



UNIVERSITY *of*
TASMANIA

**Investigations of Novel Artificial Diamond-
Based Composite Substrates for Separation
Science and Analytical Chemistry**

by

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Declaration of Originality

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List of Abbreviations

AA	Ascorbic acid
AAB	Acid anthraquinone blue
ABA	p-aminobenzoic acid
ACN	Acetonitrile
ACS	American Chemical Society
ANP	Aqueous normal phase
AP	Atmospheric pressure
APBA	3-aminophenylboronic acid
APTES	(3-aminopropyl)triethoxysilane
AR	Analytical reagent
ATR	Attenuated total reflection
BA	Benzoic acid
BDD	Boron-doped diamond
BET	Brunauer–Emmett–Teller
BSA	Bovine serum albumin
BTBA	Benzyltributylammonium chloride
CAPS	N-cyclohexyl-3-aminopropanesulfonic acid
CNTs	Carbon nanotubes
CTS	Chitosan
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
CYTC	Cytochrome <i>c</i>
DA	Dopamine hydrochloride
DAD	Diode-array detection
DC	Direct current
DGC	Diamond-graphene oxide composites
DIW	Deionised water
DLC	Diamond-like carbon
DMF	<i>N,N</i> -dimethylformamide
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid

DND	Detonation nanodiamonds
DOE	Design of experiment
DPG	Diamond/polyaniline/graphene
EC	Electrical conductivity
EDS	Energy-dispersive X-ray Spectroscopy
EG	Ethylene glycol
ESI	Electrospray ionisation
EtOH	Ethanol
FAAS	Flame atomic absorption spectroscopy
FID	Flame ionisation detection
FT ICR	Fourier transform ion cyclotron resonance
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GCE	Glassy carbon electrode
GO	Graphene oxide
HETP	Height equivalent to the theoretical plate
HILIC	Hydrophilic interactions liquid chromatography
HPHT	High pressure high temperature
HPLC	High-performance liquid chromatography
HSA	Human serum albumin
IC	Ion chromatography
ICP AES	Inductively coupled plasma atomic emission spectroscopy
ICP OES	Inductively coupled plasma optical emission spectrometry
ID	Internal diameter
IEC	Ion-exchange capacity
IMAC	Immobilised metal ion affinity chromatography
IPA	Isopropyl alcohol
LbL	Layer-by-layer
LC	Liquid chromatography
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LYS	Lysozyme

mAbs	Monoclonal antibodies
MALDI	Matrix-assisted laser desorption/ionization
MB	Myoglobin
MELDI	Material enhanced laser desorption ionisation
MeOH	Methanol
MPACVD	Microwave plasma assisted chemical vapour deposition
MS	Mass spectrometry
MSA	Methanesulfonic acid
MSDN	Microsintered detonation nanodiamond
MWCNTs	Multi-walled carbon nanotubes
NA	Numerical aperture
NDs	Nanodiamonds
NMP	1-methyl-2-pyrrolidone
OD	Outside diameter
PAHs	Polycyclic aromatic hydrocarbons
PB	Prussian Blue
PBS	Phosphate buffered saline
<i>p</i> -DMBA	<i>p</i> -dimethylaminobenzaldehyde
PDMS	Polydimethylsiloxane
PGC	Porous graphitic carbon
POPC	Palmitoyllecithin
PS-DVB	Polystyrene-divinylbenzene
PVDF	Polyvinylidene fluoride
rGO	Reduced graphene oxide
RNase B	Ribonuclease B
RP	Reversed-phase
RPLC	Reversed phase liquid chromatography
RSD	Relative standard deviation
SA	Surface area
SDS-PAGE	Sodium dodecyl sulphate polyacrylamide gel electrophoresis
SEM	Scanning electron micrographs
SP	Stationary phase
SPE	Solid-phase extraction

SPEED	Solid-phase extraction and elution on diamond
SPME	Solid-phase microextraction
TAMRA	Carboxytetramethylrhodamine
THF	Tetrahydrofuran
TOF	Time-of-flight
UHPLC	Ultra-high-performance liquid chromatography
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy

Abstract

The development of new technologies, such as ultra-high-performance liquid chromatography is an incentive for the development of advanced, pressure- and temperature-resistant adsorbents to achieve faster and more efficient separations. Carbon-based materials for separation science have been studied intensively during the last few decades. Diamonds unique properties such as chemical inertness, mechanical, thermal and hydrolytic stability, excellent thermal conductivity with minimal thermal expansion and intriguing adsorption properties make them one of the most potentially useful carbon-based adsorbents. There are currently three commercially available types of diamond: detonation nanodiamond (DND), high-pressure high-temperature (HPHT) diamond, and chemical vapour deposition (CVD) diamond. The highest surface area among these is attributed to DND, but the particles produced by this method are 5–10 nm, which is too small for high-performance liquid chromatography (HPLC) applications (micron and submicron-sized particles are used). Diamond produced by CVD is mostly used as a thin film coating, and the cost of production is significantly higher than that of HPHT and DND diamonds. The size distribution of HPHT diamond can be controlled and ranges from nm to mm, however, the shape of HPHT diamond is irregular, and the surface area is limited.

Therefore, the goal of this project was to investigate the HPHT diamond surface, modify it to adjust selectivity and increase its surface area by forming composites with other carbon materials.

To set a foundation for this study, a detailed review (Chapter 2) of the diverse array of recently developed synthetic diamond-containing composite adsorbents and their applications in solid-phase extraction and HPLC was composed. A focus was given to the most commonly used

synthetic diamond types – DND, HPHT, and CVD diamonds. The applications of these synthetic diamonds are highly diverse, and have been achieved *via* various physico-chemical modifications including covalent and non-covalent bonds, entrapping into polymer matrices and attaching selective molecular fragments for particular analytes. The developed HPLC stationary phases have been used in the vast majority of chromatography modes, indicating the tunability of the surface. The preferred forms and applications of different types of diamonds are usually governed by their surface and bulk properties, and how this facilitates or limits their use in different solid phase extraction (SPE) and HPLC based applications is discussed.

The adsorption and chromatographic properties of HPHT diamond (1–2 μm and 4–6 μm fractions) were investigated, with a particular focus on their cation-exchange capacity (Chapter 3). Adsorbents were prepared by several methods: wet oxidation of the surface of HPHT with $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ or $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixtures; oxidation in air at 700°C ; or a four-step reduction using LiAlH_4 and *n*-butyl lithium. The zeta potential profiles as a function of pH and ion-exchange capacity were measured for the prepared adsorbents as well as isotherms of adsorption. The results of potentiometric titration and zeta potential measurements showed that all diamond samples had cation-exchange properties in the pH range from 1 to 12 due to the presence of carboxylic groups upon the diamond surface. Surface concentrations of carboxylic groups in the prepared adsorbents varied from 0.65 to 2.2 nm^{-2} . The retention of metal cations increased for the studied adsorbents in the order reduced < bare < oxidised HPHT diamonds. The ion-exchange selectivity of oxidised HPHT diamond was studied towards alkali, alkaline-earth and transition metal cations. The elution order $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Cr}^{3+}$ in 20 mM nitric acid was observed and corresponded to that known for carboxylic cation-exchange resins.

For the next step of this research, HPHT diamond hydrogenated in a flow of pure hydrogen gas at high temperatures was studied and compared to oxidised HPHT diamond (Chapter 4). X-ray photoelectron spectroscopy confirmed a significant reduction of oxygen-containing groups on the diamond surface at 850°C. The chromatographic retention mechanisms specific to this new hydrogenated diamond were compared with the oxidised diamond by packing chromatographic columns and evaluating retention factors for analytes with different polarities. The composition of the mobile phase differed in pH and in the organic solvent content. The results revealed a mixed-mode retention mechanism which included hydrophobic interactions, anion-exchange, and reversed-phase interactions. Adsorbent stability was confirmed by increasing the temperature of the mobile phase to 75°C with no ill effects.

To increase the effectiveness of the HPHT diamond adsorbent for surface area expansion, a HPHT diamond-rGO composite material was prepared and investigated. To enable the efficient synthesis of hydrogenated HPHT diamond and graphene oxide (GO), GO reduction was investigated by monitoring the hydrazine concentration in the GO suspension (Chapter 5). In order to do so, a new ion chromatography method was developed for the monitoring of hydrazine. The method is based on the ion chromatographic separation of hydrazine (from excess ammonia) and its selective determination by electrochemical detection. The developed analytical protocol overcame the significant practical challenges of atmospheric hydrazine oxidation and minimised the matrix interference in both separation and detection which results from the excess of ammonium with respect to hydrazine (up to 5.8×10^4 times) in GO reduction experiments. Chromatographic separations were achieved using a high capacity IonPac CS16 cation-exchange column with a 30 mM methanesulfonic acid (MSA) eluent, and an analysis time of less than 20 min. The detection of hydrazine as the hydrazinium ion using an electrochemical detector was linear between 10 μ M and 4 mM, with LOD and LOQ values of 3 μ M and 10 μ M, respectively. Standard additions confirmed $103 \pm 0.8\%$ recovery. The

developed method was successfully used to determine the point of complete GO reduction with hydrazine. Reaction curves for GO reduction generated using the method were compared to results from Fourier-transform infrared spectroscopy and Raman spectroscopy to verify the utility of the approach.

The hypothesis that hydrogenated diamond should have a high affinity towards sufficiently reduced GO formed the basis for the development of a method for the synthesis of HPHT diamond-GO composite material (Chapter 6). The suggested technique comprised *in-situ* GO reduction in the presence of diamond particles. Synthesis optimisation was attempted by ultrasonification, hydrazine concentration and substance ratio variation and assessed *via* UV/vis spectrometry and scanning electron microscopy (SEM). The clustering of diamond-rGO particles resulted in uneven size distribution rendering the composite unsuitable for application as a HPLC adsorbent. Subsequently, preliminary investigations were conducted for alternate applications in analytical chemistry, with a focus on use as an electrode. Electrodes composed of HPHT diamond-rGO and boron-doped diamond (BDD)-rGO were created *via* three methods (deposited, drop cast and packed) and compared to a commercial glassy carbon electrode (GCE). Electrodes were tested for the electrochemical determination of ascorbic acid and dopamine by cyclic voltammetry. Results showed an increase in oxidation current shift in diamond electrodes compared to GCE, with HPHT diamond outperforming BDD. Oxidation potentials varied between electrode construction methods, with lower peak potential voltage readings recorded for drop cast electrodes. Overall results indicate that the reaction process on diamond-rGO modified glassy carbon is more efficient than that on standard commercial GCE.

This research advanced the knowledge of oxidised and hydrogenated HPHT diamond surfaces *via* liquid chromatography. A new ion chromatography method was developed in an attempt to increase the effectiveness of the HPHT diamond adsorbent *via* GO attachment with a high

surface area. The synthesised HPHT diamond-rGO composite was deemed unsuitable for liquid chromatography but proved to be suitable for electrochemical applications. Hence, this thesis shows the usefulness of synthetic diamond in many areas of separation science and electrochemistry.

“People always ask me if I believe diamonds are a girl’s best friend. Frankly, I don’t.”

- Marilyn Monroe.

CHAPTER 1

General Introduction

1.1. Introduction

1.1.1. Synthetic diamond: a unique material

Synthetic diamond is not just a gemstone competing with natural diamond within the jewellery market. Instead laboratory made diamonds have found applications across many fields of science and technology, including, industrial applications (cutting and machining tools) [1], use within fields of biomedicine (drug delivery platforms) [2], within optical systems (lasers, synchrotrons) [3], in various electronics (semiconductors, light-emitting diodes) [4], as thermal conductors (diodes, transistors) [5], within quantum applications [6] and throughout various fields of fundamental and applied chemistry [7]. The reasons for such a broad range of applications lie behind diamond's unique physical and chemical properties. These properties include exceptional hardness (diamond being the hardest naturally occurring material), and high mechanical stability and density. Additionally, diamond is optically transparent and characterised by extremely high thermal conductivity, combined with a very low coefficient of thermal expansion.

There are numerous ways to synthesise diamond. The detonation of explosives, to produce detonation nanodiamond [8], high-pressure high-temperature synthesis [9] and chemical vapour deposition [6], are the three methods used to produce diamond (both microparticulate and nanoparticulate) on a commercial scale. Additionally, ultrasound cavitation [10], heating electrochemically produced carbon nanostructures in molten lithium chloride [11], ion bombardment [12] and laser bombardment [13] are also produce diamond nanostructures and diamond-like carbon. In the lab, diamond can be produced with the inclusion of additional elements (e.g. boron, nitrogen, phosphorus), known as diamond doping. In the case of boron-doped diamond, for example, this doping process changes the properties of the resultant diamond from an insulating material to one which is conducting [14].

1.1.2. Diamond in analytical chemistry

The widespread applications of analytical chemistry influence our daily lives in an enormous variety of ways, from materials and pharmaceutical development, environmental monitoring and analysis, quality control in all aspects of manufacturing, to forensics and toxicology, to name but a few. Synthetic diamonds, since their first creation in the 1950's, have been employed in the development and enhancement of an extensive array of analytical methods, through exploitation of its unique physio-chemical properties. These methods have largely fallen within two key analytical fields, namely separation science and electrochemistry, and are thus introduced below.

1.1.2.1. Diamond in separation science

Separation science defines a group of analytical techniques that enable the controlled separation of mixtures, the components of which, when separated, are identifiable. Key techniques include liquid chromatography, gas chromatography, mass spectrometry, and sample preparation. Synthesised diamond, most commonly used as an adsorbent, has presented a number of exciting developments and opportunities within several of these techniques.

Some important properties for next generation adsorbents include a tunable surface (to adjust selectivity towards particular substances), biocompatibility, high surface area (or adsorption capacity), mechanical stability, hydrolytic stability, thermal stability, and reversible adsorption behaviour for reuse or chromatographic applications. In terms of carbon-based adsorbents, activated carbon, graphitised carbon black, graphene, graphite, carbon nanotubes and biochar, have all received considerable attention in recent years, with regard to their application in separation science.

The growing understanding of the unique physical properties of diamond, coupled with relative ease of modern production and commercial availability, is enabling the development of new diamond-based stationary phases and separation media [15, 16]. Within a stationary phase, diamond provides superior physical and chemical stability [17], particularly under conditions of high temperature and pressure [18], as well as extremes of pH [19]. These properties present diamond as a potential adsorbent for various modes of solid phase extraction and high performance liquid chromatography (HPLC), thus expanding their existing range of analytical selectivity and application [20, 21]. The modification of the diamond surface by homogeneous initial surface termination, and the covalent and non-covalent immobilisation of different functional moieties, including the subsequent grafting of larger (bio)molecules onto previously functionalised surface, have been shown to deliver this desired selectivity, which compliments the underlying advanced physical-chemical properties of the diamond [21].

The application of diamond in chromatography is however still relatively new and intriguing. At present, only one commercially available diamond-based chromatographic column is available [22-24]. The Diamond Analytics FLARE® HPLC column, manufactured from detonation nanodiamond (DND), is promoted to expand the existing range of analytical capabilities in separation science by providing diamond-based chromatography phase, which can withstand extremes of mobile phase conditions and expand the range of applications possible within the traditional realms of reversed-phase HPLC [25]. Given there are various synthetic diamond types (DND, high-pressure high-temperature (HPHT) and chemical vapour deposition (CVD) diamonds), together with a wide variety of possible surface modification chemistries, clearly substantial opportunities remain open to develop new diamond-based materials for separation science.

1.1.2.2. Diamond in electrochemistry

Pure diamond, whether naturally occurring or synthetic is an electrical insulator. However, during the growth of synthetic diamond the intentional introduction of impurities (doping) delivers a doped diamond material possessing conductive properties. Doping significantly increases electrical conductivity, which is an essential property for all electrochemical analytical application. Various elements can be used as dopants, including boron, nitrogen, phosphorous and aluminium [26, 27]. Boron is the most popular dopant as it provides almost metal-like conductivity in diamond, and even superconductive properties [28, 29].

Diamond electrodes have unique characteristics compared to other solid electrodes, including a low and stable background current, a wide window of electrochemical potential, relatively high electron transfer rates for soluble redox systems without pre-treatment, tunable electrical resistivity, high oxygen evolution, biocompatibility, stability, considerable resistance to fouling, unique surface chemistry and long-term responses [30]. A wide variety of conductive diamond materials prepared by various approaches have been reported to date. Applications of diamond electrodes include, chemical [31] and biochemical sensing [32], environmental degradation [33], electrocatalysis [34], and electrosynthesis [35], as well as energy storage [36] and conversion [37].

To date, high-quality boron doped diamond (BDD), either grown by CVD or HPHT methods, are still considerably expensive. Subsequently, there is a demand to develop cost-effective alternatives. Such alternatives may include conductive composite materials, for instance, diamond/metal [38, 39], diamond/metal oxide [40], diamond/SiC [41, 42], diamond/carbon nanotubes (CNTs) [39, 43] and diamond/graphene [44]. Although at the present time these materials may be only marginally more cost-effective, they are attractive due to the unique combination of the features of both components of the composites and thus can potentially

expand the range of electrochemical applications. Other promising areas for further development include reliable modification methods of diamond electrode surfaces to further enhance the selectivity and sensitivity for biomolecules detection in complex systems, as well as developing sensor arrays for detecting several bio-analytes at once [45].

1.2. Aims

The primary aim of this project is to develop new diamond-based materials for separation science and related analytical applications.

The specific objectives of the project could be classified as follows:

1. To conduct a comprehensive review of diamond-based materials for separation science;
2. To develop new and advanced diamond-based materials for separation science and analytical chemistry;
3. To characterise and understand the unique adsorption properties and selectivity of the novel materials;
4. To explore other possible advantageous application areas of novel diamond-based materials.

1.3. Thesis Structure

Chapter 2 provides a comprehensive literature review on the properties of the three commercially available synthetic diamond types, DND, HPHT and CVD. Particular attention is given to surface properties and the numerous modification methods available. The review then focuses on the applications of these diamonds in solid-phase extraction and liquid chromatography.

In Chapter 3, modifications of the diamond surface by oxidation and reduction methods are explored. The ion-exchange selectivity of oxidised HPHT diamond towards alkali, alkaline-earth, and transition metal cations is studied. This chapter has been published as a research paper within *Diamond and Related Materials*. Chapter 4 describes diamond hydrogenation, with surface modifications confirmed by Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy and elemental analysis. The hydrogenated diamond is applied for the first time as a stationary phase in HPLC, and the chromatographic performance is reported.

To increase the HPHT diamond surface area for enhanced analytical performance, a diamond-graphene oxide composite material was developed. For this to occur, the kinetics of the graphene oxide (GO) reduction reaction had to be first investigated by a novel ion chromatographic method, which is described in Chapter 5. This method is developed and optimised for the sensitive determination of hydrazine concentration in excess of ammonia. This chapter has been published as a research paper within *Talanta*. Chapter 6 describes the full details of the preparation and optimisation of the diamond/GO composite material. The research is then extended to investigate the electrochemical properties of the composite, given the expanding applications of diamond-based materials in this field.

Chapter 7 summarises the thesis and provides directions for future research.

CHAPTER 2

Recent Advances and Applications of Synthetic Diamonds in Solid-Phase Extraction and High-Performance Liquid Chromatography

2.1. Introduction

High-performance liquid chromatography (HPLC), and in some cases solid-phase extraction (SPE), can involve quite challenging experimental conditions, such as elevated temperatures, strongly acidic or basic mobile/elution phases, and high fluidic pressures. The latter is particularly so for the latest ultra-high-performance liquid chromatography (UHPLC) technologies, which operate at pressures a multiple of that typical for standard HPLC only a decade or so ago. Currently, the most commonly used silica and polymeric stationary phases struggle to provide the required chemical, mechanical, and thermal stability when applied under a combination of such extreme conditions. Silica-based stationary phases are unstable in strongly acidic and basic conditions, and polymeric phases often lack both mechanical and thermal stability [46, 47]. Moreover, polymeric stationary phases typically exhibit lower separation efficiencies. They can swell or shrink in the presence of certain organic solvents and extremes of pH [48]. Carbon-based materials (such as diamonds, carbon nanotubes (CNTs), fullerenes, and graphene) can potentially address some of these general limitations, taking advantage of their inherent high chemical, mechanical, and thermal stabilities, and so deliver a new variety of adsorbents for both SPE- and HPLC-based applications.

Diamond, one of the most widely used carbon-based adsorbents, possesses several unique properties, including exceptional hardness (being the hardest naturally occurring material, ~180 times higher than CNTs, ~375 times higher than fullerenes, and ~38 times higher than graphene), high mechanical stability (Young's modulus of the diamond is ~81 and ~95 times higher than that of fullerenes and graphene, respectively), and high density (~2–3 times higher than CNTs and fullerenes, ~22k times higher than graphene) (see Table 2.1). Diamonds are also known for other important advantages significant to their application in areas of separation science, including resistance to a wide variety of organic and aqueous mobile phases, high

thermal stability, biocompatibility, reusability (due to their reversible adsorption), unique selectivity and mixed-mode retention mechanisms, and tunable surface properties. These properties suggest diamond as a potentially suitable adsorbent for many possible variants of SPE and HPLC, both with and without surface modification [20, 21].

The recent advent of relatively cheap and simple methods to produce bulk volumes of nano- and micro-diamonds, and a greater understanding of their physical and chemical properties has led to a significant rise in their applications across all areas of analytical chemistry. Within separation science (at least for chromatography and extraction), this has seen an annual increase both in the number of papers and in the number of citations (see Figure 2.1) relating to diamond-based adsorbents over the last twenty years.

The first review on diamond-based materials which included aspects of separation science was published in 2007 by Najam-ul-Haq *et al.* [49]. However, the review only briefly mentioned the application of nanodiamonds in the isolation and preconcentration of biological materials [49]. Following this, in 2010, the first comprehensive review on diamond-related materials as adsorbents across many fields of separation science was published by Nesterenko *et al.* [16]. From there no further reviews that specifically covered diamond-based adsorbents were compiled until 2014, when a critical review was published by Peristyy *et al.* [7], which was swiftly followed by a similar review in 2015 by Zhang *et al.* [15]. The former review focused on the various applications of synthetic diamonds as stationary phases in both liquid chromatography (LC) and gas chromatography (GC), however, it did not cover their applications in SPE. The latter review explicitly focused on nano-carbonaceous materials. Since that time, to the best of our knowledge, there have been no subsequent review papers comprehensively covering the use of diamond as a sorbent across both SPE and HPLC. However, for the readers' convenience, Table 2.2 summarises all the review articles published

over the past 20 years that include some reference to, or are dedicated to the application of diamond and diamond-related materials within various fields of separation science.

Thus herein, the most recent developments (past 5–6 years) in the study and application of diamond-based adsorbents within both SPE and HPLC have been reviewed and evaluated, with a particular focus upon the properties and selectivities that either facilitate or limit their use.

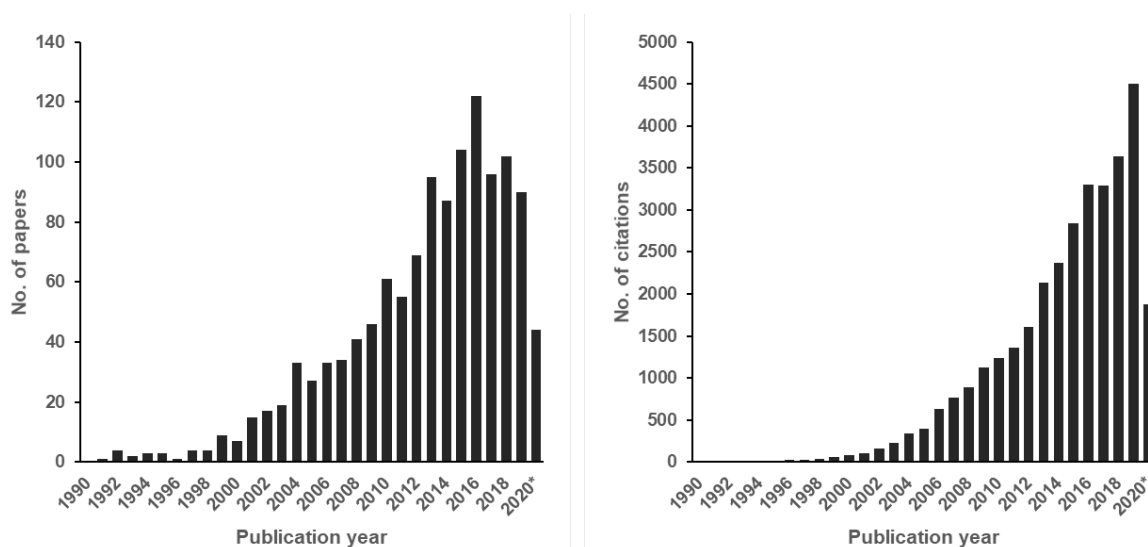


Figure 2.1. The number of publications and citations for diamond-based adsorbents over the past twenty years*: (left) the total number of publications each year and (right) the total number of citations each year. The data is based on a Web of Science search. The searched topics were diamond or nanodiamond, and SPE, chromatography or HPLC. *as at 03/06/2020

Table 2.1. Properties of diamonds and other carbon-based materials [7, 50-60].

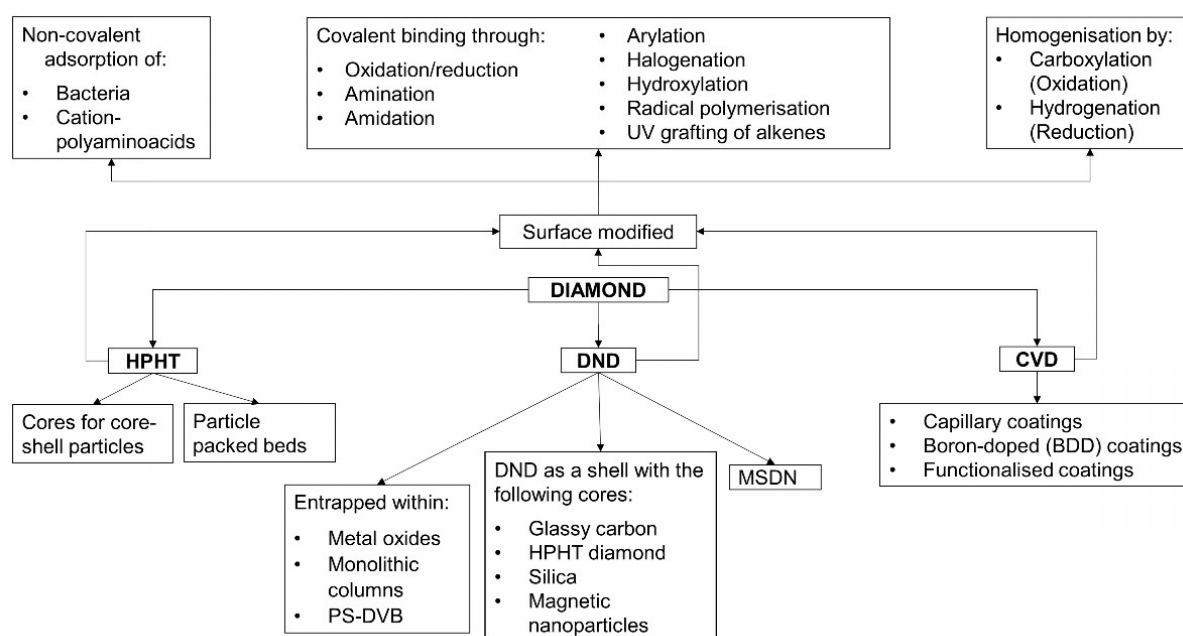
Properties	Diamond	CNTs	Fullerene	Graphene
Hardness (kg mm ⁻²)	9000	~50	~24	240
Surface area (m ² g ⁻¹)	150–350	144–662	300	62–163
Thermal stability (°C)	1000	1200	2377	600
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	800–2300	~10	0.4	~3000–5000
Young's modulus (GPa)	1050	Up to 1000	~5–13	~11
Density (g cm ⁻³)	3.51	1.33–1.40	1.65	1.6 x 10 ⁻⁴

Table 2.2. Review papers on diamond-based adsorbents published over the last twenty years (2000–2019).

Year	Focus	Ref
2019	Preparation and electrochemical properties of boron-doped diamond (BDD) film followed by mineralisation of organic pollutants on BDD electrodes	[61]
2019	Applications of bare BDD electrodes in electroanalysis of organic compounds and biomacromolecules	[62]
2017	Incorporation of nanomaterials (organic and inorganic) into LC systems	[63]
2015	Novel HPLC stationary phases modified with carbonaceous nanomaterials (e.g. CNTs, fullerenes, nanographene, and nanodiamonds (NDs)) focusing on retention and selectivity	[15]
2015	Use of nanomaterials (e.g. CNTs and NDs) for the adsorption of dyes from wastewater	[64]
2015	Surface modification techniques of nanomaterials (e.g. CNTs and NDs) with aryldiazonium salts	[65]
2014	Preparation and properties of diamond-based stationary phases and their chromatographic performance	[7]
2013	Applications of carbonaceous materials (e.g. CNTs, ND, graphene) in sample preparation (e.g. SPE, solid-phase microextraction (SPME)) focusing on graphene	[66]
2013	Applications of carbonaceous materials (e.g. CNTs, fullerenes, and NDs) in GC, HPLC, and capillary electrochromatography	[67]
2013	Nanoscale carbon materials (e.g. carbon nanofiber, ND, fullerenes, CNTs, graphene) as SPE materials in the isolation and preconcentration of protein species	[68]
2012	Surface modification (e.g. homogeneous initial surface termination, covalent and non-covalent immobilisation of functional moieties, and grafting of larger biomolecules) of nanodiamond	[21]
2011	Nanoparticles (e.g. carbon, metallic, silica etc.) in sample preparation (SPE, SPME, liquid-liquid extraction (LLE) etc.)	[69]
2010	Diamond-related materials as stationary phases in separation techniques (e.g. SPE, GC, HPLC, ion chromatography (IC)), electromodulated chromatography, affinity chromatography, electrophoresis, and microchip separations)	[16]
2010	NDs as SPE and elution media for mass spectrometry analysis of biomolecules (e.g. peptide, protein, deoxyribonucleic acid (DNA), glycan)	[70]
2007	Carbon nanomaterials (e.g. NDs, graphite, CNTs, and fullerenes) for isolation and preconcentration of biological materials (e.g. peptides, proteins, metabolites, and polymers) followed by matrix-assisted laser desorption/ionisation (MALDI)-mass spectrometry (MS) analysis	[49]

2.2. Synthetic Diamonds

Diamond has a face-centred crystal structure, and it consists of tetrahedrally bonded sp^3 carbon atoms, which provides it with exceptionally high chemical and mechanical stability [16]. However, natural diamonds can have various impurities within the crystal structure, delivering irreproducible physio-chemical properties [71]. Moreover, natural diamond's scarcity and cost exclude its application within analytical chemistry. Over many decades, significant efforts have been made to synthesise low-cost and pure diamonds for a variety of industrial applications. These materials can also be applied for analytical purposes. The synthetic diamonds which are most commonly used in SPE and HPLC are detonation nanodiamonds (DNDs), high pressure high temperature (HPHT) diamonds, or chemical vapour deposition (CVD) diamonds. Scheme 2.1 summarises the different forms of these synthetic diamonds that have been used in various SPE- and HPLC-based applications to-date.



Scheme 2.1. Classification of different types of synthetic diamonds that are used in SPE- and HPLC-based applications.

2.2.1. Detonation nanodiamonds (DNDs)

DNDs, also known as ultradispersed nanodiamonds, were first prepared in 1963 by exploding a mixture of trinitrotoluene and hexogen in a closed chamber, generating a reaction soot containing up to 2–10% DND (sp^3 carbon atoms) as well as amorphous graphite (sp^2 carbon atoms) and elemental impurities [7, 72]. This process delivers nanodiamonds with diverse surface chemistry and various characteristic features, with post-production purification processes significantly affecting the final chemical properties. This heterogeneity is evident in the differences reported in properties of DND obtained from different vendors, and indeed between different batches from the same vendor [73, 74]. The various purification processes applied (typically oxidative and acidic processing) result in a wide variety of functional groups (e.g. hydroxyl, carboxyl, carbonyl, alcohols, ethers and some amino groups) on the DND's surface [21]. The presence of these functional groups increases the polarity of the DND, which is much higher than that of CVD or HPHT diamonds, and therefore potentially makes DND suitable for application within aqueous normal phase (ANP) and hydrophilic interaction liquid chromatography (HILIC) modes of chromatography [7]. The purification process also provides a conditionally charged surface (varying between -40 and $+40$ mV in the pH range 1–14). The presence of the above-mentioned ionogenic groups also suggests that DND could also be used to produce a stationary phase for application within ion-exchange modes of chromatography and extraction [75, 76]. Moreover, these groups can additionally be utilised to anchor different side chains to obtain more selective surface functionalities, as described by Krueger *et al.* in a recent review [21]. Detonation synthesis is also responsible for the polycrystalline form, and the small particle size (typically $\sim 4\text{--}5$ nm) compared to the HPHT diamonds (Figure 2.2a) [73]. While the small size of DND makes it a promising material for the development of high-surface-area adsorbents ($150\text{--}350\text{ m}^2\text{ g}^{-1}$, $\sim 30\text{--}70$ times higher than the HPHT diamonds), agglomeration in the form of tight aggregates (up to $70\text{--}100$ nm in size) poses a significant

practical challenge in the application DND [77]. As produced, the small particle size of DND restricts its direct use in SPE- and HPLC-based applications, hence these particles have either been predominantly used to produce composites with other materials, or sintered to produce micron-sized particles, so-called microsintered detonation nanodiamonds (MSDN) [78], which are discussed below in Section 2.2.2.

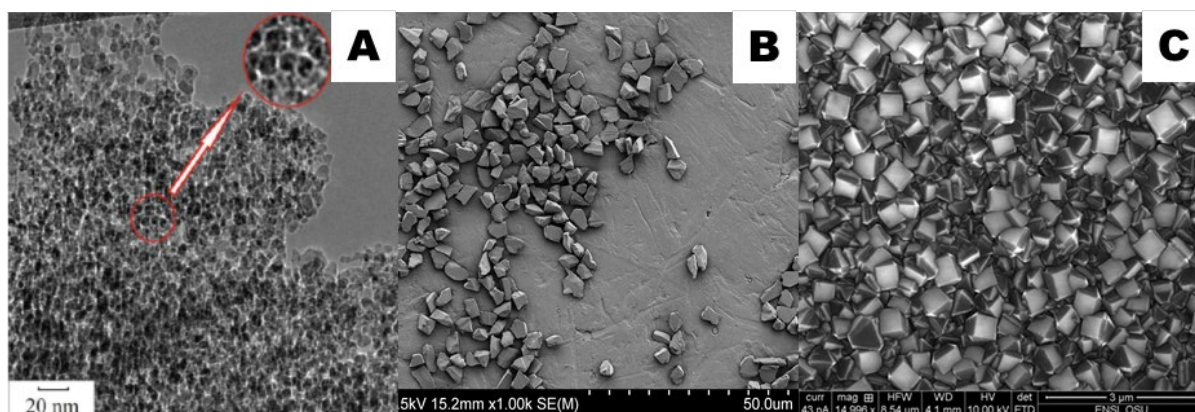


Figure 2.2. Scanning electron micrographs (SEM) of the different types of synthetic diamonds that are used in SPE and HPLC-based applications: (a) DND, adapted from [79] (b) HPHT diamonds (c) CVD diamonds, adapted from [80].

2.2.2. Microsintered detonation nanodiamonds (MSDN)

As mentioned in Section 2.2.1, the individual small particle size of the DND limits its direct use as a stationary phase within HPLC. This problem can be potentially solved by synthesising DND aggregates. Such polycrystalline aggregates are preferably prepared by sintering DND under high pressures (≥ 3 GPa) and high temperatures (≥ 1000 °C), followed by crushing the resulting agglomerates, producing the so-called MSDN [8, 81, 82]. The fractionation of the resulting mesoporous material (~ 30 – 35 μm) produces particle sizes of ~ 3 – 5 μm , with a bi- or tri-modal distribution of pore diameters with maxima at 0.7, 1.4, and ~ 3 – 8.0 nm [83]. Although the sintering process decreases the surface area of DND by $\sim 30\%$, the resultant surface area (~ 135 – 216 $\text{m}^2 \text{g}^{-1}$) is still sufficient for adsorption-based applications [83]. Similar to DND,

MSDN is also subjected to oxidative treatment to remove the residual graphite from the surface, making it polar and suitable for further chemical modifications [84]. The application of MSDN as a stationary phase for chromatography is briefly reviewed in Section 2.4.1.

2.2.3. High-pressure high-temperature (HPHT) diamonds

The static synthesis of HPHT diamonds, simulating a natural process of forming diamonds, is performed at elevated pressures ($\sim 60,000$ atm) and temperatures ($1000\text{--}1400^\circ\text{C}$) in the presence of a catalyst [85]. This highly reproducible method was first reported by Bundy *et al.* in 1955 [85]. This method has many advantages over the other methods used for synthesising diamonds, some of which are listed below. As opposed to the detonation technique, the HPHT method produces monocrystalline diamond particles that range from a few nanometres to a few millimetres in size (see Figure 2.2.b) [86]. It is the only practical method that produces diamond particles which are big enough (a few microns) for directly packing practical SPE and HPLC columns [7]. HPHT diamonds also have more homogeneous and uniform surface chemistry as compared to the DNDs [7]. While the surface of a DND is positively charged in acidic media, HPHT diamond particles are typically reported as exhibiting a negative surface charge, an observation again confirmed in recent published works [58, 87], which discussed HPHT diamond's negative surface charge across the pH range 2 to 12. It has also been shown that purified HPHT diamonds ($1.6\text{ }\mu\text{m}$ particles with $5.1\text{ m}^2\text{ g}^{-1}$ surface area) contain ca. $4.6\text{ }\mu\text{eq g}^{-1}$ of protogenic groups, predominantly carboxyl and hydroxyl groups [87]. The availability of these surface groups also suggests potential applications of bare HPHT diamonds in developing weak cation-exchange and HILIC stationary phases [87]. However, tight control over the particle size distribution during the HPHT synthesis process remains a significant challenge [88].

2.2.4. Chemical vapour deposition (CVD) diamonds

The CVD process for diamond production, consisting of thermal decomposition of carbonaceous gases (such as methane) in the presence of hydrogen, delivers the deposition of a thin film of a highly pure diamond phase onto various supporting substrates (Figure 2.2c) [89]. The advantages of the CVD process over other synthetic diamond production techniques include, (1) a lower pressure requirement compared to the HPHT method, (2) much less likely (and less common than in the case of detonation synthesis) incorporation of undesirable non-carbon impurities into the diamond lattice and on the surface, (3) the ease of doping the diamond phase with other elements (e.g. boron, nitrogen, phosphorus) to modify the properties (e.g. the electrical conductivity of boron-doped diamond (BDD)), and (4) much greater control over the dimensions of diamond particles and films than with other techniques [90]. The process also provides several other useful properties, e.g. low surface energy for deposited diamond films, which can be used to passivate different materials and composites [91], and a hydrophilic surface, if terminated with oxygen, or hydrophobic surface, if terminated with hydrogen [92]. In the case of hydrogen termination, the surface is characterised by positive electron affinity, and the material is highly resistive. The resultant hydrophobic material could potentially be exploited for use within reversed phase (RP) modes of HPLC. However, the expensive and slow deposition process has currently limited the use of CVD diamond films in most areas of separation science.

2.2.5. Boron-doped diamond (BDD)

BDD is synthesised by the CVD method on various substrates. It has the typical diamond tetrahedral robust structure; however, some atoms are substituted by boron in order to provide electrical conductivity [93]. BDD was studied as an electrode in electrochemical analysis for the first time in 1987 [94]. BDD possesses several properties that make it a useful material in

electrochemistry, including a wide potential window ($\sim 3\text{--}4$ V), a low and stable background current, less propensity to fouling compared to other solid electrode materials, and a possibility of *in-situ* electrochemical activation. There are many reviews covering BDD's applications within electrochemistry, although these applications are beyond the scope of the current review. A relatively high cost of synthesis and a limited number of functional groups on the surface make BDD less favourable for SPE- and HPLC-based applications. Nonetheless, it has been shown that BDD (e.g. a BDD porous membrane) can potentially be used for SPE applications [95] and within microchip capillary chromatography [96].

2.2.6. Diamond-like carbon (DLC)

DLC has an amorphous structure, comprising of a mix of sp^3 and sp^2 carbon atoms, which give DLC a three-dimensional structure with strength equivalent to graphene. Its properties include chemical inertness, biocompatibility, a low friction coefficient (ranging from 0.05–0.3), high thermal stability ($>700^\circ\text{C}$, comparable to diamond), and high mechanical strength of sp^3 DLC (120 GPa, similar to diamond). However, sp^2 DLC typically provides much lower mechanical strength (2–5 GPa, ~ 20 times lower than the diamond), and like diamond itself, DLC's overall hardness is dependent upon the ratio of sp^3 and sp^2 carbon atoms. DLC's microstructure also allows the incorporation of other species [97] and its properties can be tailored far more readily than those of diamond. Unlike diamond, DLC can form a very smooth surface on a nanometre scale, which makes DLC a useful material for developing coatings for biomedical applications [98]. However, its applications in HPLC and SPE has not been extensively studied, hence they have not been further discussed within this review.

2.3. Diamond Surface Modifications

Chromatographic applications of commercially available diamond-based materials (having different properties due to a variety of synthetic processes) often require a homogeneous surface [7]. Surface modification (by either physical or chemical means) is carried out to achieve this, along with removing impurities and introducing new selectivity to target specific chromatographic applications [7]. Aspects of several surface modification techniques have already been covered elsewhere (please refer to a review by Krueger *et al.* [21]), however the commonly used surface modification techniques are briefly outlined below for readers' easy reference.

2.3.1. Oxidation

Oxidative treatment both purifies diamond surfaces (e.g. the removal of non-diamond carbons and metal impurities) and increases the amount of oxygen-containing functional groups (e.g. carbonyls, carboxyls and hydroxyls) [7, 21]. The treatment most frequently involves using strong mineral acids and heating diamond in an oxygen or air atmosphere [21]. Diamond thus produced can potentially be used in cation-exchange chromatography due to the introduction of negatively charged groups [7, 76].

2.3.2. Hydrogenation

Hydrogenation is usually performed by either heating the diamond surface at high temperatures (800–900 °C) in the presence of hydrogen or treating the material within a plasma reactor (e.g. hydrogen or argon plasma) [7, 21]. However, hydrogenation at elevated temperatures (e.g. ~900 °C) may not be appropriate for diamond particles less than ~100 nm in size [21]. The hydrogenation technique enables the formation of a large number of surface C-H groups, which increases the hydrophobicity of the diamond [99].

2.3.3. Amination

Amination of the diamond surface can be performed by direct and indirect methods. The former includes the reaction of chlorinated diamond particles ($\sim 0.5\ \mu\text{m}$) with ammonia at high temperature, as performed by Ando *et al.* [100], who reported the first successful formation of ammonia groups on the diamond surface, and photochemical or plasma treatment [101, 102] with ammonia, leading to aminated nanodiamonds. The latter covers such methods as the use of aminated silanes, the immobilisation of aminated aromatic moieties, and the formation of aminomethyl groups. Surface modification of nanodiamond through direct amination is of potential interest within the chromatography community as the process provides ideal binding sites for a wide range of bioactive compounds (biomolecules) [21].

2.3.4. Amidation

The amidation of purified diamond is performed in three steps: (1) oxidation to increase the presence of carboxylic groups on the diamond surface, (2) chlorination of the oxidised diamond (e.g. by using thionyl chloride), and (3) reaction of the chlorinated diamond with diamino molecules (e.g. ethylenediamine, 1,3-propylenediamine, 1,6-hexamethylenediamine) [103]. For further explanation about these steps, please refer to the works of Reina *et al.*, who successfully amidated a nanodiamond surface to investigate the chelating behaviour of diamond particles towards cobalt in wastewater [103].

2.3.5. Arylation

Arylation using aryl diazonium salts is a particularly useful modification method for the diamond surface because it can be carried out with various functional groups [21]. It is performed either electrochemically on BDD films or chemically on nanodiamond particles.

However, diamond particles cannot be modified via electrochemical arylation when these particles are undoped and not exhibiting sufficient electrical conductivity [21].

2.3.6. Covalent and non-covalent immobilisation

Oxidised diamond has carboxylic groups on the surface, which are sufficient for both covalent and non-covalent bioconjugation [104]. Non-covalent bioconjugation has been used to form a homogeneous specific polymer shell around diamond particles [21]. The bioconjugation can be either directly utilised as a composite, or the coated diamond particles can be functionalised with a particular moiety. For example, Chang *et al.* have reported the successful preparation of non-covalent bioconjugates, using *L*-polylysine and polyarginine to coat the diamond surface, which was later functionalised, e.g. by amide formation [104].

2.3.7. Reaction with monomers

The other common way to form polymer shells around diamond particles (e.g. hydrogen and deuterium-terminated diamond) involves reactions with monomers (e.g. styrene) in the presence of a radical initiator (e.g. di-*tert*-amyl peroxide) and a cross-linking agent (e.g. divinylbenzene) [105]. Yang *et al.* report a detailed investigation of the use of both polystyrene-modified and sulfonated-styrene-modified deuterium-terminated diamonds as SPE adsorbents [105].

2.3.8. Grafting polyamidoxime

Grafting polyamidoxime on the surface of nanodiamond is carried out in three principal steps: (1) the synthesis of polyglycerol modified hyperbranched nanodiamond (ND-OH) by a microwave radiation method, allowing reaction between diamond particles and glycidol, (2) preparation of polyacrylonitrile modified hyperbranched nanodiamond (ND-CN) by reacting ND-OH with acrylonitrile and hydrogen peroxide, and (3) reaction of ND-CN with

hydroxylamine hydrochloride to functionalise the diamond with polyamidoxime (ND-AO) [106]. Li *et al.* synthesised this new material and applied it as an adsorbent for the selective separation of uranium [106].

2.3.9. Grafting ω -alkenes

Grafting ω -alkenes onto a hydrogenated diamond surface (especially onto nanodiamond films) is another useful technique that has been known for a long time [107, 108]. The photochemical ultraviolet (UV) grafting of alkenes (through the formation of single C-C bonds with a diamond surface) is also possible for submicron diamond powder and is carried out in a nitrogen atmosphere [107, 109-111].

2.4. Applications in Solid Phase Extraction

Solid phase extraction (SPE) has a dominant position in the field of sample preparation because of its low cost, simplicity, and the possibility of on-line, off-line and automated applications [112]. The performance of an SPE system is predominantly dependent upon the type of adsorbent being used. Conventional SPE adsorbents suffer from various limitations, such as varying degrees of chemical and mechanical strength and limited capacity for regeneration [112]. These limitations can be effectively circumvented with the use of diamond-based adsorbents, based upon the many physio-chemical advantages and properties already mentioned [113]. The various applications of different types of synthetic diamonds within SPE recently reported are summarised within Table 2.3, and discussed below.

2.4.1. Detonation nanodiamonds (DNDs)

The small particle size and inhomogeneous distribution of surface functional groups makes it challenging to use bare (unmodified) DND particles. However, a few attempts have been made

to use DND particles directly. For example, in 2006, Sakurai *et al.* reported the use of bare DNDs (mean particle size of 4 nm) for the selective extraction of tungstate (an oxoacid anion) from an artificial river water sample. The extraction was followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which resulted in a mean recovery of 99% [114]. They also reported on the ability of DNDs to adsorb other anions, such as $\text{Cr}_2\text{O}_7^{2-}$ and MoO_4^{2-} [114]. Moreover, Wang *et al.* further investigated the application of bare DND (mean crystal size of 3–5 nm) for the selective adsorption of azo dye Acid Orange 7, reporting high adsorption capacity for DNDs ($1288 \text{ mmol kg}^{-1}$) [115], which was found to be significantly higher than granular activated carbon and CNTs (~ 5 times higher), titanium dioxide (~ 7 – 26 times higher), hematite (~ 2 times higher), and goethite nanoparticles (~ 13 times higher) [116–118]. Wei *et al.* reported the direct use of bare DND for peptide enrichment, where the maximum adsorption capacity was found to be 130 mg g^{-1} , which was comparable to carboxylated or oxidised DND [119]. The direct analysis of DND-bound peptides via matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was performed to minimise the sample load and analysis time. It was possible to eliminate the elution step due to the DNDs' inherent optical transparency. Multiple theoretical and practical investigations have suggested that during extraction with both oxygen- and hydrogen-terminated diamond particles, electrostatic forces resulting from intrinsic surface charge of DND play a significant role in determining the adsorption dynamics, attachment, and conformation of proteins [120].

However, DNDs for SPE are mostly applied as composites, as DND-based composites typically either surpass bare DND in terms of adsorption capacity or provide higher selectivity. For example, in a study by Yang *et al.*, the adsorption of Congo Red (an anionic azo dye) onto ionic liquid-DND composites (maximum adsorption capacity $\sim 227 \text{ mg g}^{-1}$) was found to be significantly (~ 4 times) higher than bare DND (maximum adsorption capacity $\sim 61 \text{ mg g}^{-1}$)

[121]. Raeiszadeh *et al.* also developed a composite by incorporating DND within chitosan (CTS). It was shown that the methyl orange (also an anionic azo dye) adsorption capacity of CTS-DND was considerably greater (~3 times higher) than that of the neat CTS. The authors further mentioned that the composite's high adsorption capacity (for the dye) was most probably attributed to DND's oxygen-containing groups, which interact with the dye molecules via hydrogen bonding and electrostatic interactions [122]. In another interesting article, Hussain *et al.* demonstrated how the incorporation of DND particles (ranging from 5–80 nm) within the metal oxide crystals (see Figure 2.3) increased the selectivity of metal oxides (e.g. lanthanum oxide La_2O_3 and samarium oxide Sm_2O_3) to biomolecules (e.g. phosphopeptides) [123]. The composites thus formed enabled highly selective extractions of phosphopeptides from standard proteins, namely β -casein and bovine serum albumin (BSA), as compared to the bare metal oxides [123]. The authors estimated DND- La_2O_3 selectivity up to 1:3000 for β -casein/BSA mixture and sensitivities of down to 10 fmol and 20 fmol for DND- La_2O_3 and DND- Sm_2O_3 , respectively [123]. The composites also resulted in excellent enrichment efficiencies when used for the extraction of phosphopeptides from complex matrices (such as human serum and non-fat milk) [123]. Similarly, Baghban *et al.* synthesised DND- MoS_2 composite nanorods to selectively extract heavy metals (e.g. lead (II) and copper (II)) from natural water sources [124]. The composites were coupled with flame atomic absorption spectroscopy (FAAS) to develop a highly sensitive method, providing up to 95% recovery of the metals and limit of detection (LOD) values of $42 \mu\text{g L}^{-1}$ and $22 \mu\text{g L}^{-1}$ for lead (II) and copper (II), respectively [124]. The authors further claimed that the extraction process was fast, simple, cost-effective, and environmentally friendly [124].

An adsorbent consisting of a core of aggregated DND particles with a Cu-Prussian Blue (Cu-PB)-treated surface for the adsorption of radioactive Cs^+ was synthesised via co-precipitation from a suspension containing DND, copper chloride and potassium ferrocyanide [125].

Interestingly, while Cu-PB was shown to be only effective for the removal of Cs^+ at a neutral pH, the DND modified with Cu-PB was observed to be effective, showing no sign of a decrease in removal efficiency, across the pH range of 4–11. The authors suspected this was due to the combination of the adsorption properties of DND and Cu-PB [125]. This adsorbent was found to be capable of retaining the analyte even from soil-treated wastewater and diluted (0.07%) artificial seawater, while the analyte removal efficiency of other adsorbents for Cs^+ removal declined significantly in diluted artificial seawater [125]. However, it is unclear if there would be a reduction in the adsorbent's efficiency in undiluted seawater samples as it was not tested under such conditions. Notably, the agglomeration tendency of DNDs, together with subsequent precipitation, advantageously removed the targeted analytes from solution, thus eliminating the filtration step to separate the supernatant from the precipitates [125]. It was further reported that DND-Cu-PB's sorption mechanism for Cs^+ was most likely due to metal cation coordination to the DND surface functional groups, as well as the non-specific electrostatic interactions between the negatively charged DND surface and the metal ions [125]. The coordination mechanism of adsorption was also suggested by Khokhlova *et al.*, who suggested that adsorption of acid anthraquinone blue (AAB) (a water-soluble dye) on DND was due to a combination of mechanisms, including hydrophobic and ionic interactions, as well as coordination bonds with metal ion impurities on the DND surface [126].

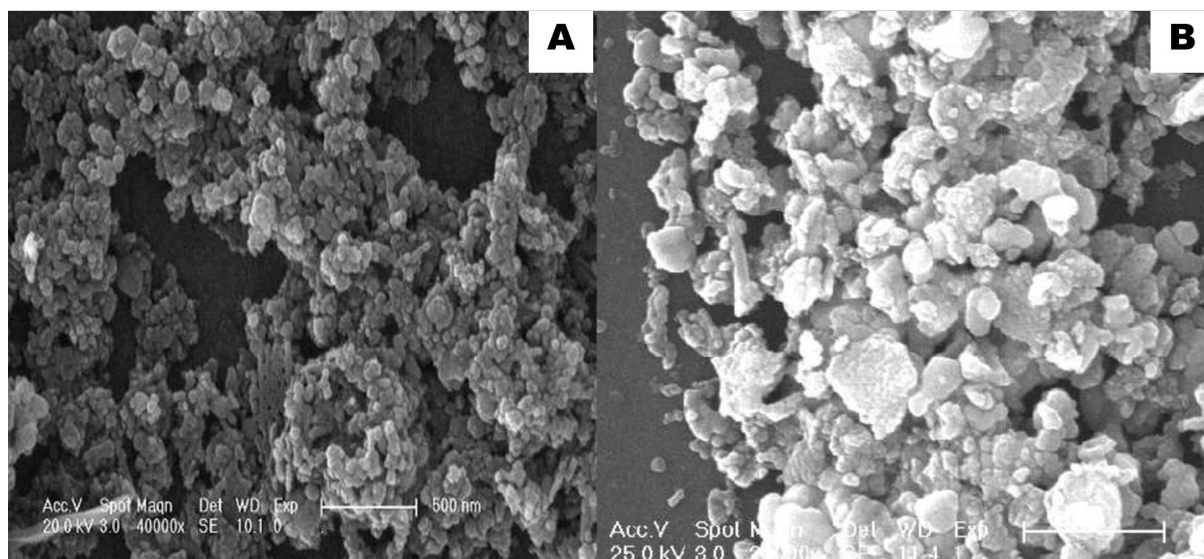


Figure 2.3. SEM of (a) diamond lanthanum oxide and (b) diamond samarium oxide nanocomposites. Reproduced from [123].

From the above discussion, it is clear that DND-based composites can be used to deliver both adsorption capacity and selectivity to different solutes. However, surface modification of bare DND can also be carried out to achieve similar sorption behaviour. Moreover, the availability of multiple functional groups on DND allows easy modification with different side chains to modulate selectivity. Hence, DND surfaces have been extensively modified for the selective extraction of different proteins, glycoproteins, and peptides [127].

Buchatskaya *et al.* employed bare, oxidised and reduced DND to adsorb radionuclides, reporting that the adsorption capacity for uranium (VI) of oxidised DND in particular was either higher than most of the commonly used sorbents (e.g. activated carbon) for radionuclide extraction or comparable to other members of the nanocarbon group (e.g. graphene oxide (GO) and CNTs) [128]. The research group partly related this radionuclide adsorption behaviour to the surface modification of the DND (e.g. oxygen-containing groups on the surface) [128]. In another study, it was noted that both original DND and carboxylated DND were able to adsorb nitrate anions and metal cations (e.g. Cu^{2+} and Pb^{2+}). However, it has also been shown that the

carboxylated DNDs' adsorption capacity was ~ 3 times higher than that of the original DND [129]. Subsequently, it was hypothesised that physical adsorption mechanisms play the dominant role in the adsorption of Cu^{2+} , while chemical adsorption mechanisms are dominant in the adsorption of NO_3^- on the surface of the DNDs.

Phenylboronic acid is an artificial receptor for saccharides, as the boronic acid moiety forms complexes with the diol groups of saccharides in basic aqueous media. Accordingly, Yeap *et al.* functionalised DND with 3-aminophenylboronic acid (APBA) to obtain specific biorecognition (see Figure 2.4) [130], which resulted in an impressively high loading capacity of 350 mg g^{-1} for ovalbumin compared to a previously reported maximum value (200 mg g^{-1}) of a similar protein [131]. An alkyl spacer chain was deposited on DND through silanisation before the boronic acid functionalisation, although Duffy *et al.* have previously revealed poor hydrolytic stability of silanised DND [132]. The spacer chain was used to form an exclusion shell around the particles to minimise the binding of non-glycated proteins and to reduce the steric hindrance between the bound glycoproteins [130]. However, non-specific binding was unavoidable due to the interaction between the non-glycosylated protein and the hydrophobic alkyl spacer. Also, due to the hydrophobic nature of the alkyl spacer, the dispersibility of particles in solution was reduced, compromising the method's analytical performance [130]. To address this problem, Xu *et al.* functionalised DND with APBA using poly-L-lysine and PEG-diglycolic acid (PEG), which improved the dispersibility of the material in aqueous solution and increased the enrichment capacity for glycopeptides [133].

Similarly, Hens *et al.* immobilised carboxytetramethylrhodamine (TAMRA) and biotin on the aminated DND surface (as shown in Figure 2.5) to selectively capture streptavidin-fluorescein isothiocyanate [134]. The authors further commented that the probes, based on irregularly shaped DND agglomerates, possessed higher surface area to volume ratios, and provided

higher extraction efficiency, than their spherical counterparts [134]. Sajid *et al.* further functionalised DND with hydrazide for the extraction of glycopeptide from complex biological samples [135] obtaining a recovery of 71% and a LOD of 10 fmol when extraction was coupled with MALDI-MS [135]. The recovery percentage was low primarily due to the non-specific interactions of non-glycopeptides with the DND [135].

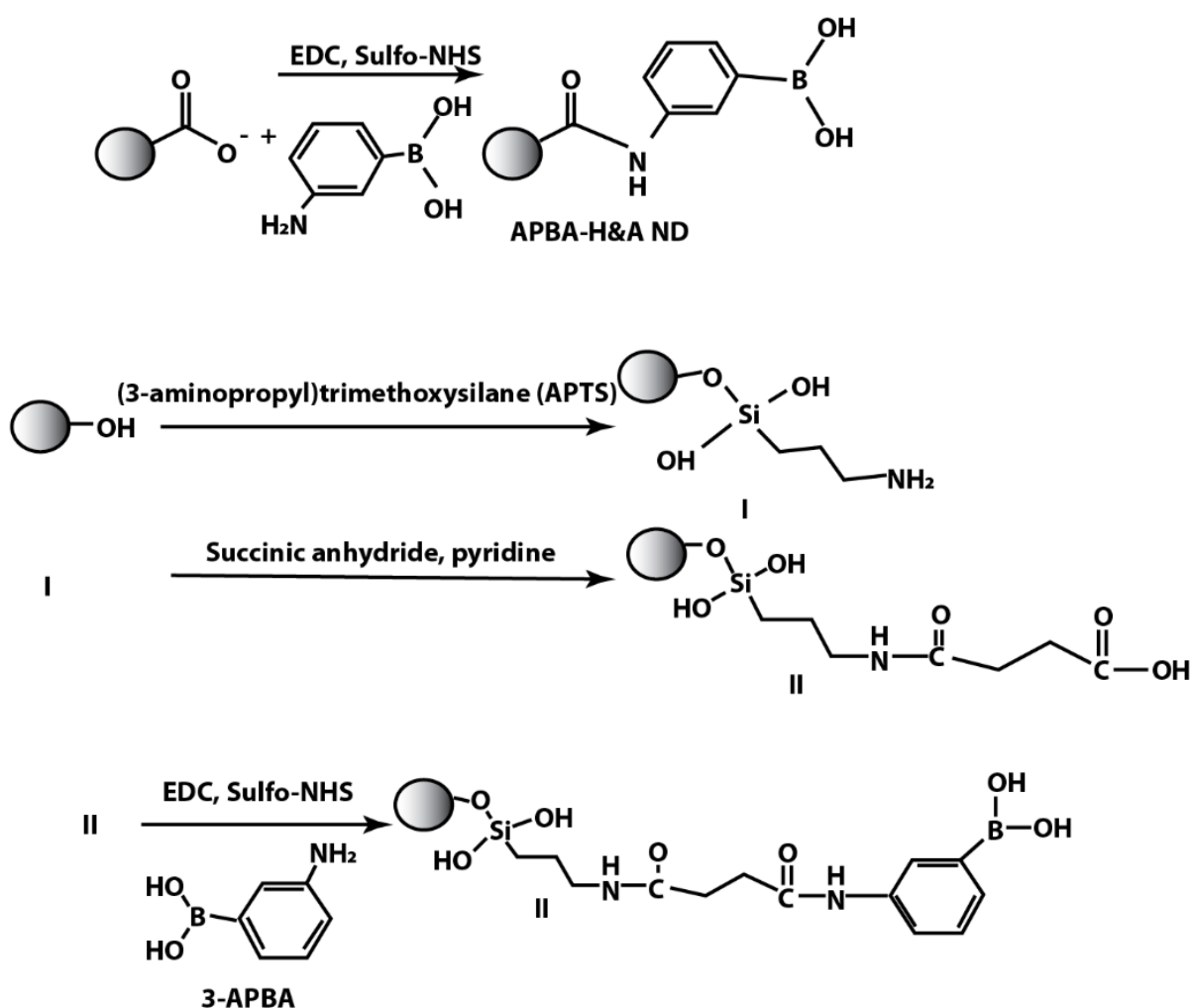


Figure 2.4. Schematic illustration of the functionalisation of DND to generate either DND-APBA or DND-spacer-APBA particles. Adopted from [130]. Copyright (2008) American Chemical Society.

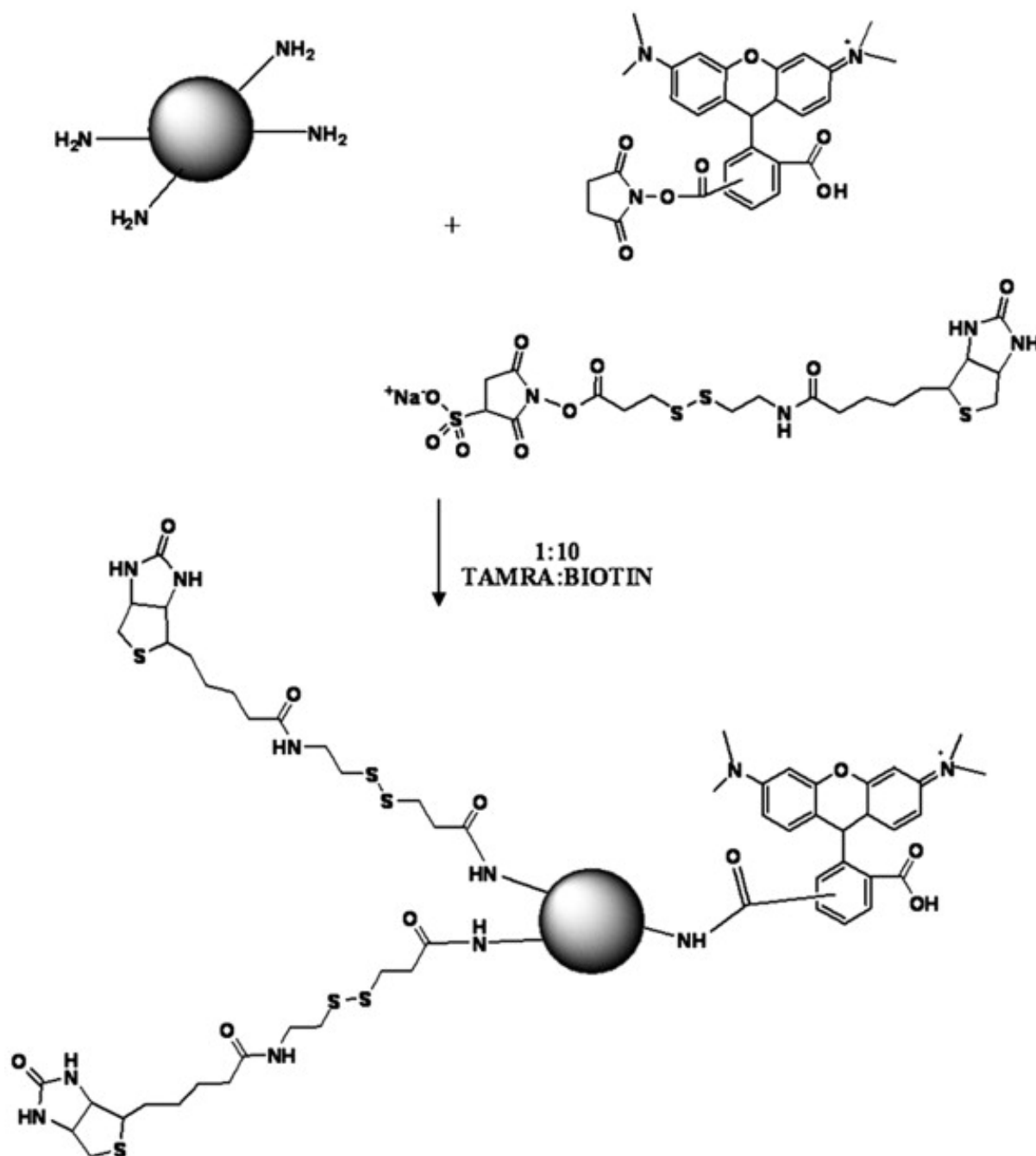


Figure 2.5. Schematic illustration of the generation of double conjugate TAMRA-DND-Biotin particles. Reproduced from [134].

It has been shown that the use of non-porous hyperbranched DND with amidoxime side chains enables a distinctively high uranium selectivity (>91%) compared with previously reported similar sorbent materials [106]. Similarly, Reina *et al.* observed very high affinity of DND functionalised with diamine chelate molecules for Co^{2+} ions. The modification increased the

adsorption capacity up to six times compared to the bare DND particles [103]. Ozdemir *et al.* produced DND particles with surface immobilised *Bacillus altitudinis* to selectively adsorb Cr^{2+} , Hg^{2+} , Pb^{2+} , and Co^{2+} from food and water samples [136]. It was shown that the pH of the sample solution significantly influenced the recovery of the heavy metals. While the highest recovery for Cr^{2+} , Hg^{2+} , and Pb^{2+} cations was observed at pH 6, for the Co^{2+} cation, the highest recovery was observed at pH 5 [136]. This bio-modified adsorbent delivered a preconcentration factor of 80 with an RSD of less than 5% and was successfully re-used at least 30 times [136].

Soriano *et al.* have functionalised aminated DND with cyclodextrin for the extraction and preconcentration of an anticancer drug (doxorubicin) from biological samples [137]. The diamond particles were modified by the covalent diazotisation of the sp^2 superficial zones of the DND followed by the attachment of cyclodextrin [137]. The modified phase was able to selectively extract doxorubicin (with an enrichment factor of ~ 10 and recovery up to 94%) from complex biological samples, such as urine, because of a perfect fit between doxorubicin and the cyclodextrin cavity [137]. The adsorbent also enabled the development of a highly precise (precision RSD $\sim 6\%$) and robust method with a LOD value down to $18 \mu\text{g L}^{-1}$ [137]. Moreover, the process resulted in an excellent batch-to-batch reproducibility (RSD $\sim 5\%$, $n = 3$) [137].

While CVD diamond is commonly used for coating substrates with diamond particles (discussed in Section 2.2.4), diamond particles synthesised via the detonation technique can also be employed for such an application. An interesting study by Ji *et al.* reported the successful coating (using epoxy resin) of stainless steel wires (32 cm length x 0.18 mm internal diameter (ID)) with micron-sized DND agglomerates [138]. The coated wires were placed into a polyether ether ketone tube for in-tube solid-phase microextraction (SPME) and later coupled with HPLC to determine polycyclic aromatic hydrocarbons (PAHs), estrogens and plasticisers

within various matrices (e.g. an aqueous solution of cigarette smoke, and a soil solution). The authors' reported that coupling the coated device with HPLC enabled the development of a robust analytical method (LOD $0.01 \mu\text{g L}^{-1}$, enrichment factors 305–2396, intra-day RSD $<2.4\%$ $n = 3$, and interday RSD $<8.4\%$ $n = 3$). The developed method had several advantages, including convenience, short analysis time, and low consumption of organic solvent [138]. Notably, the new SPME device was both structurally robust (peak areas remained unchanged following 100 extraction cycles) and stable in different solvents (e.g. ethanol, phosphoric acid and ammonium hydroxide), which showed little influence on extraction efficiency (RSD $<\sim 8\%$, $n = 3$) [138].

Recently, DND has also been increasingly used to develop core-shell particles. Researchers from Linford's group have pioneered in the field of diamond-based core-shell particles for SPE- and HPLC-based applications. They have studied various materials, such as silica [139, 140], HPHT diamond [141], and glassy carbon [19] as cores, incorporating DND in the shells, as further described in Section 2.5. Yilmaz *et al.* have incorporated magnetic nanoparticle shells around DND to allow easy removal of the DND from the solution (Figure 2.6) [142]. Magnetic nanoparticles were physically adsorbed around DND cores, and the adsorbents produced were used for the extraction (requiring <10 minutes) and preconcentration of trace amounts of Ziram pesticide (zinc bis(dimethyldithiocarbamate)) from water and food samples, providing up to 100% recovery of the solute. The extraction was followed by flame atomic absorption spectroscopy (FAAS), which resulted in a LOD of $5.3 \mu\text{g L}^{-1}$, a limit of quantification (LOQ) of $17.5 \mu\text{g L}^{-1}$, a preconcentration factor of 160, and a precision RSD of 7% ($n = 7$) [142]. Similarly, Li *et al.* synthesised DND-based superparamagnetic adsorbents to study cell secretomes [143]. Microspheres of Fe_3O_4 (~ 220 nm) were initially coated with silica through a sol-gel process, followed by modification with (3-aminopropyl)triethoxysilane (APTES) and LbL deposition of DND-polylysine up to a total thickness of 20 nm [143]. These core-shell

particles are highly selective to proteins and peptides and are able to preconcentrate these biomolecules even from diluted and complex samples, providing a promising tool for proteomics research [143].

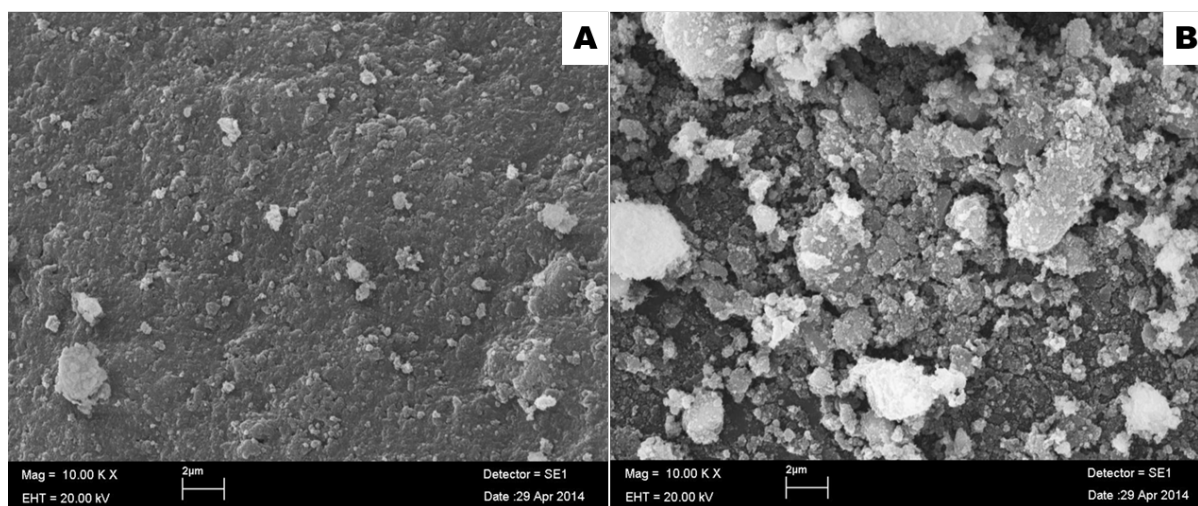


Figure 2.6. SEM of (a) carboxylated DNDs and (b) magnetised carboxylated DNDs. Adapted from [142].

2.4.2. High-pressure high-temperature (HPHT) diamonds

Researchers from Chang's group have pioneered the development of HPHT diamond-based adsorbent for SPE [131, 144]. They have observed that carboxylated and oxidised HPHT diamonds have a high affinity for amino acids with basic side-chain groups. This affinity comes from both ionic and hydrophobic interactions, hydrogen bonding, and Van der Waals forces. Such HPHT diamonds have been successfully used for the highly efficient extraction of deoxyribonucleic acid (DNA) oligonucleotides, even in the presence of high concentrations of urea, salts, and detergents [145]. Similar diamond-based adsorbents have also been used for the preconcentration of different proteins, such as cytochrome c (CYTC) [144, 146], myoglobin (MB) [144, 146], and BSA/HSA [144] from complex matrices (including human blood serum).

As mentioned above, HPHT diamonds have inherent carboxyl groups, which can be used for immobilising biopolymers through amide bonding [127]. Moreover, Huang *et al.* have also developed a simple method (which is independent of the diamond type and size) to functionalise diamond particles with amino groups [131]. Hence, polylysine- and polyarginine-coated HPHT diamonds (with a size of 100 nm) have been extensively used for the selective enrichment of different proteins and peptides and coupled with MALDI-TOF MS to develop a robust and sensitive method (e.g. the sensitivity of oligonucleotide detection increased by ~1000 times when the diamond particles were coated with polylysine) [81, 127]. These polyaminoacid-modified diamond-based phases have also been used for direct on-particle enzymatic protein digestion [113].

Strong interactions between diamonds and proteins allows for simple isolation of the bound proteins by simply centrifuging the diamond particles [144]. Moreover, due to the transparent and biocompatible nature of the diamonds, bound proteins can be directly analysed by high-sensitivity analytical techniques, such as sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) [113] and MALDI-MS [144] (Figure 2.7). These unique properties have streamlined the process for proteome analysis using diamond, and the combined process is now described as solid-phase extraction and elution on diamond (SPEED) [113]. SPEED has recently been used for various novel applications, such as the MALDI-TOF MS analysis of neutral underivatised glycans released from glycoproteins [147]. It has also been coupled with other high-sensitivity techniques, such as atmospheric pressure MALDI Fourier transform ion cyclotron resonance MS (AP MALDI-FT ICR MS) to improve the LOD to 10 fmol for purified peptides and 50 fmol for digested proteins or peptide mixtures [146].

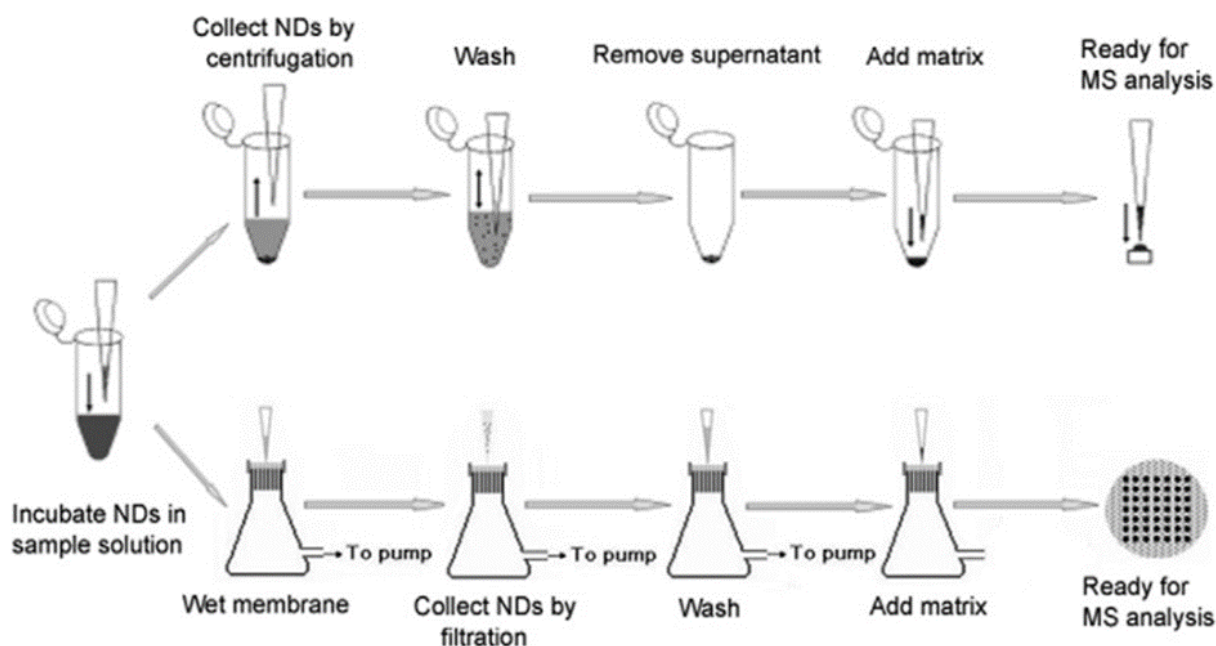


Figure 2.7. Schematic illustration of the process used for sample preparation using diamonds to enrich biopolymers for MALDI-MS analysis through centrifugation (upper) and filtration (lower). Reproduced from [70].

Surface modified HPHT diamond (treated with acids, therefore containing many oxygen groups on the surface) poorly adsorbs some of the high abundance serum proteins, facilitating the detection of low abundance proteins (which are mostly disease biomarkers) down to 400 pg mL^{-1} [148]. In addition to large biomolecules, Linford's group has also used HPHT diamonds for the extraction of small molecules [105, 149]. They have functionalised deuterium- and hydrogen-terminated HPHT diamond particles ($70 \text{ }\mu\text{m}$) using di-*tert*-amyl peroxide for cyanazine extraction. Similarly, deuterium-terminated HPHT diamonds were modified with polystyrene and sulfonated styrene for the extraction of 1-naphthylamine [105]. These stationary phases were found to be stable under both extremely acidic and basic conditions [105].

Hasan *et al.*, reported a new HPHT diamond-based adsorbent has been developed, where microdiamond particles ($2\text{--}4 \text{ }\mu\text{m}$) were dispersed within polydimethylsiloxane (PDMS). The

composite thus formed (Figure 2.8) selectively adsorbed some model solutes (e.g. esters and higher alcohol acetates) with recoveries up to 100%, and enabled a robust GC flame ionisation detection (GC-FID) method (LOD 0.6–27.3 $\mu\text{g L}^{-1}$) for such analysis [17].

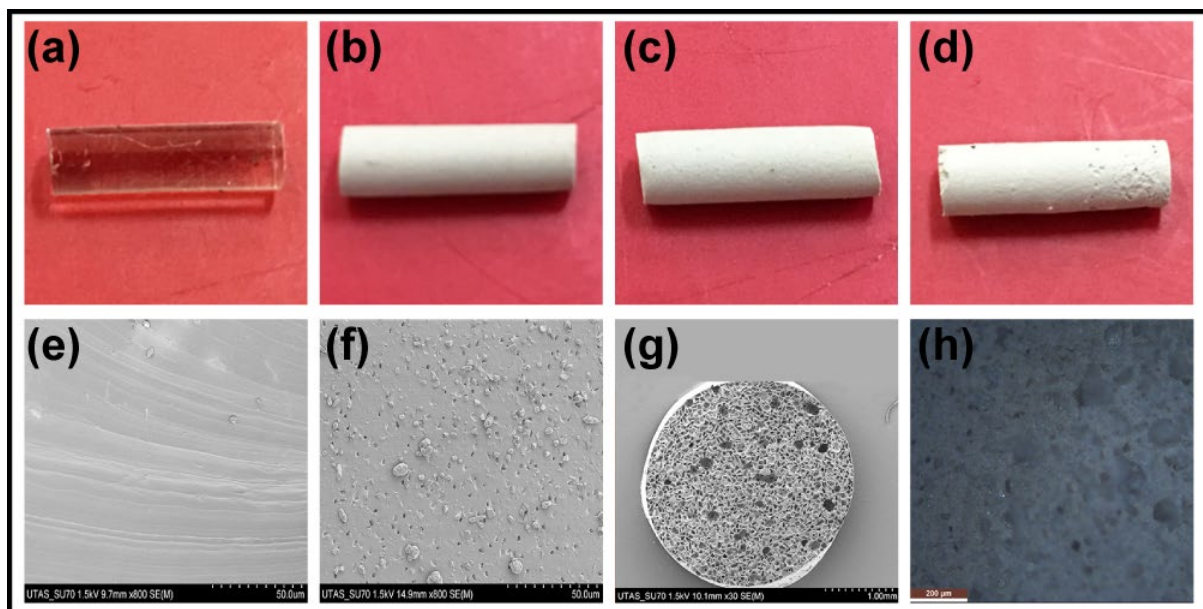


Figure 2.8. PDMS-microdiamond composites along with their microscopic images, (a) non-porous PDMS without microdiamond, (b) non-porous PDMS-microdiamond, (c) porous PDMS-microdiamond large salt particles, (d) porous PDMS-microdiamond small salt particles, (e) non-porous PDMS, (f) non-porous PDMS-microdiamond, (g) porous PDMS-microdiamond large salt particles, (h) porous PDMS-microdiamond small salt particles. Reproduced from [17].

2.4.3. Chemical vapour deposition (CVD) diamonds

In SPE based applications, CVD methods have been primarily used because of their ability to generate thin, uniform, and conformal diamond coatings. These coatings have been performed on a wide variety of materials with different surface topologies, and the shape and size of the deposited diamond particles have been found to be dependent on the substrate and the utilised reactants. For example, Ashfold *et al.* reported that CVD process involving 0.5% methane in hydrogen produced sharp angular crystals ($\sim 1 \mu\text{m}$ in size) (Figure 2.9.a), whereas a similar

process using 2.5% methane in hydrogen gave rise to nanocrystalline cauliflower-like diamond particles (Figure 2.9.b) [150].

The CVD coatings can also be doped with heteroatoms or modified with different functionalities to obtain the required selectivity and to increase the method's sensitivity. Ruffinatto *et al.* used trimethylborane and hydrogen plasma to obtain CVD coatings of BDD on glass-microfibre-based SPE membranes, which were then functionalised with tetra alkyl groups for the extraction of BSA [95]. The authors confirmed the advantages of the preparation process of this membrane, including the low cost of preparation and the highly reproducible control of pore sizes [95]. However, later when Alcaide *et al.* studied the influence of heteroatoms on the protein adsorptivity and biocompatibility of CVD diamond coatings, they found that boron doping had little to no influence on protein adsorption, cell adhesion, or cell proliferation, and that these properties were predominantly influenced by the surface topography [151].

Najam-ul-Haq *et al.* used a CVD crystal formation method to produce diamonds for the protein profiling of complex analytes [108]. A graphite or titanium chip was coated with diamonds, which were then modified with glycidyl-methacrylate followed by the immobilisation of iminodiacetic acid and Cu^{2+} ions [108]. The developed adsorbent enabled peptide mass fingerprinting for protein identification in a complex mixture using MALDI-TOF MS. Moreover, the use of graphite and titanium chips provided an electrically conductive surface to minimise the electrical noise resulting from the charge produced during the MALDI process [108]. The adsorbent was also successfully regenerated by submerging it in a 100 mM ethylenediaminetetraacetic acid solution for two hours at room temperature followed by several washes with deionised water and eventually a reloading of the diamond surface with Cu^{2+} ions for further serum profiling [108].

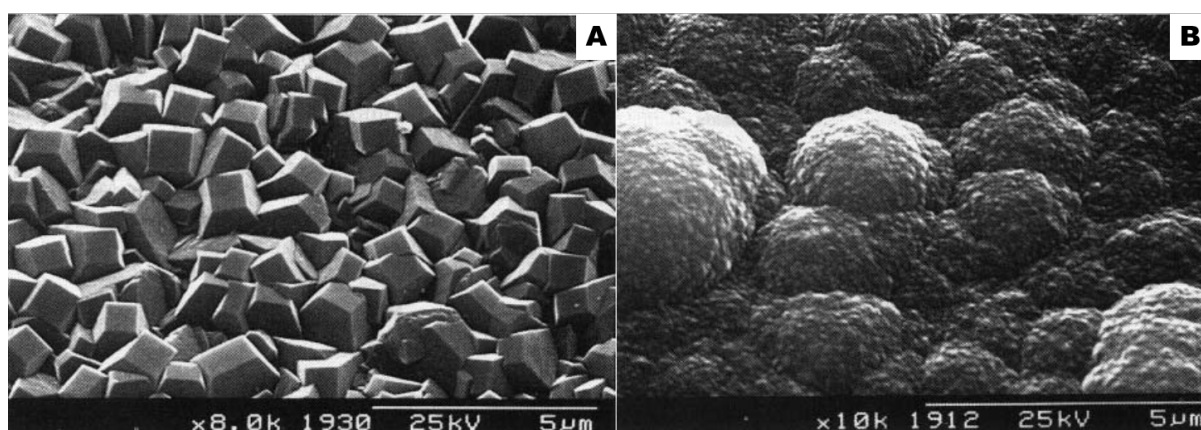


Figure 2.9. SEM images of topologically variable ideal polycrystalline diamond films deposited on a silicon substrate by the CVD method (a) angular crystals (when the ratio of CH_4/H_2 is 0.5%), and (b) cauliflower-like nanocrystalline diamond particles (when the ratio of CH_4/H_2 is 2.5%). Adapted from [150].

Table 2.3. Applications of diamond-based adsorbents in SPE.

Adsorbent	Analyte	Matrix or sample	Specific surface area (m ² g ⁻¹)	Adsorption capacity	Preconcentration factor	Employed detection technique	Ref
DND							
DND	Oxoacid anion (WO ₄ ⁻²)	Milli-Q water, artificial river water, and artificial seawater	–	-	–	ICP-AES	[114]
	Lysozyme, albumin, and calcium homopantothenate	Mili-Q water and phosphate buffer	350	12 mg g ⁻¹ (homopantothenic acid), 115 mg g ⁻¹ (lysozyme), and 392 mg g ⁻¹ (HSA)	–		[152]
	Myramistin®	Water	310	200 µmol g ⁻¹	–		[153]
	Dyes (acid orange, AAB, methylene blue (MB))	Water	260	85 mg g ⁻¹ (acid orange) 175 mg g ⁻¹ (AAB), 1.7 mg g ⁻¹ (MB)	–	Spectrophotometer, colorimeter, photo-electric	[126]
	Acid orange 7	Water	300	1288 mmol kg ⁻¹	–	UV/Vis	[115]
Magnetic silica nanoparticles functionalised with a LbL assembly of DND and magnetic carboxylated DND	Ziram	Tap/lake water, rice and cracked wheat	–	–	160	FAAS	[142]
	Digested proteins (BSA, β-casein, CYTC) and standard peptides of Lambinin B	Saline solution, serum and phenol red-free cell medium	400	70 mg g ⁻¹	–	SDS-PAGE, MALDI-TOF MS, and LC/ESI-MS	[143]
<i>Bacillus altitudinis</i> immobilised DND (10 nm)	Cations (Co ²⁺ , Cr ⁶⁺ , Hg ²⁺ , and Pb ²⁺)	Food (apple, strawberry juices, energy drink, meat, chicken, flour, honey, milk, olive, white cheese, corn, tomato, potato, and black tea) and water	–	19.5–35.2 mg g ⁻¹	80	ICP-OES	[136]
Carboxyl modified DND	Cu ²⁺ , Pb ²⁺ , NO ₃ ⁻	Water	–	three times higher than pristine DND	–	Absorption spectroscopy	[129]
	Peptides	Aqueous solution	–	130 mg g ⁻¹	–	UV spectrophotometry	[119]
Chitosan/DND	Methyl orange	Water	–	454 mg g ⁻¹	–	UV/Vis	[122]
Amidated DND	Cation UO ₂ ²⁺	Water, effluents		200 mg g ⁻¹	–	ICP-OES	[154]
	Cation UO ₂ ²⁺	Multi-ion water solution	134.6	212 mg g ⁻¹	–	ICP-AES	[106]
	Cation Co ²⁺	Wastewater	–	578 - 634 mg g ⁻¹	–		[103]
DND reduced with H ₂ and oxidised with H ₂ SO ₄ /HNO ₃ (4–5 nm)	Cations (U ⁴⁺ , Pu ⁴⁺ , Th ⁴⁺ , Am ³⁺ , and Np ⁵⁺)	Water	300	140 µmol g ⁻¹ (U ⁴⁺)	–	ICP-OES	[128]
O ₂ /H ₂ treated DND	Proteins (BSA and LYS)	Mili-Q water	198 ± 69	3.5 ng mm ⁻² (BSA) and 1.3–2.5 ng mm ⁻² (LYS)	–	ATR-FTIR	[120]

DND composite with lanthanum and samarium oxides	Digested phosphopeptides (β -casein, BSA, and endogenous serum peptides)	Non-fat milk and human serum	–	–	–	MALDI-TOF MS	[123]
Magnetic DND/GO	Sildenafil citrate	Herbal products	–	–	100	HPLC-DAD	[155]
DND-ionic liquid	Congo red	water	–	226.4 mg g ⁻¹		UV/Vis	[121]
DND-APBA (4–5 nm)	Glycoproteins (ovalbumin, fetuin, and RNase B)	A mixture of glycoproteins and non-glycoproteins	–	350 mg g ⁻¹	10	MALDI-TOF MS	[130]
DND-TAMRA-Biotin	Proteins (streptavidin)	Water	200	–	–	Electrophoresis and fluorescence microscopy	[134]
Hydrazide-functionalised DND	Glycoprotein (fetuin)	Digested proteins (fetuin, avidin, serum, BSA, and HeLa cell lysate)	–	–	–	MALDI-MS	[135]
DND/MoS ₂ nanorod	Pb ²⁺ and Cu ²⁺	Natural water sources	20.2	19.87 mg g ⁻¹ (Pb) and 49.33 mg g ⁻¹ (Cu)	35	FAAS	[124]
Cyclodextrin-modified DND	Doxorubicin	Biological samples (urine)	70.7	–	–	Fluorescence	[137]
DND shell with HPHT diamond, glassy carbon, or silica core	–	–	6.8–30.3	2 mg g ⁻¹	80	–	[141]
	Cholesterol, hexadecanedioic acid, and POPC	CHCl ₃ and isopropanol mixture	–	2.3 mg cm ⁻³	–	ESI-MS	[156]
	Cyanazine	Water	–	–	–	ESI-MS	[149]
	1-naphthylamine	Water	–	12.6 μ g g ⁻¹ (phenyl) and 32 μ g g ⁻¹ (cation-exchange)	–	ESI-MS	[105]
	Pesticides (cyanazine and diazinon)	Water	0.2	13–14 μ g g ⁻¹ (diazinon)	–	ESI-MS	[157]
DND/Cu-Prussian Blue	Cs ⁺	0.07% artificial seawater, soil-contained wastewater	–	759 mg g ⁻¹	–	ICP-AES, ICP-MS	[125]
DND coated stainless steel wire	PAHs, estrogens, plasticisers	An aqueous solution of cigarette smoke, soil solution	295 (before attached to the wire)	–	238–1121 (PAHs) 506–1792 (estrog.) 39–2609 (plastis.);	HPLC	[138]
HPHT Diamond							
Oxidised/carboxylated HPHT diamond (~100 nm)	Trypsin digested proteins (CYTC, BSA, and MB)	Human urine and human kidney cells	–	–	–	SDS-PAGE, MALDI-FT ICR MS, and LC-ESI-MS/MS	[113]
	Serum proteins	Serum	–	–	–	Nano-LC-MS/MS	[148]
	Proteins (CYTC, BSA, and MB)	Human blood serum	60	99 mg g ⁻¹ (CYTC)	10	MALDI-TOF MS	[144]
	CYTC trypsin digest, MB Lys C digest, and Gramicidin S	–	–	–	50	AP MALDI-FT ICR MS and ESI-MS	[146]
	Glycans released from glycoproteins (β -cyclodextrin, maltoheptaose, angiotensin I, chicken ovalbumin, and bovine pancreatic RNase B)	–	–	–	2	MALDI-TOF MS	[147]

	Membrane proteins from <i>Methylococcus capsulatus</i> and <i>E. coli</i> , and their digests	–	–	–	~20	MALDI-TOF MS, Nano-LC-MS/MS, and SDS-PAGE	[158]
	Digested membrane proteins from human cervical cancer cells and mouse myeloma cells and <i>E. coli</i>	Detergent rich milieu	–	–	–	SDS-PAGE	[159]
Polylysine- or polyarginine-coated HPHT diamond (~100nm)	CYTC	Yeast	60	97 mg g ⁻¹	–	–	[131]
	DNA oligonucleotides and digested DNA oligonucleotides	Urea, SDS, ubiquitin, and phosphate buffer	40	22 mg g ⁻¹	~1000	MALDI-TOF MS	[145]
	Trypsin digested α -casein, β -casein, CYTC, and MB	0.15% trifluoroacetic acid in ACN and water mixture	40	–	–	MALDI-TOF MS	[127]
	Digested phosphorylated proteins	Complex protein digests	40	–	~1000	SDS-PAGE, MALDI-MS, and LC-ESI-MS	[127]
	CYTC and angiotensin I	Urea, SDS, ubiquitin, and phosphate buffer	40	–	~1000	MALDI-TOF MS and MALDI-FT ICR MS	[160]
HPHT diamond-PDMS	Esters and higher alcohol acetates	Beverage	–	–	–	GC-FID	[17]
CVD Diamond		–	–	–	–	–	–
BDD porous membrane	Serum proteins	Human blood serum	–	–	–	MALDI-TOF MS, MELDI-TOF MS, and IMAC	[108]
	BSA	Water	–	–	–	LC-MS	[95]
BDD	Proteins	–	–	11 $\mu\text{g cm}^{-2}$	–	–	[151]

2.5. HPLC-Based Applications

HPLC is one of the most commonly used analytical techniques for the analysis of non-volatile analytes. As discussed above, conventional HPLC columns are based on silica and polymeric stationary phases, which are not always mechanically and thermally stable under extreme conditions. Employing diamond particles as stationary phases could potentially solve some of the inherent limitations of conventional HPLC stationary phases. Hence, recently, diamond-based adsorbents, and particularly DND-based phases, have been studied in almost every HPLC mode (reversed phase liquid chromatography (RPLC), HILIC, ANP, and ion chromatography (IC)). While HPHT diamond has been studied in ANP, HILIC, and IC modes, the use of CVD diamond has only been attempted in RPLC. Diamond provides a wide range of interactions, such as electrostatic and hydrophobic interactions, chelation, and hydrogen bonding, making it potentially useful for application in many HPLC modes. Among diamond-based stationary phases, MSDN particles and DND-shell-based core-shell particles are currently the most commonly used diamond-based adsorbents for HPLC columns as these diamond particles can deliver higher chromatographic efficiency. The various applications of different synthetic diamonds in HPLC are summarised in Table 2.4 and discussed below.

2.5.1. Detonation nanodiamonds (DNDs)

The small size (usually 4–20 nm) of DND prevents their direct use in HPLC columns, because of the resulting high backpressure. Accordingly, the earlier studies within the authors' research group has investigated the use of MSDN [75, 76, 82-84, 161-163]. MSDN are mechanically stable agglomerates of DND, which can reach a size of up to 50 μm with a well-developed porous structure (Figure 2.10) [75]. They usually have a high surface area (130–200 $\text{m}^2 \text{g}^{-1}$ for 3–6 μm particles), a bimodal pore size distribution (maxima at 1.5 nm and 3.0 nm), and a variety of surface functional groups. The surface chemistry of MSDN is similar to DND,

however MSDN particles typically contain a significant number of surface impurities such as sp^2 -carbon, chemisorbed water, metals, and adsorbed gases [73, 164, 165]. Removal of these impurities is an essential but challenging task [7]. Most commonly, MSDN particles are washed with strong mineral acids and complexing agents, or pyrolysed under an air (or O_2 or O_3) atmosphere to remove these impurities. These processes often remove metal impurities and oxidise different surface functional groups into carboxyls, however, they fail to remove the metal oxide and non-volatile impurities [166].

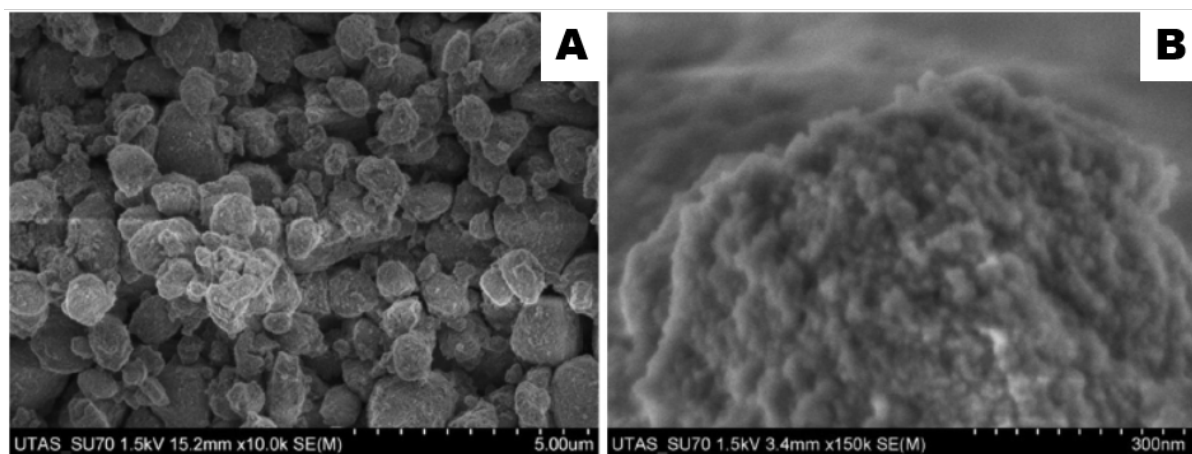


Figure 2.10. SEM of MSDN at (a) a magnification of 10k and (b) a magnification of 150k. Reproduced from [75].

MSDN particles have been successfully used for generating a wide variety of HPLC columns, ranging from cation- and anion-exchange IC columns [75] to ANP [82, 83], RP [84, 161], and HILIC [84, 161] columns. The adsorption of anions on MSDN is predominantly associated with electrostatic interactions, whereas cation adsorption likely occurs through complexation with hydroxyl and carboxyl functional groups [75]. The MSDN based IC columns demonstrate remarkably high anion adsorption capacity ($50\text{--}150\ \mu\text{mol g}^{-1}$). The availability of carboxylic and hydroxylic groups on MSDN makes these adsorbents also suitable for ANP and HILIC

chromatography modes. At the same time, non-polar analytes can be retained by π - π interactions with the diamond surface, which indicates the possibility of using MSDN in RP mode. Hence, MSDN-based columns usually demonstrate a mixed-mode retention mechanism, imparting them different selectivity compared to their conventional counterparts. Compared to the conventional ANP columns, such as silica and alumina, MSDN columns present a higher selectivity for the separation of positional isomers of xylene [82]. In the RP mode, the adsorption of phenols [84, 162], benzoic acids [161], and nitrogen-containing aromatic compounds [167] follows a parabolic relationship with the organic content, which indicates the presence of both specific and non-specific interactions between the solutes and MSDN. Some of these interactions were found to be dependent on the acidity, molecular volume, dipole moment, hydrophobicity, polarisability, and molecular refractivity of the analytes [162, 167]. The properties of MSDN-based columns can be further modulated by modifying their surface chemistry. For example, even simple conditioning of an MSDN column with acids or bases increases the adsorption of compounds containing a primary amino group by 13.5–22.0% [163].

Core-shell particles consist of a solid core and a porous shell, which provides high chromatographic performance by minimising the resistance to mass transfer and eddy diffusion, while resulting in lower backpressures. The small size of DND makes them a promising candidate for developing the shells of such core-shell particles, prompting significant interest in the development of DND based core-shell particles. Linford's group reported the first carbon core-DND shell stationary phase in 2010 [141]. In this report, HPHT micro-diamonds (1.7 μm or 5 μm) were coated in a LbL fashion (ca. 28 layers) with poly(allylamine) and 10–50 nm sized nanodiamonds. The developed core-shell particles were modified with 1,2-epoxyoctadecane to prepare C_{18} RP columns with a separation efficiency of 22,800–36,300 N m^{-1} for the separation of benzene, toluene, xylene, and mesitylene. Moreover,

the separation efficiencies for two pesticides, cyanazine and diazinon, were 40,000 N m^{-1} and 54,800 N m^{-1} , respectively. However, it was also reported that the columns were found to show signs of degradation during overnight flushing with the mobile phase (50% acetonitrile (ACN)). Later in 2011, the same group prepared core-shell particles with a glassy carbon core and similar DND-polymer shells [19]. The produced particles (4 μm in diameter) were also functionalised with C_{18} alkyl chains, which were cross-linked with 1,2,7,8-diepoxyoctane, enhancing the mechanical stability of the stationary phase under extreme conditions (pH 11.3 and 13). Compared with the non-cross-linked column, this column resulted in lower backpressures and showed efficiencies of up to 120,100 N m^{-1} and 71,000 N m^{-1} when used with UHPLC and HPLC systems, respectively. The column efficiency was later further improved by using more uniform glassy carbon cores [168].

Bobaly *et al.* [23] and Fekete *et al.* [169] further developed similar carbon-core and DND-polymer-shell particles for protein analysis. These particles were used to obtain fast protein separations by utilising rapid gradients of ACN within 15–20 minutes as compared to a required gradient time of 50–80 minutes with the comparably sized silica particles. The group studied the effect of the pore size of these core-shell particles on protein separation [169]. Three columns with particles having 120, 180, and 250 Å sized pores were evaluated, and they observed an increase in peak capacity with an increase in the pore size. The particles were further used by Hung *et al.* to perform HPLC separation of cannabinoids, showing efficiencies of up to 54,000 N m^{-1} [24]. Gupta *et al.* also investigated carbon-core DND/polyamine-shell stationary phases, reporting a stronger retention of anionic analytes for the stationary phase with 30 polyamine layers compared to the stationary phase with 15 layers due to the higher polyallylamine content within the shell. The group further observed typical RP selectivity to hydrophobic dansylated amino acids (DnsAAs) and mixed-mode selectivity to hydrophilic

DnsAAs [22]. These core-shell particles were found to be stable under extreme pH conditions, and they offered low to medium hydrophobicity and a strong ion-exchange character.

Other research groups, such as Colon's [139] and Qiu's [140], have also recently developed silica-DND core-shell particles. Colon's group attached an approximately 10-nm thick layer of DND on allyl-silica *via* UV and radical chemical initiation [139]. The selectivity of these particles was found to be dependent on the DND surface chemistry. The use of commercial DND particles, which contain a significant number of polar groups, favoured hydrophilic interactions, whereas the use of hydrogenated DND particles demonstrated hydrophobic interactions. The hydrogenated DND-based column was used to separate three model compounds, namely uracil, benzophenone, and biphenyl. Similarly, Qiu's group used an amidation reaction to obtain an approximately 30-nm thick layer of oxidised DND on APTES-modified silica particles [140]. These particles were used to separate sulphonamides and saccharides (Figure 2.11) [140].

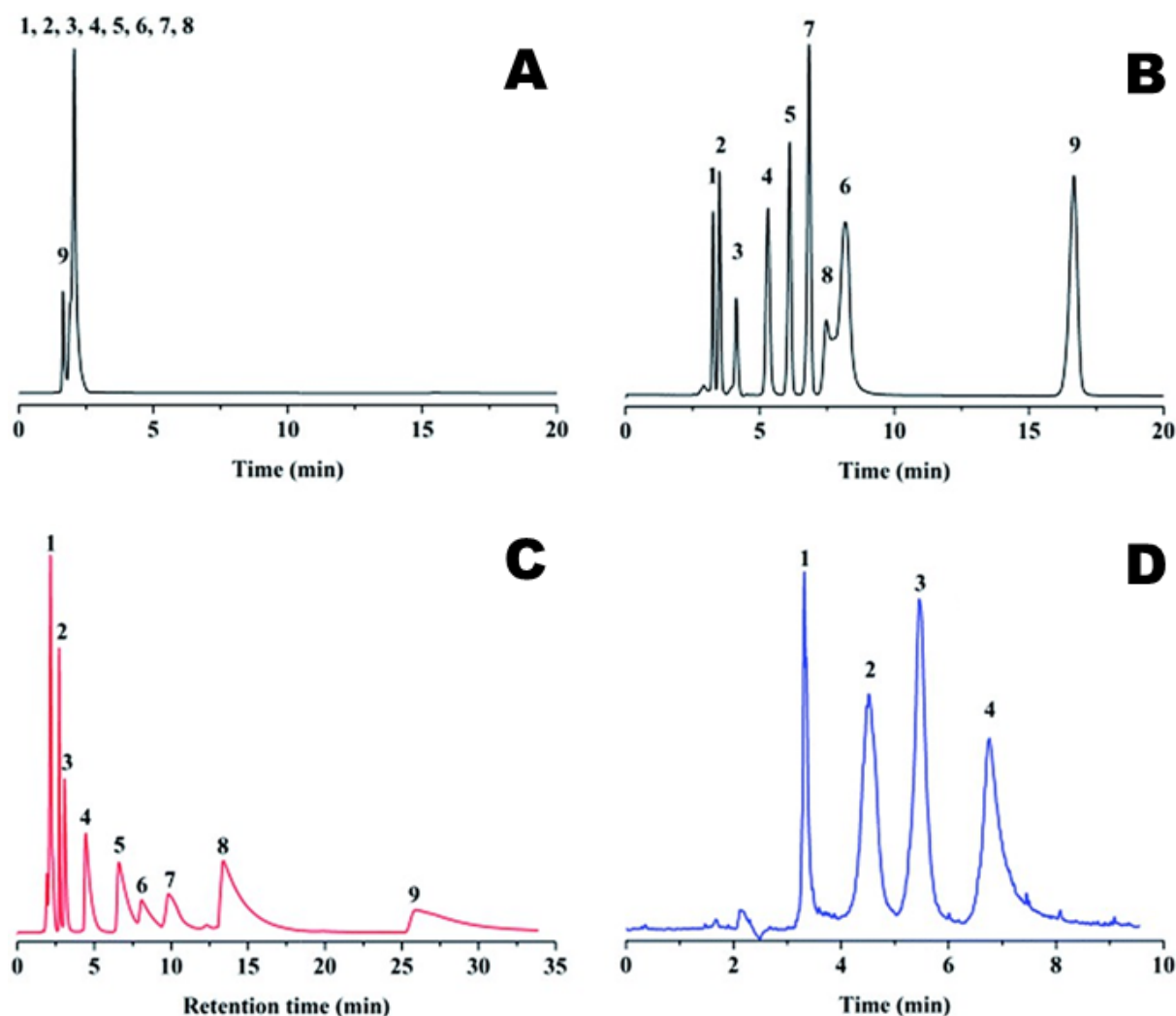


Figure 2.11. HPLC-based separation of sulphonamides and saccharides. Separation of sulphonamides using a (a) silica column, (b) amino functionalised silica column, and (c) DND-modified silica column. 1: sulphanilamide, 2: sulfapyridine, 3: sulfamethazine, 4: sulfamerazine, 5: sulfadimethoxine, 6: sulfadiazine, 7: sulfadoxine, 8: sulfathiazole, 9: sulfisoxazole. Separation of saccharides using a (d) DND-modified silica column. 1: D-ribose, 2: D-galactose, 3: sucrose, 4: lactose. Reproduced from [140].

A core-shell stationary phase with a polymer core was also proposed by Yao *et al.* [170]. Three-dimensional DNDs were chosen instead of the previously reported long multi-walled carbon nanotubes (MWCNTs) for this type of anion exchanger, as the DNDs allowed researchers to avoid joints between polystyrene-divinylbenzene (PS-DVB) beads and MWCNTs, which cause agglomeration, and decreased capacity and separation efficiency. Oxidised DNDs were quaternised multiple times by condensation polymerisation between diepoxide and amine to

achieve five layers of cationic electrolyte. Afterwards, the cationic substrate was attached to sulphonated PS-DVB beads using electrostatic interactions. In order to increase anion-exchange capacity, a subsequent hyperbranched reaction was performed. This adsorbent has been used for the separation of common inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulfate). It was also shown that the column capacity could be changed by controlling the time of cyclic reactions, which provides opportunities for synthesis of high-capacity adsorbents. The DND-modified adsorbent showed good hydrolytic stability in a wide range of pH (1–13) and mechanical stability as confirmed by tolerance to pressures up to 4000 psi. Stability in an organic solvent (methanol) was enhanced compared to a stationary phase without DND, due to the direct bond between the DND and the functional layer, which only slightly dissolved in methanol.

In addition to the core-shell particles, DND has also been used to modify monolithic columns (Figure 2.12). The monoliths modified with DND provided higher efficiency, enhanced mechanical stability and better resolution for the separation of a wide variety of acidic, alkaline, and neutral compounds (such as *o*-nitrobenzoic acid, *p*-nitroaniline, benzene, chlorobenzene, diphenylamine, *p*-aminodiphenylimide, and acenaphthylene) compared to their non-modified counterparts [171].

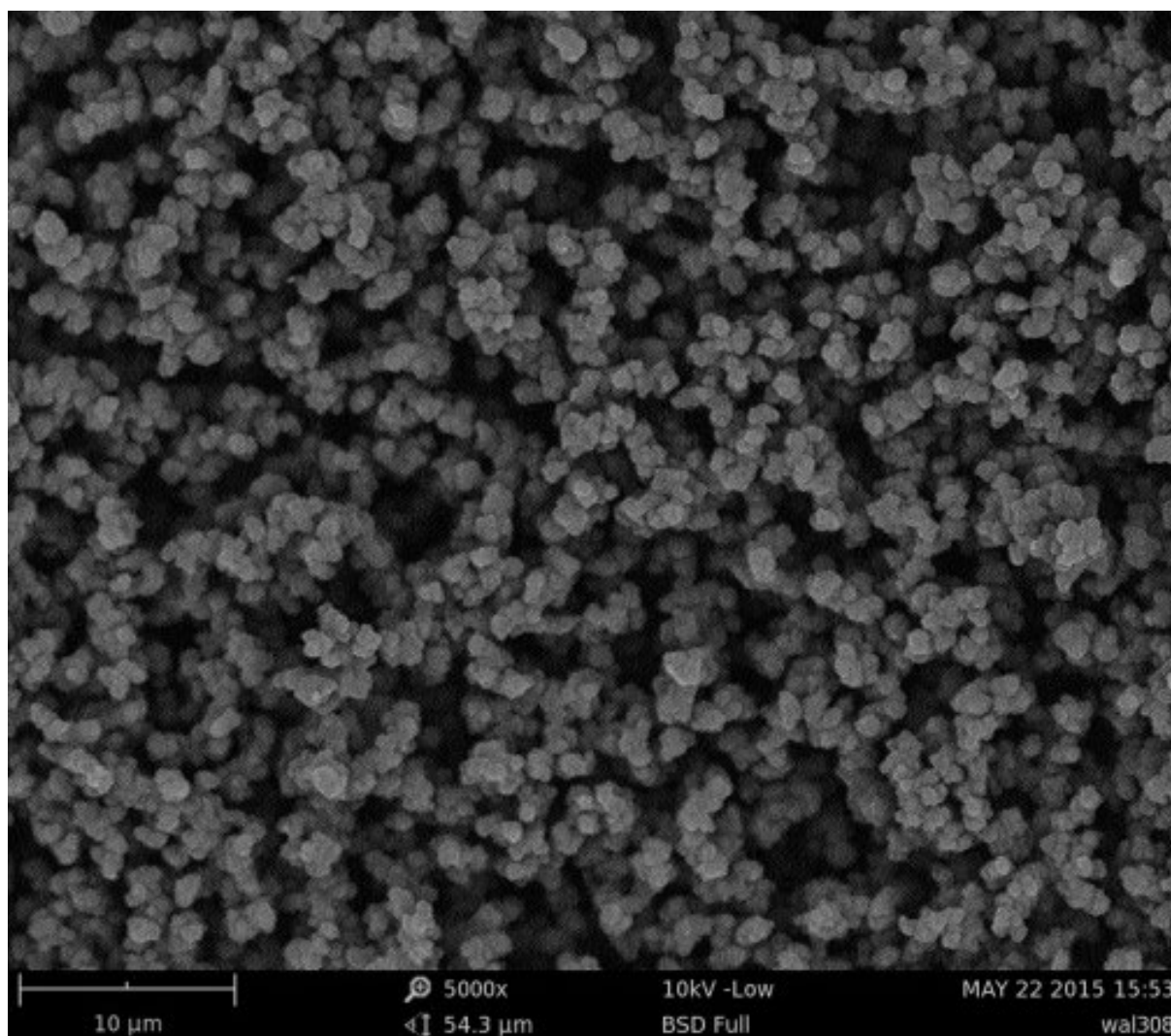


Figure 2.12. SEM of a DND-modified monolithic column. Adapted from [171].

Recently, a new DND-modified composite stationary phase was synthesised by Huang *et al.* [111]. Remarkably, the stationary phase was different from both core-shell particles and monolithic columns. PS-DVB microspheres were hybridised with oxidised DND by the method of seed swelling and polymerisation. DNDs were embedded within the 6- μm sized polymer particles, which enhanced their mechanical stability. The chromatographic column packed with unmodified PS-DVB particles showed signs of irreversible degradation at 3000 psi, whereas the DND-modified stationary phase remained stable at 4000 psi. The material was also applied in RPLC mode, separating an artificial mixture of six benzenes, although baseline separation of benzoic acid and 1,4-hydroquinone was not achieved. An improved

chromatogram of seven inorganic anions within 20 minutes, was obtained using anion-exchange mode after further quaternisation with methylamine and 1,4-butanediol diglycidyl ether (Figure 2.13). The efficiency of separation was $6820\text{--}8273\text{ N m}^{-1}$. The authors also mentioned that the material was stable across the pH range 1–14.

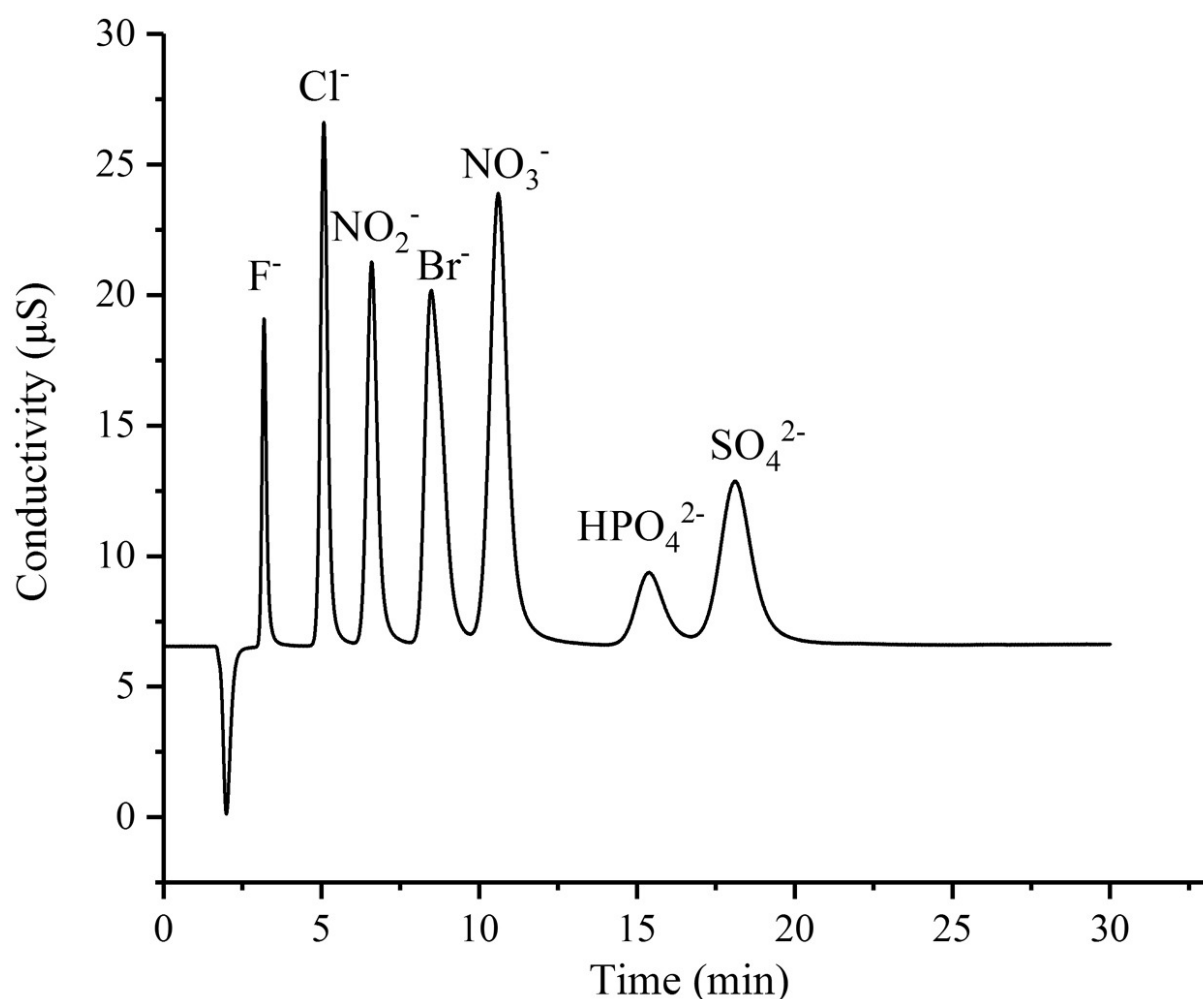


Figure 2.13. The chromatographic separation of seven inorganic anions on a PS-DVB-DND column. Reproduced from [111].

2.5.2. High-pressure high-temperature (HPHT) diamonds

The use of HPHT diamonds has also been studied in various modes of HPLC, such as ANP, HILIC, and IC [58, 87, 172]. In the ANP and HILIC modes, various retention mechanisms have been observed for HPHT diamond-based stationary phases, such as electrostatic interactions with carboxylic groups, hydrogen bonding with hydroxyl groups, and donor-

acceptor type interactions with the aromatic rings of the solutes [87, 172]. Interestingly, when applied in ANP mode, compared to other carbon-based adsorbents (e.g. MSDN and porous graphitic carbon (PGC)), these phases showed very different retention selectivity for various classes of organic compounds, such as alkylbenzenes, PAHs, alkylphenylketones, phenols, and aromatic acids and bases. Both oxidised and reduced HPHT diamonds have been studied for cation-exchange IC [58]. As expected, oxidised diamonds gave a higher ion-exchange capacity because of the higher density of carboxylic groups, as compared to their reduced counterparts [58]. Again, in the ion-exchange mode, different retention orders were observed for the HPHT diamond ($\text{Mn}^{2+} < \text{Cd}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Cr}^{3+}$) and MSDN ($\text{Cd}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Mn}^{2+} < \text{Cu}^{2+} < \text{Fe}^{3+} < \text{Al}^{3+}$) based stationary phases [58]. However, HPHT diamond-based stationary phase only produced efficiencies of up to $27,000 \text{ N m}^{-1}$ for the separation of five metal cations (Li^+ , NH_4^+ , K^+ , Cs^{2+} , Mg^{2+}) [58].

2.5.3. Chemical vapour deposition (CVD) diamonds

As discussed above, CVD is usually performed only to obtain thin diamond layers. However, Kondo *et al.* have also successfully produced micrometre-sized mesoporous CVD diamond particles [99]. The particles were deposited through microwave plasma assisted CVD on 5-nm sized DNDs (Figure 2.14), and the pore size was controlled by modulating the size of the nanodiamonds. The deposited particles were found to be both chemically and physically stable. However, when they were used for RPLC separations, these particles resulted in poor chromatographic efficiency ($4,667\text{--}11,333 \text{ N m}^{-1}$). Poor efficiency makes CVD diamond a challenging material with which to develop HPLC-based applications.

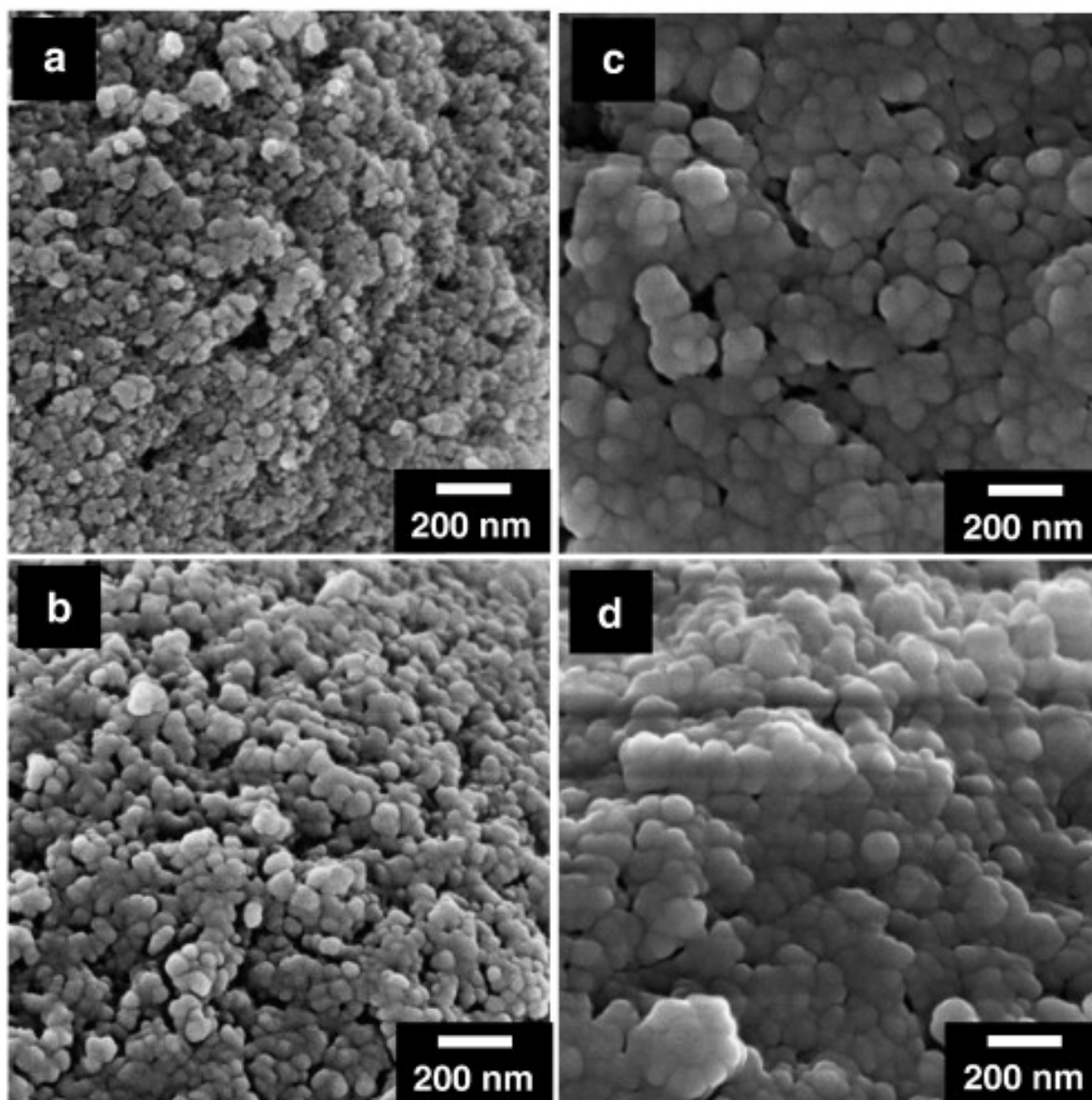


Figure 2.14. SEM of CVD mesoporous diamond particles after a deposition period of (a) 0 min, (b) 10 min, (c) 30 min, and (d) 60 min. Reproduced from [99].

Table 2.4. The applications of different diamond-based adsorbents in HPLC.

Adsorbent	Structure	Column size (L × ID)	Mobile phase	Analytes	Mode of separation	Ref
DND						
DND-modified silica	Organo-silica core (0.9, 4 μm) and DND shell (5–10 nm particles with 30–35 nm layer thickness.	150 × 4.6 mm and 30 × 3 mm	ACN/NH ₄ Ac at pH = 6.6–7.7 and ACN/water	Sulfonamides, saccharides, benzene, acetylsalicylic acid, salicylic acid, uracil, benzophenone, and biphenyl	RP-HPLC, and HILIC	[139, 140]
DND entrapped polymeric monoliths	Porosity was 75%, and median pore size was 1.56 μm	50 × 4.6 mm	ACN (20–85%)/water and methanol (85%)/water	PAHs	RP-HPLC and HILIC	[18, 173, 174]
MSDN	Particle size was 3.5–4.5 μm, surface area was 190 m ² g ^{−1} , and pore size was 3.7–3.9 nm.	150 × 4.6 mm, 150 × 4.0 mm, and 50 × 4.0 mm	ACN/water	Phenols, nitrogen-containing aromatic compounds (aniline, pyridine derivatives), transition metal cations, and inorganic anions	HILIC and ion-exchange	[75, 162, 167]
Core-shell particles with a carbon core and DND shell	Particle size was 3.6±0.06 μm, pore size was 180 Å, and surface area was 7.73 m ² g ^{−1}	100 × 2.1 mm and 33/100/150 × 4.6 mm	Acids, bases, and phosphate and ammonium formate buffers	Large proteins (interferon α-2A), benzenes, mAbs, therapeutic proteins, antibody-drug conjugates, cannabinoids (tetrahydrocannabinolic acid, bubble hash extract), inorganic anions, organic acids, anionic, cationic, and ampholytic organic compounds	RP-HPLC, ion-exchange, and HILIC	[19, 22-24, 169]
PS/DVB beads with entrapped DNDs	Particles size was 6 ± 2 μm, pore size was 50 Å, and surface area was 755 m ² g ^{−1}	120 × 4.6 mm and 150 × 4.6 mm	Methanol (85%) /water; 2 mmol L ^{−1} carbonate and 2 mmol L ^{−1} bicarbonate	Benzenes (toluene, benzaldehyde, phenol, benzoic acid, 1,4-hydroquinone, methyl p-hydroxybenzoate); Inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, hydrogen phosphate, sulfate)	RPLC, anion-exchange	[111]
PS/DVB beads with quaternised DNDs attached to the surface	Particle size was 7 μm	150 × 4.6 mm	2 mmol L ^{−1} carbonate and 2 mmol L ^{−1} bicarbonate	Inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, hydrogen phosphate, sulfate)	Anion-exchange	[170]
HPHT Diamond						
HPHT diamond particles	1.2 μm, 1.6 μm, and 1 μm non-porous particles	100/50 × 4.6 mm	<i>n</i> -hexane-2-propanol, ACN/water, methanol/water, and nitric and oxalic acids	Alkylbenzenes, PAHs, alkylphenylketones, phenols, aromatic acids and bases, benzoic and benzenesulfonic acids, nitrophenols, chlorophenols, organic bases, quaternary ammonium, and inorganic anions	ANP, HPLC, HILIC, and ion-exchange	[58, 87, 172]
CVD Diamond						
CVD coated DND and HPHT particles	Particle size was 20–60 nm, pore size was 4–10 nm, and surface area was 85–200 m ² g ^{−1} .	–	ACN/water	<i>n</i> -alkylbenzenes, uracil, methyl benzoate, toluene, and naphthalene	RP-HPLC	[99]

2.6. Conclusions

The three types of synthetic diamonds that are widely used in SPE and HPLC-based applications are DNDs, HPHT diamonds, and CVD diamonds. Both HPHT diamonds and DNDs typically have negatively charged surface groups (e.g. carboxyl and hydroxyl), which enable the selective adsorption of proteins and the development of cation-exchange and HILIC type phases. Moreover, the transparent and biocompatible nature of diamonds and their strong interaction with proteins allows easy and direct analysis of bound proteins with high-sensitivity analytical techniques. The micrometre size range of HPHT diamonds also allows their direct use in IC and HILIC type modes of extraction and separation, while the nanometre size range of DNDs requires their use in the form of MSDN, core-shell particles, or composites. DND-based core-shell particles have been developed using a variety of cores, such as silica, glassy carbon, and HPHT diamonds. The adsorption capacity of DND for cations is higher than most of the commonly used sorbents for radionuclide extraction. The use of CVD diamonds has been predominately limited to surface coatings because of the necessary expensive and slow deposition process. However, recently micrometre-sized mesoporous CVD diamond particles have also been developed. Since the advent of diamond-based adsorbents, interest in the use of diamond for various SPE and HPLC-based applications has increased considerably. Such adsorbents have great potential in the realisation of novel analytical applications due to their unique chemical and mechanical properties, and no doubt will provide new phases for specialist applications in the coming years.

CHAPTER 3

Ion-Exchange Properties of High Pressure High Temperature Synthetic Diamond

3.1. Abstract

The adsorption and chromatographic properties of microparticulated diamond (1-2 μm and 4-6 μm fractions) from high pressure and high temperature synthesis (HPHT diamond) are investigated, with a focus on their cation-exchange capacity. Several adsorbents were prepared, either by wet oxidation of the surface of HPHT with $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ or $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixtures, or by oxidation in air at 700°C , or following a four-step reduction using LiAlH_4 and *n*-butyl lithium. The zeta-potential profiles as a function of pH and ion-exchange capacities were measured for the prepared adsorbents as well as isotherms of adsorption. The ion-exchange selectivity of oxidised HPHT diamond was studied towards alkali, alkaline-earth and transition metal cations.

3.2. Introduction

Over the last decade, synthetic diamonds have attracted attention due to their unique physical and chemical properties, suitable for various applications [16, 175]. The exceptional hardness, optical transparency, extremely high thermal conductivity, combined with a very low coefficient of thermal expansion, facilitate the use of synthetic diamond as a useful material for the construction of heat exchangers [176, 177], polymer and metal composites [178, 179], electrodes [93], electronic devices [180], sensitive elements of analytical instruments [181], efficient chromatographic adsorbents [7], support for the preparation of catalysts [182] and other applications.

For many of the above listed applications the knowledge of the surface chemistry of synthetic diamond, including adsorption and ion-exchange properties is vital. The majority of investigations on the ion-exchange properties of synthetic diamond have been conducted using

detonation nanodiamond (DND) [76, 129, 183-185]. Bogatyreva *et al.* reported on the nature of cation-exchange properties of DND, occurring from the presence of negatively charged oxygen-containing groups [186]. The authors found that transition metals may be adsorbed by DND and observed the selectivity series: $\text{Fe}^{3+} > \text{Ni}^{2+} > \text{Cr}^{3+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ [186]. Such selectivity differs from typical ion-exchange selectivity, known for carboxylic cation-exchangers, and indicates the presence of a chelation mechanism during adsorption. Adsorption of di- and tri-valent metals cations and inorganic anions from aqueous solutions on microdispersed sintered detonation nanodiamond (MSDN) was carefully investigated by Peristyy *et al.* [75]. Surprisingly, significantly higher adsorption capacity for anions ($50\text{--}150\text{ }\mu\text{mol g}^{-1}$) in comparison with cations ($9\text{ }\mu\text{mol g}^{-1}$) was found under acidic conditions, which was connected with the occurrence of a high positive ζ -potential ($+40\text{ mV}$) on the DND surface [75]. The adsorption of transition metal cations by positively charged MSDN particles was attributed to complexation with surface carboxylic groups. Nesterenko *et al.* made similar conclusions regarding the adsorption mechanism for alkaline-earth and transition metal cations on MSDN and demonstrated its suitability as a promising stationary phase for ion chromatography [76].

There is sufficient information on adsorption and ion-exchange properties of DND and MSDN but significantly less data has been reported for other types of synthetic diamond such as high pressure high temperature (HPHT) diamond. However, the surface chemistry of DND differs from HPHT diamond microparticles, so such information is important for some common applications of HPHT diamond, including preparation of new adsorbents, catalysts, and other materials. In particular, in liquid chromatography, where the stationary phases with new selectivities are always in demand, HPHT diamond is considered a promising adsorbent [7]. The lack of information on the ion-exchange properties for HPHT and natural diamond is connected with low values of specific surface area ($2\text{--}5\text{ m}^2\text{ g}^{-1}$ for $1\text{--}2\text{ }\mu\text{m}$ particles) as compared to $150\text{--}350\text{ m}^2\text{ g}^{-1}$ for DND, which complicates the characterisation of the surface

properties. However, due to the density of 3.5 g cm^{-3} (comparing to the $\sim 1.0 - 1.2 \text{ g cm}^{-3}$ for silica) columns packed with diamond possess sufficient total area per column can be sufficient for the applications in chromatography. It was found for HPHT particles of size 500 nm that approximately 50 ppm out of $1.56 \times 10^{15} \text{ cm}^{-2}$ of surface carbon atoms present ionisable functional groups [183]. The surface charge of HPHT diamond can vary from +40 mV to -40 mV with pH, and its isoelectric point is 6.6. It should be noted that the reasons for the occurrence of an overall positive charge are not yet clear.

The electrophoretic mobility and zeta potential of submicron particles (particle size, $d_p < 0.5 \text{ }\mu\text{m}$) of synthetic (CVD) and natural diamond were measured using the electrokinetic sonic amplitude technique [187]. The measurements were conducted for aqueous colloidal suspensions containing 0.2 g L^{-1} of diamond particles. Zeta potential of natural diamond varied from -6 mV at pH 2.0 to -38 mV at pH 12 and from +9 mV at pH 2 to -11 mV at pH 12 for CVD synthetic diamond. Isoelectric points of 3.5 and 4.5 were obtained for CVD and natural diamond, respectively, showing weak acid properties of the surface functional groups.

To the best of our knowledge there are no publications on the adsorption properties of HPHT diamond. Therefore, the aim of this investigation was to characterise the ion-exchange properties of synthetic HPHT diamond, with an emphasis placed upon the ion-exchange selectivity and adsorption mechanism for the potential use in liquid chromatography. Several modified HPHT diamond samples were studied.

3.3. Experimental

3.3.1. Materials and reagents

Two batches (B1 and B2) of bare HPHT diamond differing in d_p (1-2 μm and 2-4 μm , according to the manufacturer) were purchased from Hunan Real Tech Superabrasive & Tool Co. Ltd. (Changsha, Hunan, China). Non-carbon impurities in these batches of HPHT diamond were determined as previously described by Mitev *et al.* [73, 164].

Deionised water (DIW) from Milli-Q® Integral Water Purification System (Millipore, North Ryde, Australia) was used for the fractionation of particles by sedimentation and preparation of solutions. HNO_3 (70 wt. %, RCI Labscan Limited, Thailand), NaOH (The British Drug Houses Ltd, England), KOH (Sigma-Aldrich, Castle Hill, NSW, Australia), and oxalic acid (AnalaR, Nowra, NSW, Australia) were used for the preparation of the eluent for ion chromatography, fractionation and purification of HPHT diamond, and for pH adjustment during zeta potential measurements and acid-base potentiometric titration.

Aqueous solutions of lithium, sodium, magnesium, barium nitrates (The British Drug Houses Ltd, England), potassium, calcium nitrates (Ajax Finechem Unilab, Sydney, NSW, Australia), rubidium, cesium nitrates (Hopkin & Williams Ltd, Swansea, Wales, United Kingdom), ammonium nitrate (Prolabo, Paris, France), strontium nitrate (Griffin & George Ltd, England) were used as cation standard solutions. An aqueous solution of potassium hydrogen phthalate (Ajax Finechem Unilab, Sydney, NSW, Australia) was used for normalisation of aqueous solutions of NaOH , which in turn was used for normalisation of HCl (36 wt. %, RCI Labscan Lt, Thailand). Normalised solutions were used for the acid-base potentiometric titration of the HPHT diamond samples with a Titrando 809 autotitrator (Metrohm, Switzerland).

3.3.2. Instrumentation

Zeta potential measurements were conducted using a Model Zen 3600 Nanoseries Zetasizer (Malvern Instruments, Malvern, Worcestershire, UK). Surface area was calculated using the Brunauer-Emmett-Teller (BET) method from data on low-temperature nitrogen adsorption/desorption, collected using a TriStar II 3020 instrument (Micromeritics Gemini, Georgia, USA). Images of magnified HPHT diamond particles are obtained using a Hitachi SU-70 (Hitachi Ltd., Chiyoda, Tokyo, TKY, Japan) field emission scanning electron microscope (SEM) and (1.5 keV) electron beam. Titrand 809 autotitrator (Metrohm, Switzerland) was used for the determination of the ion-exchange capacity of modified HPHT diamond samples by acid-base potentiometric titration (details are presented in the Supplementary Section 3.6.2). FTIR spectra of HPHT diamond were obtained using Bruker MPA infrared spectrometer (Billerica, MA, USA) under the Diffuse Reflectance mode. Prior to measuring FTIR spectra, HPHT diamond powder was dried overnight at 100 °C in a vacuum (0.4 atm) oven. Potassium bromide tablets containing 2.25 w/w % of dried diamond powder were used for collecting spectra. Raman spectra were measured with Bruker FRA 106 Raman spectrometer coupled with a Raman Scope (microscope) (Billerica, MA, USA).

An Accela 1250 (Thermo Fisher Scientific, Waltham, MA, USA) chromatographic system equipped with a spectrophotometric detector and a Model 430 conductivity detector (Waters Corporation, Milford, MA, USA) coupled with a PowerChrom 280 analog-to-digital converter (eDAQ, Denistone East, NSW, Australia) was used to study the adsorption properties of HPHT diamond. Data collection and processing was performed using ChromQuestTM software (Thermo Fisher Scientific, Waltham, MA, USA) and PowerChrom software (eDAQ, Denistone East, NSW, Australia). A simplified method for the calculation of the adsorption isotherms from the chromatographic data was used, as presented in the Supplementary Section 3.6.3.

Unless otherwise stated, retention times were recorded at peak maximum and the void time was determined via baseline disturbance from the injection of the mobile phase.

Empty stainless-steel columns (Phenomenex, Lane Cove West, NSW, Australia) were used for packing of oxidized HPHT diamond. After packing was completed, the columns were equilibrated with mobile phase (aqueous HNO_3) until retention times were stable ($\pm 1\%$).

3.3.3. Preparation and modification of diamond samples

3.3.3.1. Fractionation of HPHT particles on size

Initially the bare HPHT diamond was carefully washed with 10 mM KOH and 10 mM HNO_3 solutions. The fractionation of the HPHT diamond particles based upon size was performed according to a slightly modified procedure first described by Peristyy *et al.* [172] with 5 mM KOH used as sedimentation medium. The particle size (d_p) distribution was obtained by analysis of SEM images of isolated fractions using Image J software (National Institute of Health, USA). The so-prepared HPHT diamond was then subjected to various treatments as described below, in order to modify surface chemistry. The abbreviations for the prepared samples are explained in the footnote to the Table 3.1.

3.3.3.2. Oxidation with Piranha mixture (PIF sample)

Oxidation of diamond particles was performed using slightly modified method described by Torrenge *et al.* [188]. 200 g of HPHT diamond were placed into 1 L glass beaker, then 60 mL of DIW water, 90 mL of 50 wt.% H_2O_2 (Sigma Aldrich, USA) and 450 mL of 98 wt.% H_2SO_4 (Merck, Germany) were added and the suspension was heated in water bath for 1 hour at 100 °C. After the suspension had sedimented, the clear liquid layer was decanted, and then 600 mL of DIW were added using an ice bath. Again, after the precipitation of the diamond particles,

the liquid was decanted and another 600 mL of DIW water was added. This washing procedure was repeated 3-4 times until pH 2-3 in the washing waters achieved, and then the precipitate was dried overnight at 100 °C in oven.

3.3.3.3. *Oxidation using HNO₃/H₂SO₄ mixture (NS1F and NS2F samples)*

A mixture of 10 mL of 70% HNO₃ and 10 mL of 98% H₂SO₄ was added to 5 grams of HPHT diamond and the obtained suspension was boiled for 1 hour as described in [189]. Then, the HPHT diamond was washed with DIW until a neutral pH of the washing waters was achieved, and then dried at 80 °C in the oven.

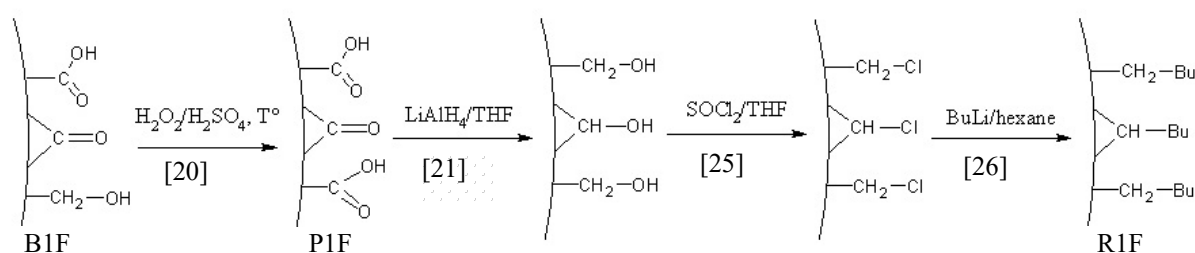
3.3.3.4. *Oxidation in an air (A1 sample)*

HPHT diamond was heated in air using a Woodrow AF-3 furnace (Woodrow, Kilns, Bankstown, NSW, Australia). The heating rate was 5 °C per minute until a target temperature of 700 °C was reached. Sample was then kept at this temperature for 1 hour and cooled down to room temperature at a rate of 10 °C per minute.

3.3.3.5. *Reduction with LiAlH₄/butyl lithium (R1F and R2F samples)*

For a reduction of the HPHT diamond surface, a four-step method was suggested, as shown in the Scheme 3.1. In the first step, HPHT diamond was oxidised using Piranha mixture, as described in the Section 3.3.3.2. Then 20 g of the prepared diamond was dried overnight at 100 °C. The dry oxidised diamond was then suspended in 20 mL of tetrahydrofuran (THF, Merck, Germany). Then a solution of 0.5 g of LiAlH₄ (97%, Alfa Aesar, USA) in 20 mL of THF was added dropwise to the suspension and reaction mixture was left for 1 hour [190]. 10 mL of 5 M HNO₃ were then added to quench the reaction until the disappearance of bubbles. 100 mL of 1 M NaOH was then added and the mixture was heated in a water bath for 15 minutes. The diamond was decanted and washed with 0.1 M sodium citrate (pH 6.4) and several times with

DIW until neutral pH. Complete removal of Al was confirmed by the Raman spectroscopy of the prepared sample (see Supplementary Figure 3.8) by absence of Raman shift in the region $300 - 700 \text{ cm}^{-1}$ characteristic for aluminium oxides and hydroxides [191, 192]. At this step carboxylic groups on the surface of HPHT diamond were converted to hydroxyls and the prepared product was dried overnight at 100°C .



Scheme 3.1. Four-step modification procedure for HPHT diamond used in this work.

In the next step, a mixture of 30 mL of THF and 5 mL of thionyl chloride (Ajax Finechem Unilab, Sydney, NSW, Australia) was added to the hydroxylated HPHT diamond and the suspension was left overnight [193]. Following this, 150 mL of DIW was added, the solution decanted, and after washing the obtained product, now with hydroxyls converted to chloro-groups, dried overnight at 100°C . Finally, the chlorinated HPHT diamond was suspended in 30 mL of *n*-hexane and reacted with 5 mL of 1.6 M *n*-butyl lithium in *n*-hexane (Sigma Aldrich, USA) overnight at room temperature [194]. The final product was washed with isopropanol and DIW and dried at 100°C . At this stage it was expected that all chloro- groups were converted into butyl groups.

3.4. Results and Discussion

3.4.1. Fractionation of HPHT diamond particles on size

According to the manufacturer's passport for the obtained samples B1 and B2 had particles within ranges from 1.0 to 2.0 and from 2.0 to 4.0 μm , respectively, but a much broader distribution of particles of size (0.1-2.5 μm for B1 and 2.0-6.0 μm for B2) was found experimentally (see Supplementary Table 3.5 and Supplementary Figure 3.6). This may cause extra peak broadening and high backpressure in chromatographic experiments as well as additional difficulties in handling HPHT diamond particles in other experimental work. Therefore, the diamond particles were fractionated using repetitive sedimentation procedures from 5 mM KOH solution (see details in Supplementary Section 3.6.1) prior to modification and adsorption tests. As result (Supplementary Figure 3.6), the complete removal of the fine particles with $d_p < 0.7 \mu\text{m}$ in B1F sample (F in sample name means fractionated) and of particles with $d_p < 3 \mu\text{m}$ and $d_p > 5.7 \mu\text{m}$ for B2F sample. The average particle size ($d_{p,mean}$) increased slightly from 1.27 to 1.38 μm , for the B1F sample, but did not change significantly for the B2F sample, with size of 4 μm (see Supplementary Table 3.5). The ratio of D_{90}/D_{10} decreased for both samples by $\sim 35\%$.

3.4.2. Characterisation of HPHT diamond

3.4.2.1. Surface area

The ion exchange capacity of an adsorbent depends on the density of ion-exchange groups at the surface and its specific surface area. The values of specific surface area (S_{BET}) for the studied samples, as well as the values of ion exchange capacity and surface concentrations of ionic groups are presented in Table 3.1. As expected, the removal of the fine particles during fractionation results in a significant decrease of the S_{BET} values for both B1F and B2F. At the

same time, the chemical modifications did not affect the surface area values significantly, which confirms the stability of HPHT diamond particles under the harsh oxidation and reduction conditions applied. S_{BET} values for HPHT diamond particles varied within 1.00 – 1.04 m² g⁻¹ and 2.0 – 2.3 m² g⁻¹ for the 2F and 1F sets of samples. This is significantly less than for many commercial ion-exchangers and complicates the investigation of the ion-exchange properties of HPHT diamond, and would be a probable reason for the lack of data on this aspect. For this reason, HPHT diamond particles with d_p of 1-2 μm, with the higher surface area, provide greater retention of analytes in chromatographic columns and allow more accurate determination of adsorption parameters, so they were used here for the characterisation of these ion-exchange and adsorption properties. The use of particles with $d_p < 1$ μm is more challenging and requires significantly higher pressures applied to the chromatographic columns.

Table 3.1. BET specific surface area (m^2g^{-1}) and surface concentration of protogenic groups (groups nm^{-2}) of HPHT diamond samples used in this work.

Sample	S, m^2g^{-1}	IEC, $\mu\text{eq g}^{-1}$	Surface concentration, groups nm^{-2}	Column dimensions, length $\times$ ID (mm)
B1	5.6 $\pm$ 0.2	-	-	-
B1F	2.32 $\pm$ 0.11	3.1 $\pm$ 0.3	0.8 $\pm$ 0.2	50 $\times$ 4.6
A1	5.1 $\pm$ 0.2	9.4 $\pm$ 0.6	1.1 $\pm$ 0.3	-
P1F	2.01 $\pm$ 0.13	7.0 $\pm$ 0.4	2.1 $\pm$ 0.4	100 $\times$ 4.6
NS1F	2.12 $\pm$ 0.13	-	-	-
R1F	2.12 $\pm$ 0.13	2.5 $\pm$ 0.2	0.7 $\pm$ 0.1	-
B2	1.65 $\pm$ 0.10	-	-	-
B2F	1.04 $\pm$ 0.08	1.6 $\pm$ 0.2	0.9 $\pm$ 0.2	50 $\times$ 4.6
P2F	1.00 $\pm$ 0.07	3.7 $\pm$ 0.3	2.2 $\pm$ 0.5	-
NS2F	1.01 $\pm$ 0.08	3.0 $\pm$ 0.3	1.8 $\pm$ 0.4	-
R2F	1.01 $\pm$ 0.07	1.8 $\pm$ 0.2	0.7 $\pm$ 0.1	-

* In the sample abbreviations, letter(s) preceding the number stand for the type of surface modification (B = bare (unmodified), P = oxidised with Piranha (Section 3.3.3.2), A = oxidised in air (Section 3.3.3.4), NS = oxidised with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (Section 3.3.3.3), R = reduced (Section 3.3.3.5)). Numbers stand for the particle size (according to the manufacturer; “1” for 1-2 μm and “2” for 2-4 μm batches), and the letter “F” at the end indicates whether the sample was subjected to the size fractionation by sedimentation (see Supplementary Section 3.6.1) or not. For the calculation of surface concentration of protogenic groups see section 3.6.2.

3.4.2.2. FTIR

All procedures used in this work for modification of diamond surface have been previously described in the literature (see Scheme 3.1 and references there), it was important to confirm the preparation of intended products. This is not a trivial task because of small specific surface area (2-3 m^2g^{-1}) of HPHT diamond microparticles used in this work. The maximum concentration of functional groups (e.g. carboxylic) in fully oxidised is about 2.3 groups/ nm^2 , which is equivalent of 7.6-11.2 micromoles per gram of HPHT diamond particles. In reality, absolute amounts of target functional groups in HPHT diamond is even less. For example, for

FTIR analysis maximum 2.25 % and 10 % of diamond powder in potassium bromide pellet tablets method and in a mixture with potassium bromide in diffusive reflectance mode, respectively. This means that the changes in HPHT surface chemistry must be detected at sub-micromolar concentration level, which is very close to limits of possibilities of FTIR. Also, it explains very limited literature data available on surface characterisation of HPHT diamond microparticles using FTIR, Raman and XPS. Supplementary Figure 3.7 presents the FTIR spectra of samples B1F, P1F, R1F samples, along with the intermediate samples treated with LiAlH_4 and SOCl_2 (see Section 3.3.3.5).

Firstly, the oxidation with $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ results only in slight increase in intensity of $\text{C}=\text{O}$ bands at 1725 and 1790 cm^{-1} . At the same time, such oxidation treatment increases ion-exchange capacity (IEC) from 3.1 for B1F to 7.0 $\mu\text{eq}\cdot\text{g}^{-1}$ for P1F sample (see Section 3.3.3.2 and Table 3.1). This indicates that the surface of initial B1F sample (bare diamond particles as obtained and washed with alkali and acid) is already fairly oxidised and contains some carbonyl groups, so further oxidation treatment with $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ results in conversion of $\text{C}=\text{O}$ into COOH (sample P1F), thus increasing IEC. This is in agreement with the data of XPS study of samples B1F and P1F (see Supplementary Figure 3.9 and Supplementary Table 3.6). Clearly, the XPS spectra before and after oxidation are nearly identical, and surface oxygen content is the same within the error. The following reduction of P1F with LiAlH_4 causes appearance of bands at 1005, 1365 and 3435 cm^{-1} in a spectrum of R1F sample, which can be attributed to O-H bend, C-O stretch, and C-O-H in-plane bend, respectively. Clearly, this is due to the appearance of elevated concentration of hydroxyl groups at the surface after the reduction. The further treatment with SOCl_2 results in the appearance of a band at 730 cm^{-1} , related to C-Cl stretch, due to the substitution of hydroxyls with chlorine. Finally, FTIR spectrum of R1F shows C-H related bands in 2850 – 3000 cm^{-1} region, confirming presence of butyl moieties upon HPHT diamond surface.

3.4.2.3. Zeta potential and acid base potentiometric titration

Figure 3.1 presents plots showing changes in zeta potential (ζ) with the pH for the different HPHT diamond samples. As expected, negative ζ -potentials over the entire pH range were recorded for all samples with instantly increasing ζ values with higher pH. A maximum negative surface charge (-70 mV) was recorded for the P1F sample prepared by oxidation of the HPHT diamond with the Piranha mixture, while other oxidised samples did not show significant differences as compared with the bare diamond (B1F). The surface of the reduced diamond, R1F, was substantially less charged as compared with other samples, especially at neutral pH, but had a similar charge under alkaline conditions, as compared to B1F sample. Such an effect was also noted by Shergold and Hartley who reported no difference in the electrophoretic mobilities of bare and methylated HPHT diamond samples [195].

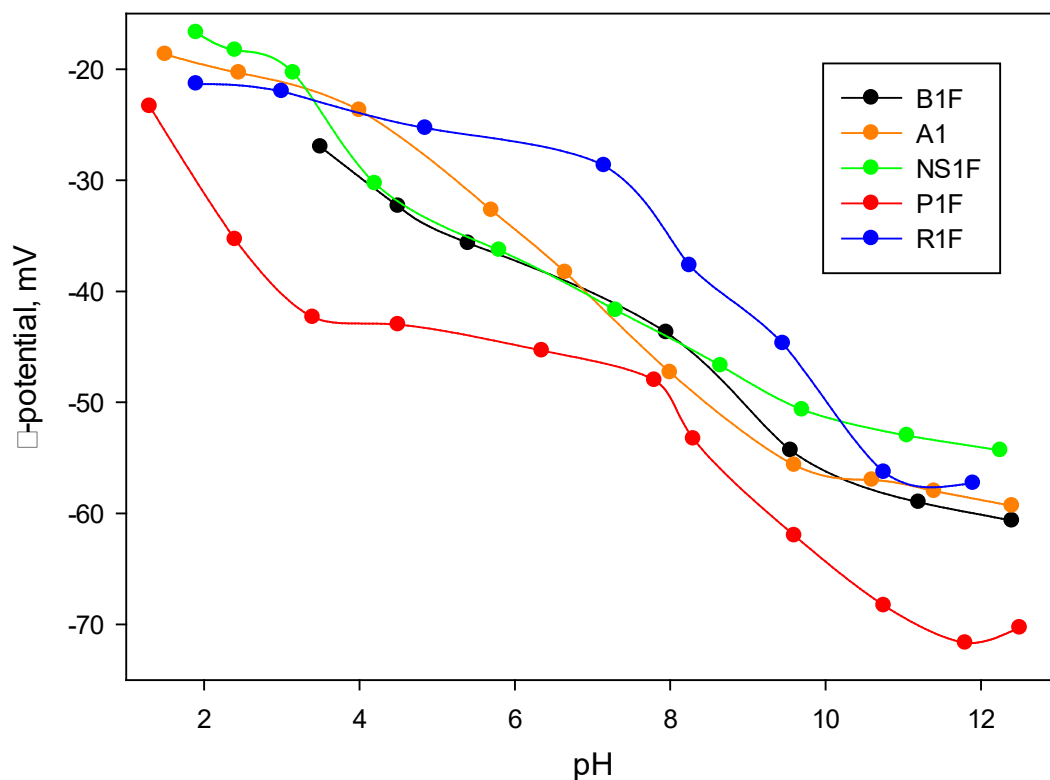


Figure 3.1. ζ -potential v pH dependences for differently treated HPHT diamond samples. 25°C, $\mu = 0.01$ M, pH adjusted with HNO_3/KOH .

There are data in the literature on the ζ -potential of DND [196-199], and natural diamond [129, 200, 201], but much less attention has been paid to the surface charge measurement for CVD diamond [129] and HPHT diamond [195]. The dissociated carboxyl- and hydroxyl- groups are unambiguously responsible for the negative surface charge of various types of diamond [195, 202, 203]. At the same time, positive ζ -potential can be normally observed under acidic conditions for DND due to the presence of impurities or carbonyls in sp^2 carbon surface layer, but not for HPHT diamond [196]. Overall, the data in Figure 3.1 suggests that oxidation with Piranha mixture had the strongest effect on the surface charge of the HPHT diamond, which was also confirmed by the following experiments using potentiometric acid base titrations.

The results of the acid-base titration of HPHT diamond samples showed that the surface concentration of carboxylic groups was highest for the P1F and P2F samples. Other oxidation methods increase the ion-exchange capacity (IEC) of HPHT diamond but to a lesser degree. Apparently, the reduction of the HPHT diamond surface, as described in Section 3.3.3.5, was not complete, since the concentration of acidic groups in the B1F and R1F samples differs insignificantly. As expected, the IEC of the P1F sample was nearly twice that for P2F, reflecting the difference in the surface area for these samples. This fact suggests that particle size does not influence the reactivity of the HPHT diamond surface during oxidation and reduction reactions. Again, the data from acid-base titrations confirmed that the treatment of HPHT diamond with the Piranha mixture provided the most efficient oxidation of the surface. The concentration of 2.1-2.2 carboxylic groups per nm^2 obtained with Piranha treated samples is higher than the values of 1.40 and 1.49 acidic groups per nm^2 reported for MSDN and oxidized activated carbon, respectively [75, 204].

3.4.3. Ion-exchange properties

Due to the very low ion-exchange capacities of the prepared HPHT diamond samples, the investigation of the adsorption of alkaline, alkaline-earth and transition metal cations and selectivity of ion-exchange was studied under chromatographic conditions with the adsorbents packed in short (50 x 4.6 mm ID) stainless steel columns. The retention factors (k) of cations are calculated as:

$$k = t_R/t_0, \quad (\text{Eqn. 1})$$

where t_R and t_0 are retention times of ions and non-retained solvent. The retention factors are proportional to the distribution constant K_D

$$k = K_D \cdot \varphi, \quad (\text{Eqn. 2})$$

where φ is phase ratio, constant for the selected chromatographic column.

3.4.3.1. Influence of oxidation and reduction

Table 3.2 compares the separation selectivity $\alpha = k_2/k_1$ obtained for alkali and alkali earth metal ions for the columns packed with B1F, P1F and R1F adsorbents. The retention order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ was observed for all columns, reflecting the typical ion-exchange selectivity of carboxylic cation-exchangers [205]. The metal cations were significantly (~40%) stronger retained on the column packed with oxidised diamond P1F, as compared to bare diamond B1F, due to the higher IEC (see Table 3.1 and Figure 3.1). Similarly, an approx. ~30% reduction in retention of these cations on the reduced diamond R1F was noted, as compared to B1F. Good separation selectivity ($\alpha_{\text{NH}_4^+/\text{K}^+} \approx 2.3$) for NH_4^+ and K^+ was achieved with all columns.

Table 3.2. Selectivity of retention of alkali and alkali earth metal cations on columns packed with B1F, P1F and R1F, relative to Li^+ . Flow rate 0.5 mL min^{-1} , 25°C , injections of 10 mM of cation (in nitrate form) in eluent.

Conditions	Cation	Selectivity, α		
		B1F	P1F	R1F
Eluent: 10 mM HNO_3 , Inj. volume: $5 \mu\text{L}$	Li^+	1.00	1.00	1.00
	Na^+	1.61	1.63	1.33
	NH_4^+	1.78	2.19	1.44
	K^+	4.17	5.31	3.11
	Rb^+	4.67	6.75	3.78
	Cs^+	5.22	7.88	4.33
Eluent: 50 mM HNO_3 , Inj. volume: $10 \mu\text{L}$	Mg^{2+}	1.00	1.00	1.00
	Ca^{2+}	1.20	1.51	0.68
	Sr^{2+}	1.78	1.80	0.74
	Ba^{2+}	2.84	2.72	1.42

In the case of alkaline earth metal cations, similar separation selectivity, with retention order $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$, was observed for both B1F and P1F adsorbents. However, the R1F adsorbent exhibited stronger retention for Mg^{2+} than for Ca^{2+} and Sr^{2+} . This type of separation selectivity indicates that the reduction of the HPHT diamond surface changes the coordination of alkaline earth metal cations by the carboxyl groups. For example, the retention due to complexation at the surface of carboxylic cation exchangers may result in the retention order $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$, which is orthogonal to that known for a pure ion-exchange mechanism [206, 207]. Therefore, in the case of R1F, the modification of the surface could result in a relatively larger contribution of the hydrophobic properties of the surface into the retention for alkaline earth metal cations, with resulting intermediate selectivity $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Mg}^{2+} < \text{Ba}^{2+}$. A reason for this is possible changes in the size of the hydrated radii of cations approaching such hydrophobic surfaces and related changes in the strength of electrostatic interactions between cation and carboxylic group.

3.4.3.2. Adsorption isotherms

The adsorption isotherms for metal cations were calculated from the corresponding chromatographic peaks according to the method described within the Supplementary Section 3.6.3. For all metals, the classic Langmuir type adsorption isotherm was observed. Figure 3.2 presents the adsorption isotherms for P1F adsorbent, and Table 3.3 lists the parameters obtained for the Langmuir isotherm (Eqn. 3):

$$A = \frac{A_{max}K_L C}{1 + K_L C} \quad (\text{Eqn. 3})$$

where A_{max} is maximum adsorption achieved with increasing solute concentration (C), K_L is a slope of adsorption isotherm in the area of low concentration, and A is adsorption.

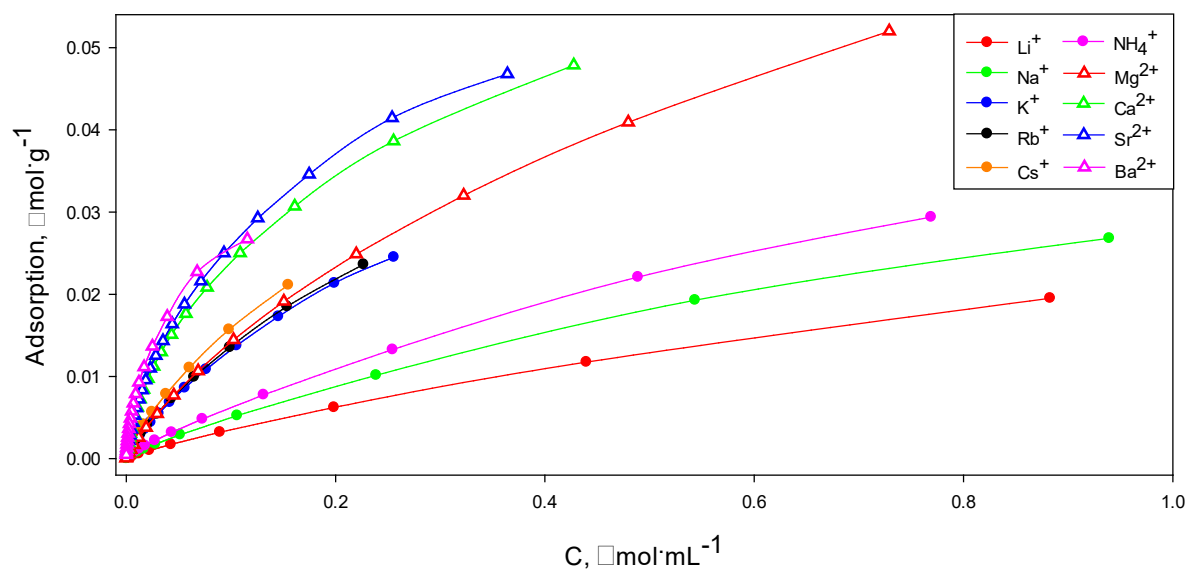


Figure 3.2. Adsorption isotherms for alkali and alkali earth metals cations on P1F diamond obtained from chromatographic peak (see Supplementary Section 3.6.3). Eluent 50 mM HNO₃, 0.5 mL min⁻¹, 25°C, 5 μL injections of 100 mM of cation as nitrate salt dissolved in the eluent.

Table 3.3. Calculated parameters of approximation of adsorption isotherms in Figure 3.2 with Langmuir model (Eqn. 3) and ionic radii of cations.

Cation	A_{max} , nmol g ⁻¹	K_L , mL g ⁻¹	R ²	Ionic radius, pm	Hydrated radius, pm
Li ⁺	46±3	0.80±0.05	1.000	94 ^a	382 ^a
Na ⁺	57±4	0.93±0.05	1.000	117 ^a	358 ^a
NH ₄ ⁺	67±4	1.00±0.07	1.000	148 ^a	331 ^a
K ⁺	48±3	3.97±0.26	0.999	149 ^a	331 ^a
Rb ⁺	48±3	4.18±0.28	0.999	163 ^a	329 ^a
Cs ⁺	43±4	6.02±0.39	0.999	186 ^a	329 ^a
Mg ²⁺	104±9	1.43±0.13	0.999	90 ^b	800 ^b
Ca ²⁺	59±8	7.83±0.48	0.990	140 ^b	600 ^b
Sr ²⁺	59±8	8.71±0.50	0.993	170 ^b	500 ^b
Ba ²⁺	32±5	33.8±3.3	0.992	210 ^b	500 ^b

Values of ionic radii of cations are adapted from (a) -Volkov *et al.* [208] and (b) - Kielland [209].

Maximum adsorption for alkali metal cations was around 50 nmol g⁻¹, which indicates that their adsorption was due to cation exchange on carboxylic groups, when IEC is proportional to the concentration of carboxylic groups upon the surface [207]. A slightly higher maximum of adsorption was noted for NH₄⁺, which can be explained by the occurrence of specific interactions between NH₄⁺ and oxygen containing groups at the surface [210]. For alkaline earth metals, A_{max} value decreased in the series Mg²⁺ > Ca²⁺ > Sr²⁺ > Ba²⁺, which is similar to the results of Gordeev *et al.* [211], who reported a higher maximum adsorption capacity for Ca²⁺ as compared with Ba²⁺ for oxidised diamond. In the latter work the authors proposed the adsorption of monovalent cations in the form of [MOH]⁺ ions on isolated carboxylic groups.

K_L values (see Table 3.3) are proportional to the distribution coefficients (K_D) obtained for diamond in diluted nitric acid as an eluent. For alkali metal cations, K_L values increase in the series Li⁺ < Na⁺ < NH₄⁺ < K⁺ < Rb⁺ < Cs⁺, and Mg²⁺ < Ca²⁺ < Sr²⁺ < Ba²⁺, which is in

accordance to their ionic radii listed in Table 3.3. This observation is in agreement with the ion-exchange retention mechanism common for carboxylic cation-exchangers [207].

Both oxidation of B1F with the Piranha mixture and reduction with n-butyl lithium can substantially change the surface ζ -potential and the IEC, and therefore affect the adsorption isotherms for metal cations. The adsorption isotherms for K^+ and Mg^{2+} ions on B1F, P1F, and R1F samples are shown in Figure 3.3. Clearly, the shape of adsorption isotherms was similar for all HPHT diamond samples, indicating the main adsorption mechanism does not depend on the surface treatment. Supplementary Table 3.6 presents the parameters for adsorption isotherms shown in Figure 3.3 and approximated using Langmuir model (Eqn. 3). For K^+ and Mg^{2+} , the A_{max} values did not change significantly after oxidation or reduction treatment. This indicates that the total concentration of various functional groups upon the surface had not changed significantly, but their ratio is varied. This hypothesis is in agreement with the obtained K_L values, which increase in the series $R1F < B1F < P1F$. Clearly, oxidation leads to a proportionally higher amount of acidic groups on the surface of the P1F sample, which interacts stronger with metal cations, while reduction causes the opposite effect for R1F sample. Interestingly, according to the data in Supplementary Table 3.6 and Supplementary Table 3.7, the A_{max} values are in the range $30 - 100 \text{ nmol g}^{-1}$, which is ~ 100 times lower than IEC values of $2 - 10 \text{ } \mu\text{eq g}^{-1}$ obtained by acid-base titration (Table 3.1). This difference is due to the fact that IEC values were obtained under alkaline conditions, where more functional groups are dissociated and are available for interaction with metal cations. Accordingly, under acidic conditions ($\text{pH} \sim 1.3$ in Figure 3.2 and Figure 3.3), only a small proportion of these groups can coordinate metal cations, which decreases the apparent A_{max} values.

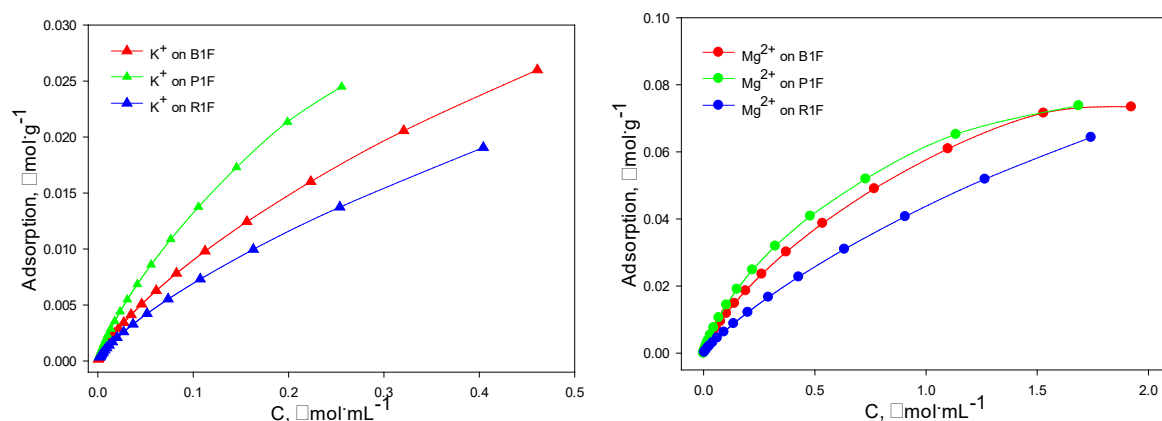


Figure 3.3. Adsorption isotherms for K^+ (left) and Mg^{2+} (right) on B1F, P1F, and R1F diamond obtained from chromatographic peak (see Section 3.4.3.3). Eluent 50 mM HNO_3 , 0.5 mL min^{-1} , 25°C , $5\text{ }\mu\text{L}$ injections of 50 mM of cation as nitrate salt dissolved in the eluent.

3.4.3.3. Retention of transition metals and influence of eluent concentration

As mentioned in the Introduction, there is no data on adsorption of transition metal cations by HPHT diamond. As shown in Table 3.4 the retention of transition metals on P1F increases in the series $Mn^{2+} < Cd^{2+} < Ni^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Cr^{3+}$. This is different from the selectivity $Cd^{2+} < Pb^{2+} < Cr^{3+} < Ni^{2+} < Fe^{3+}$ previously reported by Bogatyreva *et al.* for DND [186, 212] and the selectivity series $Cd^{2+} < Ni^{2+} < Co^{2+} < Zn^{2+} < Mn^{2+} < Cu^{2+} < Fe^{3+} < Al^{3+}$ known for MSDN [75], but is close to the selectivity $Mn^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$ reported by Strelko and Malik for oxidised carbon [213]. Clearly, the adsorption of transition metal cations on HPHT diamond is due to ion exchange interactions, as can be concluded from the results of ζ -potential measurements and acid base titrations (Section 3.4.2).

Table 3.4. The slopes of $\log k - \log C_{\text{HNO}_3}$ dependences for metal cations c for P1F diamond as approximated with Eqn. 4 and k values.

Cation	x/y (tg α)	R^2	k
Li ⁺	0.71	0.994	0.24 ^a
Na ⁺	0.58	0.986	0.35 ^a
NH ₄ ⁺	0.56	0.988	0.49 ^a
K ⁺	0.48	0.984	1.11 ^a
Mg ²⁺	1.04	0.986	3.12 ^a
Cr ³⁺	2.52	0.995	9.4 ^b
Mn ²⁺	1.69	0.994	0.68 ^b
Co ²⁺	1.72	0.997	1.29 ^b
Ni ²⁺	1.86	0.992	0.92 ^b
Cu ²⁺	1.79	0.998	2.05 ^b
Zn ²⁺	1.68	0.995	0.99 ^b
Cd ²⁺	1.6	0.998	0.89 ^b

^a in 5 mM HNO₃^b in 50 mM HNO₃

The indirect evidence for these dominant ion exchange interactions can be obtained from analysis of the relationship between the logarithms of k and eluent concentration [214-216]. According to the equivalent ion exchange of metal cations with H⁺ at carboxylate groups, the retention of cations should obey the following equation:

$$\log k = C_1 - \left(\frac{x}{y}\right) \cdot \log[H^+] \quad (\text{Eqn. 4})$$

where $[H^+]$ – is the molar concentration of the eluent influencing the retention, x and y are the charges of exchanging cations, and C_1 is a constant relating to the properties of the column.

The $\log k - \log[H^+]$ dependences obtained for different cations with the P1F adsorbent were linear (Figure 3.4) with the slope and correlation coefficients (R^2) given in Table 3.4. The calculated values of x/y varied in the range from 0.48 to 0.71 for monovalent metal cations,

1.04 for the divalent magnesium cation, in the range from 1.6 to 1.84 for the doubly charged transition metal cations, and 2.52 for trivalent cation Cr^{3+} . For all cations these values are below theoretically expected, which can be explained by the variation of IEC of the column during experiment. In this set of experiments (Figure 3.4), the concentration of HNO_3 ranged from 1 to 65 mM, which corresponds to the pH change from 3.0 to 1.2. Accordingly, the ζ -potential for P1F adsorbent changes from -40 to -23 mV (Figure 3.1). In the case of divalent and trivalent metal cations, the possibility of complexation with two carboxylic groups on the surface can be taken into consideration [217], and may also affect slopes. However, the obtained retention selectivity for P1F adsorbent suggests that the contribution of complexation to the retention of transition metal cations was insignificant.

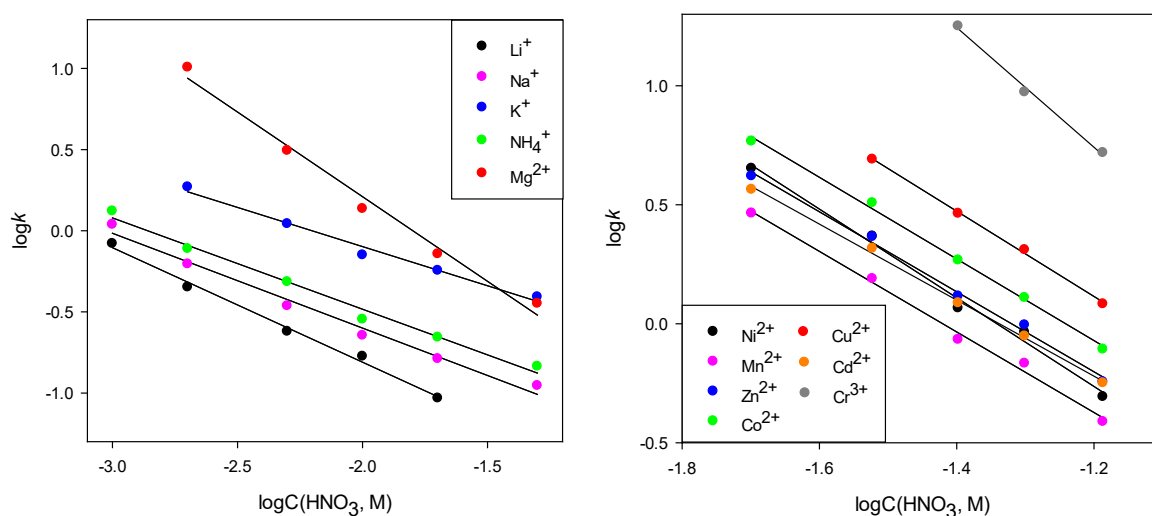


Figure 3.4. $\log k - \log C_{\text{HNO}_3}$ dependences for retention of alkali and alkali earth (left) and transition metals cations (right) on P1F diamond. Eluent flow rate – 0.5 mL min^{-1} , 25°C , injections of 10 mM of cation as nitrate salt dissolved in the eluent, injection volume 5 μL (left figure) or 2 μL (right figure).

3.4.3.4. Application of HPHT diamond for separation of cations

The high selectivity obtained for the column packed with oxidised HPHT diamond can be used for the liquid chromatographic separation of metals cations and charged molecules. The stainless steel column 50×4.6 mm ID was well-packed with P1F diamond sample and had separation efficiency of 36,740 plates m^{-1} as calculated from the chromatographic peak of cytosine in a test chromatogram of shown in Figure 3.5a. The complete separation of 4-hydroxybenzenesulphonic acid, cytosine, benzyltributylammonium chloride and benzyltrimethylammonium chloride was achieved in less than 10 minutes using mixture of 85 % acetonitrile – 15% 10 mM NaOH in water as the eluent.

Figure 3.5b presents the separation of a mixture of Li^+ , NH_4^+ , K^+ , Mg^{2+} and Cs^+ using a longer (100×4.6 mm ID) column packed with the P1F adsorbent and 10 mM HNO_3 as the eluent. This column demonstrated good separation selectivity of metal cation, but distorted peaks of for two last eluted peaks of Cs^+ and Mg^{2+} was observed. This effect is due to partial overloading effect of the chromatographic column. The problem was solved by using 12 mM oxalic acid as the eluent, which provides a better separation selectivity of metal cations and improves peak shape for Mg^{2+} . Clearly this effect is related to the ability of oxalic acid to form complexes with alkaline earth metals. Accordingly, addition of oxalate to the eluent improved peak shape for Mg^{2+} . The column efficiency calculated from the chromatographic peak of Na^+ with 12 mM oxalic acid was 27,000 plates m^{-1} , which is slightly less than mentioned above value of column efficiency obtained for cytosine. Probably, the lower efficiency observed for metal cations is defined by slow kinetics of ion exchange itself, which for some reason is a rather slow process for the oxidised diamond.

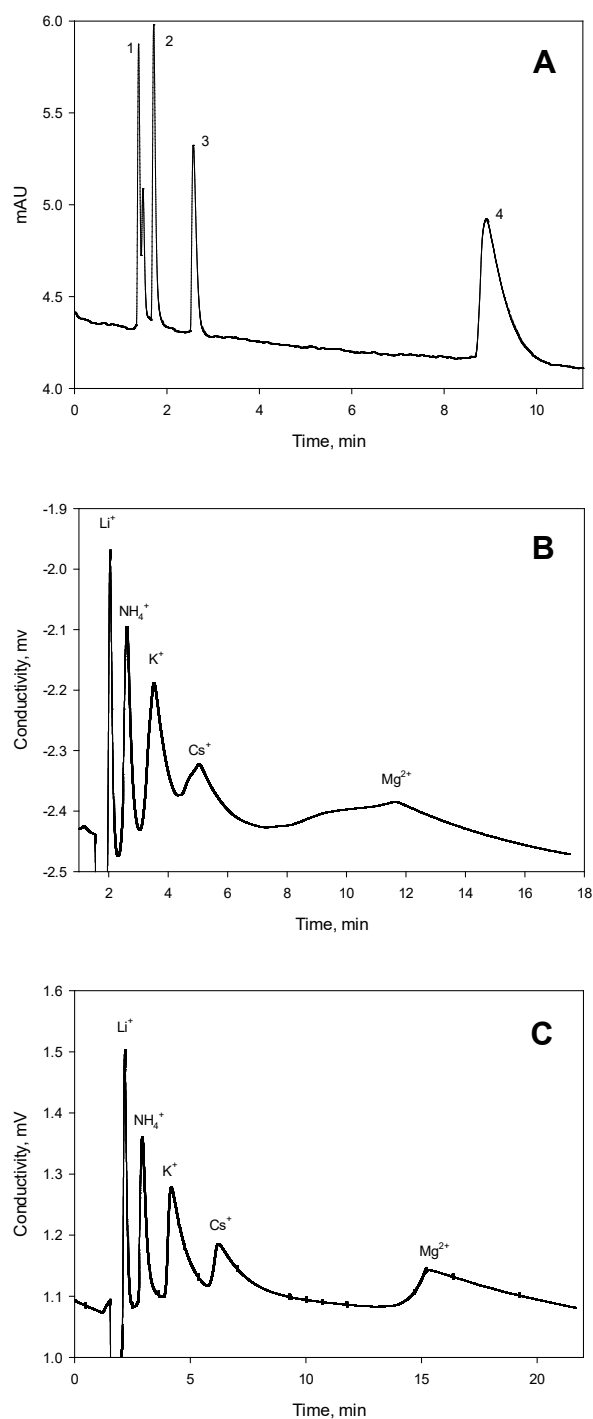


Figure 3.5. Separation of test mixtures on 50×4.6 mm ID (a) and 100×4.6 mm ID (b,c) columns packed with P1F diamond. a) Eluent: 15% 10 mM NaOH – 85% acetonitrile, 0.5 mL min⁻¹, 25°C, UV detection at 254 nm. 1 – 4-hydroxybenzenesulphonic acid, 2 – cytosine, 3 – benzyltributylammonium chloride, 4 – benzyltrimethylammonium chloride; b) Eluent: 10 mM HNO₃, 0.5 mL min⁻¹, 25°C, 5 μL injection of cations as nitrate salt dissolved in the eluent (4 mM Li⁺, 5 mM NH₄⁺, 10 mM K⁺, Cs⁺, and Mg²⁺); c) Eluent: 12 mM oxalic acid, 0.5 mL min⁻¹, 25°C, 5 μL injection of cations as nitrate salt dissolved in the eluent (4 mM Li⁺, 5 mM NH₄⁺, 10 mM K⁺, Cs⁺, and Mg²⁺).

3.5. Conclusions

For the first time ion-exchange properties of HPHT synthetic diamond and its oxidised and reduced derivatives were systematically investigated. Results of potentiometric titration and zeta potential measurements showed that all diamond samples had cation-exchange properties in the pH range from 1 to 12 due to presence of carboxylic groups upon diamond surface. The surface concentration of carboxylic groups in the prepared adsorbents varied from 0.65 to 2.2 per nm⁻². The greatest oxidation of diamond was achieved using a hot H₂O₂/H₂SO₄ mixture. The retention of metal cations increased for the studied adsorbents in the series: reduced < bare < oxidised HPHT diamonds.

A new method for the calculation of adsorption isotherms from the shapes of chromatographic peaks was proposed for the studied adsorbents. This method allowed calculation of maximum adsorption values for metal cations, which were in the range from 50 to 70 nmol g⁻¹ for alkali metal cations, and from 30 to 100 nmol g⁻¹ for alkaline-earth metal cations.

The possibility of simultaneous separation of five metal cations using column packed with oxidised HPHT diamond particles was demonstrated. The elution order Li⁺<Na⁺<NH₄⁺<K⁺<Mg²⁺<Mn²⁺<Cd²⁺<Zn²⁺<Ni²⁺<Co²⁺<Cu²⁺<Cr³⁺ in 20 mM nitric acid was observed and corresponded to that known for carboxylic cation exchange resins. Future research in this area should focus on the diamond surface modification to improve ion exchange kinetics, which together with high-temperature applications could result in a greater exploitation of the outstanding stability of HPHT diamond adsorbents.

3.6. Supplementary

3.6.1. Fractionation of HPHT diamond particles

The fractionation of the HPHT synthetic diamond was accomplished using previously reported method [172]. It was noticed that amount of the diamond that can be fractionated is limited by the total volume of suspension and by the concentration of KOH used as medium. If this limit was exceeded, the formation of pseudo liquid layer was noted in the precipitate at the bottom of the cylinder, which resulted in inconsistency of the particle sedimentation velocity. In this work, 5 mM NaOH was used instead of 10 mM NaOH as suggested before [172]), which allowed increasing HPHT diamond slurry concentration up to 100 g·L⁻¹. The particle size distribution plots obtained before and after fractionation of B1 and B2 diamond samples are shown in Figure 3.6 and Table 3.5.

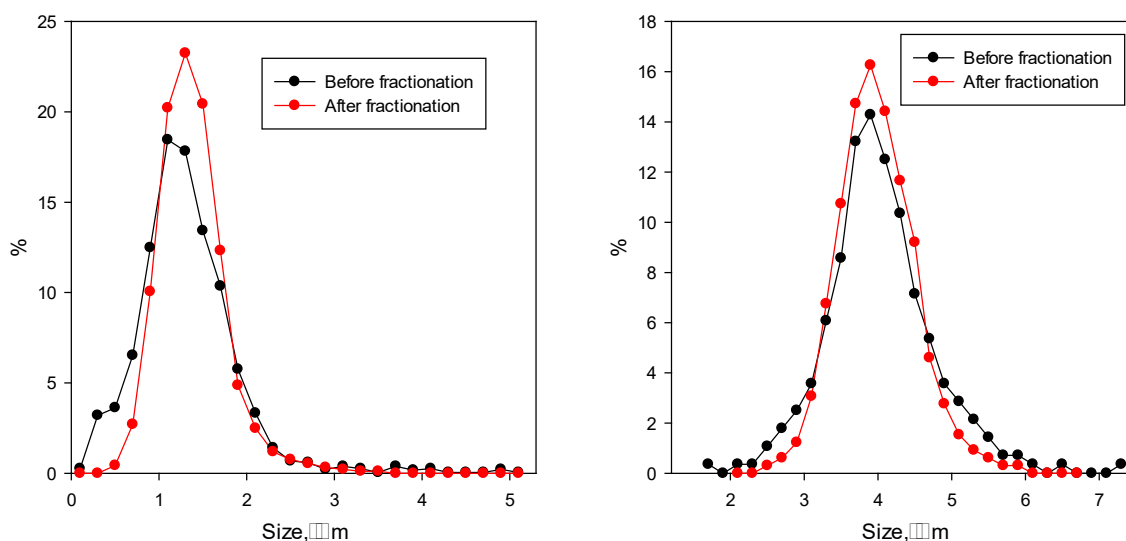


Figure 3.6. Particle size distributions for B1 and B1F (left) and B2 and B2F (right) diamond.

Table 3.5. Fractionation of B1 and B2 diamond on size.

	B1	B1F	B2	B2F
Mean particle size, μm	1.27	1.38	4.02	3.99
$D_{90/10}$	3.33	2.29	1.61	1.39

3.6.2. Acid-base potentiometric titration

Ion-exchange capacity (IEC) of the HPHT diamond and concentration of protogenic groups on the diamond's surface were calculated according to the difference between concentrations of NaOH (C_{NaOH}) before and after reaction with the diamond sample of mass m . For measurement samples of mass 5 g of bare, oxidised or reduced diamond were washed with 2 mM HCl, decanted and dried overnight at 80 °C. Then 20 mL of 2 mM NaOH were added to each sample and IEC was calculated using the following formula:

$$IEC = \frac{C(\text{NaOH}) \times V(\text{NaOH}) - V(\text{HCl}) \times C(\text{HCl}) \times \frac{V(\text{NaOH})}{V(\text{aliquote})}}{m(\text{HPHT diamond})},$$

where V_{NaOH} and V_{HCl} are volumes of NaOH and HCl used and C_{HCl} is concentration of HCl.

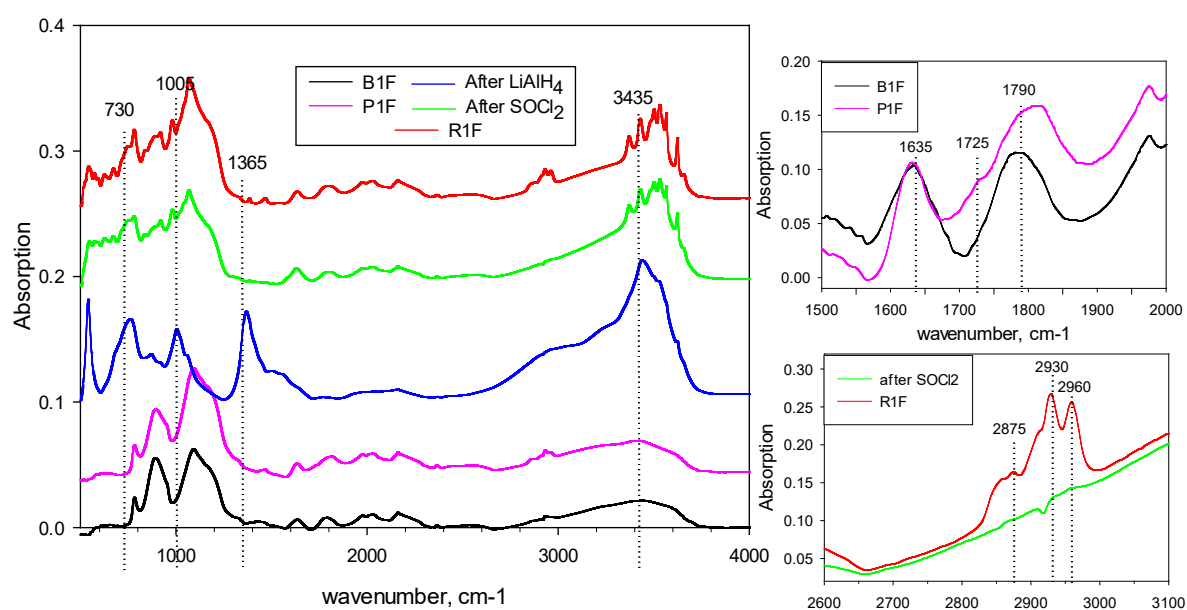


Figure 3.7. FTIR spectra of HPHT diamond samples before and after surface modification.

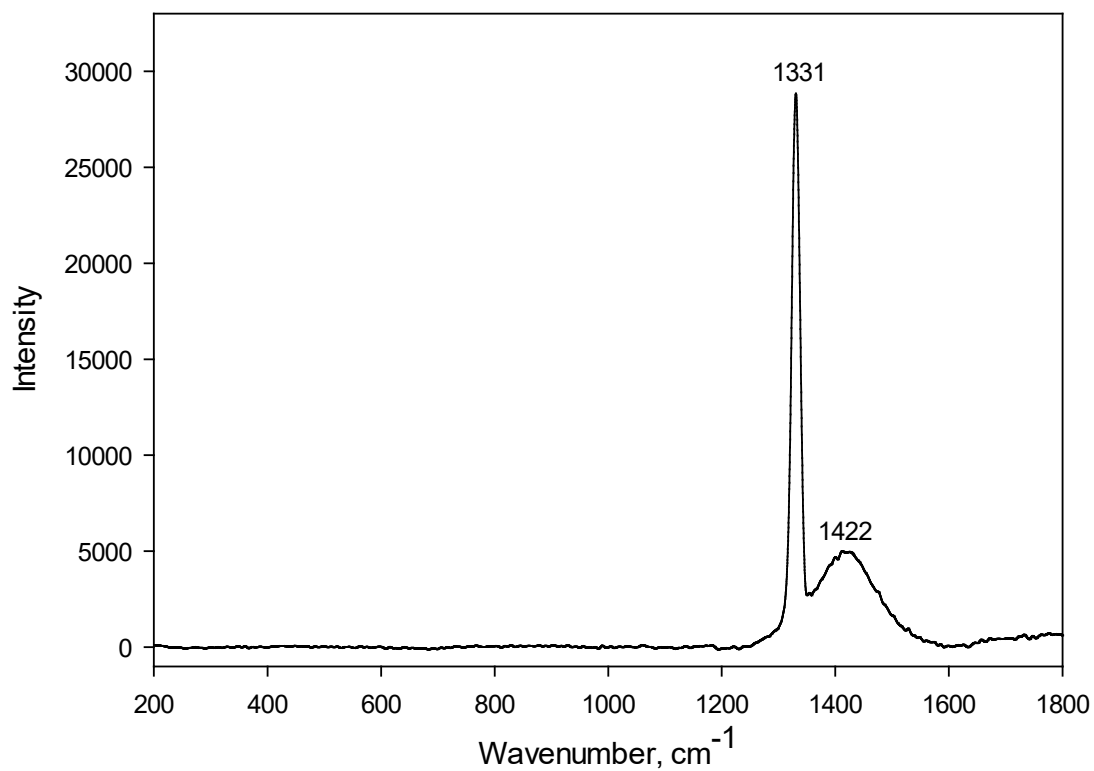


Figure 3.8. Raman spectrum of HPHT diamond after reduction with LiAlH₄. Absence of peaks in the region 300 – 700 cm⁻¹ indicates that no Al left on the surface.

3.6.3. Calculation of isotherms of adsorption

There are several methods described the literature for calculation of the isotherms of adsorption from the elution profile or chromatographic peak. The earliest work in this area was published by Glueckauf [218], who proposed the calculation of the adsorption isotherms in gas chromatography (GC) and ion-exchange chromatography. This was followed by a simplified method of Neumann [219], which could be applied only to GC as it was based on measurement of the changes in the volume of carrier gas due to the adsorption of solute on the stationary phase. Later, two similar approaches were suggested by Jonsson and Lovkvist [220] and Dose *et al.* [221]. Both of them were based on the initial hypothesis about the adsorption isotherm parameters, and further numerical calculations in order to achieve the best fit for the experimental data.

The main drawback of the above-mentioned methods was the fact that they did not consider the effect of chromatographic peak broadening due to “non-adsorption matters” (non-ideal packing, contribution of diffusion, etc.). Also, these methods could only be used if the type of adsorption isotherm was predetermined, which is unlikely event in practice. Recently, an improved method was suggested by Lanin *et al.* , who accounted for these effects and was able to achieve good agreement between calculated and experimentally measured adsorption isotherms [222]. Unfortunately, this method could be used only in GC, and required multiple injections in order to obtain sufficient number of points on the adsorption isotherm, but it applicable to the tailing peaks.

The method which was used in the current work is based on the two assumptions. Firstly, it exploits the mass balance of the solute, meaning that the sum of the amounts of the solute adsorbed on the stationary phase and present in the eluent is equal to the total amount of injected solute. This total amount is known from the volume and the concentration of injected

analyte, which is directly proportional to the chromatographic peak area. Secondly, the ratio of the amounts of the solute in stationary and mobile phases (distribution coefficient K_D) is directly proportional to the retention factor k . Also, this method is only valid if three conditions are satisfied including:

1. The chromatographic column is not overloaded.
2. Peak tailing reflects the adsorption on heterogeneous surface, and is not related to the quality of column packing or strong to the contribution of longitudinal diffusion.
3. The concentrations of the solute distributed between mobile and stationary phases are corresponding to complete equilibrium by the time when the first portion of solute is leaving the column.

To build the adsorption isotherm, the chromatographic peak was divided into large number of small segments as shown in Scheme 3.2, so that the detector response at the beginning with time t_n and in the end of each segment (t_n) can be accepted as the same, which means that the concentration of solute in this segment can be accepted as constant. For convenience, the segment “ n ” is a segment within time window from t_n to t_{n+1} (see Scheme 3.2). The amount of solute (N_n) which elutes within the segment “ n ” is proportional to the ratio of the area of this segment (S_n) to the total peak area (S_{total}):

$$N_n = V_{inj} * C_{inj} * \frac{S_n}{S_{total}} \quad (\text{Eqn. S1})$$

where V_{inj} and C_{inj} are the volume and concentration of injected solute. When leaving the column, this amount of solute N_n is dissolved within the corresponding volume of the effluent V_n :

$$V_n = F * (t_{n+1} - t_n) \quad (\text{Eqn. S2})$$

where F is the flow rate of the eluent. In the last segment of the chromatographic column the amount of solute N_n is distributed between the volume of the eluent V_n and the mass of the stationary phase m_n , which is in contact with this volume of the eluent:

$$N_n = C_{SP,n} * m_n + C_{MP,n} * V_n \quad (\text{Eqn. S3})$$

where $C_{SP,n}$ and $C_{MP,n}$ are the concentrations of the solute in mobile phase and stationary phase, respectively, within the segment “ n ”. m_n can be calculated as follows:

$$m_n = \beta * V_n \quad (\text{Eqn. S4})$$

where β is the column phase ratio, defined as the ratio of the total mass of stationary phase (m_{total}) to the total volume of mobile phase (V_{total}) in the column:

$$\beta = \frac{m_{total}}{V_{total}} = \frac{m_{total}}{F * t_0} \quad (\text{Eqn. S5})$$

where t_0 is the void time. In order to build the adsorption isotherm, it is required to determine the values $C_{SP,n}$ and $C_{MP,n}$ for every segment “ n ”. Since it was assumed that the equilibrium between mobile and stationary phases is achieved before solute leaving the column, the following is true:

$$\frac{C_{SP,n}}{C_{MP,n}} = K_{D,n} \quad (\text{Eqn. S6})$$

where $K_{D,n}$ is the distribution coefficient for the segment “ n ”, which can be expressed as:

$$K_{D,n} = \frac{k_n}{\beta} = \frac{\frac{t_n+t_{n+1}-1}{2t_0}}{\beta} = \frac{t_n+t_{n+1}-2t_0}{2\beta t_0} \quad (\text{Eqn. S7})$$

where k_n is the retention factor for the middle of the segment “ n ”. By combining Eqns. S1, S2 and S4 within Eqn. S3, and Eqns. S6 and S7, the new equations S8 and S9 can be written:

$$\frac{V_{inj} * C_{inj} * S_n}{S_{total}} = F * (t_{n+1} - t_n) * [C_{SP,n} * \beta + C_{MP,n}] \quad (\text{Eqn. S8})$$

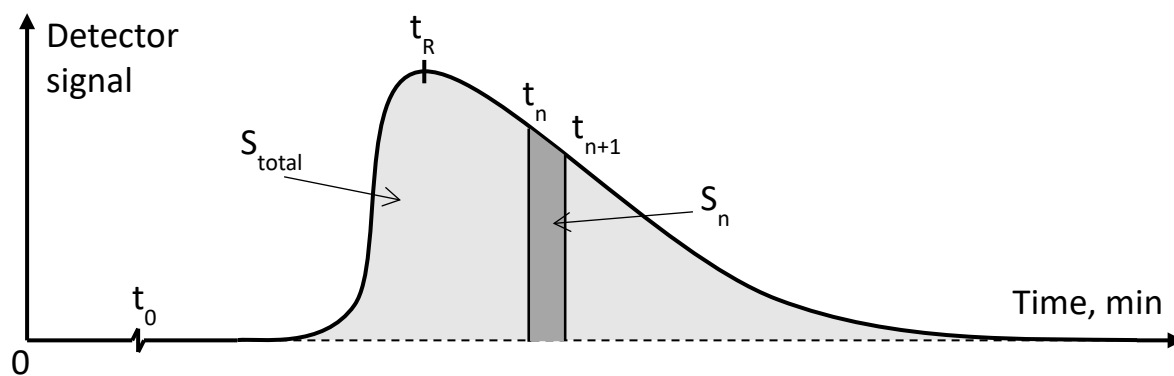
$$\frac{C_{SP,n}}{C_{MP,n}} = \frac{t_n+t_{n+1}-2t_0}{2\beta t_0} \quad (\text{Eqn. S9})$$

The solution of this set of equations, and using Eqn. S5 provides the following expression for the values of $C_{SP,n}$ and $C_{MP,n}$ as following:

$$C_{MP,n} = \frac{2t_0 * V_{inj} * C_{inj} * S_n}{S_{total} * F * (t_{n+1}^2 - t_n^2)} \quad (\text{Eqn. S10})$$

$$C_{SP,n} = \frac{t_0 * V_{inj} * C_{inj} * S_n}{S_{total} * m_{total}} * \left[\frac{t_n+t_{n+1}-2t_0}{t_{n+1}^2 - t_n^2} \right] \quad (\text{Eqn. S11})$$

Finally, plotting $C_{SP,n}$ versus $C_{MP,n}$ for different n yields the adsorption isotherm. Clearly, in the case of tailing peak, only part of the peak after t_R should be used to derive the adsorption isotherm data (see Scheme 3.2). In this work, the n values were chosen in a way that peaks were divided into ~20 segments, resulting in ~20 points on the adsorption isotherm.



Scheme 3.2. Calculating the adsorption isotherm from the peak shape.

Table 3.6. Calculated parameters for approximation of adsorption isotherms in Figure 3.3 with Langmuir model (Eqn. 3).

		B1F	P1F	R1F
K^+	$A_{max}, \text{nmol} \cdot \text{g}^{-1}$	50 ± 4	48 ± 3	50 ± 4
	$K_L, \text{mL} \cdot \text{g}^{-1}$	2.27 ± 0.18	3.97 ± 0.26	1.60 ± 0.12
Mg^{2+}	$A_{max}, \text{nmol} \cdot \text{g}^{-1}$	113 ± 11	104 ± 9	141 ± 14
	$K_L, \text{mL} \cdot \text{g}^{-1}$	1.04 ± 0.10	1.43 ± 0.13	0.47 ± 0.06

3.6.4. X-ray photoelectron spectroscopy study of HPHT diamond.

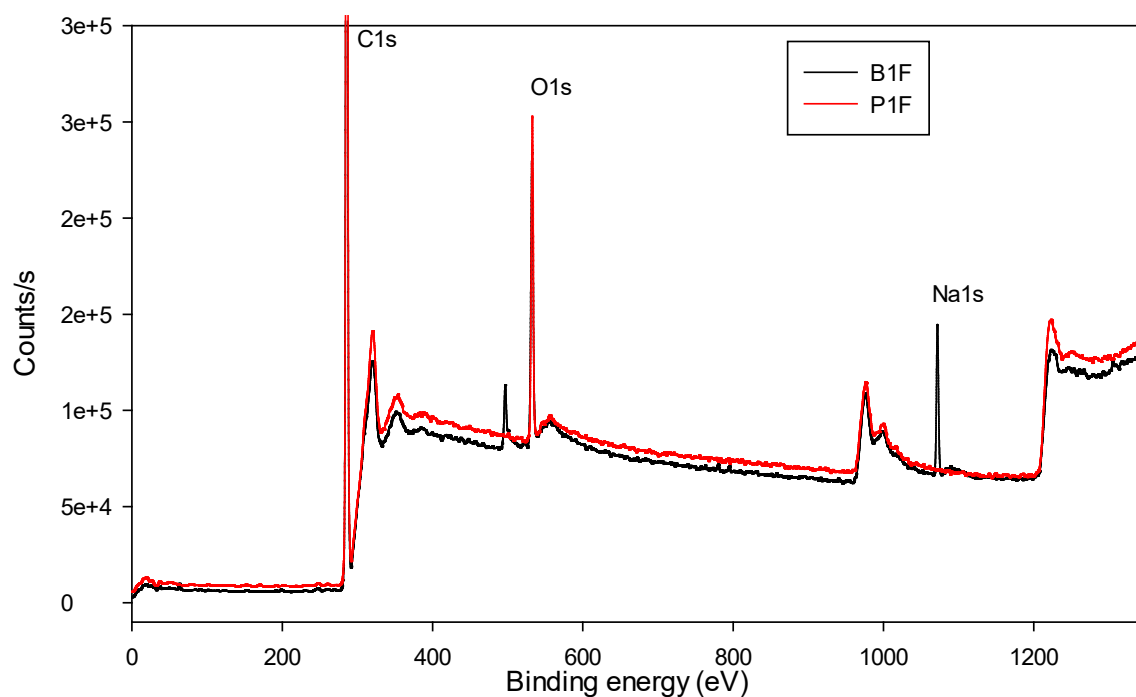


Figure 3.9. XPS spectra of samples B1F and P1F. XPS was performed on an Escalab250Xi X-ray photoelectron spectrometer (Thermo Scientific, Waltham, MA, USA) with Al K α incident radiation (1486.6 eV) at 150 W (13 kV, 12 mA).

Table 3.7. Surface content of carbon, sodium and oxygen in B1F and P1F samples, calculated from XPS spectra (Figure 3.9).

	B1F	P1F
C1s	89.3 $\pm$ 2.5	91.4 $\pm$ 2.6
O1s	8.9 $\pm$ 0.9	8.6 $\pm$ 0.9
Na1s	1.8 $\pm$ 0.2	-

CHAPTER 4

Chromatographic Performance of Hydrogenated HPHT Diamond

4.1. Introduction

Continual development and refinement of analytical techniques leads to greater applications, increased efficiencies through reduced analysis times, improved reproducibility, and lower limits of detection. In liquid chromatography, the use of diamond particles as stationary phases (SPs) offers a potentially useful alternative to the commonly used silica- and polymer-based phases (Chapter 2). Potential advantages include superior mechanical [17], hydrolytic [19] and thermal stability [18], thermal conductivity [223], and unique adsorption properties. The surface chemistry and adsorption properties of diamond-based SPs have been intensively studied by several research groups, across reversed-phase, normal-phase, hydrophilic interaction and ion chromatographic modes of HPLC [140, 141, 172]. The variety of investigated applications of diamond-based SPs is due to the significant diversity of possible surface interactions, including electrostatic and hydrophobic interactions, and selective hydrogen bonding and chelation type selectivity.

To date, of the three commercially available types of diamond, namely detonation nanodiamond (DND), high-pressure high-temperature (HPHT) diamond, and chemical vapour deposition (CVD) diamond, DNDs are the most chemically diverse, widely studied and perhaps the most successfully applied diamonds in the preparation of SPs. The size of DND is too small for direct applications in HPLC, therefore DNDs are used as composite materials. One composite, microdispersed sintered detonation nanodiamond (MSDN), prepared by sintering DNDs at high pressure, was used as an SP and characterised by Fedyanina *et al.* [82, 84, 161]. Separation of polar and non-polar compounds has been performed on this SP proving both hydrophobic and hydrophilic interactions are characteristic of DND.

Columns packed with core-shell pellicular particles, formed from a carbon core and a DND shell coating, were first reported by Linford's research group [23, 169, 224]. Consecutive layers

of DND and amine-containing polymer were deposited onto carbon cores. The thus formed SP showed good mechanical, hydrolytic and thermal stability as well as good separation efficiency of essential oils (up to $112,000 \text{ N m}^{-1}$) [168]. Later these columns became commercially available under trade name Flare (Diamond Analytics, USA) and were used for protein separation, showing mixed-mode hydrophobic and anion-exchange mechanisms due to the presence of C18 chains and protonated amino groups [23]. Preparations of polystyrene-divinylbenzene beads with quaternised DND anion exchangers were also reported by Zhu's research group [111, 170], and the performance of this composite was investigated for the separation of inorganic anions. The authors showed that the addition of DND improves the mechanical stability of adsorbents, that the ion-exchange capacity can be tuned, and the SPs are stable in the pH range 1 to 13 [170]. Monolithic polymer columns with entrapped DNDs have been recently developed and characterised by Yan's research group. [18, 171, 174]. They also reported that the addition of DND improved the mechanical stability of the prepared SP, furthermore better separation efficiency (up to $24,350 \text{ N m}^{-1}$) was achieved due to the bigger surface area of the composite monolithic column functionalised with DND, compared with the non-functionalised column. Although a reversed-phase retention mechanism was shown for these adsorbents, it was induced by the polymer's properties rather than those of the DND. The use of organo-silica core particles modified with a DND shell was reported by two research groups at a similar time [139, 140]. In these cases, the DND not only enlarged the surface area of the packing material but also introduced new functional groups. Cai *et al.* [140] demonstrated the separation of sulfonamides on silica functionalised with oxidised DND and revealed electrostatic interactions corresponding to HILIC behaviour. Xue *et al.* [139] compared the selectivity of silica SPs functionalised with oxidised DND to those with hydrogenated DND and showed that the latter favoured hydrophobic interactions, and the former, hydrophilic.

Comparatively, research into the applications of chemical vapour deposition (CVD) and HPHT diamond in the field of separation science are far fewer. While the CVD method has been used to develop specialised thin, uniform, and conformal diamond coatings on a wide variety of materials of different surface topology [150], its wider use, including in separation science, has been predominately limited because of the slow and expensive deposition process. Similarly, the use of raw HPHT diamond has been restricted to just a few studies, primarily related to the limited surface area and irregular particle size and shape of the HPHT diamond.

Initial investigations have pointed to the significant potential of HPHT diamond for use as a SP within aqueous normal-phase (ANP), hydrophilic interaction liquid chromatography (HILIC) and ion chromatographic (IC) systems [58, 87, 172]. However, considerable uncertainty still exists about which retention mechanisms are specifically involved in adsorption onto the HPHT diamond surface. Without this knowledge, the further development of HPHT-based SPs is severely hindered. Also, in contrast with DNDs, there is yet no significant evidence that HPHT diamond can be used in reversed-phase chromatography, due to its reported predominantly oxidised surface. Hydrogenation was previously used to introduce hydrophobic properties to DNDs [139], and a similar method can be applied to HPHT diamond. Therefore, this chapter reports a detailed investigation into the selectivity and retention mechanisms for a range of selected test solutes on an hydrogenated HPHT diamond SP as compared to common HPHT diamond by analysing the retention times of various types of analytes under different chromatographic conditions.

4.2. Materials and Methods

4.2.1. Diamond hydrogenation

HPHT diamond (monocrystalline diamond powder, MSY 0-0.5 & 1.5–2.5 micron, Microdiamant AG, Lengwil, Switzerland), 10 g was placed into a Carbolite tube furnace STF 15/180 (Chelmsford, United Kingdom) at 850–950°C, under hydrogen atmosphere (high purity grade 99.98%, BOC (NSW, Australia)) at a flow rate of 1–2 L min⁻¹ for 5 hours. Heating and cooling were carried out under a pure nitrogen atmosphere, at a flow rate 3–4 L min⁻¹.

4.2.2. Diamond oxidation

Oxidation of diamond particles (as above) was performed using a slightly modified method described by Torrenco *et al.* [188]. Specifically, 200 g of HPHT diamond was placed into a 1 L glass beaker, then 60 mL of deionised water (DIW), 90 mL of 50 wt.% H₂O₂ (Sigma-Aldrich, USA) and 450 mL of 98 wt.% H₂SO₄ (Merck, Germany) were added. The resultant suspension was heated in a water bath for 1 hour at 100°C. After the suspension had sedimented, the supernatant was decanted, then 600 mL of DIW water was added using an ice bath. This washing procedure was repeated 3–4 times until the rinsing water measured pH 2–3. The particles were dried overnight at 100°C.

4.2.3. Fourier-transform infrared spectroscopy (FTIR)

Before measuring the FTIR spectra, the HPHT diamond powder was dried overnight at 100°C in a vacuum (0.4 bar) oven. Samples were prepared by grinding and mixing the dried diamond powder (0–0.5 µm) with potassium bromide (FTIR grade, ≥99% trace metal basis, Merck, Darmstadt, Germany) to give a concentration of 5 wt. %. The infrared spectra were recorded on a Bruker Vertex 70 in diffuse reflectance mode using a Pike AutoDiff (Billerica, Massachusetts, United States). The spectral range was 500–4000 cm⁻¹ at a spectral resolution

of 4 cm⁻¹. One hundred and twenty-eight scans were used for the samples and the potassium bromide background, and the spectra were corrected using the atmospheric compensation algorithm within the OPUS software (Bruker, Billerica, Massachusetts, United States).

4.2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed to determine the oxygen atomic abundance present on the diamond surfaces prior to and after modification treatments. Photoelectron spectra were acquired using a non-monochromatic Mg K α radiation source, ($h\nu$ = 1253.6 eV) The spectra were acquired using a Kratos AXIS Ultra DLD X-ray Photoelectron Spectrometer (Shimadzu, Kyoto, Japan).

4.2.5. Elemental analysis

The HPHT diamond (0.5 μ m) was subjected to elemental analysis. The analysis for total nitrogen, carbon, hydrogen, and sulfur was carried out using a Thermo Finnigan EA 1112 Series Flash Elemental Analyser (ThermoFisher, Waltham, Massachusetts, United States). Between 0.7 and 1.7 mg of sample was weighed into a tin capsule using a Sartorius SE2 ultra-microbalance with an accuracy of 0.1 μ g. Combustion of the pressed tin cups was achieved in ultra-high purity oxygen at 1000°C (the actual combustion temperature would be several hundreds of degrees higher due to the tin cup combustion) using tungstic oxide on alumina as an oxidising agent followed by reduced copper wires as a reducing agent. The results were calibrated using a certified sulfanilamide standard.

4.2.6. Column packing conditions

A slurry containing 2 (1.5–2.5) μ m hydrogenated diamond at a concentration of 66.7 mg mL⁻¹ was prepared in 50% aqueous 2-propanol (HPLC grade, Fisher Scientific, Hampton, NH, USA) or methanol (HPLC grade, Sigma-Aldrich, St. Louis, MO, USA) 50% 2-propanol was used as

the pump fluid. The slurry containing oxidised (with Piranha mixture, see Section 3.3.3.2 [58]) diamond was prepared in 10 mM aqueous sodium hydroxide (analytical grade, Chem-Supply, SA, Australia). 10 mM nitric acid (70%, AR, RCI Labscan, Bangkok, Thailand) was used as the pump fluid. In all cases, stainless steel UHPLC columns (50×4.6 mm ID, Modular Systems, IDEX Health & Science, Middleborough, MA, USA) equipped with 0.5 µm frits were packed using the pneumatic air-driven fluid pump (Haskel International Inc, Burbank, CA, USA) at pressure 15000 psi (10^8 Pa) until 0.25 L of pump fluid had passed through the column.

4.2.7. HPLC methods

Methanol and acetonitrile (for HPLC, $\geq 99.9\%$, Sigma-Aldrich) were used as organic modifiers for the preparation of mobile phases. *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS) ($\geq 99\%$, Sigma-Aldrich), sodium hydroxide (pellets, 97%, Chem-supply), hydrochloric acid (37%, ACS reagent, Scharlau), and sodium and potassium chloride ($\geq 99\%$, ACS reagent, Honeywell Fluka) were used to adjust the pH and ionic strength of mobile phases. An Accela 1250 UHPLC with ChromQuest™ software (Thermo Fisher Scientific, USA) was used for the evaluation of the modified HPHT diamond columns. All separations were carried out in triplicate with an injection volume of 5 µL, at 30°C and a flow rate of 0.3 mL min⁻¹, with photometric detection at 254 nm, unless otherwise stated.

4.2.8. Design of chromatographic experiments to investigate the selectivity of prepared stationary phases

In liquid chromatography, the selectivity of the chromatographic separation is primarily defined by the surface chemistry of the SP adsorbent. To a lesser extent, it is affected by parameters of the mobile phase, such as pH, organic content, and ionic strength. Thus, by characterising the selectivity of the SP under different chromatographic conditions, it is possible to gain a greater understanding of the specific retention mechanisms involved in

producing the resultant separation. In order to maximise the efficiency of this type of exploratory experimental work, a two-level full factorial design (2^3) for three factors [225] in triplicate was applied herein. (Figure 4.1). Two levels of each variable were defined – low and high (Table 4.1), which resulted in eight test conditions for investigation.

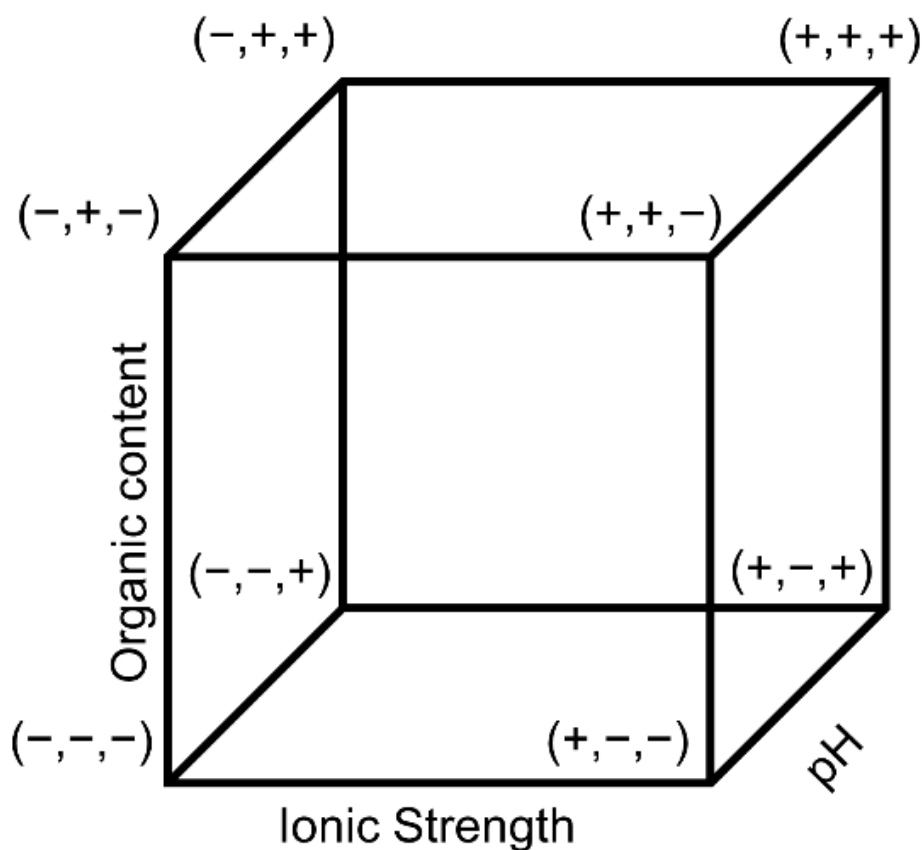


Figure 4.1. Schematic of a two-level full factorial design (2^3) matrix for three input factors.

Table 4.1. The two-level full factorial design (2^3) table for three input factors.

Variables	Factors	Units	Experimental region	
			Low (-)	High (+)
X	Ionic strength	mmol L ⁻¹	1	10
Y	Organic content	%	25	75
Z	pH	–	2	10

4.3. Results and Discussion

4.3.1. Bulk and surface characterisation of hydrogenated diamond

4.3.1.1. *Elemental analysis*

According to elemental analysis data, a sample of bare diamond contains 0.05% nitrogen. This value does not change after oxidation, but slightly decreases after hydrogenation (0.04%). It is widely accepted that the nitrogen present stems from nitrogen defects in the diamond lattice rather than from nitrogen-containing groups, and is thus uniformly distributed through the bulk of the material [8]. Nitrogen was not seen within the XPS analysis, which confirms that the amount on the surface is negligible. The carbon content was shown to increase in the order of oxidised (98.22 wt. %), bare (98.54 wt. %), and hydrogenated diamond (99.28 wt. %), which indirectly points to the replacement of heavy oxygen atoms by hydrogen, assuming that there are no other elements present in the bulk of the material.

4.3.1.2. *Fourier transform infrared spectroscopy*

In order to compare the adsorption properties and retention mechanisms of differently treated HPHT diamond particles, different samples were prepared. Diamond was hydrogenated at two different temperatures, 850 and 950°C, based on previous studies [226]. Diffuse-reflectance FTIR spectra of each of the diamond powders are shown in Figure 4.2. The initial spectrum of the diamond before hydrogenation treatment showed bands at 1803 and 1630 cm^{-1} and a weak broad band at 2900–3740 cm^{-1} (Figure 4.2a). The bands at 1803 cm^{-1} and 1603 cm^{-1} are likely due to moieties containing carbonyl (C=O) groups, which can be attributed to the C=O vibrations of carboxylic acid (COOH), carboxylic anhydride (COOCO), cyclic ketone (–CO–) or lactone (COO) structures [227]. This bare diamond spectrum (Figure 4.2a) indicates that the diamond surface is predominantly oxidised either during the synthesis and purification

procedure or generally from atmospheric oxygen. The two peaks attributed to C=O vibrations disappear following the hydrogenation treatment (Figure 4.2b, 2c). A broad O-H stretching band at 2900–3740 cm^{-1} (Figure 4.2a) is caused by physically absorbed molecular water. Oxidised diamond surfaces readily absorb atmospheric water on polar C=O groups [227]. A weak sharp peak at 3698 cm^{-1} that disappeared after hydrogenation may be assigned to the O–H vibration of hydroxy groups on the diamond surface. After hydrogenation of the sample in H_2 at 850 and 950°C, the spectra showed two sharp peaks at 2837 and 2933 cm^{-1} (Figure 4.2b, and 4.2c respectively), which are absent in the spectrum of the bare diamond. The former peak corresponds to the symmetric stretching vibration of aliphatic CH_2 groups, and the latter peak to the asymmetric stretching vibration of aliphatic CH_2 groups. This data confirms desirable changes on the diamond surface and would suggest a significant reduction in surface polarity. The diffuse-reflectance FTIR spectra of the two samples hydrogenated at different temperatures did not reveal any significant changes between them, and thus the lower temperature was chosen to save energy and time.

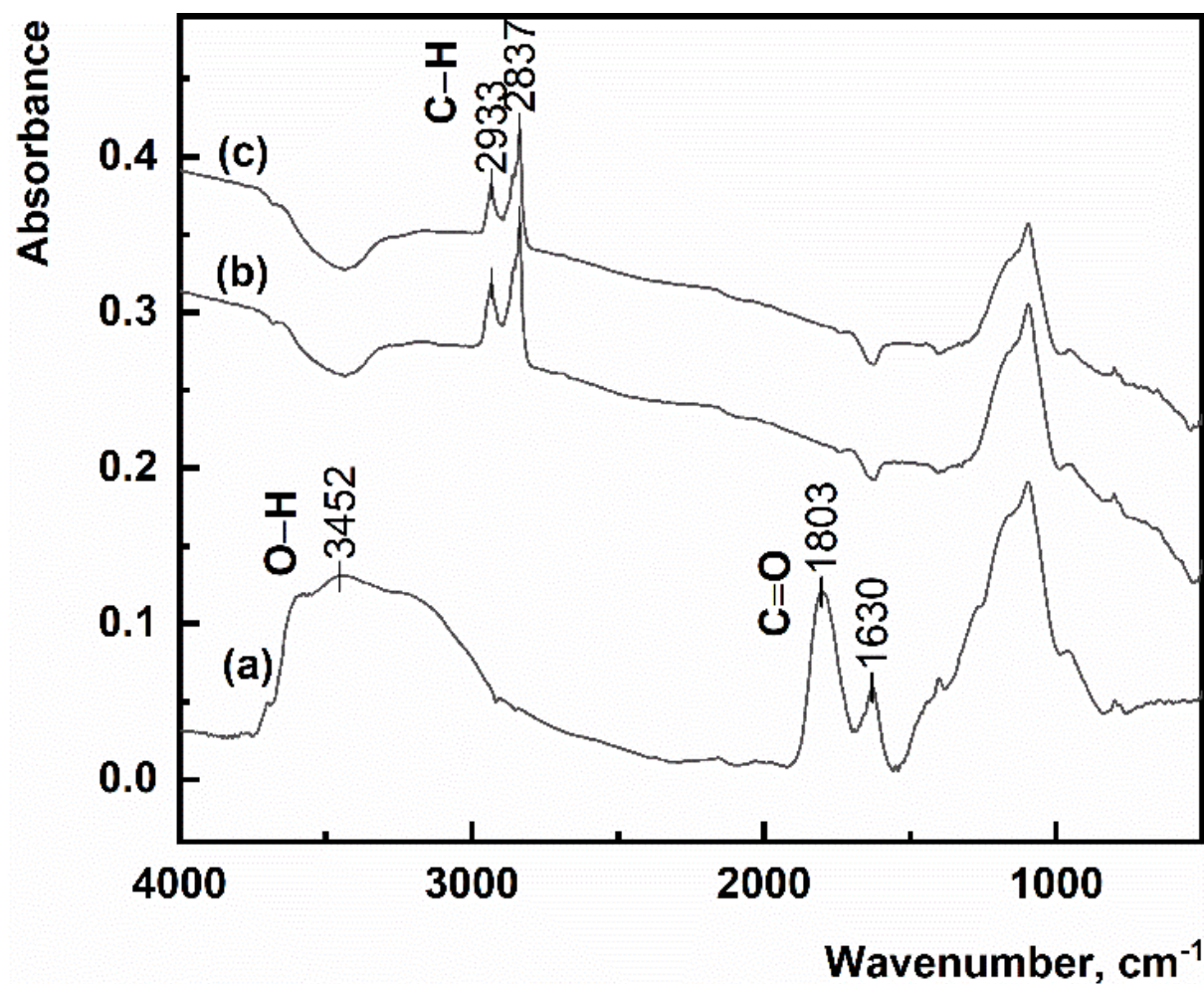


Figure 4.2. FTIR spectra of 0.025 (0–0.05) μm HPHT diamond (a) bare; (b) hydrogenated at 850°C; (c) hydrogenated at 950°C.

4.3.1.3. *X-ray photoelectron spectroscopy*

In order to further confirm the surface chemical modifications, XPS spectra were measured, and the results are presented in Figure 4.3. The XPS spectra were dominated by the C 1s peak at approximately 289 eV, with a full-width half maximum value of 2.06 eV for the bare diamond, 2.00 eV for the oxidised diamond and 1.61 eV for the hydrogenated diamond (Figure 4.3b). Also present were O 1s peaks at 537 eV for the oxidised HPHT diamond, due to the presence of oxygen-containing groups on the diamond surface (Figure 4.3a). The peak shift between bare, oxidised and hydrogenated diamond is due to the different chemical

environments of the C 1s and O 1s electrons with respect to the hybridisation of the orbital. Fitting these peaks to suitable functions in future would allow this bonding information to be extracted, although this has not been carried out herein as this was not the primary purpose of this work. For the oxidised diamond, the O 1s/C 1s atomic concentration ratio is about 10.3 at %, as calculated from the relevant peak area in the recorded spectrum divided by an appropriate bulk atomic sensitivity factor. This value is comparable with the reported values for the diamond surfaces treated by oxygen [228] and not significantly different from the value calculated for the bare diamond (8.1 at %), which indicates that the surface of bare diamond is also moderately oxidised in its ‘native’ state. In stark contrast, for the hydrogenated diamond, the O 1s/C 1s ratio is approximately 1.0 at %, and this is also comparable with reported values for hydrogen-terminated diamond of between 0.9 [229] and 1.0 ± 0.3 at % [230]. Considering the XPS detection depth of $\sim 2\text{--}3$ nm, the oxygen content is extremely low, even though the samples were stored in air. Apart from oxygen and hydrogen, each of the diamond surfaces appeared to be relatively free of other elements.

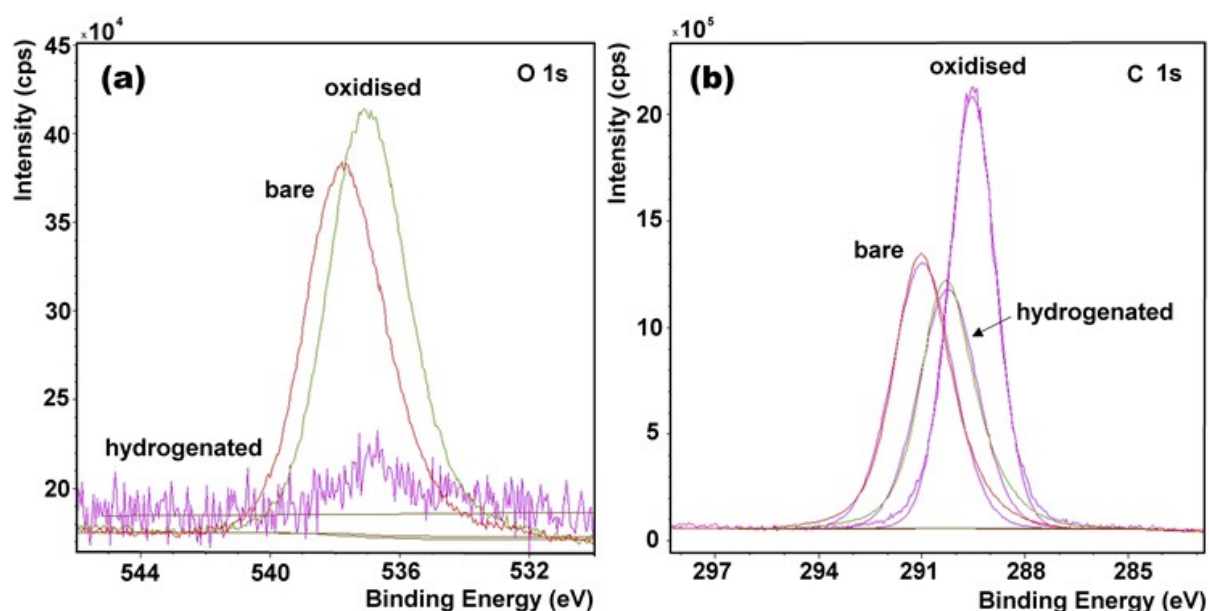


Figure 4.3. The O 1s (a) and C 1s (b) XPS spectra for bare, oxidised, and hydrogenated HPHT diamond.

4.3.2. Study of adsorption properties

4.3.2.1. Comparison of the selectivity between oxidised and hydrogenated diamond phases

The liquid chromatographic selectivities of oxidised and hydrogenated HPHT diamond SPs were compared. Seven solutes exhibiting a range of polarity and pK_a values were chosen for these scoping experiments (Table 4.2). Benzenesulfonic acid (BSA) was modelled as the ionised form, being the predominant form at both experimental pH values investigated. Carboxylic acid (benzoic acid, BA) and aromatic base (aniline) were modelled as both ionised and unionised species, to represent the different experimental pH conditions used. Benzyltributylammonium chloride (BTBA) was modelled as the charged benzyltributylammonium cation and *para*-Aminobenzoic acid (p-ABA), an amphiphilic compound, was used for comparison.

Table 4.2. Summary of the key properties of the seven analytes used in this study.

Solute	pK_a	LogP	Charge at pH 2	Charge at pH 10	Polarity
BSA	-6.5	-1.17	-	-	Very polar
p-ABA	2.35/4.98	0.83	0/+	-	Very polar
BA	4.2	1.87	0	-	Very polar
Toluene	41	2.73	0	0	Non-polar
Aniline	4.6	0.9	+	0	Polar
Uracil	9.5	-1.07	0	0/-	Polar
BTBA	>10	5.53	+	+	Polar

Retention factors were determined over eight different experimental conditions (see Section 4.2.8 for more details) and are presented in Figure 4.4. The retention data confirmed that chromatographic retention of all solutes on oxidised HPHT diamond was very weak, except for benzyltributylammonium (BTBA) chloride (Figure 4.4a), which is the only positively charged species among those tested across all experimental conditions. Moreover, its retention decreased with an increase of ionic strength of the mobile phase. This behaviour indicates that a cation-exchange retention mechanism is significant on oxidised HPHT diamond, due to the presence of negatively charged ionogenic groups, such as hydroxyls and carboxyls, as previously confirmed and described in detail in Chapter 2. At higher pH, more carboxylic groups on the diamond surface become deprotonated, therefore the retention of the BTBA cation is increased. However, at pH 10 and 75% methanol, the retention factor for BTBA began to increase with an increase of ionic strength. This unusual response seems to align with a hydrophilic interaction (HILIC)-like behaviour, although further experiments would be required to confirm this. Other polar solutes used in this study, such as BA and *p*-ABA, were negatively charged and so likely to be repulsed from the negatively charged diamond surface, which resulted in their limited retention.

However, very different retention behaviour was noticed on the hydrogenated diamond (Figure 4.4b). Surprisingly, the highest retention factors were observed for benzoic, benzenesulfonic and *p*-aminobenzoic acids. The retention order among the test solutes at pH 2 was BSA > *p*-aminobenzoic acid (*p*-ABA) > benzoic acid (BA) > toluene. An increase in mobile phase pH led to a decrease in the retention for all solutes possessing acidic functional groups. The hydrogenated diamond surface is more non-polar than that of the oxidised diamond, therefore non-polar interactions are likely to occur on this SP. Carboxylic groups of BA, *p*-APBA and BSA are mostly protonated at pH 2 hence hydrophobic interactions dominated the retention of

the benzoic acids, while at pH 10 these solutes became negatively charged, and their retention subsequently decreased.

The strong retention of BSA observed upon the hydrogenated diamond could be explained by the attraction of negatively charged deprotonated sulfonic acid groups and possible positively charged amino groups on the hydrogenated diamond surface, which become deprotonated at higher pH, causing the observed decrease in retention. However, in characterising the hydrogenated diamond, the existence of nitrogen-containing groups on the surface was not proven, although elemental analysis did reveal the presence of nitrogen (0.05%, Section 4.3.1.1). This nitrogen could possibly be partially exposed to the surface and there form amino groups during the hydrogenation process. With an increase of mobile phase ionic strength, the decrease of BSA retention also confirms a likely anion-exchange mechanism is now involved in retention of this compound in mobile phases at pH 2.

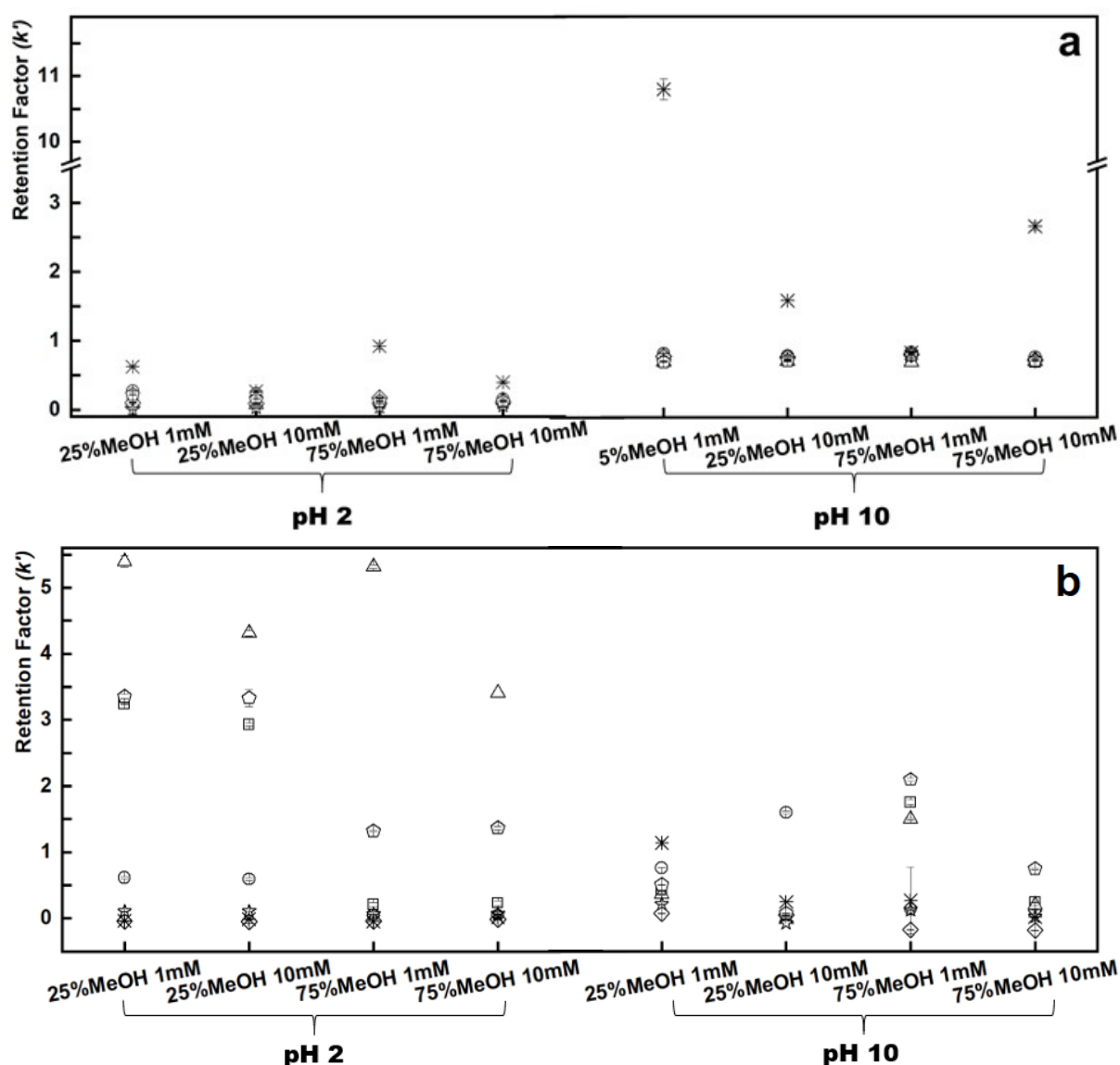


Figure 4.4. The retention factors of seven analytes on (a) oxidised and (b) hydrogenated HPHT diamond at pH 2 and pH 10. ○ – toluene; □ – BA; △ – BSA; ◇ – aniline; ☆ – uracil; ◊ – p-ABA; * – BTBA.

Retention of BA, *p*-ABA, and toluene at pH 2 was not affected by ionic strength, these solutes are protonated and predominately neutral at this pH. For these solutes, a change in organic content of the mobile phase had the most dominant effect upon retention, corresponding to a typical reversed-phase interaction mechanism. Therefore, it is likely that the benzene ring of these solutes allows hydrophobic and donor–acceptor π – π interactions with the diamond’s surface. Indeed the elution order of these compounds is similar to the previously reported data related to a porous graphitic carbon (PGC) SP [231].

An elution order quite different from that reported for PGC was observed at pH 10. Under these conditions, the retention of the benzoic acids decreased, and simultaneously the retention of the BTBA cation slightly increased. This could be explained by the presence of residual carboxylic groups on the hydrogenated diamond surface, which undergo deprotonation and so contribute some cation-exchange properties. Meanwhile, the retention of non-ionogenic solutes, such as toluene, was not affected by pH, as no electrostatic interactions were involved in their retention.

4.3.2.2. *The effect of organic solvent in the eluent and hydrophobic properties of HPHT diamond SP*

From the initial scoping experiments, it was observed that hydrogenated HPHT diamond exhibited a mixed-mode retention character, but which clearly included strong reversed-phase behaviour. As shown in the previous experiment (Figure 4.4b), the presence of hydrophobic interactions was indicated by the decrease of retention with an increase of methanol content from 25% to 75% for toluene, p-ABA and BA at pH 2, and aniline at pH 10, in other words for all non-charged solutes (see pK_a values, Table 4.2). In order to confirm this observation, a series of experiments was performed using mobile phase compositions with varying amounts of organic modifier (from 25% to 90% methanol). The results of these experiments are shown in Figure 4.5.

For the organic acids at pH 10 (CAPS buffer), an increase in retention with an increase of methanol content was observed. This behaviour is very different to that observed on Hypercarb (PGC) [161], where the retention of benzoic acids on PGC declines linearly with an increasing concentration of methanol in the mobile phase. This could possibly be explained by a solvent-enhanced ion-exchange retention mechanism. It has been shown previously that the addition of organic solvents to the eluent dramatically increases the complexity of the ion-exchange

process, as there are multiple competing effects affecting the retention [232]. In particular, the proportion of organic solvent significantly affects the pK_a values of solutes and their effective charge, the buffer capacity, pH of the organo-aqueous eluent mixture, enhanced solvation of the buffer molecules and solute solvation enthalpies [233]. It has also been previously reported by multiple researchers that unlike the addition of acetonitrile, methanol often increases the retention of solutes, e.g. n-alkylamines on alumina (Alox T10) [234], inorganic anions on a latex bonded anion-exchanger (Omnipac PAX-100) [235], and carboxylic acids on divinylbenzene-ethylvinylbenzene modified with alkylamines [236, 237].

The sharp increase in retention with the higher content of organic modifier may also be a contribution of the other hydrophilic interactions (HILIC) between the solutes and the SP. In HILIC mode, as well as ion-exchange, there are several other ways to model the separation mechanism, including partition, adsorption and size-exclusion [238]. Pore size distribution measured *via* BET, the structure of adsorbent and the nature of compounds retained make the size-exclusion mechanism irrelevant in this case. Therefore, it was decided to investigate the partition and adsorption retention mechanisms.

Due to the different mechanisms involved in adsorption and partitioning models, the mobile phase composition has a different effect on retention in HILIC mode [238]. In the case of the partitioning mechanism, a direct correlation between $\log k$ and the volume fraction of strong organic solvent should be observed (Eqn. 1), whereas the adsorption mechanism is adequately described by the Snyder-Soczewinski equation (Eqn. 2) [239]:

$$\text{Partitioning model:} \quad \log k = \log k_{org} - S \cdot \phi_w \quad (1)$$

$$\text{Adsorption model:} \quad \log k = \log k_w - A_s/n_w \cdot \log X_w \quad (2)$$

Here, k_{org} is the retention factor of the solute in an organic solvent, φ_w is the volume fraction of a strong eluting solvent (such as water), S is the slope of $\log k$ vs φ_w when fitted to a linear regression model; k_w is retention factor in water, X_w is the mole fraction of the stronger solvent (water), A_S and n_w are the cross-sectional areas occupied by the solute molecules on the surface, respectively.

Table 4.3 summarises the squared correlation coefficients for the approximation of retention vs water content dependence calculated using the models described above. As can be concluded from the data presented, the partitioning model describes the observed trends better than the adsorption model. However, there is a significant deviation from linear correlation, which indicates that even if the partition mechanism occurs on the hydrogenated diamond, ion-exchange interactions enhanced by the organic solvent also contribute largely to solute retention. More research must be done to evaluate the overall contributions of the proposed mechanisms.

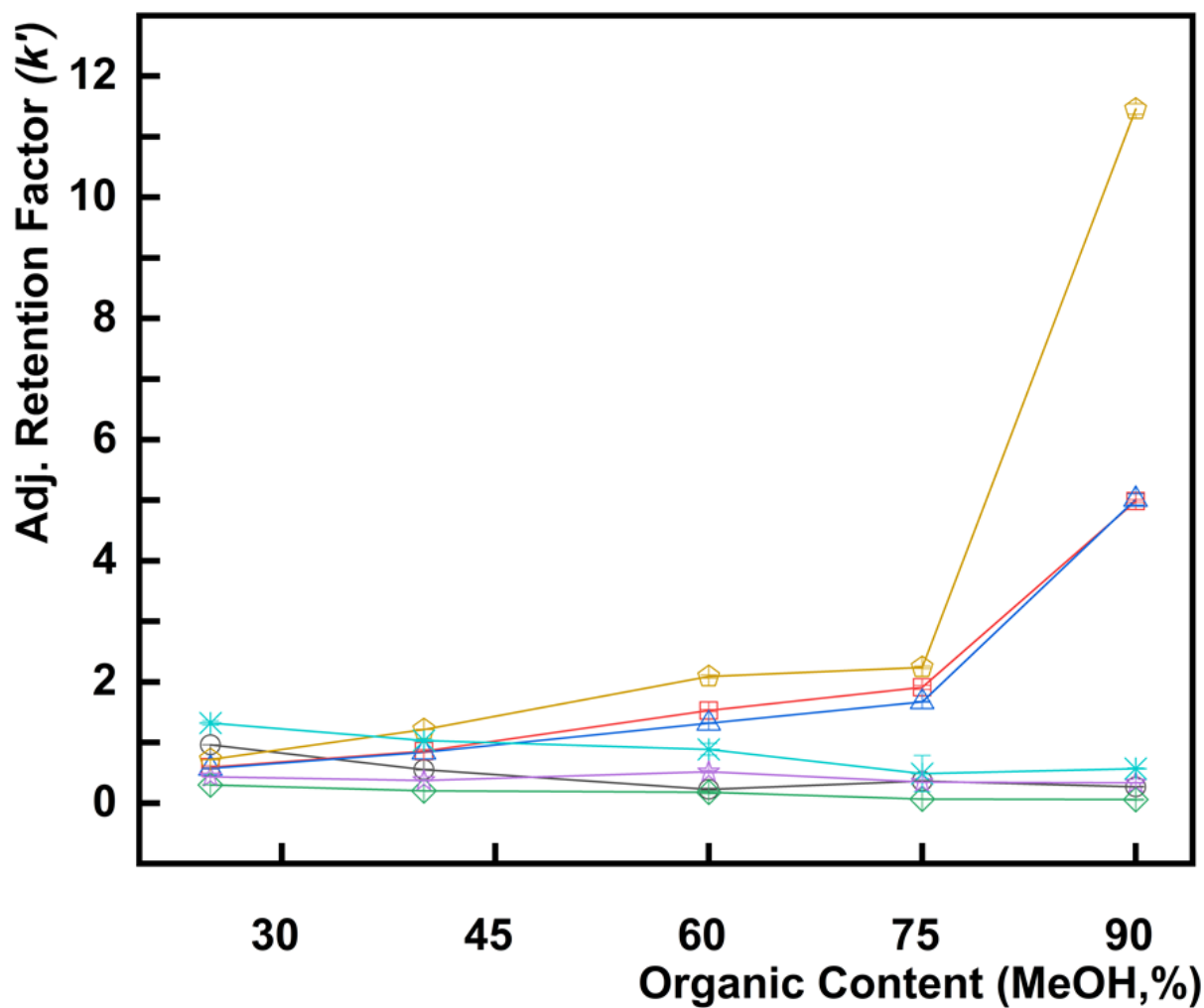


Figure 4.5. The retention factors of the seven analytes on the hydrogenated HPHT diamond at pH 10, methanol content ranging from 10% to 90%, ionic strength 1 mM. ○ – toluene; ◻ – BA; △ – BSA; ◇ – aniline; ☆ – uracil; ◻ – p-ABA; * – BTBA chloride.

Table 4.3. R^2 values ($n \geq 3$) for the approximation of retention factors obtained in the water-MeOH mobile phase (see Figure 4.5) using Eqn. 1 (partitioning model) and Eqn. 2 (adsorption model).

Analyte	Partitioning model	Adsorption model
<i>p</i> -ABA	0.7806	0.7308
BSA	0.9034	0.8694
BA	0.9160	0.8849

Hydrogenated diamond exhibited an affinity for hydrophobic compounds, unlike the oxidised diamond. For example, non-ionogenic benzene derivatives like toluene were retained on the hydrogenated diamond SP when water-organic mobile phases were used. Thus, typically reversed-phase behaviour was observed. The retention observed was not as strong as seen with graphitic carbon (Hypercarb) SPs [231], as revealed by the low organic solvent content required to observe retention in the current series of experiments. Nevertheless, to further investigate its hydrophobic properties, the retention of various benzene derivatives on hydrogenated HPHT diamond was investigated using a 6% ACN mobile phase. It was assumed that the hydrophobicity of the molecules would govern the strength of the solute–adsorbent interactions. The contribution to retention from hydrophobic interactions can be obtained from the correlation between retention and $\log P$, where the latter reflects the hydrophobic character of the organic compound, defined as the distribution coefficient in the octanol–water extraction system. The list of tested solutes and their properties is summarised in Table 4.4, and the resultant $\log P - \log k$ correlations are shown in Figure 4.6.

Table 4.4. Properties of the investigated hydrocarbon and halogen derivatives of benzene and data on their retention on hydrogenated HPHT diamond with 6% ACN in the mobile phase.

Solute	Log P^*	Log k	Solute	Log P^*	Log k
benzene	2.13	−1.46	Fluorobenzene	2.27	−0.72
toluene	2.73	−0.39	Chlorobenzene	2.84	−0.06
styrene	2.95	0.36	Bromobenzene	2.99	0.22
o-xylene	3.15	−0.06	1-fluoro-4-bromobenzene	3.08	0.40
ethylbenzene	3.15	0.28	m-dichlorobenzene	3.53	0.80
p-xylene	3.16	0.28	nitrobenzene	1.85	−0.04
m-xylene	3.20	0.25	mesitylene	3.42	0.37
cumene	3.66	0.17	4-nitrotoluene	2.37	0.65
propylbenzene	3.69	−0.31	1-phenyl-1-butyne	3.30	0.89
butylbenzene	4.38	1.16	naphthalene	3.30	1.27
sec-butylbenzene	4.57	−0.06			

*Log P values for benzene derivatives (water/octanol) were taken from the experimental data database of Environment Protection Department

In the course of this investigation, it was clearly established that retention of the investigated benzene derivatives on hydrogenated diamond depends on hydrophobicity, as well as the length of the alkyl chain, the number of substituents and their relative positions (Figure 4.6, right) and nature of the substituent (Figure 4.6, left). Linear regression coefficients (R^2) for the dependence of the logarithm of the retention factor ($\log k$) on the $\log P$ values of the four derivatives with different lengths of alkyl chains, namely, toluene, ethylbenzene, propylbenzene and butylbenzene was found to be 0.998 and the dependence described by equation $\log k = 0.952 \log P - 3.016$. The $\log k$ values for solutes in the order of benzene, toluene, xylene, where the number of methyl substitutes increases by one, depends on hydrophobicity as $\log k = 1.646 \log P - 4.939$, with $R^2 = 0.995$ (Figure 4.6, right).

Remarkably, a difference in retention of xylene isomers was noticed, and the elution order was *meta*, *para*, *ortho*, similarly to the reported data for PGC and MSDN [82]. As in the case of those SPs, the lower retention of *m*-xylene is related to the smaller number of contacts (three) than *o*- and *p*- xylenes (four) between the flat surface of diamond and the isomer [240]. The difference in retention between the *para* and *ortho* isomers was insignificant in this study. Possibly, the greater retention of *o*-xylene may be due to a higher charge transfer interaction, or a greater ability to induce a significant dipole on the diamond surface. Separation of isomers is a significant challenge for analytical chemistry, and this finding contributes to the idea that certain types of carbonaceous adsorbents are a possible future solution to this problem.

For the halogen benzene derivatives, a correlation between hydrophobicity and retention was also found. The tested compounds included fluorobenzene, chlorobenzene, bromobenzene, 1-fluoro-4-bromobenzene and *m*-dichlorobenzene. The equation describing the correlation, in this case, is the following: $\log k = 1.2 \log P - 3.5$, with $R^2 = 0.986$ when the mixed halogen derivative 1-fluoro-4-bromobenzene is included, and 0.996 otherwise (Figure 4.6, left).

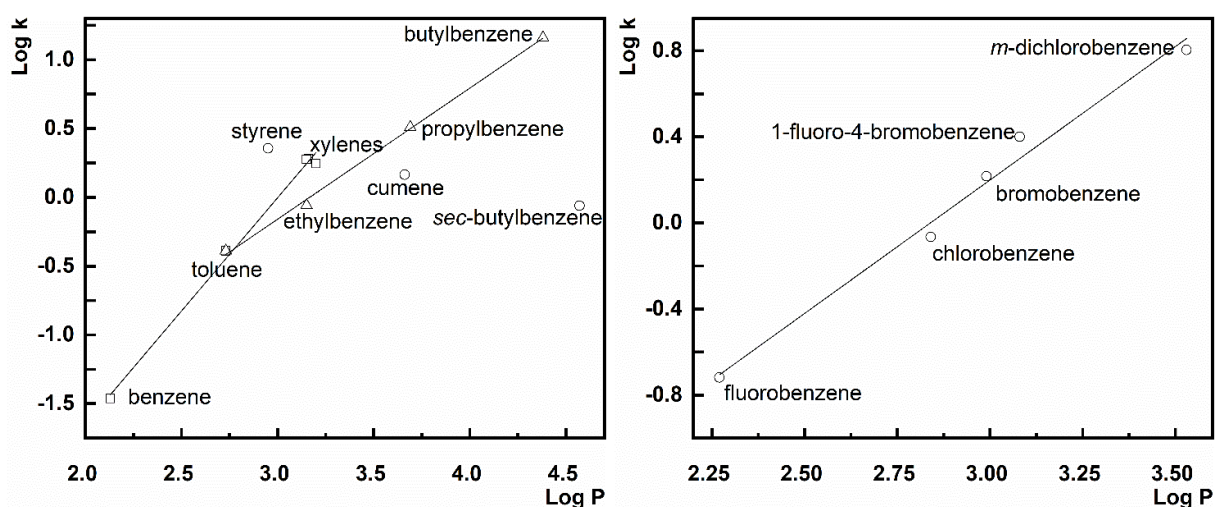


Figure 4.6. LogP–log k correlation for hydrocarbon (left) and halogen (right) derivatives of benzene. Hydrogenated HPHT diamond. Eluent: 6% ACN, □ – methylbenzenes; △ – alkylbenzenes; ○ – other benzene derivatives.

As shown in Chapter 3, the size fractionation of diamond particles by multiple sedimentations can reduce diamond particle size distribution leading to higher column efficiencies (up to 36,740 plates m^{-1}). This fractionation has not been performed for the investigated adsorbent in the present study because the achievement of high separation efficiency was not the study's aim. Nevertheless, in order to show the potential of hydrogenated diamond in RP HPLC, separation of the model mixture (benzene (0.02 mg mL^{-1}), sec-butylbenzene (0.1 mg mL^{-1}), p-xylene (0.1 mg mL^{-1})) in 6% ACN was performed (Figure 4.7).

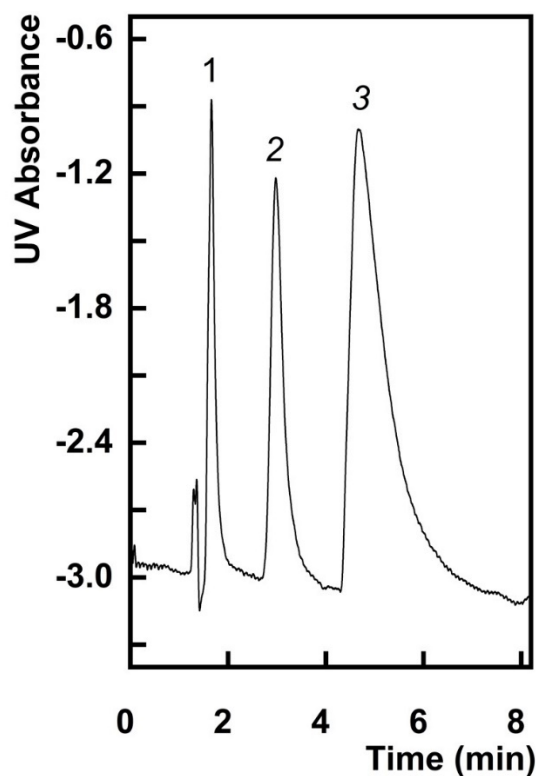


Figure 4.7. Separation of model mixture of benzene derivatives (1 – benzene (0.02 mg mL^{-1}), 2 – sec-butylbenzene (0.1 mg mL^{-1}), 3 – p-xylene (0.1 mg mL^{-1})) on hydrogenated HPHT diamond. Eluent 6% ACN. All analytes were prepared in the eluent.

4.3.2.3. *Electrostatic interactions*

The influence of the ionic strength on the retention of seven solutes (toluene, BA, benzenesulfonic acid, aniline, uracil, p-ABA and BTBA) was more fully investigated. For collecting experimental data, mobile phases containing 75% methanol and 25% 0.01M CAPS buffer ($\text{pH} = 10$) with ionic strengths of 1, 2, 4, 6, and 10 mM adjusted with sodium chloride were prepared, (other conditions are described in Section 4.2.8). The retention factor of the selected solutes was plotted against ionic strength and the results are shown in Figure 4.8. The general trend for anionic compounds is a decrease in retention time with an increase of ionic strength of the mobile phase. This confirms early observations that electrostatic interactions play a significant role in the retention mechanism. Higher ionic strength results in the suppression of such interactions and decreases the retention of acids.

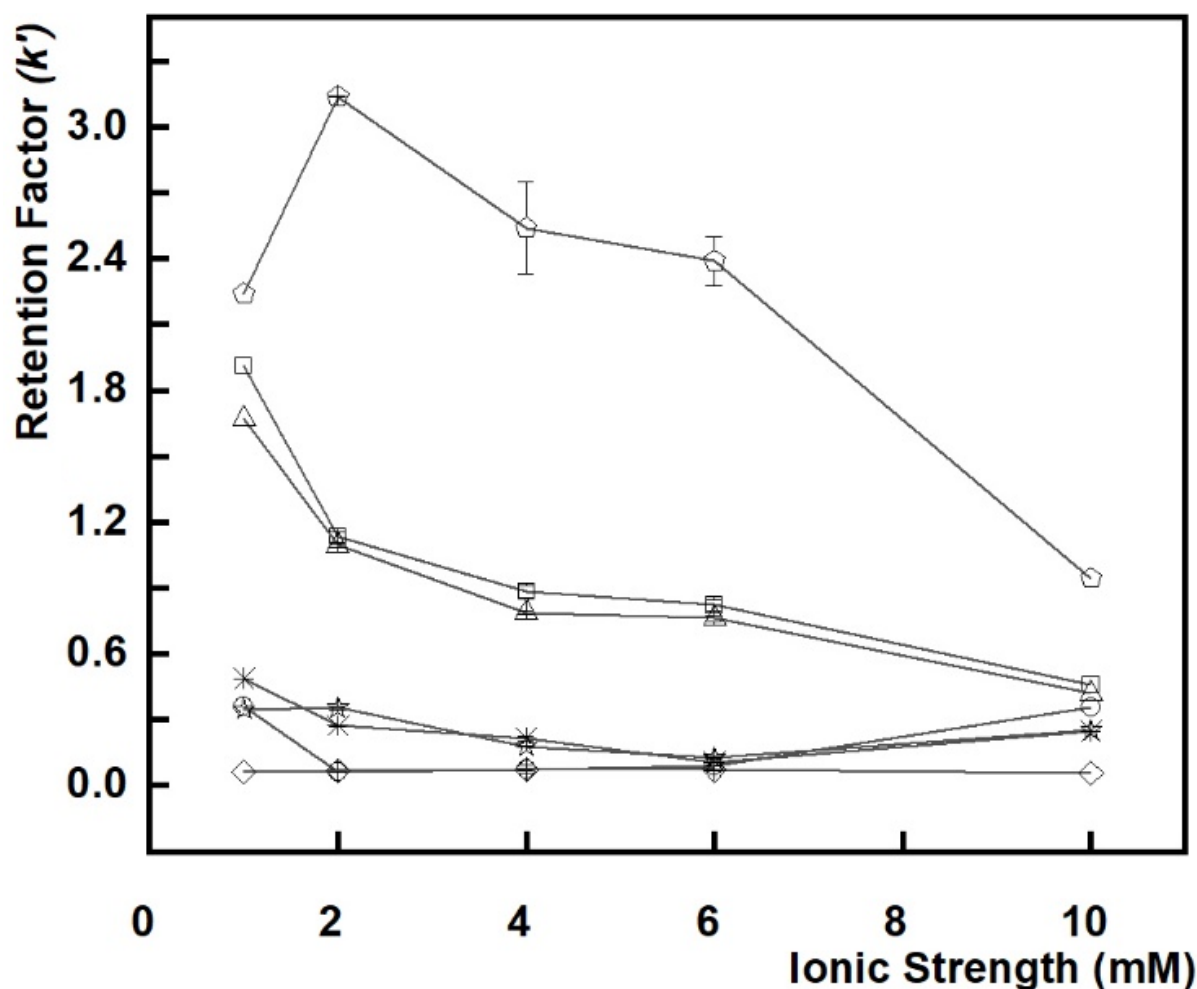


Figure 4.8. The retention factors of seven analytes on hydrogenated HPHT diamond at pH 10, eluent: 75% MeOH, ionic strength 1 to 10 mM. ○ – toluene; □ – BA; △ – BSA; ◇ – aniline; ☆ – uracil; ◇ – p-ABA; * – BTBA chloride.

4.3.2.4. Column efficiency

As previously mentioned, the main goal of this study was an investigation of the adsorption properties of hydrogenated diamond and not the preparation of a highly efficient adsorbent for HPLC. Nonetheless, column efficiency was investigated to make some conclusions about the optimum flow rate for our experiments. The Van Deemter curve for the hydrogenated diamond column (stainless steel, 50×4.6 mm ID) is depicted in Figure 4.9. The data was collected using BA as the injected solute (in triplicate) to calculate standard deviations. The mobile phase contained 90% methanol and 10% CAPS buffer (pH = 10) to ensure substantial solute retention for accurate calculations. A linear velocity range from 0.01 to 0.2 cm s^{-1} was examined. The

results indicated that the best efficiency for this chromatographic column could be obtained at a flow rate below 0.1 mL min^{-1} , but such a low flow rate would be impractical to use for further experiments. The overall efficiency was clearly poor, as expected ($H_{\text{min}} = 100 \text{ }\mu\text{m}$ for BA), which is a result of poor column packing, and broad particle size distribution ($1.5\text{--}2.5 \text{ }\mu\text{m}$ according to manufacturer), and the irregular HPHT diamond particle shape and non-porous structure. Thus, the flow rates used for the experiments within this chapter were chosen as a compromise between efficiency and practicality.

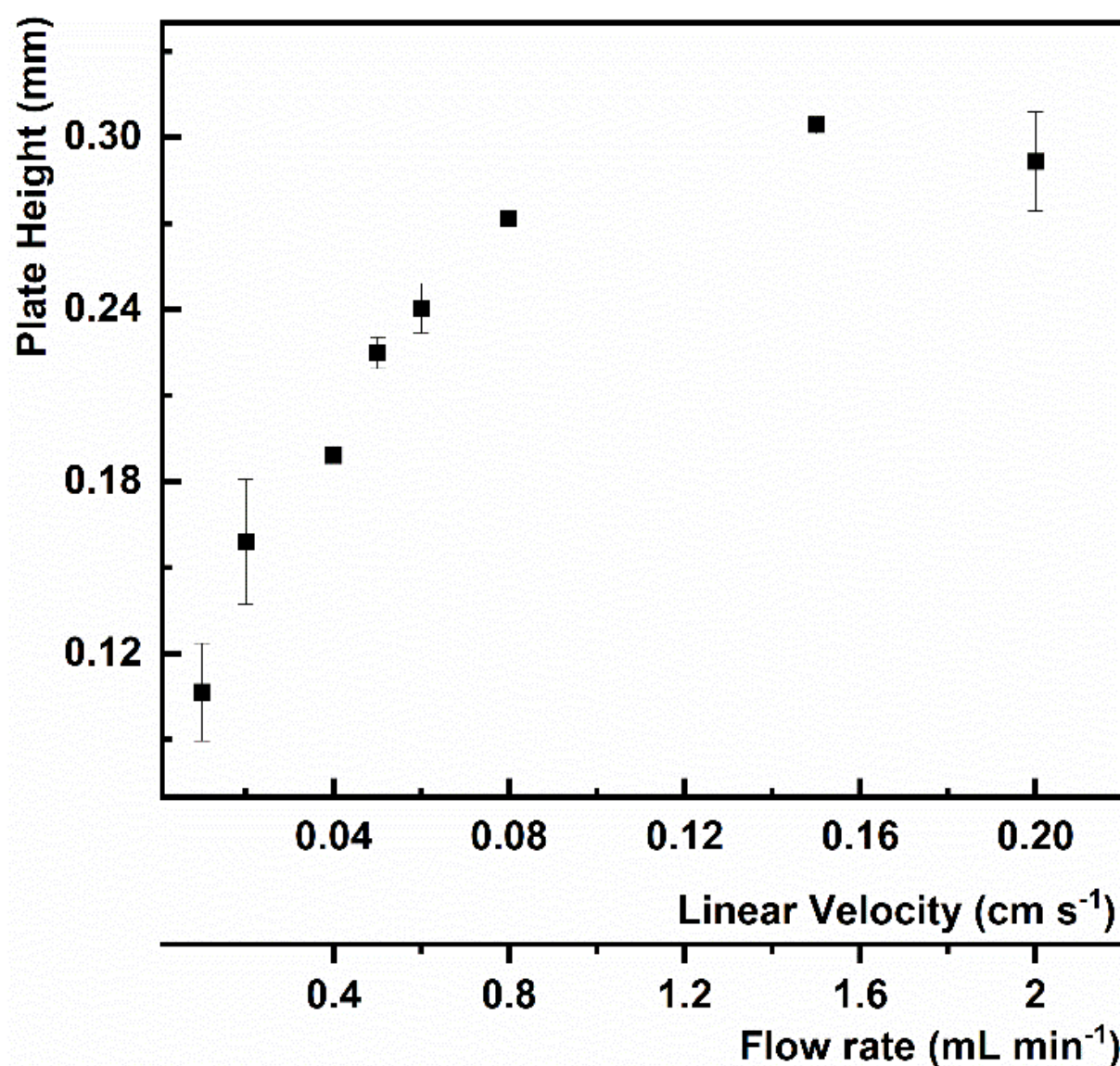


Figure 4.9. Van Deemter curve for the hydrogenated diamond column. Analyte – BA; Eluent: 90% MeOH – 10% 0.01M CAPS buffer pH 10.

4.3.2.5. *Effect of temperature*

Valuable knowledge about interactions between solutes and the surface of the hydrogenated diamond can be obtained from the parameters within the Van't Hoff equation (Eqn. 3):

$$\ln k = -\Delta H^\circ/RT + \Delta S^\circ/R + \ln \beta, \quad (3)$$

where k is the retention factor, ΔH° is the change in enthalpy, ΔS° is the change in entropy, T is the absolute column temperature (K), R is the gas constant, and β is the column phase ratio (volume). The equation can be used to calculate the enthalpy of interaction of analytes with the retention of various benzoic acids on the SP. Retention factors were measured at different temperatures in a range between 30 and 75°C.

As shown in Figure 4.10 and Table 4.5, the obtained Van't Hoff plots reveal linear relationships for the three investigated compounds, which means that the retention mechanisms for the solutes are constant at all temperatures under the mobile phase conditions applied. All ΔH° values are negative, which indicates the exothermic character of interactions.

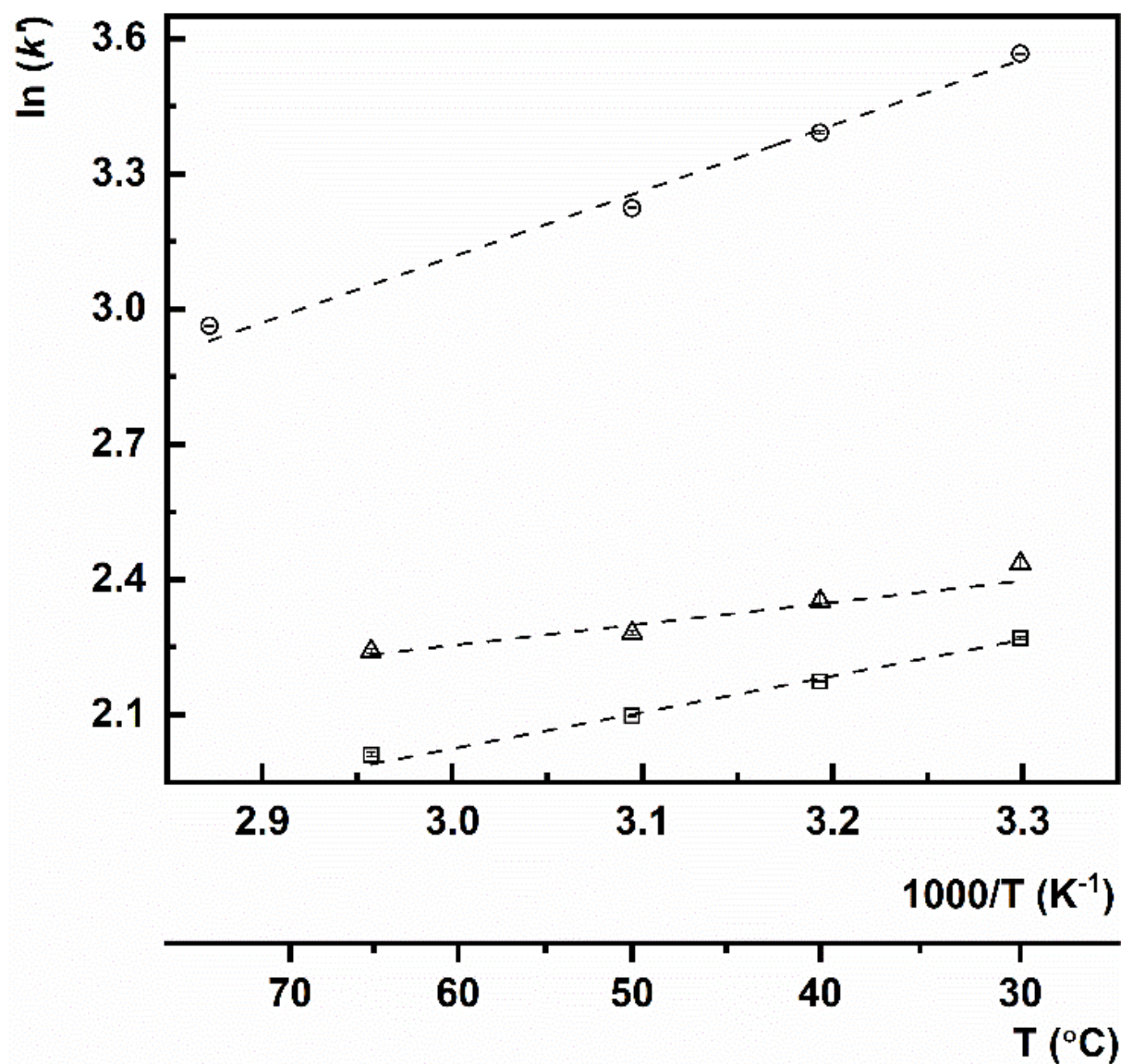


Figure 4.10. Van't Hoff plots obtained for hydrogenated diamond. Mobile phase: 90% MeOH – 10% 0.01M CAPS buffer, pH 10. □ – BA; ○ – p-ABA; △ – BSA.

Table 4.5. Parameters of the Van't Hoff plots for model compounds and coefficients of linear regressions R^2 .

Compound	ΔH° , kJ mol ⁻¹	$\Delta S^\circ/R + \ln\beta$	Linearity, R^2
BA	-6.7±0.4	-0.39	0.993
BSA	-4.0±0.9	0.82	0.899
p-ABA	-12.1±1.0	-1.26	0.988

4.4. Conclusions

In this study, the HPHT diamond was hydrogenated, and its surface changes were confirmed by FTIR, XPS, and elemental analysis. The resulting adsorbent was packed into chromatographic columns, and its selectivity investigated and compared with that of oxidised diamond under various mobile phase compositions.

Oxidised diamond, as expected, showed dominant cation-exchange properties, while retention on the hydrogenated diamond was significantly more complex. Anion-exchange retention appears to play a role in the retention of carboxylic acids on the hydrogenated diamond SP, with the change of ionic strength noticeably affecting the acids' retention factors. The gradual increase in carboxylic acid retention with the addition of methanol into the mobile phase points towards a possible combination of HILIC and solvent-enhanced ion-exchange behaviour. Yet, it is unclear which of these mechanisms prevails and what surface chemistry of the hydrogenated diamond is causing these interactions. Therefore, further investigation is required to explain this phenomenon.

Even though hydrophobic interactions are not entirely dominant on the investigated SP, as it was expected, they also play an essential role in retention. It has been shown that 21 non-ionogenic derivatives of benzene could be retained from the mobile phase, which contained 6% ACN, and the retention factors correlated with the polarity ($\log P$) of the solutes. The efficiency of separation was poor ($H_{\min} = 100 \mu\text{m}$ for BA), as improving separation efficiency was not a goal for this study.

Furthermore, the thermal stability of the adsorbent and immutability of retention mechanisms involved was confirmed by linear Van't Hoff plots for the investigated compounds.

CHAPTER 5

Ion Chromatographic Determination of Hydrazine in Excess Ammonia for Monitoring Graphene Oxide Reduction Reaction

5.1. Abstract

A new ion chromatography method has been developed to study graphene oxide (GO) reduction by monitoring hydrazine concentration in the GO suspension. The method is based on ion chromatographic separation of hydrazine (from excess ammonia) and its selective determination by electrochemical detection. The developed analytical protocol overcame the significant practical challenges of atmospheric hydrazine oxidation and minimised the matrix interference in both separation and detection which result from the excess of ammonium with respect to hydrazine (up to 5.8×10^4 times) in GO reduction experiments. Chromatographic separations were achieved using a high capacity IonPac CS16 cation-exchange column with a 30 mM methanesulfonic acid (MSA) eluent, within an analysis time of less than 20 min. Detection of hydrazine as hydrazinium ion using electrochemical detector was linear between 10 μ M and 4 mM, with LOD and LOQ values of 3 μ M and 10 μ M, respectively. Standard additions confirmed $103 \pm 0.8\%$ recovery. The developed method was successfully used to determine the point of complete GO reduction with hydrazine. Reaction curves for GO reduction generated using the method were compared to results from Fourier-transform infrared spectroscopy and Raman spectroscopy to verify the utility of the approach.

5.2. Introduction

Over the last decade, chemically reduced graphene oxide (rGO) has attracted a great deal of attention from researchers across many fields, as it exhibits unique properties for which there are many potential applications [241, 242]. One of the most common approaches to the preparation of rGO is via reduction of exfoliated GO using hydrazine [243-246]. Hydrazine is a highly reactive base and a strong reducing agent; hence it is widely used in organic synthesis as a reducing agent [247]. Hydrazine was first used for the reduction of GO by Ruoff *et al.*

[243]. The exact mechanism for the reduction of GO with hydrazine is however still unclear; although it is proposed to be through a direct nucleophilic attack of hydrazine on the epoxide groups, where hydrazine is converted into diamine and water [244]. There is also some contradiction in the rate of the reduction reaction, and more specifically, how to control and monitor the reduction process to identify the time-point of complete reduction.

The surface of GO presents several oxygen-containing functional groups, such as hydroxyl, epoxide, carbonyl, and carboxyl. Peng-Gang *et al.* observed that during GO reduction with hydrazine at 95 °C, carboxyl and carbonyl groups were reduced within 1 to 2 hours, however, the complete reduction of epoxide groups could take up to 3 hours [246]. The reduction of these groups has been typically studied through either Fourier-transform infrared spectroscopy (FTIR) [246], Raman spectroscopy [248], X-ray photoelectron spectroscopy (XPS) [248], UV-Vis spectroscopy [245], or four-point probe conductivity measurements [249]. Each of these semi-quantitative methods, with the possible exception of UV-Vis spectroscopy, are restricted to off-line measurements and require the removal of rGO sheets from the reactor prior to each subsequent measurement. In addition to the above spectroscopy and physical methods, some attempts at separation-based methods have also been reported, such as capillary electrophoresis, but with limited success [250].

UV-Vis spectroscopy methods are based on the measurement of the redshift of $\lambda_{\max}$ for GO sheets from 230 nm to 270 nm during their reduction. The termination of the redshift is considered as the time required for complete GO reduction. However, the difference in the $\lambda_{\max}$ of GO sheets over time during the reduction process is relatively small, such that it can result in the determination of a false endpoint for the GO reduction process [245]. Previous studies that have used UV-Vis spectroscopy to study the endpoints for GO reduction using hydrazine have often suggested much shorter times for complete GO reduction, such as 60 minutes [245]

and 15 minutes [251], as compared to that proposed in studies that have used XPS or FTIR studies (3 hours [246]), at the same reaction temperature of 95 °C. These contradictory results suggest a new method for monitoring GO reduction is required that offers the potential for both accurate and on-line determination of the reduction endpoint, and this can be achieved by developing a method to monitor the hydrazine consumption in the GO reduction solvent.

An accurate measurement of hydrazine consumption during the GO reduction process would help to provide a better insight into GO reduction kinetics and the point of complete reduction. Moreover, the development of a chromatographic method to monitor the hydrazine consumption would facilitate the future development of an on-line system for monitoring GO reduction, which is especially required in the study or control of GO reduction kinetics and to obtain stable aqueous suspensions of maximally reduced GO [250].

The reduction of GO by hydrazine is often performed in the presence of excess ammonia to minimise the aggregation of the rGO sheets [245, 250, 252]. Hence, given the reactive nature of hydrazine and the large excesses of ammonia present in such solutions, this presents quite a significant analytical challenge towards accurately quantifying the hydrazine concentration. Analytical approaches reported to-date involving the determination of hydrazine in the presence of ammonia have been reviewed and are summarised within Table 5.1 below. The range of analytical techniques applied includes, flow-injection analysis [253-256], gas chromatography [257] ion chromatography [258-261], titration [262-264], and fluorescence-based assays [265-267]. The most sensitive of these reported methods involves fluorescence, based upon the reaction of hydrazine with 2,3-naphthalene dicarboxaldehyde. The method is indeed highly selective for hydrazine [266], however, it requires precise control of the sample derivatisation conditions, its response is highly dependent upon pH (optimum pH = 2.5), and the reagent is very expensive. A second similarly sensitive spectrophotometric method has been

reported, which is based upon the reaction with *p*-dimethylaminobenzaldehyde (*p*-DMBA) [256]. However, in this case, the method was set-up and designed for industrial applications, and the reagent is not highly selective for hydrazine; hence interference from excess ammonia would be significant. From Table 5.1, it can be seen that the maximum tolerance to excess ammonium from published methods (where stated) is at a ratio of 1:2500 [259]. For our study and the desired application, this is well below the requirement.

Obviously, chromatographic separation provides the possibility to achieve greater tolerances to high ammonia levels, ideally combined with sensitive (and selective) detection. Ion-chromatographic methods developed for hydrazine to-date, using either conductivity or amperometric detectors, provide slightly less sensitivity than some alternative methods discussed above, but obviously do not involve expensive reagents, or require sample pre- or post-column derivatisation [268]. In the following study, we sought to determine the time required for the complete reduction of exfoliated GO sheets with hydrazine monohydrate in ammonia environment by monitoring the hydrazine content in the solution during the reaction. To achieve this, an ion-chromatographic method for the determination of hydrazine in ammonia environment was developed. Application of this method to the determination of the point of complete GO reduction was validated using FTIR and Raman spectroscopy. Hydrazine is a highly reactive reducing agent, therefore, a competing reaction with oxygen could significantly affect the results of the study. For this reason, great attention in this work was paid in optimising the experimental and sampling conditions.

1 Table 5.1. Existing methods for the determination of hydrazine in the presence of ammonia.

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Method	Studied concentrations of N ₂ H ₄ (µg/L)	The maximum studied ratio of NH ₃ :N ₂ H ₄	LOD for N ₂ H ₄ (µg/L)	Samples	Ref.
Flow injection spectrophotometric detection with <i>p</i> -DMBA	25 to 300	60	0.2	A mixture of ammonia and hydrazine	[253-255]
Flow injection spectrophotometric detection with <i>p</i> -DMBA	1×10 ⁴ to 4.86×10 ⁵	100	10	Water from the steam cycle of the son Reus plant (Spain)	[256]
Fluorescence detection with dichlorofluorescein and resorufin acetates	<1.6×10 ⁶	-	2.88 and 26.28, respectively	Aqueous solutions (tap water)	[265]
Fluorescence detection with 2,3-naphthalene dicarboxaldehyde	< 1000	NH ₃ does not interfere	0.05	Artificial water mixtures	[266]
Fluorimetric determination with 2-hydroxybenzaldehyde azine	800 to 3.2×10 ⁴	150	-	Artificial model mixtures	[267]
Ion chromatography with suppressed conductivity detection	100 to 4000	2.5	11	Air	[258]
Ion chromatography with conductivity and amperometric detection	10 to 50	2500	2.3	Simulated nuclear power plant wastewater matrix	[259]
Ion chromatography with electrochemical detection	1 to 1000	5	-	Artificial water mixtures	[260]
Ion-exclusion chromatography with conductivity detection	1 to 1×10 ⁵	-	0.64	Real boiler water sample	[261]
Colourimetric flow titration with electrogenerated bromine	64 to 3.5×10 ⁴	250	1.92	A mixture of N ₂ H ₄ and NH ₃ and spiked water samples	[262]
Titration with direct iodine/iodate	3.2×10 ⁴ to 3.2×10 ⁷	0.07	3.2×10 ⁴	A mixture of 44% N ₂ H ₄ and 3% NH ₃ in water	[263]
Titration with bromate	1600 to 4800	393	-	An aqueous mixture of N ₂ H ₄ and NH ₃ in water	[264]

5.3. Materials and Methods

5.3.1. Materials

A Dionex ICS-2000 ion chromatograph (Dionex, Thermo Fisher Scientific, Sunnyvale, CA, USA) equipped with a UI20 Universal Interface and a PC with Chromeleon 6.8 software was used for the chromatography. The instrument was used with an IonPac CS16 cation-exchange (250 × 5 mm ID) column, a Dionex CSRS300 (4-mm) cation self-regenerating suppressor, a Dionex DS6 heated conductivity cell detector, and a Dionex ED40 electrochemical detector. Disposable plastic 1-mL syringes and reusable gas-tight 250 µL syringes (Trajan Scientific and Medical, Melbourne, VIC, Australia) were used for sample loading. Millipore 0.45 µm type HA membrane filters were used to vacuum filter the rGO. Gas-tight vials (10 and 20 mL) with Polytetrafluoroethylene/Silicone septa (Supelco, Bellefonte, PA, USA) were used for sample preparation. The reagents used to prepare eluents, buffers, and stock solutions were: methanesulfonic acid, hydrazine monohydrate 64-65%, hydrazine sulfate, sodium phosphate dibasic, sodium phosphate monobasic (Sigma Aldrich, Castle Hill, NSW, Australia), sodium tetraborate (Merck, Darmstadt, Germany), ammonia 28-30% (Chem-Supply, Gillman, SA, Australia), and lithium nitrate (≥98%, Hopkin & Williams, Swansea, England). GO suspension (17 mg/mL) was kindly provided by the University of Wollongong (Wollongong, NSW, Australia).

5.3.2. Ion chromatography

All hydrazine solutions were prepared in gas-tight vials and were transferred using gas-tight syringes to minimise their atmospheric oxidation. Working standards were freshly prepared each day, and the stock standards were prepared monthly and stored in a fridge at 5 °C. The chromatographic column was rinsed at the end of each day with 30 mM MSA for 30 min.

Borate buffer (20 mM, pH 9.5) was prepared by dissolving sodium tetraborate in Millipore water and adjusting the pH with sodium hydroxide. It was mixed on-line with the eluent stream at a flow rate of 0.3 mL/min as shown in the schematic representation of the experimental setup (Figure 5.1), which resulted in the mobile phase pH of 1.85. The column temperature was maintained at 30 °C. A Dionex ICS-2000 Ion Chromatographic instrument controlled using Chromeleon® software (version 6.80) was used during this work. All the instrumental components including Virtual Column Separation Simulator [269] were obtained from Dionex (Sunnyvale, CA, USA).

The electrochemical detection was performed using a Dionex ED40 detector (Dionex, Thermo Fisher Scientific, Sunnyvale, CA, USA), which is a three-electrode system with titanium as the counter electrode and Ag/AgCl as the reference electrode. As mentioned above, the mobile phase pH was found to be acidic, hence, Pt was used as the working electrode over the more sensitive Au electrode, because latter requires basic eluent pH [259]. The active cell volume was 0.2 μ L. The detector was used in DC amperometry mode. It was coupled with a UI20 Universal Interface (Dionex, Thermo Fisher Scientific, Sunnyvale, CA, USA), which converted the analog current (input) into digitized voltage (output).

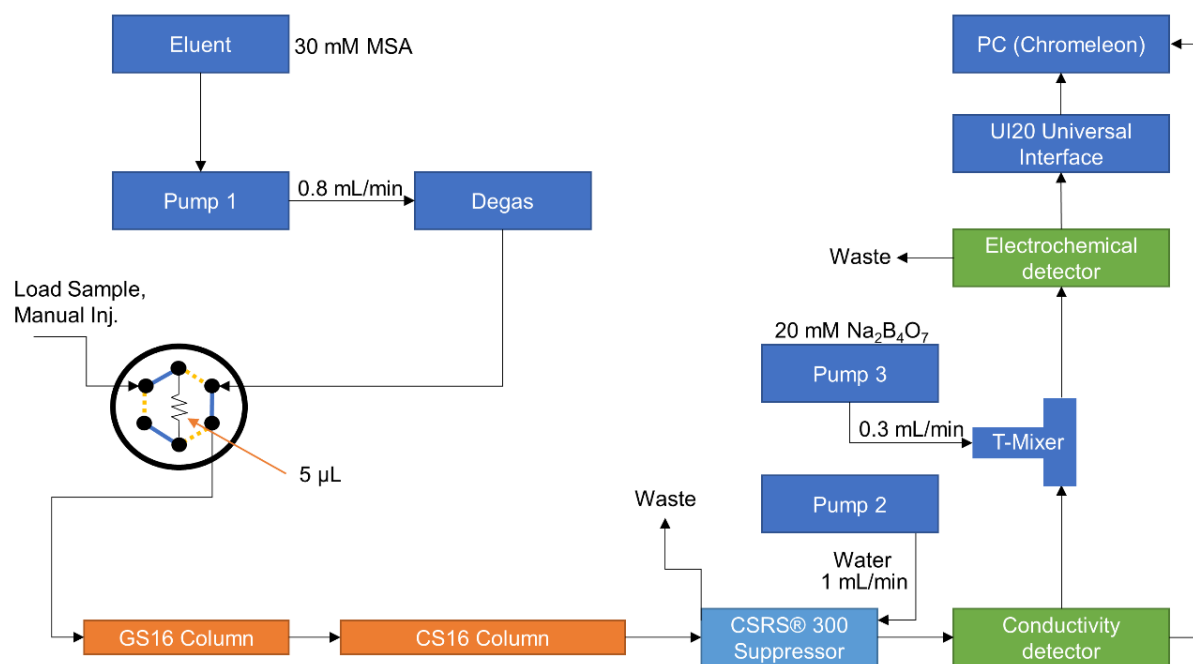


Figure 5.1. A schematic representation of the experimental setup for the ion chromatographic determination of hydrazine.

5.3.3. Fourier-transform infrared spectroscopy

The reaction mixture was vacuum filtrated using 37 mm diameter silver membrane filters with 0.45 μm pore size (Sterlitech, Washington, USA). The FTIR spectra were recorded on Bruker Vertex 70 spectrometer coupled to a Hyperion 3000 microscope using a Bruker Macro ATR Germanium crystal and a 20x reflection objective with an aperture of 124x124 μm^2 . The spectral range was 600-4000 cm^{-1} with a spectral resolution of 4 cm^{-1} using 64 scans for background and sample acquisition. The spectra were treated with atmospheric compensation and concave rubberband correction using 10 iterations and 500 baseline points.

5.3.4. Raman spectroscopy

The Raman spectra were recorded between 105-2732 cm^{-1} on a Renishaw inVia spectrometer with Streamline using a frequency doubled Nd:YAG laser 532 nm and a x20 (0.40 numerical

aperture (NA)) objective focusing the beam to a spot size of about 3.5 μm in diameter (5 μm in depth) with an adjusted laser power of 180 μW under the sample. Acquisition time was 1000s using a grating of 1200 l/mm resulting in a spectral resolution of about 2.5 cm^{-1} .

5.4. Results and Discussion

5.4.1. Ion chromatography

As listed in Table 5.1, various ion chromatographic methods have been developed previously for the determination of hydrazine in the presence of ammonia. However, these methods were not developed to separate hydrazine (as hydrazinium) from exceptionally high concentrations of ammonium, which is required here to determine the levels of hydrazine and ammonia typically applied in GO reduction processes. Hence, herein, the previously described methods [258-260, 268] for the ion chromatographic determination of hydrazine have been further adapted to minimise the interference from excess ammonia.

The presence of disparate concentrations of ammonia in relation to hydrazine in the GO reduction solvent necessitates the use of high capacity columns to tolerate high salt concentrations. Initially, Virtual IC Column Separation Simulator was used to identify suitable ion-exchange columns for the study [269]. The optimisation program suggested the use of either an IonPack CS18 or CS16 column for the desired separation. Both columns are based upon carboxylate-functionalised silica, however, they offer very different column capacities: CS18 (290 $\mu\text{eq}/\text{column}$) and CS16 (8400 $\mu\text{eq}/\text{column}$) [270]. Moreover, the CS16 (250 $\times$ 5 mm ID) column provides 4.6 times higher ion-exchange capacity compared to the CS18 (250 $\times$ 2 mm ID) column [271]. Accordingly, the CS16 column resulted in better peak shapes for ammonium and hydrazine (as hydrazinium), as compared to the CS18 column. Moreover, the high capacity of the CS16 column avoided its overloading from the excess ammonium. The

maximum cation concentration within the samples was 254 meq/L. Hence, a 5 μ L injection loop resulted in the use of less than 0.016% of the column capacity, which is well below the recommended 5% column loading limit [272]. The manufacturer recommended flow rate for the CS16 (250 $\times$ 5 mm ID) column was 1.0 mL/min. However, a slightly smaller Height Equivalent to the Theoretical Plate (HETP) was observed for hydrazine at the flow rate of 0.8 mL/min (27.1 μ m) compared to 1 mL/min (28.9 μ m) with 30 mM MSA as the eluent.

5.4.2. Electrochemical detection

The optimised ion chromatographic separation of standard mixtures still resulted in the partial overlapping of peaks for hydrazinium and the tail of the ammonium peak, particularly when a high excess of ammonia was present. Similar partial coelution has also been observed previously [259]. As mentioned above, in GO reduction solutions, the concentration of hydrazine is far lower than ammonia, which results in complete masking of the hydrazinium peak by the large ammonium peak when using standard conductivity detection (Figure 5.2a), and so this detection mode is not suitable for the quantitative determination of hydrazine in such solutions. However, electrochemical detection provides a selective determination of hydrazinium, even in the presence of a high concentration of ammonium (Figure 5.2b and Figure 5.2c).

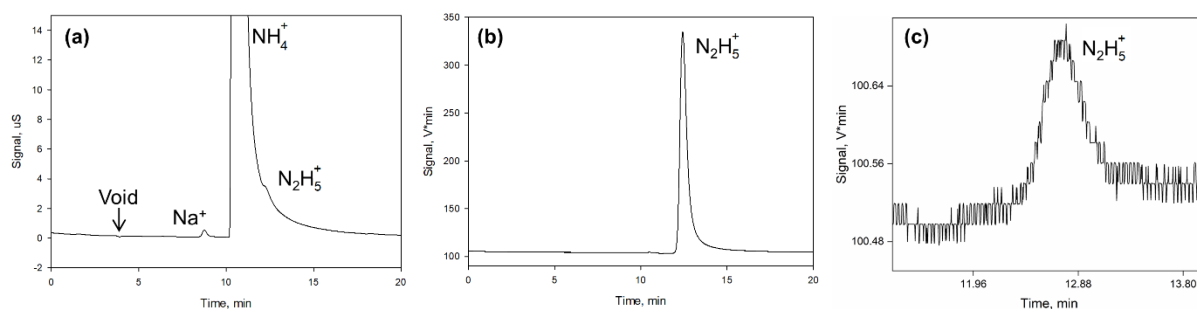


Figure 5.2. Ion chromatographic separation of the hydrazine and ammonia mixture: (a) conductometric detection of 1.6 mM hydrazinium, (b) electrochemical detection of 1.6 mM hydrazinium, and (c) electrochemical detection of 5×10^{-3} mM hydrazinium. Concentration of ammonia: 250 mM. column: CS16 (5×250 mm ID), eluent: 30 mM MSA, flow rate: 0.8 mL min^{-1} , column temperature: 30°C , injection volume: $5 \mu\text{L}$, and 20 mM $\text{Na}_2\text{B}_4\text{O}_7$ buffer at a flow rate of 0.3 mL min^{-1} was used in the post-column reactor.

The effect of ionic strength of the eluent on the electrochemical detection of hydrazine was studied by using the different concentration of borate buffer as a post-column reactor (Figure 5.1). As shown in Figure 5.3a, the use of Pt electrode based amperometry detection minimised any influence of the ionic strength on the electrochemical determination of hydrazine. The effect of electrode potential on the signal to noise ratio for hydrazine was also determined. As shown in Figure 5.3b, the response for hydrazine increased steeply from 0.1 V to 0.3 V, and plateaued after 0.3 V up to 0.7 V. However, the noise continued to increase up to 0.7 V. Hence, an electrode potential of 0.4 V was used to ascertain maximum and stable signal without introducing the high levels of noise.

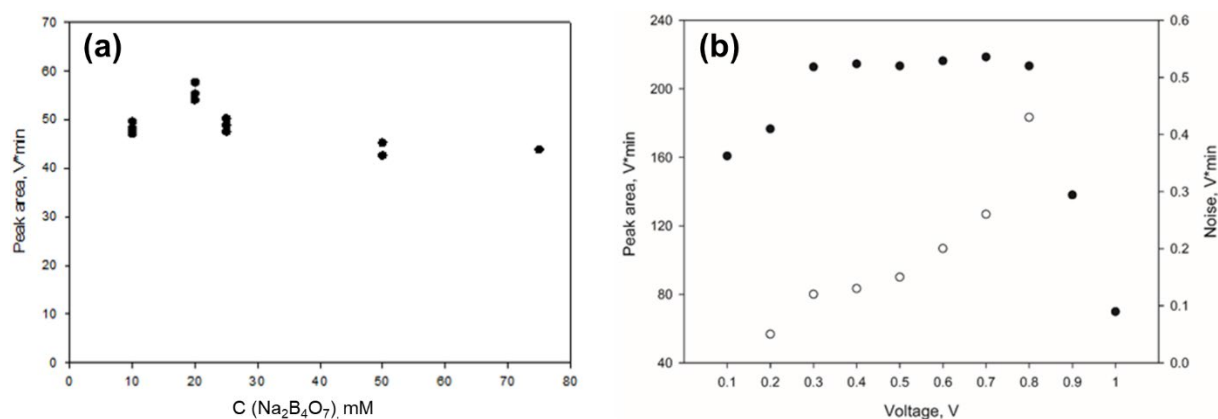


Figure 5.3. Dependence of the electrochemical response for hydrazine on (a) the concentration of borate buffer at an electrode potential of 0.7 V and (b) the electrode potential at the borate buffer concentration of 50 mM: peak area (●) and noise (○).

5.4.3. Quantitative determination of hydrazine in the presence of ammonia

A calibration plot was prepared for the electrochemical detection of hydrazine in the presence and absence of ammonia. Concentrations of hydrazine (from hydrazine monohydrate) from 0.5 μM to 4 mM resulted in a linear calibration plot ($R^2 = 0.9999$) with a slope of 101.55 (Figure 5.4). The calibration plot was cross-validated with standards produced from hydrazine sulphate, as hydrazine monohydrate can be unstable and degrade over time. However, as shown in Figure 5.4, no significant differences were observed between the two calibration plots.

The presence of excess (0.25 M) ammonia in the standard solutions resulted in a decrease in the slope of the calibration plot from 101.55 to 83.79, indicating that high concentration of ammonia negatively impacted ($\sim 20\%$) the sensitivity of the electrochemical detector for hydrazine (Figure 5.4). Hence, quantitative determination of hydrazine in the presence of ammonia requires a standard addition calibration approach, or a matrix matching of calibration solutions, to ensure the same concentration of ammonia as present in the experimental samples.

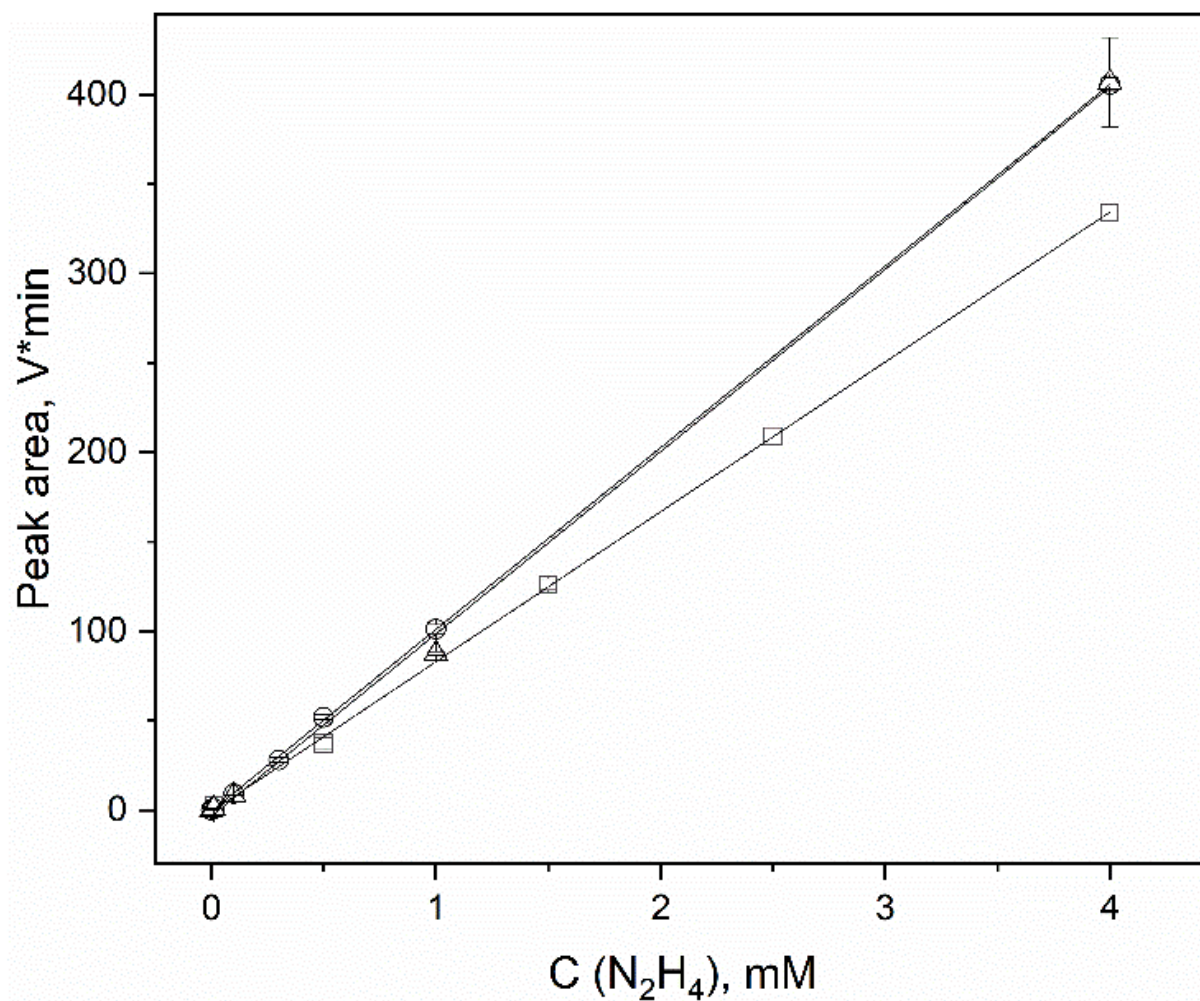


Figure 5.4. Calibration plot for hydrazine (peak area with respect to concentration). Hydrazine monohydrate (○), hydrazine sulphate (Δ), and hydrazine monohydrate in the presence of 0.25 M ammonia (□).

Under optimised conditions, the LOD ($S/N=3$) and LOQ ($S/N=10$) values for hydrazine in the presence of ammonia were estimated as 3 μM and 10 μM , respectively. To further validate the LOD and LOQ values, 5 μM hydrazine was studied, which resulted in a $S/N>3$, as shown in Figure 5.2c. Using the standard addition approach, an average ($n=3$) recovery of $103 \pm 0.8\%$ was observed for hydrazine from 10 μM to 20 μM in the sample matrix. These values were found suitable for the qualitative and quantitative determination of hydrazine to study GO reduction.

5.4.4. Study of GO reduction

GO sheets were reduced in the presence of 1.6 mM hydrazine and 0.25 M ammonia at 80 °C. The reduction was performed in gas-tight vials, as previous experiences with relatively open reactors, such as a three-neck flask (Figure 5.5) resulted in unwanted exposure to oxygen. Exposure to atmospheric oxygen resulted in the significant oxidation of hydrazine, which prevented any conclusive study of hydrazine concentration during the reduction process. The change in hydrazine concentration with respect to time in a three-neck flask is shown in Figure 5.6a. The use of gas-tight vials considerably reduced the atmospheric oxidation of hydrazine as shown in Figure 5.6b. However, since the atmospheric oxidation was still not completely eliminated, a blank experiment was always performed along with the GO reduction experiments to adjust the final concentration of hydrazine. Moreover, care was taken to minimise the number of punctures in a vial septum to ensure a gas-tight seal. It was observed that any more than 10 punctures resulted in significant degradation of the stored hydrazine solution. Hence, the reaction was simultaneously performed in multiple vials when more than 10 samples were required during the course of the study. The samples were collected using gas-tight syringes that were fitted with a 22 µm pore size filter paper between the syringe and the needle.

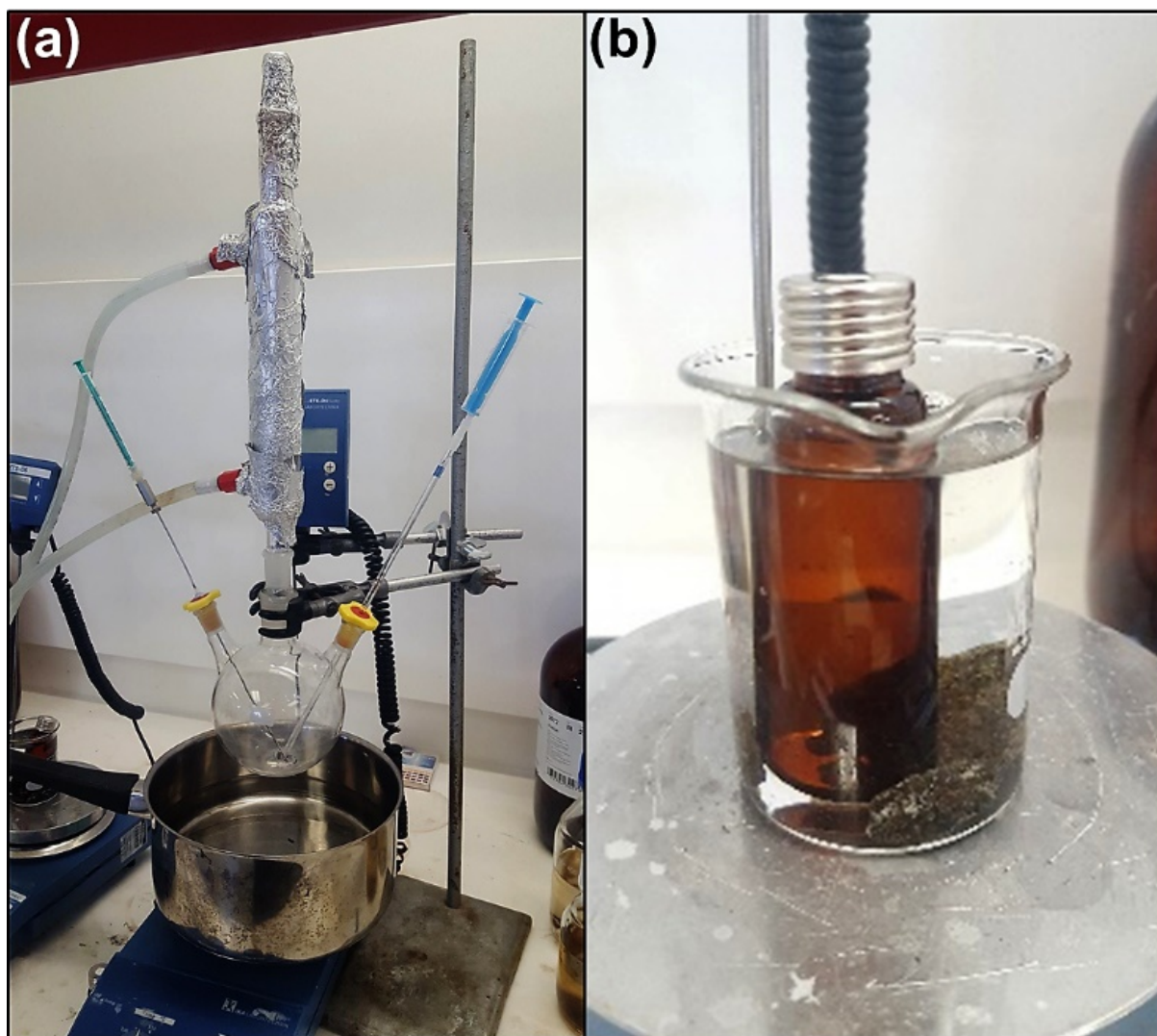


Figure 5.5. GO reduction assembly based on a (a) three-neck flask, which includes a magnetic stir bar and a thermostat, a reflux condenser, a capillary with a syringe for sampling, and a glass pipette to supply nitrogen and (b) gas-tight vial with a magnetic stir bar and a thermostat.

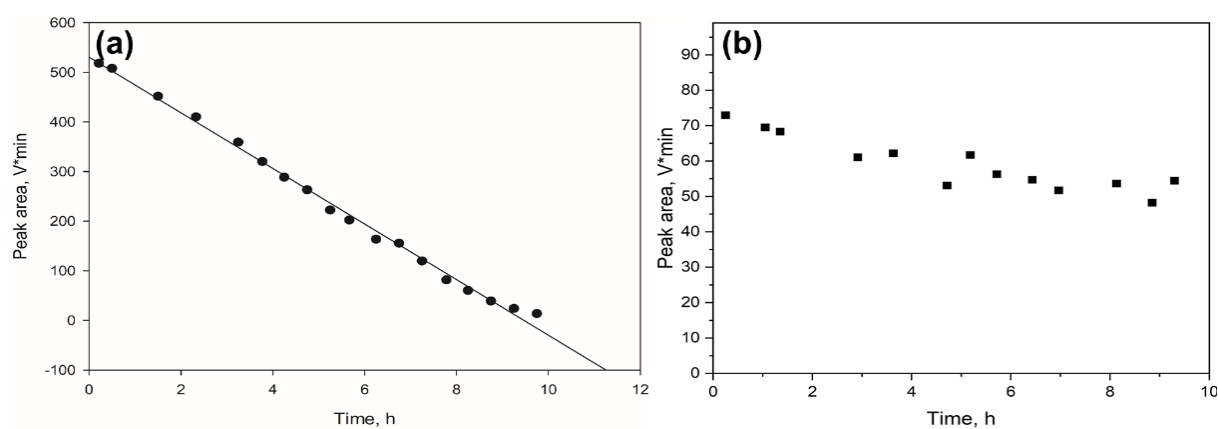


Figure 5.6. Depletion of hydrazine over time in the (a) three neck flask based assembly and (b) gas-tight vial-based assembly.

The consumption of hydrazine was monitored throughout the GO reduction process by analysing hydrazine concentration at regular time intervals using the developed ion chromatographic method described above. As shown in Figure 5.7, the hydrazine concentration continued to decrease for a period of ca. 6 hours, after which there was no significant change observed for up to 10 hours. These initial results suggested that under the applied conditions, the GO was completely reduced in ca. 6 hours. Three separate reactions were monitored in this way to understand the stability and reproducibility of the process. Reaction 1 and 2 were studied using the Dionex ED40 detector described above, and reaction 3 was studied using a miniaturised pulsed amperometric detector, described elsewhere [273]. All three reactions resulted in similar observations in terms of the reaction endpoint (Figure 5.7).

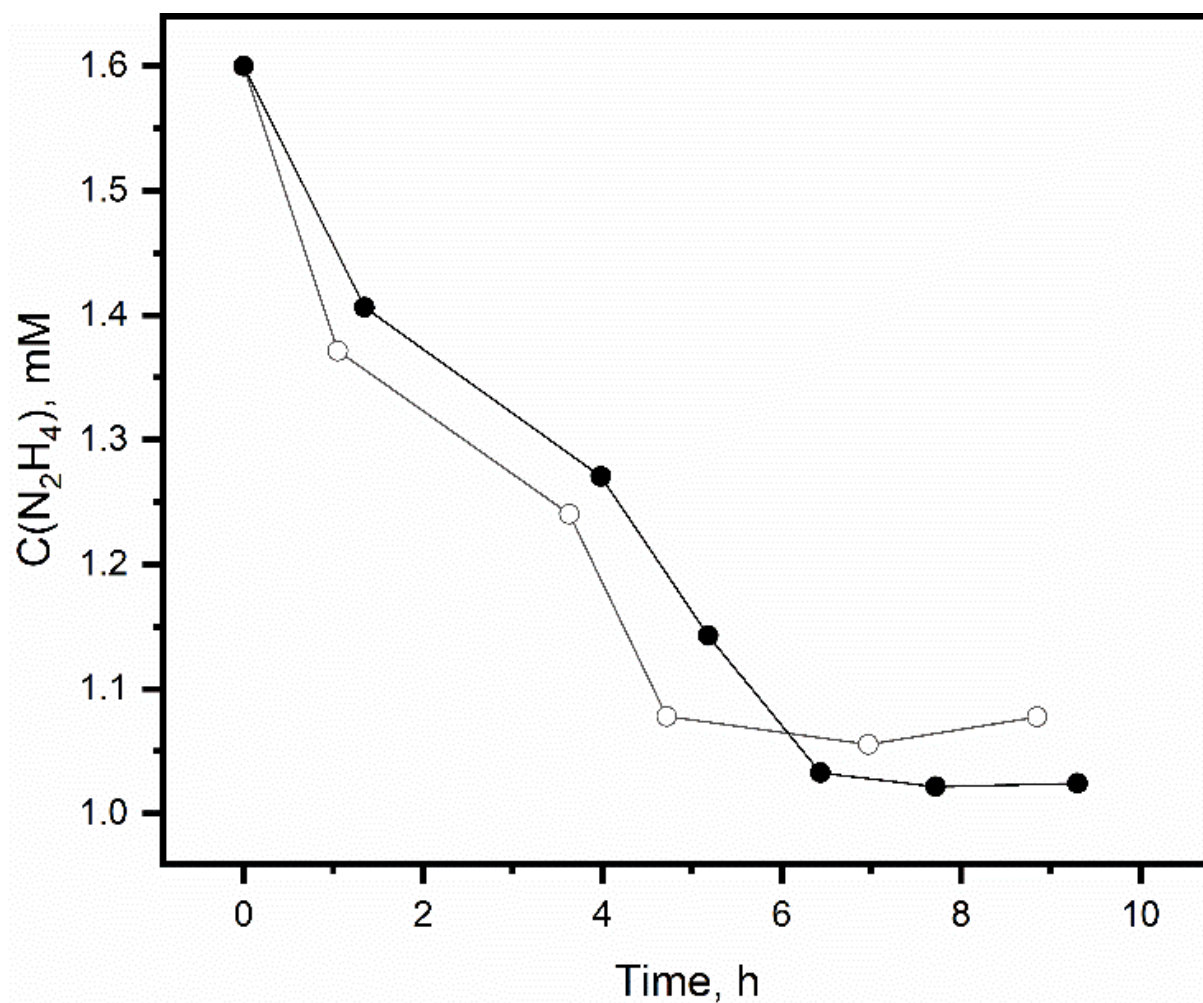


Figure 5.7. Monitoring hydrazine concentration during the GO reduction process. Reaction 1 (○), reaction 2 (●), and reaction 3 (■). The concentration of GO was 2 mg mL⁻¹, the starting concentration of hydrazine was 1.6 mM, the concentration of ammonium hydroxide was 0.25 M, and the temperature was 80°C.

To cross-validate these observations, the reduction endpoint obtained by monitoring hydrazine consumption was also investigated with FTIR and Raman spectroscopy. The FTIR spectroscopy of the un-reduced GO sheets showed C=C (1621 cm⁻¹), C-O (988 cm⁻¹ and 1044 cm⁻¹), C=O (1700-1780 cm⁻¹), and C-H (2850-2925) bonds stretching (Figure 5.8). The spectrum was found consistent with the previous FTIR spectra reported for GO [246]. The GO sheets that were reduced for 2 hours showed a shift in the aromatic C=C stretching peak (1621 cm⁻¹ to 1590 cm⁻¹) (presumably, due to the loss of C_{sp2}-O conjugation and an increase in delocalisation of the C=C bonds), a significant reduction in the oxygen functional groups (C=O

and C-O), and a concomitant increase in the C-H groups. The sheets that were reduced for 4 and 6 hours showed minimal changes in the C=C and C=O groups compared to the sheets reduced for 2 hours. A small peak for C-O groups was observed in the sheets that were reduced for 2, 4, and 6 hours, and it disappeared in the sheets reduced for 8 hours. This also suggests that GO was fully reduced after ca. 6 hours, which is in correspondence with the endpoint obtained by monitoring the hydrazine consumption. Raman spectroscopy also demonstrated a significant increase in the D/G band ratio for the sheets that were reduced for 6 hours compared to the un-reduced sheets, indicating a highly reduced state of GO after 6 hours (Figure 5.9). The endpoint obtained by monitoring hydrazine consumption also agreed with the previous observations made by other groups using XPS and FTIR analysis [246].

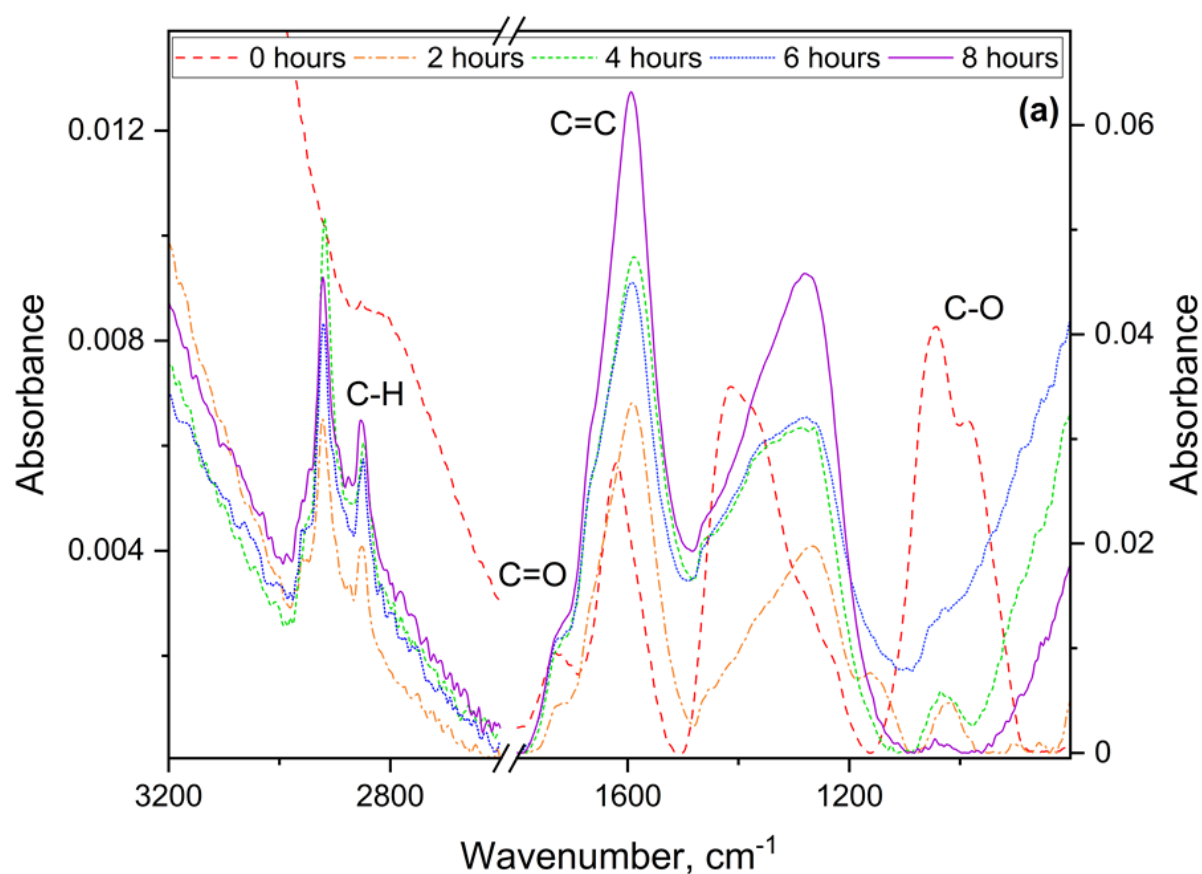


Figure 5.8. FTIR spectra of GO that was reduced for different time periods as indicated in the legend. The left Y-axis is for the wavenumbers from 3200 cm^{-1} to 2600 cm^{-1} , and the right Y-axis is for the wavenumbers from 1800 cm^{-1} to 800 cm^{-1} .

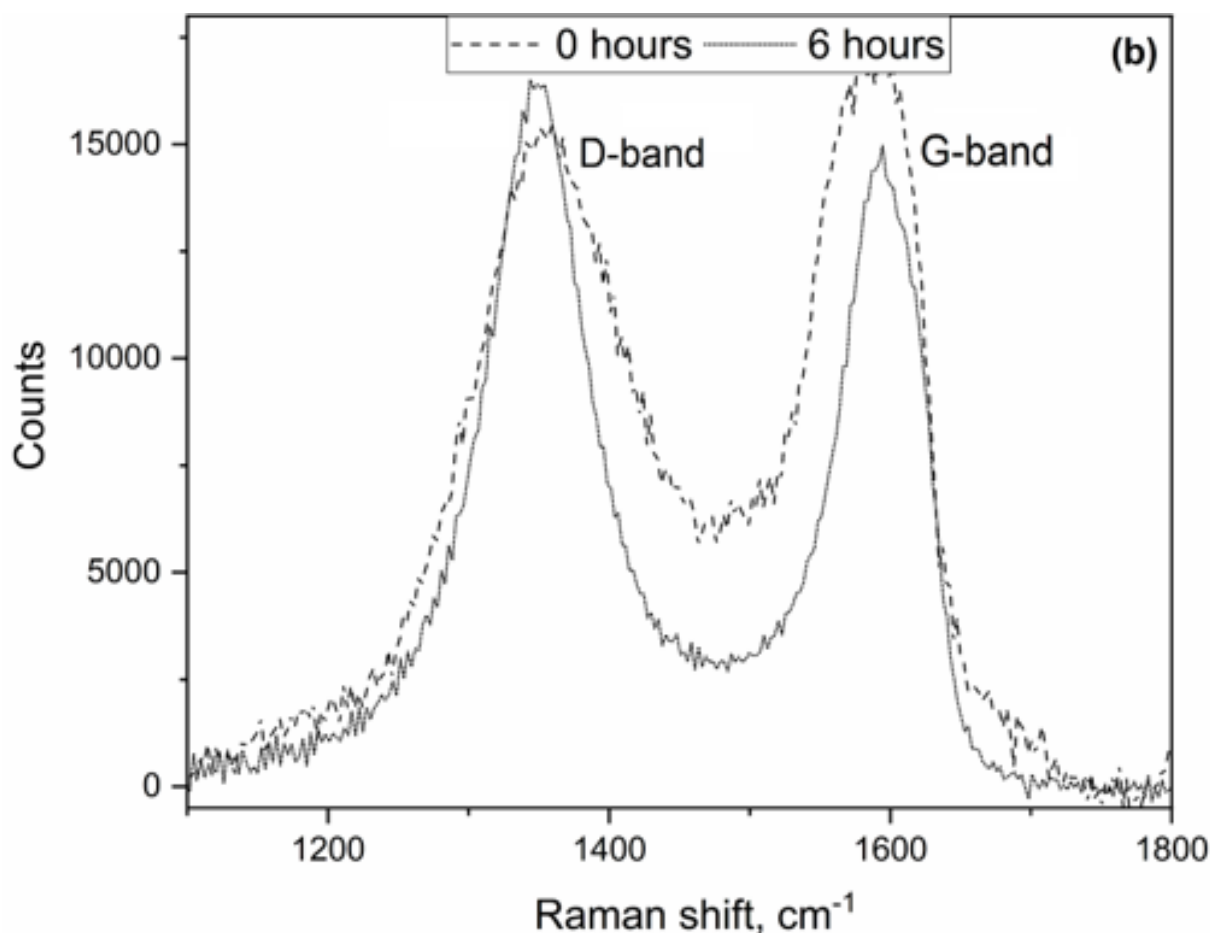


Figure 5.9. Raman spectra of GO before (0 hours) and after (6 hours) reduction with hydrazine. The concentration of GO was 2 mg mL⁻¹, the starting concentration of hydrazine was 1.6 mM, the concentration of ammonium hydroxide was 0.25 M, and the temperature was 80°C.

Although providing some support of the hydrazine consumption method, the differences observed in the FTIR spectrum of the sheets reduced for 2 to 6 hours were so small that they could be easily overlooked without proper data processing. Raman spectroscopy is also not suitable for quantification of GO reduction, and simple electrical conductivity measurements suffer from irreproducibility due to variations in area-selection, measurement methods, test equipment, and other process parameters [250]. Therefore, monitoring the consumption of hydrazine using ion-exchange chromatography clearly presents the most viable and reproducible approach to monitor the full reduction process (Figure 5.7).

5.5. Conclusions

A new method has been developed to study GO reduction with hydrazine by monitoring the hydrazine consumption. The concentration of hydrazine was monitored over time using ion-exchange chromatography with electrochemical detection. The use of electrochemical detection allowed selective determination of hydrazine even in the presence of up to 5.8×10^4 times excess ammonia. The method resulted in an LOD and LOQ of 3 μM and 10 μM , respectively for hydrazine in the presence of 0.25 M ammonium hydroxide. The reduction endpoint obtained with the study of hydrazine consumption was found in correspondence with the FTIR and Raman spectroscopy and with the previous reports of similar reduction processes. Monitoring hydrazine consumption by chromatography during GO reduction can offer various advantages, such as the development of an on-line system to monitor the GO reduction process, ease of quantifying the different stages of rGO, unequivocal determination of the reduction endpoint, and new insights into the GO chemistry.

CHAPTER 6

Reduced Graphene Oxide–High-Pressure High-Temperature Diamond Composite Material: Preparation and Electrochemical Characterisation

6.1. Introduction

Diamond-based electrodes have unique characteristics compared to other solid electrodes, including a low and stable background current, a wide window of electrochemical potential, relatively high electron transfer rates for soluble redox systems without pre-treatment, tunable electrical resistivity, high oxygen evolution, biocompatibility, stability, considerable resistance to fouling, unique surface chemistry and long-term responses [30]. A wide variety of conductive diamond materials for applications within analytical chemistry, prepared by various approaches have been reported to date. These applications include chemical [31] and biochemical sensing [32], environmental degradation [33], electrocatalysis [34] and electrosynthesis [35], as well as energy storage [36] and conversion [37].

Diamond itself is characterised by extremely low electrical conductivity (EC) unless it is doped with boron [26] or on rare occasions with other atoms [27]. Doping can significantly increase EC, which is an essential property for any electrochemical application. However, the cost of high-quality doped chemical vapour deposition (CVD) diamond is considerable, therefore there is a significant demand for cost-effective alternatives. Such alternatives may include conductive composite materials, for instance, diamond/metal [38, 39], diamond/metal oxide [40], diamond/SiC [41, 42], diamond/carbon nanotubes (CNTs) [39, 43] and diamond/graphene [44]. Although at the present time these materials may be only marginally more cost-effective, they are often attractive due to the unique combination of the properties of both components and thus can potentially expand the range and selectivity of electrochemical applications.

For example, nanodiamonds were used to reinforce mechanical properties of ZrB₂-SiC composites by Fattahi *et al.* [42]. They found that because diamond was thermodynamically a

more powerful reducing agent than SiC, a lower temperature was needed for ZrB₂ synthesis. This feature helped to eliminate oxide layers on ZrB₂ particles, as well as unwanted surface phases on the SiC particles, especially SiO₂. In electrochemical applications, incorporating SiC with boron-doped diamond (BDD) can reduce the background current of the composite electrode by 20% compared to a pure diamond film [41]. Fabrication of the composite electrode consisting of both the insulating and the conductive phases allows the electrical properties, as well as the performance of the electrode, to be controlled.

Su *et al.* prepared a hybrid nanodiamond/CNT/metal electrode by spark plasma sintering [39]. Incorporated metals and CNTs enhanced the final mechanical properties and EC of the electrode and served as concrescence media for nanodiamonds. Thus, the prepared electrode was conductive without boron doping and cheaper than CVD-grown diamond-based electrodes. In other work, Jafarpour *et al.* used CNTs and nanodiamond to adjust the properties of styrene-butadiene rubber [274]. Varying the ratio between nanodiamonds and CNTs allowed the adjustment of the mechanical properties of the polymer and its EC. Addition of CNTs alone dramatically increased the EC, which is unhelpful for many applications. Moreover, the addition of nanodiamonds alone was less effective than the nanodiamond-CNT addition for the enhancement of tensile properties. It was also shown that hybridisation of CNTs and nanodiamonds exhibited synergistic effects on thermal stability and thermal conductivity [274].

Peleyeju *et al.* brought together properties of diamond and graphene for the sensitive detection of 2,4-dichlorophenol. A diamond/polyaniline/graphene (DPG) composite was prepared by the *in-situ* oxidative polymerisation of aniline in the presence of diamond and graphene. Aniline was used as a fixative, while the presence of graphene resulted in improved surface area (SA) of the composite material when compared to pristine diamond. Here, diamond was believed to

act as an anti-passivating agent because of its low susceptibility to passivation. The DPG modified glassy carbon electrode (GCE) showed significantly improved electrochemical properties over bare GCE [44].

In previous chapters, the surface properties of variously modified diamond, including hydrogenated high-pressure high-temperature (HPHT) diamond were studied in detail. It was shown in Chapter 4 that hydrogenated HPHT diamond retains hydrophobic solutes in reversed-phase liquid chromatography (RPLC) mode when used as a stationary phase, indicating that hydrogenated HPHT diamond has a relatively hydrophobic surface. This property resulted in the hypothesis that hydrogenated HPHT diamond may attract the hydrophobic reduced graphene oxide (rGO) (Chapter 5). An addition of graphene has the potential to increase the SA and may remove some of the limitations each of these materials have in analytical chemistry applications, similar to the diamond/graphene/polyaniline composite discussed above.

Thus, the primary objective of this Chapter is to bring together the inherent properties of diamond and graphene. First, the preparation of diamond-rGO composites (DGC) *via in-situ* reduction with hydrazine is reported. Optimisation of the suggested technique and characterisation of the physical and electrical properties of DGC are also included. Particular emphasis is placed on its electrochemical properties, inspired by the work of others on similar composites [275-278].

6.2. Experimental

6.2.1. Chemicals and reagents

Monocrystalline synthetic HPHT diamond, 99.5% purity, precision size range, 1.5–2.5 μm was purchased from Microdiamant AG (Lengwil, Switzerland). BDD powder, 2–3 μm , doping level 800 ppm, was purchased from Changsha 3 Better Ultra-hard materials Co., Ltd. (Changsha, Hunan, China). Graphene oxide (GO) aqueous suspension (20–21 mg g^{-1}) was obtained from the University of Wollongong, Australia. Hydrogen gas, high purity grade 3.8 (99.98%) (BOC, North Ryde, NSW, Australia) was used for the hydrogenation of the diamond particles. Ammonia solution, analytical reagent (AR), 28–30% (Ajax-Finechem (UNIVAR), Thermo Fisher, Scoresby, VIC, Australia), ethylene glycol (EG), AR and hydrazine monohydrate, N_2H_4 64–65%, reagent grade, 98% (both from Sigma-Aldrich, Castle Hill, NSW, Australia) were used for the preparation of composite materials. Pellets of poly(vinylidene fluoride) (PVDF) average $M_w \sim 530,000$, N,N-dimethylformamide (DMF), anhydrous, 99.8% and methanol (MeOH), for high-performance liquid chromatography (HPLC), $\geq 99.9\%$ (all from Sigma-Aldrich, Castle Hill, NSW, Australia) were used for the preparation of membranes. ColorFabb HT (clear) filament (All3DP, Munich, Germany) was used for 3D-printing. Solvents used for the investigation of the suspension stability included tetrahydrofuran (THF), HPLC, grade; ethanol (EtOH), undenatured, 100%, AR; isopropyl alcohol (IPA), HPLC grade (all three from Chem-Supply, Gillman, SA, Australia); 1-methyl-2-pyrrolidone (NMP), for headspace gas chromatography; acetone, ACS reagent; acetic acid (glacial) 100%, ACS reagent (all three from Supelco Inc., Bellefonte, Pennsylvania, USA); dimethyl sulfoxide (DMSO), anhydrous, $\geq 99.9\%$; acetonitrile (ACN), HPLC grade $\geq 99.9\%$; 1,4-dioxane, ACS reagent (last three from Sigma-Aldrich, Castle Hill, NSW, Australia); and propan-1-ol (Ajax-Finechem (UNILAB), Thermo Fisher, Scoresby, VIC, Australia). For the preparation of test solutions for

cyclic voltammetric (CV) measurements the following chemicals were used: potassium dihydrogen orthophosphate, $\geq 99.0\%$; dipotassium hydrogen orthophosphate, $\geq 99.0\%$ (both from Ajax-Finechem (UNIVAR), Thermo Fisher, Scoresby, VIC, Australia); disodium hydrogen orthophosphate (BDH chemicals, Murarrie, QLD, Australia); sodium chloride, ACS reagent, $\geq 99.0\%$; potassium chloride, ACS reagent, $\geq 99.0\%$ (both from Honeywell Fluka, North Ryde, NSW, Australia). L-ascorbic acid (AA), ACS reagent, 99% and dopamine hydrochloride (DA) (both from Sigma-Aldrich, Castle Hill, NSW, Australia) were used as test analytes. Deionised water obtained from a Milli-Q (USA) system was used for the preparation of all tested solutions for CV.

6.2.2. Hydrogenated diamond (H-diamond) preparation

Diamond particles (as received) were placed into a ceramic boat to form a thin layer (not more than 5 g at a time), which was then placed into a Carbolite furnace STF 15/180 (Carbolite Gero, Hope Valley, UK). Hydrogen was purged through the furnace at a flow rate of $1\text{--}2\text{ L min}^{-1}$ for 5 hours at 850°C and then cooled down to room temperature in a nitrogen atmosphere at a flow rate of $3\text{--}4\text{ L min}^{-1}$ (Figure 6.1).

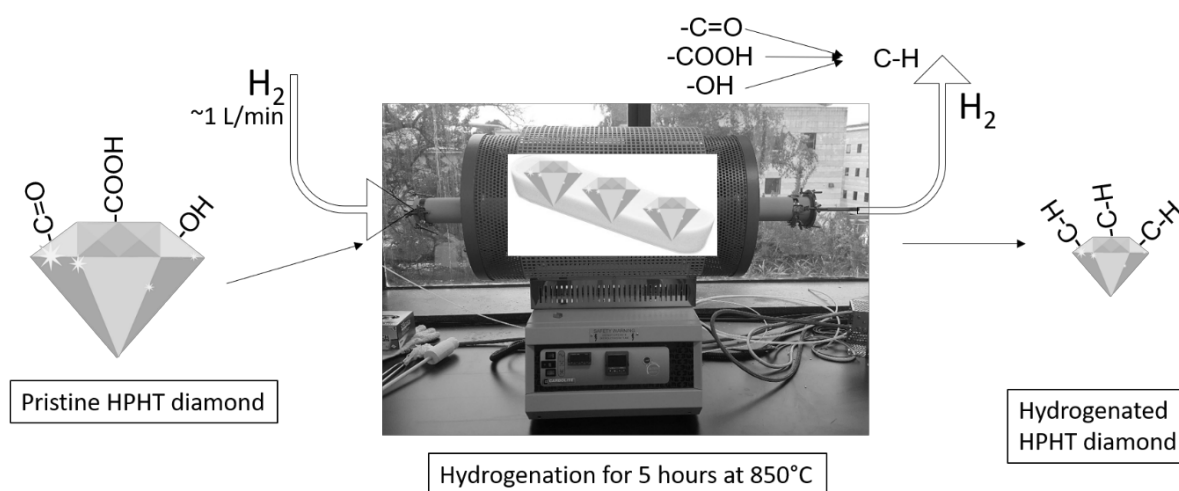


Figure 6.1. A schematic illustration of the diamond hydrogenation procedure.

6.2.3. Design of experiments (DOE) for Diamond-rGO composite (DGC) preparation optimisation

Factorial DOE (2^3) was used to optimise the experiment [225]. Three independent variables were included, namely the ratio between diamond and GO, the concentration of reducing agent, and the sonication mode. Two levels for each variable were chosen and coded as – (low) and + (high). A total of eight experiments were carried out (Figure 6.2).

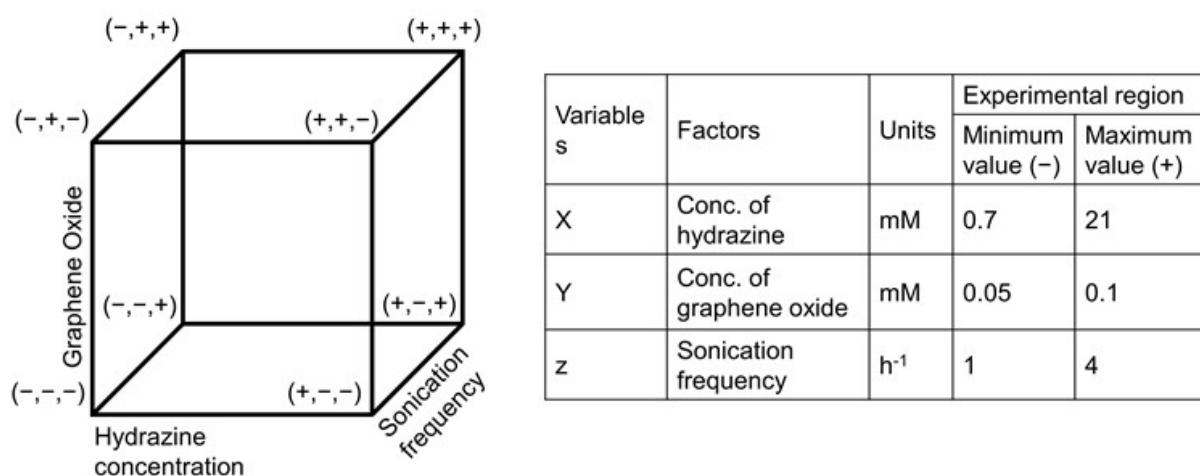


Figure 6.2. 2^3 factorial DOE with three independent variables and two levels of each variable, giving eight test conditions.

6.2.4. Diamond-rGO composites (DGC)

GO aqueous suspension was dispersed in EG. The dispersion was subsequently sonicated *via* sonotrode for 1 min at maximum power to ensure good exfoliation of GO sheets and even particle distribution throughout the mixture. Similarly, the H-diamond powder or BDD was also suspended in EG and then added to the GO suspension. After combining into 50 mL polypropylene centrifuge tubes (GO/diamond ratios 0.04, 0.08 and 0.12), the total mixture was sonicated one more time under the same sonication conditions. Then ammonia (340 μ L) and hydrazine (0.7 mM or 21 mM) were added to the mixture, and the tube was capped and placed into a thermostated oil bath, which was set at 80°C for 6 hours. A Teflon stirrer was not used

here, as previous experiments showed rGO agglomeration on the Teflon surface. After the reaction was completed, the H-diamond-rGO (D-rGO) or boron-doped diamond-rGO (BDD-rGO) was centrifuged, washed with MeOH (40 mL) and dried in the vacuum oven at 40°C overnight.

6.2.5. DGC-Polyvinylidene fluoride (PVDF) membranes

The DGC adsorbent (150 mg) was suspended in 1 g of PVDF/DMF (7.5 wt.% PVDF) and sonicated for 30 min in an ultrasonic bath. The suspension was cast on a Petri dish (50 mm internal diameter (ID)) and placed in the oven for 1 hour at 75°C to evaporate the solvent. Finally, the dried membrane was removed from the glass with a few drops of MeOH.

6.2.6. Scanning electron microscopy (SEM)

Imaging of the composite materials and membranes was carried out using a Hitachi SU-70 (Hitachi Ltd., Chiyoda, Tokyo, TKY, Japan) field emission analytical SEM with acceleration voltage of 1.5 kV. Non-conductive samples were platinum-sputtered before analysis. An Oxford AZtec 2.3 Energy-dispersive X-ray Spectroscopy (EDS)/Electron Backscatter Diffraction system was used for the investigation of membrane composition.

6.2.7. Electrical conductivity (EC) measurements

The EC of the constructed electrodes was measured with a Hewlett Packard 34401A multimeter (Keysight Technologies, Mulgrave, VIC, Australia). The cathode and anode probes were fixed at a distance of 18.92 mm and were placed randomly at three different locations upon the membranes to record the voltage.

6.2.8. Preparation of working electrodes

The working electrodes used in this study are:

6.2.8.1. *Diamond-PVDF (D-PVDF) and DGC-PVDF chips*

The preparation method was adopted from [279]. Diamond or DGC (150 mg) was dispersed in 1.0 g of a PVDF/DMF solution (7.5 wt.% PVDF) and sonicated for 15 min. The final dispersion was cast onto the side of a spectrophotometric cuvette to obtain a similar-sized rectangular shape for all electrodes (10×45 mm). Teflon tape was used to prevent the solution from flowing out. The solvent was evaporated by placing the cuvettes in the oven at 70°C for 1 hour and the resulting electrode chips (ca. 0.5 mm thick) were delaminated from the quartz substrate by adding a few drops of MeOH. Finally, all chips were cut down to 20 mm length.

6.2.8.2. *Diamond-rGO composite modified glassy carbon electrodes*

Approximately 100 mg of DGC slurry in MeOH was deposited on the GCE, excess edges were carefully removed to precisely match the 3 mm surface diameter of the GCE, and the electrode was left to dry naturally overnight.

6.2.8.3. *Drop-cast - diamond-rGO composite modified glassy carbon electrodes*

The surface of the GCE was polished using Al_2O_3 powder and a polishing pad, then sonicated in deionised water and dried. A suspension of the DGC (1 mg mL^{-1}) was prepared in MeOH, and a 5 μL droplet was cast on the GCE surface and left to dry for 15 min. The drop-cast (DC) was repeated three times before usage.

6.2.8.4. *Diamond-rGO composite electrodes*

Hollow cylinders (6×60 mm, 3 mm ID, 6 mm outside diameter (OD)) were 3D-printed using ColorFabb filament material and a Prusa 3D printer (Prusa Research, Prague, Czech Republic).

The copper wire (75×1 mm) was wrapped with Teflon tape coated with super glue and placed in the middle of the cylinder. Particular attention was paid to keeping the ends of the copper wire clean. From one of the ends of the cylinder a 2 mm space was left to be filled with the produced conductive material. The filling with DGC powder, slightly moistened by MeOH, was performed using a micro-spatula. The material was tightly rammed and left to dry overnight.

6.2.9. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was performed at room temperature using a Metrohm Autolab PGSTAT-101 (Utrecht, Netherlands) and data were acquired with Metrohm Autolab, Nova 2.0 software. Phosphate buffered saline (PBS), 0.1 M, pH 7.5, or 0.1 M KH_2PO_4 were prepared and used as supporting electrolytes. A conventional three-electrode configuration was employed. Silver/silver chloride (Ag/AgCl, 3M KCl) and platinum wire (1 mm diameter) were used as the reference electrode and auxiliary electrode, respectively. Working electrodes are described above.

6.3. Results and Discussion

6.3.1. Material preparation and characterisation

To the best of the author's knowledge, there is no well-established method for attaching graphene/GO to the diamond surface. Some of the previously reported methods for the preparation of diamond-graphene based materials include co-polymerisation with polyaniline [44], catalytic annealing of diamond [280, 281], electrochemical deposition [282], CVD diamond growth [278], DC [283], esterification [284], vacuum filtration [285, 286], electrostatic attachment [287] and hydrothermal reduction [275, 288-291]. Wang *et al.* [275] synthesised a nanodiamond/rGO composite *via* hydrothermal reduction for a supercapacitor application. Inspired by the concept of the reduction of GO in the presence of diamond particles, a new method is developed herein, employing micron-sized HPHT diamond.

The first stage of this study was to design and optimise the preparation of a DGC material, which could be stable in the majority of common solvents. First of all, an aqueous suspension of exfoliated GO was mixed with HPHT diamond and dried, and the resulting material was examined by SEM (Figure 6.3). From the resulting micrographs, it was clear that the affinity between diamond particles and GO sheets was not enough to form a stable composite material. The likely reason behind this observation is that the various negatively charged oxygen-containing groups on the surface of the diamond and the GO repel each other. Some theoretical studies suggest that the Van-der-Waals interactions of diamond with graphene are more substantial with H-terminated diamond (with an adsorption energy -10.6 eV) than with F-, O- and OH- terminated surfaces [292, 293]. Therefore, to test these suggestions, subsequent diamonds discussed within this chapter were first hydrogenated in a flow of hydrogen gas [226] before further experiments.

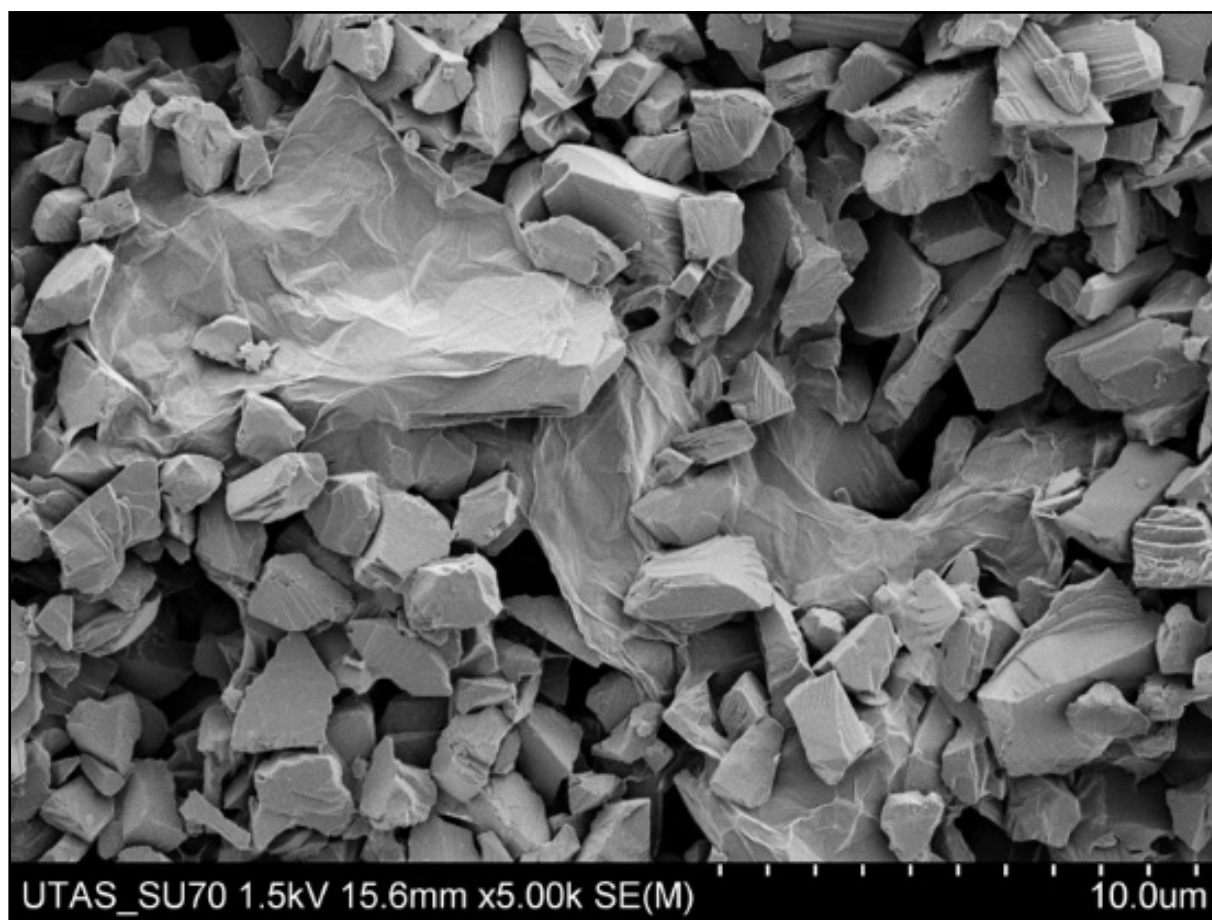


Figure 6.3. SEM image of the mechanical mixture of HPHT diamond and GO.

Along the same lines, to increase the affinity to the diamond surface, the GO sheets should be reduced. There are several reducing agents suggested for GO, although hydrazine has been found to be the most efficient [294]. However, reduction of GO prior to combination with diamond particles would lead to agglomeration of the GO sheets. Agglomerated material may cause an uneven distribution of rGO within the resultant composites. Therefore *in-situ* GO reduction with diamond particles was investigated for the composite preparation, in line with a previously reported method for a similar substrate [252].

The solvent for the reaction mixture should maintain the formation of a stable suspension. The maximum degree of exfoliation of GO was obtained in water, DMF, THF and NMP, in which the dispersion remained stable for three weeks (Figure 6.4) [295]. There was no available literature data on the dispersion stability of micron-size HPHT diamond. Therefore, herein 16 solvents or solvent mixtures were tested, namely: EtOH, 50% EtOH in water, IPA, 50% IPA in water, DMSO, propan-2-one (acetone), MeOH, 50% MeOH in water, THF, acetic acid, propan-1-ol, water, ACN, DMF, 1,4-dioxane, NMP and EG (Figure 6.5). The results of this experiment revealed that the most prolonged micro-diamond dispersion stability was obtained in three of the tested solvents, which increased in the order: DMSO, 50% IPA in water, EG (Figure 6.6). EG kept ca. 90% of the micron-size diamond particles in suspension for up to three hours, and after 24 hours at least half of the particles were still in suspension. The reduction process required for the composite preparation was six hours long. To keep the diamond particles in suspension for that period of time, sonication was performed every hour. This was considered sufficient for the preparation process.

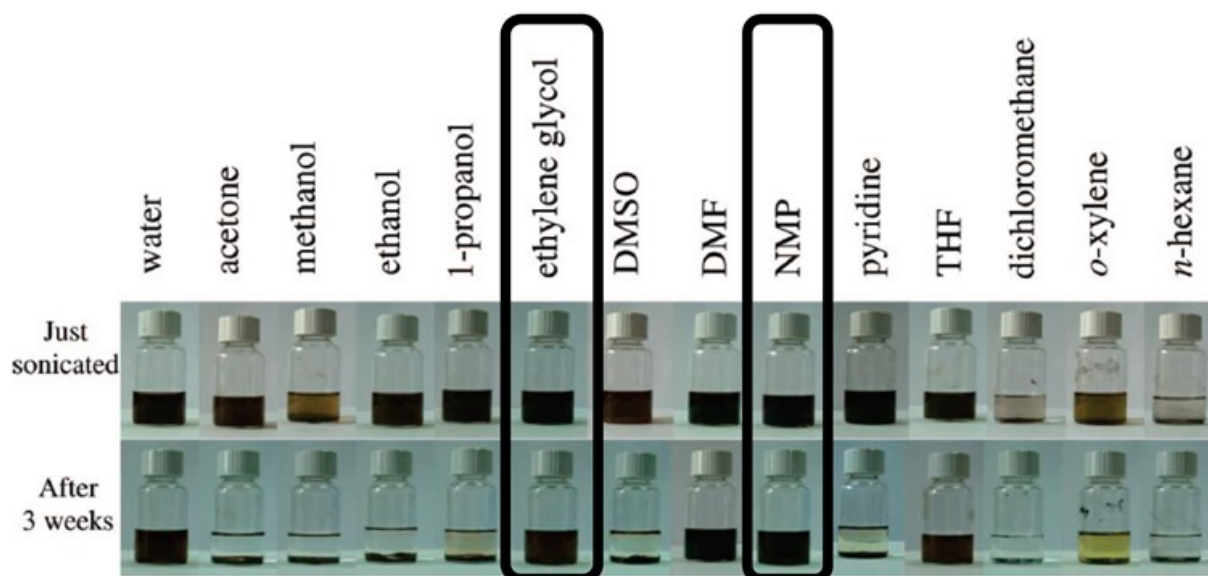


Figure 6.4. GO suspended in different solvents just after sonication and three weeks after sonication, adapted from [295].



Figure 6.5. Hydrogenated HPHT diamond (2 μm , 50 mg) suspended in various organic solvents (2 mL), just after sonication.

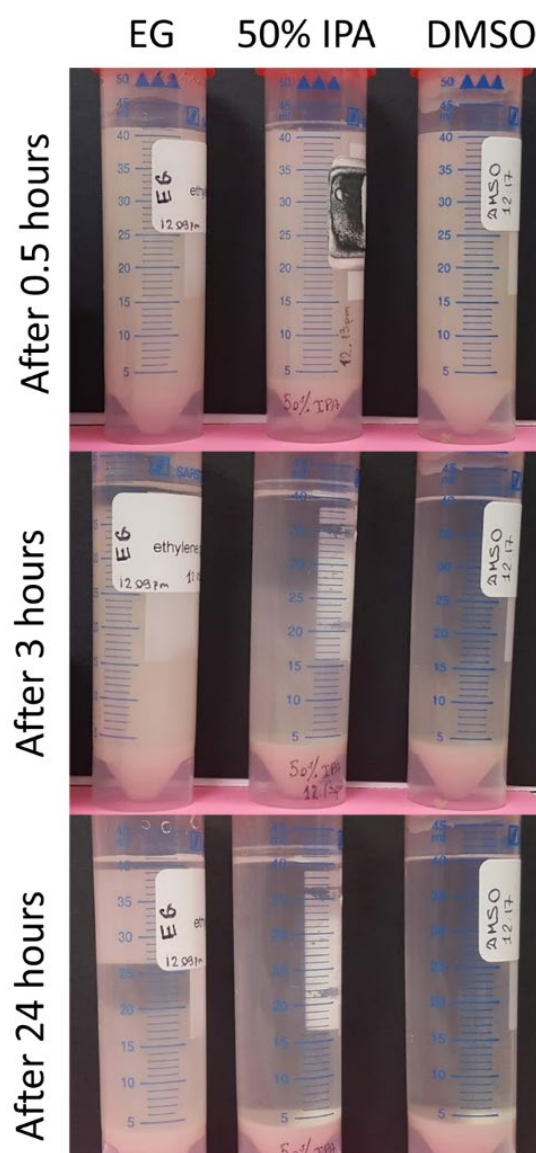


Figure 6.6. H-diamond suspended in EG, 50% IPA and DMSO – 0.5, 3 and 24 hours after sonication.

A factorial DOE was used to optimise the other conditions of the preparation, all of which may affect the structure of the produced material (Figure 6.2). The three independent variables included the ratio between diamond and GO, the concentration of reducing agent, and the sonication mode. In an attempt to cover the diamond surface with a thin layer of rGO, the ratio of diamond and GO was adopted from [252], taking into account the fact that the SA of the diamond measured by Brunauer–Emmett–Teller (BET) was $2.32 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$. Thus, the GO/diamond mass ratio variables were set as 0.04 (–) and 0.08 (+). The Teflon stirrer was not used during the reduction to avoid rGO agglomeration on its surface. Therefore, sonication was employed, and its frequency was considered as an essential factor to uniformity of the composite. The levels of sonication frequency in this set of experiments were set as one per hour (–) and four per hour (+). It has been shown that the concentration of hydrazine is responsible for the degree of GO reduction, or, in other words, for the amount of oxygen-containing functional groups on to GO surface [296]. The kinetics of the reduction process does not necessarily depend on the reactant concentrations but depends on the temperature [297]. The most commonly used temperature for GO reduction is 80°C, and the results within Chapter 5 revealed that it takes six hours to complete the reduction process at this temperature. Therefore conditions of 80°C temperature, six hours and two different concentrations of hydrazine (0.7 mM [298] and 21 mM [297]) were chosen for these tests.

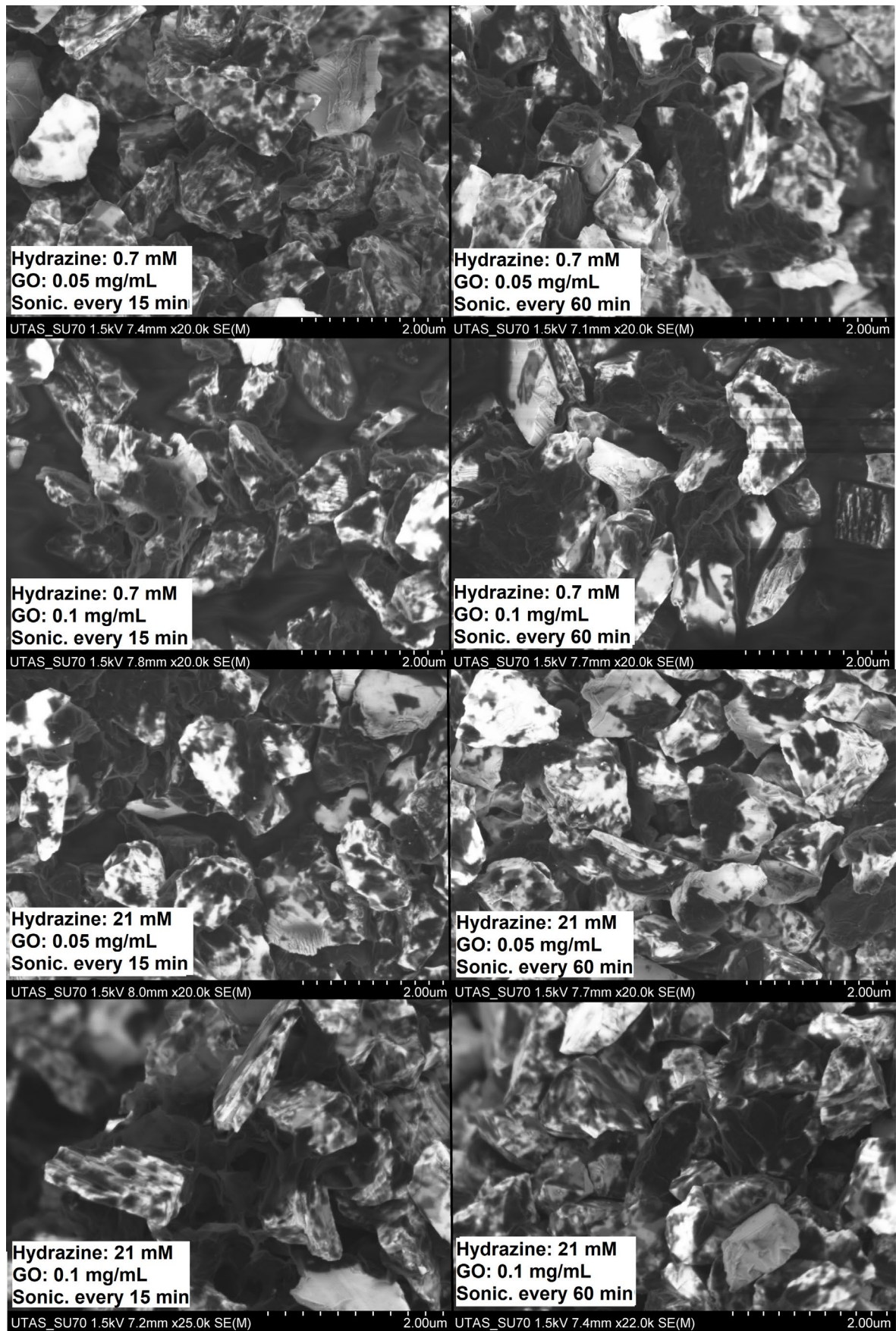


Figure 6.7. SEM images of eight diamond-rGO composite materials produced under the experimental conditions established in the factorial DOE.

Thus, eight composite materials were produced and further investigated by SEM (Figure 6.7). Remarkably, no Pt coating was required for SEM analysis of these samples as their EC increased compared to bare diamond, where Pt coating was necessary. Micrographs did not reveal any difference in coverage between the two sonication frequencies, therefore less frequent sonication was acceptable. The supernatant from all reaction mixtures was subjected to UV-Vis spectrophotometry (Figure 6.8). At higher concentrations of hydrazine, the overall absorbance was higher. The absorption peaks shifted from ~ 215 nm at a lower hydrazine concentration (0.7 mM) to ~ 225 nm at the higher (21 mM), which indicated a greater reduction of GO [299, 300]. The small secondary peak at 285 nm was unknown, however I suggest it may be a result of excess of hydrazine or contribution of microdiamond entrapped by reduced graphene oxide. An attempt to repeat the experiment to further investigate was prevented by COVID restrictions.

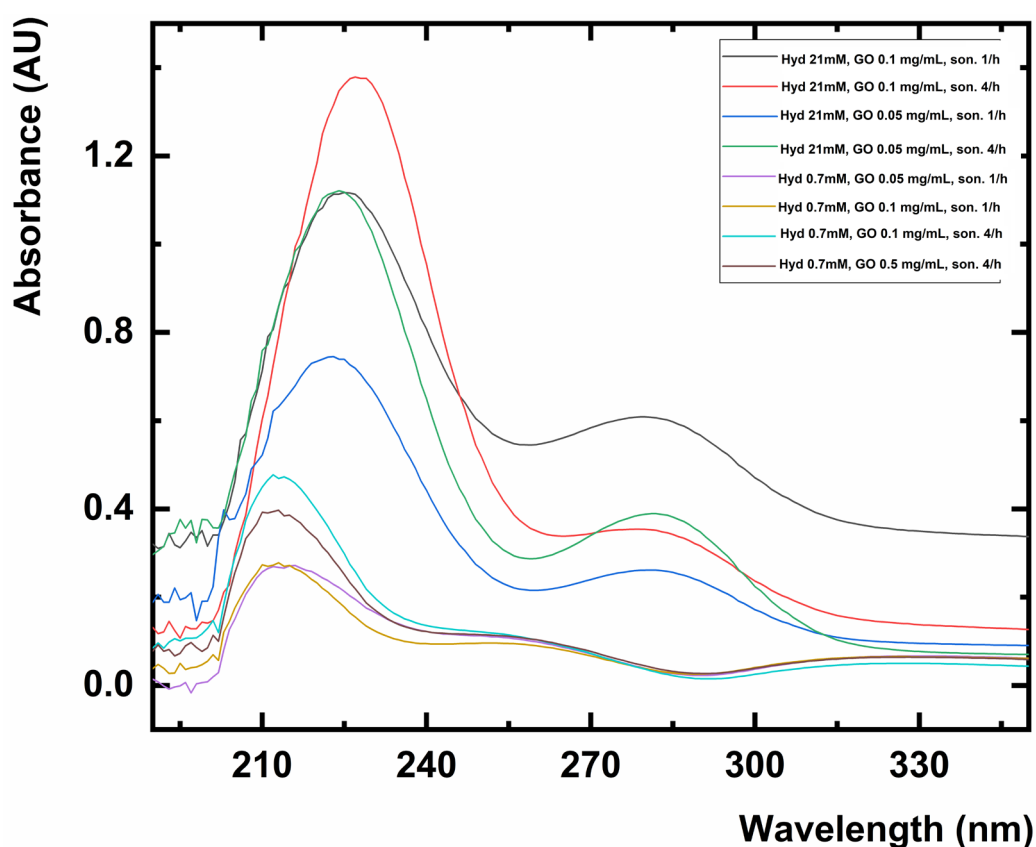


Figure 6.8. UV-Vis absorption spectra of rGO after reduction at eight different experimental conditions.

Based on the SEM micrographs, higher GO concentration provided better coverage than lower. Another experiment was carried out to compare the uniformity of rGO distribution by adding GO (2 mg) layer-by-layer four times compared with adding 8 mg of GO at once. The SEM micrographs revealed no significant difference between the four layers and the one-time deposition of the same overall mass of GO. Therefore, the latter approach has been used in further experiments. The SEMs of the as-received diamond (A) and prepared adsorbent (rGO/diamond ratio 0.16) (B) are shown in Figure 6.9.

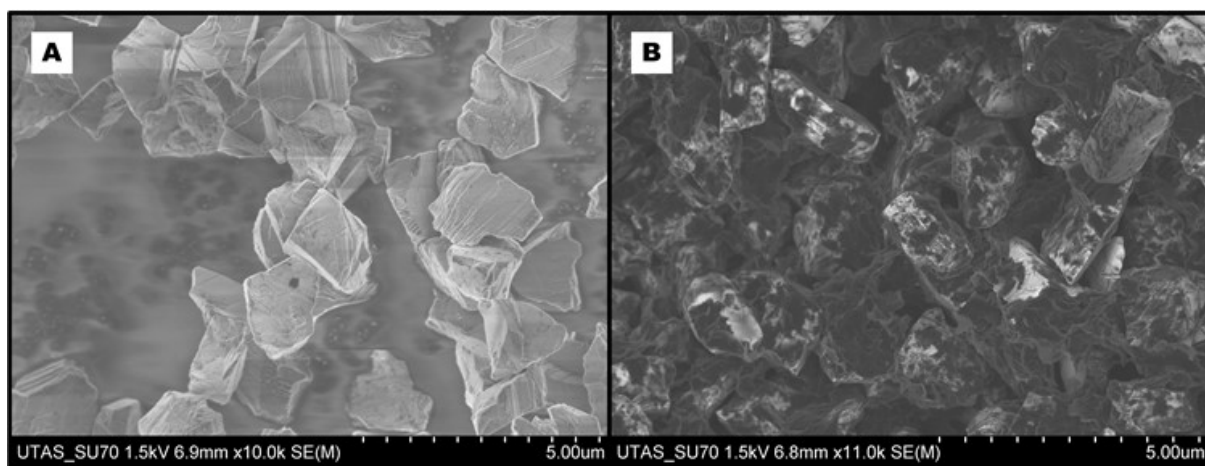


Figure 6.9 SEM of the (A) as-received HPHT diamond (B) D-rGO composite material (rGO/diamond ratio 0.16)

For further characterisation of the material, the SA was measured by BET, and the results supported an approximately 60% increase in SA compared to bare diamond. Specifically, for the bare diamond, the SA was measured as $2.32 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$, and for the D-rGO, it was $3.62 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$.

The mechanism of attraction between the reduced diamond surface and the GO is not readily apparent. Most composite materials reported earlier employed detonation nanodiamond, which compared to the HPHT diamond used in this study, has a smaller size (ca. 5 nm) and more

diverse surface chemistry (which can be positively charged) and is more prone to self-agglomeration. It is reasonable to assume that the affinity to GO is due to the hydrophobic nature of both materials as well as the Van der Waals interactions between the surfaces. The surface of reduced graphene oxide, rich with pi-electrons, can induce electric dipoles on hydrogenated diamond surface (Figure 6.10).

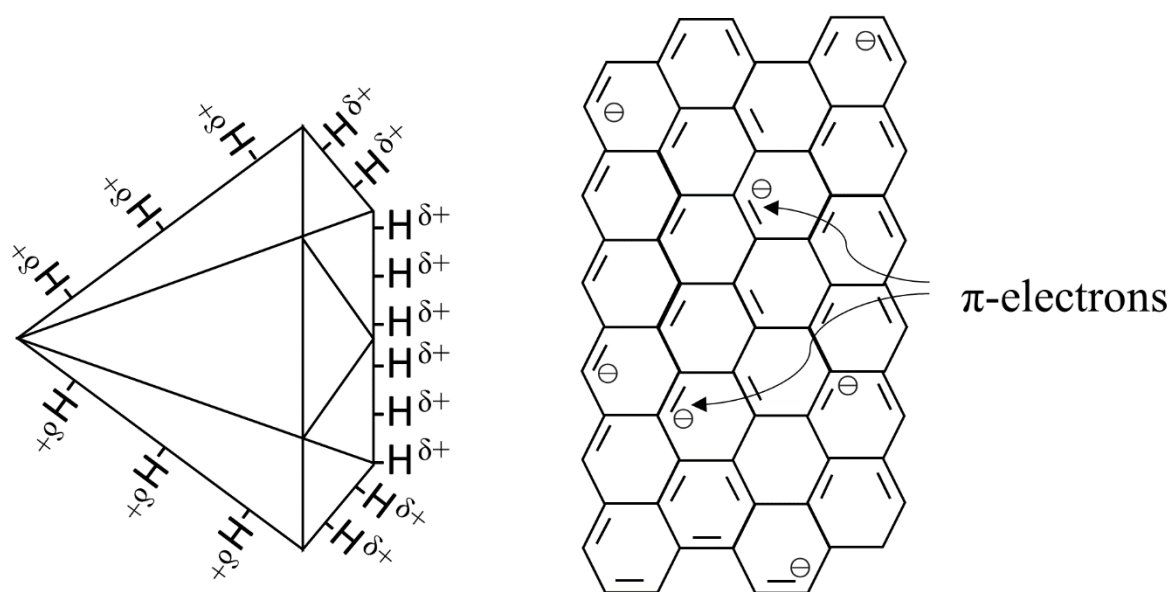


Figure 6.10. Schematic illustration of the possible charge distribution on the surfaces of H-diamond and rGO.

All early tests were carried out with minimal amounts of materials (50 mg of diamond and 2–8 mg of GO). To produce a sufficient amount of the composite for further investigations, a scale-up study was carried out with a 5, 10, 15 and 20 times increase of components in the reaction vessel (Figure 6.11). It was noticed that higher concentrations caused a higher agglomeration of rGO on the diamond, as the supernatant after centrifugation became clearer as the amounts of the components increased (Figure 11).

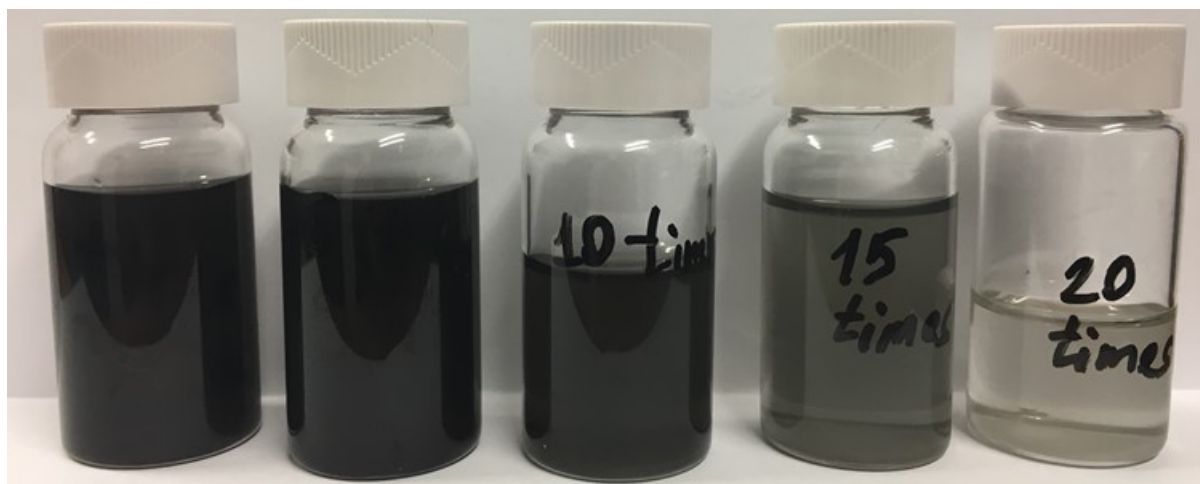


Figure 6.11. The scale-up study shows that the increase in the mass of diamond and GO per volume of EG leads to an increased rGO amount entrapped in the composite material.



Figure 6.12. Photo of D-rGO-PVDF on a nylon filter membrane.

In order to investigate the feasibility of making chips/membranes of any shape using the produced material, a polymer was incorporated into the structure, to play the role of a concrescence medium in the DGC. For extra support, some membranes were cast on a nylon filter (Figure 6.12). PVDF was chosen as a matrix (33.3 wt. % of a polymer).

The membranes were analysed by SEM (Figure 6.13 A, C) and EDS (Figure 6.13 B, D) in order to evaluate the morphology. For the membrane that was cast on glass, PVDF tightly filled up any gaps, and even though there were quite a few deep cracks on the surface, it did not appear to be highly porous (Figure 6.13 A, B). The membrane on the nylon filter had a significantly more porous structure. The capillary forces induced by the filter support absorbed the PVDF, which contributed to the formation of a porous structure with more adsorbent exposed on the surface (Figure 6.13 C, D).

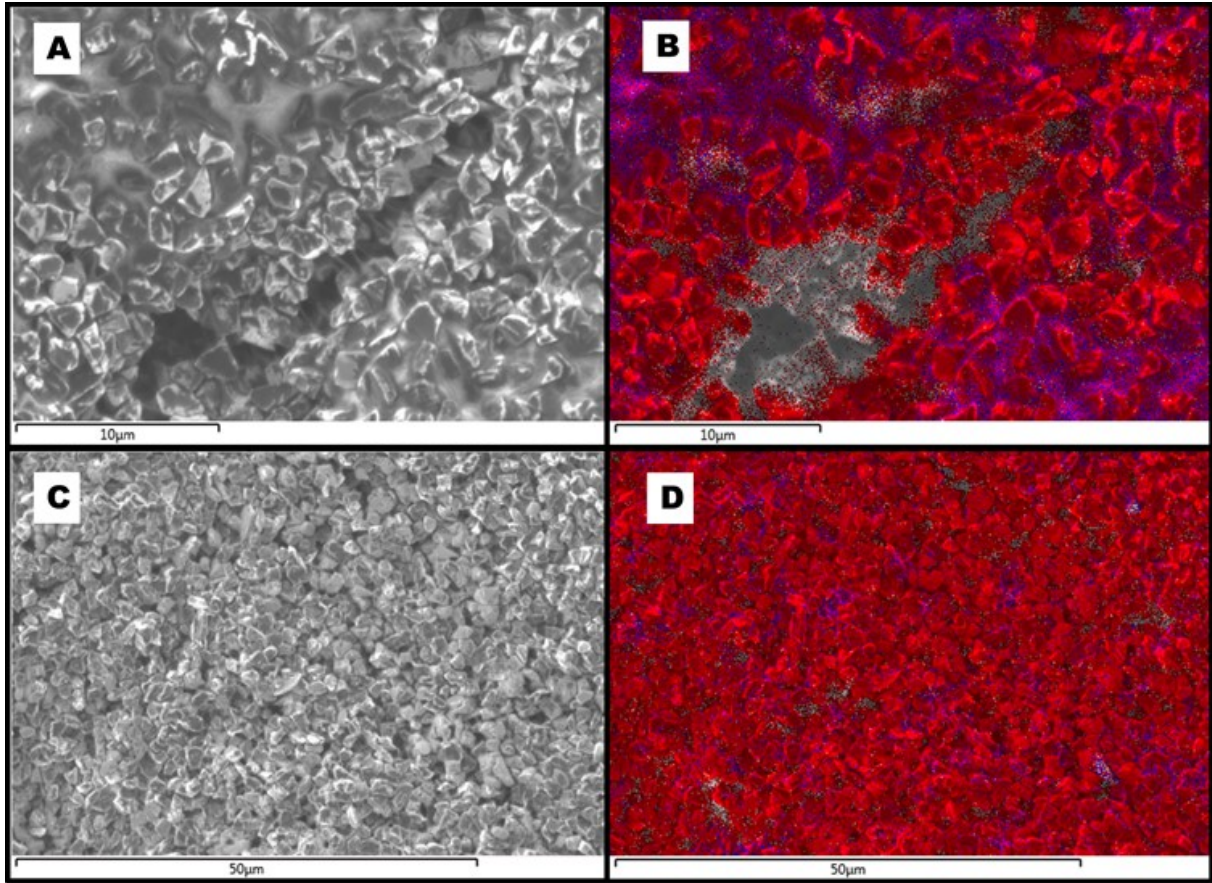


Figure 6.13. The D-rGO-PVDF membrane on glass (A – SEM, B – EDS) and on a nylon filter (C – SEM, D – EDS). Carbon (red) and fluorine (blue) signals are overlapped on the micrographs.

During SEM analysis, it was discovered that these membranes were conductive (as expected), as a Pt coating was not required to achieve high-quality images. A multimeter was used to measure the EC of the obtained membranes. The readings were taken by placing two probes on the substrate and measuring the distance between probes, and the resistance. These values were then used to calculate the resistivity of membranes by the following equation (1):

$$\rho = R \times A/l \quad (1)$$

where ρ is electrical resistivity ($\Omega \times \text{m}$), l is a distance between two electrodes (cm), A is a cross-section area (cm^2), R is the resistance reading from the multimeter-voltage detector (Ω). EC is the inverse of electrical resistivity (2):

$$\sigma = 1/\rho \quad (2)$$

In this experiment, the distance between the two electrodes was 1.892 cm, the thickness of the membrane was 30 μm (without support), and 970 μm (on the nylon filter), the length of the membrane was 2 cm. For the D-rGO-PVDF membrane without nylon support, an average resistance was $1.9 \times 10^5 \Omega$, and the average EC was 0.17 S m^{-1} according to equations (1) and (2) (actual calculations shown in equations (3) and (4)).

$$\rho = R \times A/l = 188000 \times 0.02 \times 0.00003 / 0.01892 = 5.96 \Omega \quad (3)$$

$$\sigma = 1/\rho = 1/5.96 = 0.17 \text{ S/m} \quad (4)$$

Table 6.1 provides EC values for the materials used in this study.

Table 6.1. EC of different materials.

Material	EC, S m^{-1}	Reference
D-rGO-PVDF	0.17	This work
D-rGO-PVDF on nylon support	6×10^{-4}	This work
rGO	200	[243]
PVDF	0.01	[301]
Glassy carbon	2	[302]

6.3.2. Investigation of electrochemical properties

The rGO-diamond composite in the PVDF matrix allows the casting of conductive membranes of different shapes. Therefore, the suitability of the composite as an electrode for CV was tested. Four electrodes were cast in rectangular shapes using a quartz cuvette as a mould, followed by cutting them into $1 \text{ cm} \times 2 \text{ cm}$ segments (Figure 6.14). AA was chosen to estimate the performance of the electrodes.



Figure 6.14. Images of the D-PVDF, BDD-PVDF, D-rGO-PVDF and BDD-rGO-PVDF electrodes.

CVs of 3.5 mM AA in 0.1 M dipotassium phosphate (K_2HPO_4) as the supporting electrolyte (pH 5.2) on the cast electrodes are shown in Figure 6.15. The D-PVDF electrode, as expected, showed no current due to the high resistance of this material. The CV obtained using the BDD-PVDF electrode showed background current due to the EC properties of BDD. However, the oxidation peak of AA was not observed using this electrode (Figure 6.15, BDD-PVDF). In contrast, both the D-rGO-PVDF and BDD-rGO-PVDF electrodes showed potential as CV electrodes. However, it was observed that the peaks were rather broad (compared to the BDD-PVDF electrode) potentially due to large double-layer capacitances (Figure 6.15, HPHT D-rGO-PVDF and BDD-rGO-PVDF). These experiments show that composites containing rGO have a much higher electrochemically active area. Thus, they are promising materials for

electrochemical applications. The current related to AA oxidation was slightly higher for D-rGO than for BDD-rGO, with both of them higher than the current for GCE (Figure 6.15, GCE).

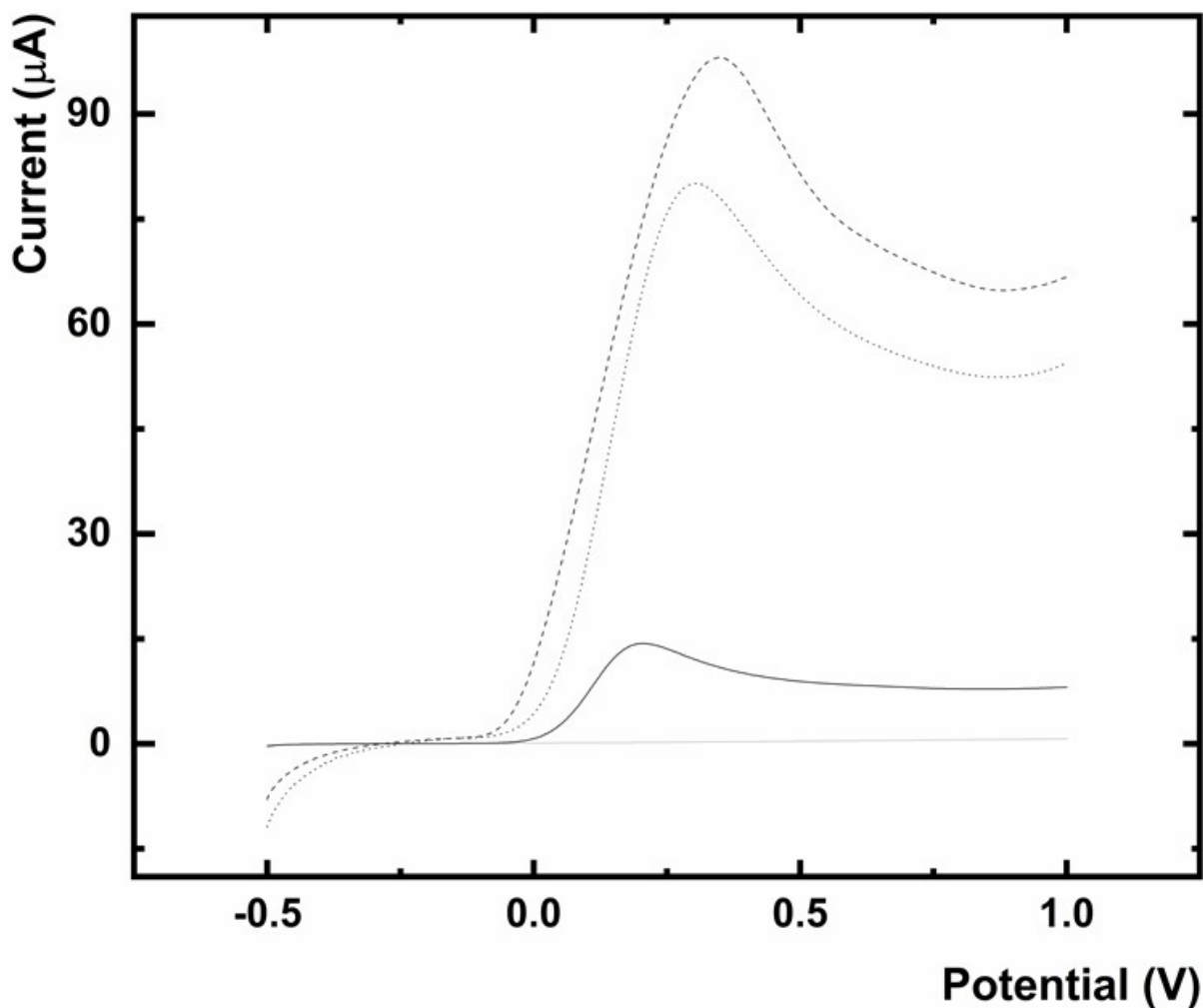


Figure 6.15. CV of AA (3.5 mM) in 0.1 M dipotassium phosphate (K_2HPO_4) at a scan rate of 50 mV s^{-1} for (from bottom to top) BDD-PVDF (grey solid line —), GCE (black solid line —), BDD-rGO-PVDF (dotted line •••), and D-rGO-PVDF (dashed line ---) electrodes.

It appears that the inclusion of D-rGO into the PVDF matrix provides increased SA and increased roughness. Unfortunately, no BET measurements of PVDF-based electrodes were made. During the preliminary drying of the samples under vacuum at elevated temperature, the structure of the membrane changed as the amorphous polymer in its composition filled the

pores, thereby distorting the experimental results. As expected, the signal varies with the size of the SA of an electrode immersed in a solution. The Randles-Sevcik equation (5) describes how the peak current i_p (A) is calculated for electrochemically reversible electron transfer processes involving freely diffusing redox species [303]:

$$i_p = 0.446nFAC^0(nFvD_o/RT)^{1/2} \quad (5)$$

Where v is a scan rate ($V s^{-1}$), n is the number of electrons transferred in the redox event, A (cm^2) is the electrode SA (usually treated as the geometric SA), D_o ($cm^2 s^{-1}$) is the diffusion coefficient of the oxidised analyte, C^0 ($mol cm^{-3}$) is the bulk concentration of the analyte, F is the Faraday constant ($C mol^{-1}$), R is the gas constant ($J K^{-1} mol^{-1}$), and T is the temperature (K).

The higher the SA of an electrode, the higher the current, which follows from equation (5). However, a larger electrode size causes broadening and tailing of CV peaks, which is due to inconsistencies in electron transfer resistance as electrons travel through the solution from the working electrode to the reference electrode. In order to get more defined peaks and higher sensitivity in a smaller concentration range, it is necessary to reduce the size of the electrode. At the same time, it was significantly difficult to ensure the consistency of the immersed SA using rectangular chips. Therefore, two approaches were tried to ensure a small and consistent SA of working electrodes. The first approach was to deposit a layer (~ 0.5 mm) of each of the composite materials onto a GCE (DGC-GCE) (Figure 6.16, photo), and the second was to make the entire electrodes from scratch (DGC electrodes). PVDF was not used in either method, as the composite DGC adsorbents formed a reasonably stable cluster while remaining adhered to the GCE surface or even when employed as an electrode without GCE support.

Calibration curves (measured current *vs* concentration) for AA in a range of concentrations from 0.1 to 10 mM in 0.1 M potassium dihydrogen phosphate were obtained using the GCE and DGC-GCE electrodes (Figure 6.16). This series of experiments was not performed in triplicate, and no standard deviations were calculated on this occasion as it was performed as a proof of concept. From the presented curves and their linear fits, it is evident that higher concentrations of AA give greater currents when the modified electrodes are used. The slope for the DGC-GCE electrode is greater than that for GCE, which suggests this electrode more sensitive to a change of AA concentration in solution. However, the response of the DGC-GCE electrode in the low-concentration range was poor due to the background current flow, which is significantly lower for the GCE. This can be explained once again by the Randles-Sevcik equation as the SA of the DGC-GCE electrode is greater than that of the GCE. This gives rise to broader peaks, which in turn reduces practical utility at low concentrations, which necessitates a further reduction in electrode SA.

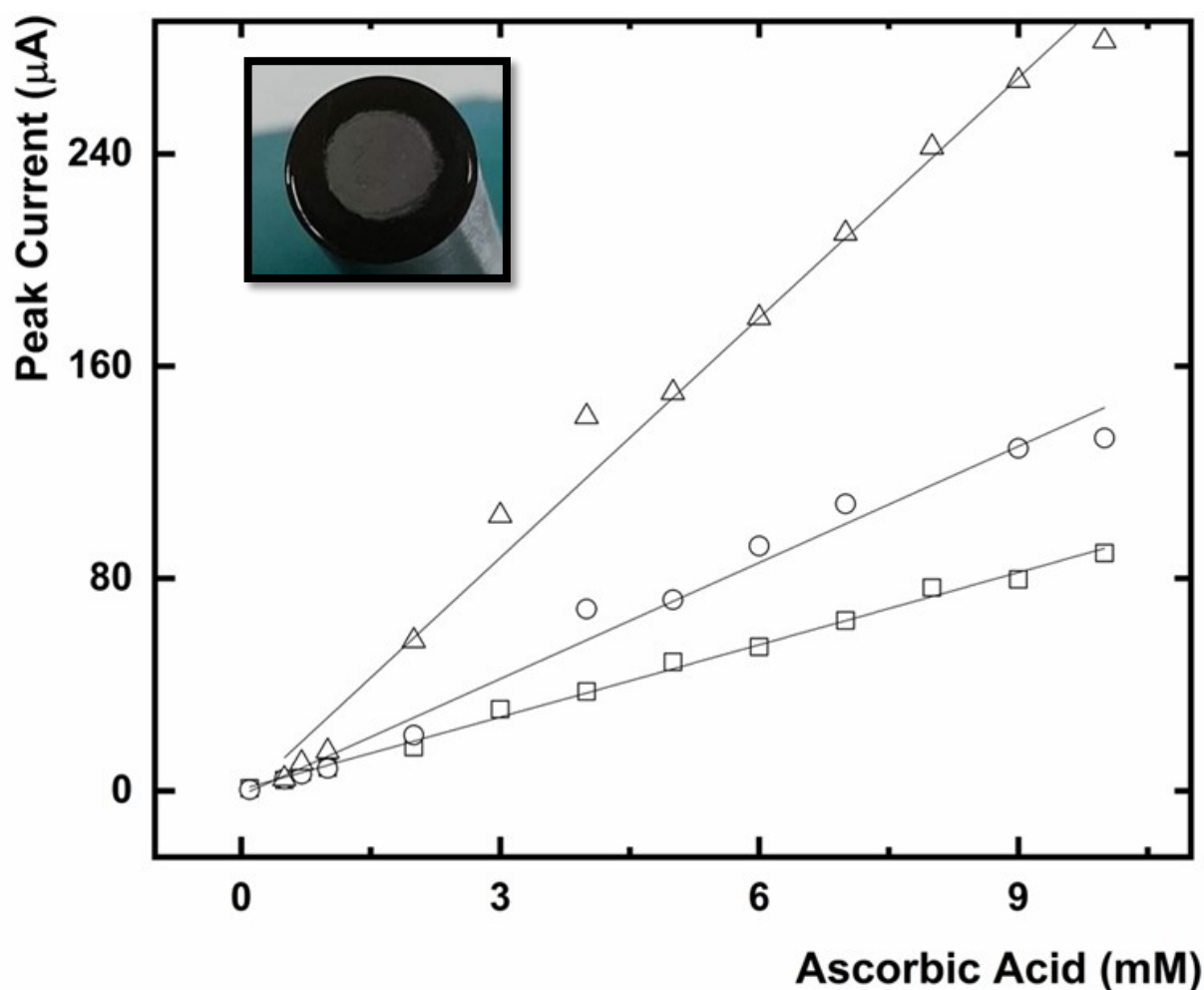


Figure 6.16. Calibration plots of AA in 0.1 M KH_2PO_4 using (a) GCE, and DGC-GCE electrodes: (b) D-rGO (c) BDD-rGO at a scan rate of 50 mV s^{-1} . $\square$ – GCE; $\circ$ – D-rGO-GCE; $\triangle$ – BDD-rGO-GCE.

A third series of experiments was carried out with drop-cast (DC)-DGC-GCE electrodes. This time, a GCE was modified with an ultra-thin layer of DGC by drop casting from a MeOH suspension. These electrodes were used to obtain another series of calibration plots for AA, which are shown in Figure 6.17. These experiments mirror our previous results with the modified GCE showing a higher peak current at a given concentration of AA. Moreover, although increases in concentration resulted in smaller increases in the current, the overall calibrations are more linear and values more stable. The reduced increase in current is due to the thinner layer of modified diamond composite. Given the minimal variation between the

responses on the electrodes prepared by DC, but a significant variation on the electrodes prepared by deposition, the effect of increasing DC layer thickness by increasing the concentration of the MeOH suspension during electrode construction, or increasing the number of layers, needs to be further investigated. The more linear values of the DC method suggest that this technique of construction of modified electrodes may be superior.

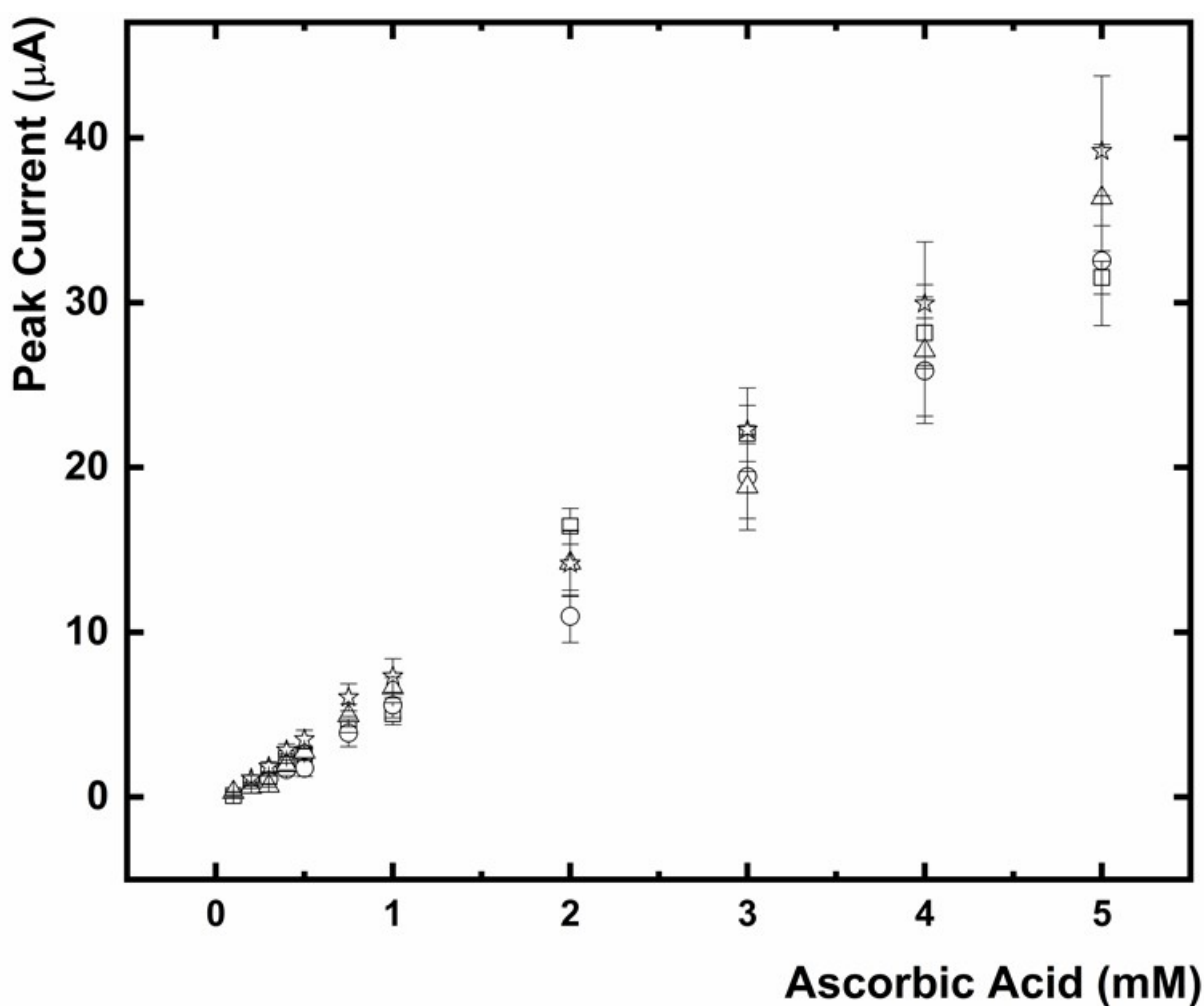


Figure 6.17. Calibration plots of AA in 0.1 M KH_2PO_4 using DC-DGC-GCE electrodes at a scan rate of 50 mV s^{-1} . $\square$ – GCE; $\circ$ – DC-rGO-GCE; Δ – DC-D-rGO-GCE; $\star$ – DC-BDD-rGO-GCE.

CVs of 1 mM AA on DC-modified electrodes are shown in Figure 6.18. For comparison, GO was drop cast onto a GCE surface from a 1 mg mL⁻¹ aqueous suspension. After that, it was reduced with hydrazine using the method used for the preparation of the DGC and rinsed with water before being used for the electrochemical application. The DC-rGO-GCE has a capacitive current much higher than that of GCE due to the higher specific SA and enhanced EC properties. The ability of graphene to accumulate charge is a beneficial property for capacitors and supercapacitors, where graphene attracted much interest during the last decade. However, the high capacitance of the material causes more prominent noise, less accurate peak detection, and lower sensitivity. As shown in Figure 6.18, the capacitances of DC-DGC-GCE are much smaller than that of DC-rGO-GCE, and this reduction allows greater elucidation of oxidative peaks of AA using the composite electrodes.

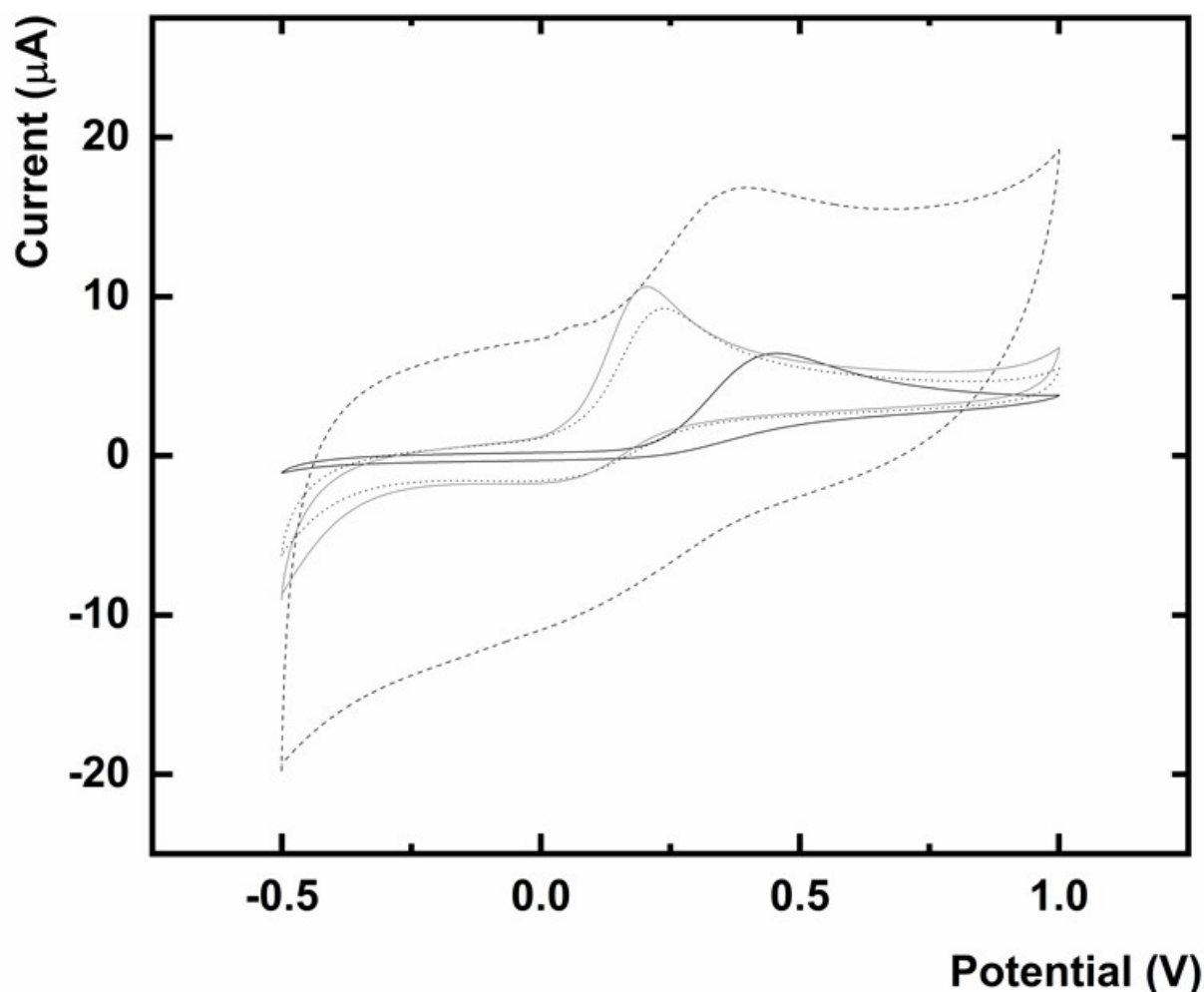


Figure 6.18. CVs of 1 mM AA in 0.1 M KH_2PO_4 using drop-cast modified GCE: GCE (solid black line —), DC-rGO-GCE (dashed line ---), DC-D-rGO-GCE (dotted line •••), DC-BDD-rGO-GCE (solid grey line —).

Though the modified GCE electrodes had overall increased sensitivity, the issue remained with consistency, with regards to the SA and morphology. The significant deviation from linearity trends for the modified electrodes was assumed to be caused by inconsistencies of depositions. Therefore, DGC electrodes with more consistent dimensions were suggested (see more detail in Section 6.2.8.4). The tip (2 mm) of a 3D-printed hollow cylinder (60 mm $\times$ 3 mm ID, 6 mm OD) was packed with the DGC (Figure 6.19). In this case, the electrode SA exposed to analytes is equal to the ID of the cylinder. Electrodes constructed this way are similar to and comparable with the commercial GCE. (These electrodes were also tested for the determination of AA concentrations.)

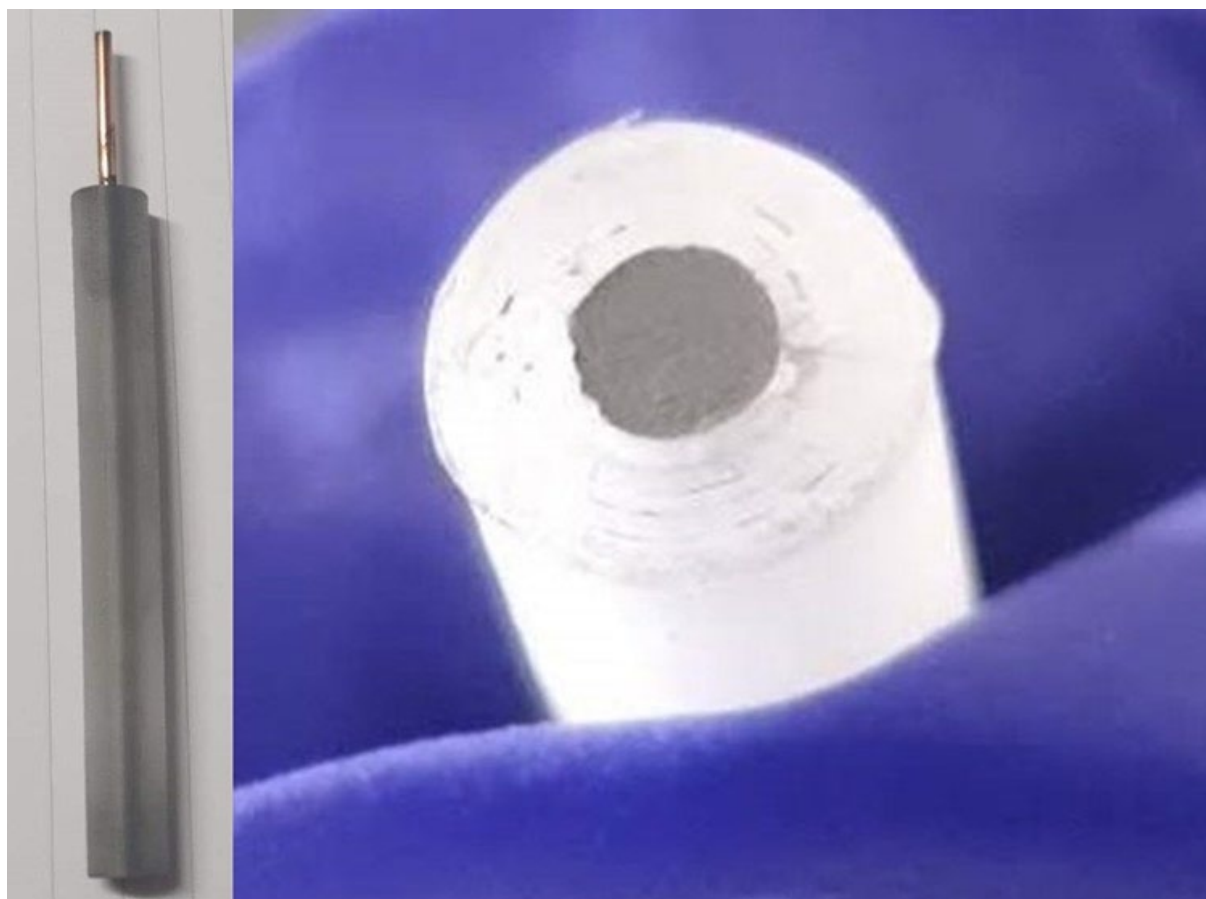


Figure 6.19. In-house prepared electrode.

AA oxidation peak potentials for analyte concentrations between 0.1 mM and 5 mM on six different electrodes are shown in Figure 6.20. It has been shown that a lower peak potential equates to a more efficient reaction process. Introducing rGO on the surface of the GCE shifts the oxidation potential to the left towards negative values compared to the unmodified GCE, and an even more significant shift was observed on GCE modified with composite materials. These shifts show that the reaction is better facilitated by the composites, which may be due to an increased active SA or a reduction in the resistance to electrons transitioning in and out of the electrode surface. In the case of the self-made electrodes, the peak is shifted towards higher values of applied potential, which more reflects the non-ideal construction of the electrodes.

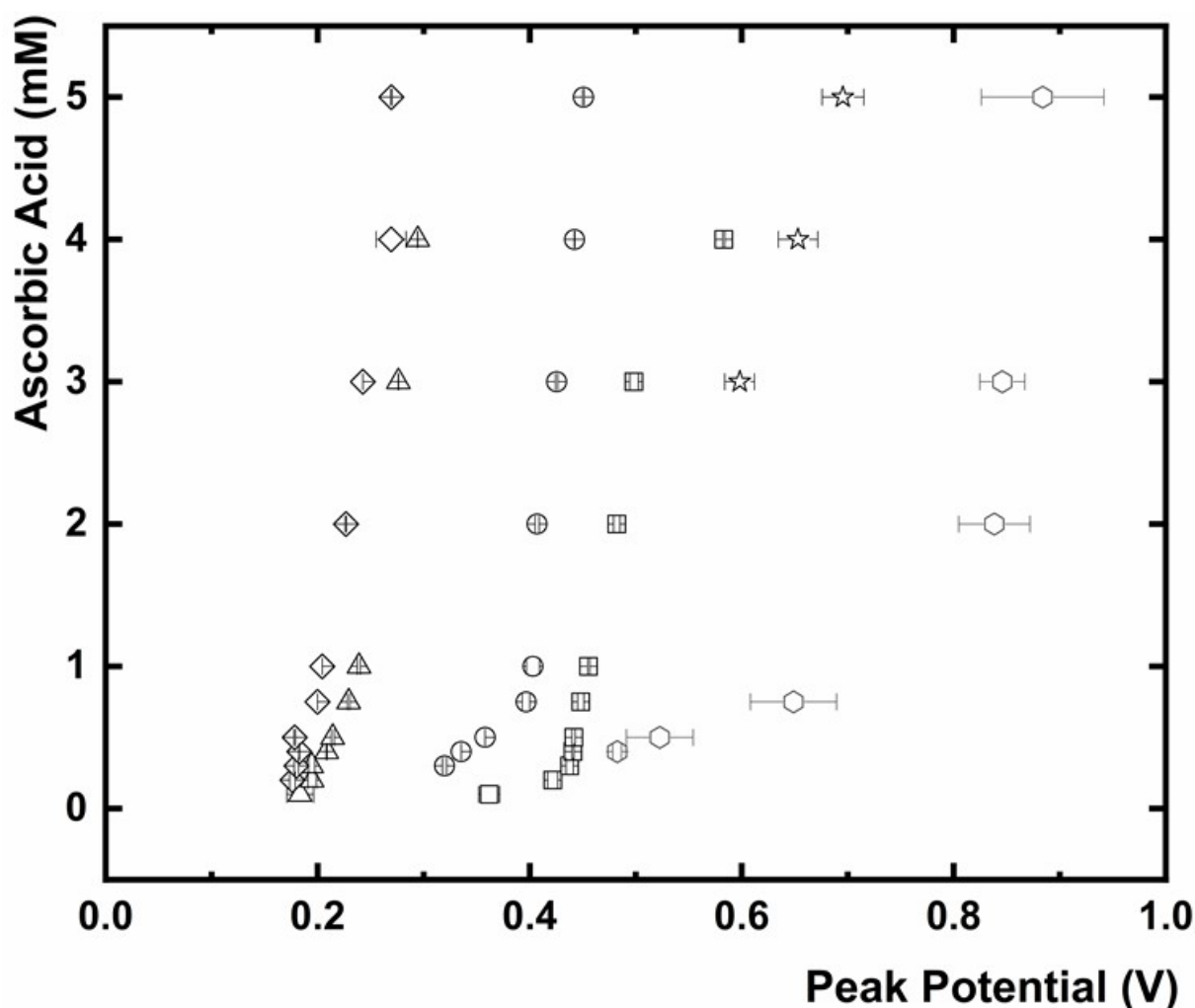


Figure 6.20. Oxidation potentials of AA from the solutions of different concentrations on various electrodes. □ – GCE; ○ – DC-rGO-GCE; △ – DC-D-rGO-GCE; ◇ – DC-BDD-rGO-GCE; ○ – D-rGO; ☆ – BDD-rGO.

As tests using AA determined that the composite materials could be used in electrochemistry, the DGC electrodes (D-rGO and BDD-rGO) were next tested for their behaviour in biologically relevant systems. Dopamine (DA) in PBS (pH 7.5) was chosen as the analyte. The resulting CVs for the 200 μ M DA solution on three electrodes (GCE, D-rGO and BDD-GO) are shown in Figure 6.21. Again, the DGC electrodes have a higher current draw when compared to GCE, showing greater SA due to higher electrical capacity. This means that there is potential that the DGC electrodes may be more sensitive at lower concentrations of DA.

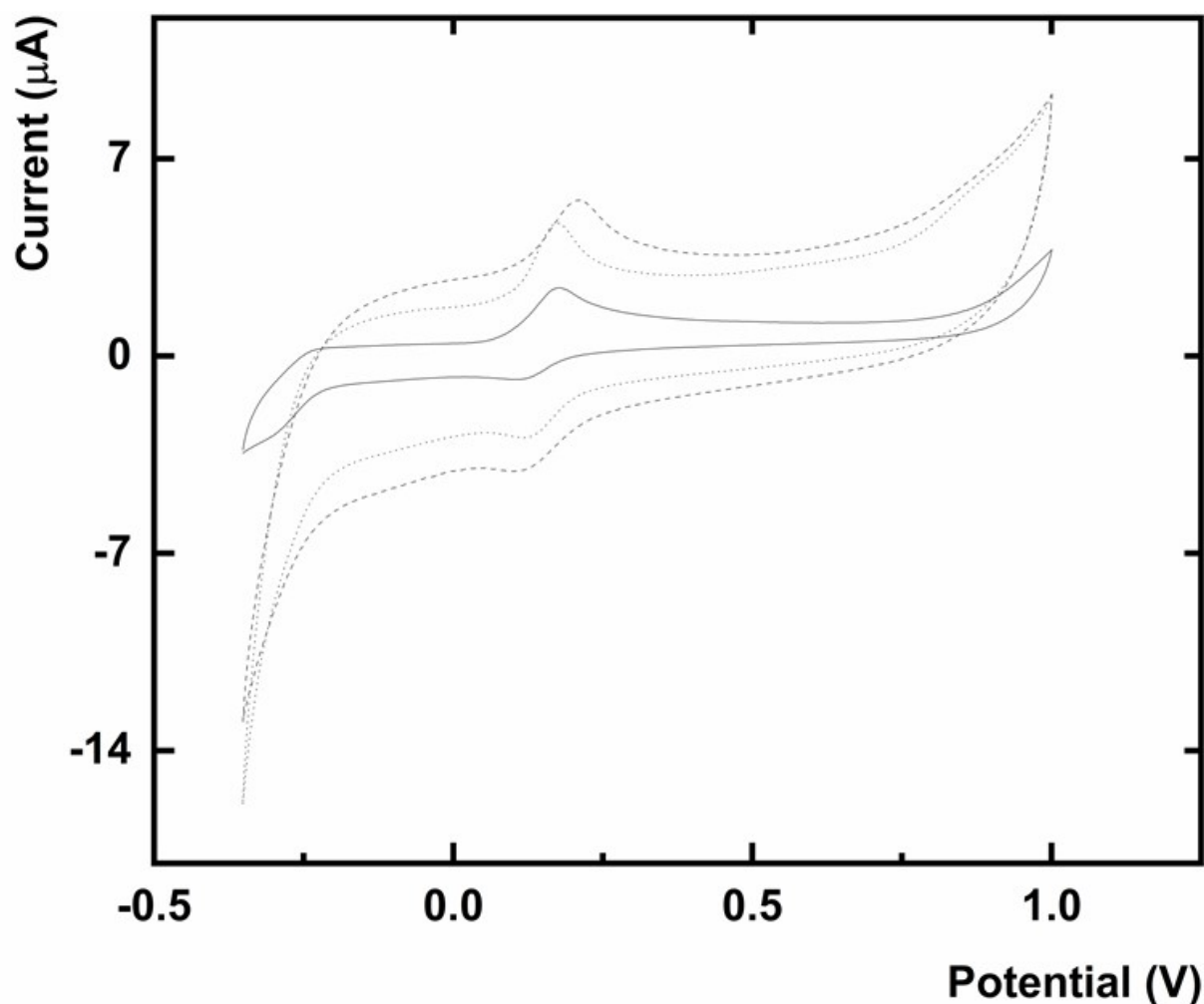


Figure 6.21. CVs of 200 μM DA in PBS, pH 7.5 on GCE and D-rGO and BDD-rGO electrodes. GCE (solid line —); BDD-rGO (dashed line ---); D-rGO (dotted line •••).

Calibration plots for DA on the three electrodes (GCE, D-rGO, BDD-rGO) are presented in Figure 6.22. The linearity ranges for all the tested electrodes are similar and are up to ca. 200 μM . Two-parameter saturation growth models applied to the data depict the flattening of the curve for all electrodes at concentrations $> 200 \mu\text{M}$. The D-rGO electrode outperformed the other two electrodes, with a capacity to return more sensitive measurements, as depicted by the steeper calibration plot. This difference may be attributed due to the increased SA of the D-rGO electrode, which would facilitate a superior number of reactions, due to lower resistance

on the electrode. A similar response to this was expected from the BDD-rGO electrode. However, the calibration curve and saturation levels of the BDD-rGO electrode were more similar to those of the GCE, which may be attributed to issues in the construction of consistent electrodes by hand. The positive results from the D-rGO electrode indicate that diamond-based electrodes have potential benefits in electrochemistry and warrant further investigation.

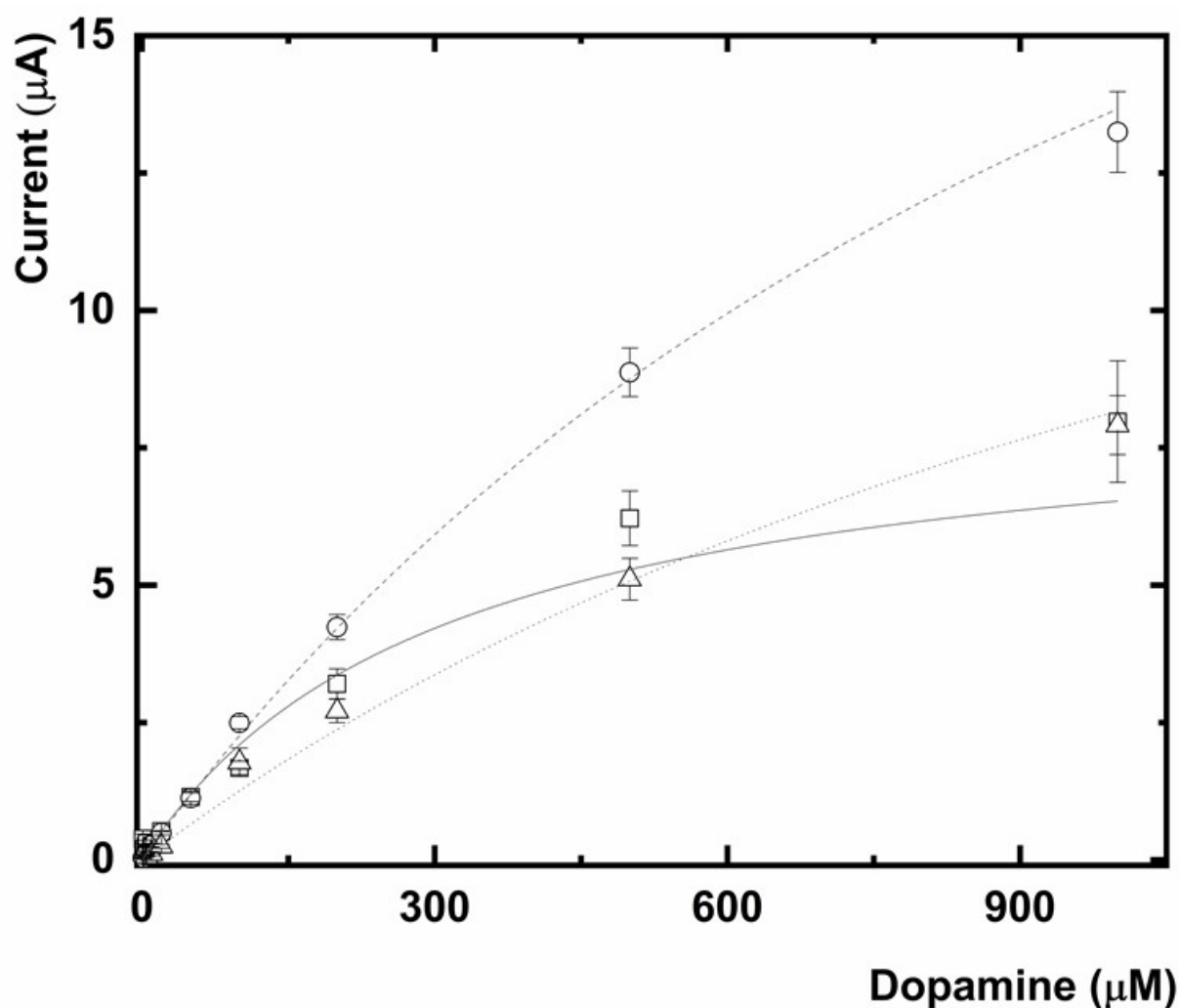


Figure 6.22. Calibration plots for DA in 0.1 M PBS, pH 7.5. Two-parameters saturation growth fit. $\square$, solid line – GCE; $\circ$, dashed line – D-rGO; $\triangle$, dotted line – BDD-rGO.

6.4. Conclusions

A satisfactory method for the preparation of a DGC material has been developed and optimised. This method includes a full reduction of GO with hydrazine on an H-diamond surface. EG was selected from a wide range of solvents based on the ability of the solvent to form a stable suspension for the reaction mixture. A factorial DOE was applied to optimise other variables of the preparation technique such as the ratio between diamond and GO, the concentration of the reducing agent and sonication frequency. The final preparation conditions were selected based on SEM images of the produced materials and UV-Vis spectrophotometry of the supernatant. The resulting conditions for the preparation of the composite were 21 mM hydrazine concentration, hourly sonication and a mass ratio of GO to diamond equal to 0.16. Comparison of the layer-by-layer self-assembly approach and the bulk mixture did not reveal significant differences in the structure of the composites. A further scale-up study showed a higher level of entrapping of rGO into the resulting material with an increase of concentrations of all components of a mixture.

At the next stage, DGC was entrapped into a PVDF matrix to produce a flow-through porous membrane. The morphology of the obtained membrane was investigated via SEM, and its EC was measured as $0.17 \text{ S} \cdot \text{m}^{-1}$. Based on these investigations, the produced materials were tested as electrodes for CV.

DGC-PVDF chips, DGC-GCE, DC-DGC-GCE and in-house made DGC electrodes were tested for AA and DA determination. Notably, no polymer was needed to modify the GCE or the in-house made DGC electrodes as the materials themselves were able to form stable clusters. The performance of the new electrodes was comparable to that of a commercial GCE.

The PVDF chips had some unfavourable features, which necessitated a redesign to provide uniformity. The new design was similar to a commercial GCE, and these electrodes provided good linearity in their response over a range of DA concentrations up to 200 μM . However, there were some issues regarding large peak areas being formed from large capacitance, and thus current flow. Therefore, these electrodes could be redesigned to minimise the peak area, which can be achieved by further reducing the amount of material used in each electrode.

Thus, it has been shown that these composites are an alternative substrate to GCE. When compared directly to GCE using an approximately equal cross-sectional area, these electrodes are showed the potential for better performance than the commercially available GCE. Therefore, being able to use less substrate, these electrodes can be quickly assembled in-house to obtain fully customisable fit-for-purpose electrodes, which can be used in analysis on a nanomolar, and up to a molar scale. The DGC, therefore, lends itself to be used as a potential bulk-electrolysis electrode, showing that DGC is an easily assembled multi-use composite with regards to electrochemistry.

CHAPTER 7

Conclusions and Future Outlook

7.1. General Conclusions

The incorporation of diamonds in composite materials is receiving considerable attention because of their exceptional physico-chemical properties. The use of diamonds composite materials in various aspects of analytical chemistry applications may lead to aspects of increased performance, robustness, reproducibility, and analytical selectivity and sensitivity. However, to achieve these potential benefits a better understanding of the diamond surface chemistry, followed by the development of new composite materials is necessary, which will then deliver upon broaden applications. This project aimed to explore and characterise modified diamonds, and, in an adaptive manner, create new composite materials and investigate the application of such composites.

As a foundation for this study, a comprehensive literature review was conducted on the application of diamonds within analytical chemistry (Chapter 2), with a specific focus on applications in solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC), highlighting advances in this field over the six years since the last detailed review on this topic was published. The applications of diamond were classified by the three most commonly used types of synthetic diamonds: detonation nanodiamonds (DNDs), high-pressure high-temperature (HPHT) diamonds, and chemical vapour deposition (CVD) diamonds. The variations in the surface chemistry, size and typical applications of these different types of diamond was a key focus of the review.

A number of general observations could be concluded from the above review and related reviews published elsewhere. For example, DND's high concentration of negatively charged oxygen-containing groups enables efficient surface binding of large biomolecules, such as proteins and their subsequent detection using high-sensitivity analytical techniques. However,

the small size (ca. 5 nm) of DND renders it unsuited for most chromatographic methods in their nature forms. Larger microsintered detonation nanodiamonds (MSDN), core-shell particles or monolithic columns are required for such applications. The recent commercialisation of one type of detonation-based core-shell particle has demonstrated the potential for diamond-containing materials in liquid chromatography.

HPHT and CVD diamonds are available across a wide size range, and therefore can theoretically be used directly for HPLC applications. However, the use of CVD-diamond-based materials for separation science is constrained by the required expensive manufacturing technique and the passivated surface means that CVD based materials for separation science applications is not ideal. The literature revealed that the selectivity of bare HPHT diamond has been studied in aqueous normal-phase and hydrophilic interaction liquid chromatography (HILIC) modes, producing promising, but limited, results. Based on this, it was decided to expand our knowledge about the HPHT diamond surface chemistry, and subsequently undertake to modify its surface to deliver new chromatographic selectivities and to potentially expand the scope of its applications.

Five types of modifications were performed on HPHT diamond surfaces and the resultant properties of these modified adsorbents were systematically investigated (Chapters 3 and 4). The modification methods included oxidation with Piranha mixture, oxidation by air, oxidation by a mixture of concentrated nitric and sulfuric acid, reduction by lithium aluminium hydride and further modification with *n*-butyllithium ($\text{LiAlH}_4/\text{BuLi}$), and reduction in a hydrogen atmosphere. The changes on the surface were confirmed by Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and elemental analysis.

All of the modified HPHT diamond phases produced in this study exhibited ion-exchange properties. In particular, cation-exchange properties were observed within all of the oxidised diamonds, as well as the $\text{LiAlH}_4/\text{BuLi}$ modified diamonds, due to the negatively charged groups (e.g. carboxyls and hydroxyls). This was evident from the results of potentiometric titration and zeta potential measurements across the pH range from 1 to 12. The surface concentration of carboxylic groups in the prepared adsorbents varied in the range of $0.65\text{--}2.2\text{ nm}^{-2}$, with the greatest oxidation of diamond being achieved through a hot Piranha mixture oxidation process. In contrast, the hydrogen-terminated surface predominantly exhibited anion-exchange properties at basic pH. Relatively strong retention of carboxylic acids under these conditions decreased with an increase in the mobile phase ionic strength, indicating the possible presence of positively charged nitrogen-containing groups. The retention of metal cations increased for the prepared adsorbents in the order: hydrogenated < $\text{LiAlH}_4/\text{BuLi}$ modified < bare < oxidised HPHT diamonds. For the obtained adsorbents, a new method was developed for calculating adsorption isotherms from the shapes of chromatographic peaks. This method allowed the calculation of maximum adsorption values for metal cations on oxidised diamond, from $50\text{--}70\text{ nmol g}^{-1}$ for alkali metal cations, and from $30\text{--}100\text{ nmol g}^{-1}$ for alkaline-earth metal cations. The possibility of the simultaneous separation of five metal cations using a column packed with Piranha-oxidised HPHT diamond particles was demonstrated. The elution order $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Cr}^{3+}$ in 20 mM nitric acid was observed and corresponded to that known for carboxylic cation exchange resins.

The retention mechanism on hydrogenated diamond was found to be significantly more complicated than that on oxidised diamond. Apart from simple ion-exchange properties, hydrogenated diamond also exhibited weak reversed-phase interactions, which was confirmed by the retention of non-polar solutes. It was demonstrated that 21 non-ionogenic derivatives of benzene could be retained with a mobile phase, (which contained 6% ACN), and the retention

factors of the solutes were shown to correlate with their polarity ($\log P$). In addition, an increase in the retention of ionogenic aromatic compounds with a significant increase of organic modifier in the mobile phase also revealed what is surmised to be solvent-enhanced ion-exchange response, or even HILIC-like retention mechanisms in play.

The efficiency of chromatographic separations on oxidised diamond phases achieved in this study peaked at $36,740 \text{ N m}^{-1}$, as calculated for cytosine, following a size fractionation of the stationary phase by a series of sedimentations in 10 mM sodium hydroxide. Poorer efficiency was observed on hydrogenated diamond ($9,630 \text{ N m}^{-1}$ as calculated for benzoic acid), however, improving separation efficiency was not a significant goal for this particular study. The thermal stability of the hydrogenated diamond stationary phase and the immutability of the retention mechanisms involved was confirmed by linear Van't Hoff plots for all investigated compounds, a fact expected to be relevant to other adsorbents.

In an attempt to increase the HPHT diamond surface area, a stable diamond-graphene oxide composite material was constructed by *in-situ* reduction with hydrazine and fully characterised (Chapter 6). For the composite material to be synthesised the kinetics of graphene oxide (GO) reduction was first investigated by a novel ion chromatographic method (Chapter 5). The research was then further extended by the electrochemical characterisation of the resultant diamond/GO composite (DGC) material.

At first, to investigate the kinetics of GO reduction with hydrazine, a new method was developed for monitoring hydrazine consumption during the reaction process. Ion-exchange chromatography with electrochemical detection was employed for this purpose. The use of electrochemical detection allowed the selective determination of hydrazine in the presence of excess ammonia, even up to 5.8×10^4 times the hydrazine concentration. The method resulted

in an LOD and LOQ of 3 μM and 10 μM , respectively, for hydrazine in the presence of 0.25 M ammonium hydroxide. The reduction endpoint obtained with the study of hydrazine consumption was found to correspond with Fourier transform infrared (FTIR) and Raman spectroscopy and with published reports of similar reduction processes. Monitoring hydrazine consumption by chromatography during GO reduction can offer many advantages, such as the development of an on-line system to monitor the GO reduction process, the ease of quantifying the different stages of rGO, unequivocal determination of the reduction endpoint, and new insights into GO chemistry. As a result of the application of the developed method for controlling the concentration of hydrazine in the reaction mixture, it was found that it takes six hours for complete reduction of GO under the studied conditions. This finding was significant for the subsequent synthesis of DGC material.

The method for the preparation of DGC includes the full reduction of GO with hydrazine in presence of hydrogenated diamond particles. Ethylene glycol was chosen as a reaction medium based on its ability to support a reasonably stable suspension of GO and diamond. A factorial experimental design was applied to optimise the variables of the preparation technique, such as the ratio between diamond and GO, the concentration of the reducing agent and the sonication frequency. The final preparation conditions were selected based on scanning electron microscopy (SEM) images of the produced materials and ultraviolet (UV) spectrophotometry of the supernatant. These were as follows: 21 mM hydrazine concentration, hourly sonication and a mass ratio of graphene to diamond equal to 0.16. A layer-by-layer self-assembly approach and a bulk mixture approach were also compared and no significant differences in the structure of the final composites was revealed. A further scale-up study showed a higher level of entrapping of graphene into the resulting material with an increase in concentration of all components of the mixture. The obtained composite adsorbent demonstrated good stability in common organic solvents. The surface area of the DGC

measured by the Brunauer-Emmett-Teller (BET) method increased by 60% compared to bare HPHT diamond. Although the material was deemed to be unsuitable for column liquid chromatographic applications at this point, due to the agglomeration of the particles, it has clearly the potential to be used as an SPE sorbent.

At this stage in the project it was evident that the conductivity of the prepared DGC was comparable with boron-doped diamond (BDD), and so resulted in its electrochemical properties being investigated. DGC electrochemical properties were studied *via* the modification of a glassy carbon electrode (GCE) and as a free-standing electrode – either entrapped into polyvinylidene fluoride (PVDF) or as an electrode made in house. When compared directly to GCE for the detection of ascorbic acid and dopamine using an approximately equal cross-sectional area, these electrodes were found to facilitate the reaction faster and better than the commercially available GCE. This finding indicates that smaller sized electrodes made from DGC are possible. Additionally, the DGC electrode can be quickly assembled in house to obtain a fully customisable fit-for-purpose electrode which can be used in analyses of nanomolar up to molar scale. The performance of the DGC was also compared with a similar DGC made with BDD; however, no significant difference in electrochemical response between these two electrodes was noted.

7.2. Future Outlook

While this project delivered advances in the characterisation and application of HPHT diamond materials, several key areas of further work were identified and are warranted.

Chapter 4 revealed that further investigations of the H-terminated diamond surface are required to identify the specific contributions of HILIC-like selectivity, and the nature of other solvent-enhanced modes of interactions, to the overall retention mechanism of the stationary phase.

The adsorption properties of the composites developed in Chapter 6, namely diamond-rGO and BDD-rGO, should be thoroughly investigated and expanded to practical applications for this material, and/or further define directions in which to advance these novel adsorbents. In the area of electrochemistry, the electrode configuration should be further optimised to improve the linearity of response. Bulk electrolysis and capacitor applications for this type of composite should also be explored, given the relatively simple method for preparation and electrode construction developed, and the positive results of initial electrochemical characterisation.

Development of highly thermally stable ($>100^{\circ}\text{C}$) and efficient diamond-based adsorbents with improved adsorption kinetics remains a challenge and an area to assign further dedicated efforts. Adsorbents with such high stability and (potential) efficiency may be useful to the pharmaceutical industry as it could be applied under supercritical conditions for the separation of chiral molecule. Catalytic annealing of the diamond surface appears to be a relatively cheap and easy modification method. Therefore, such developed materials could have an increased surface area, thus positively affecting the adsorption capacity of the diamond without affecting the thermal stability of the adsorbent. The resulting porous surface may also deliver a positive effect on the kinetics of retention and the separation efficiency.

The comprehensive literature review highlighted the limited use of CVD diamond in chromatography and sample preparation due to the high cost of production. Likely, the cost of production will decrease in the coming years, which will present new opportunities for diamond-based adsorbents with highly controllable surface morphology provided by such CVD methods. Although it was not covered in the review, it has been noticed that the use of conductive BDD diamond is particular of interest for the development of selective and sensitive biosensors, and new chemical surface-modifications need to be developed for controlling adsorption and electron-transfer kinetics.

Finally, conductive diamonds can also be applied for the development of electrochemically modulated liquid chromatography stationary phases due to the unique combination of their adsorption and conductivity properties. This unusual mode of chromatography gained some attention in the past, but never gained mass appeal, new conductive stationary phases may help reignite this area of research in the future.

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