.1.1, the potential drop can only be measured with the help of the RE as previously described, at which point the Nernst equation becomes:

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{\alpha_A}{\alpha_B} \right), \quad (2.6)$$

where E is the equilibrium potential drop across the electrode-electrolyte interface, E^0 is the standard electrode potential of the reaction and all other terms are defined as in Eq. 2.5.[5]

Dynamic electrochemistry

Many electrochemical experiments rely on the application of an external potential to induce current flow, which results in dynamic rather than equilibrium electrochemistry. Two main factors affect the induced electrolytic current: electrode kinetics and mass transport. Electrode kinetics describes the rate of charge transfer between the electroactive species and the solid electrode, while mass transfer describes the transfer of the electroactive reagent (A) and electrolytic product (B) from the bulk solution to the electrode.[5]

To induce current flow, the applied potential E must be larger than the equilibrium potential E_{eq} . The difference $\eta = E - E_{\text{eq}}$ between these potentials is called the overpotential.[5] If an overpotential is applied to the reaction in Eq. 2.4 to drive the reduction of A to B, a current will flow:

$$I_{\text{red}} = AFk_{\text{red}}[A], \quad (2.7)$$

where A is the electrode area, F is Faraday's constant, k_{red} is the heterogeneous rate constant of electron transfer for the reduction reaction and $[A]$ is the concentration of the reagent at the electrode surface. An analogous equation can be written for the oxidative current [5] so that the net current flowing is described by

$$I = I_{\text{ox}} - I_{\text{red}} = FA(k_{\text{ox}}[B] - k_{\text{red}}[A]). \quad (2.8)$$

To a good approximation, electrochemical electron transfers can be treated as chemical

¹These activities can be related to their concentrations, $\alpha_A = \gamma_A c_A$, where γ_A is the activity coefficient. At low concentrations (c_A), however, the activity coefficient tends to unity and so the concentration of species A can be used instead of the activity of species A in the Nernst equation.[4]

electron transfers and therefore be described by the Arrhenius equation:[5]

$$k_{\text{red}} = Z e^{\frac{-\Delta G_{\text{red}}^{\ddagger}}{RT}}, \quad (2.9)$$

where $\Delta G_{\text{red}}^{\ddagger}$ is the Gibbs energy of activation, R is the universal gas constant, T is the temperature and Z is a “frequency factor” that accounts for the rate of collision between the electroactive molecules and the electrode surface. An analogous equation can be written for the oxidative case using the rate constant of the oxidation reaction and the Gibbs energy of oxidation. Since the Gibbs energy of activation depends on the potential difference between the electrode and the electrolyte, the rate constant in Eq. 2.9 can be written in terms of the overpotential η :

$$k_{\text{red}} = k_0 e^{\frac{-\alpha F \eta}{RT}}, \quad (2.10)$$

and likewise for the oxidation reaction,

$$k_{\text{ox}} = k_0 e^{\frac{1-\alpha F \eta}{RT}}, \quad (2.11)$$

where k_0 is the standard electrochemical rate, α is the dimensionless transfer coefficient with a value $0 < \alpha < 1$.

The overall expression for the current, Eq. 2.8, can be expressed in terms of the overpotential and transfer coefficient:

$$I = I_0 \left(\frac{[B]_0}{[B]_{\text{bulk}}} e^{\frac{(1-\alpha)F\eta}{RT}} - \frac{[A]_0}{[A]_{\text{bulk}}} e^{\frac{-\alpha F \eta}{RT}} \right) \quad (2.12)$$

Eq. 2.12 is called the Butler-Volmer equation. It gives the current response as a function of the overpotential and the transfer coefficients, and shows that no current will flow when $\eta = 0$. If the solution is stirred, the surface concentrations of the reagents, $[A]_0$ and $[B]_0$, will equal the bulk concentrations, $[A]_{\text{bulk}}$ and $[B]_{\text{bulk}}$. I_0 is a scaling factor that is proportional to the electrode area, the rate coefficient, k_0 and the bulk concentrations, $[A]_{\text{bulk}}$ and $[B]_{\text{bulk}}$. There are two limiting cases to Eq. 2.12: large I_0 and small I_0 . [5] When I_0 is large, only a small overpotential is needed to drive the redox reactions and current flows readily in both the

cathodic and anodic directions.² Reactions with a large I_0 are considered reversible. When I_0 is small, a large overpotential is required to drive the reaction, which is then considered irreversible.

Mass transport

Mass transport is the second factor that determines the induced current in dynamic electrochemistry. The overall mass transfer during an electrochemical reaction is given by the Nernst-Planck equation. For a one-dimensional case in the x -direction, this equation is given by

$$j_i(x) = \frac{q_i F}{RT} D_i c_i \frac{\partial \phi_i(x)}{x} + c_i \nu(x) - D_i \frac{\partial c_i(x)}{\partial x}, \quad (2.13)$$

where $j_i(x)$ is the flux of species i at a distance x from the surface, D_i is the diffusion coefficient, c_i is the analyte concentration, $\frac{\partial c_i}{\partial x}$ is the concentration gradient along the x -axis, $\nu(x)$ is the velocity of a volume element, q_i is the charge, and $\frac{\partial \phi_i(x)}{\partial x}$ is the potential gradient. The three components of Eq. 2.13 correspond to the three sources of mass transport: migration, convection and diffusion.

The migration of species i to or from the electrode surface—the first term in Eq. 2.13—occurs when a potential gradient, such as the gradient that arises naturally from the potential drop between the electrode and electrolyte, exists in the electrolyte. Furthermore, when a charge-transfer process occurs, the local electric field at the electrode surface changes, which also causes the migratory flux to change. The combined effects of electrolysis and migration makes the mass transport due to migration difficult to model and the electrochemical reaction difficult to interpret. Migration is therefore suppressed in practice by including a chemically and electrochemically inert, highly conducting supporting electrolyte at concentrations of around 0.1 M or around 100 times more concentrated than the analyte.[5] The supporting electrolytic ions maintain electroneutrality and prevent electric fields from building up, which makes the effect of migration negligible to the overall mass transport. The supporting electrolyte also increases the overall conductivity of the electrolyte.[5]

²A cathodic current is when the current flows from the WE to the electrolyte and causes reduction of the electroactive species, and an anodic current is when the current flows from the electrolyte to the WE with the electroactive species being oxidised.

Convection, also known as hydrodynamic transport, can either be natural or forced. If the convection is natural, the transport occurs along thermal or density gradients. The contribution of natural convection to mass transport can be reduced by using stagnant solutions devoid of the gradients associated with convection. This is achieved by limiting the experimental time and preventing mechanical vibrations from ambient conditions. If, on the other hand, convection is desired during the course of the electrochemical experiment, mechanical stirring or rotating electrodes can be used.[2, 4]

Diffusion is the mass transport component that is the most common in electrochemical experiments. As given in the third term of Eq. 2.13, diffusion is the movement of species i along the concentration gradient, $\frac{\partial c_i(x)}{\partial x}$, which is created by the redox processes at the electrode surface. The negative sign indicates that the diffusion occurs from a region of high concentration, usually the bulk solution, to a region of low concentration, usually the depletion region near the electrode surface. The region of diffusion is called the “diffusion layer”. The thickness of this layer, δ_d , extends from the electrode surface to where the concentration of the electroactive species i is equal to the bulk concentration of i . [2, 4]

2.1.3 Electrochemical methods

This section describes the working principles of the electrochemical techniques used in this thesis: linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), square-wave voltammetry (SWV), and chronoamperometry.

Linear sweep voltammetry (LSV)

LSV is the simplest potential sweep method. In this method, the potential is first started at a value for which no electrolysis occurs and is then increased or decreased at a constant rate. The potential at any given time, $E(t)$, is therefore given by the initial potential plus the product of the scan rate and time:

$$E(t) = E_0 + \nu t, \quad (2.14)$$

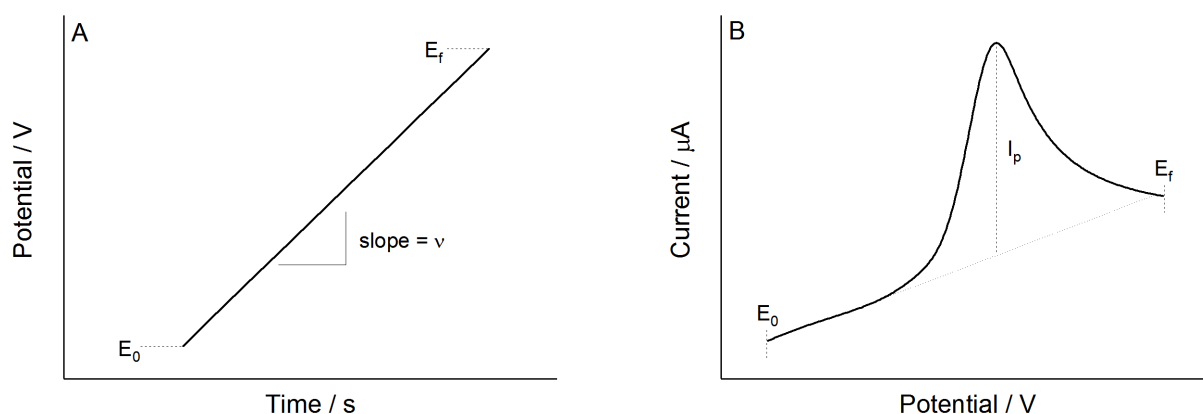


Figure 2.3: A) shows the change in potential with respect to time and B) is the LSV voltammogram of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KCl at a scan rate of 50 mV s^{-1} .

where E_0 is the starting potential, ν is the scan rate and t is the time elapsed. When the potential reaches the value at which electrolysis begins, the faradaic current starts to flow.^[2] As the potential changes, the electroactive species at the electrode surface is oxidised or reduced, causing the concentration of the reagent to decrease until the concentration of the reactant at the surface approaches zero. At this point, the rate of mass transfer of the reactant from the bulk solution to the surface reaches a maximum, which appears in a plot of the current versus potential as a maximum value in the current, I_p (Fig. 2.3). Beyond this point, depletion of the reagent causes the diffusion layer to thicken and the current to decrease.^[2]

Cyclic voltammetry (CV)

CV is one of the most common techniques used to characterize the behaviour of a particular redox couple with respect to a specific electrode. As with LSV, the potential always changes at a constant scan rate. In CV, however, the potential is first increased and then decreased (or vice-versa; see Fig. 2.4A).

In both LSV and CV, the redox process occurs only in the region of the potential for which electron transfer is kinetically and thermodynamically favourable. Because CV probes both the oxidation and the reduction regimes, CV provides more information than LSV; the peak-to-peak separation, ΔE_p in Fig. 2.4B, gives the kinetics of the electron transfer in

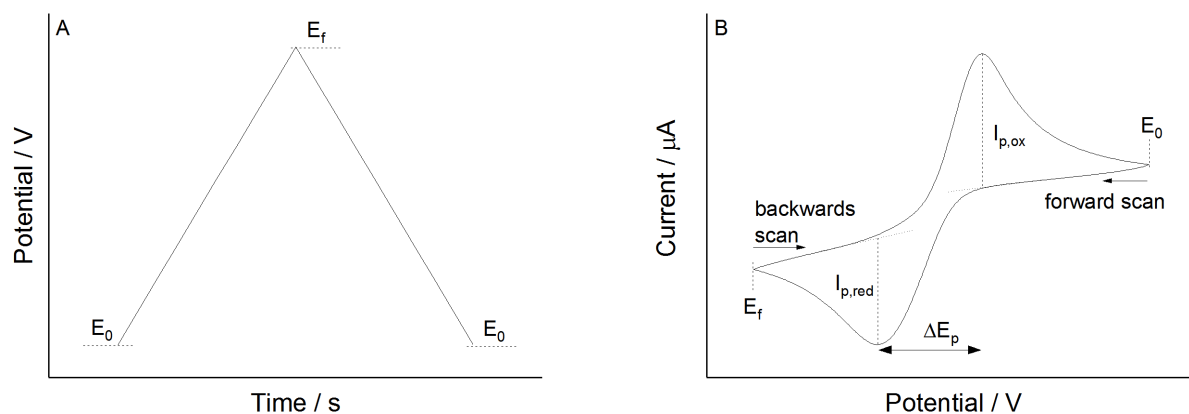


Figure 2.4: A) shows the change in potential with respect to time and B) shows the CV of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KCl at a scan rate of 50 mV s^{-1} . $I_{p,\text{red}}$ and $I_{p,\text{ox}}$ are the peak currents of reduction and oxidation, respectively.

addition to information on the reaction mechanism.

More specifically, when the electron transfer is fast, i.e. ΔE_p is close to its lower limit of 57 mV,³[2] the peak current I_p is given by the Randles-Sevcik equation [4]

$$I_p = 0.446FA[A]_{\text{bulk}}n \left(\frac{nFD\nu}{RT} \right)^{1/2}. \quad (2.15)$$

At room-temperature, this equation reduces to

$$I_p = 2.69 \times 10^5 n^{3/2} AD^{1/2} [A]_{\text{bulk}} \nu^{1/2}, \quad (2.16)$$

where n is the number of electrons transferred, A is the surface area of the electrode, D is the diffusion coefficient, $[A]_{\text{bulk}}$ is the bulk concentration of the reagent, ν is the scan rate, F is Faraday's constant, R is the universal gas constant and T is the temperature of the solution. Typically, n , A , D and $[A]_{\text{bulk}}$ are kept constant in a series of experiments in which the scan rate ν is varied. In this case, a plot of the peak current against $\nu^{1/2}$ will be linear. The linear correlation can be used both to test the reversibility of a given redox couple and to calculate the diffusion coefficient or the electroactive surface area of the electrode.

³The value of 57 mV is a theoretical value derived from the interplay of Nernstian behaviour, diffusion equations and boundary conditions of the system.[2]

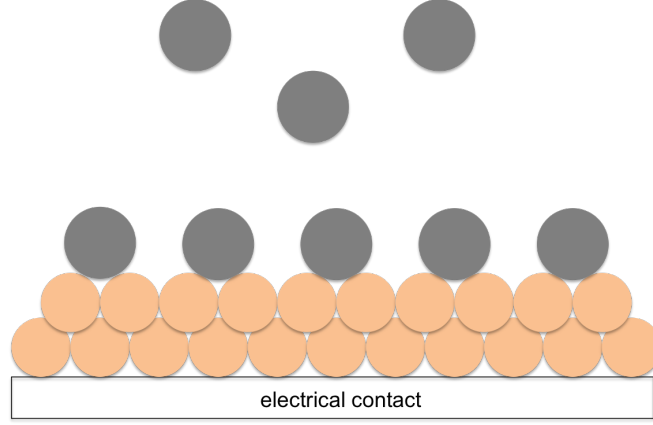


Figure 2.5: Underpotential deposition of Pb (gray circles) on Au (orange circles). Adapted from [8]

When the electron transfer is slow, the peak current is given by the irreversible Randles-Sevcik equation,

$$I_p = 0.496(n' + \alpha)^{1/2} F A [A]_{\text{bulk}} n \left(\frac{n F D \nu}{RT} \right)^{1/2}, \quad (2.17)$$

which, at room temperature becomes

$$I_p = 2.99 \times 10^5 n^{3/2} A (n' + \alpha)^{1/2} D^{1/2} [A]_{\text{bulk}} \nu^{1/2}. \quad (2.18)$$

The main difference between Eq. 2.16 and Eq. 2.18 is the inclusion of the transfer coefficient, α , and n' , the number of electrons transferred before the rate-determining step, in the latter.

Lead underpotential deposition (PbUPD)

Many techniques have been developed to provide information in addition to that obtained by CV. Some of these techniques, including lead underpotential deposition (PbUPD), probe the surface structure of metal electrodes. PbUPD is the electrochemical adsorption and desorption of a monolayer or submonolayer of Pb cations on metal surfaces.[6] The potential at which underpotential deposition occurs is more positive than the deposition of bulk Pb, but the underpotential value varies with the type of metal and, more importantly for surface characterization, the exposed crystal face of the metal due to the different surface energy associated with each crystallographic orientation.[6, 7] PbUPD on gold is shown schematically in Fig. 2.5.

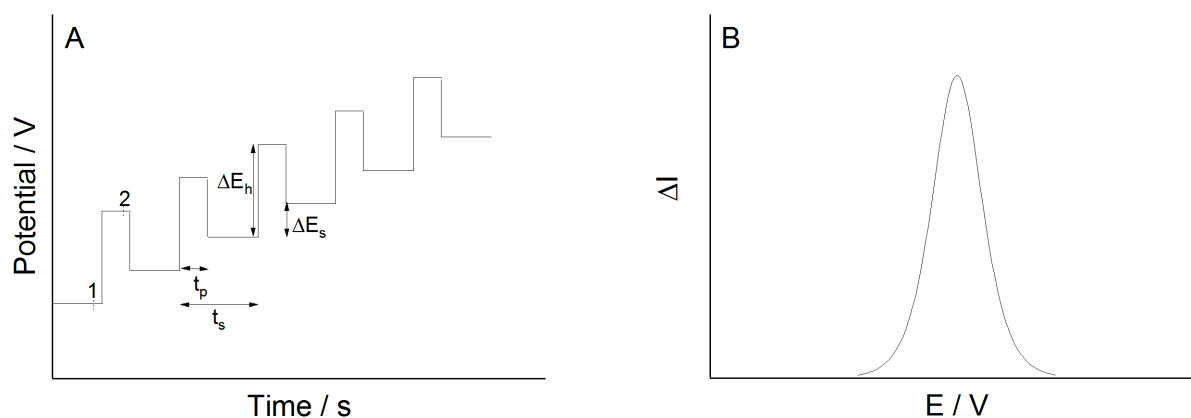


Figure 2.6: A) shows the change in potential with respect to time and B) is a schematic of the resulting DPV current response.[10]

Differential pulse and square-wave voltammetry

CV gives fundamental insight into the electrochemical system. However, greater sensitivity (i.e. better signal-to-noise ratios at low concentrations of electrolytic species) can be obtained by using pulsed-potential waveforms such as square-wave or differential-pulse voltammetry. Differential-pulse voltammetry (DPV) and square-wave voltammetry (SWV) are two pulsed voltammetrical methods that are both used to obtain high sensitivity in electrochemical sensing applications.

The improved sensitivity of these techniques arises from their enhanced response to the faradaic current relative to the non-faradaic, capacitive, current because the potential is stepped rather than scanned, which allows for the subtraction of the capacitive current from the recorded current.[4] The two techniques are in many ways similar to each other, and in some ways rather different, as explained in this section.

DPV is carried out by applying a potential in the manner shown in Fig. 2.6A.[9] Typical values for the pulse duration, t_p , and the period of the waveform, t_s , are 5–100 ms and 0.5–5 s respectively, while typical step heights, ΔE_s , and the pulse heights, ΔE_h , are around 10 mV and 50 mV, respectively.[4] The current is sampled twice during each pulse: once just before the pulse is applied (I_1 , 1 in Fig. 2.6A) and once at the end of the pulse (I_2 , 2 in Fig. 2.6A). I_1 is a capacitive current, which decays quickly after the pulse. I_2 is predominantly faradaic

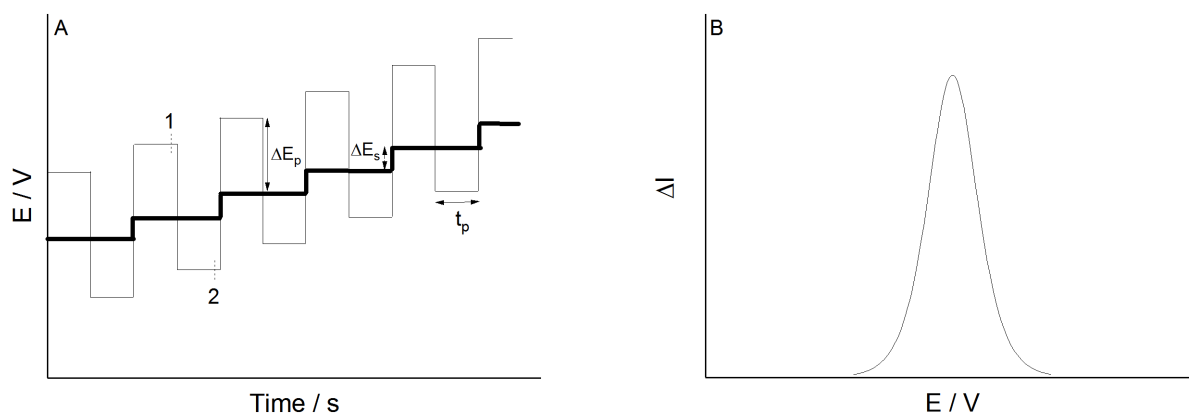


Figure 2.7: A) shows the change in potential with respect to time as well as the underlying step potential (bold) that is part of the applied potential waveform (adapted from [2]). B) is a schematic of the resulting SW voltammogram.

given that the capacitive current has diminished significantly by the time I_2 is measured. Subtracting I_1 from I_2 , $\Delta I = I_2 - I_1$, gives the current response shown in Fig. 2.6B. Note that this peak has a full width, half max (FWHM) value which has a complex dependence on the potential pulse. However, when the potential pulse is small, the FWHM is given by [10]

$$\text{FWHM} = \frac{3.57RT}{nF} \quad (2.19)$$

where R is the universal gas constant, T is the temperature, n is the number of electrons transferred and F is Faraday's constant. From Eq. 2.19, having a one-electron process at room temperature leads to a FWHM of just less than 100 mV. This puts an upper limit of about 100 mV on ΔE_h ; the peak width increases with the pulse height such that when ΔE_h becomes larger than the FWHM, Eq. 2.19 breaks down and peaks from different species may overlap; the resolution is degraded past the point of usefulness.[2] Generally, DPV allows for detection limits of at least 10^{-7} M.[4]

SWV works similarly to DPV in that the current is sampled at the beginning and end of the potential pulse, marked as 1 and 2 in Fig. 2.7A. The main difference between the pulse applied in DPV and in SWV is that in SWV the preelectrolysis period is of equal duration to the pulse time, t_p , while in DPV there is a factor ten difference in their duration. The value of the potential step, ΔE_s , determines the spacing of the data points in the resulting

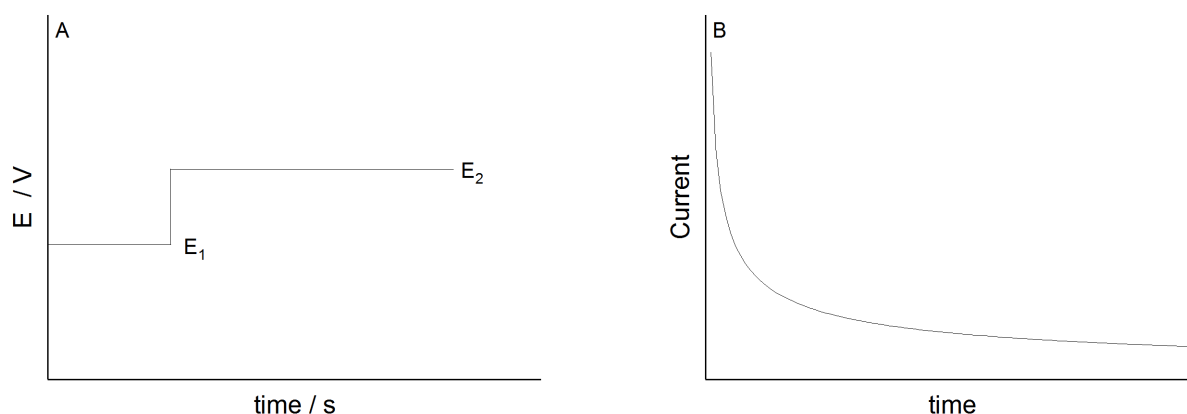


Figure 2.8: A) shows the change in potential with respect to time in chronoamperometry and B) is a schematic of the resulting current response. Adapted from [2].

voltammogram (Fig. 2.7B) and is usually significantly lower than the pulse height, ΔE_p . The value of ΔE_p determines how many features can be resolved in the voltammogram.

The resulting currents, I_1 and I_2 , are different than in the DPV case, but the resulting voltammogram of ΔI vs E has a profile that is similar to that obtained by DPV. Note that for SWV, I_1 is recorded in the direction of the potential step while I_2 is a reverse current sample, and so for this method $\Delta I = I_1 - I_2$. [2] Overall, the different sampling times in SWV makes this method better at removing the background capacitive current than DPV and can therefore be more sensitive, with limits of detection around 10^{-8} M. [4] Also, SWV allows for faster scan rates than DPV. [4]

Chronoamperometry

Chronoamperometry is a technique in which the potential is first held at a value E_1 at which no faradaic current flows and then immediately stepped to a value E_2 at which all the electroactive species near the working electrode surface are oxidised or reduced, as shown in Fig. 2.8A. [2] The resulting current variation from the time the potential has increased to E_2 (Fig. 2.8B) is given by the Cottrell equation: [4]

$$I = \frac{nFAD^{1/2}[A]_{\text{bulk}}}{(\pi t)^{1/2}}, \quad (2.20)$$

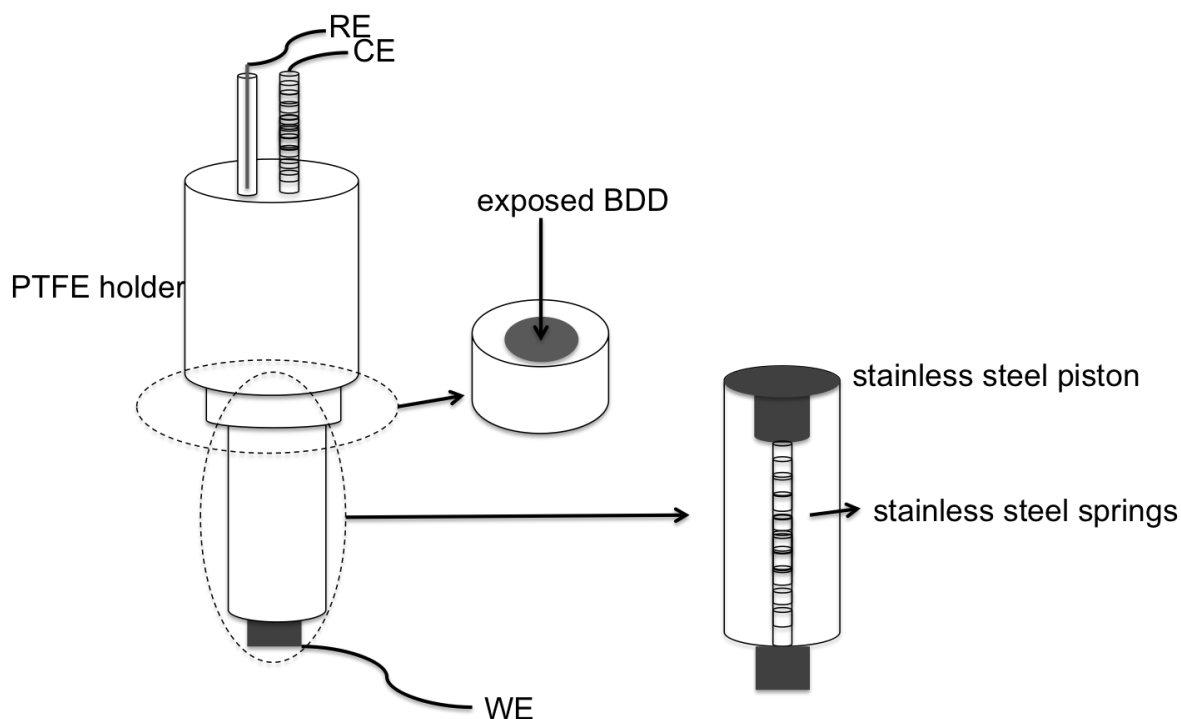


Figure 2.9: The PTFE holder consists of three hollow cylinders. The BDD wafer rests on a stainless steel piston at the top of the bottom cylinder, which forms the electrical connection from the BDD WE electrode to the Autolab. The middle cylinder masked off the BDD and prevented leakage from the electrolytic solution, held in the topmost cylinder, to the springs in the bottom cylinder that formed the electrical connection to the Autolab. The hole cut into the center of the middle cylinder left 0.46 cm^2 of the BDD growth surface exposed to the electrolytic solution.

where n is the number of electrons involved in the redox process, F is Faraday's constant, A is the surface area of the electrode, D is the diffusion coefficient, $[A]_{\text{bulk}}$ is the bulk concentration and t is the time. The rate at which the current decays for stationary electrodes and in non-stirred solutions is therefore limited by the rate of diffusion of the reagent to the electrode surface.[2] Generally, the correlation between I and $t^{-1/2}$ ("Cottrell behaviour") deviates at times greater than approximately 100 s due to convection effects.

2.1.4 Instrumentation and experimental set-up

The work described in this thesis uses a three-electrode system comprised of a Pt wire counter electrode (CE), a Ag/AgCl reference electrode (RE) and an often-decorated BDD working electrode (WE) housed in a PTFE holder, as shown in Fig. 2.9. The material properties of the BDDs purchased from Element Six are given in Table 2.1. The PTFE holder, designed

Table 2.1: The material properties of BDD purchased from Element Six (item number 145-500-0030). Data from [11]

Boron concentration / atoms cm ⁻³	2-6×10 ²⁰
Resistivity / Ohm m	0.2-1.8×10 ⁻³
Current density / A m ²	> 20000
Crystallinity	polycrystalline, including (100) and (111)

by Jingping Hu and built in the Chemistry Department's workshops, left 0.46 cm² of the BDD surface exposed to the electrolyte. The electrochemical measurements were performed at room temperature using an Autolab system (Eco Chemie, the Netherlands) controlled by GPES 4.9 software. All reported potentials are relative to the Ag/AgCl reference electrode, and Millipore water with a resistivity of at least 18 MΩ cm was used for all aqueous solutions.

2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique used to determine the elemental composition of a solid sample. The following section gives a brief overview of XPS theory as well as the instruments used to obtain the spectra. While there are many specific methods that can be employed and many effects that can be studied with XPS, this section focuses only on those used in this thesis.

2.2.1 Introduction to XPS: a brief outline of the theory

The interplay between light and the generation of electric sparks has been of interest since the late 1880s.[12] In 1905, Albert Einstein described the photoelectric effect,[13] which is the process by which electrons are emitted when a sample is irradiated with light. The energy of the photoelectron is specific to its element of origin. XPS uses X-rays to achieve photo-ionization of core electrons, as depicted in Fig. 2.10. The ejection of a core electron (A in Fig 2.10) results in a number of additional processes. For example, electron B can radiate some of its energy to occupy the hole left by electron A. The energy lost by electron

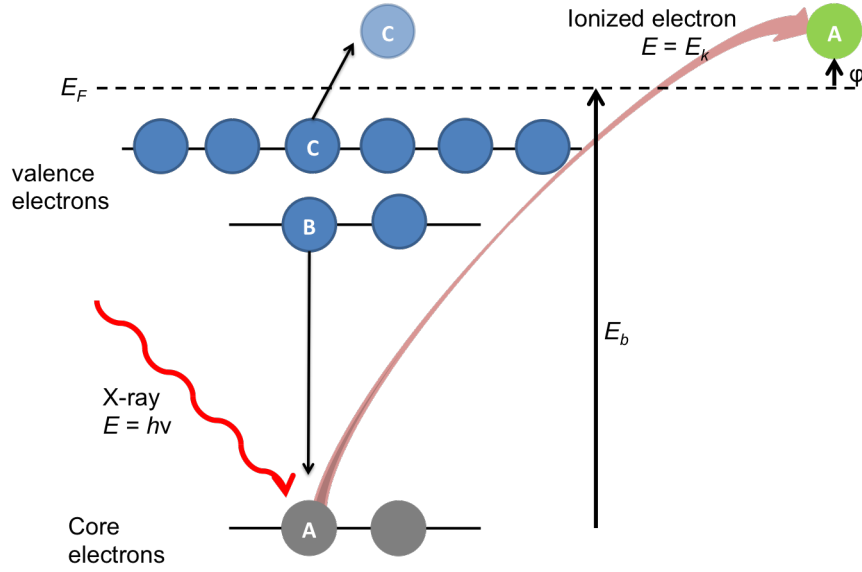


Figure 2.10: A schematic representation of the XPS process. The blue circles represent electrons that do not directly participate in the XPS process, the grey circles are core electrons that are photo-ionized by the X-rays and the green circle is the ionized photoelectron. E_F is the Fermi level, E_k means 'kinetic energy', E_b means 'binding energy' and ϕ is the work function of the sample.

B can either be released as a photon or 'donated' to electron C. In the latter case, electron C is also ionized and becomes an Auger electron. Auger effects are observed as distinct peaks in the XPS spectra, but they are easy to distinguish from XPS peaks.

Since the energy of the incident, monochromatic X-ray beam ($h\nu$) is well-known and the kinetic energy of the photoelectrons (E_k) emitted is readily measured, the binding energy of the core electron (E_b) is easily calculated from

$$E_k = h\nu - E_b - \phi, \quad (2.21)$$

where ϕ is the work function, which is defined as the energy required for an electron to completely escape the material surface. Both the sample of interest and the XPS equipment have a work function, and the term ϕ in Eq. 2.21 is properly the work function of the spectrometer, if E_b is measured with respect to the Fermi energy. Since the photon energy is well defined and the analyzer, described in section 2.2.2 measures the kinetic energy of the electrons, the binding energy is easily obtained; the work function and charging effects are compensated for by prior calibration of the obtained spectrum against a peak standard,

Table 2.2: The intensity ratio of spin-orbit split elemental peaks

shell	j	degeneracy ($2j+1$)	intensity ratio
p ($l=1$)	$\frac{1}{2}, \frac{3}{2}$	2, 4	1:2
d ($l=2$)	$\frac{3}{2}, \frac{5}{2}$	6, 4	3:2
f ($l=3$)	$\frac{5}{2}, \frac{7}{2}$	6, 8	3:4

usually C 1s at 285.0 eV.

Spectral features

The chemical environment affects the binding energy of the photoelectrons. This means that photoelectrons from the same element may have different binding energies if some photoelectrons come from the pure element while others come from an oxide or otherwise bonded atom.[12] These chemical shifts are often relatively small and broaden the main peak of the element. Fig. 2.11 shows the survey scan of a clean, oxygen-terminated diamond electrode (A) and the C 1s region (B) that has been broadened by different chemical environments.

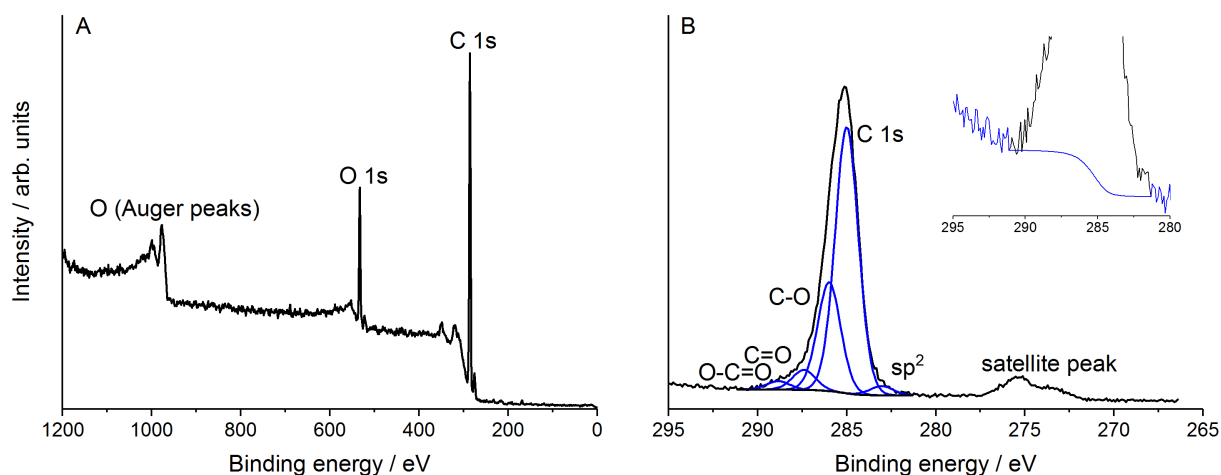


Figure 2.11: The survey scan (A) shows the peaks from all the elements present in the sample. The elements are identified by their binding energies; reference tables of the binding energies are widely available. (B) shows the C 1s region and the inset shows the Shirley background.

Electrons that originate from a core level other than an s-orbital result in a split peak due to spin-orbit coupling.[12] The difference in binding energy of the two peaks is proportional to

the atomic number, and the intensity ratio is given by their degeneracy, $2j+1$ (Table 2.2).[12]

The peak intensities of elemental lines are affected by both the amount of the element present on the surface and the sensitivity of that element to X-rays. While XPS does not directly measure the amount of an element present on the surface, it is often used to calculate the relative amount of an element compared to another element. Assuming that the sample composition is uniform with the XPS sampling depth (on the order of 5 nm), the relative amounts of element A to element B is given by

$$\frac{x_A}{x_B} = \frac{I_A/S_A}{I_B/S_B}, \quad (2.22)$$

where x_A and x_B are the mole fractions of elements A and B respectively, I_A and I_B are their measured intensities, and S_A and S_B the respective elemental relative sensitivity factors (RSFs). RSFs depend on the element detected, the sample measured and the specific instrument used in the XPS analysis.[14] Measuring RSFs using internal reference standards for each element of interest in a given sample gives the most accurate determination of mole fractions, but RSFs reported in the literature, such as the Scofield RSFs, can also be used to calculate mole fractions to good precision, if not as accurately as with internal RSFs.[14, 15] Unless otherwise stated, the RSFs used in this thesis are those calculated by Scofield and included in the CasaXPS library.[15]

Background noise and ghost features

A spectral background (noise) arises from the detection of electrons in the analyzer that have undergone inelastic scattering processes and thereby have had their kinetic energy change from the kinetic energy of the element of their origin. When measuring the intensities of the elemental XPS peaks, a background function is used to determine the baseline from which the peak intensities are measured. The background fit also gives the baseline from which the peak area is calculated. Having a realistic baseline fit is therefore important for accurate determination of the relative amounts of a given element present in the sample. Of the three most common background functions used in XPS analysis—linear, Shirley and

Tougaard—this thesis uses the Shirley (or Integral) background, which tends to be more accurate than the linear background and easier to use than the Tougaard background, which requires a large energy range (approximately 50 eV on the higher binding energy side) to give reasonable background fits.[12]

The spectral background in Figure 2.11A is larger at high binding energies (low kinetic energies). The Shirley background assumes that this is primarily due to inelastic scattering processes [16] for example, if a photoelectron from the C 1s core shell undergoes inelastic scattering the detected kinetic energy of this photoelectron will be lowered, making the electron contribute to the spectrum at a higher binding energy.[12, 17] Therefore, the Shirley background tends to have a curved shape, as shown in the inset of Fig. 2.11B.

The satellite peak in Figure 2.11B arises from non-monochromatic X-rays. These types of ghost peaks are easily discarded from spectra.[17]

2.2.2 XPS instrumentation

XPS is limited to being a surface-sensitive technique since only electrons from the top few atomic layers can escape the the surface of the material and be detected without interference from inelastic scattering processes or recombination.[12] Maintaining XPS at high vacuum conditions is therefore important in order to detect a signal to ensure there are very few atoms or molecules with which the photoelectrons can interact prior to detection. Furthermore, maintaining ultra high vacuum (UHV) conditions prevent the surface of the sample from becoming contaminated by ambient species during the course of the XPS measurement.[12, 17] Therefore, the three main components of the XPS—the X-ray gun, the analyzer and the detector—are all housed in UHV conditions.⁴

Al or Mg $K\alpha$ X-rays are the most commonly used sources in XPS because these materials

⁴To maintain UHV conditions and avoid contamination from ambient air, the sample is moved to the so-called analysis chamber by a series of intermediate steps. The sample is inserted into the XPS housing via the loading chamber, which can be flushed with N_2 gas and raised to atmospheric pressures. Once the sample is in the loading chamber, the chamber is sealed and pumped down to a low pressure (10^{-6} Torr) after which the sample is moved to the preparation (prep.) chamber. When the lock between the loading and prep. chambers is opened and the sample is moved across, the pressure in the prep. chamber increases. Therefore, after the lock is closed, the sample is held in the prep. chamber until UHV conditions are reached (i.e. pressure $<10^{-9}$ Torr) and the sample can be transferred safely from the prep. chamber to the analysis chamber. All components of the XPS discussed henceforth are connected to the analysis chamber.

yield soft X-rays that have a) sufficient energy to ionise core levels of the sample (1486.6 and 1253 eV, respectively) and b) sufficiently small line widths (< 1 eV) to give XPS spectra with good resolution.[12, 17] These X-ray sources also have minor emission lines at shifted energies that can result in ‘satellite peaks’ in the spectrum (Fig. 2.11). The intensity of these lines is reduced, if not removed, by the inclusion of a monochromator in the X-ray gun.

The kinetic energies of the photoelectrons generated when the X-rays described above irradiate the surface are measured by the analyzer. There are several kinds of analyzers available on the market. The concentric hemispherical analyzer (CHA) is one of the most common [12] and was the kind used in the work in this thesis. The photoelectrons enter the analyzer through an electron lens that reduces their kinetic energy and thereby improves the resolution of the spectrum.[17] The reduced energy is called “pass energy” — the lower the pass energy, the better the resolution.[12] In this thesis, a pass energy of 50 eV was used for the wide, or survey, scans and a pass energy of 25 eV was used for the elemental regions.

After passing through the electron lens, the photoelectrons enter the CHA. The CHA consists of two concentric semi-circular plates with a potential difference applied across them. This potential difference can either be held constant while the potential at the analyzer entrance is varied in the “fixed analyzer transmission” (FAT) mode, or the entrance potential can be fixed and the potential difference can be varied in the “fixed retard ratio” (FRR) mode.[12] While FRR is often used in Auger spectroscopy, XPS uses the FAT mode exclusively since the constant pass energy ensures consistent resolution for all kinetic energies.[17] The analyzer is connected to an electron detector with a multi-channel plate electron multiplier, which converts the current into a digital spectrum. The spectra obtained in this thesis were then analysed using XPSPEAK 4.1 and CasaXPS softwares.

2.3 Atomic force microscopy

Atomic force microscopy (AFM) is used to determine the surface morphology of the sample. The topographical image generated by AFM is based on the movement of a tip across the surface of the sample; as the tip is deflected by the surface topography, a series of height

measurements are recorded that are then digitised into a 2D image that shows the height variation as a colour gradation over the surface.[18] These height measurements are carried out either by dragging the sharp tip, which is connected to a cantilever, across the surface of the sample (“contact mode”) or by tapping the tip over the surface (“tapping mode”). In both operating modes, a laser is reflected off the back of the cantilever and the reflected beam is detected to record the vertical deflection of the tip-cantilever due to the interaction with the surface.[18, 19] The tip, usually made from silicon or silicon nitride,[18, 20] must be sharp (diameters typically range from 1 to 20 nm[21]) since bluntness of the tip causes imprecise deflection measurements; if the tip is blunt, the cantilever starts to deflect when the outer edge of the tip reaches a topographical feature on the surface rather than when the tip centre reaches the feature. Similarly, if the tip approaches a pit on the surface, a blunted tip might record the pit as shallower and narrower than the actual feature.[20]

The primary disadvantage with operating AFM in contact mode is the level of interaction between the tip and the surface; attractive van der Waals forces can cause the tip to “stick into” the surface, causing damage to the sample, the tip, or both.[21] Tapping mode AFM eschews this issue. In tapping mode AFM, the tip oscillates perpendicularly to the surface in such a way that the oscillation amplitude is constant on a perfectly flat surface. A surface with topographical features will, in contrast, cause the amplitude of the tip’s oscillation to change, which can then be detected.[18, 20] Tapping mode AFM has a better signal-to-noise ratio than contact mode AFM due to its modulated signal.[18] This thesis used tapping mode AFM to image gold nanoparticles on a polished conducting diamond substrate.

2.4 Scanning electron microscopy

Scanning electron microscopy (SEM) is another technique used to determine the morphology or topography of a sample.[22] Unlike conventional microscopes, the SEM relies on an electron beam to generate an image rather than light. An electron beam has two main advantages: improved resolution and higher magnification. The resolution of a microscope is approximately equal to half the wavelength of the light used, therefore an optical microscope

that uses visible light has a resolution of a few hundred nanometres while a microscope that uses an electron beam has a resolution of a few nanometres.⁵[23] The magnification of SEM depends on the dimensions of the electron-beam spot [23] rather than the power of objective lenses, thereby allowing SEM to obtain magnification greater than $100,000\times$ that of optical microscopy.

The electron beam, which is generated in a thermionic or field emission gun by applying a high voltage to a metallic filament, is focused through a series of condenser and objective lenses before reaching the sample. It is then either transmitted through a (thin) sample before being back-scattered or it interacts with the sample to produce secondary electrons. All the samples in this thesis were sufficiently thick to hinder transmission of the electron beam.

The back-scattered and secondary electrons can be detected and their velocity and intensity are used to create the image of the surface. Generally, the SEM is operated in a way that measures either the back-scattered or the secondary electrons depending on what surface information is desired. Since the intensity of the back-scattered electrons increases with the atomic number of the particles from which they were scattered, the back-scattered electron imaging mode (BEI) can be used to determine the chemical composition of a sample. Secondary electron imaging (SEI) mode can be used to gather information about the surface topography and crystallinity.[23] This thesis made use of SEI SEM to estimate the size of particles deposited on the BDD surface and to determine surface morphology.

⁵The wavelength of an electron beam is estimated by $\lambda = (\frac{1.5}{V_o})^{1/2}$, which for an accelerating voltage of 30 kV gives a wavelength of approximately 1×10^{-11} m.[23]

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Chapter 3

Comparing gold nanoparticles on explicitly terminated diamond electrodes

3.1 Introduction

Since Haruta discovered the catalytic properties of noble-metal nanoparticles in 1987,^[1] gold nanoparticles (AuNPs) have been used in a wide range of applications including air-freshening,^[2] biomedical applications,^[3–7] the oxygen reduction reaction,^[8] CO oxidation^[9] and sensing of heavy metals and arsine.^[10–16] It is well established that NP behaviour depends heavily on morphology, size and distribution over the supporting substrate — traits that are influenced by the NP deposition method.^[3–7, 10, 12–18] However, few studies monitor and directly compare the effects of electroless and electrodeposition methods. Drop-casting (DC) of colloidal AuNPs yields AuNPs of uniform size and morphology, while electrodeposition tends to deposit the AuNPs at the electroactive sites of the substrate but does not guarantee uniform size or distribution.^[19] These parameters affect the electrochemical performance of the AuNPs,^[19] which makes understanding the effect of the AuNP deposition method important for optimizing their use in applications such as electrocatalysis and sensing.^[17]

When modifying boron-doped diamond (BDD) electrodes with AuNPs, another consideration arises: the effect of the surface termination on the AuNP deposition. The hydrogen-terminated BDD (BDDH) has surface-induced conductivity that results in metal-like rather than semiconductor-like properties.[20] Oxygen-terminated BDD (BDDO) surfaces, on the other hand, tend to be insulating and have a positive electron affinity and negative charge due to the functional groups that could attract more positive metal ions from the solution.[21–23] Therefore, the performance of the AuNP/BDD system should be most improved by either increasing the presence of NPs on the surface or by improving the electrical contact between the AuNPs and the underlying BDD. A direct comparison between AuNP deposition on BDDO and BDDH has not been widely reported in the literature.

Mercury is a well-known environmental pollutant and toxin that occurs naturally in the Earth’s crust and is produced through human activities such as mining and coal burning.[24] The toxicity of mercury and its oxidized ions (e.g. Hg^{2+}) make it an important target for effective, quick and cheap sensing platforms.[25–27] The literature reports many uses of electrochemistry to fill this need using various electrode assemblages, including some that make use of Au.[11, 25–32] The interest in using AuNPs in the detection of Hg arises from the high affinity of Hg to Au,[27, 29, 30] which makes mercury sensing an appealing application of AuNPs and also useful for studying of the behaviour of different types of AuNPs. Previously, many researchers have used bulk Au or Au film electrodes,[25, 26, 29, 30] while others have used AuNPs supported on bulk Au [11] or on carbon-based substrates such as graphene [32] or glassy carbon [27, 28, 31] to detect Hg^{2+} and study the Au-Hg interaction. However, the use of AuNPs supported on conducting diamond electrodes have not been extensively used. The comparison of different types of AuNPs on two differently terminated BDDs in Hg^{2+} detection is a special feature of this work.

3.2 Aims of the chapter

The aim of this chapter is to explore how both the surface termination of BDD and the deposition method of AuNPs affect the electrochemical performance of the AuNP/BDD

electrodes. AuNPs were deposited on BDDO and BDDH by CV and DC. The decorated electrodes were then characterized physically by XPS and microscopy and electrochemically by CV in dilute aqua regia and Pb underpotential deposition (PbUPD). The physical stability of the AuNPs was determined by a simple sonication experiment. Finally, the decorated electrodes were tested as Hg^{2+} sensors to investigate their possible use in electrosensing.

3.3 Experimental

BDDs ($[\text{B}] > 10^{20} \text{cm}^{-3}$) were purchased from Element Six Co, catalogue number 145-500-0030. The BDDs were faceted with a grain size of $50 \mu\text{m}$ [33] and XRD detected the (111), (220) and (311) surfaces. All experiments were performed with unpolished, polycrystalline BDDs except for those used in AFM imaging, which were performed with polished BDDs. The 50 nm diameter colloidal AuNPs were purchased from BBI (Cardiff, UK) and used without further purification. 70% HNO_3 and 37% HCl were obtained from Fisher Scientific while all other chemicals were from Sigma-Aldrich. Millipore water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was used for all aqueous solutions and in sonication. Deaeration was done by bubbling N_2 through the solutions for 20 minutes.

3.3.1 BDD cleaning and termination

All BDDs were cleaned prior to first use and between each subsequent experiment. Cleaning was done by submersion in room-temperature aqua regia (3:1 v/v of HCl and HNO_3) overnight followed by sonication in water and 20 CV scans in 0.1 M HNO_3 between 2.5 and -1.7 V at 100 mV s^{-1} . If the CV scans following aqua regia showed any signs of a peak, these cleaning steps were insufficient and the electrodes were also polished in 0.1 and $0.05 \mu\text{m}$ alumina (Buehler) slurries followed by sonication in water and a 1:1 acetone-water mixture to remove the alumina from the electrode surface. Oxygen termination was achieved by refluxing the clean BDD in 70% HNO_3 for 4 hours, while hydrogen termination was accomplished by exposing the clean BDD to microwave assisted hydrogen plasma for 45 minutes at 600°C , 1.5 kW power and a pressure of 45 Torr. The resulting surface termination was checked

by XPS – the clean, oxygen-terminated BDD had an O/C ratio of around 18% while the hydrogen-terminated BDD had a O/C ratio that was less than 5%. After 45 minutes in the microwave assisted hydrogen plasma or 4 hours in 70% HNO₃ these O/C ratios no longer changed and the surface termination was considered complete. For comparison, a clean BDDO was cathodically pre-treated by applying a voltage of -1.244 V for 10 s in deaerated, dilute aqua regia (0.1 M HCl and 0.3 M HNO₃), as previously described by Holt.[34] This treatment removes some of, but not all, surface oxygen species and should be an intermediate case between oxygen- and hydrogen-terminated BDDs.

3.3.2 AuNP deposition

DC deposition was done by pipetting 50 μ L of a 50 $\pm$ 3 nm AuNP colloidal solution purchased from BBI (product number EM.GC50) prepared by a 1:2 dilution with water onto the electrode, as described by Bonanni *et al.*,[35] and leaving the sample to dry under ambient conditions. Since the commercial AuNPs were suspended in water without preservative according to the manufacturer’s data sheet, the AuNPs were used as received without further purification or characterization. CV deposition was done by a single CV scan in a deaerated solution of 1 mM HAuCl $\cdot$ 3H₂O in dilute aqua regia (0.1M HCl and 0.3 M HNO₃) between 0.7 and -0.1 V at 100 mV s⁻¹. [34]

3.3.3 XPS, AFM and SEM

XPS was performed with a VG Escalab II spectrometer using Al K α radiation (1486.6 eV) and a hemispherical analyzer for electron detection, which measured the binding energy from 0 to 1200 eV. Samples were held in place on copper stubs by carbon tape. Peaks were calibrated against the C 1s peak at 285.0 eV. Peak fitting was done using XPSPEAK 4.1.

The DC-AuNPs were imaged in tapping-mode AFM using scanning probe microscopy equipment from Digital Instruments, a Nanoscope IIIa controller and silicon nitride probes with an aluminium back-coating for extra reflectivity (Nascatec). The CV-AuNPs were imaged with an Auriga FEGSEM (Carl Zeiss) operated at a 5 kV accelerating voltage in secondary electron mode. The samples were held in place on aluminium stubs by adhesives.

While the hydrogen-terminated samples all had good conductivity, the image contrast was poor for the oxygen-terminated samples and so for the results presented in this chapter, a thin carbon coating was sputtered onto the electrode surface of all samples to make them more conductive before SEM imaging.

3.3.4 Stability

The stability of the AuNPs was tested by sonicating the decorated BDDs in an ultrasonic bath in water for 0, 2, 5 and 10 minutes and then subjecting them to ten CV scans in dilute aqua regia at 100 mV s^{-1} from 0.7 to 1.4 V, the potential range that covers the Au stripping region.

3.3.5 Pb underpotential deposition

PbUPD was performed in a 1 mM $\text{Pb}(\text{NO}_3)_2$ in 0.1 M NaOH solution, as reported by Wain,[36] to probe the crystal orientation of the deposited AuNPs. The entire Pb region was first inspected by one CV scan between -0.7 and 0.7 V starting at 0.2 V. Next, the PbUPD region, -0.7 to 0.4 V, was scanned five times starting at -0.2 V. After the experiment, a single CV scan from -0.2 to -0.7 V in 0.1 M NaOH was performed to ensure that all Pb had been removed from the surface. A scan rate of 50 mV s^{-1} was used for all scans.

3.3.6 Hg^{2+} sensing

Linear sweep voltammetry (LSV) was used to determine the behaviour of DC-AuNPs and CV-AuNPs on BDDO towards Hg^{2+} sensing. The method consisted of one LSV scan between 0.35 and 1.1 V at a scan rate of 50 mV s^{-1} after a 60 s pre-treatment at 0.35 V, as previously reported by Barrosse-Antle *et al.*[27] Square-wave anodic stripping voltammetry (SWASV) optimized from the LSV parameters above was then used to find the limit of detection of Hg^{2+} using the modified hydrogen- and oxygen-terminated BDDs. Again, a 60 s pre-treatment step at 0.35 V was used to pre-deposit Hg^0 onto the electrode surface, after which a SW scan from 0.35 to 1.1 V was performed with a potential step of 5 mV, an amplitude of

10 mV and a 10 Hz frequency in a solution of $\text{Hg}(\text{NO}_3)_2$ in 0.1 M HNO_3 . The detection limit was determined by repeatedly halving the $\text{Hg}(\text{NO}_3)_2$ concentration until the Hg^0 oxidation current was indistinguishable from the background.

3.4 Results and discussion

The results pertaining to the physical characterization of the AuNP/BDD systems are presented first, followed by the electrochemical characterizations. The use of these systems for Hg^{2+} sensing is presented last.

3.4.1 Physical characterization

XPS was used to determine the amount of Au relative to the C 1s signal on the oxygen and hydrogen-terminated electrodes for both Au deposition methods. The spectra are shown in Fig. 3.1, in which the insets show the Au 4f region with a single peak for each spin state. The relative amount of Au 4f to C 1s on each of the four electrodes was determined from the ratio of the normalized area of the Au 4f_{7/2} peak to the normalized C 1s area. Normalization of the two areas was carried out using the atomic sensitivity factors of Au 4f and C 1s, respectively. The results are given in Table 3.1. The relative ratios of Au 4f_{7/2} to C 1s given in Table 3.1 should not be directly interpreted as surface coverage ratios since these values were estimated using atomic sensitivity factors reported in the literature rather than internal standards. The ratios should mainly be used to *compare* the relative amount of Au present on the different surfaces rather than interpreted individually.

Table 3.1 shows a number of features. First, the ratio of Au 4f_{7/2} to C 1s is most similar between CV- and DC-AuNPs on BDDO than between either of the CV-AuNP or DC-AuNP samples. Second, the CV-AuNP samples show approximately three and a half times more surface Au on BDDH than BDDO despite the fact that the CV-AuNP deposition was carried out under the same conditions. Since rapid CV deposition occurs only at electroactive sites on the electrode, the difference in the amount of surface Au deposited by CV on BDDO and BDDH likely arises from the difference in electronic properties induced by hydrogen-

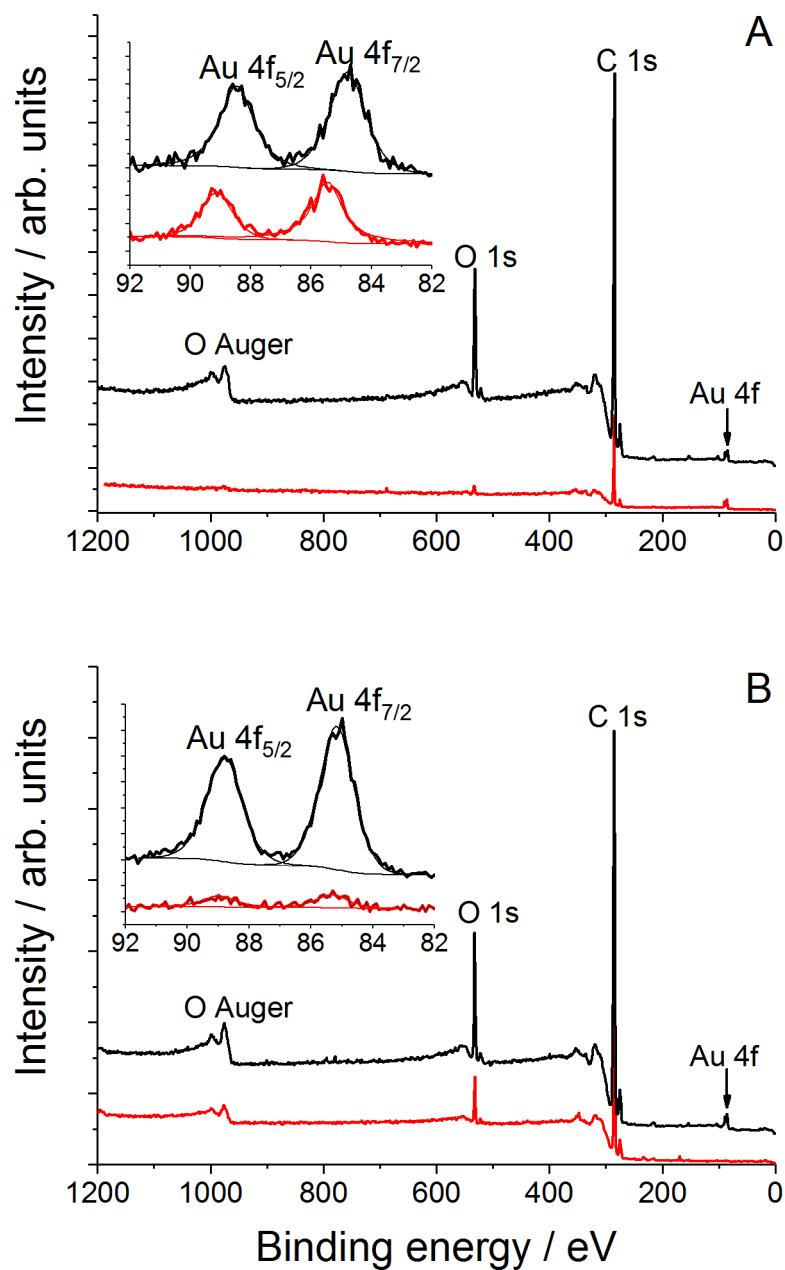


Figure 3.1: XPS of A) CV-AuNPs and B) DC-AuNPs on BDDH (red) and BDDO (black). The insets show the Au 4f peaks. Binding energies are calibrated against C 1s at 285.0 eV.

Table 3.1: The Au peak assignment and peak location for each of the four decorated electrodes.

Electrode	Binding energy / eV		Ratio of Au4f _{7/2} to C1s
	Au 4f _{7/2}	Au 4f _{5/2}	
CV-AuNPs/BDDH	85.5 (1.5)	89.1 (1.4)	0.011
CV-AuNPs/BDDO	84.8 (0.8)	88.5 (0.8)	0.003
DC-AuNPs/BDDH	85.3 (1.3)	89.0 (1.3)	0.0005
DC-AuNPs/BDDO	85.1 (1.1)	88.8 (1.1)	0.0045

The numbers in parenthesis are the shifts in peak position compared to the expected location of 84.0 eV for Au4f_{7/2} and 87.7 eV for Au4f_{5/2}. Atomic sensitivity factors of 2.8 and 0.25 were used for Au 4f_{7/2} and C 1s, respectively.[37]

terminating the BDD surface. Third, DC-AuNPs show the opposite trend; there is almost ten times more Au present on BDDO than BDDH, which suggests that DC-AuNPs have a higher physical affinity for the oxygen-terminated than the hydrogen-terminated BDD surface. Considering the positive surface charge of metal particles in general and the negative surface charge of BDDO the increased affinity of DC-AuNPs for BDDO compared to BDDH is not surprising.

The CV and DC-AuNPs on both BDDO and BDDH showed a shift in binding energy of the Au 4f orbital of approximately 1 eV from that observed in bulk elemental gold. Such shifts in binding energy have previously been attributed to the nature of the Au-BDD interaction.[22, 38, 39] Briefly, the Schottky barrier height decreases with decreasing surface oxygen species up to the point of hydrogen termination (i.e. no surface oxygen), in which case the Au is in ohmic contact with the BDD.[22, 38, 40] Hence, the 0.7 eV difference in binding energy between the CV-AuNPs on BDDO and BDDH can be explained by the difference in contact type.[22, 38, 39] Interestingly, the DC-AuNPs on BDDO and BDDH did not show different binding energy shifts — possibly due to the absence of a well-defined electrical contact between the DC-AuNPs and BDD.

Microscopy was used to determine the AuNP distribution on the electrode surfaces. Fig. 3.2A and C show SEM images of CV-AuNPs on BDDH and BDDO, while Fig. 3.2B

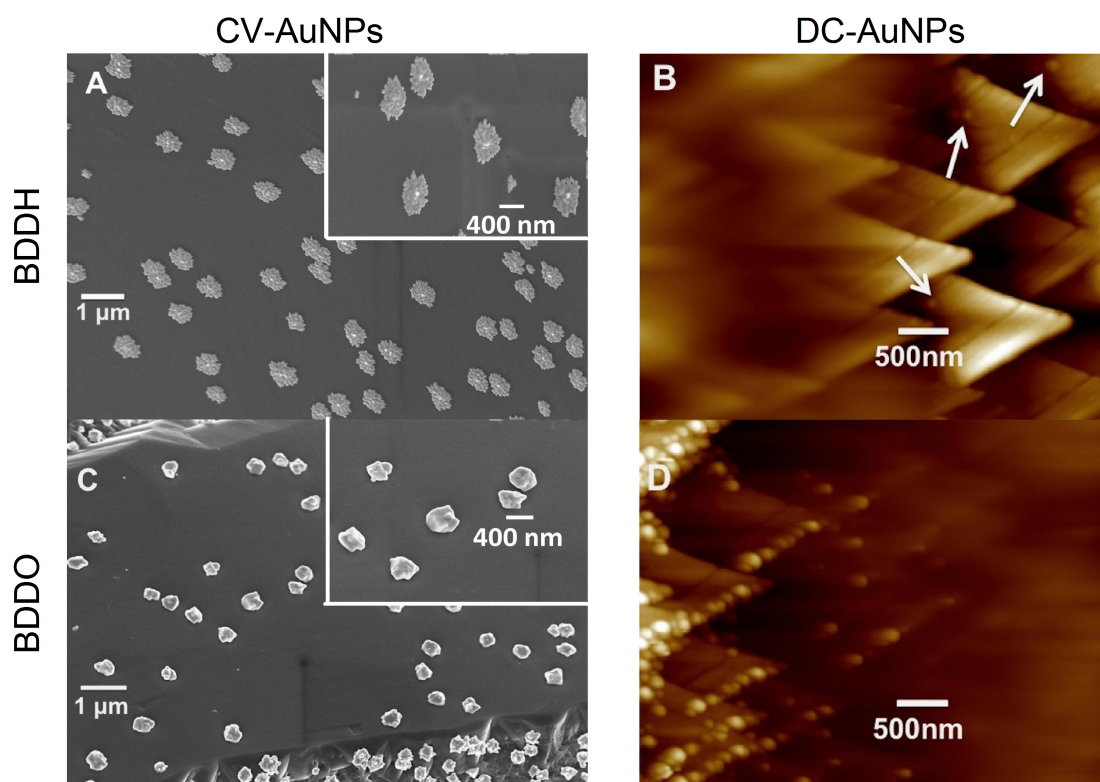


Figure 3.2: BDDH decorated with A) CV-AuNPs (SEM) and B) 50 nm DC-AuNPs (AFM) and BDDO decorated with C) CV-AuNPs (SEM) and D) DC-AuNPs (AFM). The arrows in B) point to individual DC-AuNPs dispersed on the BDDH surface.

and D show AFM images of DC-AuNPs. Fig. 3.2 shows that the diameter of the CV-AuNPs on the two electrodes were similar but the morphologies changed with electrode termination; the AuNPs had a floral shape on BDDH, which may indicate the presence of several nucleation sites in close proximity, while the CV-AuNPs were single units on BDDO. For the DC-AuNP-decorated BDDs, for which the particle morphology was predetermined, the electrode termination influenced the deposition location. For BDDO, DC-AuNPs tended to cluster together along BDD grain boundaries, whereas the DC-AuNPs dispersed over the entire grain for BDDH. AFM confirmed that significantly more DC-AuNPs adsorb onto BDDO than BDDH, as was also observed by XPS (Fig. 3.1).

3.4.2 Electrochemical characterization

The electrochemical characterization of the AuNP/BDD systems is divided into three sections: the (re)deposition and stripping behaviour, stability and PbUPD.

Electrochemical deposition and stripping behaviour

CV was used to determine the difference in (re)deposition and stripping behaviour of the AuNPs deposited on BDDO and BDDH. Deaerated, dilute aqua regia was used as the electrolyte for the pre-deposited DC-AuNPs, while clean BDDO and BDDH was used with a solution of 1 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in dilute aqua regia to probe both the initial deposition and subsequent growth of the CV-AuNPs. The results are shown in Fig. 3.3. The cathodic peak in the 0.7 to 0.1 V range corresponds to the reduction of Au,



During CV deposition of Au onto BDD, the Au typically undergoes NP nucleation followed by growth.[34] In the data presented in Fig. 3.3A and B, the nucleation-growth process is evident from the reduction-deposition potential shift from 0.1 or 0.2 V in the first scan to 0.4 V in later scans. This shift can be attributed to the Au-Au interaction exceeding the Au-BDD interaction once the electroactive sites have been seeded in the first scan.

Fig. 3.3 also shows that the Au nucleation potential depends on the electrode termination; the overpotential of CV-AuNP/BDDH is approximately 0.1 V smaller than that of CV-AuNP/BDDO, which illustrates a difference in the interaction of Au with the underlying oxygen- or hydrogen-terminated BDD. The anodic peak at 1.1 V is due to the oxidation of Au — primarily the reverse of reaction 3.1.[34, 41] The Au oxidation peak position is unaffected by scan number, but its amplitude increases with each scan because the amount of Au deposited in the early scans exceeds the amount stripped off, as shown in Table 3.2 and the insets of Fig. 3.3. The shift in overpotential of the reduction peak does not affect the amount of Au deposited by CV; the first scan deposited approximately $3.18 \mu\text{g cm}^{-2}$

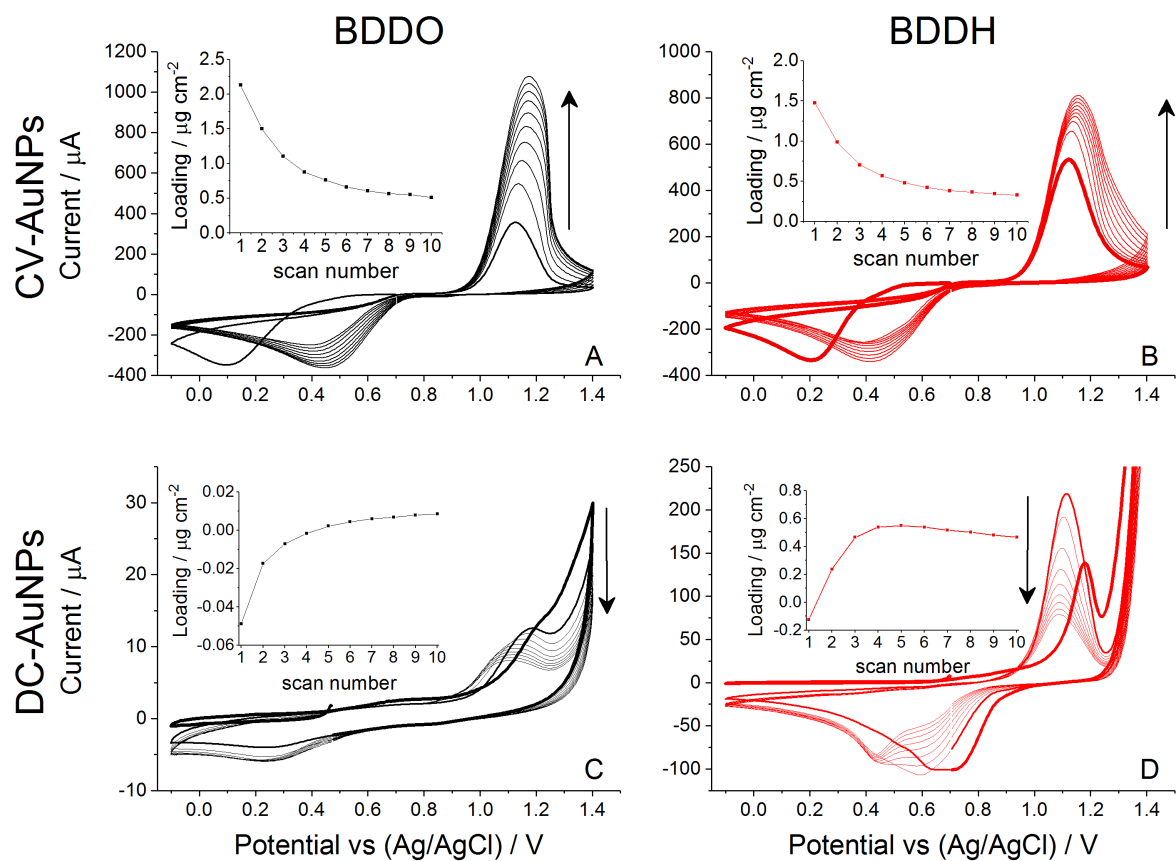


Figure 3.3: CV in dilute aqua regia at 100 mV s^{-1} starting at 0.7 V of A) CV-AuNPs/BDDO, B) CV-AuNPs/BDDH, C) DC-AuNPs/BDDO and D) DC-AuNPs/BDDH. The insets show the net Au loading after each scan, as calculated by subtracting the amount of Au stripped off the surface from the Au deposited — both of these values were calculated from the integration of the oxidation and reductions peaks, respectively. The arrows show the order of increasing scan number.

Table 3.2: The amount of Au (in $\mu\text{g cm}^{-2}$) deposited and stripped off the CV-AuNP decorated electrodes in each scan.

scan number	CV-AuNP/BDDO		CV-AuNP/BDDH	
	Deposition	Stripping	Deposition	Stripping
	$\mu\text{g cm}^{-2}$	$\mu\text{g cm}^{-2}$	$\mu\text{g cm}^{-2}$	$\mu\text{g cm}^{-2}$
1	3.18	1.05	3.19	1.71
2	3.10	1.59	3.04	2.06
3	3.16	2.06	2.96	2.25
4	3.30	2.42	2.99	2.42
5	3.47	2.71	3.06	2.59
6	3.61	2.94	3.18	2.76
7	3.75	3.15	3.31	2.92
8	3.85	3.28	3.45	3.09
9	3.95	3.40	3.59	3.24
10	4.01	3.50	3.70	3.38

The amount of Au deposited and removed in each scan was calculated from the integration of the reduction and oxidation peaks in Fig. 3.3. Note that this calculation assumes that all of the reduced Au adheres to the surface of the electrode, and that the oxidation is that and only that of the three electron process in Eq. 3.1.

of Au on both electrodes (Table 3.2). However, the first oxidation peak is larger for the CV-AuNP/BDDH sample such that the net loading after each scan is lower for BDDH than BDDO. Interestingly, the XPS data in Table 3.1 showed significantly more Au on BDDH than BDDO, which suggests that the difference in concentration is due to the strength of adhesion of the AuNPs on the different electrodes, with the adhesion of AuNPs to BDDH being stronger than that to BDDO.

Neither of the DC-AuNP samples have a reduction peak in the first scan since there were no Au ions in the solution. For DC-AuNPs/BDDH, Fig. 3.3D shows an anodic peak at 1.2 V as well as a cathodic peak at 0.7 V. These peaks correspond to the oxidation and reduction peaks associated with redox processes in Au oxide layers at bulk Au electrodes.[42, 43] At higher scan numbers, the stripping and deposition of Au from and onto the DC-AuNPs results

in peaks similar to those observed for the CV-AuNPs. The concentration of DC-AuNPs on BDDO as measured by XPS is approximately ten times higher than that measured on BDDH (Table 3.1), which likely reflects a stronger interaction of the Au with the negatively charged, hydrophilic BDDO surface than with the hydrophobic BDDH surface. The corresponding CV data for DC-AuNPs/BDDO might be expected to resemble that of DC-AuNPs/BDDH (Fig. 3.3D) but with more intense oxidation and reduction peaks due to the increased amount of Au. This is not the case. The peaks in Fig. 3.3C are at least one order of magnitude smaller than those in Fig. 3.3D. The DC-AuNPs are therefore in poorer electrical contact with BDDO than with BDDH, which may be attributed to the difference in the type of electrical contact between the AuNPs and the two diamond surfaces.[22, 38, 39, 44]

The inset of Fig. 3.3C and D shows that the net Au loading increases for the DC-AuNP decorated electrodes with each subsequent scan. The negative net loadings obtained in the first few scans are easily explained by the initial absence of Au ions in the solution, which prevents initial deposition of Au onto the surface. For the DC-AuNPs on the BDDO, the net loading after each scan eventually approaches $0.01 \mu\text{g cm}^{-2}$ while the net loading for the DC-AuNP/BDDH sample reaches a maximum after the fourth scan. These results suggest that the Au is removed from the pre-deposited colloidal NPs and redeposited at the electroactive sites on the BDD surface. The fact that the net loading of DC-AuNPs on BDDO continues to increase after each scan suggests that the colloidal NPs act as a Au source for the seeding and growing of AuNPs at electroactive sites. In contrast, the DC-AuNPs on BDDH reach a maximum net loading after the fourth scan before decreasing in a manner similar to that of the CV-AuNPs.

The extent to which the underlying surface termination of the BDD determines the redox behaviour of Au was further investigated by repeating the (re)deposition and stripping experiments on BDDs that were partially hydrogen terminated by a cathodic pre-treatment of -1.244 V for 10 s (BDDC) and then decorated with CV- or DC-AuNPs. The results are given in Fig. 3.4.

Fig. 3.4 shows that the cathodic pre-treatment resulted in a surface that was more similar to BDDO than BDDH, especially for the DC-AuNPs. For the CV-AuNPs, the initial Au

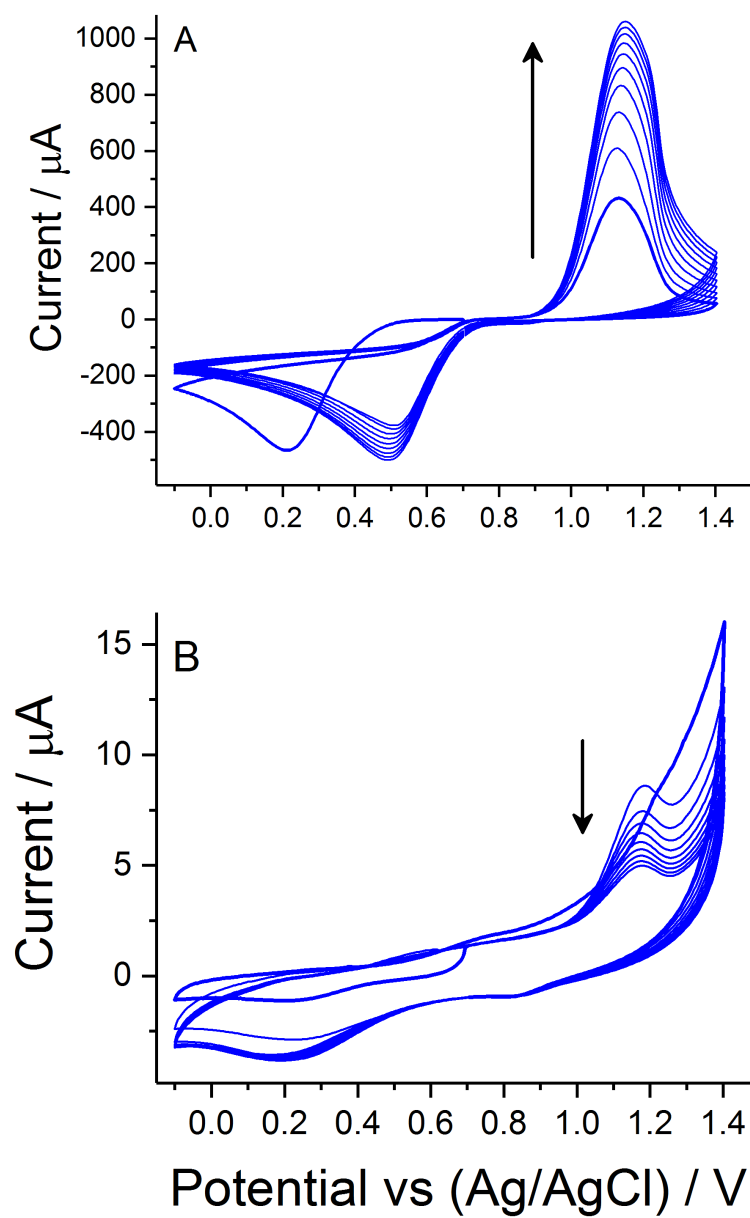


Figure 3.4: CV in dilute aqua regia at 100 mV s^{-1} starting at 0.7 V of A) CV-AuNPs/BDDC, B) CV-AuNPs/BDDC. The vertical arrows indicates the scan sequence.

deposition occurred at a potential closer to that of BDDH than BDDO, but the magnitude of the subsequent oxidation peak more closely matched that of BDDO than BDDH — even with the growth of the oxidation peak with increasing scan number. These results suggest that the degree of hydrogenation can be electrochemically tuned, but since this thesis is predominantly concerned with BDDs with the two extreme surface terminations of completely oxygen-terminated or as completely hydrogen-terminated as ambient conditions allow, these results were not pursued further.

Stability

The physical stability of the AuNPs on the surface of the BDDO and BDDH electrodes was examined for both deposition methods. The decorated electrodes were sonicated in water for 0, 2, 5 and 10 minutes, after which they were electrochemically stripped of Au using ten CV scans in dilute aqua regia between 0.7 and 1.4 V. The aim of this experiment was to estimate the amount of Au that remained on the electrodes after sonication by measuring the amount stripped off the electrode; if more Au was electrochemically removed from the BDD, then presumably more Au was left on the surface after sonication. Fig. 3.5 shows the Au loading as a function of the scan number.

The Au loading, determined by the amount of Au removed by CV, was higher on BDDH than BDDO irrespective of the deposition method. As previously discussed, this is likely due to the increased stability of AuNPs on BDDH than BDDO. Nevertheless, the bonded CV-AuNPs on both BDDO and BDDH appeared to be stable with respect to sonication since only about half of the AuNPs were removed after 10 minutes sonication. Furthermore, more CV-AuNPs were detected in the second scan than the first scan, which may indicate that the sonication process causes the AuNPs to oxidise.

DC-AuNPs showed opposite results. First, no Au loading data could be obtained for the DC-AuNPs/BDDO sample without one CV scan in dilute aqua regia being performed prior to sonication. After this activation scan, a negligible electrochemical stripping signal was observed for DC-AuNPs/BDDO due to the lack of electrical contact between the Au and the underlying electrode. Performing the activation scan after sonication did not result

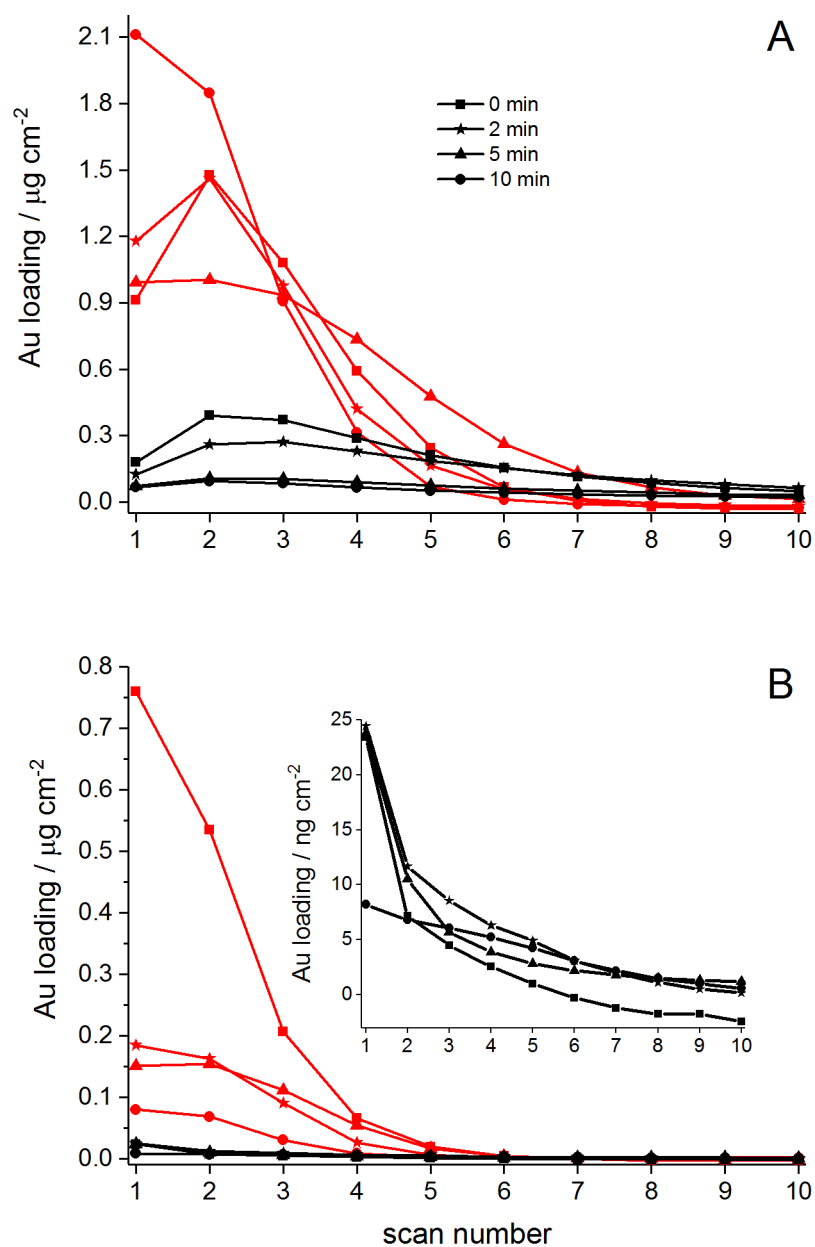


Figure 3.5: The stability is given as Au loading on BDDO (black) and BDDH (red) with respect to scan number for A) CV-AuNPs and B) DC-AuNPs. The inset in B shows the DC-AuNPs/BDDO at a smaller scale. The time legend is the same for both A and B, BDDO and BDDH.

in a detectable current, probably due to the loss of the DC-AuNPs induced by sonication. From this result, the CV scan likely improved the electrical contact between the DC-AuNPs and the BDDO electrode. Second, the DC-AuNPs were significantly less stable on BDDO than BDDH; even short sonication times resulted in complete loss of the Au oxidation signal for BDDO, while approximately 10% of the AuNPs/BDDH remained after sonication. Therefore, the DC-AuNPs were significantly less stable on the BDDs than the CV-AuNPs.

Pb underpotential deposition

PbUPD experiments were performed to determine the surface crystallinity of the AuNPs and to estimate the CV-AuNP diameter.[17, 36, 45–47] The NP diameter can be estimated by

$$\frac{A_{Au}}{S_{Au}} = \frac{\frac{2}{3}\pi r^3 \sigma n}{2\pi r^2 n}, \quad (3.2)$$

where A_{Au} is the amount of Au, S_{Au} is the surface area of Au assuming hemispherical geometry and uniform size,¹ r is the NP radius, σ is the surface density of Au and n is the number of NPs. Solving for the NP radius gives

$$r = \frac{3A_{Au}}{S_{Au}\sigma}. \quad (3.3)$$

Since Pb preferentially deposits on Au over BDD, the surface area of the detected Pb is assumed to be equal to that of the AuNPs. The amount of Au was determined by integrating the deposition peaks in Fig. 3.3, which introduced a small error due to some Au being lost between deposition and experiment (Fig. 3.5 — there was some Au loss even without sonication). The results are shown in Fig. 3.6. The reduction peaks correspond to the reduction of Pb^{2+} to Pb^0 on the Au (110), (100) and (111) surfaces, in order of decreasing potential.[36] The peaks associated with the deposition of Pb onto Au(110) is partially obscured by the background peaks of the supporting NaOH electrolyte, which explains the discrepancy in the oxidation and reduction peak magnitudes on this surface. Both CV-AuNP samples and the DC-AuNPs/BDDH sample show the Au(111) surface, while

¹These assumptions do not hold for CV-AuNPs, as shown in Fig. 3.2. Nevertheless, this approximation should give a reasonable estimate.

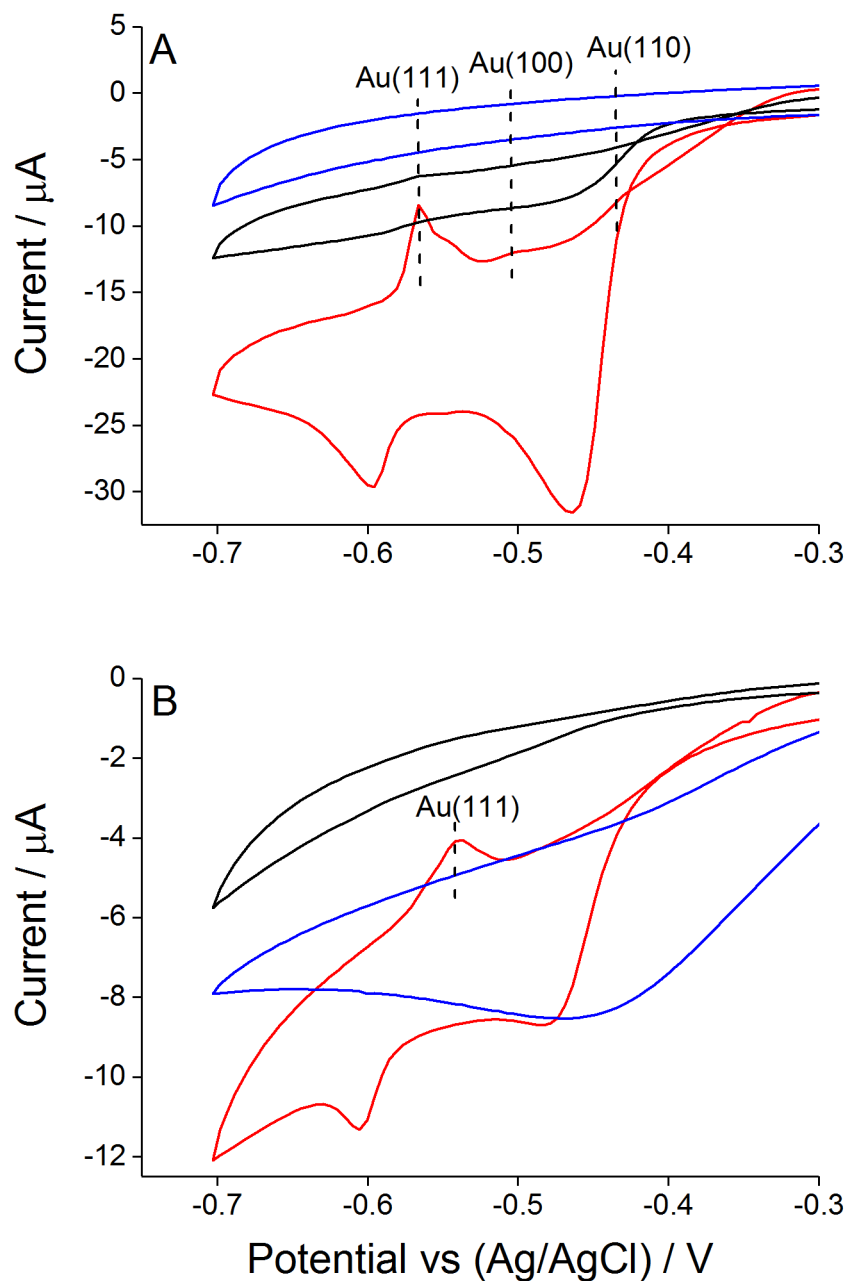


Figure 3.6: PbUPD at 50 mV s^{-1} in a $1 \text{ mM Pb(NO}_2)_3$ in 0.1 M NaOH solution on A) CV-AuNPs on BDDH (red) and BDDO (black) and B) DC-AuNPs on BDDH (red) and BDDO (black). The blue line in A) shows the PbUPD on the clean BDD and B) the effect of the 0.1 M NaOH supporting electrolyte on AuNPs/BDD.

DC-AuNPs/BDDO do not show any electrochemical response to PbUPD. The CV-AuNPs on both BDDO and BDDH also show additional Au crystal surfaces, though the peaks for CV-AuNPs/BDDO are small. The presence of multiple peaks shows that CV deposition results in AuNPs that are electrochemically active on multiple crystal surfaces, especially CV-AuNPs on BDDH, which show three Au surfaces. The diameter of the CV-AuNPs was calculated to be 200 nm for CV-AuNPs/BDDH, which is on the same order of magnitude as the SEM data (Fig. 3.2). The diameter of the CV-AuNPs/BDDO was calculated to be 3.14 μm , which is different from the SEM result. The discrepancy between the calculated and the measured diameter arises from the overestimation of deposited Au from the reduction curves – Holt *et al.* reported that the CV deposition method results in some of the Au forming colloidal particles at the BDD surface rather than on the surface and so some AuNPs are “lost” from the BDDO surface between deposition and analysis.[34]

The background slope of the voltammograms suggests that residual oxygen is interfering with the PbUPD process. This interference should not affect the overall measurement.

3.4.3 Hg^{2+} sensing

After studying the variation in characteristics of the AuNP/BDDs with Au deposition method and BDD termination, the combined effect of these characteristics was explored by testing the electrodes as heavy metal sensors. Hg was chosen as the test candidate because of its high affinity for Au arising from a strong Hg-Au bonding interaction.[27, 29, 30] Hence, any electrochemical differences observed in sensing experiments are likely due to the effect of the electrode termination and deposition method on the Au-BDD interaction. Linear sweep voltammetry (LSV) was first used to characterize the oxidation potentials of Hg^{2+} and the pre-deposition time of Hg^0 on the bare and AuNP-decorated BDDO. Since these experiments were only performed to facilitate the parameter optimization of the SWASV used later, BDDH was not used. SWASV was then used for detection at low Hg^{2+} concentrations for both AuNP deposition methods on BDDO and BDDH.

Linear sweep voltammetry

The LSV parameters reported by Barrosse-Antle [27] were used for the initial investigation of the detection of Hg^{2+} using AuNP-modified BDDO. Briefly, a pre-treatment step of 0.35 V for 60 s was used to pre-deposit Hg^0 onto the BDDO:



The LSV scan reoxidizes the deposited Hg^0 to Hg^{2+} , which is observed at approximately 0.5 V on the bare BDD of either termination and at 0.6 V and 0.8 V for DC-AuNPs and CV-AuNPs, respectively, as shown in Fig. 3.7. The LSV scan ran between 0.35 and 1.1 V at 50 mV s⁻¹.

Fig. 3.7A and B show two oxidation peaks for Hg^0 to Hg^{2+} : one peak arises from the oxidation of Hg^0 on the underlying BDDO and the other peak arises from oxidation on the AuNPs. The peak current associated with oxidation at the CV-AuNPs is appreciably larger than that for the DC-AuNPs. However, the DC-AuNP/BDDO electrode showed the largest oxidation current arising from the underlying BDDO. This result can be explained if the presence of the DC-AuNPs on the electrode surface increases the sensitivity of BDD to Hg, for instance by allowing the deposited Hg^0 to diffuse from the AuNPs onto the clean diamond surface from which the Hg^0 is reoxidised. Despite having the lowest oxidation current at the underlying BDDO, the CV-AuNP/BDDO electrode shows the smallest loss of current with reduced $\text{Hg}(\text{NO}_3)_2$ concentration. This suggests that the CV-AuNP/BDDO electrode will be best suited for the detection of low $\text{Hg}(\text{NO}_3)_2$ concentrations.

Square-wave anodic stripping voltammetry

Low concentrations of Hg^{2+} were detected by SWASV of the decorated electrode in the $\text{Hg}(\text{NO}_3)_2$ solution after a pre-concentration step at 0.35 V for 60 s. During the scan, the Hg^0 reoxidized to Hg^{2+} at approximately 0.5 V on the bare BDD of either termination and at 0.6 V and 0.8 V for DC-AuNPs and CV-AuNPs, respectively — similar to the LSV results above. A competing oxidation reaction, the formation of the mercuric dimer at 0.9 V [48, 49],

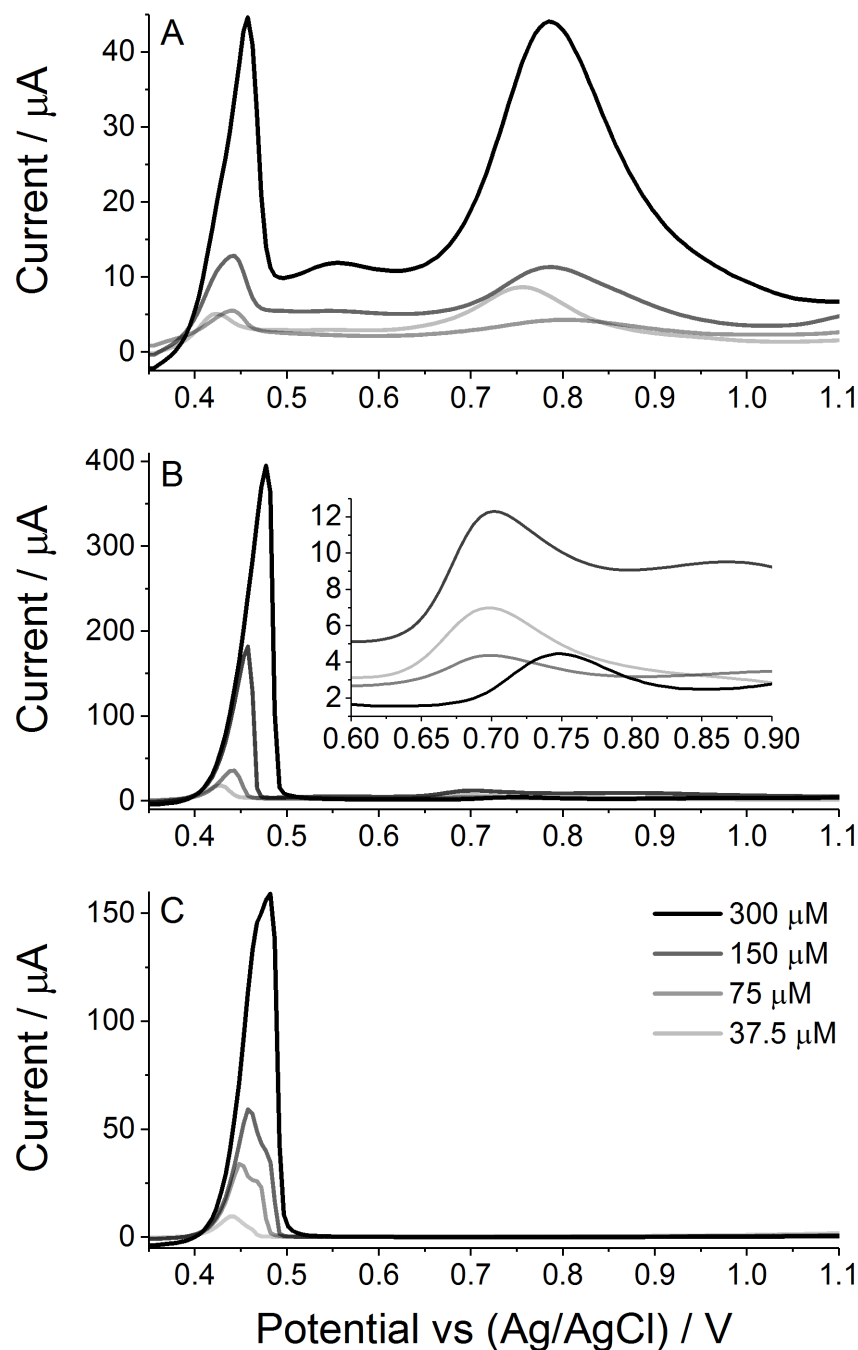


Figure 3.7: LSV at 50 mV s^{-1} in different concentrations of $\text{Hg}(\text{NO}_3)_2$ after a 60 s pre-treatment at 0.35 V on A) CV-AuNPs/BDDO B) DC-AuNPs/BDDO and C) bare BDDO. The $\text{Hg}(\text{NO}_3)_2$ concentrations are the same for all three graphs and are given in the legend of C).

occurred only on the bare BDDH or at high Hg^{2+} concentrations on the DC-AuNPs/BDDH. Fig. 3.8 shows the reoxidation of Hg^0 to Hg^{2+} obtained by using a stock concentration of 1 μM $\text{Hg}(\text{NO}_3)_2$ solution for the bare BDDs and a stock solution of 500 nM, as well as the lowest concentration of $\text{Hg}(\text{NO}_3)_2$ for which peak currents could be detected, for the decorated BDDs.

For Hg sensing, the electrode termination was more important than the AuNP deposition method. Significantly lower concentrations of Hg could be detected on BDDH decorated with either DC- or CV-AuNPs than on BDDO. The detection limits were 4 and 32 nM Hg^{2+} for the CV- and DC-AuNPs, respectively. Fig. 3.8D shows that at lower concentrations of Hg, the oxidation to Hg^{2+} primarily occurs at potentials associated with oxidation at the underlying BDDH rather than at the DC-AuNPs. Peculiarly, the Hg^0 stripping peak is only observable if the DC-AuNPs are present on the electrode, even if the reoxidation is not observed at the potential associated with Au. This suggests that the DC-AuNPs aid the reduction of Hg^{2+} onto BDDH by first depositing Hg^0 onto the DC-AuNPs and then diffusing to the BDDH, as discussed for the LSV currents in Fig. 3.7B.

The lowest limit of Hg detection with AuNPs currently reported in the literature is 0.42 nM at glassy carbon electrodes.[28] Therefore, with further optimization, the AuNPs/BDD ensembles might be capable of offering performance that is competitive with carbon-based substrates in the field of Hg sensing.

3.5 Summary

This chapter investigated the effect of BDD termination on the electrochemical activity of AuNPs deposited by both electrochemical and electroless methods. This section gives a brief summary of the most salient results.

1. *Coverage* The amount of Au present on the electrode surfaces was estimated by three distinct methods. XPS showed that there was more Au present on the hydrogen-terminated BDD than the oxygen-terminated BDD when the Au was deposited electrochemically, but that more Au was present on the oxygen-terminated BDD than

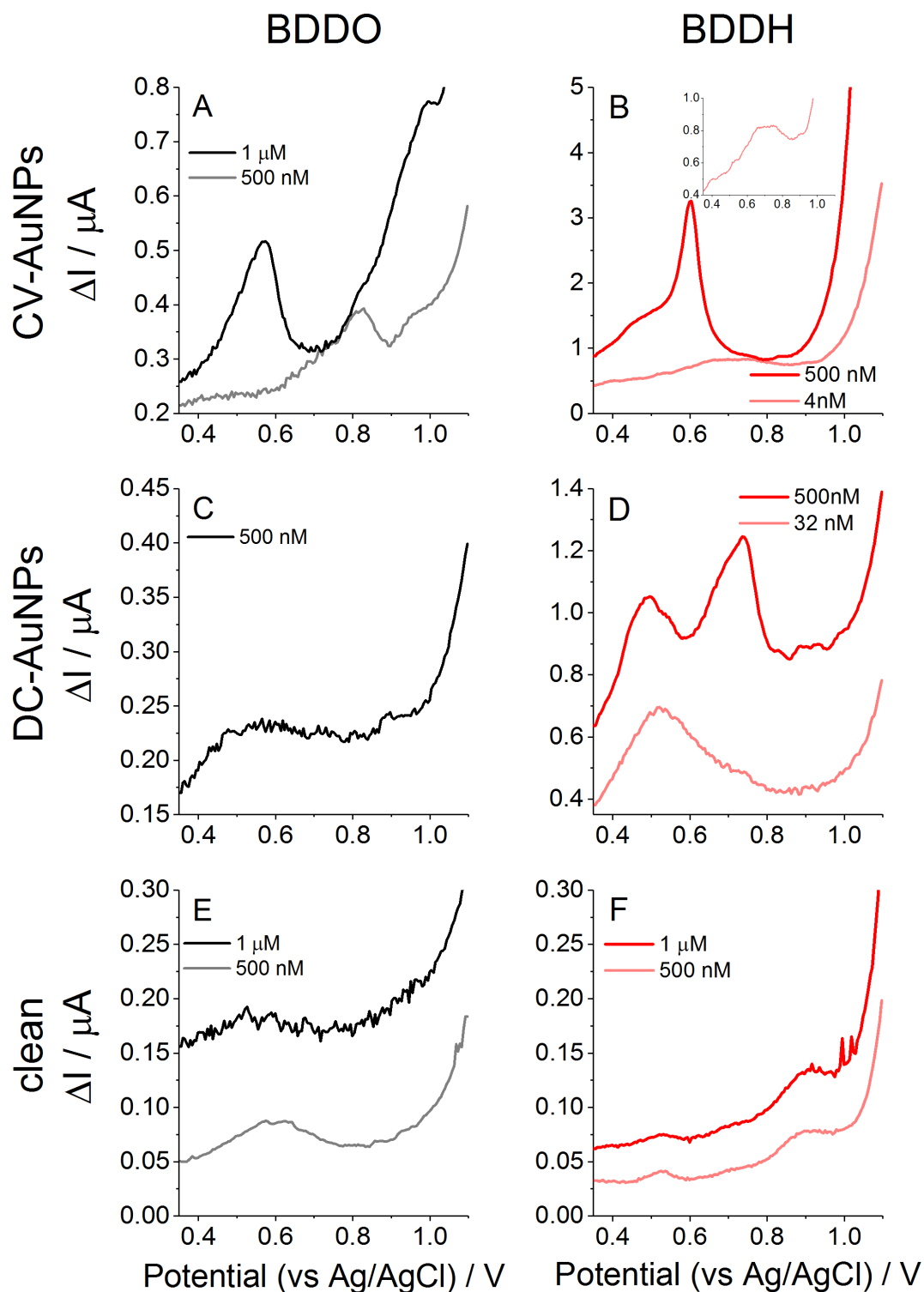


Figure 3.8: SWASV with a potential step of 5 mV, 10 mV amplitude and 10 Hz frequency after a 60 s pretreatment at 0.35 V in $Hg(NO_3)_2$ solutions on A) CV-AuNPs/BDDO, B) CV-AuNPs/BDDH, C) DC-AuNPs/BDDO, D) DC-AuNPs/BDDH, E) bare BDDO and F) bare BDDH. The $Hg(NO_3)_2$ concentrations are given in each legend. The small shoulder observed at just over 1 V corresponds to the onset of Au oxidation.

the hydrogen-terminated BDD when deposition was done by drop-casting from a colloidal solution. In order of decreasing Au 4f_{7/2} to C 1s ratios, XPS gave CV-AuNPs/BDDH > DC-AuNPs/BDDO > CV-AuNPs/BDDO > DC-AuNPs/BDDH. Microscopy, used to qualitatively estimate the amount of AuNPs on the BDD surface, corroborated this finding. However, electrochemical experiments showed different amounts of Au on the surface compared to the XPS results. The electrochemical measurements (Fig. 3.3) showed that the largest peak current, which corresponds to the most electrochemically active Au on the surface, was obtained using CV-AuNPs on the hydrogen-terminated BDD. While this result corresponds with the XPS results, more electrochemically active Au was detected on the BDD surface when the AuNPs were deposited by CV. In order of decreasing peak current, the electrochemical experiments gave CV-AuNPs/BDDH > CV-AuNPs/BDDO > DC-AuNPs/BDDH > DC-AuNPs/BDDO. The discrepancy in the amount of Au detected by XPS and electrochemistry can be explained by either a difference in stability or by a difference in an effective electrical contact between the Au and the underlying BDD.

2. *Morphology and distribution over the underlying BDD* Microscopy revealed the surface-termination of the underlying BDD to be of utmost importance in the morphology of the CV-AuNPs and in the distribution of the DC-AuNPs over the underlying BDD. The CV-AuNPs on the hydrogen-terminated surface had a shape that suggested initial deposition followed by growth, while the CV-AuNPs were single units on the oxygen-terminated surface. The DC-AuNPs were dispersed over the BDDH surface, but clustered along the BDD grain boundaries of BDDO. PbUPD showed that the surface crystallinity of the CV-AuNPs was determined by the surface-termination of the underlying BDD.
3. *Electrical contact* The electrochemical characterization indicated a more effective electrical contact between the AuNPs deposited by either method on BDDH than on BDDO. Changes in the binding energy shift in XPS showed a difference in the type of electrical contact between the CV-AuNPs deposited on BDDH and BDDO. Compari-

son with established literature suggested that the shift in binding energy was indicative of an ohmic contact for the hydrogen-terminated electrode and a Schottky barrier with the oxygen-terminated electrode.

4. *Stability* The stability experiments showed that the CV-deposited AuNPs are more stable on the electrode surface than the drop-cast AuNPs. For both deposition methods, the AuNPs were more stable on BDDH.
5. *Sensing* In the application of the prepared electrodes in the sensing of Hg^{2+} at low concentrations, the surface-termination of the BDD was found to be of greater importance than the AuNP deposition method. These experiments also suggested that Hg^0 first deposited onto the Au and then diffused to the underlying BDD before being reoxidised. The increased stability of AuNPs on BDDH and the improved electrical contact make these electrodes more stable sensing platforms than the BDDO equivalents.

3.6 Conclusion

The research into the application of AuNPs for electrochemical sensing is an active area of research, but the direct comparison between two deposition methods and two electrode terminations is unique to this study. The results presented in this chapter suggests that the performance of the electrode ensemble is tunable based on the properties required of the electrode. Distinct surface crystallinity, morphologies and surface distributions are achievable by changing the surface-termination of the underlying BDD. However, the hydrogen-terminated BDDH consistently outperformed the oxygen-terminated BDD in terms of peak currents of both Au redox and Hg sensing.

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Chapter 4

The effect of surface termination on glucose oxidation using Ni-modified diamond electrodes

4.1 Introduction

The previous chapter explored the variation in AuNP behaviour on BDD with deposition method and BDD surface termination. The results showed that the surface termination determined both the quality of the electrical contact between the AuNPs and the BDD as well as the morphology of the electrodeposited AuNPs. This chapter investigates these conclusions further by exploring if the surface termination of the underlying BDD has as great an effect when the electrodes are decorated with another class of commonly used catalysts, namely metal oxides.

Metal oxides are used in a wide range of applications from the electroreduction NO_x with various transition metal oxides including iron oxides,[1] CO oxidation with copper oxides,[2] to water electrolysis and the oxygen evolution reaction.[3, 4] Nickel oxides, for example, have also been used for water splitting,[5, 6] the oxidation of primary alcohols, including methanol, for use in green energy fuel cells,[7–10] as well as the oxidation of organic compounds such as adenine, DNA, steroid hormones and glucose for sensing purposes.[5, 11–13]

Enzymatic glucose sensing is currently the most common method of glucose sensing but suffers from the instability inherent to enzymes.[14] An alternative to enzymatic sensing is the enzyme-free oxidation of glucose, which has been investigated by several groups.[5, 7, 12, 14–18] For example, glucose can be electrooxidised to gluconolactone [19–21] by the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ catalytic redox couple,[5, 14, 17] which can be obtained from Ni oxidation in an alkali solution.[13, 17, 22, 23] Given the importance of glucose sensing in fields such as medicine, the food industry [24] and fuel cells,[15, 25–27] there is a lot of work in the literature that documents the use of Ni particles for glucose oxidation on BDD and other substrates. Wang *et al.* also reported on the use of BDD without Ni in the oxidation of glucose but found that the BDD had little effect on glucose oxidation without nanowire diamond decoration.[28] However, most of the work currently reported in the literature that studies the use of Ni particles supported on BDD for glucose oxidation exclusively uses BDDO.[5, 6, 14, 21] Toghill *et al.*, for example, showed that hydroxide-enriched Ni particles supported on BDDO had a linear current response to glucose in concentrations from 10 μM to 10 mM.[5] In this study, Toghill deposited Ni from a 1 mM $\text{Ni}(\text{NO}_3)_2$ solution for 600 s at a potential of -1.3 V versus a saturated calomel reference electrode onto a 3 mm diameter polished BDDO obtained from Windsor Scientific (Slough, UK). Deposition times of 120 and 300 s were also investigated, and the sensitivity of the electrode found to increase with Ni deposition.[5] Considering the improved surface conductivity of BDDH,[29] the work presented in this chapter aims to extend the work already conducted by Toghill by studying the performance of the Ni-decorated BDDH in glucose oxidation. The work presented here also makes use of more commercially viable BDD electrodes from Element Six. Furthermore, this work seeks to extend the research conducted by Hutton *et al.* [6] by studying various Ni loadings on both the oxygenated and hydrogenated BDDs.

4.2 Aims of the chapter

This chapter explores the use of $\text{Ni}(\text{OH})_2/\text{BDD}$ for glucose oxidation. The aims of the chapter are to determine which BDD surface termination is best suited to glucose oxidation

with the $\text{Ni}(\text{OH})_2$ acting as a catalyst, to investigate any differences in electrode performance arising from the BDD surface termination, and to determine the optimal Ni loading for each of the two BDD surfaces.

4.3 Experimental

All BDDs ($[\text{B}] > 10^{20} \text{ cm}^{-3}$) used in this work were polycrystalline, of electrochemical grade and purchased from Element Six Co (UK). The material specifications of the purchased BDDs are given in Table 2.1 and an SEM of the clean starting surface shown in Fig. 1.3. 70% HNO_3 and 37% HCl were purchased from Fischer Scientific and all other chemicals were from Sigma-Aldrich. Throughout this work, water refers to Millipore water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$. Deaeration was accomplished by bubbling N_2 through the solution for 20 minutes.

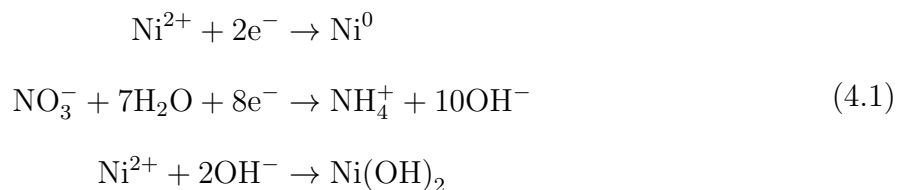
4.3.1 Electrode surface termination and cleaning

Clean BDDs were oxygen terminated by reflux in 70% HNO_3 for 4 hours or hydrogen terminated by exposure to hydrogen plasma at 600°C for 45 minutes at 1.5 kW power and a pressure of 45 Torr. The hydrogenated surface was refreshed between each use after cleaning, while the oxygen-terminated surface was maintained by 20 CV scans between 2.5 and -1.7 V at 100 mV s^{-1} in 0.1 M HNO_3 .

At the end of each experiment, the $\text{Ni}(\text{OH})_2$ was removed from the BDD surface by submerging the electrode in 6 M HCl for 30 minutes, which removed the hydroxide layers. The Ni was then removed by putting the electrodes in a 3% FeCl_3 aqueous solution twice for 10 minutes, after which cleanliness was confirmed by CV between 2.5 and -1.7 V in 0.1 M HNO_3 at 100 mV s^{-1} . If the CV revealed metal impurities, such as Fe from the FeCl_3 treatment, on the BDD surface, the electrodes were immersed in aqua regia over night. The aqua regia in this case was made of a 3:1 v/v mixture of 37% HCl and 70% HNO_3 .

4.3.2 Ni deposition and enrichment

Ni was deposited onto the clean, surface-terminated BDDs by amperometry at -1.3 V for 100, 400 or 600 s in a 1 mM $\text{Ni}(\text{NO}_3)_2$ solution with 0.1 M acetate buffer (pH=5) acting as supporting electrolyte. Given that this procedure deposits a mixture of Ni^0 and $\text{Ni}(\text{OH})_2$, [5]



the deposited Ni was then explicitly enriched with hydroxide.

The hydroxide layers were enriched by CV between 0.15 and 0.55 V in a 1 M KOH solution to oxidize the Ni metal, as previously described by Toghil [5] and Sphilevaya. [17]

4.3.3 Physical characterization

SEM was used to determine the distribution and morphology of the as-deposited Ni particles on the BDD substrates. The BDDH samples were imaged using a Hitachi S-4300 field emission scanning electron microscope as well as the 100 s Ni/BDDO. The other electrodes were imaged with a JEOL JSM-5610LV. An accelerating voltage of 20 kV was used for all samples.

XPS was used to determine relative amounts of surface Ni and was performed with a VG Escalab II spectrometer using Al $\text{K}\alpha$ radiation (1486.6 eV) and a hemispherical analyzer for electron detection, which measured the binding energy from 0 to 1200 eV. Samples were held in place on copper stubs by carbon tape. Peaks were calibrated against the C 1s peak at 285.0 eV and fitted using the CasaXPS software.

4.3.4 Glucose oxidation

The sensitivity and behaviour of the $\text{Ni}(\text{OH})_2$ /BDD systems were probed by glucose oxidation. The general redox behaviour of glucose solutions with the $\text{Ni}(\text{OH})_2$ /BDD electrodes

was observed by CV, while amperometric measurements were used to determine whether these electrodes exhibit linear increase in the oxidative current with increased glucose concentration. CV was performed using solutions containing 1–10 mM glucose in 1 M KOH between 0.2 and 0.5 V at 50 mV s^{-1} . These solutions were stirred at 700 rpm.

Amperometric measurements were then performed by keeping the $\text{Ni(OH)}_2/\text{BDD}$ electrode in a 1 M KOH solution for 50 s, after which aliquots of concentrated glucose were injected at intervals of 50 s to final concentrations either in the range of 1–13 mM or 0.1–1.3 mM glucose. The potential was held at the oxidation potential of glucose as found by CV, which was 0.47 V. The solution was stirred at 700 rpm.

4.4 Results and discussion

Ni was potentiostatically deposited at -1.3 V from a deaerated 1 mM $\text{Ni(NO}_3)_2$ in 0.1 M acetate buffer for 100, 400 and 600 s onto BDDO and BDDH. The charge equivalents of Ni deposited on each electrode are given in Table 4.1, as calculated by integration of the deposition curve. Whether the Ni at longer deposition times continued to deposit onto the

Table 4.1: Ni deposition in mC on BDDH and BDDO from a 1 mM $\text{Ni(NO}_3)_2$ solution

Electrode	100 s	400 s	600 s
BDDH	70	240	430
BDDO	65	220	310

underlying BDD or onto existing Ni particles cannot be determined from the information in Table 4.1 alone; physical characterization by SEM and XPS is also needed. Therefore, this section presents the physical characterisation first, followed by the electrochemical oxidation of glucose by both CV and amperometry. The different Ni loadings are discussed for each electrode and the two BDD terminations are discussed side by side.

4.4.1 Physical characterization

The morphology and distribution of the as-deposited Ni was investigated by SEM and Fig. 4.1 shows representative areas of the Ni-covered BDD surfaces.

The most striking difference between the Ni on BDDH (Fig. 4.1A-C) and BDDO (Fig. 4.1D-F) is the difference in particle distribution on the electrode surface; on BDDH, the Ni particles have a uniform distribution and show no preference for flat or pitted areas. In contrast, on BDDO the Ni preferentially sits in pitted areas or along ridges. The distribution of the Ni particles within these areas is random, as was also found by Toghiani.[5] As shown in Fig. 4.1A-C, BDDH has a Ni particle coverage that increases with the deposition time — these particles diminish in both size and number for the 100 s deposition. The particle size of the 600 s Ni is approximately twice as large on BDDO compared to BDDH, which shows that the difference in the amount of Ni deposited results in different particle coverages also between the two types of BDD and not only between different Ni depositions on either BDD. However, for the 100 s deposition, the particles are more than one order of magnitude larger on BDDO than BDDH. Overall, the Ni particles increase in size with deposition time on BDDH while they increase in number on BDDO. All samples have a Ni morphology that is approximately hemispherical, as was also obtained by Toghiani.[5] The more uniform coverage of Ni on the hydrogenated surface in comparison to the oxidised surface is likely caused by the additional conductivity from the so-called surface conductivity of BDDH.

The Ni-modified electrodes were then analysed by XPS to determine the different Ni environments with deposition time. Representative wide scans, C 1s and O 1s regions are shown in Fig. 4.2, while Fig. 4.3 shows the Ni 2p regions for each electrode. The peak assignments [30] are indicated on the graphs.

As shown in Fig. 4.3, the Ni was deposited in different ratios of Ni metal and Ni(OH)₂ depending on the termination of the underlying BDD. After 100 and 400 s of Ni deposition, the Ni metal to Ni(OH)₂ ratio was larger for BDDO than BDDH, while the 600 s deposition times had a larger metal to hydroxide ratio on BDDH than BDDO. Given that the Ni was deposited at the same potential and the same pH for both electrodes, the difference in Ni metal to Ni(OH)₂ ratios between the two types of BDD suggests that there is a difference

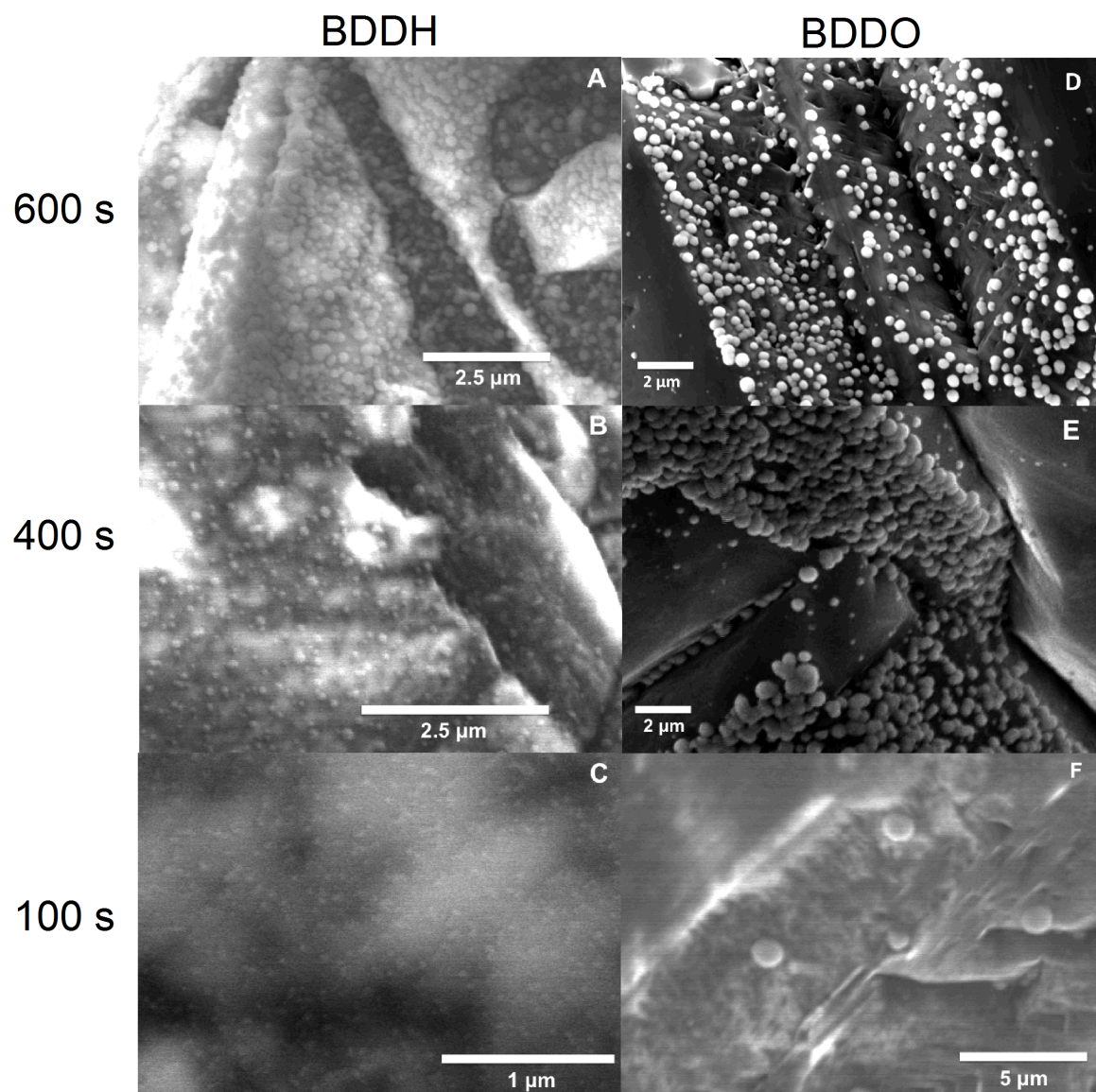


Figure 4.1: SEM images of Ni deposited at -1.3 V from a solution of 1 mM $\text{Ni}(\text{NO}_3)_2$ in 0.1 M acetate buffer onto BDDH for A) 600 s, B) 400 s and C) 100 s or onto BDDO for D) 600 s, E) 400 s and F) 100 s.

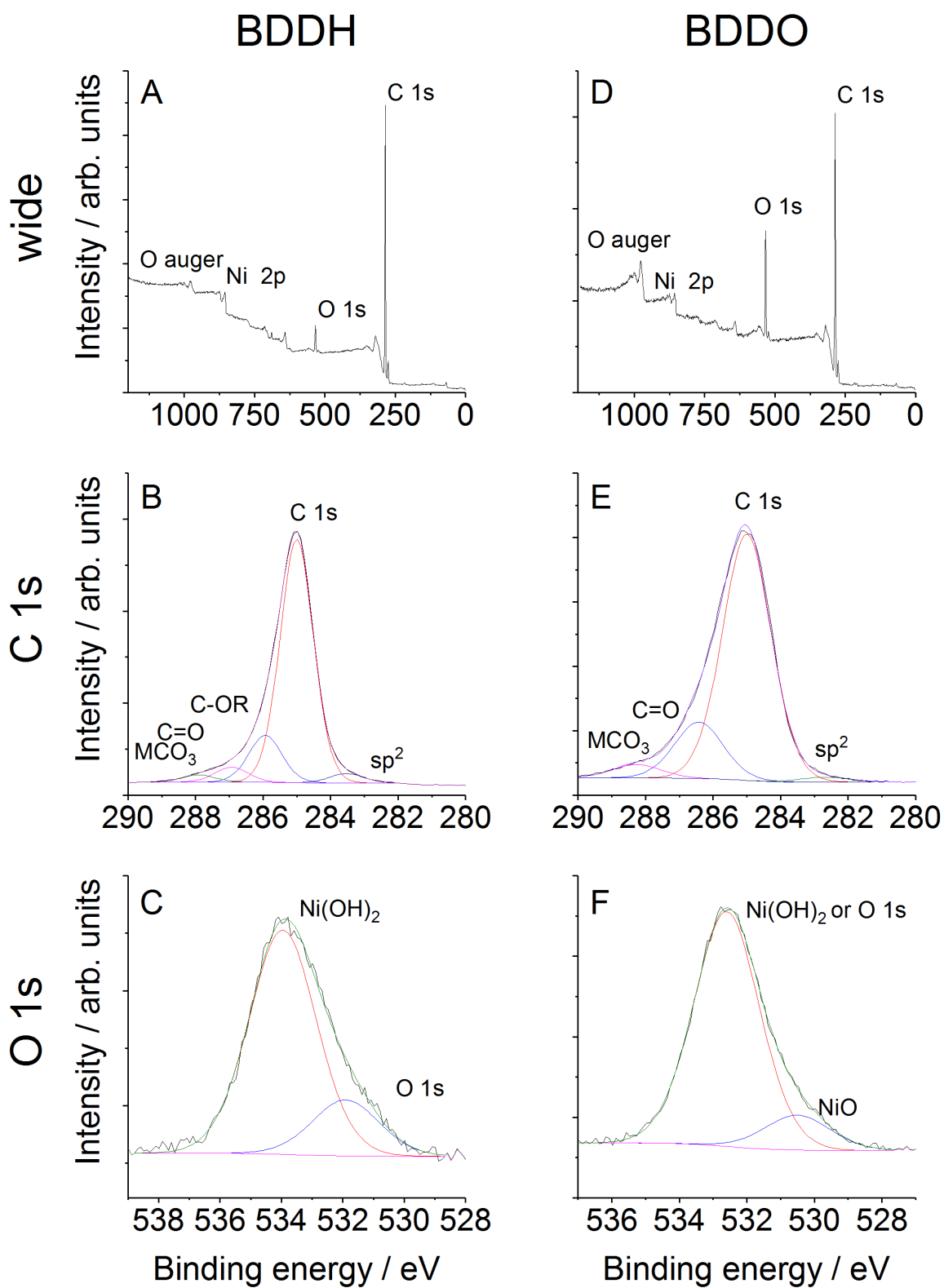


Figure 4.2: The wide survey scans, the C 1s and O 1s regions of representative Ni-decorated BDDH and BDDO.

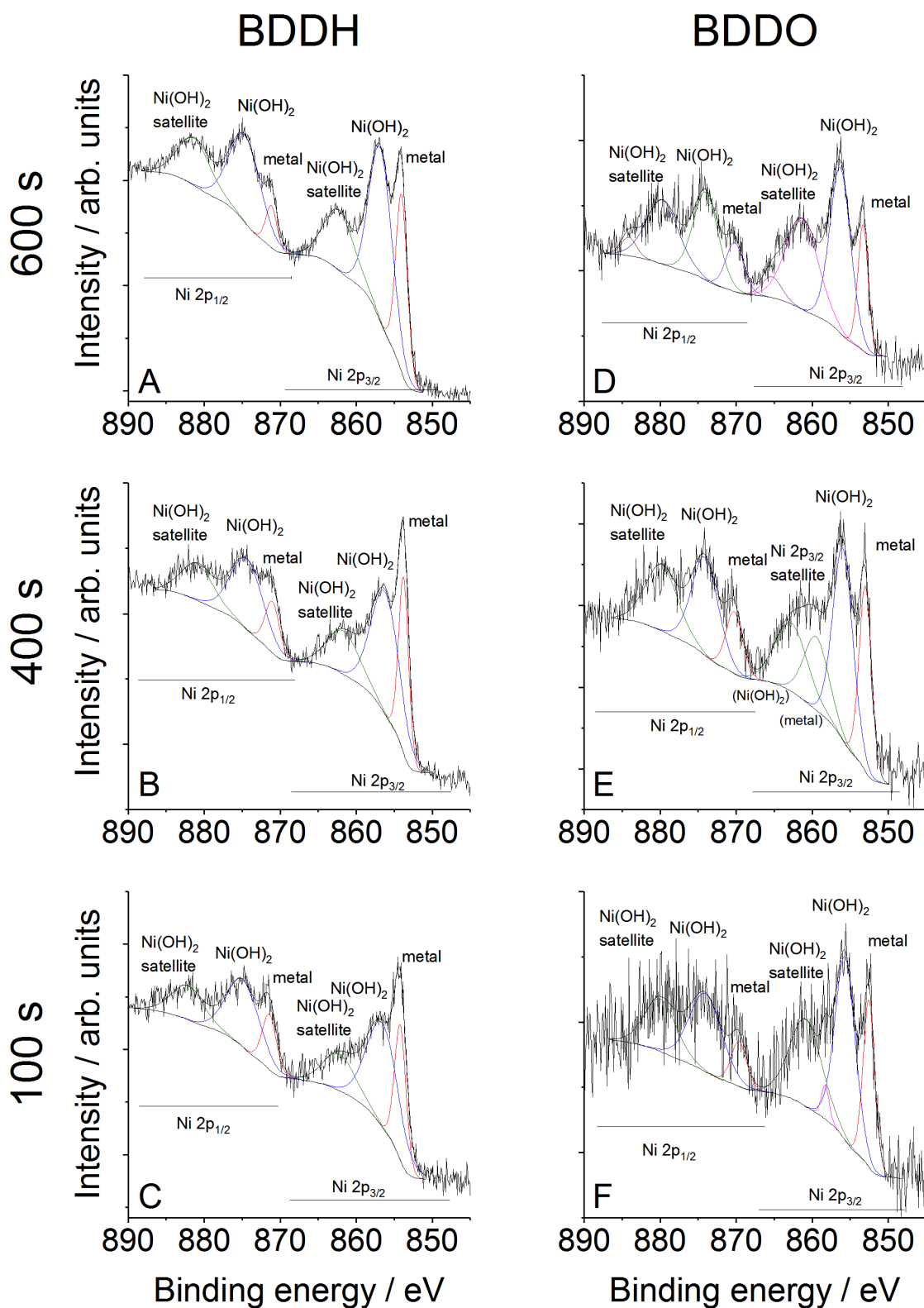


Figure 4.3: XPS of the Ni 2p region of Ni-modified BDDH for A) 600 s, B) 400 s and C) 100 s and of the Ni-modified BDDO for D) 600 s, E) 400 s and F) 100 s. The Ni metal peak contributions are fitted in red, the Ni(OH)₂ in blue and the satellite peaks are in green. Where the satellite peaks have distinct contributions from both Ni(OH)₂ and Ni metal, the assignment is indicated in parenthesis below the spectrum.

Table 4.2: Relative % amounts of O and Ni on BDDH and BDDO as calculated by XPS

Ni deposition (representative)	Ratio / % O 1s : C 1s	BDDH	BDDO
600 s	Ni : C 1s	2.60	1.44
	Ni metal : Ni(OH) ₂	50.34	37.53
400 s	Ni : C 1s	1.42	1.61
	Ni metal : Ni(OH) ₂	50.47	59.41
100 s	Ni : C 1s	1.06	0.61
	Ni metal : Ni(OH) ₂	47.19	52.57

The O 1s to C 1s ratios were calculated from the representative 400 s Ni deposition spectra and the Ni metal to Ni(OH)₂ were calculated from the 2p_{3/2} peaks, using Schofield relative sensitivity factors of 1 for C 1s, 2.8 for O 1s and 22.2 for Ni 2p.

in the interaction between the Ni and the underlying BDD with surface termination. For BDDH, the ratio was within 3% of an even split between Ni metal and hydroxide for all three samples. On BDDO, however, the ratio varied greatly from showing marginally more metal than hydroxide at shorter deposition times to indicating significantly more hydroxide than metallic Ni after the 600 s deposition.

As expected from the calculation of the amount of Ni deposited (Table 4.1), more Ni was deposited with longer deposition times. However, the 400 s Ni deposition onto BDDO showed more surface Ni by XPS than the 600 s deposition, despite that approximately 90 mC more Ni was deposited with 600 s than with 400 s deposition times.

4.4.2 Glucose oxidation: CV

Following the deposition of Ni, the Ni was enriched to Ni(OH)₂ in 1 M KOH for 500 cycles between 0.15 and 0.55 V to improve the electrochemical activity of the sample. The enriched Ni-modified BDD was then used to probe the redox behaviour of solutions with glucose concentrations between 1 and 10 mM in 1 M KOH. The voltammograms, together with current versus glucose concentration plots, are shown in Fig. 4.4 and 4.5. In the forward scan, the peak is that of Ni(OH)₂ oxidation to NiOOH. NiOOH is then reduced back to

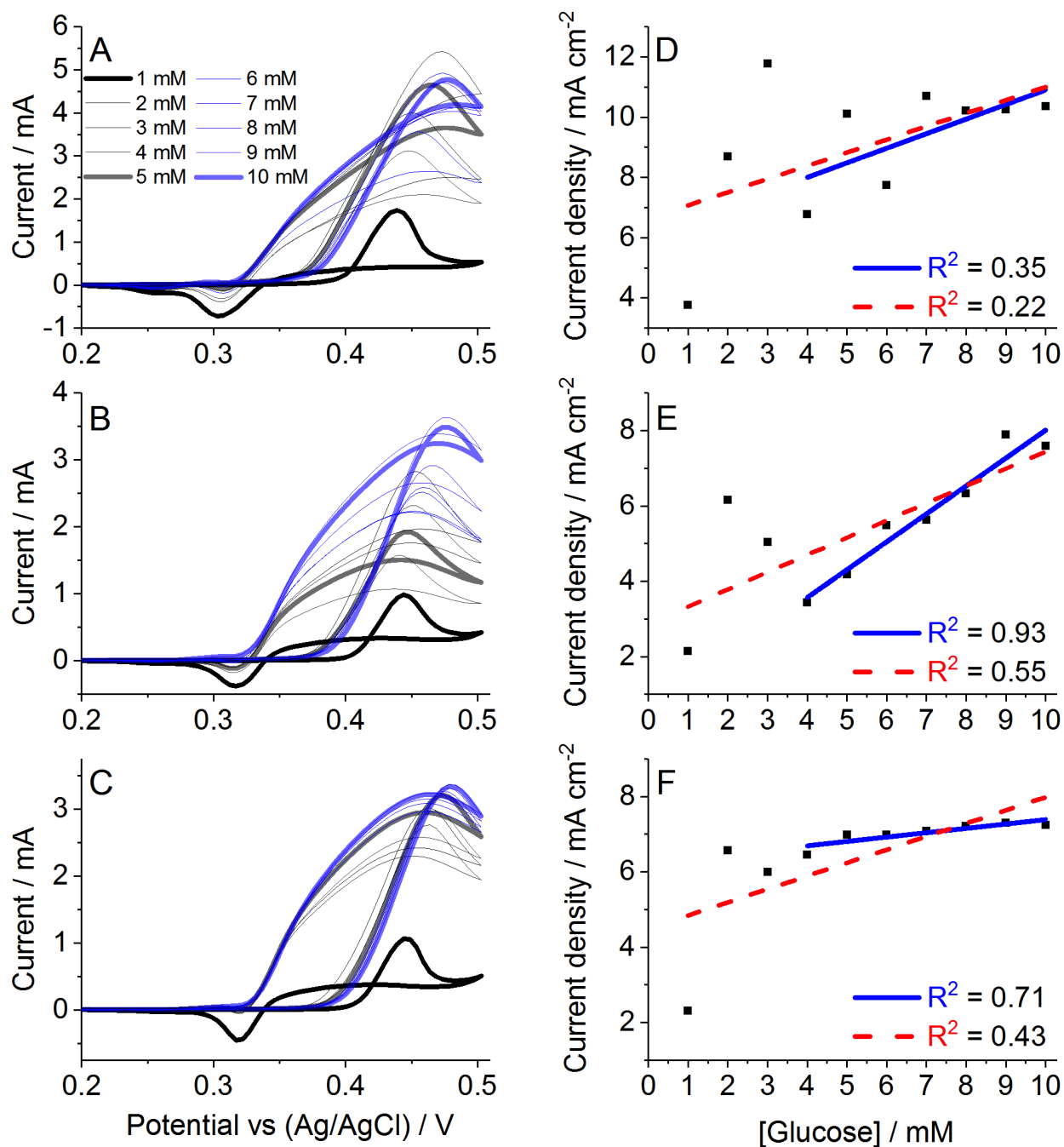


Figure 4.4: CV response of 1–10 mM glucose in 1 M KOH on A) 600 s, B) 400 s and C) 100 s Ni deposition from 1 mM Ni(NO₃)₂ solution on BDDH. These CV were recorded at a scan rate of 50 mV s⁻¹. The thick curves on each graph are for 1, 5 and 10 mM glucose. Graphs D-F show the current response with respect to glucose concentration for 600, 400 and 100 s, respectively. The solid blue line marks the linear correlation between the current density and the glucose concentration using all but the first three data points ($n=7$), while the red dashed line is the linear correlation using all ten concentrations ($n=10$).

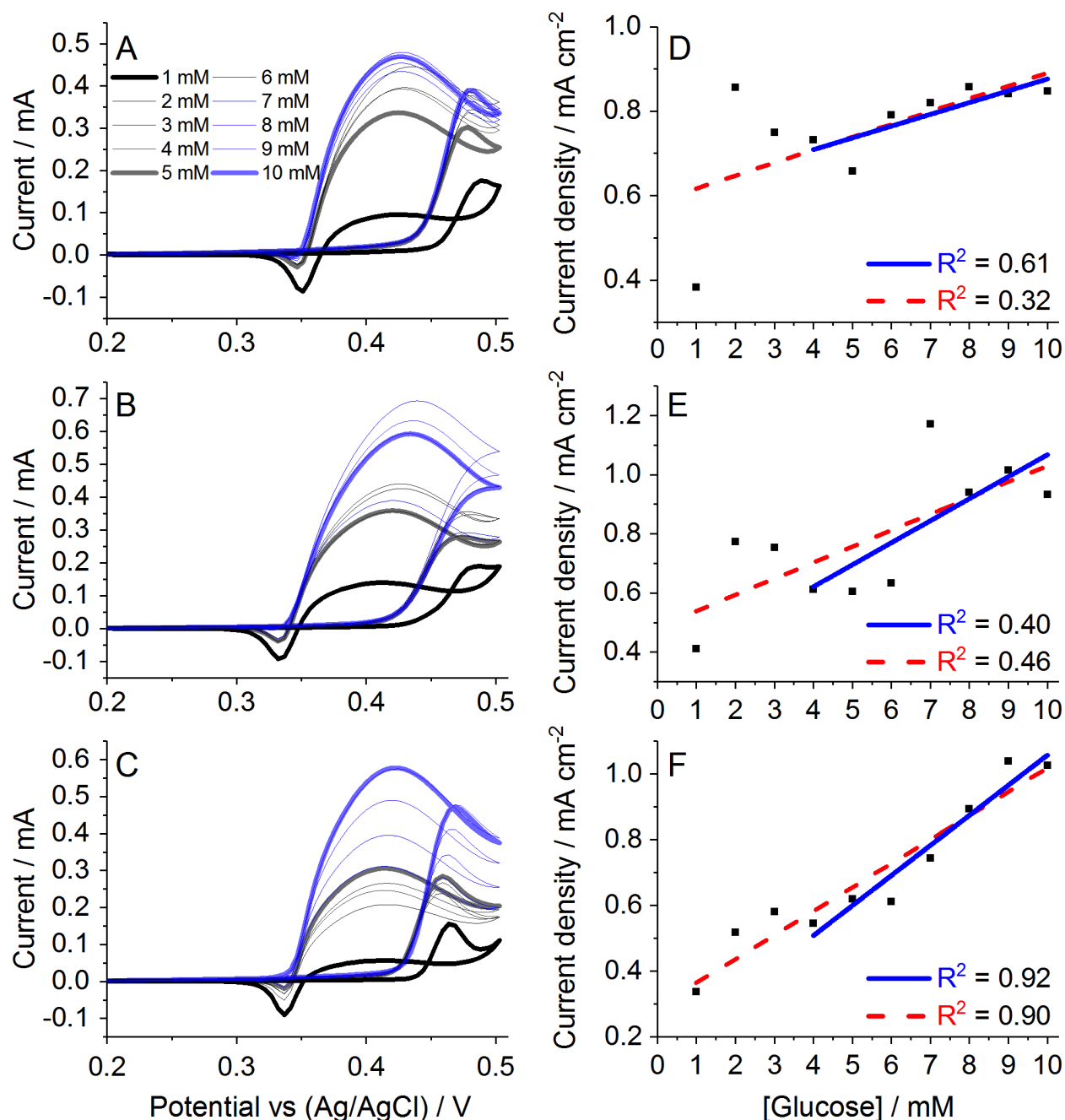


Figure 4.5: CV response of 1–10 mM glucose in 1 M KOH on A) 600 s, B) 400 s and C) 100 s Ni deposition from 1 mM Ni(NO₃)₂ solution on BDDO. These CV were recorded at a scan rate of 50 mV s⁻¹. The thick curves on each graph are for 1, 5 and 10 mM glucose. Graphs D-F show the current response with respect to glucose concentration for 600, 400 and 100 s, respectively. The solid blue line marks the linear correlation between the current density and the glucose concentration using all but the first three data points ($n=7$), while the red dashed line is the linear correlation using all ten concentrations ($n=10$).

Ni(OH)_2 by the irreversible oxidation of glucose such that Ni(OH)_2 is again oxidised to NiOOH on the backward scan. The small reduction peak is the reduction of residual NiOOH to Ni(OH)_2 .^[5]

The two fits for the current response to glucose concentration shown in Fig. 4.4 and 4.5D–F are for all glucose concentrations (red, dashed line) and for the concentration range 4–10 mM (blue, solid line). The response of $\text{Ni(OH)}_2/\text{BDDH}$ to glucose shows the strongest linear correlation to glucose concentration for the 400 s Ni deposition (Fig. 4.4B and E), while the 600 s deposition of Ni on BDDH shows the weakest correlation (lowest R^2 value, Fig. 4.4A and D). However, there is little overall correlation between the current response observed to glucose and the Ni coverage, particularly at low concentrations of glucose. The difference in R^2 values shows that the current response is more linear with respect to glucose concentration if the lowest concentrations are not included in the analysis.

Two conclusions can be drawn from the above observations. First, the oxidation of glucose at the Ni-modified BDDs is likely controlled by diffusion of glucose to the densely covered Ni particle array rather than being limited by a surface reaction at the Ni particle surface.^[6] Hence, changes in Ni particle coverage have virtually no effect on the magnitude of the oxidation current observed. Second, some other factor that is especially prominent at low glucose concentrations has a salient effect in controlling the current response as evinced by the scatter in the data presented in Fig. 4.4D, E and F. Given the sensitivity of the electrode to the conditioning that produces the Ni hydroxide layer, this is most probably associated with the level of oxidation of the surface of the Ni particles, which is difficult to maintain at a constant level as the electrode is used.

Behaviour similar to that of the Ni-modified BDDH is observed with the Ni-modified BDDO. Again, scatter in the data is observed at low glucose concentrations, for which the current response is weakly correlated to the glucose concentration, which is indicative of diffusion-controlled rather than surface-limited behaviour. However, the current density observed in the CV data is approximately one order of magnitude smaller on the oxygen-terminated than the hydrogen-terminated BDD. The simplest explanation for this current, which is seemingly independent of particle density but much lower than the diffusion limit

seen on the hydrogen-terminated surface, is that regions of dimensions on the same order of magnitude or greater than the thickness of the glucose diffusion layer are electrochemically inactive and thereby significantly reduce the current response. This explanation is also supported by the heterogeneous deposition of Ni in the SEM images (Fig. 4.1), which also suggests that significant areas of the oxygen-terminated electrode remain unmodified by the presence of Ni. The difference in Ni loading determined by SEM (Fig. 4.1) between BDDH and BDDO is approximately two-fold, which is not sufficient to account for the ten-fold difference in current response. Therefore, not all of the Ni deposited onto BDDO is likely to be in good electrical contact with the underlying BDD. Furthermore, the areas of the oxygen-terminated BDD electrode that remain unmodified by the presence of Ni also explains the discrepancy in scatter between the results presented in Fig. 4.5 and the results obtained by Toghil.[5] The BDDs used in this chapter were unpolished, while the smaller, polished BDDs from Windsor Scientific that Toghil used might not have regions of inactivity that are comparable to those observed with the BDDs used here.

4.4.3 Glucose oxidation: amperometry

The 100 s Ni samples were found to have the strongest correlation between glucose concentration and oxidative current for BDDO and the second best correlation for BDDH with CV, which makes the 100 s Ni samples the most suitable sample for comparison between the two differently surface-terminated BDDs. Therefore, the 100 s Ni/BDD samples were used to gauge the sensitivity of the Ni/BDD system with amperometry. The amperometric measurements were taken in two distinct glucose concentration ranges: 1–13 mM and 0.1–1.3 mM, as shown in Fig. 4.6. The current response was consistently higher for 100 s Ni/BDDH than for BDDO, as was also the case for the CVs. However, this increased current does not correspond to an improved sensitivity to glucose oxidation in the concentration ranges probed; both high concentrations (1–13 mM, Fig. 4.6A) and low concentrations (0.1–1.3 mM, Fig. 4.6B) can easily be detected at both the hydrogen- and oxygen-terminated, Ni-modified BDDs, but the electrodes show a marked variability in performance. This variability in performance is at odds with the results presented by Toghil for a 600 s Ni modified

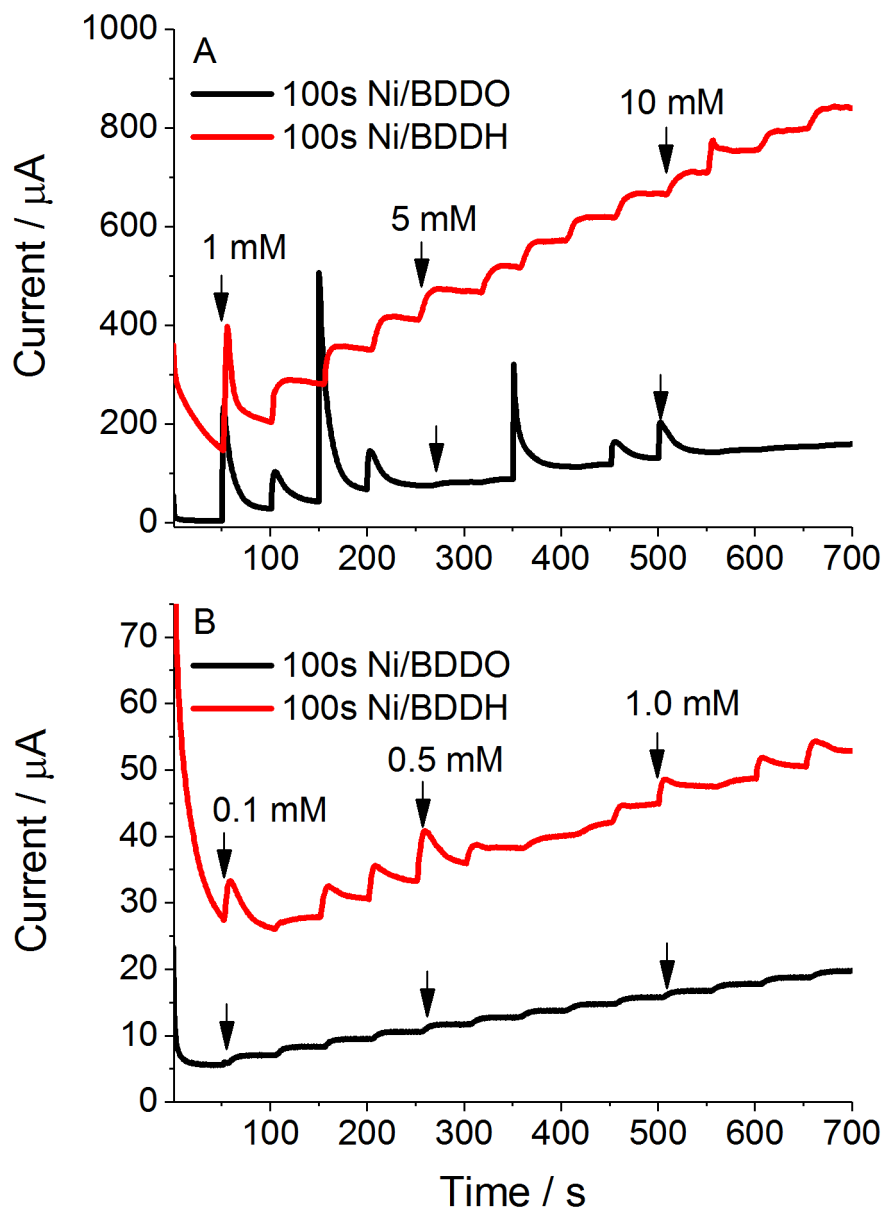


Figure 4.6: Amperometric measurements at 0.47 V in a stirred solution of 1 M KOH with glucose injections every 50 s with 100 s Ni on BDDO (black) and BDDH (red) electrodes. The glucose concentrations ranged from A) 1–13 mM and B) 0.1–1.3 mM.

BDDO,[5] but can be explained by the variability between the underlying BDDs discussed in section 4.4.2. The variability in the performance of the decorated BDDs presented here is congruent with the variability that was also observed by CV, except perhaps for the 100 s Ni/BDDO in the 0.1–1.3 mM. The perceived stability of the 100 s Ni/BDDO electrode in the amperometric measurement compared to the CV measurement suggests that some part of the decoupling between the current response and glucose concentration may have arisen from the difference in the two measurement techniques; specifically, the amperometric measurement holds the potential constant at a value that corresponds to glucose oxidation while the CV measurement scans through a range of potentials, including the potential at which Ni is reduced. The back-reduction of Ni may change the Ni particle surface in a way that reduces the stability of the electrode.

4.5 Conclusion

This work investigated the effect of BDD surface termination on glucose oxidation with hydroxide-enriched Ni particles. The Ni particles were potentiostatically deposited onto the clean, explicitly surface-terminated BDDs for 100, 400 and 600 s to achieve different Ni loadings. The as-deposited Ni was then enriched to $\text{Ni}(\text{OH})_2$ before being used for glucose oxidation. BDDH was found to have slightly higher Ni loadings than BDDO and a more uniform Ni distribution, which shows that Ni nucleates and deposits differently on BDDH than BDDO. The difference in Ni particle distribution might arise from the surface conductivity of the hydrogen-terminated surface, which tends to equalize the variations in conductivity caused by local electrical fields in the vicinity of boron sites.[31, 32]

In accordance with the higher Ni loadings and increased surface conductivity, the Ni decorated BDDH exhibited larger glucose oxidation currents in the electrochemical tests than the Ni/BDDO samples. Glucose oxidation by CV showed an approximately ten-fold increase in current for BDDH compared to BDDO, a current increase which is not explicable by the approximately two-fold difference in Ni loading. Rather, the Ni particles are believed to be in poor electrical contact with the underlying BDDO, and the lack of electrical

communication between the particles and BDDO, together with the difference in particle loading, explains the difference in current response between BDDH and BDDO. Both the CV and amperometric glucose oxidations showed considerable variation in electrode sensitivity. The variation in sensitivity was attributed to variations in Ni particle activity that depends on both the specific BDD wafer and the hydroxide layer, which XPS showed to vary in the as-deposited Ni particles between the two types of BDD. Overall, the oxidised BDD surfaces were more sensitive to glucose oxidation and showed less variability than the hydrogen-terminated counterparts.

The results obtained here were generally comparable to those obtained by Toghill [5] but were afflicted by the variability between individual BDD wafers. While extending the study to commercially viable diamond samples is of interest for the ease of use of these sensors, the variability of the underlying diamond results in unpredictable current response for some wafers. The stability of the performance of the 100 s Ni/BDDO in the amperometric oxidation of 0.1–1.3 mM glucose, and the less stable 100 s Ni/BDDH in the amperometric oxidation of 1–13 mM glucose were noteworthy in comparison to the variability exhibited by other Ni/BDD samples presented in this chapter. The marginally improved stability of the oxidised electrodes may suggest that, in addition to the effect of the underlying BDD wafer, the surrounding BDD oxides may help in stabilising the Ni hydroxide layers. In this case, the performance of the electrode is not enhanced by an increased contact between the metal deposits and the BDD surface but rather by the synergistic effect of having an oxygenated environment surrounding the metal oxide. However, the effect of the surrounding oxides is of lesser importance than the variability introduced by the underlying BDD.

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Chapter 5

Using surface-terminated, carbon-black-modified BDDs to sense acetaminophen

5.1 Introduction

Previous chapters have shown that the behaviour of metal and metal oxide systems on boron-doped diamond (BDD) is strongly affected by the surface termination of the underlying BDD. Both gold nanoparticles (AuNPs) and $\text{Ni}(\text{OH})_2$ particles were found to be in better electrical contact with a hydrogen-terminated BDD (BDDH) electrode than with an oxygen-terminated BDD (BDDO) and that the difference in the electrical contact affects the performance of the electrodes as sensors. However, one of the main modifiers used to improve the sensitivity or selectivity of electrodes is not metal based, like the AuNP and $\text{Ni}(\text{OH})_2$ systems described in the preceding two chapters, but nanocarbon. Therefore, this chapter expands the investigation of the effect of surface termination on the electrochemical performance of the BDDs by considering electrode modification with nanocarbon, specifically carbon black particles.

Carbon nanotubes (CNT) and graphene are two commonly-used forms of nanocarbon; in particular, CNTs and graphene have been investigated for the electrochemical detection

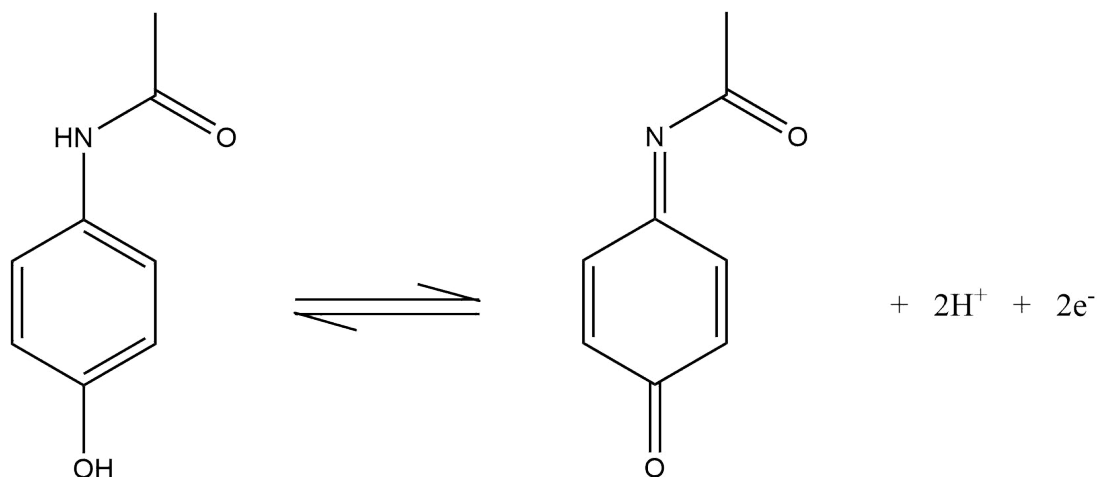


Figure 5.1: The redox process of Ac.

of biomolecules,[1, 2] such as acetaminophen (Ac, also known as paracetamol), which is a common analgesic.[3–5] In Ac sensing, modifying the underlying electrode, typically glassy carbon (GCE), with CNTs or graphene results in enhanced current responses and reduced oxidation overpotentials.[6–14] Unfortunately, CNTs and graphene often require extensive preparation or further modification to enhance the electrochemical signal. For example, Gowda *et al.* [7] found lower Ac detection limits when the multi-walled CNTs (MWCNTs) used to modify the underlying GCE were themselves modified by the inclusion of cetyltrimethyl ammonium bromide (CTAB) and Kim *et al.* [10] enhanced the performance of their activated graphene/GCE electrodes by modifying the graphene with Nafion prior to deposition onto the electrode surface. Cernat published an extensive review of Ac sensing with CNTs and graphene,[2] and some examples are given in Table 5.1. The reaction scheme of Ac oxidation is given in Fig. 5.1.

In addition to graphene and CNT, which can be complicated to work with,[2] others have obtained promising results using simple carbon blacks. Carbon black is an economically viable form of carbon that has been used for a wide variety purposes. Carbon black has been used historically as a filler in rubber products and in printer ink and toners,[15–17] but more modern applications of carbon black include uses in capacitors and Li-ion batteries,[18–22] fuel cells,[23–27] and electrochemical sensing.[28–32] In electrochemical sensing, carbon black is, like CNTs and graphene, used to modify and improve the electrochemical performance of the underlying electrode, often for the detection of organic compounds.[28, 29, 33–

[38] More recently, Ac is also an organic compound detected with carbon-black-modified electrodes.[39] Deroco, one of the few researchers who have used carbon blacks for Ac sensing, found that using Ni oxide-modified carbon-black on GCE for simultaneous detection of Ac and codeine resulted in increased current responses, lower overpotentials of oxidation and increased capacitance.[39] These observations, which were also made by Ghorbani-Bidkorbeh [40] using unmodified carbon nanoparticles on GCE, correspond to the general observations made regarding the use of CNTs and graphene for Ac sensing. These carbon black systems achieved limits of Ac detection that are comparable to the CNT and graphene systems (Table 5.1).

In addition to the work done using nanocarbon modifiers, BDD electrodes have also been effective in Ac sensing.[43–49] While the limits of detection of Ac obtained with BDD are higher than those obtained with nanocarbon-modified electrodes (Table 5.1), they are comparable to some of the simpler systems previously discussed, such as the MWCNT/GCE system.[6] Therefore, modifying the BDD surface with carbon blacks should improve the performance of the BDD in Ac detection. Another aspect of BDD that has yet to be fully explored in Ac oxidation is the possibility of changing the surface termination of the BDD. Lourenção [45] used a cathodically pre-treated, bare BDD (BDDC) to detect Ac by square wave voltammetry (SWV). However, to date, no one has explicitly studied the effect of surface termination on the ability of BDD to electrooxidise Ac. The combination of BDD modification with carbon blacks and surface termination is both promising and unexplored.

Morphologically, most carbon blacks are spherical particles made of graphene-like layers,[50] but the porosity of these particles, as well as their oxygen content, depends on the source and synthesis method of the carbon black.[50–52] Consequently, the behaviour of a carbon-black-modified BDD might vary with the type of carbon black deposited. Therefore, in this chapter, two types of carbon blacks were selected based on their surface area and oxygen content: acetylene carbon black (ACB) and Commercial Monarch 430 carbon black (CB). The properties of these materials have been previously characterized and reported by Shepherd *et al.*[53] A summary of the most important properties are given in Table 5.2.

Considering that previous chapters found that BDDH has a better electrochemical re-

Table 5.1: Limits of detection (LoD) of Ac using nanocarbons

Electrode system	Method	LoD / μM	E_{ox}^* / V	Ref
bare GCE	DPV	3.54	0.8	[41]
MWCNT/GCE	DPV	0.35	0.34	[6]
ionic liquid-MWCNT-chitosan/GCE	DPV	0.24	0.35	[8]
NiO-CB/GCE	SWV	0.12	0.6	[39]
RGO ^a -CB-chitosan/GCE	SWV	0.053	0.55	[36]
graphene/GCE	SWV	0.032	0.28	[12]
graphene-Nafion/GCE	DPV	0.031	0.35	[10]
SWCNTs/carbon ceramic electrode	DPV	0.025	0.2	[42]
graphene-Ni oxides NPs/GCE	DPV	0.02	0.26	[11]
Mg-Al layered double hydroxide-Ni hydroxide NPs-MWCNT/GCE	DPV	0.005	0.35	[9]
MWCNT-CTAB/GCE	DPV	0.00482	0.36	[7]
ERG ^b /GCE	DPV	0.00213	0.387	[13]
carbon NPs/GCE	DPV	0.0021	0.2	[40]
thin film BDDO	CV	10	0.45	[43]
BDDO	CA ^c	0.97	0.66	[44]
BDDC ^d	SWV	0.49	0.8	[45]

* oxidation potential of Ac vs Ag/AgCl ^a RGO: reduced graphene oxide ^b ERG: electrochemically reduced graphene ^c CA: chronoamperometry ^d BDDC: cathodically pretreated BDD.

Table 5.2: Properties of CB and ACB

carbon black	surface area cm^2g^{-1}	pore volume cm^3g^{-1}	density g cm^{-3}	oxygen content %
ACB	80.1	0.26	0.06-0.11	0.44
CB	72.6	0.57	1.7-1.9	1.6

The surface area was calculated by BET and the oxygen content by XPS. All values are from [53].

sponse over BDDO and that large areas of BDDO are electrochemically inactive, the low oxygen content and large surface areas of the carbon blacks could make the carbon black modified BDDO an easy-to-prepare alternative to BDDH.

5.2 Aims of the chapter

The aim of this chapter was to evaluate

1. the difference in performance of BDDO and BDDH
2. the surface modification of BDDO and BDDH with two different carbon blacks, CB and ACB
3. the possibility of using carbon black modified BDDO as a substitute for BDDH

in Ac sensing. The third aim is of considerable interest given the time-consuming and expensive procedure of hydrogen terminating a BDD wafer effectively.

5.3 Experimental

Polycrystalline, electrochemistry-grade BDDs ($[B] > 10^{20} \text{ cm}^{-3}$) were purchased from Element Six Co, Commercial Monarch 430 CB was supplied by Cabot Corporation (Billerica, MA), 70% HNO_3 was obtained by Fisher Scientific and all other chemicals were purchased from Sigma-Aldrich. Millipore water with a resistivity of $18.2 \text{ M}\Omega\text{cm}$ was used for rinsing, for all aqueous solutions and in sonication.

5.3.1 BDD termination

Clean BDDs were either oxygen terminated by reflux in 70% HNO_3 for 4 hours or hydrogen terminated by exposure to hydrogen plasma at 600°C for 45 minutes at 1.5 kW power and a pressure of 45 Torr. The hydrogenated surface was refreshed between each use after cleaning while the oxygen-terminated surface was maintained by 20 CV scans between 2.5 and -1.7 V at 100 mV s^{-1} in 0.1 M HNO_3 .

5.3.2 Carbon black deposition and removal

Carbon black suspensions were made by mixing 10 mg of either CB or ACB with 10 mL of water. These suspensions were sonicated for one hour prior to use, after which 10 μL were deposited onto the clean, surface-terminated BDD. The sample was then left to dry under ambient conditions. For the XPS experiments, the deposition method varied slightly in that 100 μL rather than 10 μL of the suspensions were deposited onto the electrodes.

After each experiment, the carbon black deposits were removed by rinsing the electrode in water followed by 20 minutes of sonication in water. The absence of carbon black deposits was visually observed, determined by CV in 0.1 M HNO_3 described in chapter 3 and double-checked for BDDO in 0.2 mM hydroquinone described in section 6.4.1.

5.3.3 XPS

XPS was performed with a VG Escalab II spectrometer using Al $K\alpha$ radiation (1486.6 eV) and a hemispherical analyzer for electron detection, which measured the binding energy from 0 to 1200 eV. Samples were held in place on copper stubs by carbon tape. Peaks were calibrated against the C 1s peak at 285.0 eV. Peak fitting was done using CasaXPS.

5.3.4 CV

The CVs of 1 mM Ac in 0.1 M phosphate buffer (PB, pH=7) were obtained at 50 mV s^{-1} between -1.0 and 1.5 V. The Randles-Sevcik type experiments were performed in the potential range of -1.0 to 1.5 V at scan rates ranging from 10 to 500 mV s^{-1} in 1 mM Ac solutions supported in 0.1 M PB. For the Randles-Sevcik type experiments, the CVs of the scan rates were recorded on the same electrode for each decoration; the electrodes were neither cleaned nor prepared anew between each scan rate.

5.3.5 DPV

Differential pulse voltammetry (DPV) was performed in Ac solutions of various concentrations supported in 0.1 M PB with a modulation time of 0.025 s, an interval time of 0.25 s, a

step potential of 0.005 V and a modulation amplitude of 0.05 V. All electrochemical experiments were performed with a Pt wire counter electrode and a Ag/AgCl reference electrode.

5.4 Results and discussion

The XPS results are presented first and discussed according to varying oxygen content between the different electrodes. This is followed by the CVs of the clean and decorated electrodes in 1 mM Ac. The changes in behaviour of the electrodes and Ac oxidation with scan rate are discussed next, and the sensitivity of the electrodes towards the oxidation of low Ac concentrations are shown last.

5.4.1 XPS

XPS was used to calculate the change in surface oxygen content with CB and ACB decoration on both BDDO and BDDH. For these experiments, 100 μL ¹ of the sonicated ACB and CB suspensions were deposited onto the clean, surface-terminated BDDs and left to dry under ambient conditions. The XPS spectra are given in Fig. 5.2 for the CB decorated BDDs and in Fig. 5.3 for the ACB decorated BDDs. Table 5.3 gives the O 1s content relative to the C 1s content of each electrode.

BDDO showed a significant reduction in surface oxygen when decorated with the carbon blacks. After modification with both CB and ACB, the oxygen content of the BDDO electrodes was comparable to that of the BDDH electrodes. The reduced amount of surface oxygen suggests that electrode modification with both carbon blacks resulted in a good surface coverage of the BDDO. The oxygen content of the BDDH remained low after modification with the carbon blacks.

Decorating the BDDs with either of the carbon blacks resulted in an oxygen peak with only one chemical environment centered at 533 eV, which is attributable to C=O.

¹10 μL was used in all other experiments presented in this chapter. 10 μL was too little to show a quantitative difference in carbon or oxygen environments by XPS, but the XPS results obtained by the larger carbon black deposition are still useful because they show the local difference between the carbon black regions and the underlying diamond of the decorated electrode.

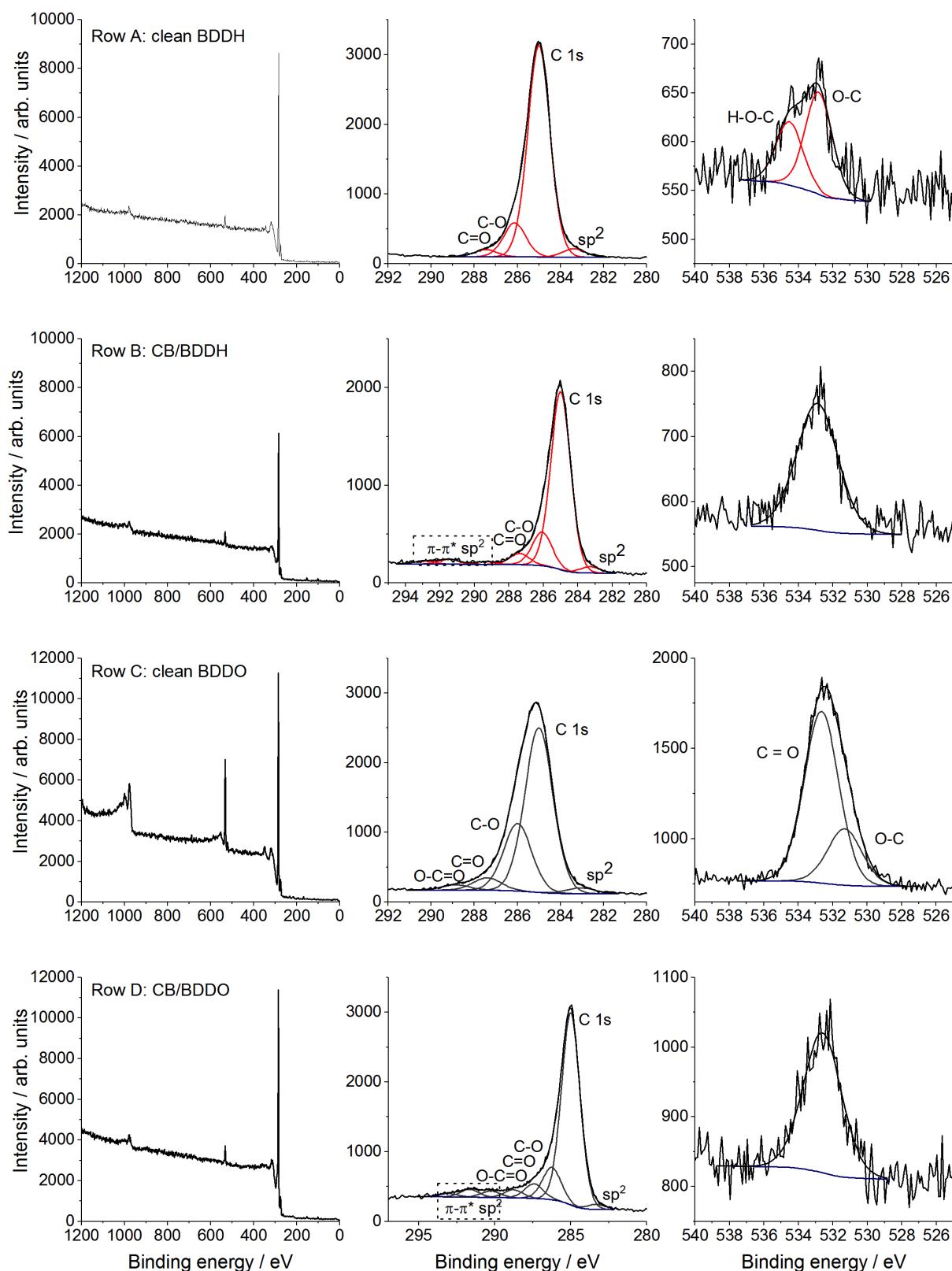


Figure 5.2: XPS of Row A) clean BDDH, Row B) 100 μL 1 mg mL^{-1} CB on BDDH, Row C) clean BDDO, Row D) 100 μL 1 mg mL^{-1} CB on BDDO. The peak fits are shown in red for the hydrogen-terminated samples and in gray for the oxygen-terminated electrodes. The Shirley backgrounds are shown in blue. All peaks have been calibrated to the C 1s peak at 285 eV.

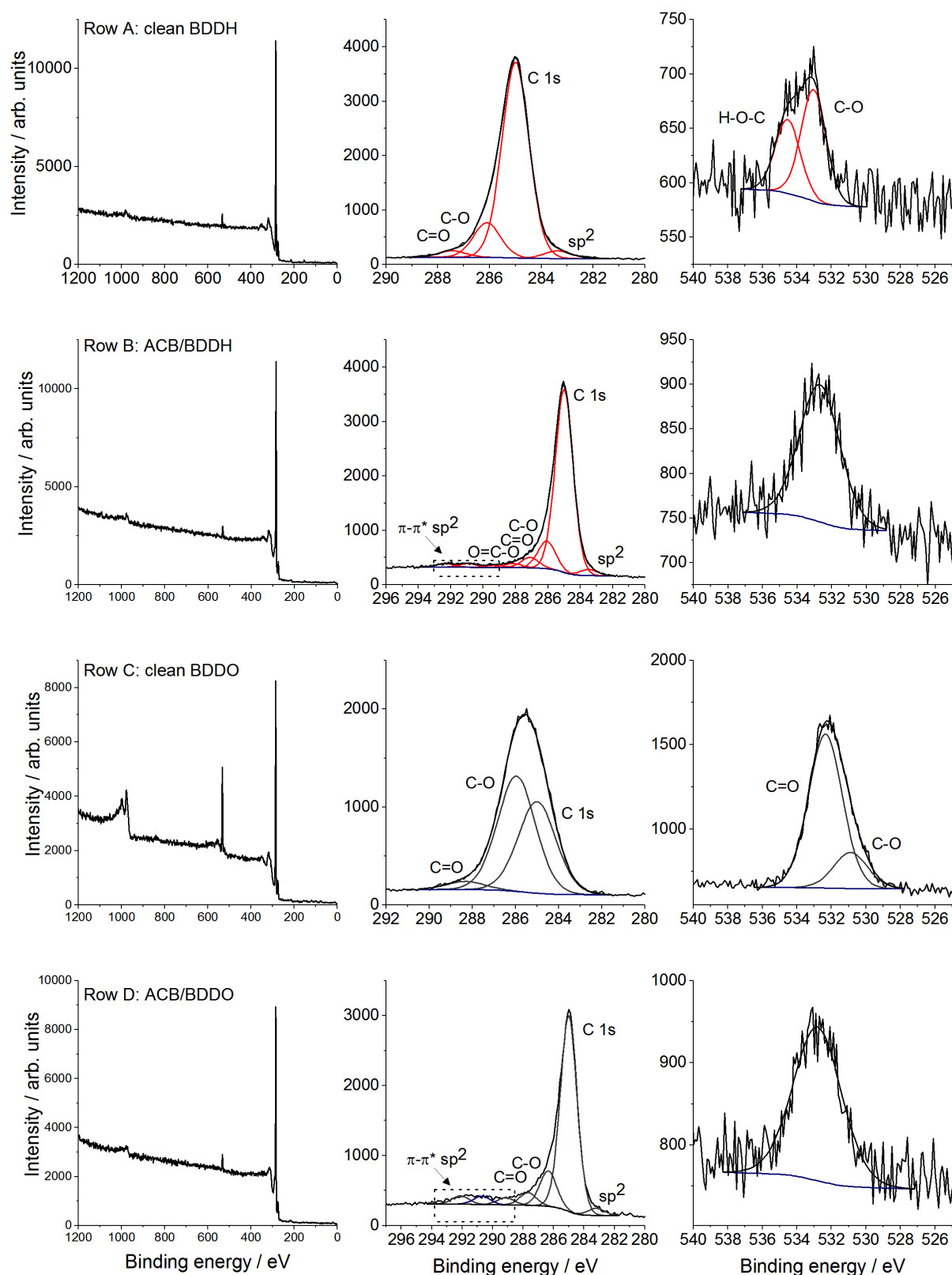


Figure 5.3: XPS of Row A) clean BDDH, Row B) 100 μL 1 mg mL^{-1} ACB on BDDH, Row C) clean BDDO, Row D) 100 μL 1 mg mL^{-1} ACB on BDDO. The peak fits are shown in red for the hydrogen-terminated samples and in gray for the oxygen-terminated electrodes. The Shirley backgrounds are shown in blue. All peaks have been calibrated to the C 1s peak at 285 eV.

Table 5.3: O 1s to C 1s ratio for each electrode

Electrode	O 1s : C 1s / %	comments
clean BDDH	2.34	similar
CB/BDDH	5.64	
clean BDDO	18.07	-
CB/BDDO	3.24	comparable to the BDDH electrodes
clean BDDH	1.79	similar
ACB/BDDH	2.55	
clean BDDO	19.57	-
ACB/BDDO	4.15	comparable to the BDDH electrodes

All peaks were corrected by their Schofield RSF of 1 for C 1s and 2.93 for O 1s in the surface area calculations.

5.4.2 Electrooxidation of acetaminophen at 50 mV s⁻¹

CV was used to investigate the behaviour of the clean and decorated BDDs towards Ac oxidation. The voltammograms obtained from a 1 mM Ac solution in 0.1 M PB at 50 mV s⁻¹ are shown in Fig. 5.4.

As shown in Fig. 5.4, the behaviours of the three oxygen-terminated electrodes were similar; the difference in capacitance and peak separation between the samples are negligible and the difference in peak current is small: $82 \pm 5.2 \mu(A)$. The similarity of the Ac redox on all three electrodes suggests that the inclusion of carbon blacks on the BDDO surface does not particularly affect the overall performance of the electrode, either because 1) the carbon blacks are physically unstable on, and are easily dislodged from the surface, 2) the carbon black particles are not in electrical contact with the underlying BDDO or 3) a combination of these two effects. The overall peak profile for the clean BDDO matches the peak profiles found in the literature,[43, 46, 49] but the CB/BDDO sample has a small shoulder on the oxidation peak in the first scan (inset in Fig. 5.4C). This peak suggests that despite not having much of an effect on BDDO, the CB is in sufficient contact to influence the behaviour of the BDDO. The potential of the main peak corresponds to that of Ac oxidation on the clean BDDO; the presence of the oxidative shoulder for the CB/BDDO sample indicates that

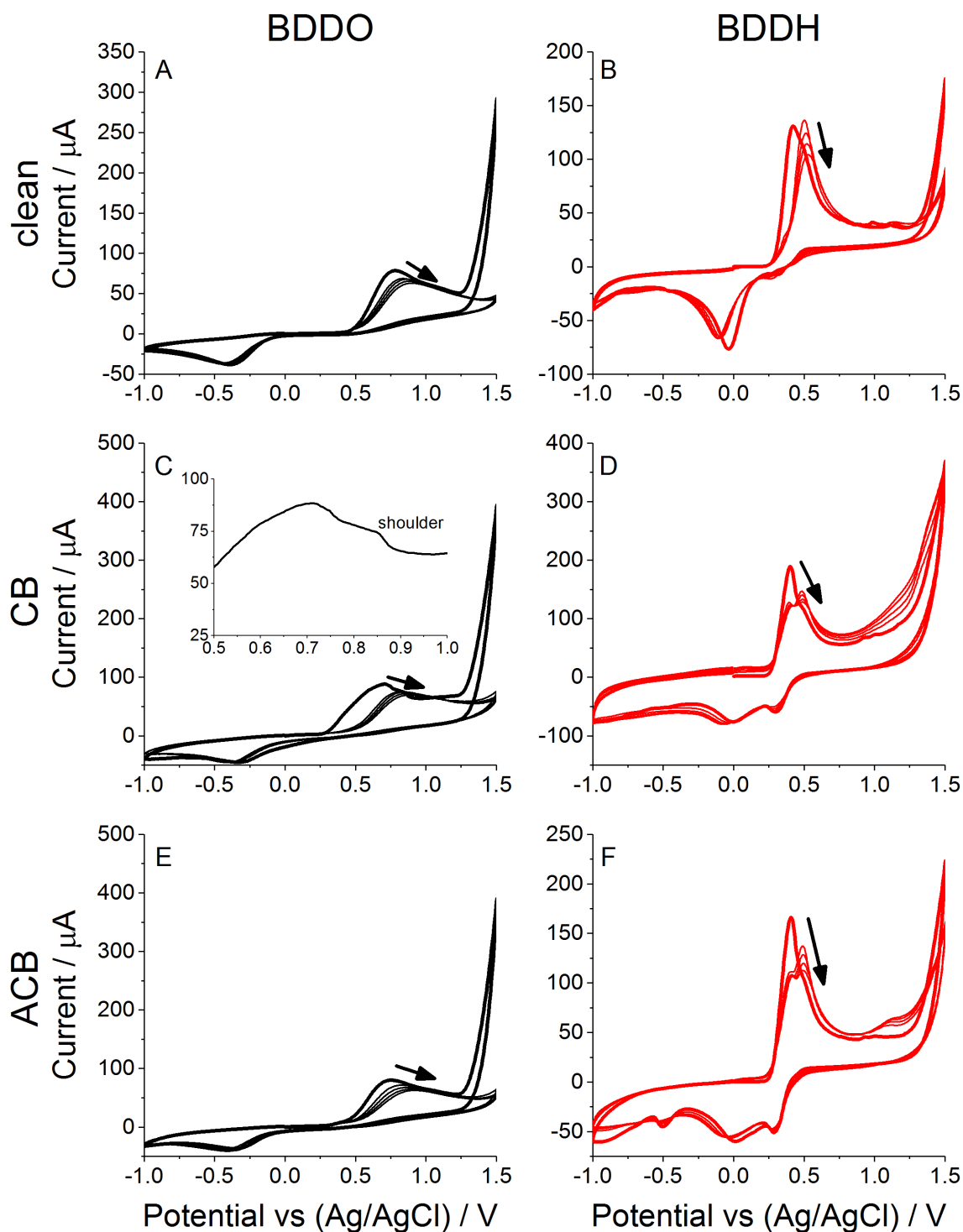


Figure 5.4: 5 CV scans of 1 mM Ac in 0.1 M PB (pH=7) at 50 mV s^{-1} on A) clean BDDO, B) clean BDDH, C) 10 μL 1 mg mL^{-1} CB/BDDO, with the inset showing the oxidation peak of the first scan, D) 10 μL 1 mg mL^{-1} CB/BDDH, E) 10 μL 1 mg mL^{-1} ACB/BDDO and F) 10 μL 1 mg mL^{-1} ACB/BDDH. The arrow indicates the order of increasing scan number.

the Ac oxidises at two distinct potentials for the underlying BDDO and the CB deposits. The peak amplitude of the main Ac oxidation peak, while close to that of the clean BDDO, was the highest of the three electrodes. The voltammogram of the ACB/BDDO sample (Fig. 5.4E) shows neither a shoulder nor increased oxidation peak current compared to the clean BDDO, probably due to a combination of the physical instability and the poor electrical contact discussed above.

The hydrogen-terminated BDDs showed more conspicuous differences in Ac oxidation with the surface preparation than the oxygen-terminated samples. Although Ac oxidises at approximately 0.4 V for all three of the hydrogen-terminated electrodes, both the CB and the ACB decorated BDDHs (Fig. 5.4D and F) have a strongly split oxidation peak. The first (i.e. lower overpotential) peak corresponds to that of the clean BDDH (Fig. 5.4B) while the second peak, in conjunction with smaller reduction peaks, suggests that Ac adsorbs onto the decorated electrode surface. The reduction peak at -0.5 V in Fig. 5.4F has been previously reported by [54] and attributed to the overreduction of Ac to quinones. Both of the oxidation potentials are the same on CB/BDDH as on ACB/BDDH, but the height ratio of the two contributing peaks is marginally larger for ACB/BDDH than CB/BDDH: 27 versus 20 μA difference in peak height for the two shoulders. However, the CB/BDDH has a larger peak magnitude (189 μA) in the first scan than ACB/BDDH (166 μA). Considering the peak ratio and overall peak height together, CB increases the current response of the BDDH while ACB shows stronger adsorption.

Overall, the hydrogen-terminated BDDs showed faster kinetics and increased capacitance than the oxygen-terminated BDDs. The peak potentials were 0.1–0.2 V higher and the peak currents lower on BDDOs than BDDHs. This shift corresponds well with the potential shift found by Lourenção when changing from a flat BDDO to a porous one,[49] which they attributed to an improved electronic transfer.[49] The decorated BDDs also showed clear signs, and the clean BDDH hints, of adsorption. When the clean BDDs that had been used for CV in the 1 mM Ac solution (Fig. 5.4) were rinsed with water and then immediately used for CV in the 0.1 M PB supporting electrolyte (Fig. 5.5), the clean BDDH still exhibited oxidation and reduction peaks associated with Ac (Fig. 5.5B). The presence of these peaks

shows that some Ac adsorbs onto the BDDH electrode.

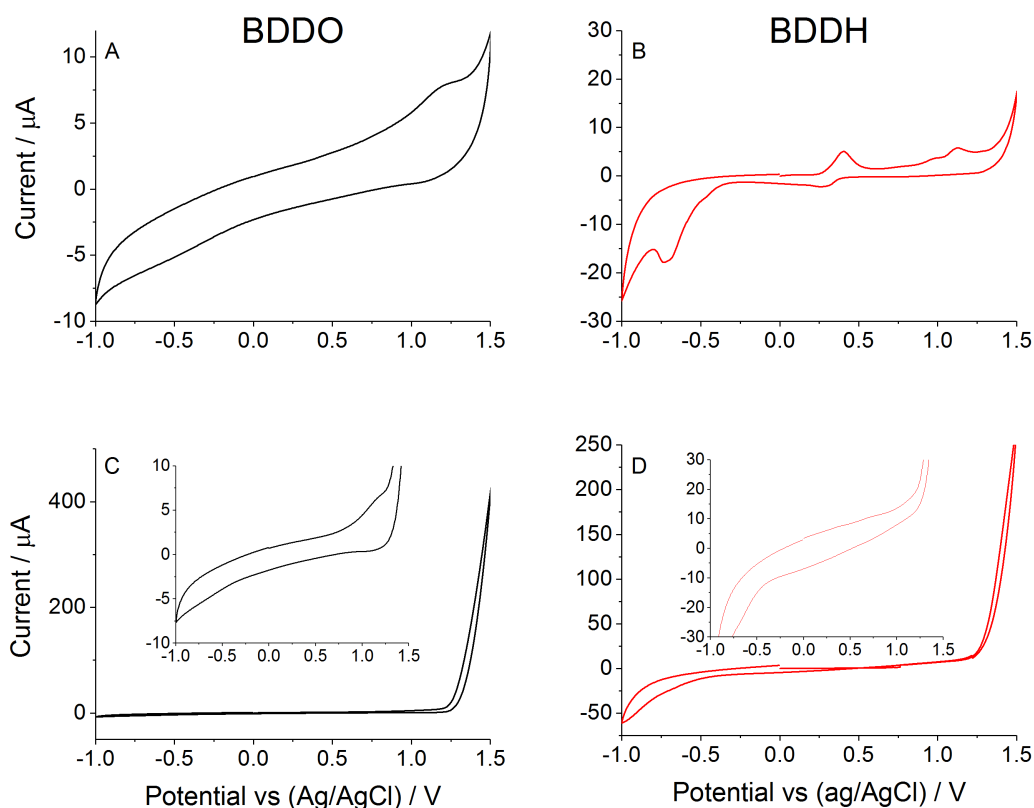


Figure 5.5: CV in 0.1 M PB at 50 mV s^{-1} directly after 5 CV scans in 1 mM Ac in 0.1 M PB on A) clean BDDO and B) clean BDDH, and CV in 0.1 M PB at 50 mV s^{-1} with unused clean C) BDDO and D) BDDH.

5.4.3 Randles-Sevcik experiments

The CV scan of the previously-used clean BDDs in 0.1 M PB shown in Fig. 5.5 suggested that Ac adsorbs onto the underlying BDDH. Due to the poor adhesion of the CB and ACB to the underlying BDD, the CV of the previously-used decorated BDDs in 0.1 M PB could not be performed. However, redox couples that are under diffusional control have peak currents that are linearly proportional to the square root of the scan rate, while adsorption controlled species have peak currents that are linearly proportional to the scan rate.[55] Therefore, Randles-Sevcik type experiments were performed in a 1 mM Ac solution in 0.1 M PB at scan rates from 10 to 500 mV s^{-1} . The results are shown in Fig. 5.6 for the oxygen-

terminated BDDs and in Fig. 5.7 for the hydrogen-terminated BDDs.

The CVs obtained using the clean BDDO and the CB/BDDO sample are similar to those shown in Fig. 5.4A and C but have smaller peak amplitudes. Fig. 5.4 showed a reduction in peak amplitude with successive scan number, which suggests that the electrodes are fouled during the CV scan. The smaller peak amplitudes observed in Fig. 5.6A-C are therefore likely a result of surface poisoning by repeated scans on the same electrode. The good linear fit between the peak current and the square root of the scan rate indicates that both the clean BDDO and CB/BDDO operate under diffusion control. The CVs obtained with the ACB-decorated BDDO are markedly different from those shown in Fig. 5.4E. In addition to the redox couple at approximately 0.8 and -0.4 V, there is a second set of peaks centred around 0.4 V. This latter set of peaks corresponds well with the Ac oxidation and reduction peaks found in Fig. 5.5B that were attributed to the adsorption of Ac onto BDDH. The presence of these adsorption peaks suggests that some Ac also adsorbs onto the ACB/BDDO electrode. This claim is supported by the excellent linear correlation between the peak currents of these inner peaks and the scan rate (Fig. 5.6G). The reason for the absence of these Ac adsorption peaks in Fig. 5.4E can be explained if the adsorption occurs at a slower rate than the diffusionally controlled oxidation at 50 mV s^{-1} . When the experiment is started at 10 mV s^{-1} , Ac has time to adsorb onto the ACB/BDDO electrode and the outer peaks of the ACB/BDDO sample are under diffusional control like the clean BDDO and CB/BDDO sample.

Although the clean BDDO has the smallest and CB/BDDO has the largest slope, all three of the oxygen-terminated electrodes have similar slopes. Assuming the diffusion coefficient of Ac, $6.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, [56] is the same for all three samples, the difference in slope indicates a difference in the electroactive surface area between the samples.

$$\frac{\text{slope}_{\text{CB/BDDO}}}{\text{slope}_{\text{BDDO}}} = 1.28 \qquad \frac{\text{slope}_{\text{ACB/BDDO}}}{\text{slope}_{\text{BDDO}}} = 1.08 \qquad (5.1)$$

Given that ACB has a larger surface area than CB (Table 5.2), the fact that CB/BDDO appears to have a larger surface area than ACB/BDDO would be surprising except that,

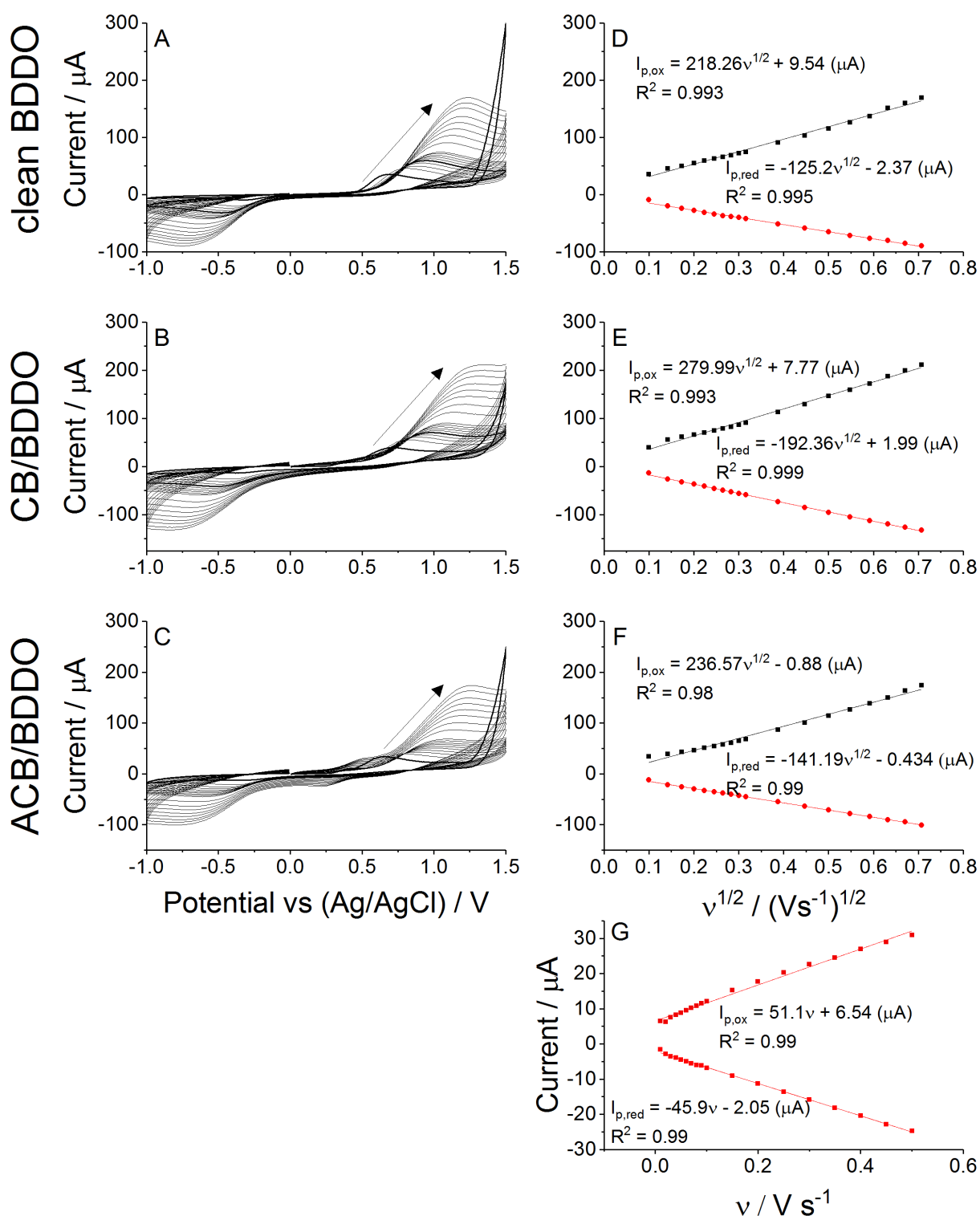


Figure 5.6: CVs of 1 mM Ac in 0.1 M PB (pH=7) at scan rates from 10 to 500 mV s^{-1} on A) clean BDDO, B) CB/BDDO and C) ACB/BDDO, with the arrow indicating the increasing scan rate. D-F show the corresponding plots of peak current against the square root of the scan rate, with the slope given in units of μA per mV s^{-1} . Plot G shows the fit of the peak current against the scan rate for the ACB/BDDO sample.

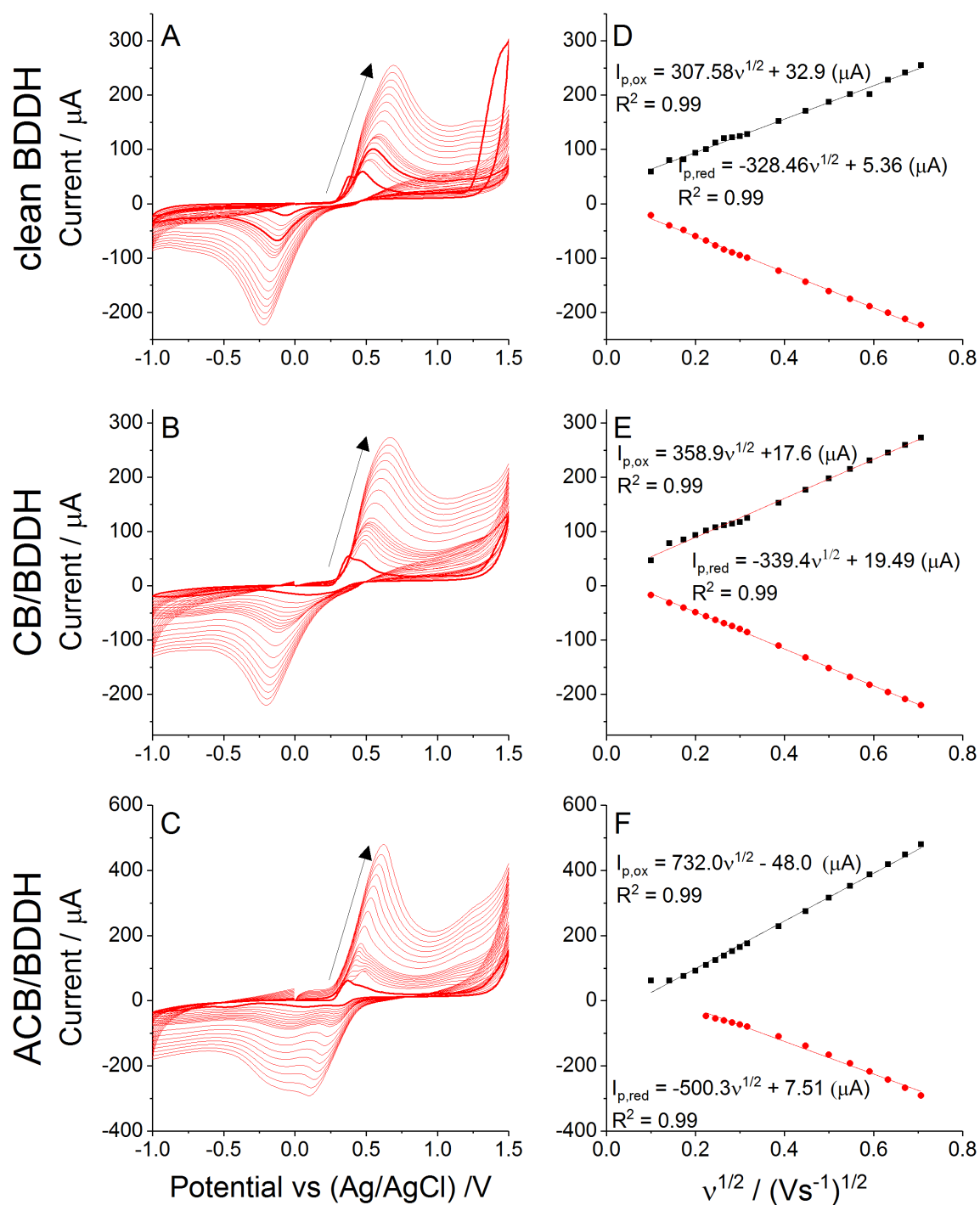


Figure 5.7: CVs of 1 mM Ac in 0.1 M PB (pH=7) at scan rates from 10 to 500 mV s⁻¹ on A) clean BDDH, B) CB/BDDH and C) ACB/BDDH. D-F show the corresponding plots of peak current against the square root of the scan rate, with the slope given in units of μA per mV s⁻¹. The arrows indicate the increasing scan rate.

as previously discussed, the ACB appears less stable on the electrode surface than CB and more of the ACB is lost from the electrode surface during the course of the experiment.

The three hydrogen-terminated BDDs behave quasi-reversibly with strong linear correlations between the peak current and the square root of the scan rate (Fig. 5.7). Of the hydrogen-terminated samples, ACB/BDDH has the largest surface area, and the clean BDDH has the lowest surface area.

$$\frac{\text{slope}_{\text{CB/BDDH}}}{\text{slope}_{\text{BDDH}}} = 1.17 \qquad \frac{\text{slope}_{\text{ACB/BDDH}}}{\text{slope}_{\text{BDDH}}} = 2.38 \qquad (5.2)$$

However, the difference in surface area between the two types of carbon black is not sufficient to account for the increased electroactive surface area of ACB/BDDH compared to CB/BDDH. Both the CB/BDDH and ACB/BDDH samples show the split in the oxidation peak in these Randles-Sevcik experiments (see Fig. 5.4D and F), but the split appears to be more palpable for the CB/BDDH sample, where the peak profile broadens at higher scan rates. For the ACB/BDDH sample, the split is evident at low scan rates but less evident at high scan rates. This difference in sensitivity towards Ac oxidation at the distinct surface regions of the electrodes may help explain the large difference in electroactive surface area.

5.4.4 Acetaminophen concentration variation with CV

Following the characterisation of Ac electrooxidation at a single concentration, the next set of experiments probed the sensitivity of the electrodes to different concentrations of Ac. The CVs and the corresponding scatter plots of peak current versus the Ac concentration are given in Fig. 5.8 for the clean BDDO and Fig. 5.9 for the clean and decorated, hydrogen-terminated electrodes. Given that the main source of error in these experiments arise from the physical instability of the carbon black deposits on the electrode surfaces rather than errors in peak magnitude or concentration measurements, the scatter plots in Fig 5.9 are not fitted with error bars.

The clean BDDO detected Ac at concentrations of 7.5 μM , which is close to, but slightly lower than, the 10 μM previously reported by Wangfuengkanagul in 2002 using CV on a

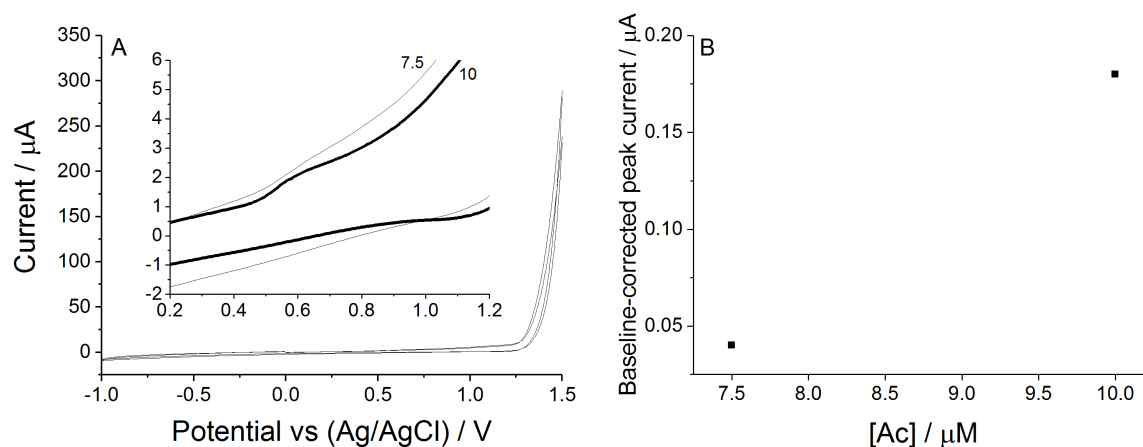


Figure 5.8: CV of Ac in 0.1 M PB (pH=7) at 50 mV s^{-1} on A) clean BDDO, B) the corresponding scatter plot of the peak current against Ac concentration in μM .

clean BDDO.[43] The dependence of current response with Ac concentration could be better probed with more Ac concentrations; this was not done in the work presented here due to time constraints and that these CV measurements were a starting point for the more accurate DPV measurements. Considering the limited effect that ACB and CB decoration has on the performance of BDDO, the decorated BDDO electrodes were not investigated in this experiment.

Congruent with previous experiments, all BDDH samples detected Ac at lower concentrations than was possible with BDDO. At lower Ac concentrations, the oxidation peaks obtained with the CB and ACB decorated BDDH do not have a shoulder peak, unlike the CV at 1 mM Ac (Fig. 5.4D and F). However, the oxidation occurs at approximately 0.05 V lower potential than at the clean BDDH. Both the clean BDDH and CB/BDDH showed a possibly linear correlation between the peak current and the Ac concentration. At low Ac concentrations, the correlation is linear (blue fit), but at high concentrations of Ac the fit deviates from the peak response (red fit). For the clean BDDH, the current response is lower than expected from the linear fit at low Ac concentrations (blue line) whereas the current response is higher than expected at high Ac concentrations for CB/BDDH. This suggest that there may be a saturation point for Ac oxidation on the clean BDDH such that larger Ac concentrations do not necessarily result in larger oxidation currents. The peak currents were again larger for CB/BDDH and ACB/BDDH than the clean BDDH, but all three electrodes

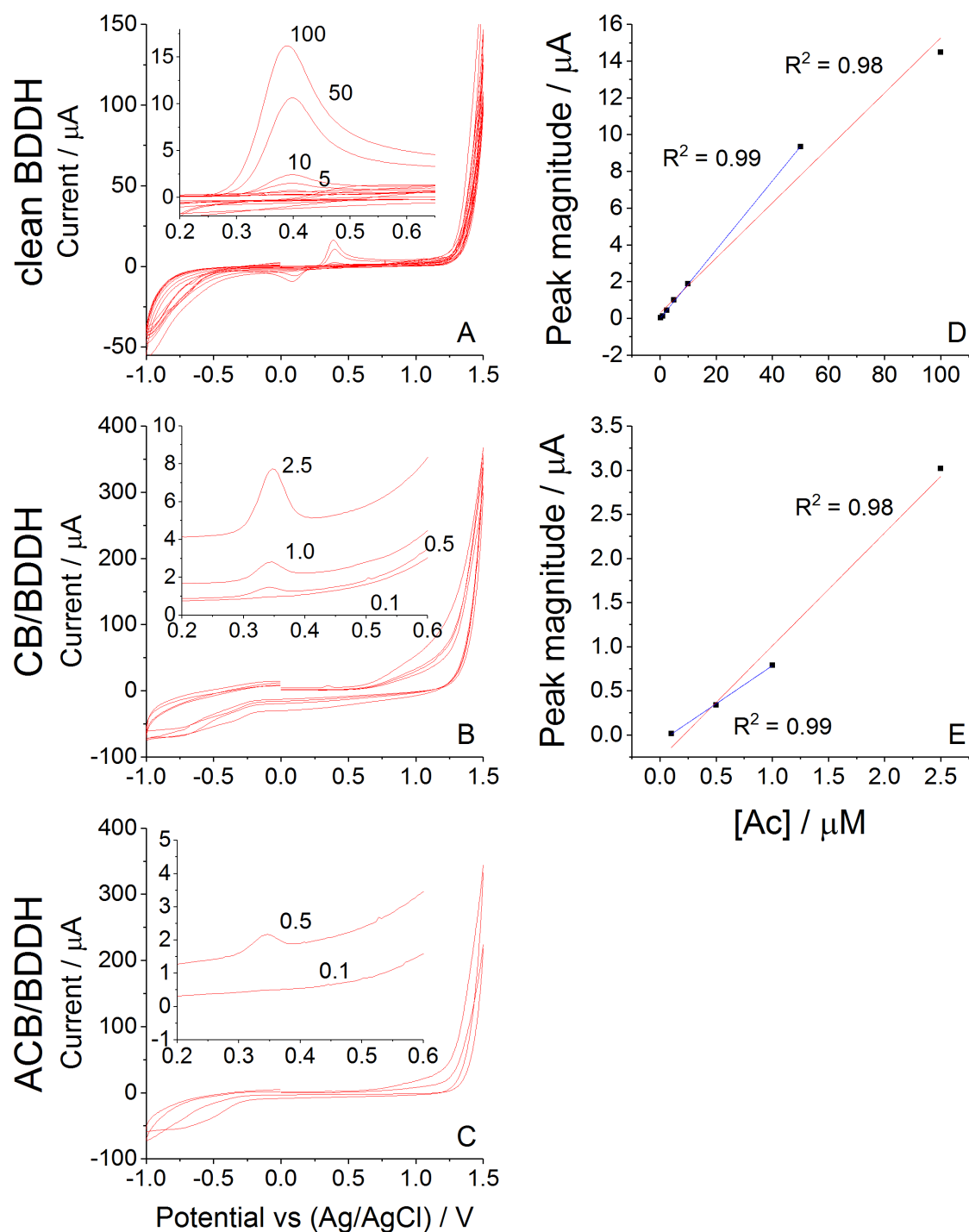


Figure 5.9: CV of Ac in 0.1 M PB (pH=7) at 50 mV s⁻¹ on A) clean BDDH, B) CB/BDDH and C) ACB/BDDH. The insets show the Ac oxidation peaks with the Ac concentration given in μM noted by each line. D and E give the corresponding scatter plot of the peak current against Ac concentration.

detected Ac down to a concentration of $0.5 \mu\text{M}$.

5.4.5 Acetaminophen sensing with DPV

DPV was used to determine the lowest concentration of Ac that is detectable with the clean and carbon black-modified BDDs. All DPVs were recorded at a modulation time of 0.025 s, an interval time of 0.25 s, a step potential of 0.005 V and a modulation amplitude of 0.05 V. The results are shown in Fig. 5.10 for the oxygen-terminated electrodes and Fig. 5.11 for the hydrogen-terminated electrodes. Again, the largest source of error arises from the instability of carbon black deposits on the electrode surfaces, which is not readily measured, so the scatter plots in Figs 5.10 and 5.11 do not show the error bars caused by uncertainty in Ac concentration or the peak current due to the fact that the former is a less significant source of error than the carbon black instability and the latter is strongly related to the carbon black instability. The lowest detectable Ac concentrations with each electrode are summarised in Table 5.4.

Table 5.4: Lowest detectable Ac concentration at each electrode

Electrode	Ac concentration	units
clean BDDO	7.5	μM
CB/BDDO	1.0	
ACB/BDDO	2.5	
clean BDDH	100	nM
CB/BDDH	30	
ACB/BDDH	10	

These values are the lowest concentrations of Ac that yielded a detectable peak current in the DPV experiments. The usual method of calculating the limit of detection from the slope of the peak currents against the concentration was not considered appropriate given the poor linear correlation of many of these samples.

As shown in Fig. 5.10, the oxygen-terminated BDDs were capable of detecting a few μM of Ac, with CB/BDDO being the most sensitive of the three oxygen-terminated electrodes. The potential at which the Ac is oxidised changes with the electrode surface decoration; both

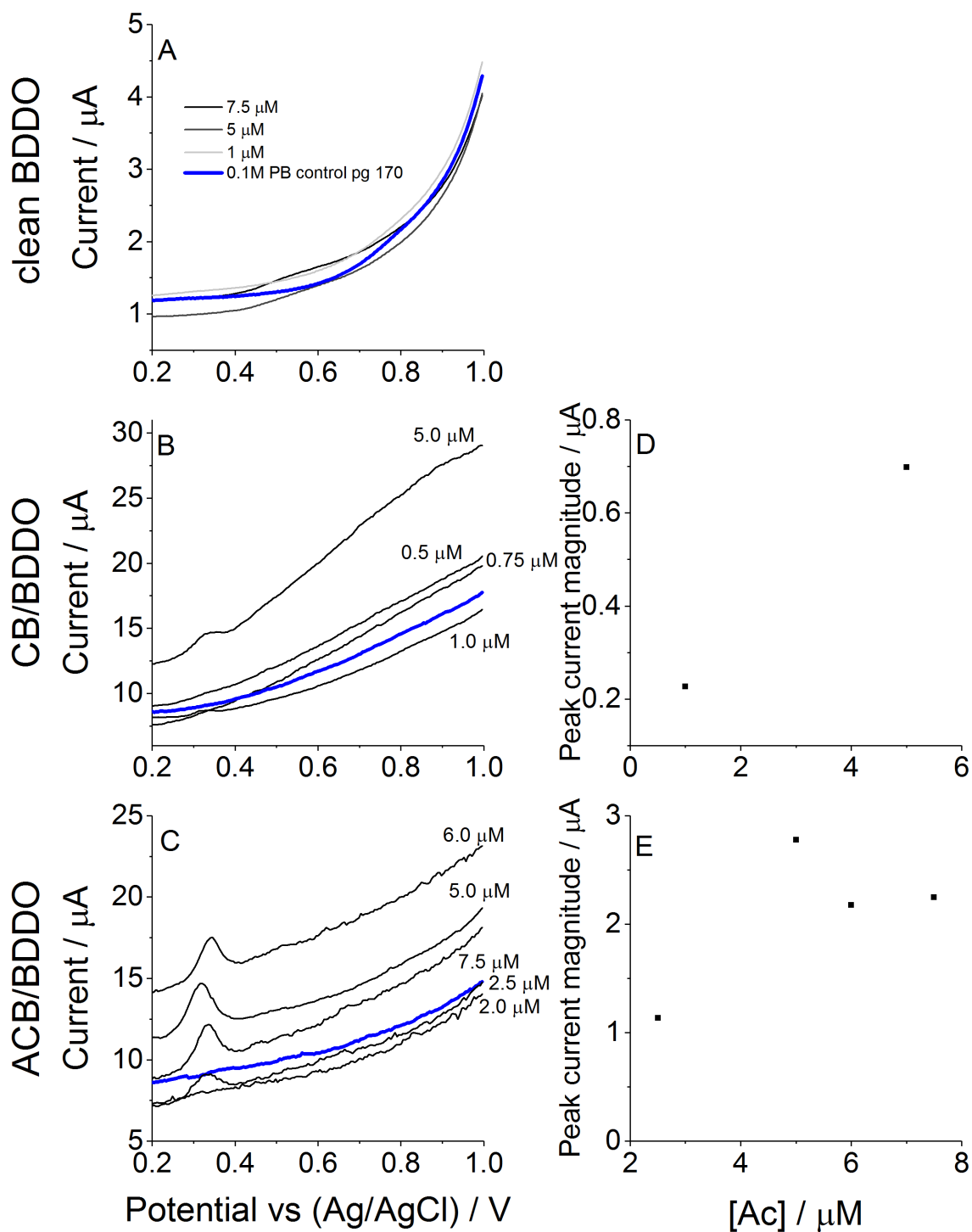


Figure 5.10: DPVs of Ac at various concentrations in 0.1 M PB (pH=7) on A) clean BDDO, B) CB/BDDO and C) ACB/BDDO. The Ac concentrations are given in μM next to each line and the blue line in each DPV shows the DPV response of the electrode in the absence of any Ac (i.e. 0.1 M PB only). D) and E) show the correlation between the peak current and the Ac concentration for CB/BDDO and ACB/BDDO, respectively.

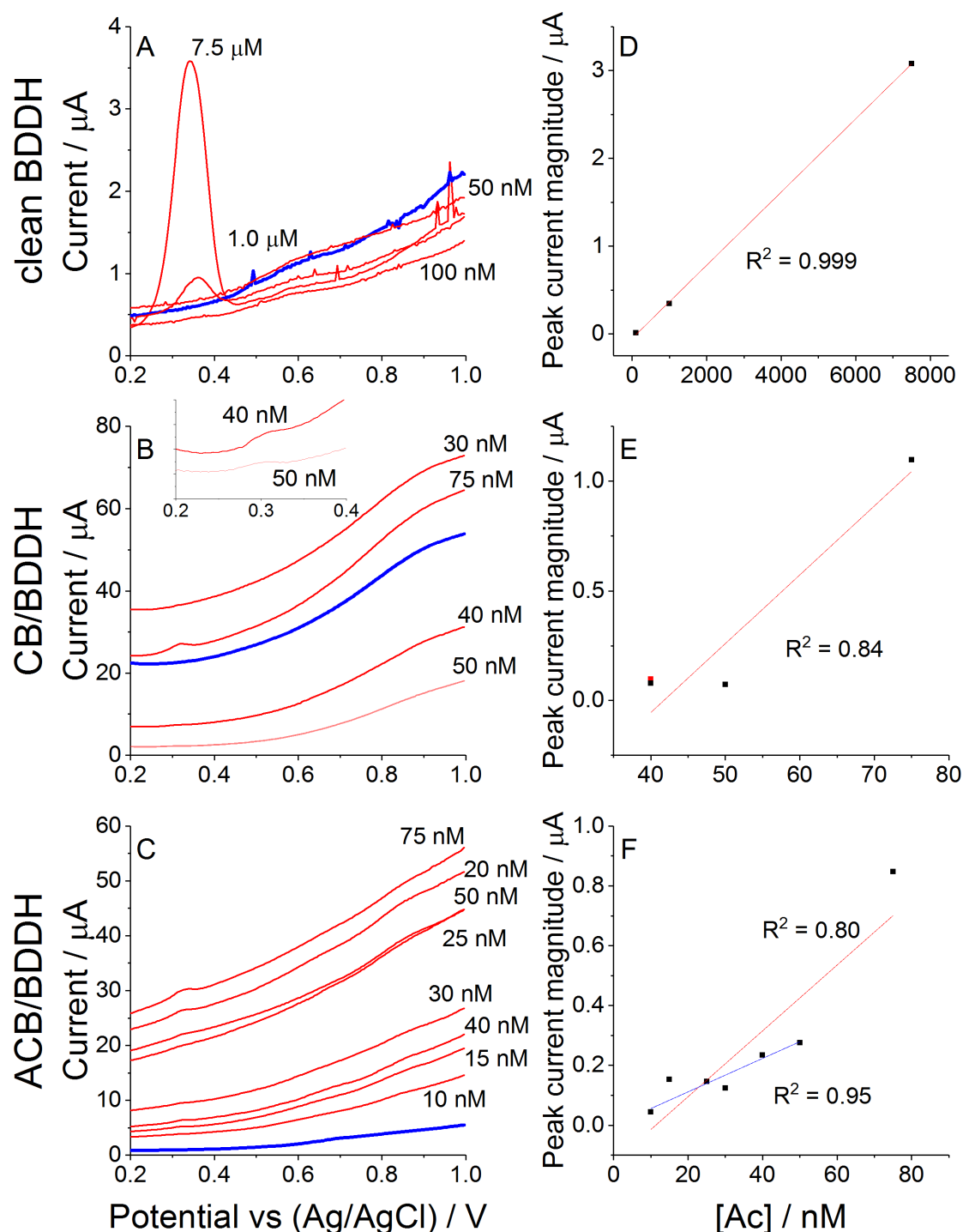


Figure 5.11: DPVs of Ac at various concentrations in 0.1 M PB (pH=7) on A) clean BDDH, B) CB/BDDH (inset shows the current response of 50 and 40 nM Ac, respectively) and C) ACB/BDDH. The Ac concentrations are given in μM next to each line and the blue line in each DPV shows the DPV response of the electrode in the absence of any Ac (i.e. 0.1 M PB only). D), E) and F) show the correlation between the peak current and the Ac concentration for clean BDDH, CB/BDDH and ACB/BDDH, respectively. The blue fit in F) is the correlation when the highest concentration of Ac is excluded from the analysis.

of the carbon black-decorated BDDOs oxidise Ac at just below 0.4 V while the clean BDDO oxidises Ac at just over 0.6 V. The lower oxidation potential of the carbon black decorated electrodes matches the potential of the adsorptive peaks in Fig. 5.6C and the oxidation peaks of the hydrogen-terminated BDDs. This suggests that, at low Ac concentrations, oxidation occurs solely on the carbon black deposits and not on the underlying diamond. Whether this is the case should be probed using a larger concentration range to see at which point the linear correlation between Ac concentration and peak current either breaks or switches to fit a different trend when the underlying BDDO starts to participate in the oxidation process. The improved detection limit of CB/BDDO compared to ACB/BDDO is congruent with the increased electroactive surface area of CB/BDDO compared to ACB/BDDO (Eq. 5.1). The detection limit obtained with the clean BDDO was higher than that obtained with bare GCE [41] and the 0.97 μM reported by Cofan,[44] who performed Ac sensing experiments using chronoamperometry with a BDD mounted in a teflon tube from Windsor Scientific and a Britton-Robinson buffer of pH 1.96. The CB/BDDO electrode achieved a detection limit of 1.0 μM , which is comparable to Cofan's work and 0.51 μM higher than the detection limit obtained with a cathodically pre-treated (partially hydrogenated) BDDO by Lourenção.[45]

The hydrogen-terminated electrodes are consistently more sensitive towards Ac oxidation than the oxygen-terminated BDDs. The achievable detection limits of the BDDH samples are at least two orders of magnitude lower on BDDH than BDDO. All three of the hydrogen-terminated electrodes had a moderate to strong linear correlation between the Ac concentration and the peak current. The clean BDDH had the strongest correlation but the highest detection limit, which suggests that although this electrode is not the most sensitive of the samples, it is the most reliable. The detection limit obtained with a simple, clean BDDH is significantly better than the detection limits obtained using BDD reported elsewhere in the literature (Table 5.1) and compares well with many of the detection limits reported using decorated GCE. ACB/BDDH detected the lowest Ac concentration of all six electrodes with a limit of detection of 10 nM — a detection limit comparable with some of the best decorated GCE electrodes found in the literature (Table 5.1). The improvement in the detection limit of ACB/BDDH compared to both the clean BDDH and CB/BDDH can be explained by the

increased electroactive surface area (Eq. 5.2).

Both CB and ACB are capacitative materials, which accounts for the increase in background current for the decorated BDD electrodes (Fig. 5.8 and 5.11).

5.5 Conclusion

This chapter investigated Ac oxidation with oxygen- and hydrogen-terminated BDD electrodes. The behaviour of Ac oxidation was found to vary drastically with BDD surface termination; specifically, Ac oxidation with BDDH showed better charge transfer than BDDO given that the overpotential was smaller and the peak currents larger with BDDH than BDDO. Ac was also found to lightly adsorb on BDDH but not on BDDO.

This chapter also investigated the effect of CB- and ACB-decorated BDDO and BDDH on Ac oxidation. Inclusion of CB and ACB on the BDDO surface had a small effect on the performance of the electrode in Ac detection by DPV, but the CB and ACB were otherwise largely inactive on this surface, as evinced by the negligible changes in CV peak profile. CB and ACB decoration on BDDH, on the other hand, resulted in increased capacitance, larger peak currents with some evidence of fouling, and improved Ac detection limits by DPV. The Ac adsorption observed on clean BDDH also became more prominent with CB and ACB decoration. In terms of Ac detection, both carbon blacks detected lower Ac concentrations than was possible with clean BDDH. The clean BDDH obtained a detection limit of 100 nM, which is better than any of the detection limits obtained with BDD currently reported in the literature and comparable to many of the decorated GCE electrodes listed in Table 5.1. CB/BDDH achieved a detection limit of 30 nM, similar to the detection limit of graphene-decorated GCE reported by Kim.[10] ACB/BDDH detected Ac down to a concentration of 10 nM, which is lower than most of the detection limits reported in the literature (Table 5.1).

Considering the limited effect of CB and ACB inclusion on BDDO, CB or ACB-decorated BDDO does not appear to be a viable substitute for the more electrochemically active BDDH. At low concentrations of Ac however, CB and ACB were found to have a small but non-negligible effect on Ac oxidation. At low Ac concentrations oxidation with the carbon-

black-modified BDDOs occurred at a potential that corresponds to Ac oxidation on the hydrogen-terminated electrodes. While other results from this chapter suggest that much of the CB and ACB is inactive on the BDDO electrode, some of the carbon black deposits are in electrical contact with the BDDO and enabled the detection of lower Ac concentrations than is possible with the clean BDDO. Given this result, a similar investigation to the one presented in this chapter but with a molecule that is less polar than Ac, and therefore more sensitive to changes in electrode surface hydrophobicity, could show a carbon-black-decorated BDDO to be a viable substitute for the BDDH electrodes in the detection of some compounds.

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Chapter 6

Hydroquinone oxidation with carbon-black-decorated, surface-terminated diamond

6.1 Introduction

Chapter 5 investigated the difference in acetaminophen (Ac) oxidation with clean, explicitly surface-terminated boron-doped diamond (BDD) electrodes and with carbon-black-modified BDDs. Both of the clean BDDs were active surfaces for Ac oxidation, but the clean hydrogen-terminated BDD (BDDH) showed evidence of faster charge transfer than the clean oxygen-terminated BDD (BDDO). Decorating BDDH with acetylene carbon black (ACB) or Monarch 430 carbon black (CB) increased the peak current and electrode capacitance as well as caused a split in the oxidation peak indicative of electrode fouling. On BDDO, both carbon blacks were found to be largely inactive to Ac oxidation at high Ac concentrations. However, at low Ac concentrations ($1 - 7 \mu\text{M}$), the CB or ACB-modified BDDOs detected Ac at a potential consistent with oxidation at the hydrogen-terminated electrode. This result suggests that some of the ACB and CB was active on the BDDO surface. The best Ac detection limits were obtained using the hydrogen-terminated BDDs, of which ACB/BDDH detected the lowest Ac concentration of 10 nM while the clean BDDH had a detection limit

of only 100 nM but the strongest linear correlation. The aim of this chapter is to extend the study presented in chapter 5 to include other organic compounds. Hydroquinone (HQ) was selected as the test compound for investigation in this chapter because of its structural similarity to Ac and because the fact that it undergoes a similar two-electron oxidation process [1, 2], which makes the oxidation behaviour of HQ on different types of electrodes comparable to that of Ac. At the same time, however, HQ is non-polar, which makes it more sensitive to changes in electrode hydrophobicity. The latter characteristic is of particular interest given that the results from chapter 5 showed that the decorated BDDOs were better than clean BDDO for the detection of low concentrations of Ac but not as efficient as the hydrogen-terminated BDDs; if HQ is more sensitive to the carbon black deposits, the carbon black modified BDDO might be a viable substitute for BDDH, which is time-consuming and expensive to prepare.

HQ is a compound that has been used historically in photographic developers, the manufacture of dyes, rubber antioxidants, hair dyes and skin lightening creams.[3–5] However, HQ is now known to be an environmental pollutant that causes drastic damage to aquatic environments[6]. HQ is also a suspected carcinogen.[5, 7] Therefore, many groups have worked to develop electrochemical sensing platforms for HQ and related compounds. Some of these groups have used metal-based electrode materials,[8–12] whereas others have used carbonaceous substrates. For example, Jiang reported the simultaneous detection of HQ and dihydroxybenzene using glassy carbon electrodes (GC) decorated with nanodiamond, graphene and CB. The results obtained with CB-modified GC showed that the inclusion of CB on the GC surface improved the sensitivity of the electrode towards HQ oxidation.[13] Yuan *et al.* used graphitic mesoporous carbon modified glassy carbon electrodes (GMC/GC) for the joint detection of HQ and catechol. They found that decorating the GC with GMC significantly reduced the peak-to-peak separation of the HQ redox couple,[14] an observation also made by Yin *et al.* with chitosan and graphene-chitosan modified GC.[15]

Some work has also been reported using BDD and modified BDDs for the oxidation of HQ. Ramesham and Rose performed kinetic studies of HQ oxidation on BDDO at HQ concentrations higher than 2 mM in hydrochloric acid and sodium sulphate.[16] They found

HQ oxidation to be irreversible but that the peak-to-peak separation decreased with the resistivity of the BDD. Nasr *et al.* used a clean, polarized BDD to measure the current response of 13.5 mM HQ in phosphate buffer at pH=2.[17] Their interest was the oxidation pathway of HQ, resorcinol and catechol on the electrode surface rather than detection or sensing. On the polarized surface, they determined that HQ has a reversible quinonic form with an oxidation potential of approximately 1.35 V and a corresponding reduction potential of approximately -0.8 V vs a saturated calomel electrode. They observed the anodic oxidation peak to be larger than the cathodic reduction peak, which they attributed to an initial electrooxidation step followed by a second chemical process. They considered this second process to likely be a polymerization step that resulted in the loss of the oxidised product. Nasr and co-workers did not investigate the effect of BDD surface termination or surface modification on HQ oxidation. Sopchak *et al.* studied the oxidation of HQ to smaller fragments.[1] Although they determined that BDD is better for HQ fragmentation than the metal electrodes studied, they did not consider the effect of surface termination or modification. Neither of these two works used BDD as a sensing platform for HQ.

Cunha *et al.* is one of the few research groups that has used BDD as a sensing platform for HQ. Using batch injection analysis with amperometric detection, they reported detection limits as low as 0.016 μM in sulfuric acid.[18] Another group that has used BDD for the detection of HQ is Zhao *et al.*, who reported a limit of detection of HQ at 1.67 μM with differential pulse voltammetry and clean BDD.[19] Again, Cunha and Zhao investigated only the clean BDD for HQ detection without extending the work to cover surface-terminated or modified BDD electrodes. Table 6.1 gives the detection limits of HQ obtained with carbon-based electrodes currently reported in the literature. The reaction scheme of HQ oxidation is given in Fig. 6.1

Considering the difference observed in the oxidation of Ac on BDDO and BDDH in chapter 5, and the promising results of using BDD-based electrodes as sensing platforms for HQ reported by Cunha [18] and Zhao [19], this chapter also aims to extend the work of using BDD-based HQ sensors to investigate the behaviour of BDDH in HQ oxidation and compare this to that of BDDO. The enhanced electrode performance reported by Jiang [13] and

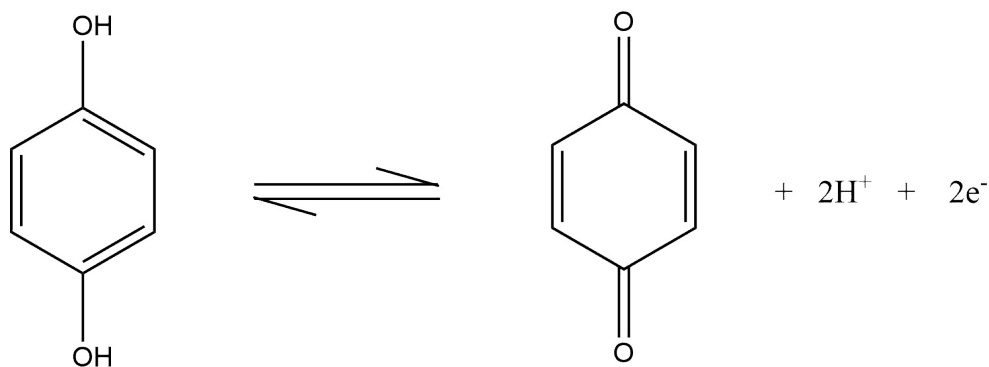


Figure 6.1: Reaction scheme of HQ oxidation.

Table 6.1: HQ limits of detection (LoD) currently reported in the literature

Electrode	LoD / μM	Ref
GC	3.9	[20]
graphene screen printed electrodes	2.7	[21]
AuNP-mesoporous silica modified carbon paste electrode	1.2	[8]
poly-amidosulfonic acid/MWCNT	1.0	[22]
chitosan/GC	0.75	[15]
GMC/GC	0.37	[14]
AuNP-MWCNT/ionic liquid composite film/GC	0.2	[23]
BDD	1.67*	[19]
BDD	0.016**	[18]

*obtained by DPV **obtained by batch injection analysis

others [14, 15] when the electrode surface is modified with carbon black makes the study of carbon-black-modified BDD a natural extension of existing research and a promising avenue of investigation for the development of a simple HQ sensor. If the small enhancement in sensitivity observed in chapter 5 for the detection of Ac with CB- or ACB-decorated BDDO is also observed for HQ, carbon-black-modified BDDO might be of interest as a substitute for BDDH.

6.2 Aims of the chapter

There were two aims of this project. The first aim was to determine if CB modification enhances the ability of BDD electrodes to detect HQ in aqueous solutions, including whether the differences in Ac redox that arose due to the carbon black decoration in chapter 5 are also present for HQ. The second aim was to see if the increased electrochemical response observed with BDDH can be replicated with the less expensive and lower maintenance CB/BDDO for the detection of a non-polar compound.

6.3 Experimental

All chemicals were sourced from the same providers as in chapter 5. The electrode termination, cleaning and CB deposition procedures were also the same as in chapter 5. Millipore water was used for all aqueous solutions, for rinsing and in sonication.

6.3.1 Cyclic voltammetry

CVs of the HQ redox profile on all four electrodes were recorded in a solution of 0.2 mM HQ in 0.1 M phosphate buffer (PB, pH=7) between -0.4 and 0.4 V at a scan rate of 50 mV s⁻¹. Randles-Sevcik type experiments were performed using the same parameters but with a scan rate that ranged from 10 to 100 mV s⁻¹.

6.3.2 Square-wave voltammetry

Square-wave voltammetry (SWV) was conducted in HQ solutions supported in 0.1 M PB at a 110 Hz frequency with a wave amplitude of 0.025 V and a potential step of 0.00045 V.

6.4 Results and discussion

The electrochemical characterisation results are presented first in section 6.4.1, together with a discussion about the CV profile characteristics of each electrode. After the electrochemical

characterisation test, the use of the electrodes as HQ sensors was investigated by varying the HQ concentration. These results are presented in section 6.4.2.

6.4.1 Cyclic voltammetry

The electrochemical performance of the CB decorated BDDs was investigated by means of CV in 0.2 mM HQ in 0.1 M PB at a scan rate of 50 mVs^{-1} . The results are shown in Fig. 6.2.

Fig. 6.2 shows the distinct behaviour of BDDO and BDDH: the clean BDDH oxidises HQ while the clean BDDO is completely inactive. All four of the decorated samples (Fig. 6.2B-F) also oxidised HQ. Of the five active samples, the current response decreased in the following order:

$$\text{CB/BDDH} > \text{CB/BDDO} > \text{ACB/BDDH} > \text{clean BDDH} > \text{ACB/BDDO}. \quad (6.1)$$

Eq. (6.1) shows that for both the oxygenated and hydrogenated case, the inclusion of CB on the electrode surface improves the ability of the electrode to electrooxidise HQ. Table 6.2 lists the peak current responses and peak separation for each electrode.

Table 6.2: Peak current and peak separation of HQ redox profile for each electrode

Electrode	$I_{\text{p,ox}} / \mu\text{A}$	$I_{\text{p,red}} / \mu\text{A}$	$\Delta E_{\text{p}} / \text{V}$
clean BDDO	n/a	n/a	n/a
CB/BDDO	35.7	35.2	0.063
ACB/BDDO	17.8	15.5	0.313
clean BDDH	24.8	29.1	0.112
CB/BDDH	42.4	41.1	0.049
ACB/BDDH*	31.7	31.9	0.059

$I_{\text{p,ox}}$ is the oxidative peak current, $I_{\text{p,red}}$ is the peak current of reduction and ΔE_{p} is the separation between the oxidation and reduction peak centers.

*The peak currents and ΔE for ACB/BDDH correspond to the main peak and not the oxidative/reductive peak shoulders.

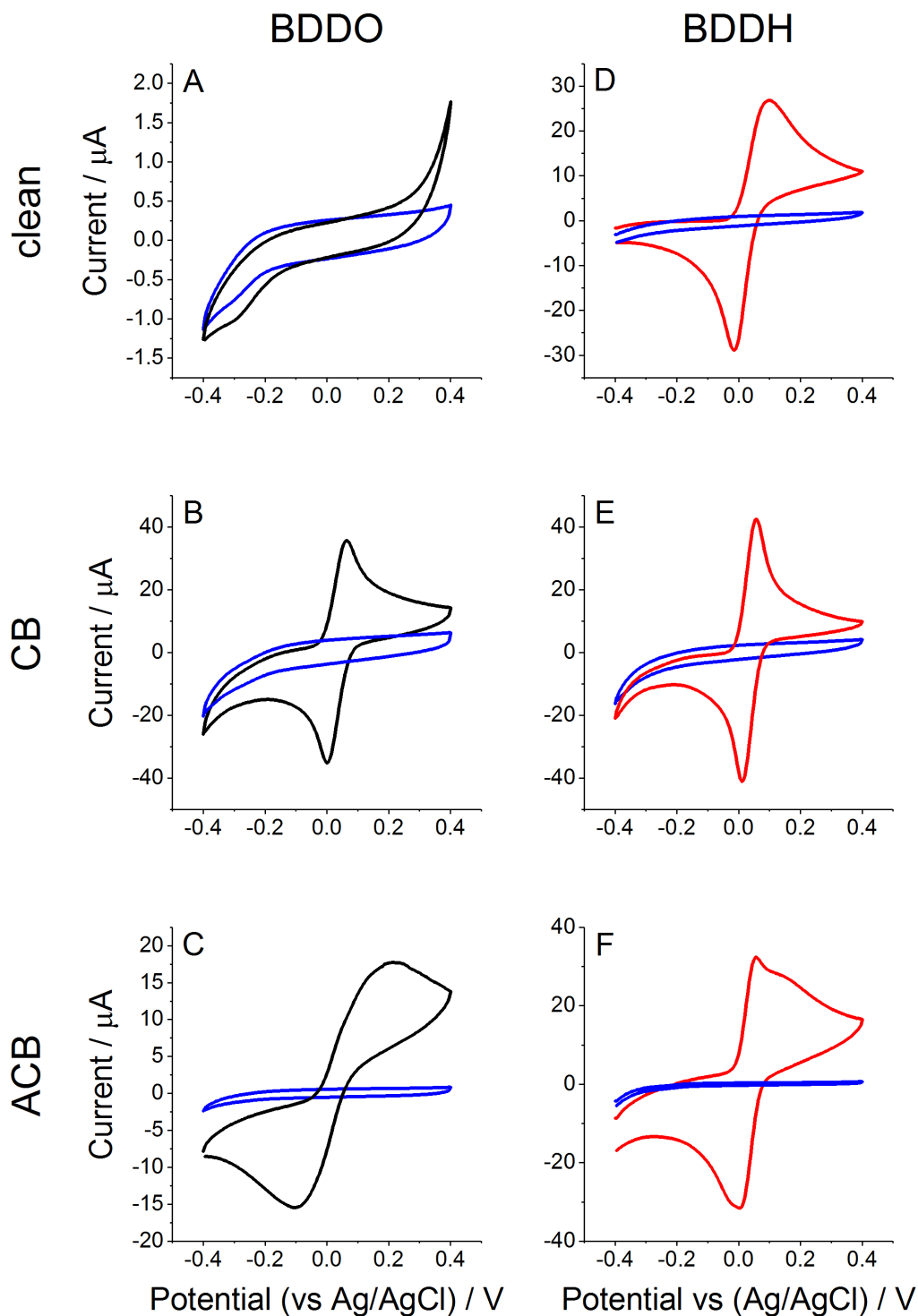


Figure 6.2: CVs of 0.2 mM HQ in 0.1 M PB at 50 mV s^{-1} on A) clean BDDO, B) $10 \mu\text{L } 1 \text{ mg mL}^{-1}$ CB on BDDO, C) $10 \mu\text{L } 1 \text{ mg mL}^{-1}$ ACB on BDDO, D) clean BDDH, E) $10 \mu\text{L } 1 \text{ mg mL}^{-1}$ on BDDH and F) $10 \mu\text{L } 1 \text{ mg mL}^{-1}$ ACB on BDDH. The blue lines show the CV in 0.1 M PB only.

Adding CB to the BDDO surface changes the electrode from being incapable of HQ oxidation to behaving comparably with BDDH. The inclusion of 10 μg CB increases the peak current from 0 (no response) to approximately 35 μA with a peak-to-peak separation of 63 mV. Both of these values indicate that CB/BDDO behaves comparably with CB/BDDH and better than the clean BDDH. Decorating BDDO with ACB, on the other hand, results in a detectable redox current for which the peak-to-peak separation is almost five times larger than with CB. While the HQ redox peak potentials with ACB/BDDO are closer to those observed with glassy carbon,[13] the peak-to-peak separation suggests more sluggish behaviour than that observed for CB/BDDO, possibly due to the electrode resistivity.[16]

The considerable improvement in electrode response shown with carbon black decoration (Fig. 6.2B and C) compared to the clean BDDO (Fig. 6.2A) suggests that the conclusion from chapter 5 — that much of the carbon black is inactive on BDDO — needs to be revised. While the results from chapter 5 indicated the inactivity of the carbon black, the results presented here suggest that the carbon blacks are, in fact, in electrical contact with the underlying BDDO. This apparent discrepancy can be explained given that the underlying BDDO itself was active towards Ac oxidation but not for HQ oxidation. Given the inactivity of the underlying BDDO towards HQ oxidation, even if only a fraction of the deposited carbon black is in good electrical contact with the underlying BDDO, this small improvement in electroactive surface regions could have a drastic effect on the electrode performance.

Adding CB to the BDDH surface improves the current response and reduces the peak-to-peak separation by 63 mV, or about 43%. The reduction in peak-to-peak separation in HQ oxidation is consistent with the behaviour reported for carbon-black-decorated GC electrodes[14, 15] and indicates a reduction in surface resistivity,[16, 24] which suggests that the CB is in good electrical contact with the underlying BDDH. Decorating BDDH with ACB results in a split oxidation peak, as was also observed for Ac oxidation in chapter 5 (Fig. 5.3F). The oxidation peak at the lower overpotential matches the peak obtained with CB/BDDH in Fig. 6.2E. ACB/BDDH shows a larger oxidation current than the clean BDDH but smaller than CB/BDDH. Likewise, the peak-to-peak separation of ACB/BDDH is between that of the clean BDDH and CB/BDDH, which suggests that ACB modification

does not enhance the electrochemical performance of BDDH to the same extent as CB modification.

As shown in Fig. 6.2 and summarised in Table 6.2, the ACB-modified BDDs showed less improvement in both peak currents and peak-to-peak separation over the clean BDDs than the CB-modified BDDs. This result, together with the poorer observed physical stability of the ACB-modified electrodes, made the CB-modified BDDs the main focus of the rest of this chapter. No further experiments were conducted with ACB.

Randles-Sevcik

In addition to the CVs of the CB-decorated BDDs in 0.2 mM HQ at 50 mV s⁻¹, which are presented in Fig. 6.2, Randles-Sevcik type experiments were performed in 0.2 mM HQ in 0.1 M PB at scan rates ranging from 10 to 100 mV s⁻¹. The purpose of these experiments was to determine if the HQ redox processes were diffusion or adsorption controlled. As shown in Fig. 6.3, both CB/BDDO and CB/BDDH exhibited a strong linear correlation between the peak current and the square-root of the scan rate, which shows that the HQ oxidation is reversible and diffusion controlled. Given that the process is reversible, the Randles-Sevcik equation can be used to estimate the value of the electroactive surface area:

$$A = \frac{I_p}{2.69 \times 10^5 n^{3/2} C D^{1/2} \nu^{1/2}} \quad (6.2)$$

where $n = 2$, $D = 7.5 \times 10^{-6}$ cm²s⁻¹ [25, 26] and $C = 2 \times 10^{-7}$ mol cm⁻³. Using the slopes in Fig. 6.3B and D in amps, 2.142×10^{-4} and 2.166×10^{-4} A (V s⁻¹)^{-1/2} for BDDO and BDDH, respectively, gives

$$A_{\text{CB/BDDO}} = 0.51 \text{ cm}^2 \text{ and} \quad (6.3)$$

$$A_{\text{CB/BDDH}} = 0.52 \text{ cm}^2. \quad (6.4)$$

The calculated area of the CB/BDDO is close to, but smaller than, the area of CB/BDDH. This suggests that CB/BDDO might be a practical substitute for the more cumbersome hydrogen-terminated electrodes.

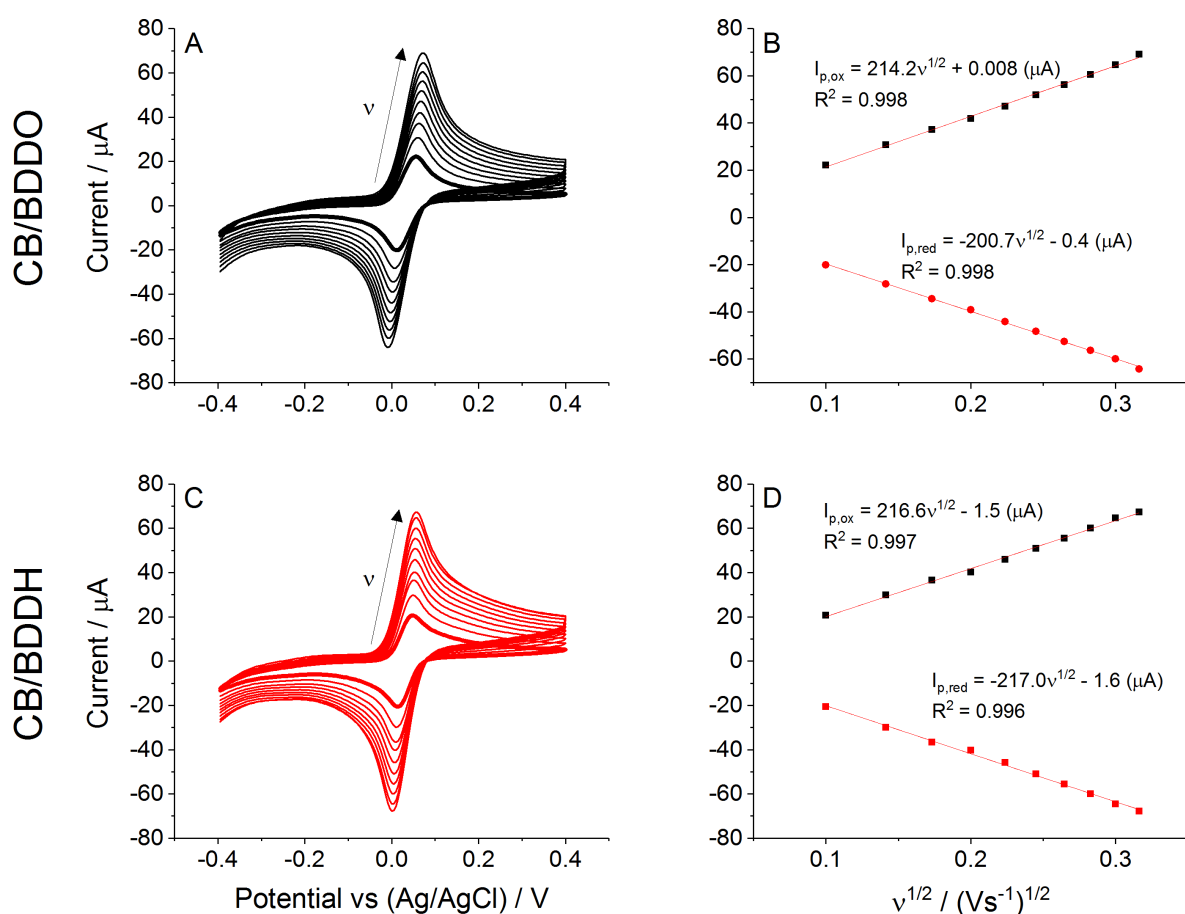


Figure 6.3: CVs and associated plot of peak current against the square root of the scan rate for A and B) CB/BDDO and C) and D) CB/BDDH.

6.4.2 HQ concentration variation

There are two main factors that determine whether a stable electrode can be used for HQ sensing. The first factor is the ability of the electrode to have a current response that is predictable and proportional to the HQ concentration. The second factor is the ability of the electrode to detect very low concentrations of HQ. To determine the suitability of the CB-decorated BDDs as HQ sensors, CV was used to establish the correlation between peak current and HQ concentration while SWV was used to determine the minimum concentration of HQ detectable with these electrodes.

Cyclic voltammetry

The CV experiment described in section 6.4.1 was repeated using the same scan parameters for a HQ concentration ranging from 0.025 to 0.4 mM. The results are given in Fig. 6.4.

At 0.2 mM HQ, the CVs for the CB/BDDO and CB/BDDH electrodes showed the greatest similarity in peak position and peak current (Fig. 6.2). The clean BDDH also had a similar profile but slightly smaller peak amplitudes and a wider FWHM compared to CB/BDDH. The similarity in peak position and current implies that there is no significant energetic preference for HQ oxidation on one electrode over the other and that both electrodes oxidise comparable quantities of HQ. However, when the HQ concentration increased beyond 0.2 mM, the the peak-to-peak separation and the FWHM of CB/BDDO increased in a manner not observed for CB/BDDH. With these shifts, CB/BDDO behaves less like the hydrogenated electrodes and CB/BDDH becomes more comparable to the clean BDDH than CB/BDDO. Therefore, the CB/BDDO might not be a suitable substitute for hydrogenated BDDs at a larger HQ concentration range.

Although the behaviour of CB/BDDO and CB/BDDH were most congruent at 0.2 mM HQ (Fig. 6.2), their behaviour over a range of HQ concentrations diverged. At high HQ concentrations, CB/BDDO had peak magnitudes that were smaller than those at the clean and CB-modified BDDH. Of the clean BDDH, CB/BDDH and CB/BDDO, CB/BDDO had the smallest peak current increase with HQ concentration (Fig. 6.4F). Coupled with a flatter slope and poorer linear correlation than the clean BDDH, this made CB/BDDO a less reliable HQ sensor. The small slope suggests CB/BDDO is less sensitive to the specific HQ concentration and the poorer linear correlation suggests that the electrode itself suffers from variability: a fresh CB/BDDO electrode was prepared for each measurement, but the physical instability of the CB on the BDD surface — discussed in chapter 5 — introduced an uncertainty in the measurement, particularly at 0.05 mM HQ in Fig 6.4F, which is not present with the clean BDDH.

CB/BDDH had the largest overall peak amplitudes and the steepest slope of all three samples. Moreover, the peak profile remained consistent with increasing HQ concentration for CB/BDDH, unlike for CB/BDDO where the peak profile changed. The steep slope suggests

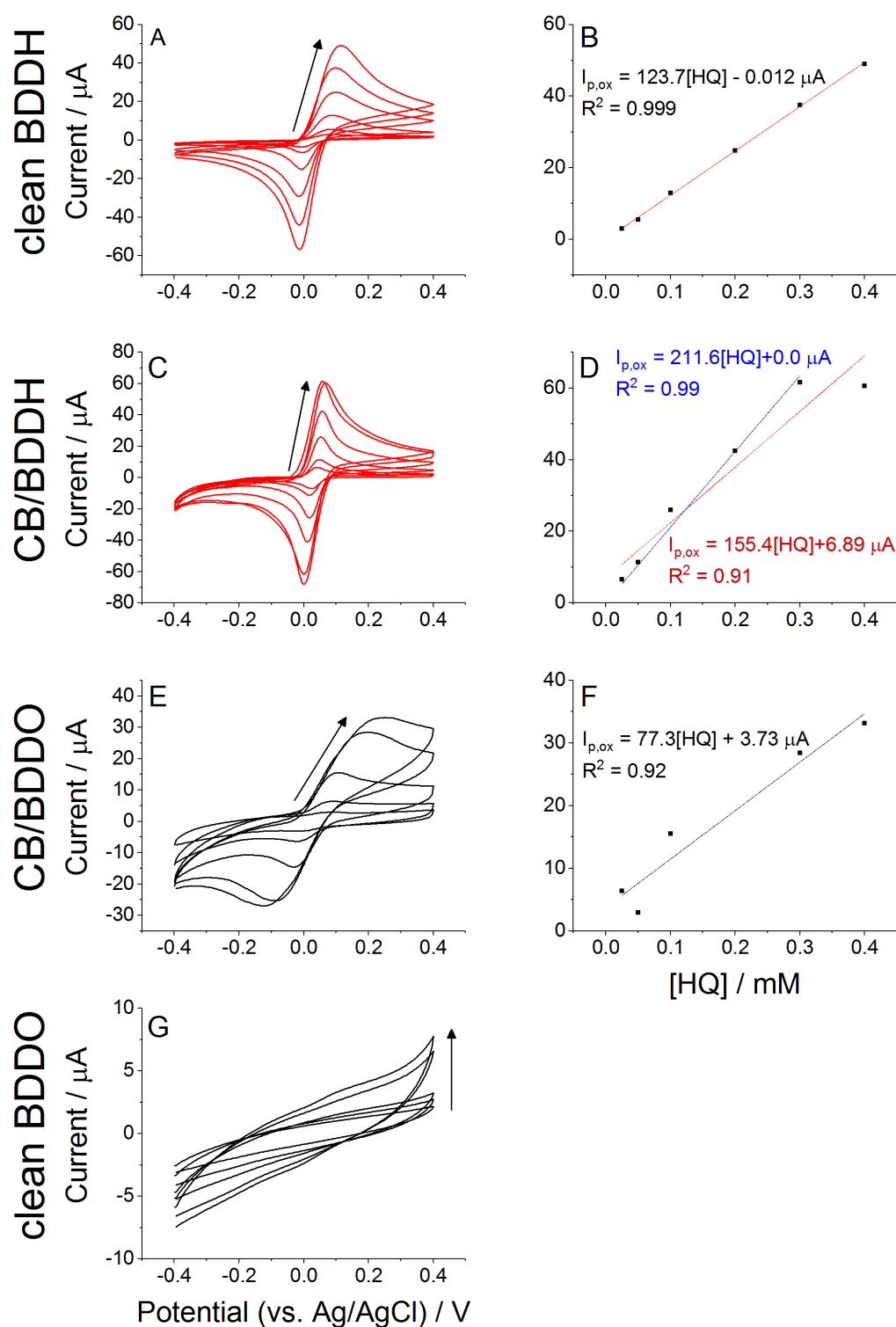


Figure 6.4: The CV of HQ at 0.025, 0.05, 0.1, 0.2, 0.3 and 0.4 mM HQ in 0.1 M PB on A) clean BDDH, with the corresponding scatter plot shown in B, C) CB/BDDH with the corresponding scatter plot shown in D (the red fit includes all data points, the blue fit excludes 0.4 mM HQ), E) CB/BDDO with the corresponding scatter plot shown in F and G) clean BDDO which did not catalyse HQ oxidation even at higher concentrations. The arrow indicates the order of increasing HQ concentration.

that CB/BDDH is the most sensitive to changes in the HQ profile, but the poorer correlation compared to the clean BDDH indicates that CB/BDDH suffers from the same variability observed with CB/BDDO, which explains the odd point at 0.4 mM HQ in Fig. 6.4D.

Like CB/BDDH, the peak profile of the clean BDDH did not change with increasing HQ concentration. The clean BDDH had peak currents that, at high HQ concentrations, were slightly larger than CB/BDDO, but the increase in peak current with HQ concentration (Fig. 6.4B) was closer to that of CB/BDDH (Fig. 6.4D) than CB/BDDO (Fig. 6.4F). The difference between the clean BDDH and CB/BDDO suggests that CB/BDDO is not an appropriate substitute for the clean BDDH, regardless of the promising initial results. Of all the electrodes, the clean BDDH had the strongest linear correlation because of the reproducibility of the surface.

The clean BDDO (Fig. 6.4G) was inactive to HQ oxidation at all the HQ concentrations tested.

Square-wave voltammetry

To make a viable electrochemical sensor, the electrode needs to be able to reliably detect low concentrations of the analyte. Since SWV is better at eliminating non-faradaic current contributions than CV, this technique was used to determine the lowest HQ concentration detectable with the CB-decorated BDDs and the clean BDDH. Given that the clean BDDO does not catalyze HQ oxidation at any of the concentrations probed in section 6.4.2, the clean BDDO was not tested with SWV. The results from the CB-decorated BDDs and the clean BDDH are shown in Fig. 6.5.

As shown in Fig. 6.5, the clean BDDH was able to detect the lowest concentrations of HQ despite the fact that CB/BDDH had the largest peak currents in the CV HQ concentration variation experiment (Fig. 6.4C). Despite the initial promise of similarity in behaviour of CB/BDDO to the hydrogenated BDDs, CB/BDDO was not able to detect particularly low concentrations of HQ. The lowest limit of detection currently reported in the literature using a similar system is 1.67 μM [19], which is comparable to the results obtained for the clean BDDH shown in Fig. 6.5. The fact that the limit of HQ detection with CB/BDDO was an

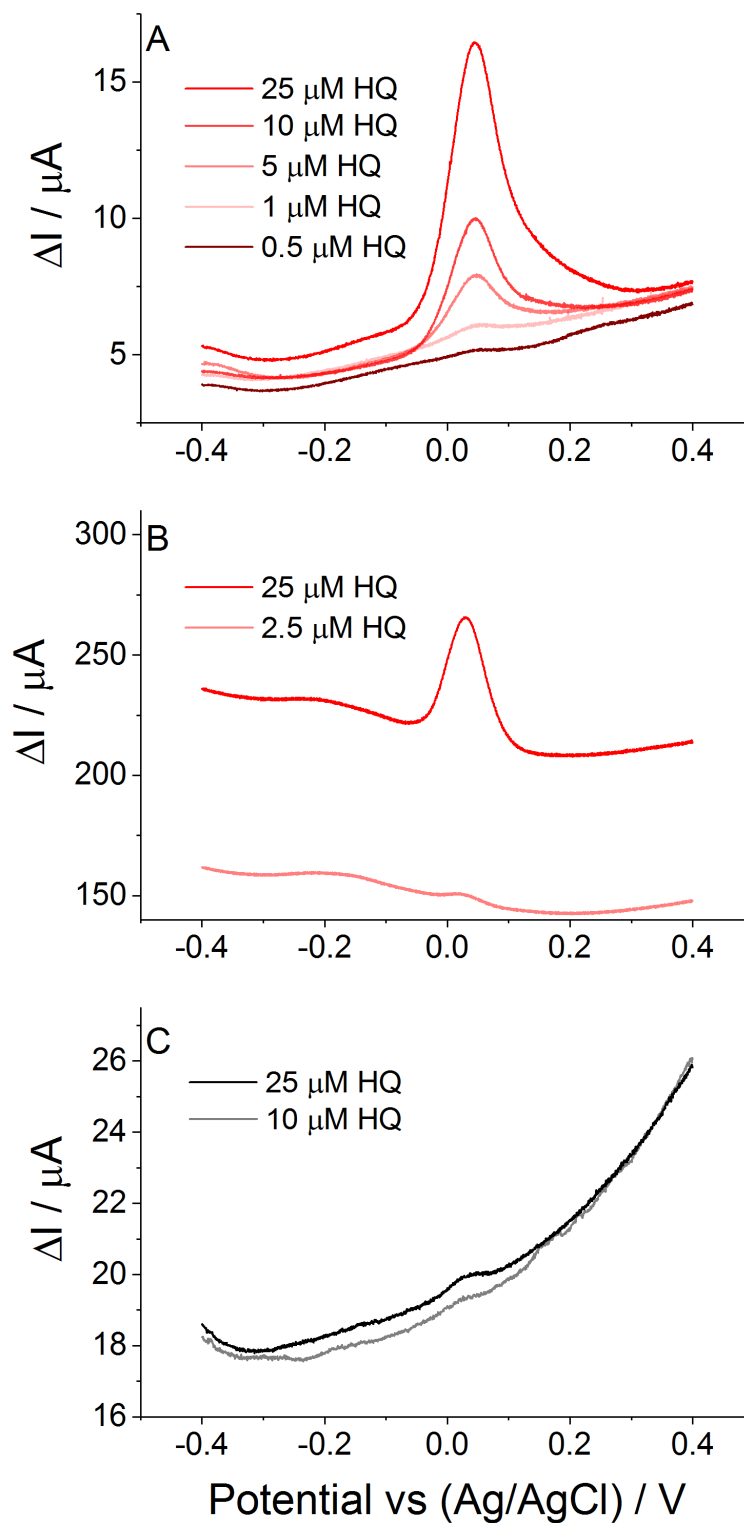


Figure 6.5: SW of HQ in 0.1 M PB with A) clean BDDH, B) CB/BDDH and C) CB/BDDO. The HQ concentration is given in the legend in each plot.

order of magnitude higher than the clean BDDH demonstrates that CB-modification is not sufficient to make an oxygenated BDD a suitable alternative to BDDH.

6.5 Conclusion

The work presented in this chapter was performed with the aim of establishing if:

1. the clean BDDH behaves differently from the clean BDDO in terms of HQ oxidation and if CB-modification enhances the ability of the BDD electrodes to detect HQ; and
2. the better electrochemical response obtained with BDDH can be reproduced using CB/BDDO.

The clean BDDH behaved very differently from the clean BDDO in that the clean BDDH was active to HQ oxidation while the clean BDDO was consistently inactive.

CB did not enhance the ability of BDDH to detect HQ; of the three electrodes (clean BDDH, CB/BDDH and CB/BDDO) that were tested as low concentration detectors of HQ, the clean BDDH performed best. The clean BDDH was able to detect HQ at concentrations as low as $0.5\ \mu\text{M}$, which is better than the BDD sensors currently reported in the literature and comparable to the detection limits obtained with decorated GC electrodes (see Table 6.1). The detection limit obtained with the clean BDDH was up to five times lower than was detectable with CB/BDDH and an order of magnitude smaller than that detected with CB/BDDO. At larger HQ concentrations, clean BDDH showed both the strongest linear correlation between the HQ concentration and the peak current and the second steepest peak current magnitude increase with HQ concentration. This suggests that the clean BDDH was more sensitive to the amount of HQ present in the solution and is a more reliable sensor.

CB did enhance the ability of BDDO to detect HQ but not enough to make CB/BDDO a viable substitute for the hydrogenated electrodes. The clean BDDO was consistently inactive to HQ oxidation, while CB/BDDO had a CV profile that, at concentrations of $0.2\ \text{mM}$ or lower, were comparable to the hydrogenated BDDs. CB, therefore, enhanced the ability of BDDO to sense HQ, but CB modification of BDDO was not sufficiently able to mimic

the behaviour of BDDH in the oxidation of low HQ concentrations to make CB/BDDO an alternative to clean BDDH. The drastic improvement in electrochemical response observed with CB/BDDO compared to the clean BDDO suggests that more of the CB is active on the electrode surface than believed from the results in chapter 5. This is explained by the increase in electrochemical surface area combined with the hydrophobic CB environment on the decorated BDDO that makes CB/BDDO active to HQ oxidation while even the bare BDDO is active towards Ac oxidation making any slight improvement from CB less important for Ac oxidation.

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Chapter 7

Summary and outlook

This thesis focused on the effect of boron-doped diamond (BDD) surface termination on the electrochemical performance of particle-decorated BDD electrodes. Throughout this thesis, the electrochemical behaviour of particle-modified, hydrogen- and oxygen-terminated BDDs have been compared directly. Three distinct types of particles — metal, metal oxide and carbon black — were used to decorate the BDDs to determine the extent to which the influence of BDD surface termination on the characteristics of the particles and the performance of the electrode can be generalised. Overall, the hydrogen-terminated BDD showed a stronger interaction between the BDD surface and the deposited particles. The oxygen-terminated BDD showed that regions of the electrode surface remain electrochemically inactive even when the surface is decorated with active particles. The following four paragraphs summarize the main results and conclusions from each chapter, after which a brief discussion of future work is presented.

7.1 Summary

Chapter 3 explored how the performance of a gold-nanoparticle-decorated BDD is affected by the BDD surface termination and the nanoparticle deposition method. The performance was evaluated in terms of cyclic voltammetry profiling; physical stability; physical characteristics of the gold nanoparticles such as surface crystallinity, particle size and distribution over the underlying BDD; and mercury sensing. Overall, gold nanoparticles were found to be in bet-

ter electrical communication with hydrogen-terminated BDDs than with oxygen-terminated BDDs, which resulted in higher currents and lower mercury detection limits being achieved with hydrogen-terminated than with oxygen-terminated BDDs. The mercury detection limit reached with the hydrogen-terminated BDD decorated with electrodeposited gold nanoparticles was similar to mercury detection limits reported for other carbon-based electrodes in the literature. The BDD surface termination affected the distribution of colloidal gold nanoparticles of the BDD surface, with greater dispersion and agglomeration being evident on the hydrogen-terminated and oxygen-terminated BDD, respectively. On the other hand, the BDD surface termination determined both the morphology and surface crystallinity of electrodeposited gold nanoparticles. Additionally, the gold nanoparticles were found to be more physically stable on the hydrogen-terminated BDD.

Chapter 4 extended the study to the use of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox couple supported on an oxygen-terminated BDD for glucose sensing previously reported by Toghill [1] and Hutton [2] to include also the hydrogen-terminated BDD. The BDD surface termination affected the amount of Ni deposited during the time limited, potentiostatic deposition step as well as the distribution of the deposited Ni particles on the BDD surface. The Ni decorated, hydrogen-terminated BDD electrode consistently yielded larger peak currents than the oxygen-terminated counterparts, but the Ni decorated, oxygen-terminated BDD electrodes showed less variability than the hydrogen-terminated BDD.

Chapter 5 investigated the use of two different types of carbon black on both hydrogen- and oxygen-terminated BDD for acetaminophen sensing. The clean, surface-terminated BDDs had different CV profiles for acetaminophen oxidation, with the hydrogen-terminated BDD having larger peak currents and smaller peak-to-peak separations. Adding carbon black to the electrode surface increased the peak currents of the hydrogen-terminated BDD but had very little effect on the oxygen-terminated BDD. While most of the carbon black deposits were inactive on the oxygen-terminated BDD, carbon black modification enabled the detection of lower amounts of acetaminophen than was possible with the clean BDD. On the hydrogen-terminated BDD, the detection limit for acetaminophen decreased from 100 nM on the clean BDD to a state-of-the-art 10 nM when the BDD was modified by CB.

Chapter 6 studied the use of carbon-black-decorated and explicitly terminated BDDs for hydroquinone sensing. The possibility of using a carbon-black-modified, oxygen-terminated BDDO as a substitute for hydrogen-terminated BDD was also considered. The clean, oxygen-terminated BDD was found to be inactive with respect to hydroquinone oxidation in the potential range studied, while the hydrogen-terminated BDD was found to be able to detect hydroquinone down to concentrations as low as $0.5\ \mu\text{M}$. This detection limit is comparable to, and better than, detection limits reported for other carbon-based electrodes. While carbon black decoration did not improve the detection limits of the hydrogen-terminated BDD, carbon black modification made the oxygen-terminated BDD active to hydroquinone oxidation. At $0.2\ \text{mM}$ hydroquinone, the CV profile of the carbon-black-decorated, oxygen-terminated BDD was comparable to the profile of the hydrogen-terminated electrodes. However, the carbon-black-modified, oxygen-terminated BDD was only able to detect hydroquinone down to a concentration of $10\ \mu\text{M}$. Overall, carbon-black modification was found to enhance the performance of the oxygen-terminated BDD but not sufficiently to make this electrode a viable alternative to the hydrogen-terminated BDD.

The overall conclusion is that BDD surface termination has an important role in controlling electrochemical performance with better results in general being obtained at the less frequently used hydrogen-terminated material.

7.2 Outlook

There are a number of ways in which the work presented in this thesis can be further developed. Chapters 3 and 4 both dealt with metal particles on the oxygen-terminated BDD that were in poor electrical contact with the underlying BDD. Additional impedance measurements would show if and how the resistivity of the electrode varies with different surface terminations. Due to the complex interplay between BDD crystal orientation, surface structure, surface termination and electrochemical response, as discussed in chapter 1, continuing the comparison between particle decoration on explicitly terminated BDDs begun in this thesis on single-crystal BDDs would offer insight into the effect of individual BDD crystal

surfaces on the electrochemical behaviour of the particle-modified BDD ensemble.

In this thesis, oxygen termination was achieved by refluxing BDD wafers in HNO_3 , which resulted in several oxygen functional groups being present on the electrode surface. The electrochemical behaviour of these electrodes was then compared to that of hydrogen terminated electrodes and, in general, the oxygen-terminated electrode was found to have a poorer electrochemical response than the hydrogen-terminated BDD. Therefore, it would be interesting to explore whether this effect is due to a specific oxygen-terminated surface — specific by functional group, crystal orientation/reconstruction, or both — and how each type of oxygen-terminated surface compares to that of the hydrogen-terminated surfaces.

The results from chapters 5 and 6 suggest that the simple modification of oxygen-terminated BDD with carbon black to achieve the electrochemical behaviour of hydrogen-terminated BDD is possible but not yet unrealized. Possibilities of continuing research in this area include the use of surfactants to improve the physical stability and uniform distribution of the carbon black on the BDD surface. Care would have to be taken to avoid making the surface modification of the carbon black overly complicated and thereby undermining the purpose of a simple, cost-effective method of fabricating a hydrogen-terminated-like BDD electrode.

Chapter 5 showed that, at low Ac concentrations, Ac oxidation occurs only on the carbon black deposits and not on the underlying BDDO. The most natural continuation of this work is to complete the Ac concentration range and determine whether there is a critical point in concentration at which the underlying BDDO begins to participate in the oxidation process.

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