

Electrode surface modification using iron(II)
phthalocyanine immobilized via electrografting and click
chemistry and clicked onto azide-functionalized quantum
dots: Applications in electrocatalysis

A thesis submitted in fulfilment of the requirements for the degree of

Master of Science

Of

Rhodes University

By

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December 2015

Dedicated to:

My late grandmother, Doris Mpofu

My loving parents, Israel and Sharon Nxele

My bestfriends, my sisters, Pearl and Rachel Nxele

**“...You cannot hold on to your seed. You must sow it and reap
anew...” Robert Collier**

Acknowledgements

The work reported in this thesis would have not been possible without the following people:

My supervisor, Professor Tebello Nyokong who has always been so supportive, encouraging and provided me with opportunities I could have never imagined were going to cross my path so soon. Thank you for your guidance and amazing leadership. I have learnt so much from you including the realisation of my true potential. Thank you for always believing in me and trusting me with representing you, S22 and Rhodes University at other universities in different parts of the world.

Thank you to the research laboratories I visited in Japan (Prof Nagao Kobayashi) and France (Dr Fethi Bedioui and Dr Anne Varenne). Thank you for being amazing hosts and for taking time to contribute to my growth in research.

Thank you to Dr Philani Mashazi for helping me with XPS analyses as well as electrochemistry as a whole. I truly appreciate the moments you have taken the time to just discuss my work and giving me insight on the ideas I put forward. Thank you to my S22 colleagues who have always been so helpful. A special thank you to my mentors, Dr Audacity Maringa and Mr Stephen Nyoni (soon to be Doctor) for being great and helping me throughout my MSc with electrochemistry. Thank you to my friends for their love, support and encouragement. Thank you to Mr Unako Mpiti for the support and conversations contributing to a better understanding of my work and chemistry as a whole. To my mother, my father and my two older sisters, you are truly

amazing. The love and encouragement throughout my entire life has played a part in becoming who I am today. No words can describe how thankful I am.

Abstract

Tetrakis(5-hexynoxy)Fe(II) phthalocyanine was used alone and in combination with quantum dots (QDs) in order to test the electrocatalytic ability with hydrazine and paraquat as the analytes of interest. This novel phthalocaynine was successfully synthesised and characterized using various characterisation techniques. The QDs used were the well-known core-shell CdSe/ZnS nanostructures. The fabrication of glassy carbon electrodes involved covalent attachment by electrochemical grafting and click chemistry for the first part of the work and the second part involved the conjugation of the synthesised QDs and the phthalocyanine by click chemistry. This approach of conjugating these nanostructures introduced another aspect of novelty to the work reported in this thesis. The immobilisation of this conjugate on a glassy carbon electrode (GCE) was achieved by adsorption. Characterisation techniques such as infrared spectroscopy, x-ray diffractometry, UV/vis spectroscopy, transmission electron microscopy and x-ray photoelectron spectroscopy were used to characterise the molecules and conjugates of interest. With respect to the electrocatalytic part of the work, electrode surface characterisation involved scanning electrochemical microscopy and cyclic voltammetry to determine changes in the nature of the surface as well as reactivity of the surface at different modification steps. Detection limits and the sensitivity determined for the electrocatalysts fabricated here proved to be an improvement compared to other reported work involving phthalocyanines and the test analytes chosen for application. With respect to the conjugate, the electrocatalytic ability was improved when the QDs and phthalocyanine were combined using click chemistry compared to using the phthalocyanine alone.

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List of Abbreviations

ACN	Acetonitrile
TBABF ₄	Tetrabutylammonium tetrafluoroborate
QDs	quantum dots
Pc	phthalocyanine
MPcs	metallophthalocyanines
GCE	glassy carbon electrode
GCP	glassy carbon plate
GSH	glutathione
EDC	1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide
NHS	N-hydroxysuccinamide
PQ	paraquat
CE	capillary electrophoresis
LDE	laser Doppler electrophoresis
DLS	dynamic light scattering
SECM	scanning electrochemical microscopy
XPS	x-ray photoelectron microscopy
TEM	transmission electron microscopy

XRD	X-ray diffraction
CV	cyclic voltammetry
DPV	differential pulse voltammetry
UME	ultramicroelectrode
LoD	limit of detection
Redox	reduction/oxidation
IMAC	interim maximum acceptable concentration

List of Symbols

A	Electrode surface area
ε	Extinction coefficient
E	Energy
cm^{-1}	Wavenumber
Φ	Work function
ΔE	Peak potential separation
d	Distance
e-	Electron
λ	Wavelength
$\text{\AA}$	Angstrom
E_p	Peak potential
K	Constant
I_p	Peak current
C	Concentration
T	Temperature
V	Scan rate
M	Molar concentration

k_{cat}	Catalytic rate constant
k	Empirical constant
n_{α}	Number of electrons in rate determining step
R	Universal gas constant

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Chapter 1:

Introduction

1. Introduction

This work reports on the use of phthalocyanines as electrode modifiers when alone or in combination with quantum dots. Phthalocyanines are attached to electrodes and to quantum dots by click chemistry and the modified electrodes are characterized by several techniques including X-ray photoelectron spectroscopy, scanning electrochemical microscopy and voltammetry. Capillary electrophoresis, laser Doppler electrophoresis and dynamic light scattering are also some of the techniques used to characterize the synthesized quantum dots and their conjugates. The modified electrodes are employed for the electrocatalysis of hydrazine and paraquat as test analytes with the aim of developing functional sensors.

1.1 Phthalocyanines and their application as electrocatalysts

Phthalocyanines are macrocyclic compounds with a planar structure and a conjugated 18 π -electron system. These macrocycles have been studied for many years, and may be modified to suit a wide range of applications. **Fig. 1.1A** shows an unsubstituted phthalocyanine structure and **Fig. 1.1B** indicates the positions which may be modified on the molecule. Phthalocyanines have proven to be highly stable ligands which have the ability to coordinate with a number of metals (**M on figure**) to form metallophthalocyanines (MPcs). Depending on the charge of the central metal, axial ligation is also possible. Peripheral (**β**) and non-peripheral (**α**) substitution is also possible in order to improve the functionality of these molecules for applications in areas such as photodynamic therapy (PDT) of cancer [1], optical limiting and non-linear optics [2], fluorescence imaging [3], photocatalysis [4] and electrocatalysis [5].

Substitution of the ring may also be carried out with the aim of conjugation of these macrocycles with other molecules.

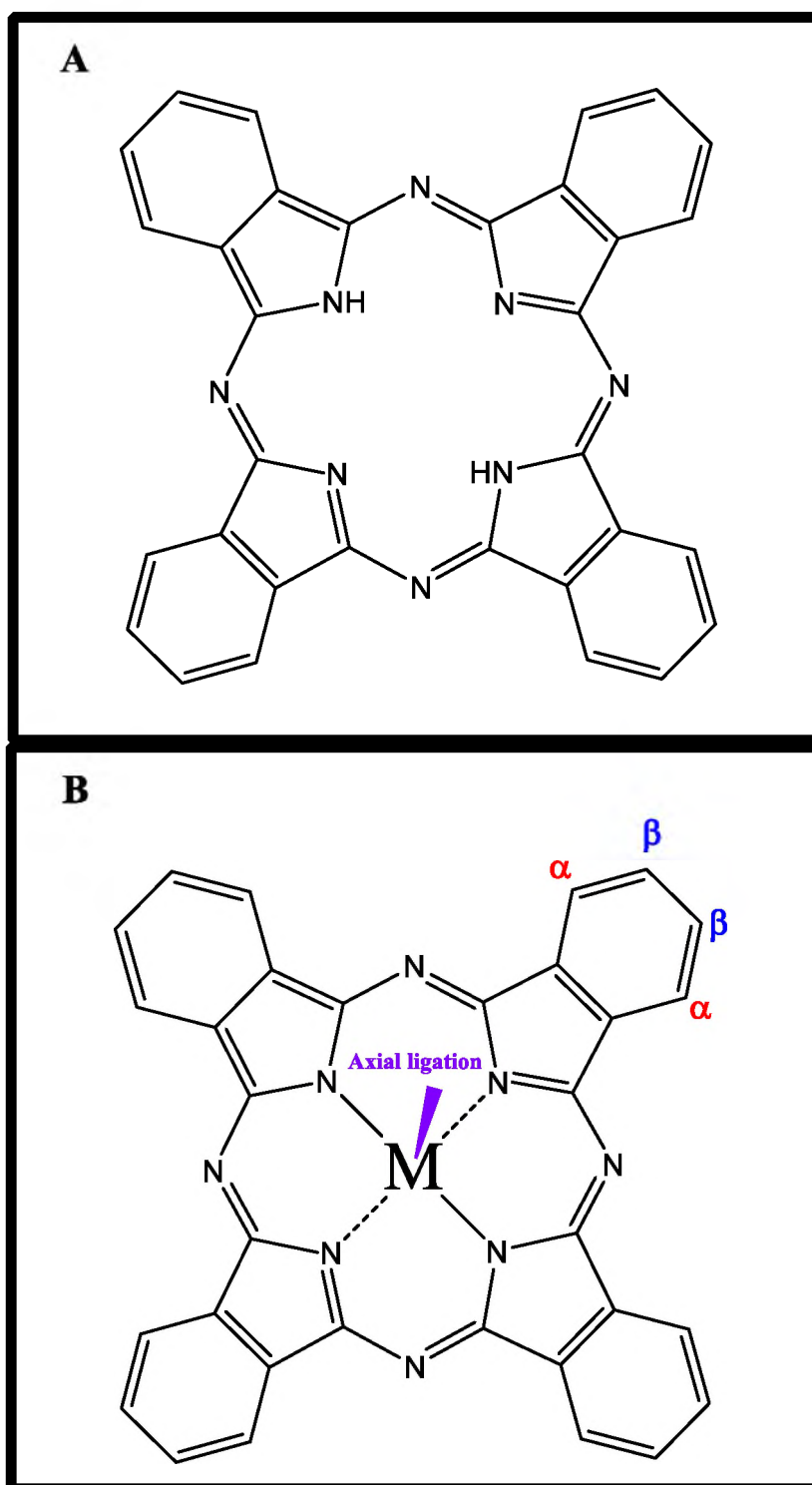


Fig. 1.1: Structure of (A) unsubstituted Pc and (B) possible modifications of Pc structure.

The focus of this thesis lies in the electrocatalytic ability of an MPc containing Fe(II) as the electroactive central metal and modified with terminal alkyne groups as the peripheral substituents for the purpose of conjugation via click chemistry. An electrocatalyst is a molecule that is able to increase the rate at which an electrochemical reaction takes place by lowering the applied potentials and increasing the current produced. Electrocatalysts in electrochemistry are generally immobilized on solid, conducting materials to enhance or rather improve the electrocatalytic reaction. **Fig. 1.2** [6] illustrates how using an electrocatalyst enhances the currents and lowers the energy (overpotential) needed for the reaction to take place.

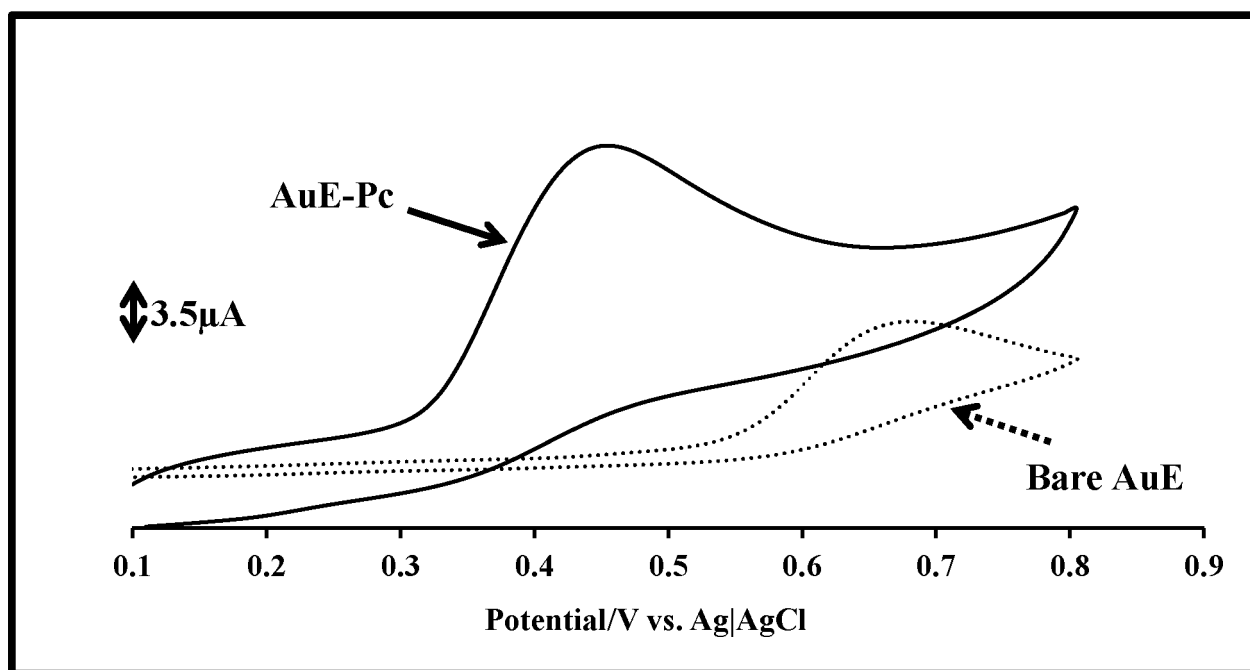


Fig. 1.2: Illustration of improvement of currents and energy required for electrocatalytic reaction using electrocatalysts. Electrodes in 200 μM carbofuran solution (pH 4). Scan rate: 100 mV/s vs Ag/AgCl [6]. Au-E= Au electrode.

There have been numerous electrochemical sensors which have been fabricated using MPcs for the electrochemical detection of various electroactive analytes such as dopamine [7-9], glutathione [10-12], amitrole [13-15], hydrogen peroxide [16-18], paraquat [19,20] and hydrazine [21-23] just to name a few. Nanomaterials in particular have played a huge role in the fabrication of electrochemical sensors with the aim of miniaturisation, lowering the applied potential and lowering detection limits. Metallophthalocyanines (MPcs) in particular, especially those with electroactive central metals such as Fe, Co and Mn [24] have proven time and time again their impressive capability of producing desirable results as electrocatalysts. **Fig 1.3** [25] illustrates how MPcs work as electrocatalysts when immobilized on an electrode. During electrocatalytic reactions, the central metal, in its 2⁺ state for example, is generally oxidised to its 3⁺ state and in turn reduced to its 2⁺ state by the analyte (**Fig. 1.3**). In addition, combining these MPcs with other nanomaterials such as carbon nanotubes [26], gold nanoparticles [27] and QDs [28] has been a subject of interest in order to improve the electrocatalytic behaviour of MPcs. In this work, a combination of alkynyl FePcs linked to QDs by click chemistry has been used.

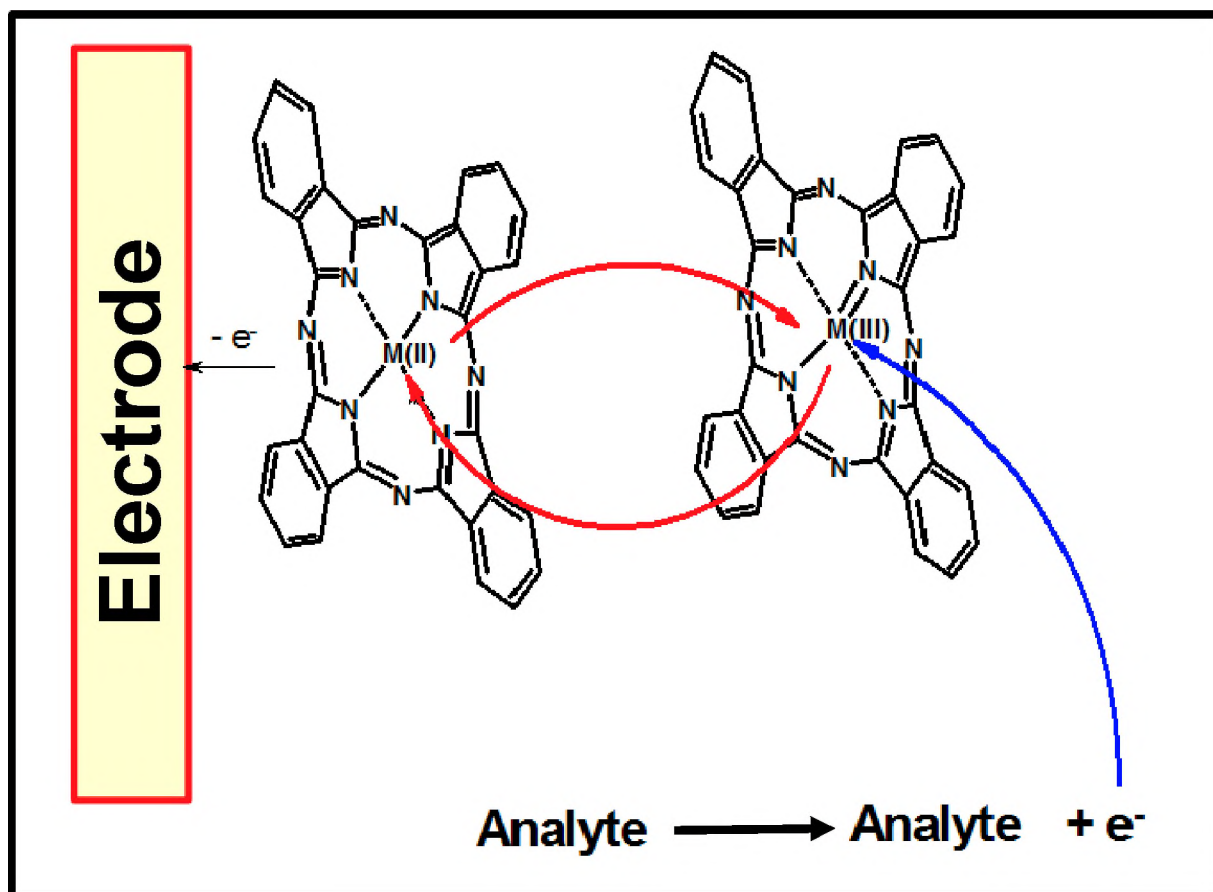


Fig. 1.3: Typical electrocatalytic process of metallophthalocyanines immobilized on electrodes. Scheme adapted from Zagal et al. [25].

1.2 Methods of electrode modification using the phthalocyanine reported in this work

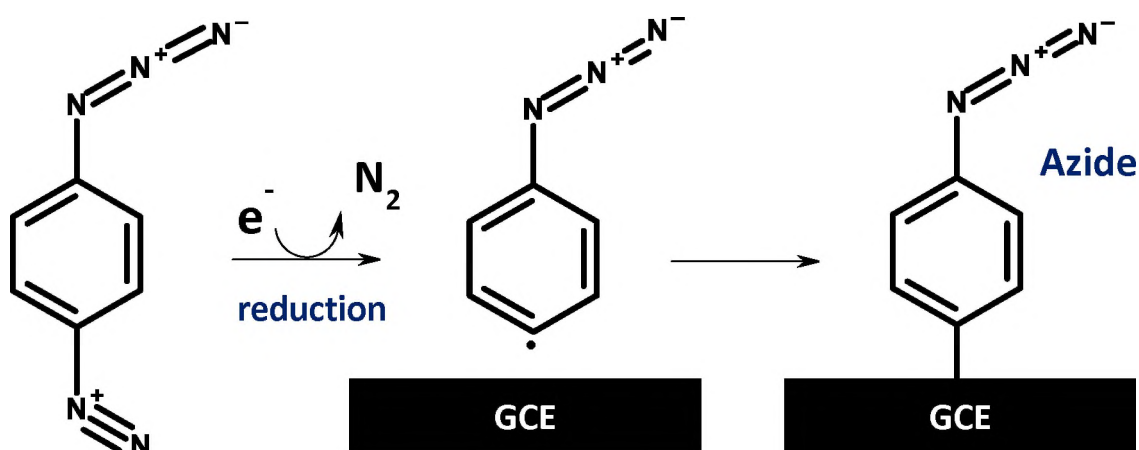
Electrode modification has played a vital role in the improvement of electrocatalytic reactions that take place on the surface. Some modification methods that have been used are (1) electropolymerization [29, 30] which involves forming a polymer film on the electrode surface by oxidation or reduction of a monomer, (2) electrodeposition [31, 32] which involves the immobilization of chemical species on an electrode surface by an applied potential, (3) self-assembled monolayers (SAMs) which involves the spontaneous assembly of molecules on an electrode surface and has been used for immobilizing thiol-modified molecules on gold surfaces due to sulphur having an

affinity for gold [33, 34] and (4) adsorption [35]. Other modification methods which have been used for electrode surface modification include covalent bonding by electrochemical grafting [36, 37]. In this work, electrochemical grafting followed by click chemistry, as well as adsorption, are employed in the modification of the electrodes and are discussed in detail next.

1.2.1 Electrochemical grafting by reduction

Grafting involves electrochemical reduction of a molecule forming a radical, after which a covalent bond is simultaneously formed between the electrode surface and the molecule. Reducing phenyl azide or phenyl acetylene diazonium salts by electrochemical methods results in the grafting of azido or ethynyl groups onto an electrode surface [38]. The interest of this work lies in achieving terminated azide groups on a glassy carbon electrode in order for these groups to react with the terminal alkyne groups of the FePc of interest. The 4-azidobenzenediazonium salt that has been synthesized in this work is of particular interest in this study because it is known to react with any compound with a terminal alkyne group under mild conditions with high specificity [39]. **Scheme 1.1** illustrates the reaction that occurs on the electrode surface during electrografting using the diazonium salt. The number of phenyl azide groups on the electrode surface is unknown but the concentration of the diazonium solution used plays a vital role as well as the number of scans that are run to reach the outlined goal. Passivation of the electrode surface by the phenyl azide groups is expected, but by optimizing the reaction parameters such as number of cycles during the electrochemical reduction process, a layer not too thick, so as to not limit the electron transfer once the alkynyl FePc has been immobilized on the electrode surface via the described ‘click’ reaction, may be formed. Moreover, this method of electrode modification allows for

a more 'ordered' electrocatalyst layer on the GCE surface. The covalent bonds formed increase the stability of the sensor which promotes the reproducibility of the electrocatalyst.

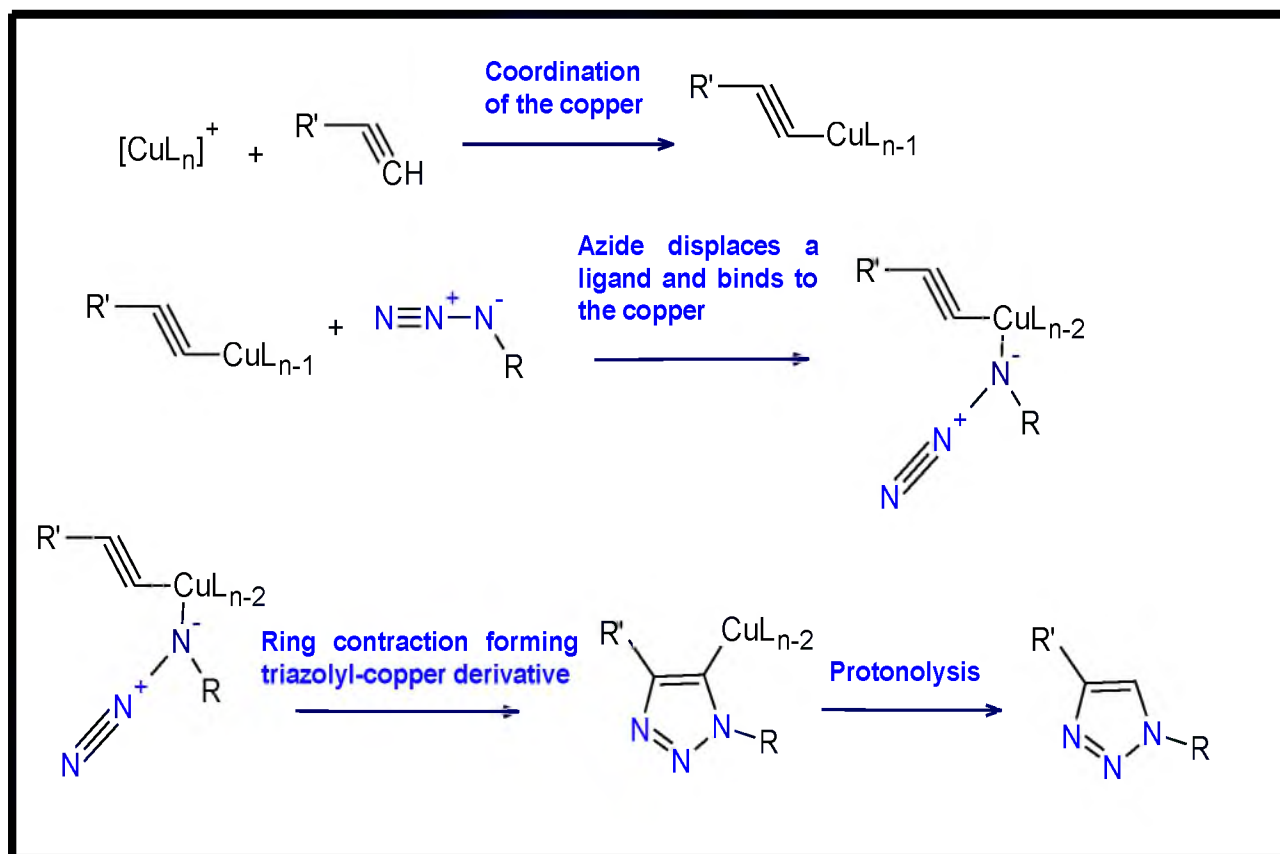


Scheme 1.1: Approach to attachment of phenyl azide groups onto a GCE by electrochemical reduction.

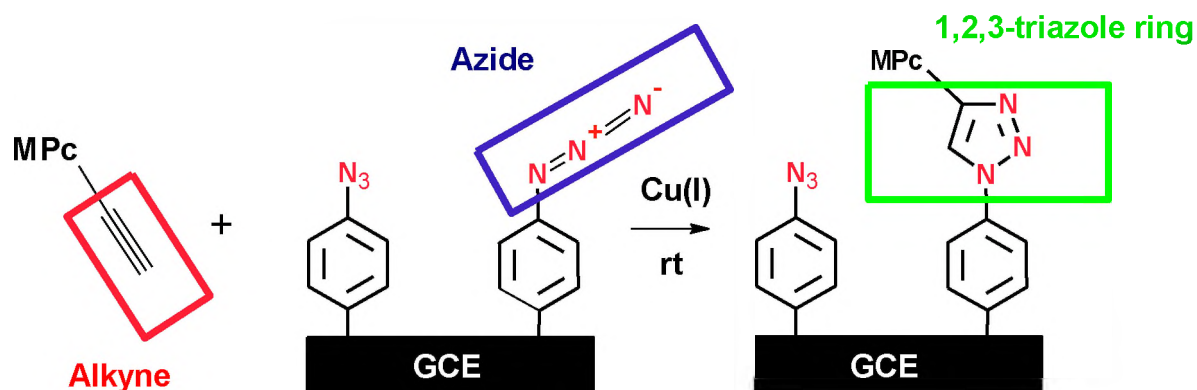
1.2.2 Click Chemistry

The click chemistry reaction involves Cu(I) as a catalyst which has been described by Sharpless [40]. This reaction is carried out at room temperature and does not require inert conditions. **Scheme 1.2** illustrates the steps of the reaction where the copper temporarily coordinates with the terminal alkyne group displacing a ligand, followed by the azide group displacing another ligand and in turn coordinating with the copper. Thereafter ring contraction takes place forming a 1,2,3-triazole ring (**Scheme 1.2**). Finally, protonolysis takes place yielding the final product. Initially the copper that is used is in

its 2^+ state and therefore a reducing agent is used to form Cu(I) which catalyzes the click reaction. **Scheme 1.3** illustrates the click reaction on a GCE which was done in this work. The reaction may occur with more than one immobilized phenyl azide group and with one or more of the peripheral substituents on the alkynyl FePc. Various surface characterization techniques were employed to prove the success of this reaction.



Scheme 1.2: Basic illustration of Cu(I)-catalyzed click chemistry reaction.



Scheme 1.3: Click reaction between terminal alkyne groups of an MPc and phenyl azide groups immobilized on a GCE.

The FePc functionalized with terminal alkyne groups is clicked onto the terminated phenyl azide groups and thus immobilized on the surface of the glassy carbon electrode.

Fig. 1.4 illustrates the clicked FePc-modified electrode used in this work. The other part of the work involves click chemistry of the alkynyl FePc with the azide groups on the QDs followed by electrode modification by adsorption which will be discussed in the next sub-section.

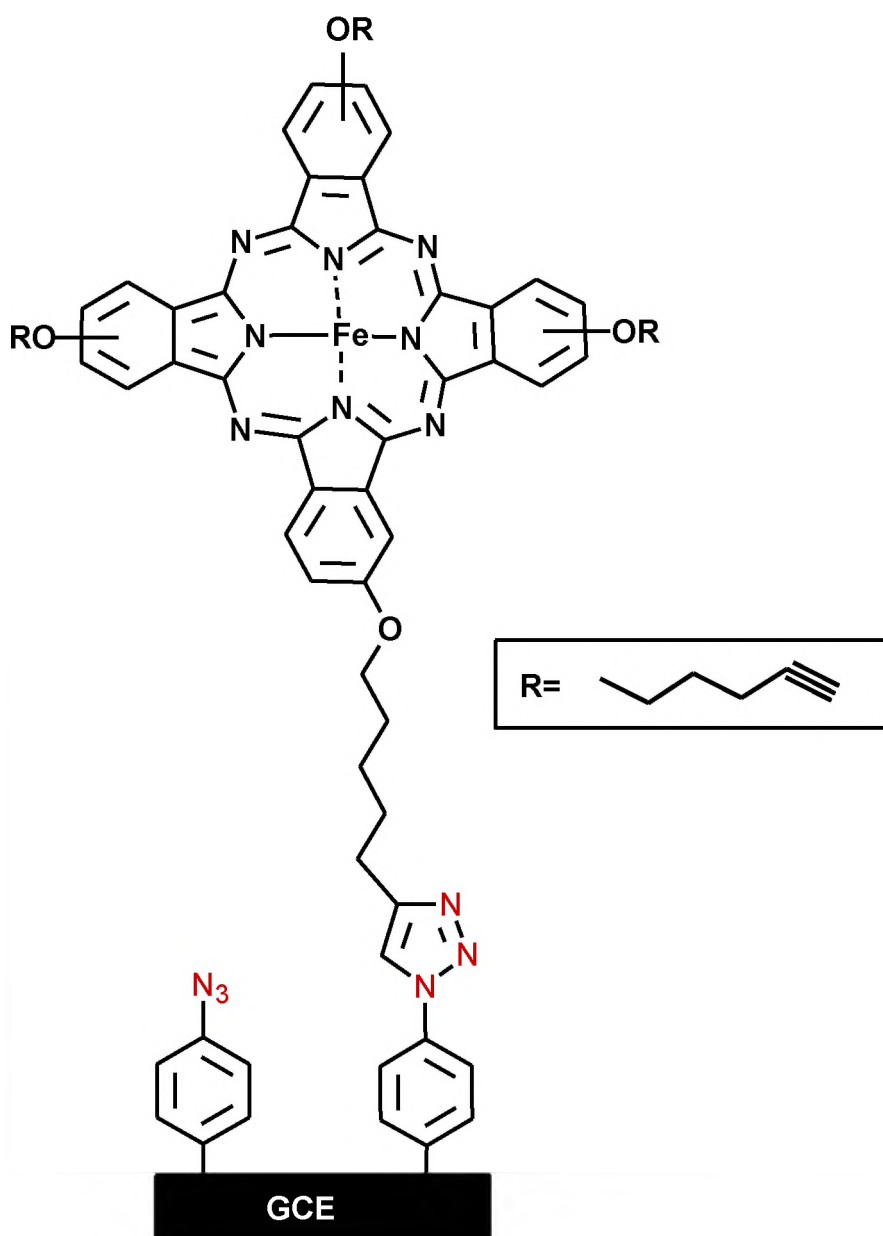


Fig. 1.4: Schematic representation of final electrode for the electrocatalytic oxidation of hydrazine.

1.2.3 Adsorption by ‘drop and dry’ modification technique

In the work involving the immobilization of QDs and their conjugates with the alkynyl FePc, adsorption methods were used to modify a glassy carbon electrode using the synthesized quantum dots and their conjugate with the alkynyl FePc by click chemistry. Physical adsorption does not involve formal bonds between the electrode surface and the modifiers but there is just a physical interaction between the surface and the molecule without changing the electronic structure of the molecule. To obtain the modified surfaces, a drop and dry method was employed by dissolving the different modifiers in a suitable solvent and applying a drop of a certain volume on the electrode surface (Fig. 1.5).

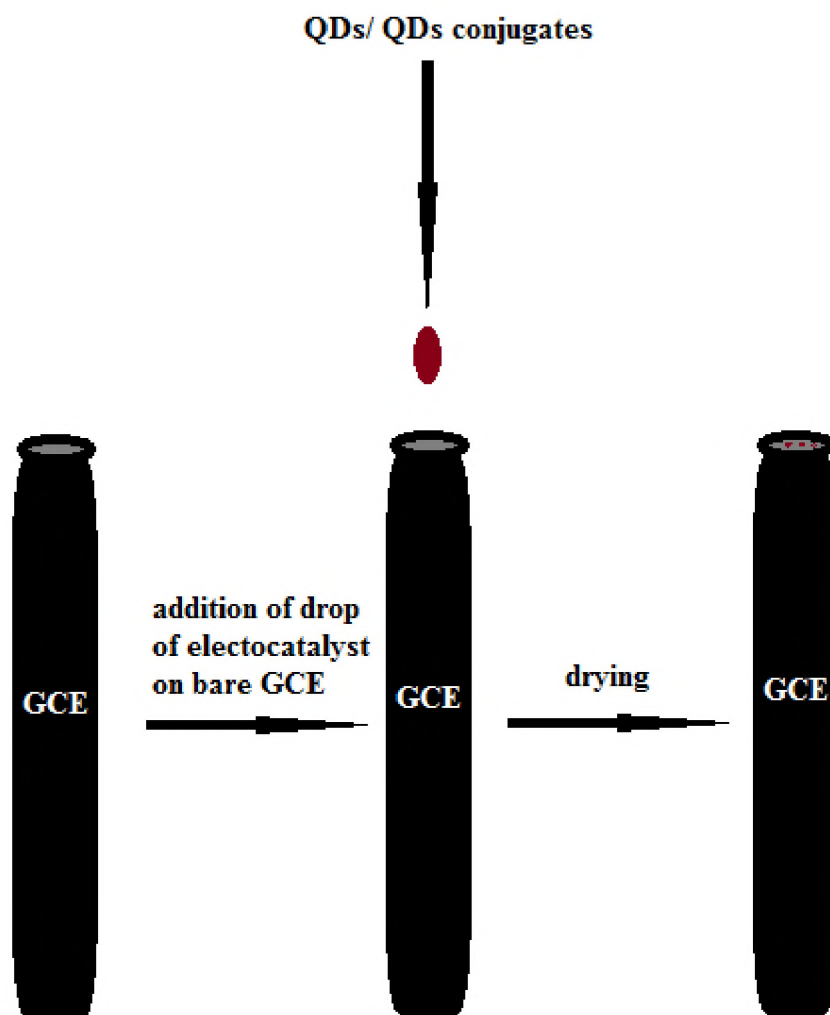


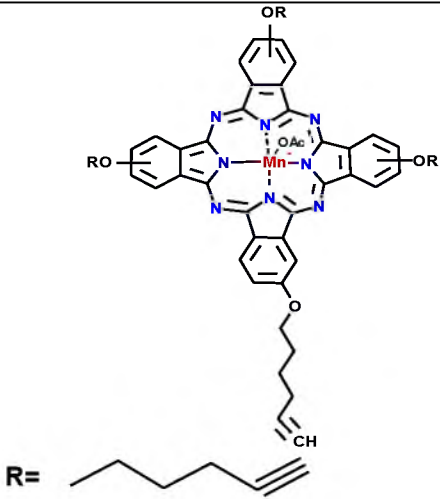
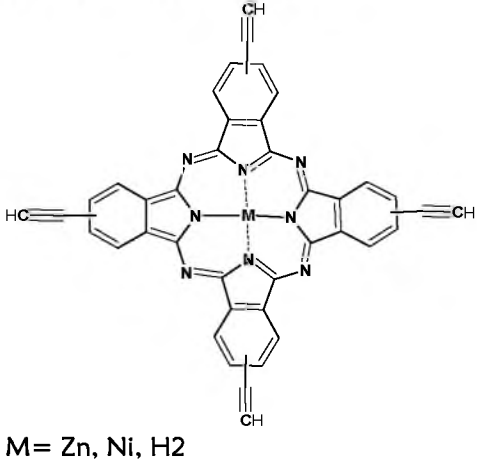
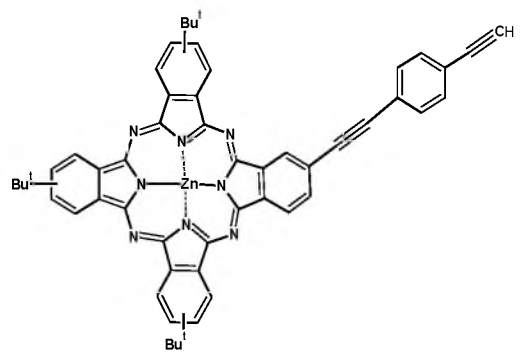
Fig. 1.5: Illustration of fabrication method of a GCE with the GSH-QDs and their conjugates.

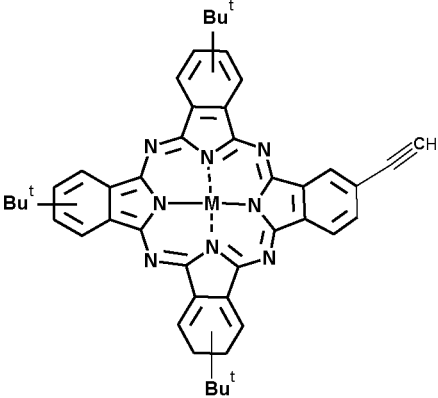
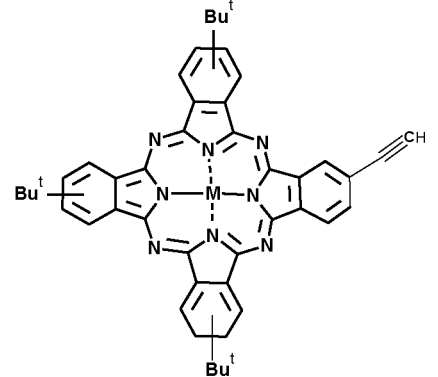
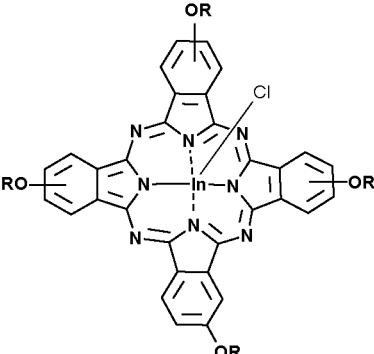
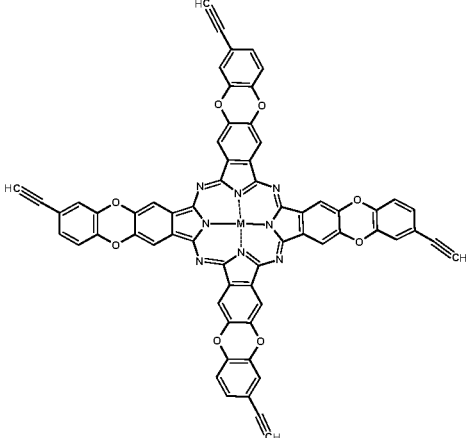
1.3 Terminal-alkyne modified phthalocyanines and their applications

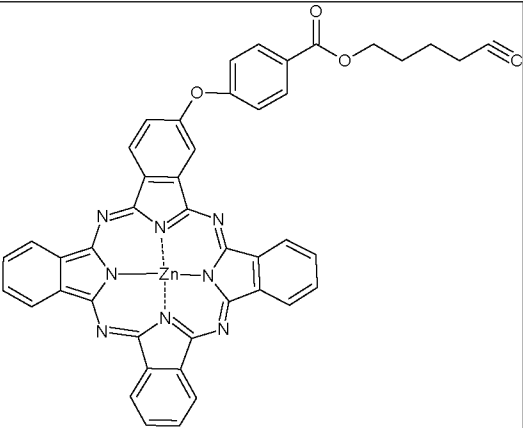
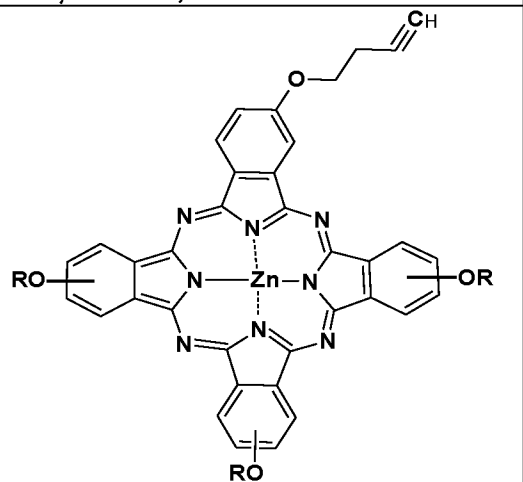
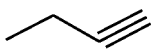
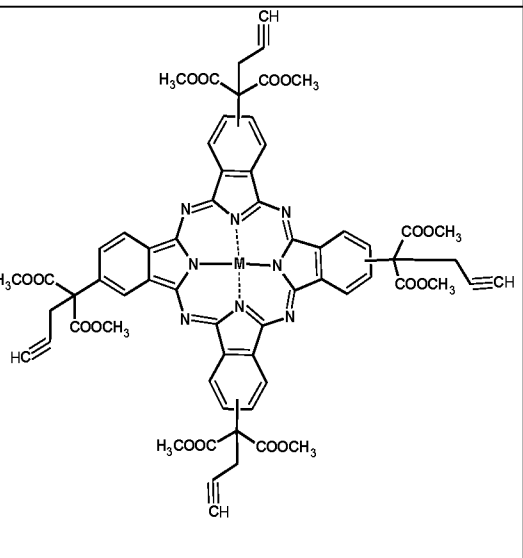
In this work we focus on the central metal which is iron(II) as well as the peripheral substituent which is a six-carbon chain with a terminal alkyne group. There are reported phthalocyanines functionalized with terminal alkyne groups for various applications as shown in Table 1.1 [41-53]. It is clear from this table that a number of MPcs containing

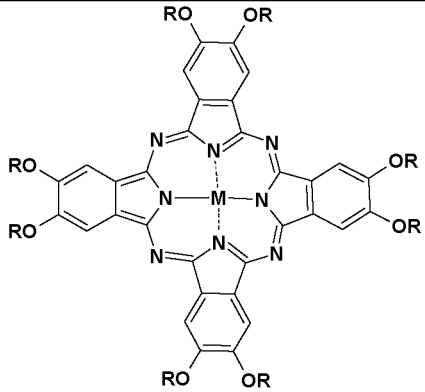
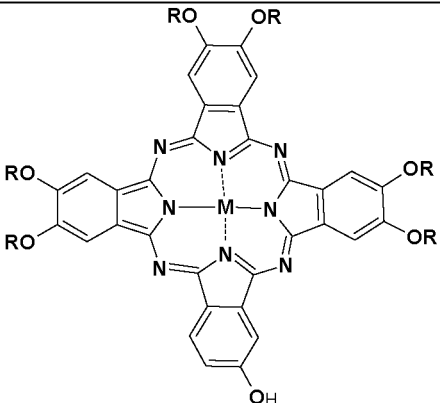
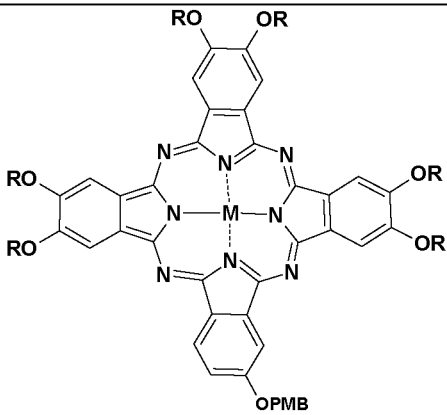
terminal alkyne groups have been synthesized and reported in literature but there are only three examples (last three entries in **Table 1.1**) where the molecules have been used to modify electrodes by click chemistry.

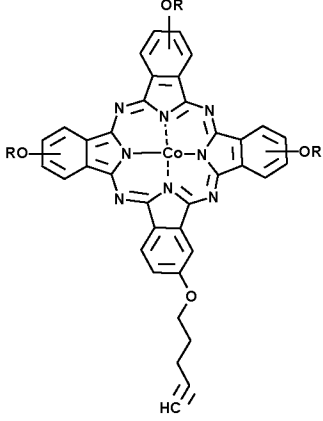
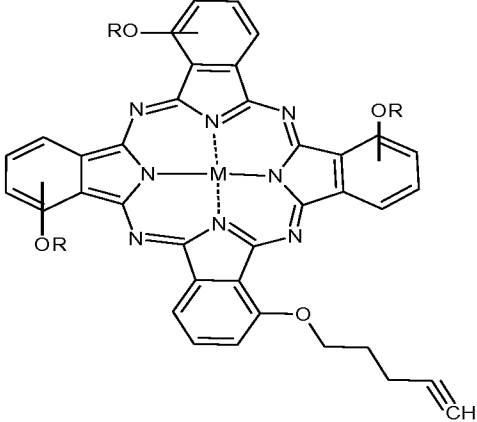
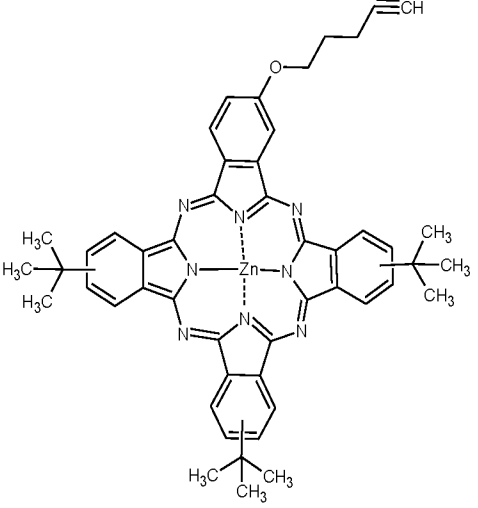
Table 1.1: Terminal alkyne-functionalized phthalocyanines and their applications.

Molecule structure	Application ^a	Reference
 R = <chem>CCCCC#C</chem>	Cyclic voltammetry and spectroelectrochemistry	[41]
 M = Zn, Ni, H₂	Linking phthalocyanines to other molecules	[42]
	Linking Phthalocyanine to other molecules	[42]

 M= Co, Zn	Optical limiting and synthesis of other Phthalocyanine derivatives	[43]
 M= Zn, Ni, Co	Linking to another phthalocyanine	[44]
 R= $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$ / $\text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{CH}$	Non-linear optical and photophysical properties	[45]
 M= H2, Zn, Cu	Synthesis and characterization	[46]

 (Non-peripherally substituted derivative also synthesized)	Determination of photophysical properties	[47]
 R = 	Change of functionality of molecule for comparison with unclicked terminal alkynyl MPc for non-linear optics	[48]
 M = Cu, H2	Further functionalization of molecule by click chemistry	[49]

 $M = H_2, Zn$ $R = H_3C-C_6H_4-O-(CH_2)_4-C\equiv CH$	Precursors for synthesis of asymmetric hexatriazolyl-monohydroxyphthalocyanines via click chemistry reaction	[50]
 $M = H_2, Zn$ $R = H_3C-C_6H_4-O-(CH_2)_4-C\equiv CH$	Precursors for synthesis of asymmetric hexatriazolyl-monohydroxyphthalocyanines via click chemistry reaction	[50]
 $M = H_2, Zn$ $OPMB = -O-(4-methoxybenzyl)$ $R = H_3C-C_6H_4-O-(CH_2)_4-C\equiv CH$	Precursors for synthesis of asymmetric hexatriazolyl-monohydroxyphthalocyanines via click chemistry reaction	[50]

 tetrakis(pent-4-ynoxy)Co(II) phthalocyanine R= <chem>CCCC#C</chem>	Clicked with azidoaniline electropolymerised on GCE for electrocatalysis	[51]
 tetrakis(pent-4-ynoxy)Phthalocyanine. M= Zn(II), Co(II) R= <chem>CCCC#C</chem>	Clicked with azidoaniline electropolymerised on GCE for electrocatalysis	[52]
	Conjugation of mono-substituted ZnPc to polymer via click chemistry. Platinum electrode modified and used in a DCM/TBAP and DMSO/TBAP system	[53]

^aDCM/TBAP = dichloromethane/tetrabutylammonium perchlorate, DMSO/TBAP=

dimethylsulfoxide/ tetrabutylammonium perchlorate, GCE= glassy carbon electrode.

One of the synthesized MPcs reported in literature is clicked with an azide-modified polymer and tested in a dichloromethane/tetrabutylammonium perchlorate system and dimethylsulfoxide/ tetrabutylammonium perchlorate system using a platinum electrode [53]. Other examples involve the electropolymerization of azidoaniline onto a GCE then clicking of the alkynyl MPc with the azide groups [52]. The chain length employed was five carbons with the central metals being cobalt and zinc [52]. Here we take a novel approach by clicking a terminal-alkyne substituted Fe(II)phthalocyanine directly onto phenyl azide groups electrochemically immobilized onto a GCE by electrochemical grafting. As already stated, Fe(II) is also used for the first time as a central metal with respect to terminal-alkyne substituted phthalocyanines that have been reported in literature.

Table 1.2 [39, 54, 55] only shows three examples of the use of non-alkynyl MPcs for electrode modification using click chemistry. The difference lies in the modification method. In all three examples, the FePc is not substituted with terminal alkyne groups but is rather axially ligated via the central metal to ethynyl pyridine clicked on an electrode with phenyl azide groups. The modification process used in this work provides a shorter and simpler route of electrode modification and enhanced stability.

Table 1.2: Click chemistry reaction involving FePcs (not terminal alkyne-substituted) for electrode modification and electrocatalysis.

MPc	Electrode*	Modification route	Ref.
Unsubstituted FePc	SWCNT-GCE for hydrazine detection	Clicked ethynyl pyridine followed by axial ligation with MPc	[39]
FeTCPc	GCE for hydrazine detection	Axial ligation with ethynyl pyridine clicked on grafted electrode	[54]
Unsubstituted FePc	GCE for hydrazine detection	Clicked ethynyl pyridine followed by axial ligation with MPc	[55]

*SWCNT= Single-walled carbonnanotubes, FeTCPc=Iron tetracarboxyphthalocyanine.

1.4 A brief review on QDs

QDs are semiconducting nano-sized particles which have been mainly used for applications such as photophysical studies. Some of the common applications of QDs include *in vivo* imaging [56], molecular diagnostics of cancer [57] and biological labelling [58]. It is only recent reports that have shown that these particles may be useful in electrocatalysis. This is the first time that QDs are linked to MPcs by click chemistry. The work involves reacting GSH-capped CdSe/ZnS QDs with azidoaniline to obtain azide-QDs. These conjugates will further be reacted with a terminal alkyne-substituted Fe(II)phthalocyanine to obtain the final conjugate referred to as clicked FePc-QDs.

1.4.1 Quantum Dots as electrocatalysts

Quantum dots have only recently been used in combination with other electroactive molecules for electrocatalysis. Recent work has shown that combining QDs with other molecules for electrocatalysis can result in favourable electrocatalytic detection of various analytes [59-62]. The mechanism behind the electrocatalysis by QDs has not yet been defined and proves to be difficult to explain although these QDs have been studied by electrochemical techniques. However, the novel combination of QDs with an alkynyl FePc via the click chemistry reaction takes this aspect of QDs research a step further.

1.4.2 Click chemistry involving QDs

QDs have been involved in click chemistry reactions but as already mentioned, they have never been linked to MPcs via click chemistry emphasizing the novelty of the work presented here. **Table 1.3** [63-66] lists QDs functionalized with phenyl-azide groups. As can be observed, not much work has gone into conjugating QDs to other molecules using click chemistry. CdSe/ZnS core-shell QDs were chosen since they have been used in click chemistry reactions before, **Table 1.3**.

Table 1.3: Azide-modified QDs and their involvement in click chemistry.

QDs	Molecule used to achieve azide function	Compound used for click reaction	Application	Ref.
CdSe/ZnS core-shell	NH ₂ -PEG-azide	Transferrin using Cyclooctyne	Biological activity testing	[63]
CdSe/ZnS core-shell	N ₃ -PMAH	PMAH attached to virus	Virus labelling & imaging	[64]
CdSe/ZnS core-shell	N ₃ -PEG ₄ -NHS	DBCO-virions	Virus labelling & imaging	[65]
CdSe/ZnS core-shell	N ₃ -PEG	Acetylene	Linking of molecules via click chemistry	[66]

PMAH= poly(maleic anhydride), PEG= polyethylene glycol, NHS=N-

hydroxysuccinamide, DBCO= dibenzocyclooctynes.

1.4.3 Conjugation of QDs to MPcs

QDs have been linked to phthalocyanines via an amide bond for electrocatalytic applications [67, 68]. It has been shown that combining QDs with phthalocyanines improves the electrocatalytic ability of the latter [67-69]. **Table 1.4** [28, 68, 70] lists the QDs-MPc conjugates that have been reported in literature and none of them involve click chemistry as a conjugation method. The clicked FePc-QDs conjugate that is synthesized in this work is shown in **Fig.1.6**.

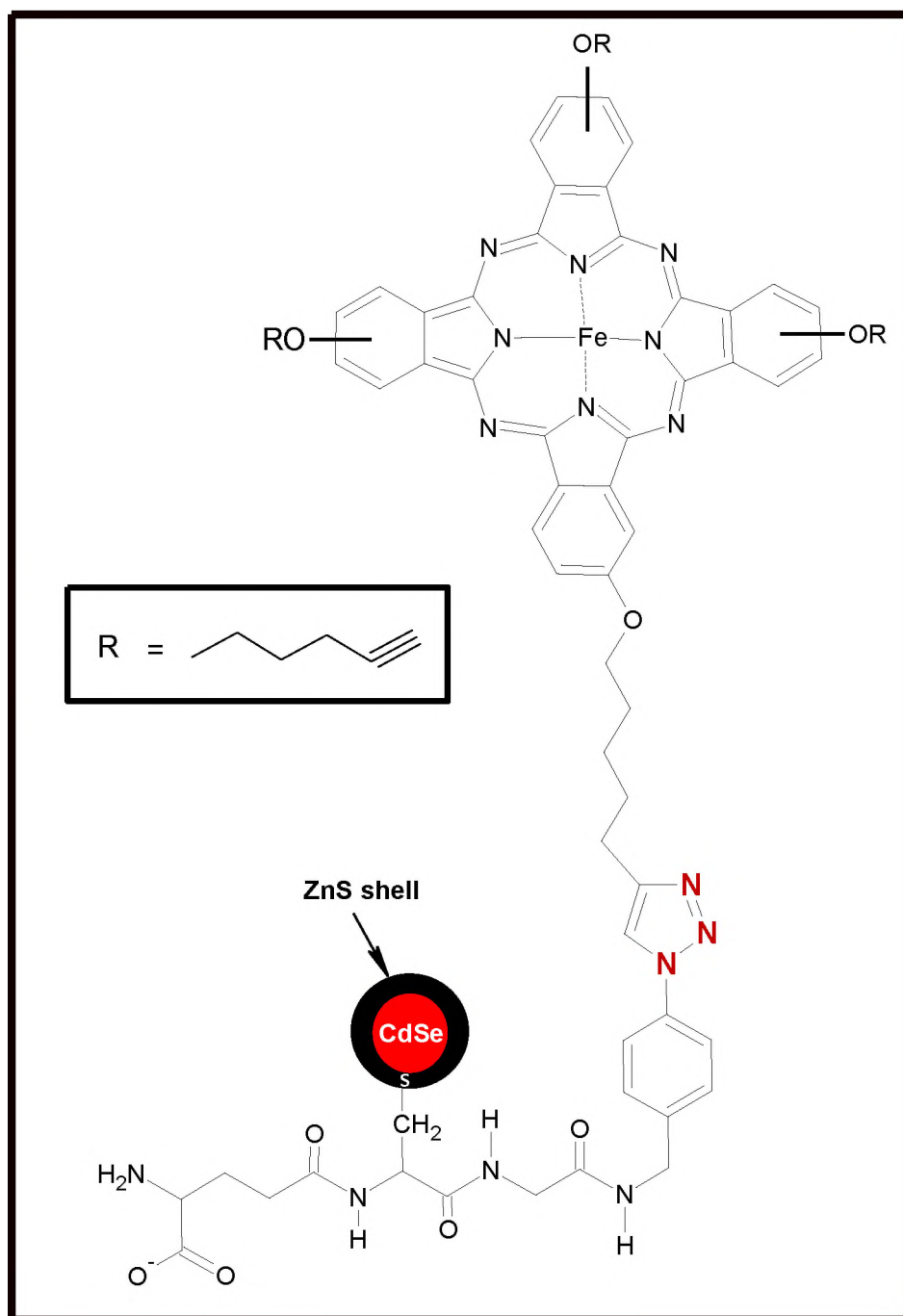


Fig.1.6: Illustration of the QDs-MPc conjugate used in this work.

Table 1.4: MPc-QDs conjugates for electrode modification and electrocatalysis.

Electrode	QD/conjugate	Conjugation method	Ref.
AuE	CdTe capped with thioglycolic acid-peripherally substituted nickel tetraamino phthalocyanine (NiTAPc)	Linked via amide bond	[68]
GCE	Graphene/CdSe Quantum Dots-Co Phthalocyanine Nanocomposite	Mixing (no conjugation)	[28]
GCE	nickel octadecylphthalocyanine (NiPc(C ₁₀ H ₂₁) ₈) NiPc(C ₁₀ H ₂₁) ₈ -SWCNT-QDs	Adsorption onto CNTs	[70]

CNTs= Carbon nanotubes.

1.5 Analytes of interest relevant in this work

The test analytes used for the application of the new modified electrodes reported in this work are hydrazine (**Fig.1.7A**) and paraquat (**Fig.1.7B**). Hydrazine, also known as diazine or tetrahydridodinitrogen is a compound which has been used in industry for many years [71]. It is a highly toxic agent and therefore monitoring its concentration is necessary, hence the need to develop reusable, easy to use, stable sensors. Paraquat on the other hand, formally known as 1,1-dimethyl-4,4-bipyridinium dichloride is a toxic pesticide that is highly resistant to biodegradation. Thus it is imperative to improve the sensing ability of electrocatalysts for these analytes which will be done in this work and the results will be compared to other electrocatalysts designed for the same purpose. Electrocatalysis is mediated by the redox process in MPcs.

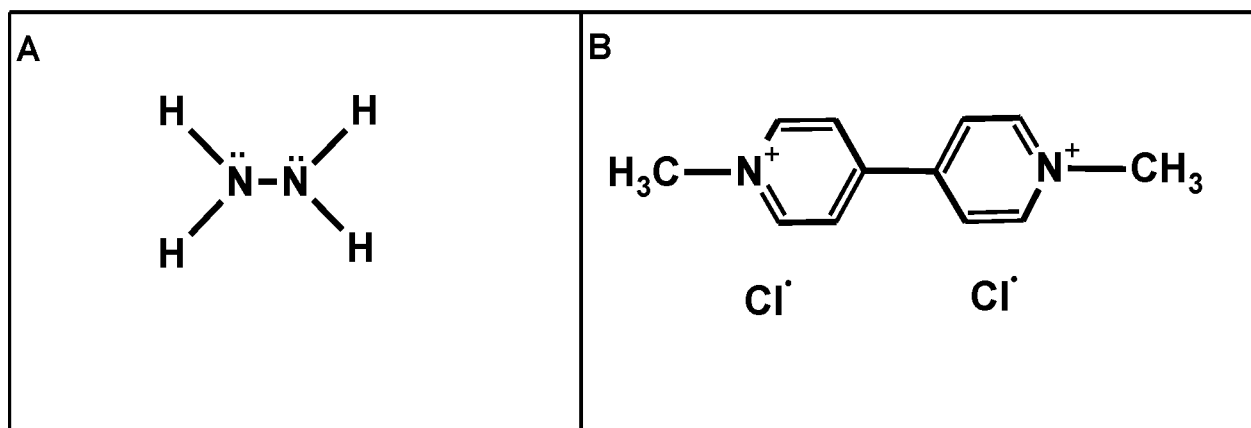
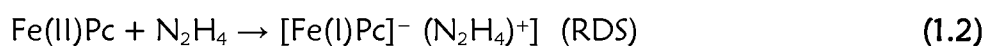
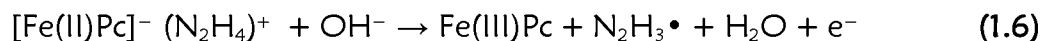
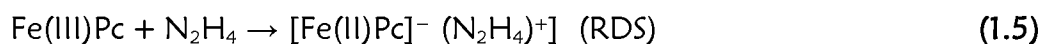


Fig. 1.7: Structure of (A) Hydrazine and (B) paraquat.

1.5.1 Mechanism for the electrooxidation of hydrazine on MPcs

The Fe(III)/Fe(II) or the Fe(II)/Fe(I) ion pair may be involved in this electrocatalytic process. The electrocatalytic reaction that takes place for the oxidation of hydrazine has been proposed by Zagal [72]. Both Fe(III)/Fe(II) [73] and the Fe(II)/Fe(I) couples [74-77] may be involved and the mechanism has been shown by Eqn.1.1-1.6. In both cases, the active electrocatalyst is regenerated to reproduce its original state by reduction of the central metal.





The first step is the oxidation of the central metal of the phthalocyanine (Eqn. 1.1, 1.4) followed by the coordination of hydrazine (Eqn.1.2 and Eqn.1.5) and its oxidation (Eqn.1.3 and Eqn.1.6).

1.5.2 Electroreduction of paraquat

Due to the structure of paraquat, the electrocatalytic reaction between the catalyst and analyte is a reduction process. Reduction of paraquat occurs through two redox pairs which are a result of the simultaneous reduction of the two positively charged nitrogens the molecule possesses. The basic reaction that takes place is shown by Eqn.1.7-1.8 [78]:



1.6 Summary of aims of reported work

In summary, this work focuses on modifying glassy carbon electrodes for the electrocatalytic detection of paraquat and hydrazine. **Table 1.5** lists the electrodes and the analytes for each electrode used in this work. In addition, the end goal is to produce electrocatalysts which will improve detection limits and show high stability as well as electrocatalysts that will require low applied potentials.

Table 1.5: Summary of fabricated electrodes used in this work and the test analytes of interest tested with each electrode.

Electrode	Purpose of electrode
Azide-GCE (electrografted)	Hydrazine electrooxidation
Azide-GCE clicked with FePc	Hydrazine electrooxidation
QDs-FePc mix-GCE	Paraquat electroreduction
FePc alone-GCE	Paraquat electroreduction
Azide-QDs clicked with FePc-GCE	Paraquat electroreduction

Every molecule synthesized in this work is characterized using various techniques that will be described in detail in the second chapter. In addition, with each modified electrode used, the surface is characterized using various techniques.

Part A: Electrografting and clicking of alkynyl FePc on electrode

- Synthesize and characterize novel tetrakis(5-hexynoxy)Fe(II) phthalocyanine.
- Synthesize and characterize diazonium salt for the electrografting of GCE.
- Modify GCE surface by electroreduction to immobilize phenyl azide groups.
- Perform click reaction between azide groups on GCE and synthesized alkynyl FePc.
- Characterize electrode surface at each modification step.
- Electrocatalyse hydrazine as a test analyte.

Part B: Adsorption of clicked-QDs on electrode

Synthesize and characterize glutathione capped CdSe/ZnS core-shell QDs.

- Modify CdSe/ZnS QDs with azide groups using azidoaniline.
- Use the synthesized alkynyl Fe(II)Pc to produce a conjugate with QDs via click chemistry.
- Modify GCE using all molecules involving QDs and test electrocatalytic ability.
- Characterize the electrode surfaces.
- Electrocatalyse paraquat as a test analyte.

Chapter 2:

Materials and Experimental

2. Materials and experimental

This chapter briefly outlines the materials used as well as the syntheses carried out. It also briefly outlines the equipment used for characterization purposes.

2.1 Materials

Iron(II) chloride, triethylamine, bromotris(triphenylphosphine) copper(I) ($\text{Cu}(\text{PPh}_3)_3\text{Br}$) and 1-pentanol, 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), N-hydroxyl succinimide (NHS), sodium ascorbate and 4-azidoaniline hydrochloride were purchased from Sigma-Aldrich. Acetonitrile (ACN) and dimethylformamide (DMF) were purchased from Merck. Tetrabutylammonium tetrafluoroborate (TBABF_4) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Fluka. $\text{K}_3[\text{Fe}(\text{CN})_6]$ and copper(II) sulphate (CuSO_4) were purchased from Saarchem. Sodium hydroxide was purchased from Minema. 4-Azidobenzenediazonium tetrafluoroborate was synthesized as reported in literature [79]. The synthesis of 4-(hex-5-yn-oxy) phthalonitrile (1) has also been reported [80]. Glutathione (GSH) capped CdSe/ZnS QDs were synthesized as reported before [81]. For the electrocatalytic studies, the analytes of interest were both tested in a deaerated 0.1 M NaOH solution. For electrophoretic studies and dynamic light scattering analyses, an initial concentration of 150 mM of phosphate buffer solution using appropriate ratios of Na_2HPO_4 and NaH_2PO_4 was prepared and thereafter diluted as required. All other reagents were of analytical grade and used as received.

2.2 Equipment

Ground state electronic absorption spectrum was obtained at room temperature using a Shimadzu UV-2550 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter.

Infrared spectra were obtained using a Bruker alpha model FT-IR spectrometer with platinum attenuated total reflectance (ATR).

Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer.

Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using a m/z range of 400–1200 amu. The spectrum was obtained using alpha-cyano-4-hydroxycinnamic acid as the MALDI matrix and a 354 nm nitrogen laser.

Transmission electron microscope (TEM) micrographs of the QDs were obtained using a Zeiss Libra 120 TEM operating at 80 kV.

X-ray powder diffraction patterns were recorded on a Bruker D8 Discover equipped with a LynxEye detector, using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Data were collected in the 2θ range of 5° - 60° , scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a zero background silicon wafer slide. The X-ray diffraction data were treated using EVA (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern.

Cyclic and differential pulse voltammetry experiments were run using the Autolab PGStat electrochemical workstation. A three-electrode system comprising of a pseudo

Ag/AgCl reference electrode, a platinum (Pt) counter electrode and a glassy carbon electrode (GCE) as the working electrode was employed.

Scanning electrochemical microscopy (SECM) experiments were conducted using Uniscan equipment, model 370. Approach curve analysis and constant height imaging was employed using the 15 μm Pt ultramicroelectrode (UME) together with a Pt counter electrode and Ag/AgCl wire as the pseudo-reference electrode. For the approach curve analyses, the UME was moved along the z-axis towards the surface of the glassy carbon plate while maintaining positions along the X-Y plane. With regards to surface imaging, the microelectrode tip was maintained at a constant height (z-axis) and the desired area scanned along the X-Y plane. Changes were monitored in the steady state current of $\text{K}_3[\text{Fe}(\text{CN})_6]$ oxidation at 0.1 V vs. Ag/AgCl as the tip travels.

X-ray photoelectron spectroscopy (XPS) was done using a Kratos Axis Ultra DLD, with the Al (monochromatic) anode, equipped with a charge neutraliser. For wide XPS scans, the following parameters were used: emission 10 mA, anode (HT): 15 kV, operating pressure below 5×10^{-9} Torr, hybrid lens, and resolution to acquire scans was at 160 eV pass energy in slot mode. The centre used for the scans was at 520 eV and the width at 1205 eV, with steps at 1 eV and dwell time at 100 ms. For the high resolution scans, the resolution was changed to 40 eV pass energy in slot mode. Centre was at 402 eV and width at 12 eV for N(1s), with step size at 0.05 eV and dwell time at 500 ms.

Glassy carbon plate electrodes (1 cm x 1 cm and 2 mm thick) obtained from Goodfellow, UK, were used for the SECM and XPS analyses.

The size of the CdSe@ZnS QDs as well as the conjugates were determined using dynamic light scattering measurements with a Nano ZS Zetasizer instrument (Malvern Instruments, South-borough, MA), which is based on the intensity fluctuations of back-

scattered (178°) laser light, caused by the Brownian motion of the nanostructures reported in this work.

Electrophoretic separations were performed with a 7100 model Capillary Electrophoresis System (Agilent Technologies, Waldbronn, Germany). Fused-silica capillaries (50 μm internal diameter $\times$ 45 cm with a detection length of 21 cm for fluorescence analysis and 36.5 cm for absorbance analysis) from Polymicro Technologies (Phoenix, AZ, USA) were used after activation by successive flushes (925 mbar) with 1.0 M NaOH (15 min), 0.1 M NaOH (15 min) and H_2O (5 min), respectively. Injections were performed hydrodynamically by applying a pressure of 20 mbar at the capillary inlet for 10 s (approx. 10 nL) unless otherwise specified. Successive injection zones were performed in the following order: neutral marker (DMF), particle sample and electrophoretic buffer. The applied voltage was 14 kV, with positive polarity at the capillary inlet for bare fused-silica capillaries. The temperature of the capillary cartridge was set at a temperature of 25 °C. The detection wavelength was 200 nm for absorbance and >520 nm for fluorescence (excitation source 480 nm). GSH-QDs, azide-QDs and azide-QDs clicked with FePc were separated in bare fused silica capillaries after a preconditioning sequence by fluxing with 0,1 M NaOH for 2 minutes, water for 2 minutes, and finally with the background electrolyte for 3 minutes (925 mbar). The electrophoretic mobility of the GSH-QDs, azide-QDs and the clicked FePc-QDs was obtained from the migration time measured at the centre area distribution of the peaks. The mathematical model to convert the electrophoretic mobility obtained by both CE and LDE into zeta potential is Ohshima's equation [82] with modification proposed by Pyell and co-workers [83] referred to as the Ohshima–Pyell equation.

2.3 Synthesis

2.3.1 Synthesis of tetrakis(5-hexynoxy)Fe(II)phthalocyanine, Scheme 3.1

The synthesis of tetrakis(5-hexyn-oxy)Fe(II)phthalocyanine (**2**) was carried out using the procedure for tetrakis(5-hexyn-oxy)MnPc [80] by dissolving 4-(hex-5-yn-oxy)phthalonitrile (**1**) (0.1 g, 0.450 mmol) and FeCl₂ (0.026 g, 0.149 mmol) in 1-pentanol (3 mL). DBU (35 μ L) was added and the mixture stirred for 12 h under argon atmosphere while refluxing at 140 °C. The green mixture was left to cool and precipitated out using a methanol-water mixture and collected by centrifugation. The collected precipitate was washed several times with 1 M HCl, methanol and finally millipore water and collected again by centrifugation. UV-Vis [DMF] λ_{max} /nm (log ϵ): 706; 643; 582. IR: KBr $\nu_{\text{cm}^{-1}}$: 747, 832, 989, 1081(Pc ring), 1127, 1239, 1281, 1387 (C-O-C), 2192 (C $\equiv$ C), 3307 (C-H, alkyne). Anal. calcd. for C₅₆H₄₈FeN₈O₄.4H₂O: C 65.62, H 5.51, N 10.93 %. Found: C 65.09, H 4.85, N 10.32%. MALDI-TOF-MS (m/z): amu found= 952.56 amu; calcd. [M]⁺ = 952.88 amu.

2.3.2 Functionalization of the CdSe/ZnS QDs with azide, Scheme 3.2

The conjugation reaction carried out was adapted from a method in literature [84]. The covalent linkage was carried out as follows: GSH CdSe/ZnS QDs (40 mg) were dissolved in 2 mL of water. Thereafter EDC (0.019 g, 0.1 mmol) and NHS (0.012 g, 0.1 mmol) were introduced into the solution in order to activate the carboxyl functional moiety of the GSH capping the QDs. The reaction was left stirring at room temperature for 2 h after which 2 mL solution of 20 mg (0.117 mmol) of 4-azidoaniline hydrochloride were added. The solution was left stirring for 24 h thereby leading to the formation of the carbonamide linkage between the GSH QDs and 4-azidoaniline

hydrochloride. The QDs were precipitated out of solution with ethanol and were successively purified with methanol. The QDs are represented as azide-QDs.

2.3.3 Functionalization of the azide-QDs with FePc by click chemistry, Scheme 3.3

Alkynyl FePc (9.50 mg, 1.00 mmol), azide QDs (130.0 mg), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 mg, 5.00 mmol,) and sodium ascorbate (79.0 mg, 40.0 mmol) were dissolved in 10 mL of dimethylformamide (DMF). The use of CuSO_4 and sodium ascorbate was due to their availability as opposed to the $\text{Cu}(\text{PPh}_3)_3\text{Br}$ and trimethylamine used for the click reaction of the alkynyl FePc onto the electrode as discussed below. The mixture was stirred at room temperature for 48 h under Ar. The reaction mixture was then poured into 100 mL of cold water. The precipitate was filtered off and washed with water, until the filtrate was neutral. The crude residue was crystallized from methanol to give the desired product which was the clicked FePc-QDs. IR ATR $\nu_{\text{max}}/\text{cm}^{-1}$: 1464, 1621 (triazole N_3); 3201 ($\text{C}\equiv\text{CH}$); 2167 ($\text{C}\equiv\text{C}$), 2926(NH_2); 1607 (carbonamide).

2.4 Electrode modification

Prior to any modifications made to the GCE surface, the GCE was cleaned by polishing on a Beuhler 1200 grit Microcut® Disc using 3 μm and then 0.25 μm diamond paste (MetaDi® supreme polycrystalline diamond suspension, Beuhler) followed by polishing on a Beuhler felt pad using aluminium oxide powder (<10 μm). In addition, all solutions were purged with argon gas for 20 minutes to eliminate the dissolved oxygen before each cyclic voltammetry analysis, and the argon atmosphere was maintained throughout the period of analysis to ensure that no disturbances occurred during the analyses due to oxygen.

2.4.1 Electrode fabrication by electrografting and click chemistry

2.4.1.1 Electrografting, Scheme 1.1

The bare glassy carbon electrode was grafted by reductive electrodeposition by scanning three cycles from + 0.50 V to -1.0 V at 50 mV/s in a 1 mM solution containing 4-azidobenzenediazonium tetrafluoroborate (1 mM in 0.1 M TBABF₄ in acetonitrile). The blocking capability of the salt was then tested in a K₃[Fe(CN)₆] solution (2 mM K₃[Fe(CN)₆] in 0.1 M KCl solution). The grafted GCE was then rinsed thoroughly with milli-Q water.

2.4.1.2 Click Chemistry, Scheme 1.3

Modification of a glassy carbon electrode by click chemistry was carried out by immersing the grafted GCE in DMF containing complex **2** (1 mM), triethylamine (10 mM) and Cu(PPh₃)₃Br (2 mM) for 18 h at room temperature. The use of these reagents for the click reaction was merely a case of their availability at the time. Thereafter, the electrode was thoroughly rinsed using milli-Q water before further use.

2.4.2 Electrode modification with QDs-based electrocatalysts by adsorption

The electrode was modified by the drop dry method whereby a 1 μ L drop of sample in DMF was placed on the electrode followed by drying. The electrode was rinsed thoroughly using milli-Q water before further use. The modifiers employed are alkynyl FePc alone, GSH-QDs alone, premixed FePc-QDs, Azide-QDs and clicked FePc-QDs.

Publications:

The work presented in this thesis has been published or submitted to the following peer reviewed journals:

1. Siphesihle Robin Nxele, Philani Mashazi, Tebello Nyokong, Electrode Modification Using Alkynyl Substituted Fe(II) Phthalocyanine via Electrografting and Click Chemistry for Electrocatalysis, *Electroanalysis* 2015, 27, 2468-2478.

2. Siphesihle Robin Nxele, Tebello Nyokong, The Conjugation of Azide-functionalized CdSe/ZnS Quantum Dots with Tetrakis(5-hexyn-oxy)Fe(II) phthalocyanine via Click Chemistry for Electrocatalysis, *Electrochimica Acta*, 2015, Submitted and under peer review.

Chapter 3:

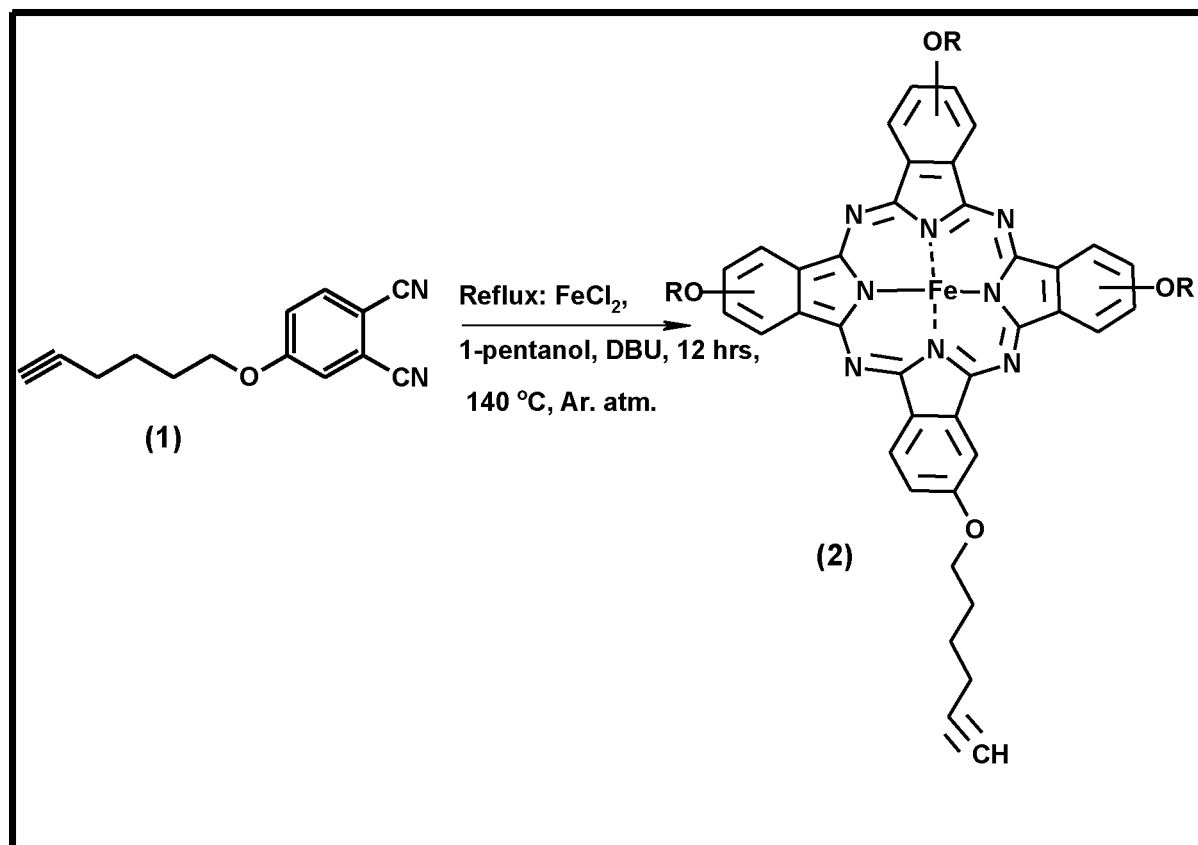
Characterization of alkynyl

Fe(II)phthalocyanine and its conjugates

3. Characterization of alkynyl FePc and its conjugates

Here, the characterization of the synthesized molecules and conjugates are presented.

3.1 Characterization of tetrakis(5-hexyn-oxy)Fe(II) phthalocyanine (2).



Scheme 3.1: Synthetic pathway of tetrakis(5-hexyn-oxy)Fe(II)phthalocyanine.

The synthetic route of the tetrasubstituted alkynyl FePc used in this work is illustrated in **Scheme 3.1**. Complex **2** (**Scheme 3.1**) was prepared by the template reaction of 4-hex-5-ynoxyphthalonitrile (**1**) precursor with Fe (II) chloride as the source of the central metal in the presence of DBU. Characterization was carried out using spectroscopic methods and elemental analysis. The presence of $\text{C}\equiv\text{CH}$ at 3307 cm^{-1} and $\text{C}\equiv\text{C}$ at 2192 cm^{-1} was confirmed by FTIR analysis. The mass spectrum and elemental analysis of the

predicted structure confirm the purity of the synthesized complex. In addition, elemental analysis results are in agreement with the reports that phthalocyanines are often isolated as solvates [85]. A mixture of four possible structural isomers is expected for complex 2. The four probable isomers can be designated by their molecular symmetry as C_{4h} , C_{2v} , C_s and D_{2h} , and they are known to occur in an expected statistical mixture of 12.5% C_{4h} , 25% C_{2v} , 50% C_s and 12.5% D_{2h} for peripherally substituted complexes [86]. The isomers are known to be difficult to separate therefore no attempt was made to separate them in this work.

The UV-Vis spectrum of complex 2 in DMF is shown in **Fig. 3.1**. The UV-visible spectral analysis of the FePc molecule and its derivatives, has been a subject of extensive research due to the wide range of species that may form in solution. The reaction of perchlorinated Fe(II)phthalocyanine dissolved in DMF, resulting in oxidation and formation of a μ -oxo species, $(Pc-2)Fe^{III}-O-Fe^{III}-(Pc-2)$, has been reported [87]. The μ -oxo species has also been proposed for the iron tetrasulfonated phthalocyanine. Therefore, according to the results obtained for the FePc synthesized in this work, the spectrum shown in **Fig. 3.1** is typical [87] of FePc molecules containing μ -oxo species (near 590 nm), with some monomeric species (near 630 nm) and a shoulder near 700 nm. In an attempt to reduce the μ -oxo species and enhance the peak due to the monomeric species, reduction with $NaBH_4$, as well as bubbling of argon through the solution was carried out but with no success thus no significant changes in the spectrum were observed.

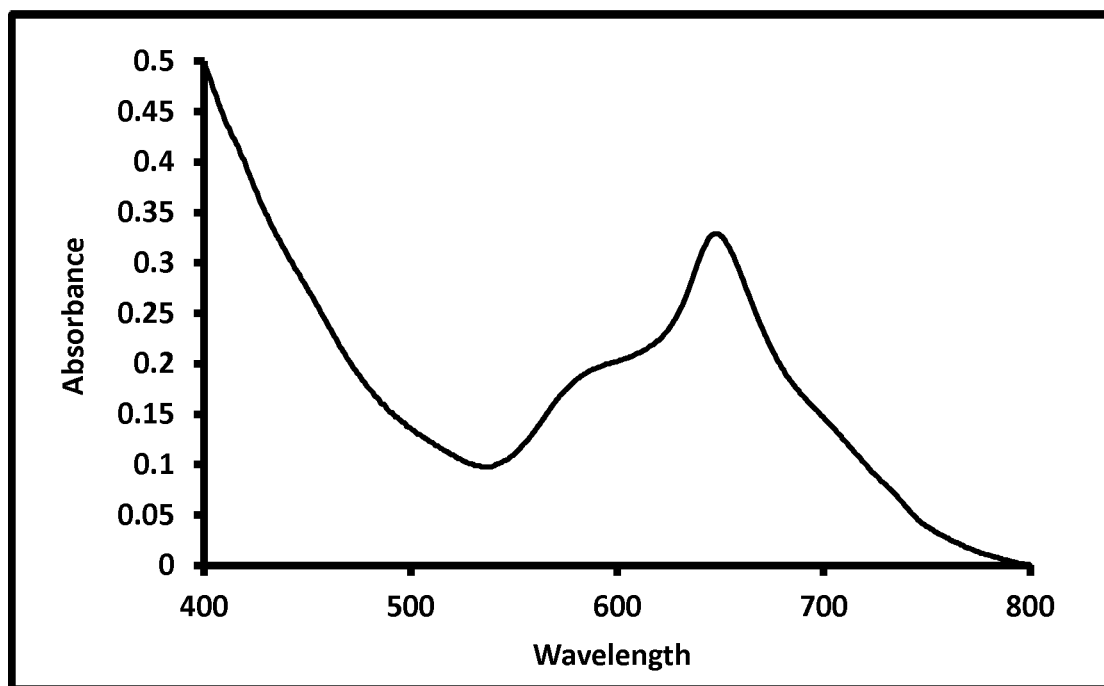
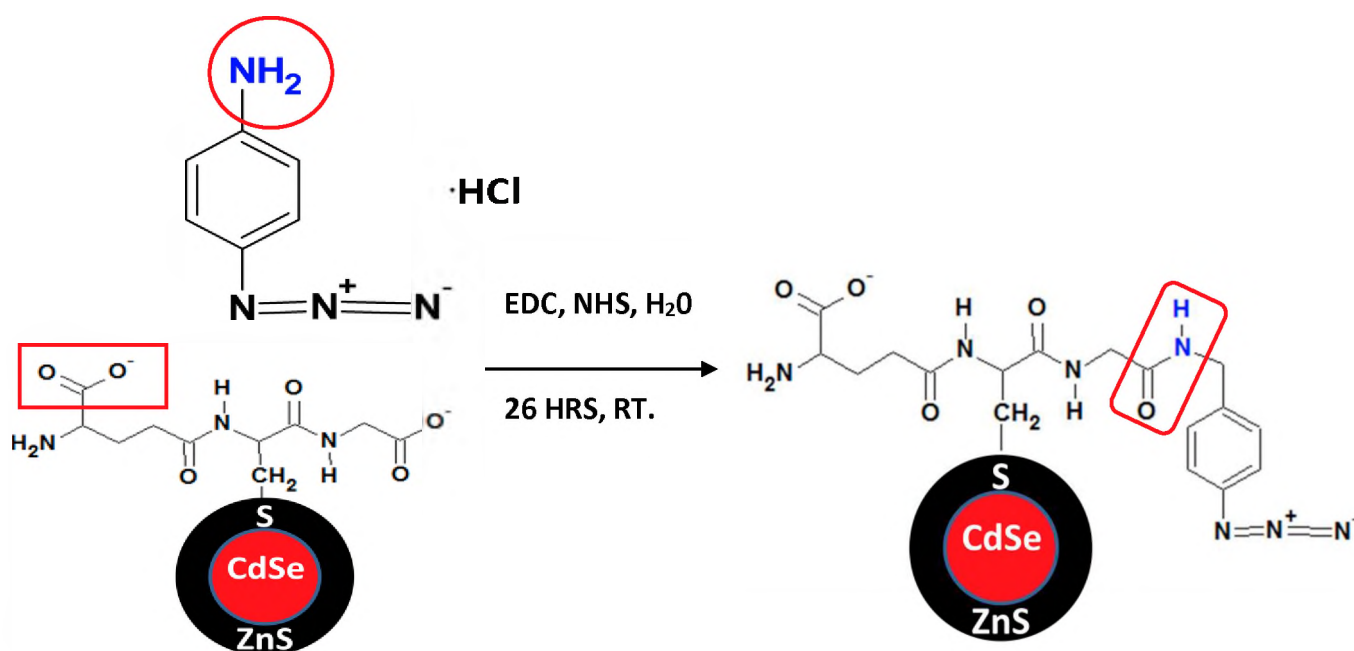


Fig. 3.1: UV-Vis spectra of complex 2 in DMF.

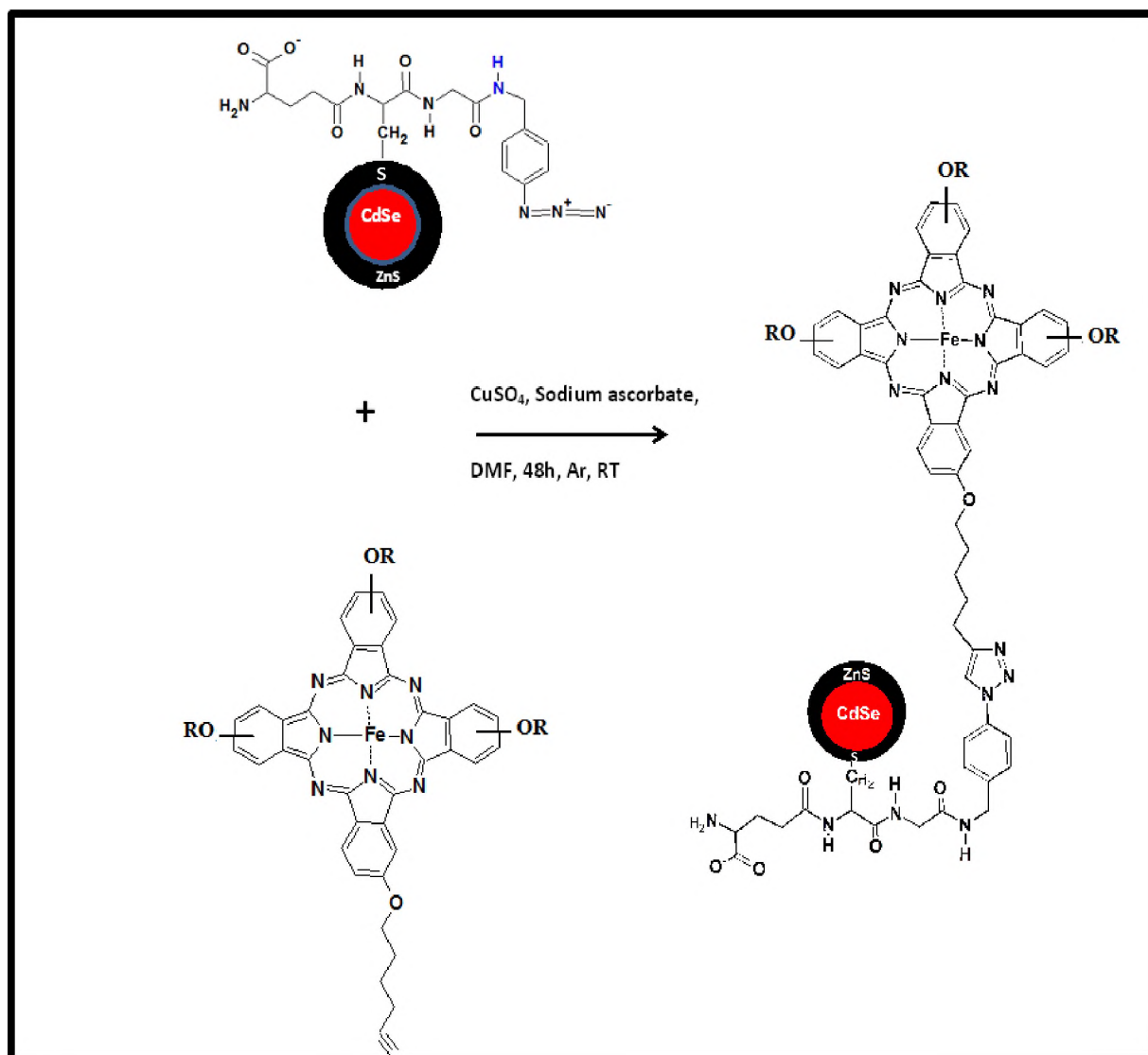
3.2 Characterization of CdSe/ZnS QDs and their conjugates

In this section, the characterization of the CdSe/ZnS QDs and their conjugates is presented. For the functionalization of the GSH-QDs with phenyl azide groups, EDC and NHS are used in combination to activate the carboxyl moieties of the GSH forming an active ester intermediate, **Scheme 3.2**. Using both the EDC and NHS is said to improve the speed and efficiency of the reaction [88]. It is important to note that in order for the click reaction to be successful, the phenyl azide group needs to be present on the QDs to selectively react with the terminal alkyne groups of the FePc. **Scheme 3.3** shows the route for the click reaction between the alkynyl FePc and the azide-functionalized CdSe/ZnS QDs. The size of the phthalocyanine molecule is approximately of 1 nm while the size of the quantum dots is larger as will be observed from the results obtained from other characterization techniques used. Hence, it is likely that more than

one phthalocyanine molecule can be bonded to the QDs considering the size of the phthalocyanine relative to the QDs. The reverse where more than one QD binds to a phthalocyanine is unlikely due to size considerations. The number of phthalocyanine molecules bonded to the QDs was estimated to be 60:1 (Pc:QDs) following literature methods, but using absorption instead of fluorescence [89].



Scheme 3.2: Schematic representation of the conjugation reaction between the GSH-capped CdSe/ZnS QDs and 4-azidoaniline hydrochloride to produce azide-QDs.



Scheme 3.3: Click chemistry between alkyne FePc and azide-QDs.

3.2.1 UV/vis and Emission Spectra

Fig. 3.2 illustrates the (i) absorption and (ii) emission spectra of the synthesized GSH-QDs which absorb at 596 nm and emit at 605 nm. The spectra show the typical [90, 91] broad absorption spectrum and a narrow emission spectrum of QDs.

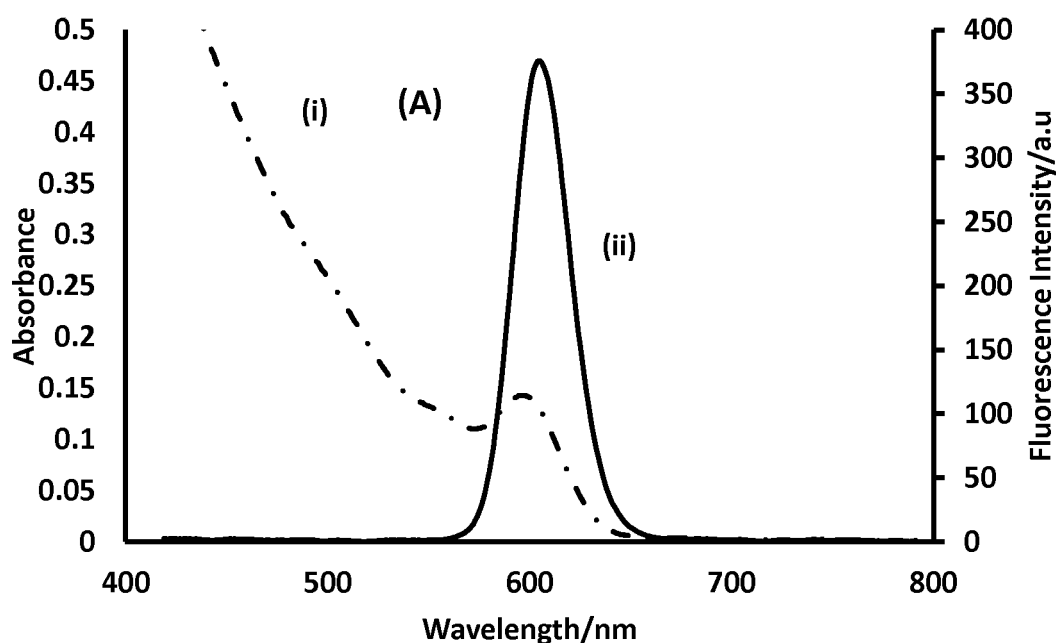


Fig. 3.2: UV/vis (i) and emission (ii) spectra of GSH-CdSe/ZnS QDs in chloroform.

As stated and shown above, the spectrum for the alkynyl FePc is broad (Fig. 3.1) and on linking this alkynyl FePc to QDs via click chemistry, there is a clear split in the Q band, as observed in Fig. 3.3. A split Q band and a shifting of one of the Q band components to longer wavelengths is typical of the oxidation of Fe(II)Pc to Fe(III)Pc derivatives [92]. Fig. 3.3 suggests the presence of both Fe(II)Pc and Fe(III)Pc species.

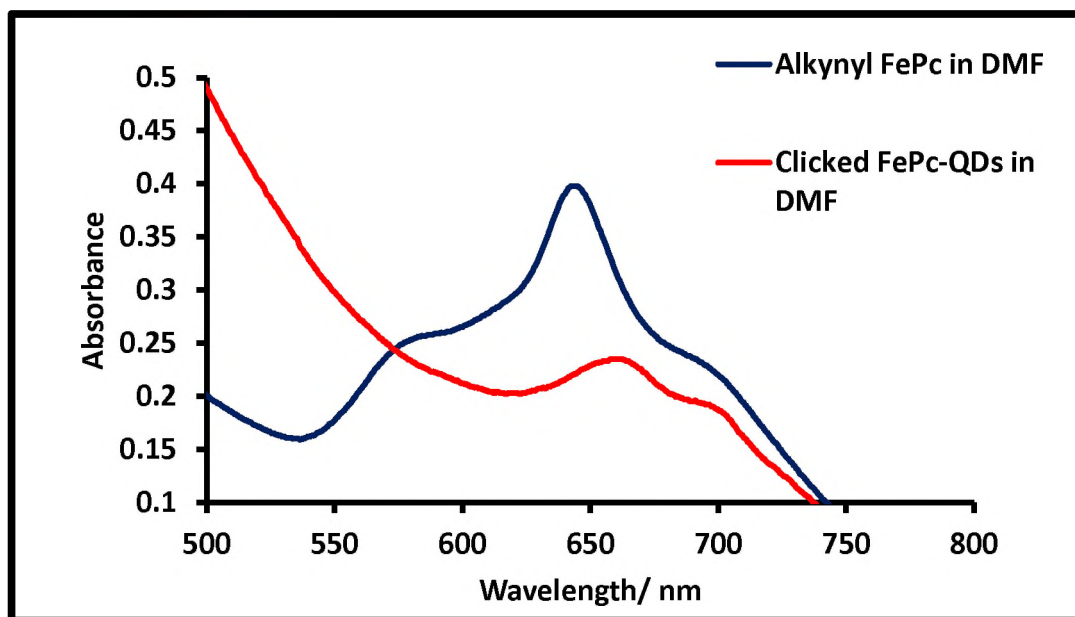


Fig. 3.3: UV/vis spectra of alkynyl FePc alone and clicked FePc-QDs, both in DMF.

3.2.2 X-ray Diffraction: GSH-QDs

XRD was also used to characterize the GSH-QDs in order to confirm the success of the synthesis and to determine the size of the GSH-capped CdSe/ZnS QDs. The diffractogram obtained is shown in Fig. 3.4. The three characteristic peaks of these nanostructures were observed as is typical of QDs [84]. The peaks were observed at 2θ values of 26.3, 43.7 and 51.3 which have been reported to be in accordance with a zinc blend crystal and cubic structure at 110, 220 and 311 respectively [93]. The slight deviations of the 2θ values obtained from those reported in literature are likely due to size differences. The sizes of the QDs were also estimated using the Scherrer equation Eqn.(3.1) [94]:

$$d \text{ (\AA)} = \frac{k\lambda}{\beta \cos \theta} \quad (3.1)$$

where λ is the wavelength of the X-ray source (1.5405 Å), k is an empirical constant equal to 0.9, β is the full width at half maximum of the diffraction peak and θ is the angular position. The size of the CdSe/ZnS was determined to be 5.8 nm which does not vary too much with the average size determined from TEM below. Although it has not been done in this work, conjugating MPcs to QDs has been shown to result in XRD peak shifts with a very broad peak attributed to the phthalocyanine molecule [90] and in another case, the peak due to the phthalocyanine overlaps with the peak due to the QDs at 2θ values around 25° (110) [93]. Therefore the diffractogram for the clicked FePc-QDs is likely to not differ much from the diffractogram of the unconjugated QDs.

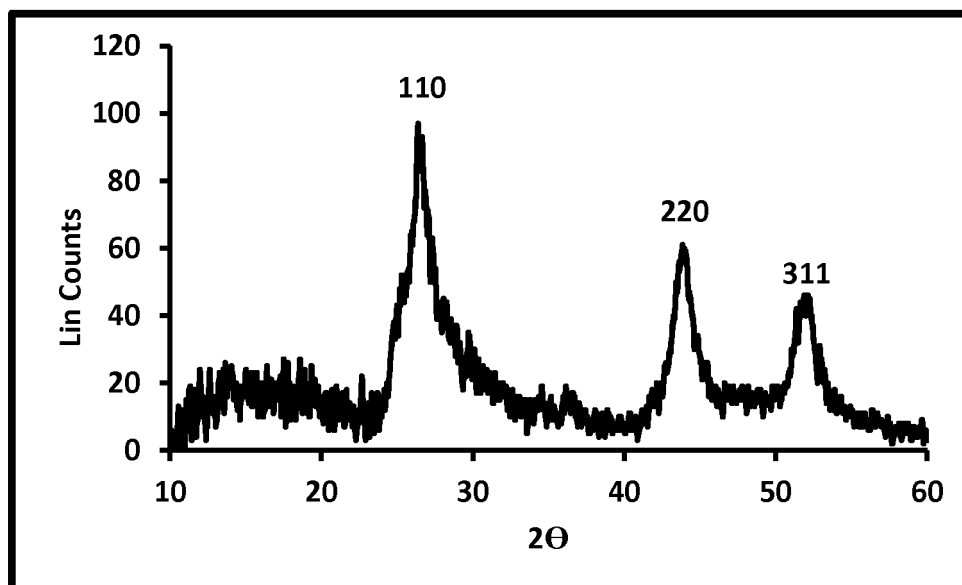
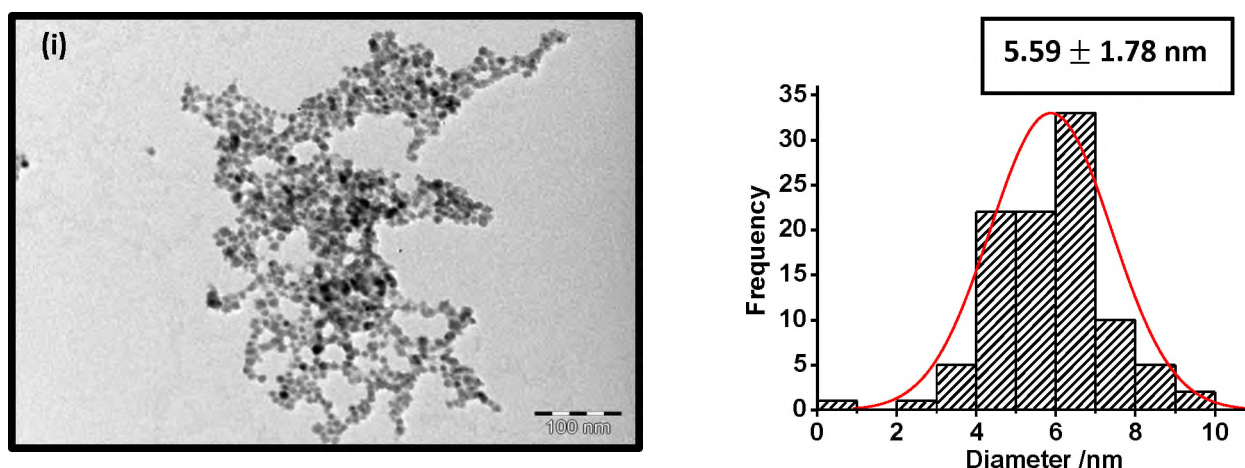


Fig. 3.4: XRD patterns of GSH-CdSe/ZnS QDs.

3.2.3 Transmission Electron Microscopy (TEM)

Fig. 3.5 (i)-(ii) shows the TEM images and size distribution of the GSH-CdSe/ZnS QDs and the azide-functionalized QDs respectively. It is evident that some aggregation has occurred in (i) but some degree of monodispersity is observed. The average size was determined as 5.59 nm with a standard deviation of 1.78 nm from Fig. 3.5 (i). The histogram beside Fig. 3.5 (i) shows that the majority of these nanocrystals fall in the size range of 4-7 nm. Upon functionalization with phenyl azide groups, the particle distribution as well as particle size slightly increases by approximately 0.55 nm as shown by Fig. 3.5 (ii) and the corresponding histogram. Fig. 3.5 (iii) shows an image of the clicked FePc-QDs which shows a high degree of aggregation making it difficult to estimate the particle size after conjugation. Phthalocyanines in general are known to aggregate [92], likely due to π - π stacking of the phthalocyanine rings via the interaction of the clicked FePc-QDs on neighboring azide-QDs.



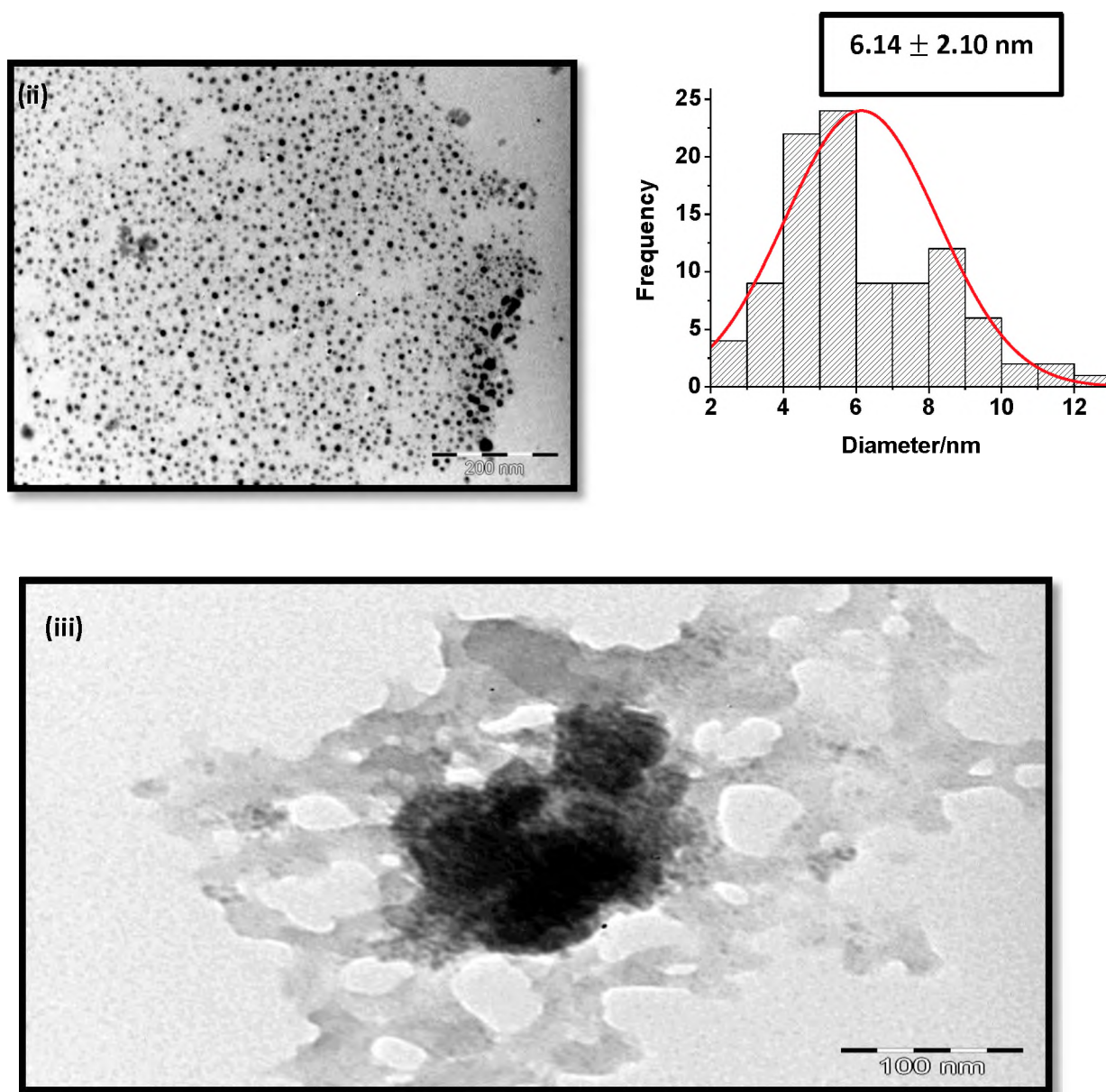


Fig. 3.5: TEM images of (i) GSH-CdSe/ZnS QDs in water (with corresponding histogram), (ii) Azide-QDs in DMF (with corresponding histogram) and (iii) clicked FePc-QDs in DMF.

3.2.4 Infrared Spectroscopy

Fig. 3.6 shows the FTIR spectra of the GSH-CdSe/ZnS QDs, 4-azidoaniline hydrochloride, azide-QDs, alkynyl FePc alone and clicked FePc-QDs. The characteristic amine (NH_2) stretch and carbonamide stretch at 2926 cm^{-1} and 1607 cm^{-1} respectively, are observed on the GSH-capped QDs spectrum. For the azide QDs, a small stretch at 2142 cm^{-1} is observed and may be attributed to the azide groups. This peak is also observed in the spectrum of 4-azidoaniline hydrochloride. The NH_2 stretch observed at 2926 cm^{-1} in GSH-QDs has almost disappeared in the azide-QDs spectrum and the peak due to the amide bond observed at 1607 cm^{-1} has decreased in intensity with the peak splitting. These observed changes and differences in the spectra are an indication of changes of the molecules with each modification step. Once the azide-QDs had been clicked with the alkynyl FePc, the azide peak initially observed at 2142 cm^{-1} , seems to have almost disappeared. However, the NH_2 peak due to the GSH capping of the QDs at 2926 cm^{-1} appears to be intense again which may be a result of the NH_2 being more exposed following conjugation. This is an indication that not all the reactive functional moieties of the GSH groups or azide groups on the QDs had reacted upon conjugation. Weak stretches due to the terminal alkyne groups of the FePc at 3201 cm^{-1} are still observed and shifted from 3303 cm^{-1} which implies that not all the alkynyl groups were involved in bonding but some degree of functionalization has taken place. The most important peaks observed after conjugation of the azide-QDs with the alkynyl FePc are the peaks due to the triazole ring observed at 1621 cm^{-1} and 1464 cm^{-1} [95]. This gives confirmation of the success of the click reaction. However, XPS will also be used in order to further prove the success of the conjugation reactions as well as the extent of functionalization.

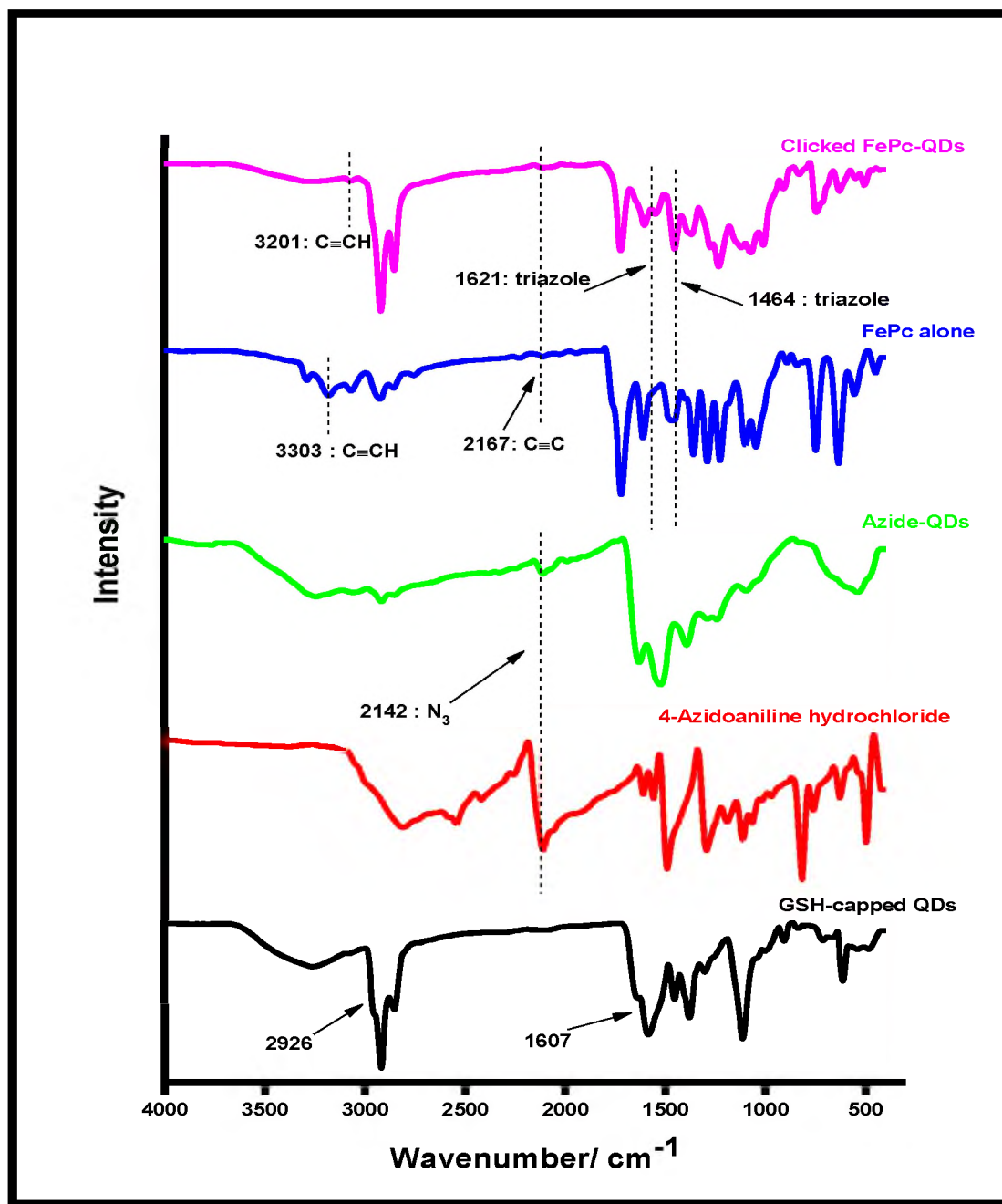


Fig. 3.6: FTIR spectra of the GSH-CdSe/ZnS QDs, 4-Azidoaniline hydrochloride, azide QDs, alkynyl FePc and clicked FePc-QDs.

3.2.5 X-ray Photoelectron Spectroscopy (XPS)

3.2.5.1 Theoretical aspects

XPS is a very useful technique due its surface sensitivity. It provides information on the chemical nature of the surface being analyzed. In this section specifically, this technique is used to confirm the click reaction between the azide functional moiety of the azide-QDs and terminal alkyne groups of the FePc. **Fig. 3.7A** is a basic representation of the instrument and the main components whereas **Fig. 3.7B** illustrates the mechanism of the technique in terms of orbitals and information obtained from the analysis. The basic principal involves the bombardment of the surface using an X-ray source resulting in the emission of an electron. The kinetic energy is measured, which then allows for the calculation of the binding energy using the x-ray photon energy, kinetic energy of the emitted electron and the work function. This calculation is shown by **Eqn.3.2** [96]:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \Phi) \quad (3.2)$$

where E_{binding} is the binding energy, E_{photon} is the energy of the x-ray photons, E_{kinetic} is the kinetic energy of the electron measured and Φ is the work function.

The binding energy is a measure of the energy required to break a bond in a molecule. This binding energy will be different for different molecules and atoms, hence the determination or prediction of the chemical structure on the surface [96]. The surface analysis by XPS requires an ultra-high vacuum.

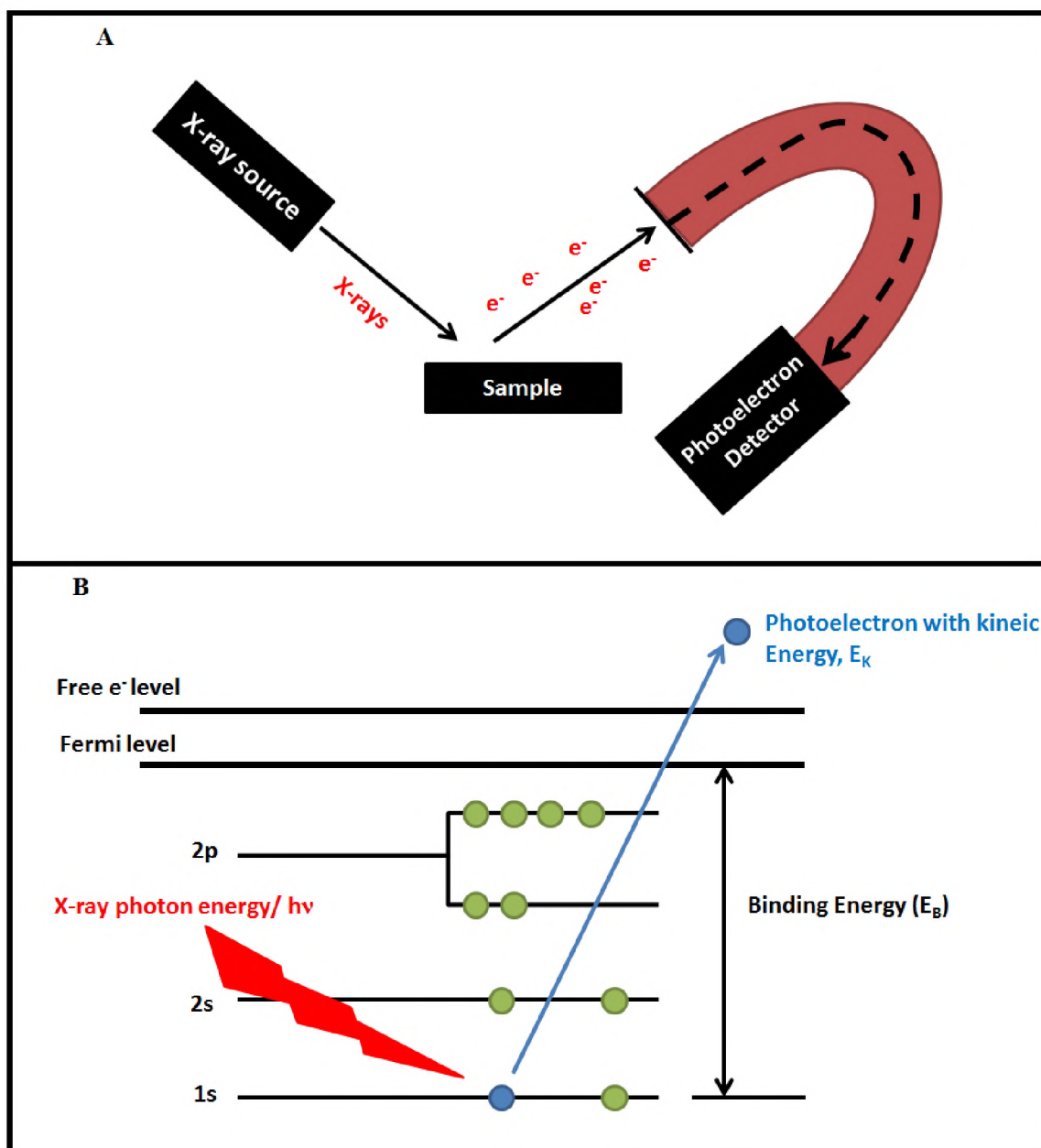


Fig. 3.7: (A) Schematic representation of the main components of XPS and (B) Illustration of mechanism of XPS analysis in terms of molecular orbitals and binding energy determination.

3.2.5.2 Characterization of QDs and conjugates with alkynyl FePc by XPS

The azide-QDs and the azide-QDs clicked with alkynyl FePc were prepared separately then adsorbed onto a glassy carbon plate for this analysis as opposed to grafting and performing the click reaction directly onto the electrode surface which will be discussed in chapter 4. The wide scans are illustrated by **Fig. 3.8**. The bare glassy carbon plate (GCP) shows the expected carbon peak as well as with an oxygen peak, the latter due to adsorbed oxygen. These peaks are also observed on the other plates but with differing intensities due to the nature of the surface. The characteristic peaks due to the molecules being analyzed are observed for all QD-derivatives confirming the success of their synthesis. For the CdSe/ZnS core-shell QDs, the characteristic Zn(2p), S(2p), Cd(3d) and Se(3d) peaks are observed. The presence of these peaks confirms the presence of the GSH-capped QDs on the surface of the GCP. After functionalizing the QDs with azidoaniline groups, the same peaks due to the QDs are observed but the peak intensities are lower. The observation of the N(1s) peak at a binding energy of 400 eV is due to the presence of nitrogens in the GSH-QDs as well as the azide-QDs and clicked FePc-QDs. For the QDs clicked with alkynyl FePc, the Fe(2p) peaks are not intense but are still observed around 700 eV. The intensities change due to the change in the surface chemistry and extent of exposure of these groups upon analysis.

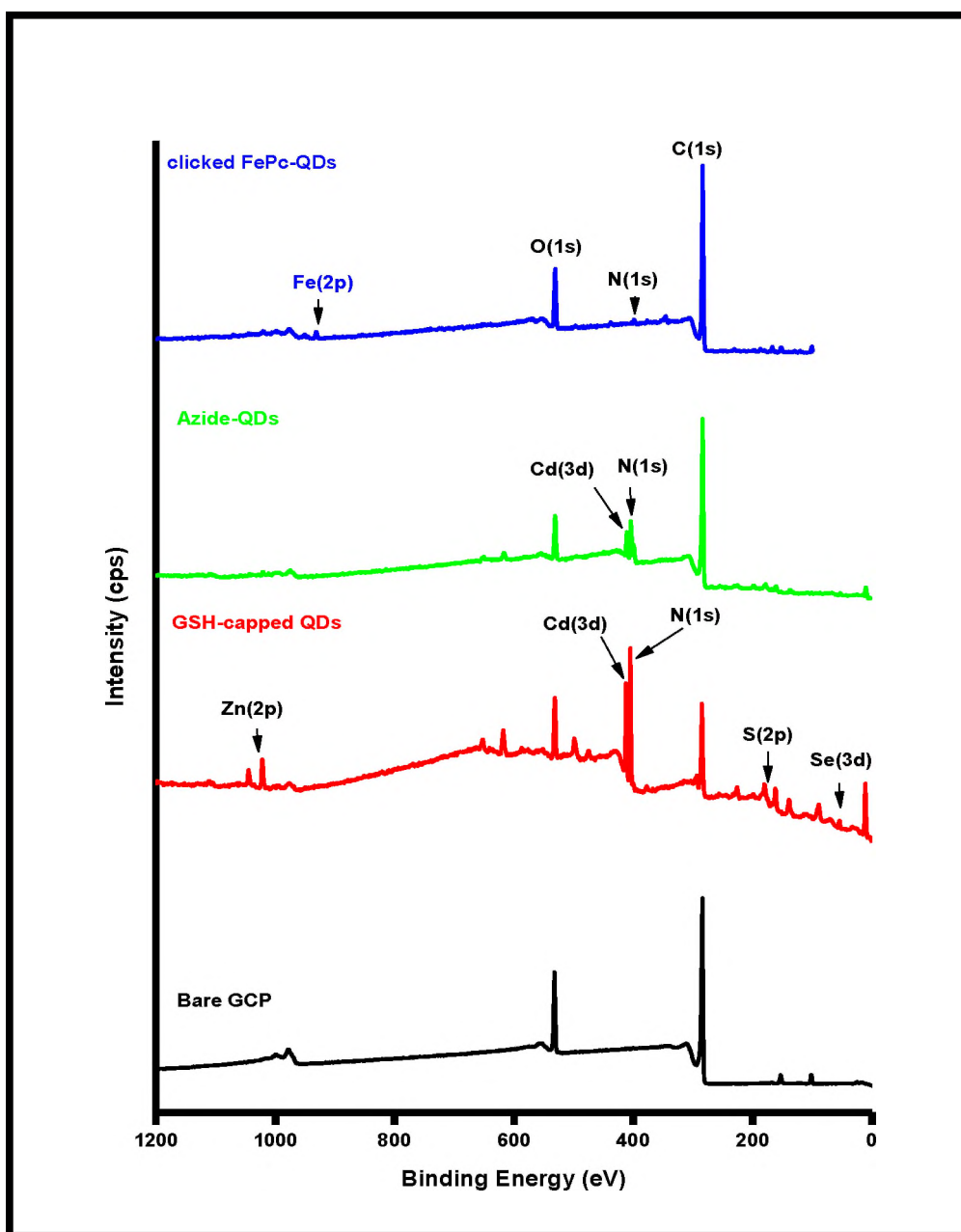
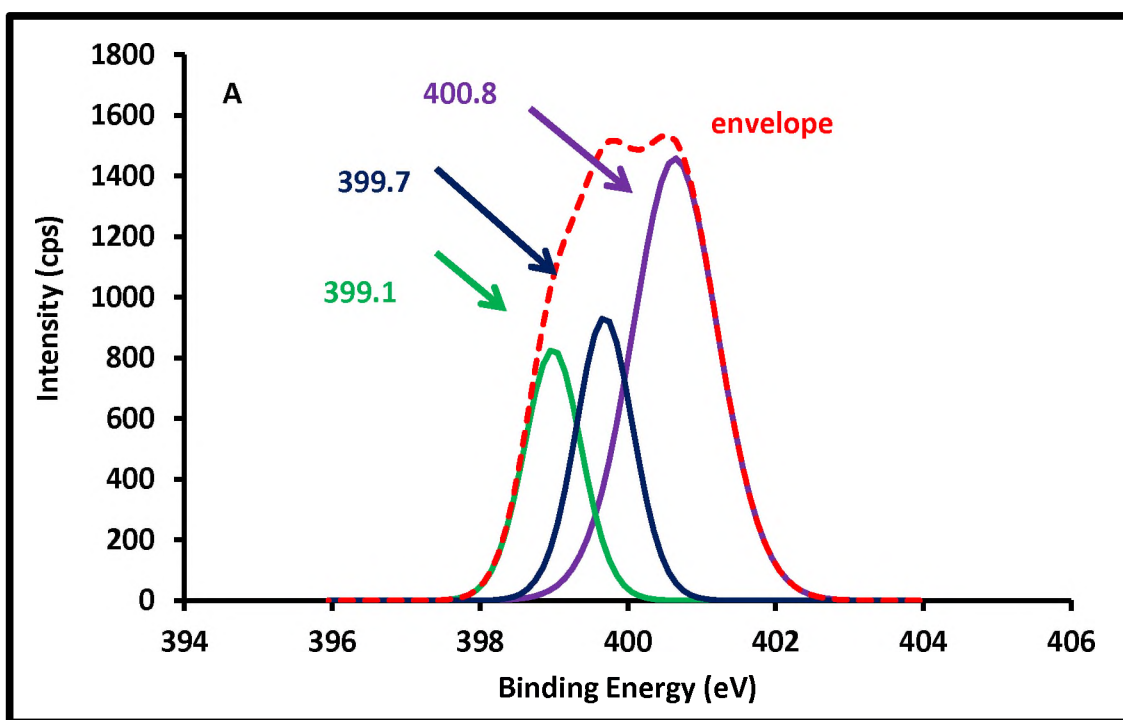


Fig. 3.8: XPS wide scans of Bare, CdSe/ZnS QDs, Azide functionalized QDs and Azide-QDs clicked with FePc on a GCP.

Fig. 3.9A shows the high resolution scan of the N(1s) region of the GSH-CdSe/ZnS QDs. The main peak appears at a binding energy of 400 eV and seems to split into two. By deconvoluting this peak, three peaks are observed at binding energies of 399.1 eV, 399.7 eV and 400.8 eV. The peak at the lowest binding energy (399.1) is due to the N-

H of the GSH capping of the CdSe/ZnS-QDs. The peak at 400.8 eV may be attributed to the C-N of the GSH capping [97]. The peak observed at 399.7 eV may be a combination of the C-N and N-H signals as the value lies between the other two values already assigned. **Fig. 3.9B** shows the high resolution N(1s) spectrum of the azide-functionalized QDs as well as the spectrum for the clicked FePc-QDs. The peak due to the electron deficient central nitrogen is observed at a binding energy of 404.6 eV. According to an XPS database [98], the binding energy at which the nitrogen peak is observed depends on the environment from which it originates, thus there is a range of binding energies that may be obtained. The value obtained in this work lies within the reported range. The peak at 399.6 eV is due the two outer nitrogens of the azide group (neutral and negatively charged nitrogens) [89, 92, 94, 97, 99-104]. It is possible that if there is GSH-capping still exposed it may contribute to the nitrogen signal as well but the binding energies observed suggest the presence and dominance of the azide groups on the surface. The ratio of these peaks is expected to be 2:1 [102] but deviations have been observed in some studies [99, 104, 105] and said to be a result of degradation after a certain period of analysis under the destructive XPS conditions [106]. Upon clicking the QDs with the alkynyl FePc, the intensities of these peaks decreases and there is a chemical shift observed. This change is an indication of the change in the surface chemistry and thus may be an indication of the success of the click reaction. The peak observed at a binding energy of 399.4 eV which is also observed from the azide-QDs at a binding energy of 399.6 eV may be assigned to a combination of unreacted azide groups (specifically the nitrogens adjacent to the central nitrogen), pyrrolic and aza-nitrogens of the alkynyl FePc and the nitrogens of the triazole ring. The broad peak at an estimated binding energy of 405.5 eV may be a result of the intense conjugation of

the phthalocyanine molecule as a peak in the same region will also be observed for other XPS analyses done in this work, with some contribution from unreacted azide groups of the azide-QDs. It may also just be a result of unreacted azide groups only. The assignment of this peak (405.5 eV) is indefinite due to its broadness.



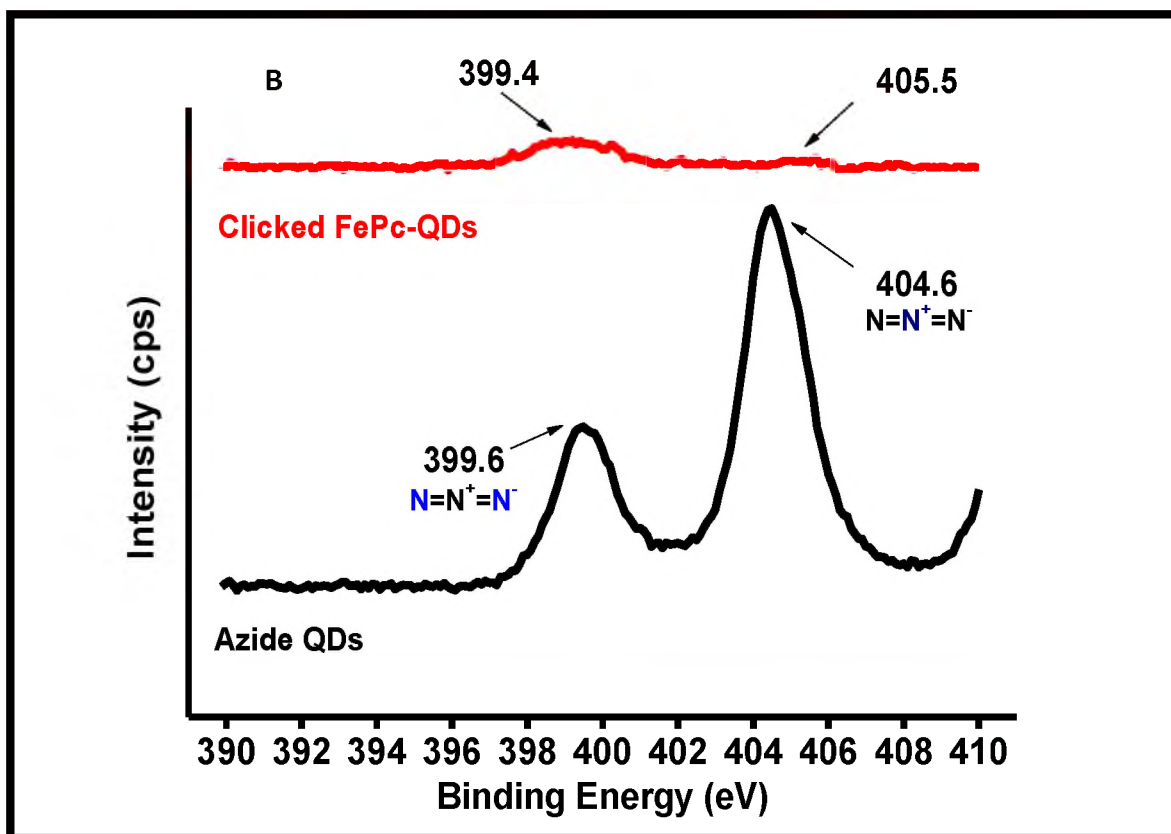


Fig. 3.9: High resolution N(1s) scans of (A) GSH-CdSe/ZnS QDs (deconvoluted), (B) azide-functionalized CdSe/ZnS QDs and clicked FePc-QDs.

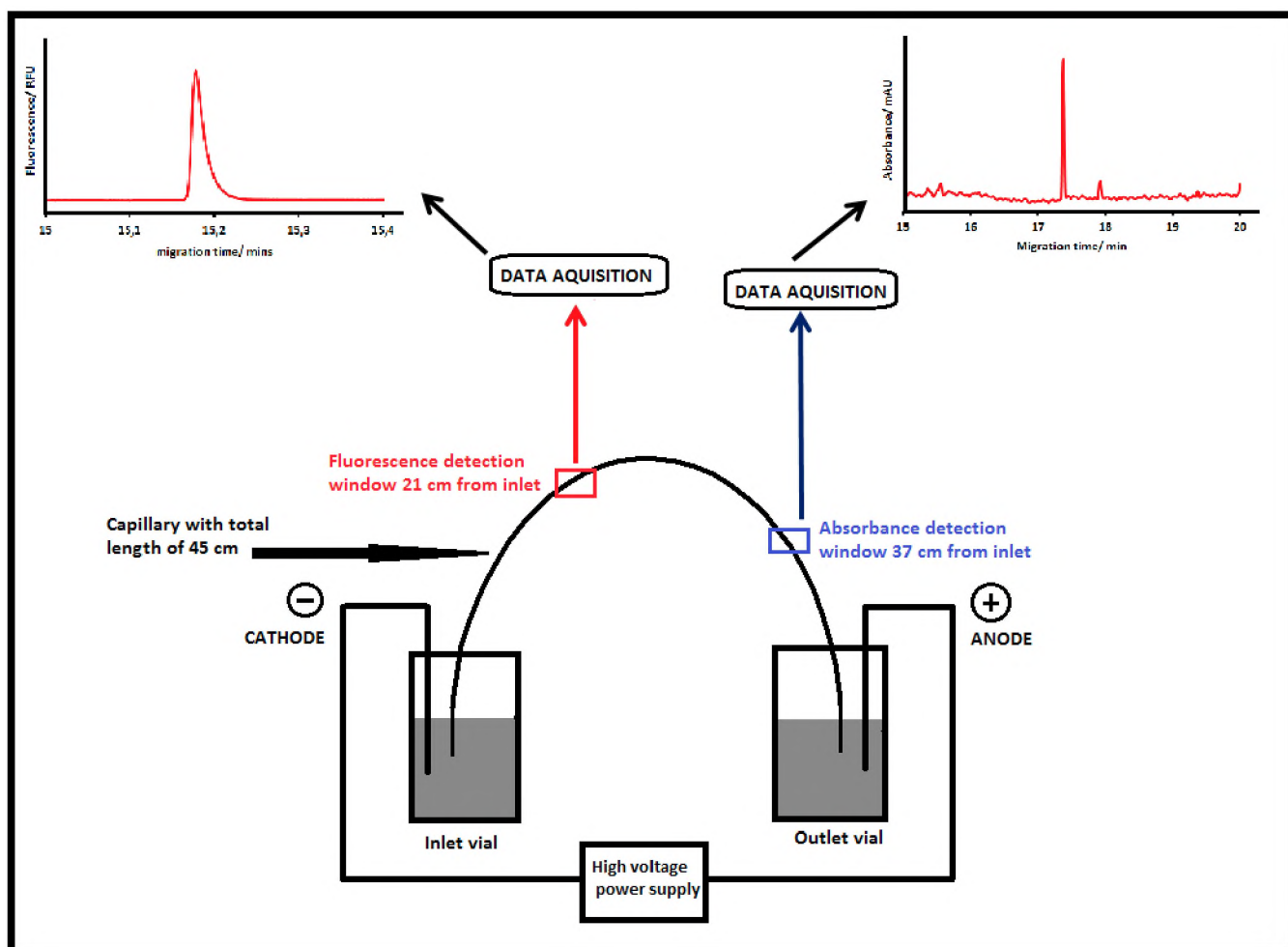
3.2.6 Capillary electrophoresis and laser Doppler electrophoresis

Capillary electrophoresis (CE), laser Doppler electrophoresis (LDE) and dynamic light scattering (DLS) were used to characterize the QDs and their conjugates in solution. The information obtained includes electrophoretic mobility, zeta potential and hydrodynamic size. The results also provided an idea of the behaviour of the particles in solution with respect to aggregation and the extent at which it occurs. The use of these different techniques is to see if these analytical techniques, especially the ones involving electrophoretic separation, would provide the same information on the QDs and their conjugates or it would become apparent that only one technique would

provide useful information to determine the characteristics the nanostructures studied possess.

3.2.6.1 Capillary electrophoresis: Absorbance and fluorescence detection

In this work capillary electrophoresis with laser induced fluorescence was used to analyze the molecules of interest due to the high sensitivity of this technique and increased selectivity [107]. With capillary electrophoresis, the migration time of particles is measured and using this information, the electrophoretic mobility may be calculated. The interaction of the particles in solution will determine the time it takes to move through the capillary and reach the detector. **Scheme 3.4** represents the basic setup of the electrophoresis instrument. Note that in this case, a long capillary of 45 cm is used in order to carry out detection by absorbance and fluorescence. The capillary length for just absorbance detection is shorter. The migration time in the electropherogram obtained by fluorescence detection is less than the migration time taken when detection by absorbance is used. This is merely due to the fact that the fluorescence detector is closer to the inlet. When determining electrophoretic mobility from the two plots, they should be the same or at least in close range to one another.



Scheme 3.4: Schematic representation of electrophoresis analysis setup and the data acquired from both absorbance and fluorescence detection.

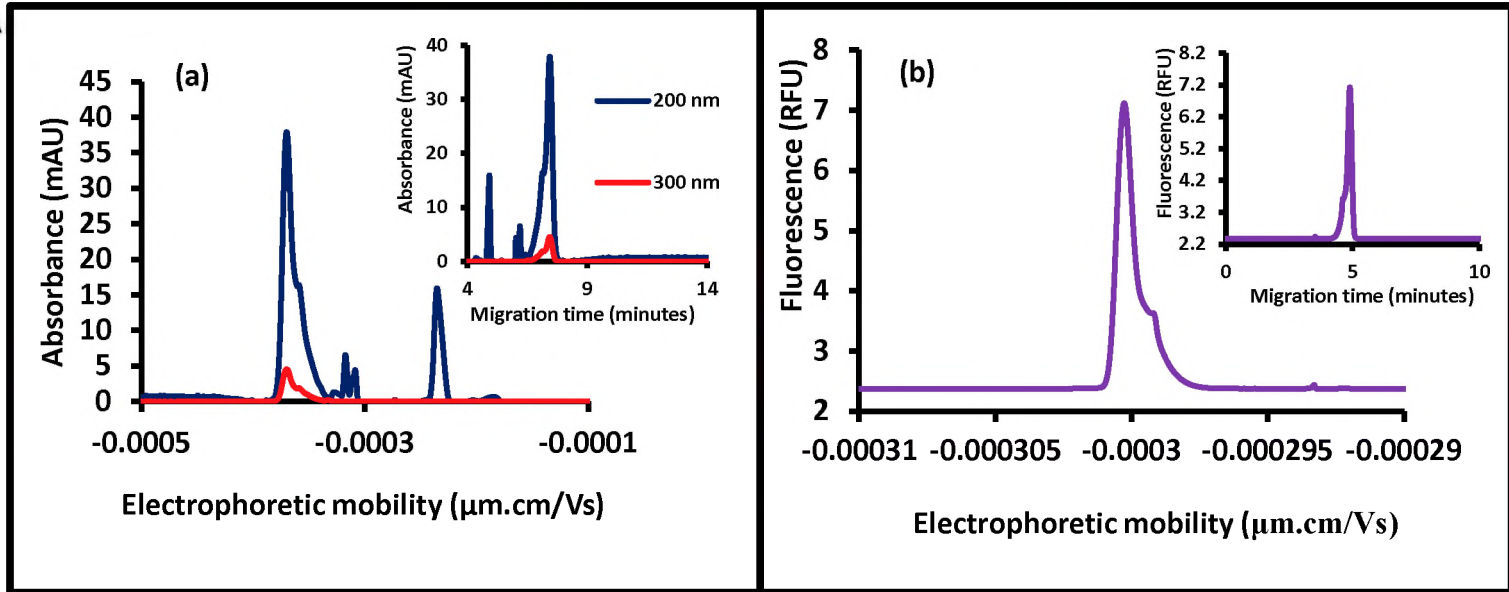
Fig. 3.10 shows the electropherograms obtained and plotted in terms of electrophoretic mobility with inserts corresponding to each electropherogram plotted in terms of migration time. Fig. 3.10A to Fig. 3.10C refers to the electrophoretic data obtained for GSH-QDs, azide-QDs and clicked FePc-QDs respectively. Traces (a) and (b) in Fig.10 correspond to absorbance and fluorescence detection respectively. The most obvious observation is the slight shifts in electrophoretic mobility as the surface of the QDs change. The GSH-QDs peak shown in Fig. 3.10A (a) appears to have a shoulder which may indicate a different population of QDs in the solution that have a slightly higher

electrophoretic mobility. Furthermore, at a 200 nm wavelength, impurities are observed which may be attributed to the precursors used to functionalize the core-shell QDs with the GSH capping. At 300 nm however, these unwanted peaks seem to disappear but the intensity of the GSH-QDs peak is largely decreased. Similar behaviour is observed with the azide-QDs as observed in **Fig. 3.10B (a)**. However, the difference here is that the peak shows a sign of aggregation [108] which is proven by the ‘spiked’ peaks observed on the main peak due to the azide-QDs. This may be attributed to the aggregation of the QDs in solution. The aggregation of the GSH-QDs may be due to non-covalent interactions between particles when suspended in solution. Literature has also suggested that the aggregation of GSH-capped QDs may be a result of cross-linking of QDs via an amine and carboxyl functional moiety or merely poor non-covalent interactions between the surface of the QDs and the ligand [109]. The interaction of aromatics as reported in literature [110] led to the assumption regarding the azide-QDs that the aggregation may possibly be due to the extra benzene ring of the azidoaniline resulting in π - π stacking. Sonication was used in an attempt to alleviate the extent of aggregation which turned out to be futile.

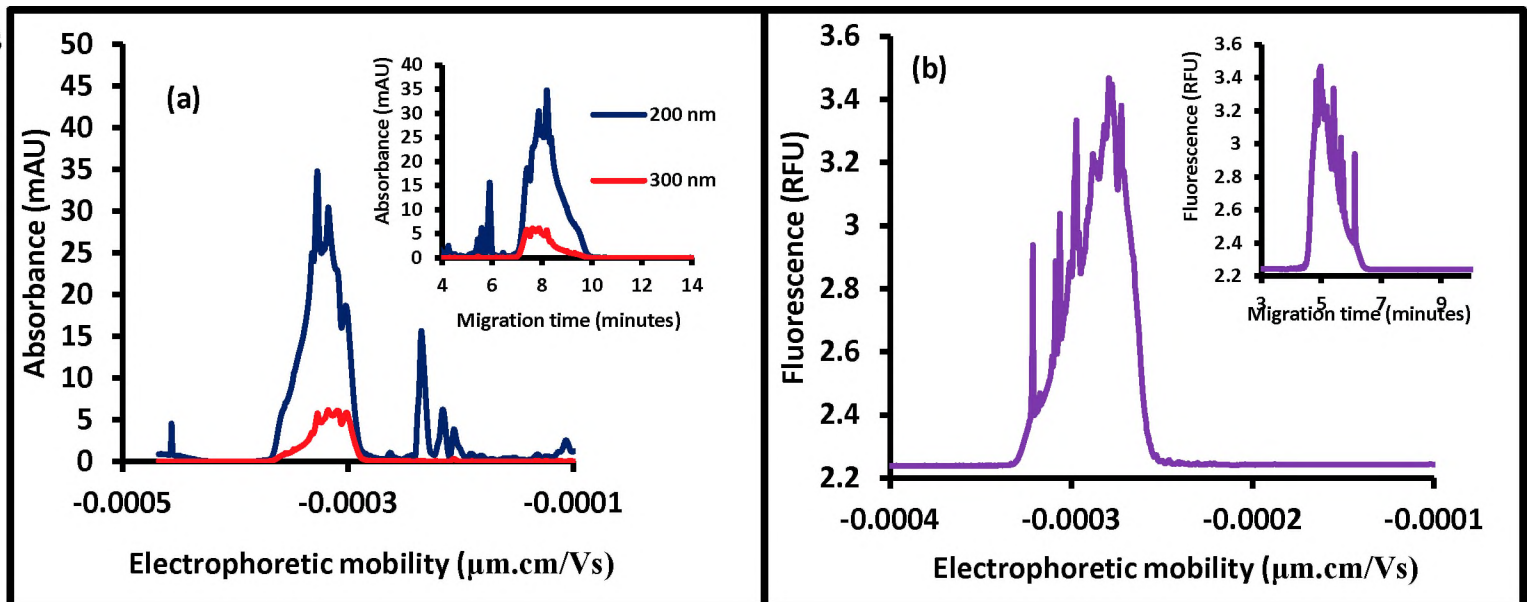
With respect to the clicked FePc-QDs analyzed via absorbance detection, **Fig. 3.10C (a)**, a number of small signals are observed which is also indicative of aggregation but a broad peak characteristic of QDs is observed at a low intensity compared to unconjugated QDs. The aggregation of phthalocyanines is known to be due to π - π stacking between the rings of the phthalocyanine [92]. The fluorescence electropherograms only show the peaks due to the QDs and the conjugates and no impurities are observed as illustrated by **Fig. 10A (b)**, **Fig. 10B (b)** and **Fig. 10C (b)**. Literature reports discuss the electrophoresis results in terms of migration time and not

electrophoretic mobility as done in this work [111, 112]. By comparing the migration times, the time observed for the QDs reported in this work (see inserts in **Fig. 3.10**) is longer than that reported in literature [111]. Looking at another report, the migration time of unconjugated QDs is similar to that obtained in this work [112] prior to converting it to electrophoretic mobility. The clicked-QDs were detected after more minutes which may have been due to aggregation, thus slowing down as the QDs moved through the capillary. Other reasons that the values obtained in this work differ from values in literature may be the solution used for analysis as well as the differences in the conjugates analyzed.

A



B



C

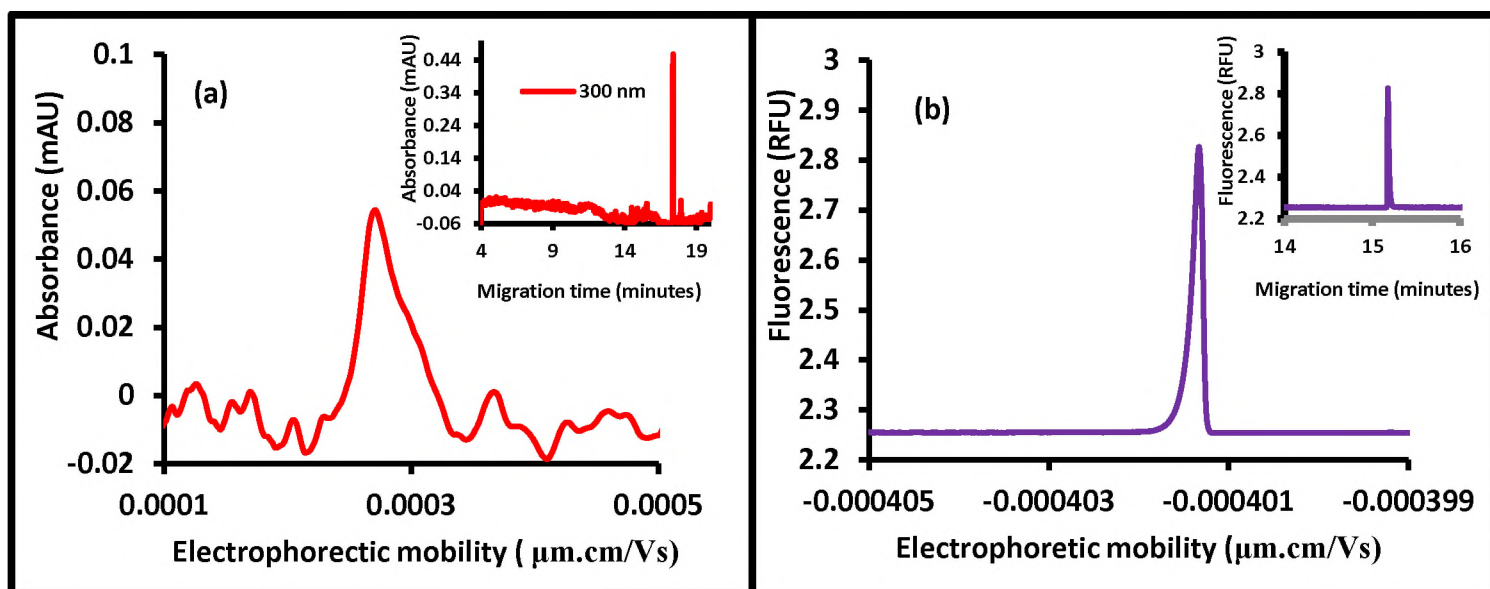


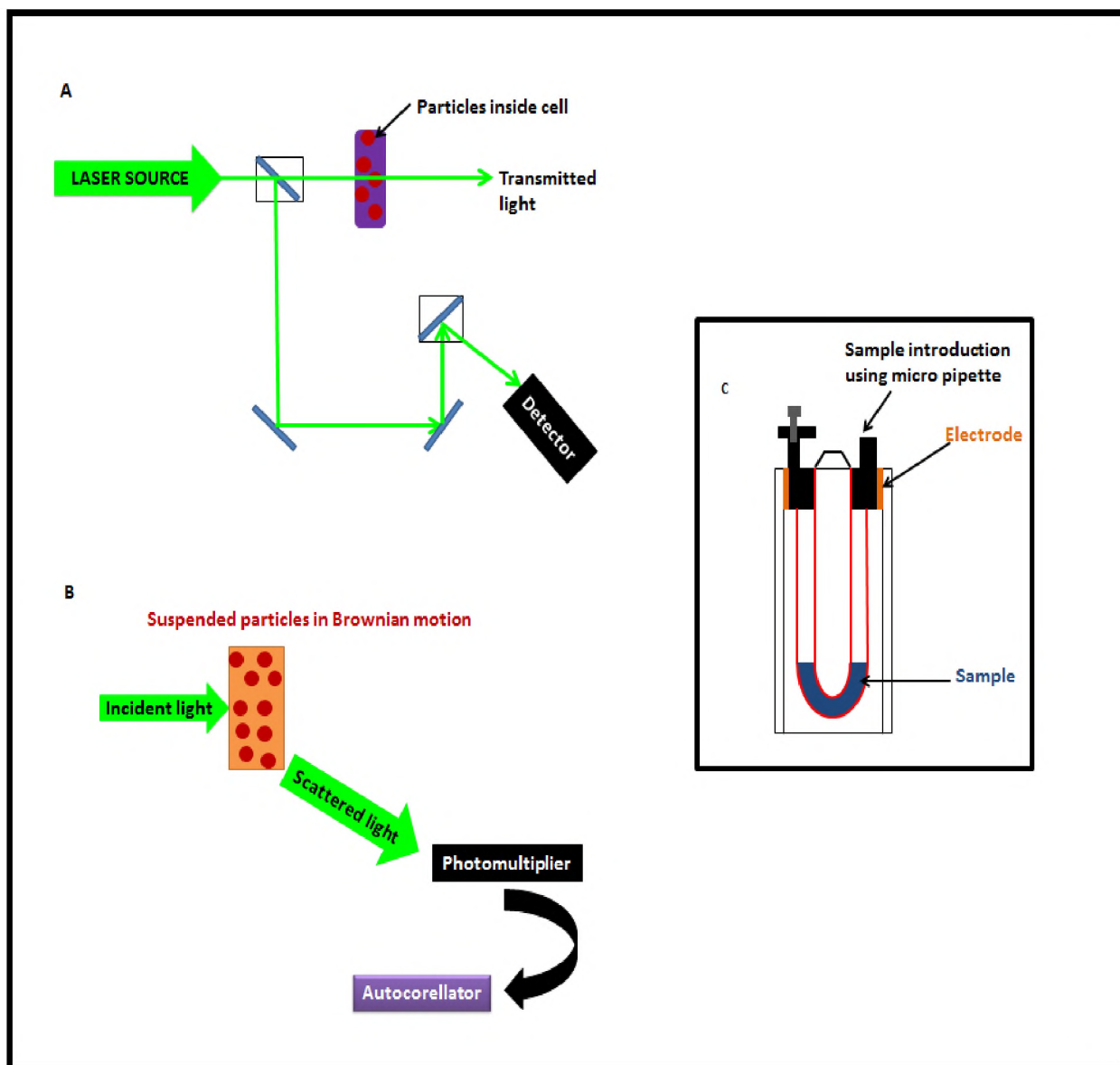
Fig. 3.10: Electropherograms of (A) GSH-QDs, (B) azide-QDs and (C) clicked FePc-QDs.

(a) absorbance and (b) fluorescence detection. Conditions: fused-silica capillaries, 50 μm internal diameter; 45 cm total length. Absorbance detection = 36.5 cm (200 nm), fluorescence detection = 21 cm (>520 nm; excitation source = 480 nm). 0.1 M NaOH running buffer with 10 s injection at 20 mbar. Applied voltage = 14 kV, Temperature = 25°C .

3.2.6.2 Laser Doppler electrophoresis (LDE) and dynamic light scattering (DLS)

By using the LDE technique, electrophoretic mobility and zeta potential was obtained. As already explained above, the use of a different technique for the determination of electrophoretic mobility was to compare the results obtained and to determine whether or not the same result would be obtained. DLS was used to determine the average hydrodynamic size of the QDs and their conjugates. **Scheme 3.5** illustrates how (A) LDE works for zeta potential determination as well as electrophoretic mobility and (B) how DLS works for the determination of the hydrodynamic diameter of particles in solution.

The cell setup is shown by **Scheme 3.5C**. With respect to LDE (**Scheme 3.5A**), the electrophoretic mobility is determined by relating the measured velocity of the particles (which is measured by light scattering) with the known electric field [113, 114]. Once the electrophoretic mobility is calculated, the zeta potential can be determined. Zeta potential refers to the net charge on the particle surface thus allowing for the prediction of the interactions occurring between particles in solution. The hydrodynamic size of the particles may be determined using DLS (**Scheme 3.5B**) which is based on the understanding that larger particles diffuse slower than smaller particles therefore the size can be determined by light scattering intensity fluctuations [115].



Scheme 3.5: Schematic representation of mechanism of (A) LDE and (B) DLS. (C) Illustration of the cell setup.

The LDE studies and DLS analyses were run by using a 50 mM buffer solution as well as a 15 mM buffer solution. **Table 3.1** serves to compare the sizes of the nanostructures determined using DLS and TEM and show the difference in the hydrodynamic behaviour of the GSH-QDs, azide-QDs and clicked FePc-QDs. It also summarizes the

electrophoretic mobility obtained as well as the zeta potential determined for the QDs and their conjugates.

The size determined using DLS appeared to be very large compared to the size determined from TEM (**Table 3.1**). This implies that there is some difference in interaction of the particles in solution. A factor that could play a role in these observed differences is that for TEM analysis, the azide-QDs were prepared in a purely organic solvent whereas for electrophoresis the azide-QDs and clicked azide-QDs were prepared in a mixture of buffer solution and DMF for analysis. It has been reported that selectivity can be changed in electrophoretic separation by organic solvents compared to pure aqueous solvents such as buffer solutions thus altering the migration time and electrophoretic mobility [116]. The aggregation of the azide-QDs and clicked FePc-QDs obviously also plays a role in the data obtained from electrophoretic analyses.

Zeta potential results obtained showed that the particles were, overall, negatively charged in solution except for the azide-QDs in 50 mM PBS where a positive value was obtained. The negative and positive signs just mean that the particles analyzed are negatively or positively charged at the surface. In addition, the value obtained provides information on the stability of the particles in solution. The higher the value obtained, the greater the hydrodynamic stability [117]. Unfortunately it was not possible to calculate the zeta potential from CE analysis results due to the aggregation that was present.

Table 3.1: Comparison of average size obtained using DLS and TEM, electrophoretic mobility and zeta potential obtained from LDE using two different concentrations of buffer solution.

Nanostructure (conc. Of PBS for DLS and LDE)	TEM: Avg. Size/ nm	DLS: Avg. Size/ nm	Avg. Electrophoretic mobility/ $\mu\text{m.cm/Vs}$	Avg. Zeta potential/ mV
GSH-QDs (50 mM)	5.59	74.9	-0,00029	-37.6
GSH-QDs (15 mM)	5.59	65.6	-0,00025	-31.1
Azide-QDs (50 mM)	6.14	57.0	-0,00028	36.2
Azide-QDs (15 mM)	6.14	958,5	-0,00026	-10.1
Clicked-QDs (50 mM)	aggregated	329.5	-0,00037	-47.7
Clicked-QDs (15 mM)	aggregated	453,9	-0,00043	-49.7

^aAvg. = average, conc. = concentration

3.2.6.3 Summary of results obtained from the techniques discussed

In the work reported, the electrophoretic mobility of the QDs and conjugates were determined using CE by absorbance detection and fluorescence detection as well as LDE.

Table 3.2 summarises the results obtained using these different techniques and the values only vary slightly. The exception lies with the clicked-QDs where the electrophoretic mobility obtained from using the absorbance detector produced a positive value which means the overall surface charge of the conjugate was positive. Using fluorescence detection and LDE, the surface charge is shown to be negative and the two values lie in close proximity to one another. As already explained, aggregation of the particles in solution resulted in the inability to confirm the presence of a peak due to the clicked QDs-FePc conjugate in **Fig. 3.10C**. However, comparing the

electrophoretic mobility obtained using a fluorescence detector and an absorbance detector in Fig. 3.10, the fluorescence detection is a better method of characterizing these conjugates as fewer signals due to other particles that are not of interest are observed.

Table 3.2: Comparative table of electrophoretic mobility of the QDs and conjugates ($\mu\text{m.cm/Vs}$) obtained using CE (fluorescence and absorbance detection) and LDE.

Nanostructure	CE (absorbance)	CE (fluorescence)	LDE
GSH-QDs	-0.00036	-0.00030	-0.00025
Azide-QDs	-0.00032	-0.00027	-0.00026
Clicked-QDs	0.00027	-0.00041	-0.00043

3.3 Conclusion

To conclude this chapter, the alkynyl FePc of interest was successfully synthesized and characterized using various analytical techniques. Moreover, the QDs and their conjugates were also successfully synthesized and XPS was of the most importance as it confirmed the presence of all the atoms present in each molecule as well as showing the changes that have occurred at the surface of these molecules. From the results obtained in the analyses involving electrophoresis and dynamic light scattering analytical techniques, it can be concluded that there is an issue of aggregation once the QDs are functionalized with azide groups and clicked with the alkynyl FePc. In addition, using CE and LDE allows for the comparison of data to determine which technique may

produce results that are a better reflection of the characteristics of the molecules of interest. Capillary electrophoresis, LDE and DLS showed similar results with respect to the behaviour of the QDs and conjugates in solution. By comparing TEM results and the results electrophoresis results, information is provided on the behavioural differences of the QDs and their conjugates between hydrodynamic as well as solid state. In terms of improving these results, parameters such as electrolyte concentrations, pH of solutions and hydrodynamic stability need to be optimized in order to obtain more accurate results with respect to the molecules being studied. Using such sensitive techniques provides a clearer and better understanding of molecules in different environments under different conditions.

Chapter 4:

Electrode modification and surface characterization

4. Electrode modification and surface characterization

In this chapter, the methods of electrode modification will be described and discussed. Furthermore, the characterization of the modified electrode surfaces at each modification step will be shown and elaborated on. This chapter will be divided into two parts (4.1 and 4.2). Sub-section 4.1 focuses on the electrografting of a glassy carbon electrode following by clicking of the alkynyl FePc with the terminated phenyl-azide groups and sub-section 4.2 will focus on the adsorption of the QDs-based electrocatalysts.

4.1 Electrografting and Click chemistry with FePc

4.1.1 Electrode modification by electrochemical grafting and click chemistry

The immobilization of phenyl azide groups on the electrode surface was achieved using cyclic voltammetry, with passivation of the surface being observed after three reductive cycles. Fig. 4.1 shows the cyclic voltammograms obtained during this modification process which are similar to those reported in literature whereby the intensity of the reduction peak decreases by successive cycling [118-120]. Following this process, the click reaction between the azide groups on the electrode surface and the terminal alkyne groups of the FePc (complex 2) was carried out. It is important to note that the reaction of the alkyne groups with the azide groups on the electrode surface may occur through one or more of the peripheral substituents depending on the orientation of the alkynyl FePc molecule. Scheme 4.1 shows conjugation through only one substituent for illustrative purposes.

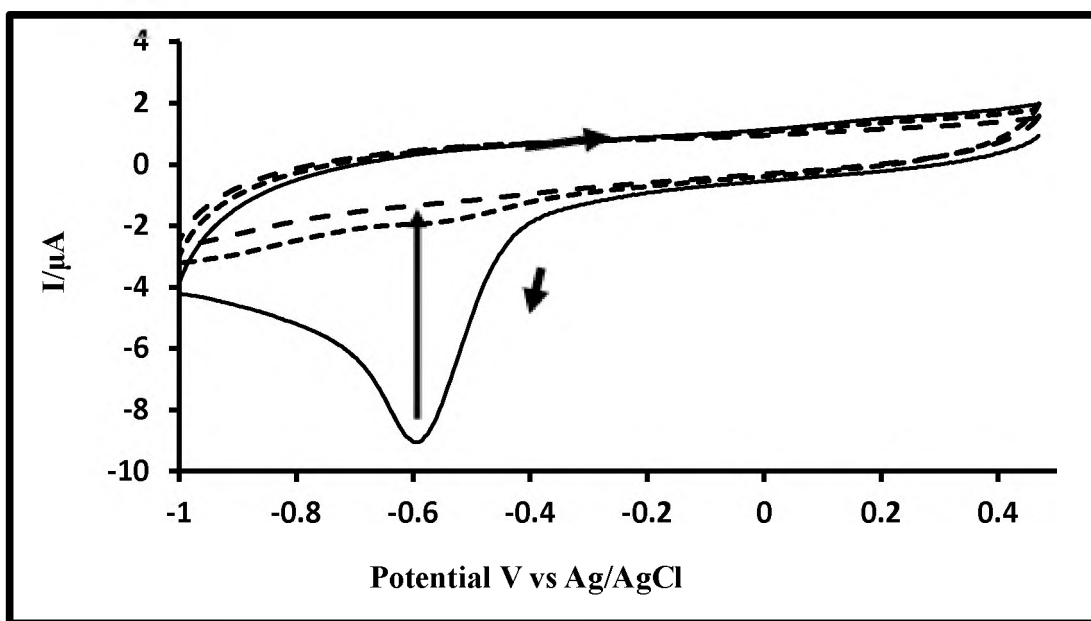
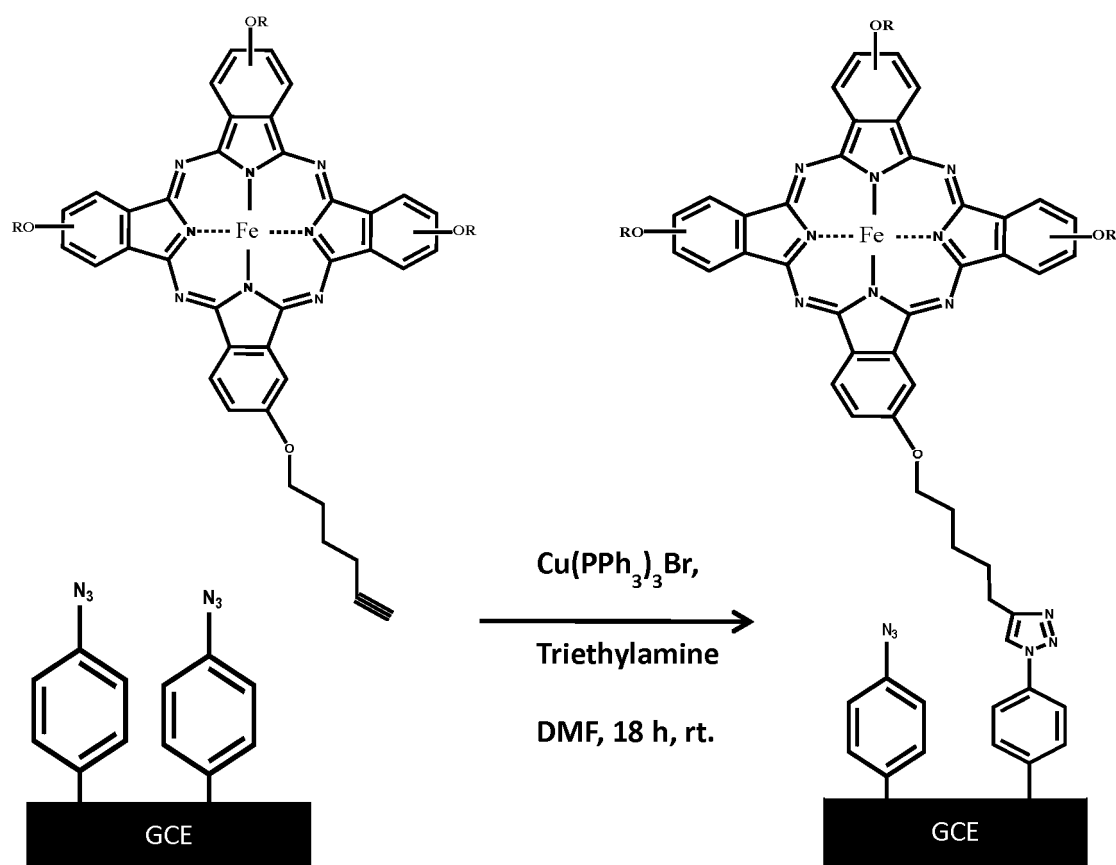


Fig. 4.1: Cyclic voltammogram showing the grafting of a GCE electrode by 3 reductive cycles from +0.50 V to -1.0 V in 1 mM 4-azidobenzene diazonium salt in 0.1 M TBABF₄ in ACN. Scan rate = 50 mV/s.



Scheme 4.1: Immobilization of alkynyl FePc on electrografted glassy carbon electrode via click chemistry through one or more peripheral ring substituents. (R = 5-hexynyl group).

4.1.2 Cyclic voltammetry

Ferricyanide solutions are known to be good redox mediators as well as being sensitive towards electrode surface kinetics [121, 122]. Thus, ferricyanide was chosen in this work as a first step to characterize the electrode surfaces of interest. The bare glassy carbon electrode, grafted electrode and the electrode clicked with the alkynyl FePc were tested in a $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution.

Fig. 4.2A (i) illustrates the response of the bare GCE towards $\text{K}_3[\text{Fe}(\text{CN})_6]$. The reversible redox couple observed for the bare GCE in this solution is typical [15, 19]. The

passivating behaviour of the phenyl azide groups on the electrode surface towards $K_3[Fe(CN)_6]$ is shown by **Fig. 4.2A (ii)**. Weak redox peaks are still visible between 0.08 V and 0.15 V which indicates inhomogeneity of the electrode surface. However, grafting by many reductive cycles may result in a layer too thick which would create a greater distance between the conductive surface and the electrocatalyst. This would reduce the efficiency of the electrocatalyst [39]. The clicked electrode was also tested in the $K_3[Fe(CN)_6]$ solution showing good blocking behaviour, as illustrated by **Fig. 4.2A (iii)**. Using cyclic voltammetry only confirms the change in the nature of the electrode surface making the use of other surface characterization techniques necessary.

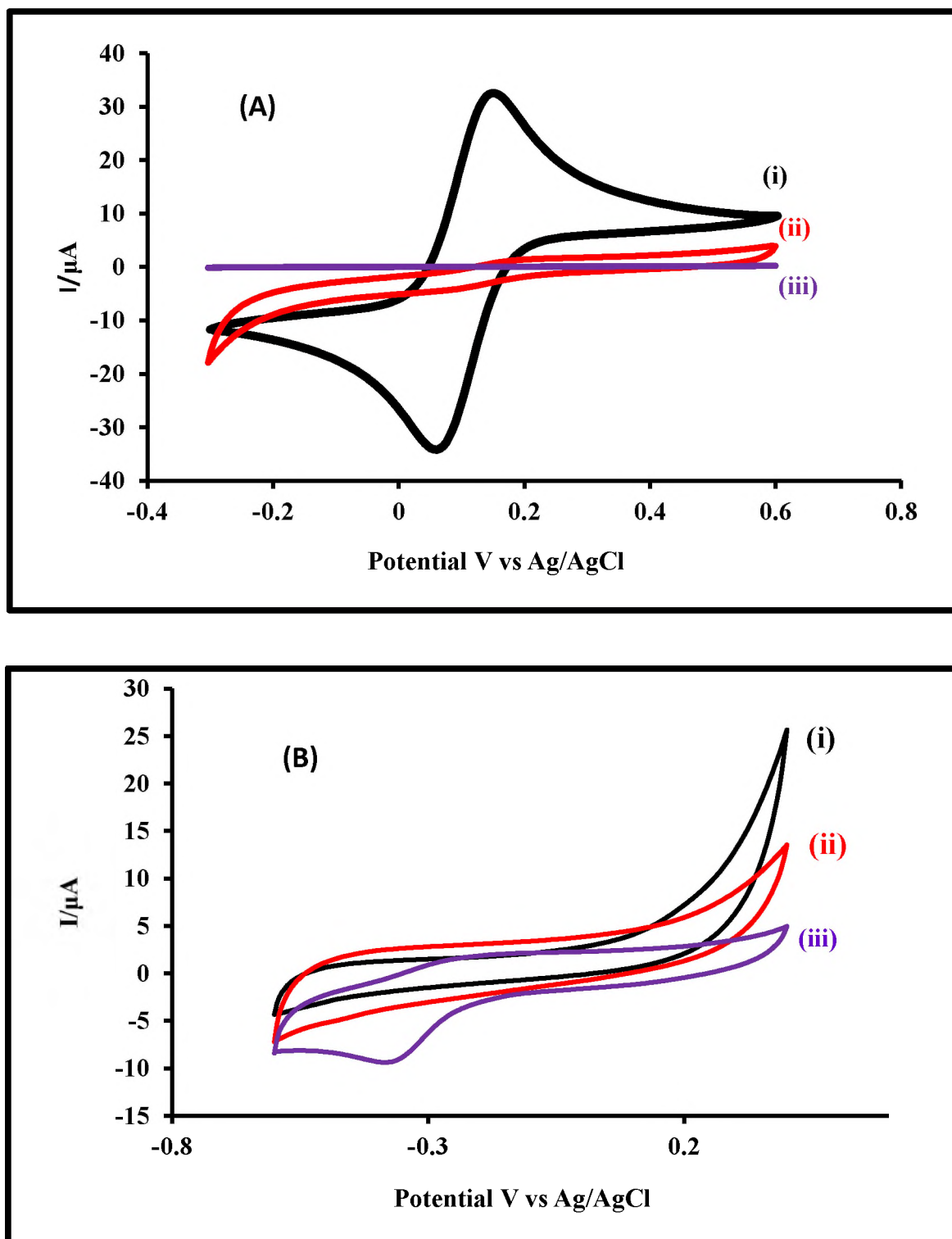


Fig. 4.2: Cyclic voltammograms of (i) bare GCE, (ii) grafted GCE and (iii) grafted GCE after click chemistry with alkynyl FePc. Analysis carried out in (A) 2 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl and (B) deaerated 0.1 M NaOH solution. Scan rate = 100 mV/s.

The bare electrode and modified electrodes were also tested in a 0.1 M NaOH solution, in which hydrazine (the analyte of interest) would be dissolved (**Fig. 4.2B**). The purpose of this is to ensure that there are no interferences when using the chosen electrocatalyst to test for hydrazine as well as to observe the behaviour of the final electrocatalyst which is expected to show redox activity in such solutions. No peaks were observed relating to the bare and grafted electrodes when tested in the NaOH solution. The electrode clicked with alkynyl FePc on the other hand showed a response in NaOH where a very broad oxidation peak was observed at approximately -0.14 V and a reduction peak at a potential of -0.38 V which may be assigned to the Fe(II)/Fe(I) pair in FePcs [74-76, 123]. This redox pair is expected to be involved in the electrooxidation of hydrazine.

4.1.3 Scanning electrochemical microscopy (SECM)

SECM is a useful surface characterization technique due to its ability to provide information on the reactivity, conductivity and topography of a substrate [124, 125]. SECM has proven to be a very unique and useful electrochemically-based surface characterization technique. The modes used in this work were the constant height imaging to obtain the area scans and the feedback mode to obtain the approach curves. The feedback mode can further be divided into the positive feedback mode where the current increases the closer it gets to the substrate surface and the negative feedback mode where the current decreases as it approaches the substrate surface. **Fig. 4.3** illustrates the feedback modes of analysis using SECM described above. **Fig. 4.3A** illustrates the positive feedback mode and **Fig. 4.3B** the negative feedback mode. **Fig. 4.3(C)** shows the typical approach curves obtained as the ultra-microelectrode approaches the surface being analyzed along the z-axis. The approach curves are

illustrated in Fig. 4.3C Fig. 4.3C (i) shows the result obtained as a result of the conducting nature of the surface hence the current increases as the UME approaches the substrate and Fig. 4.3C (ii) results from insulating surfaces as the current decreases when the UME approaches the substrate.

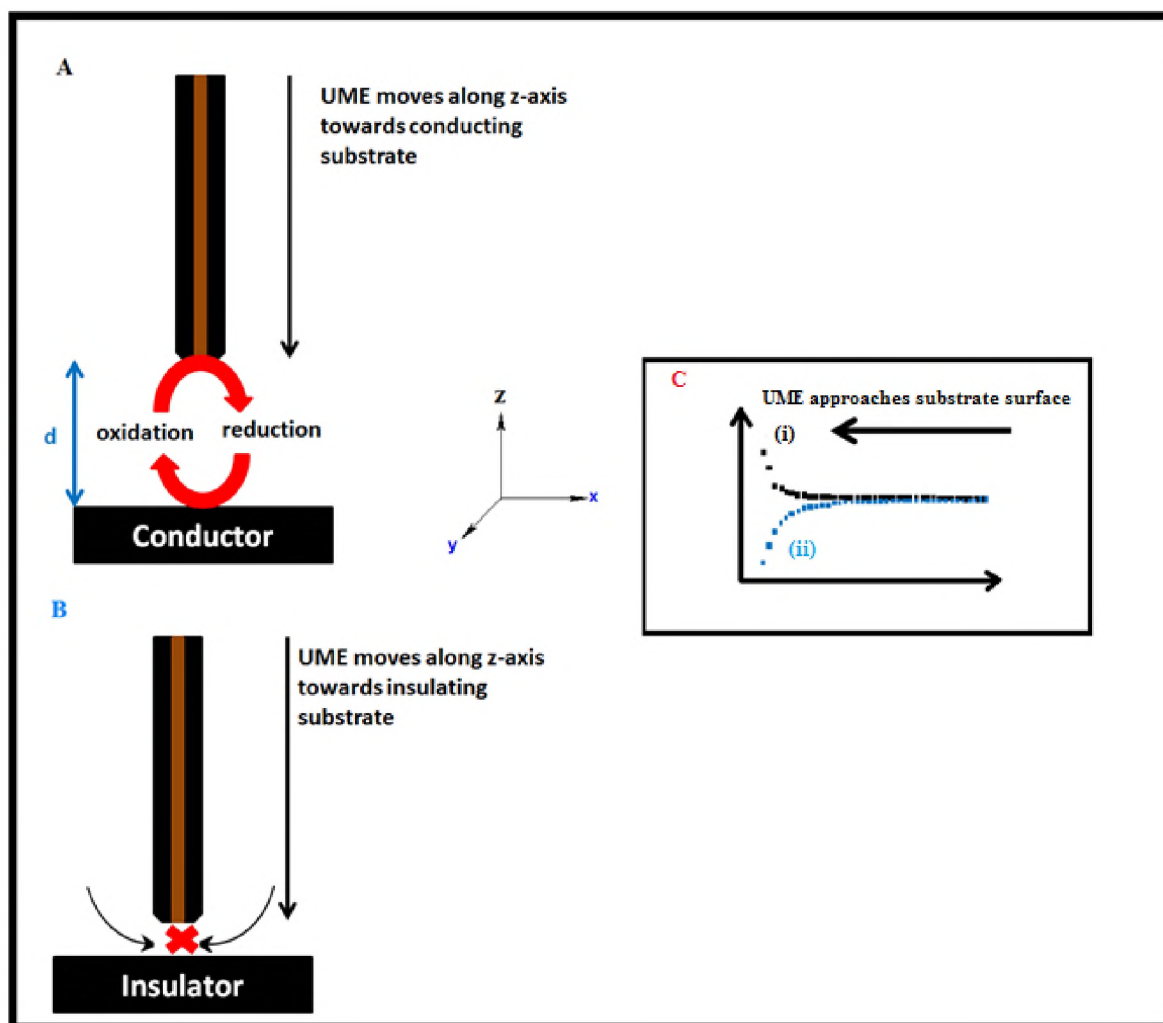


Fig. 4.3: Illustration of (A) positive and (B) negative feedback modes of SECM analysis in $K_3[Fe(CN)_6]$. (C) Approach curves obtained for (i) negative and (ii) positive feedback modes.

As mentioned in chapter 2, glassy carbon plates were used for SECM analyses but were modified in the same way and order as the conventional glassy carbon electrodes. Only half of the glassy carbon plate was grafted and so the assumption was made that upon immersion of the entire plate in the alkynyl FePc solution, only the grafted half of the plate would undergo the click reaction. The redox probe used was $K_3[Fe(CN)_6]$ for the characterization. The bare glassy carbon plate, **Fig. 4.4 (i)**, proved to be conducting towards the redox probe. However, the grafted and clicked glassy carbon plates, illustrated by **Fig. 4.4 (ii)** and **Fig. 4.4 (iii)** respectively, proved to be insulating towards the $K_3[Fe(CN)_6]$ solution. The phenyl azide groups are known to be insulating [118] and therefore the result obtained for the grafted electrode was expected. The insulating nature observed for the clicked-FePc may be due to insufficiently exposed Fe. For **Fig. 4.4 (i)**, **(ii)** and **(iii)**, the current and distance were normalised in relation to the limiting current (I_{lim}) and the radius of the ultra-micro electrode (UME).

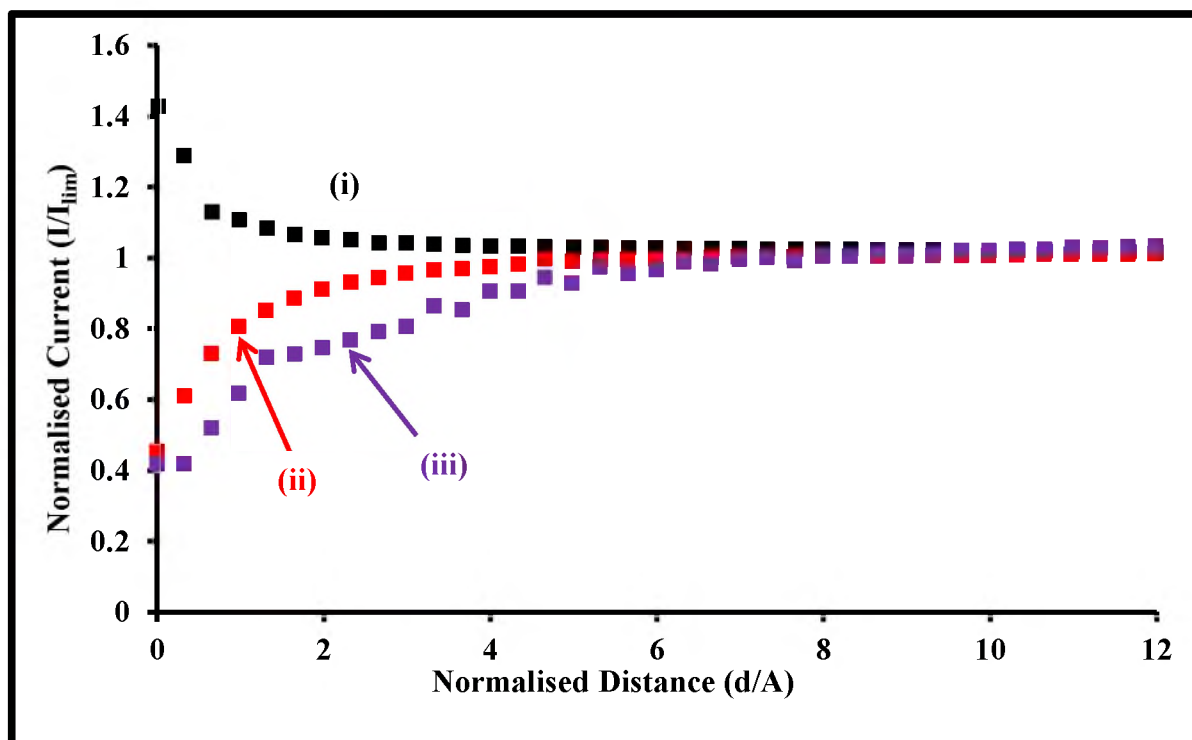
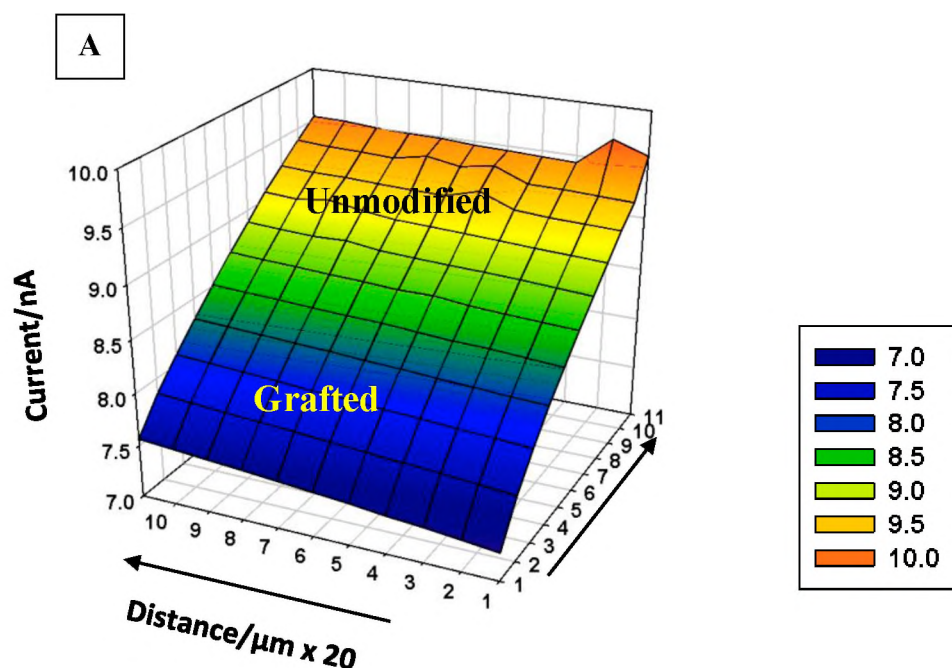


Fig. 4.4: SECM approach curves of (i) bare GCE, (ii) grafted GCE and (iii) grafted GCE after click chemistry with alkynyl FePc in 2 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at 0.15 V vs Ag/AgCl.

A specific area of the glassy carbon plate was scanned on each glassy carbon plate with the UME maintained at a constant height. For the sake of consistency and maintaining as reliable a result as possible, the same area was scanned after each modification step. Images of the different electrode surfaces were obtained thereafter (Fig. 4.5). Fig. 4.5A shows lower currents after electrochemical grafting compared to the unmodified section of the glassy carbon plate. As previously mentioned, the grafted layer is expected to be insulating [118] due to the phenyl azide groups not being conductive. The observation made here corresponds with the results obtained in the cyclic voltammetry experiments as well as the data obtained from the approach curves. Fig. 4.5B illustrates the surface after click chemistry between the terminated phenyl-azide groups and the terminal

alkyne groups of the FePc. The currents are lower for the section analyzed after grafting and click chemistry compared to the unmodified section, thus the observations made in the cyclic voltammetry experiments and results shown in the approach curves are confirmed. The unmodified section of the glassy carbon plate in **Fig. 4.5A** shows lower currents compared to the corresponding section illustrated in **Fig. 4.5B** which may be due to the distance between the UME and the substrate surface being greater [39] or insufficiently exposed Fe to facilitate the transfer of electrons between the substrate surface and the UME.



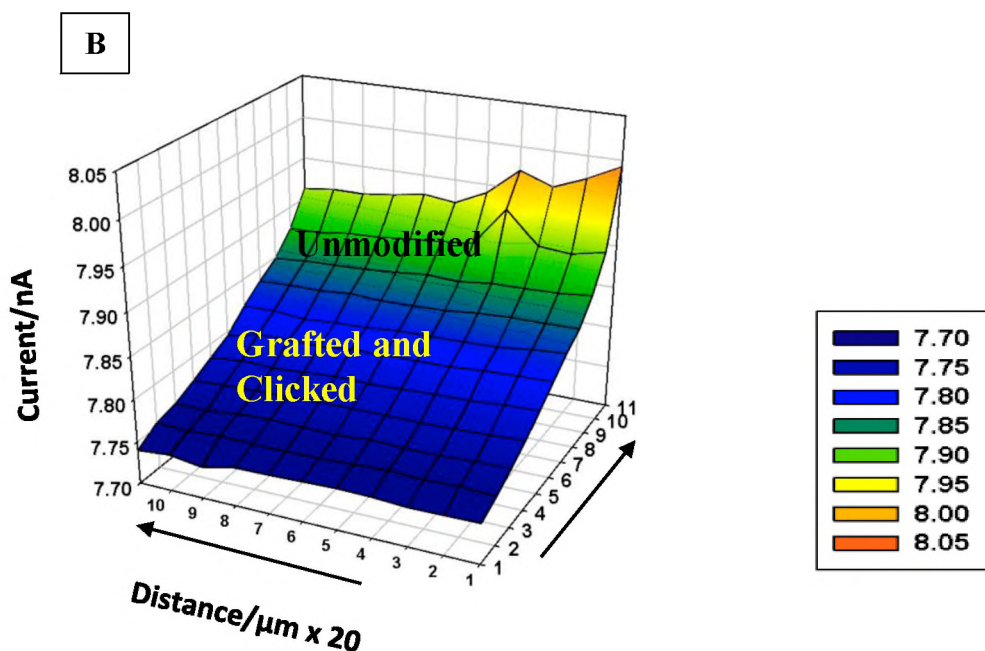
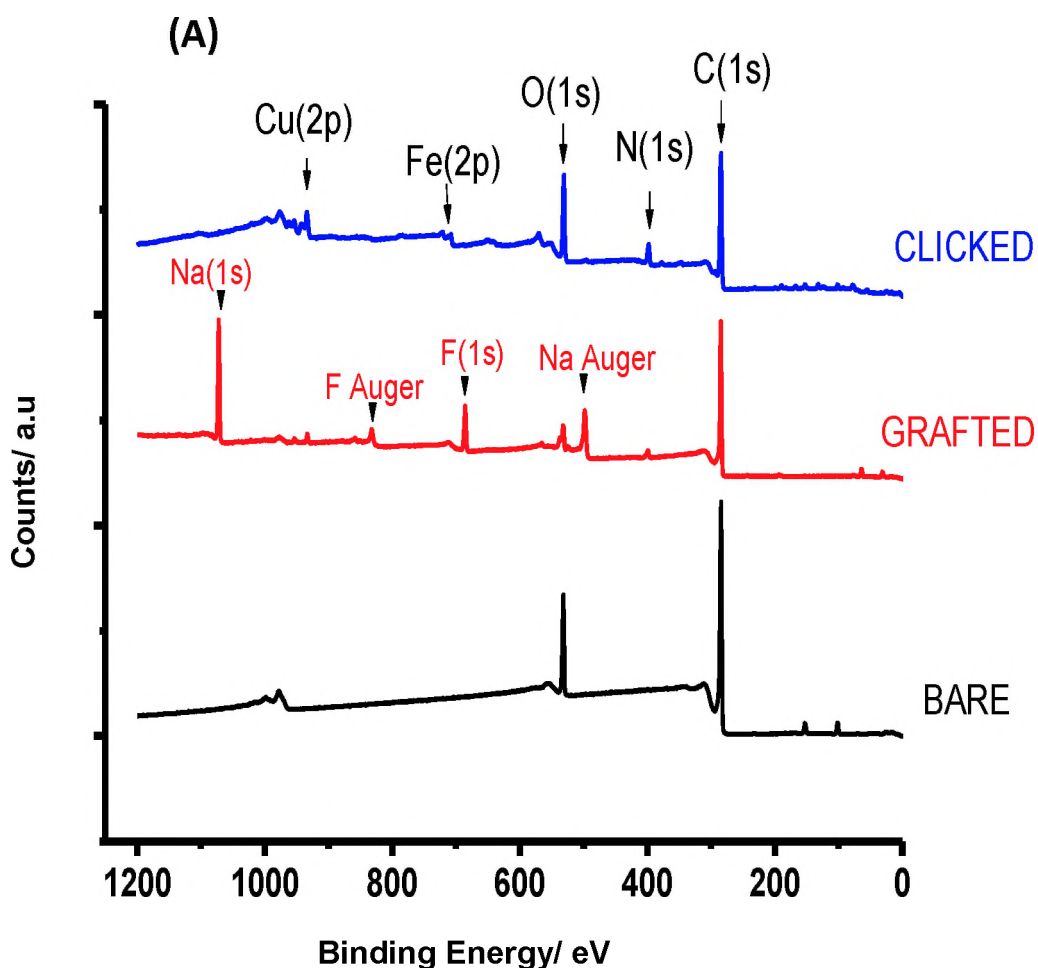


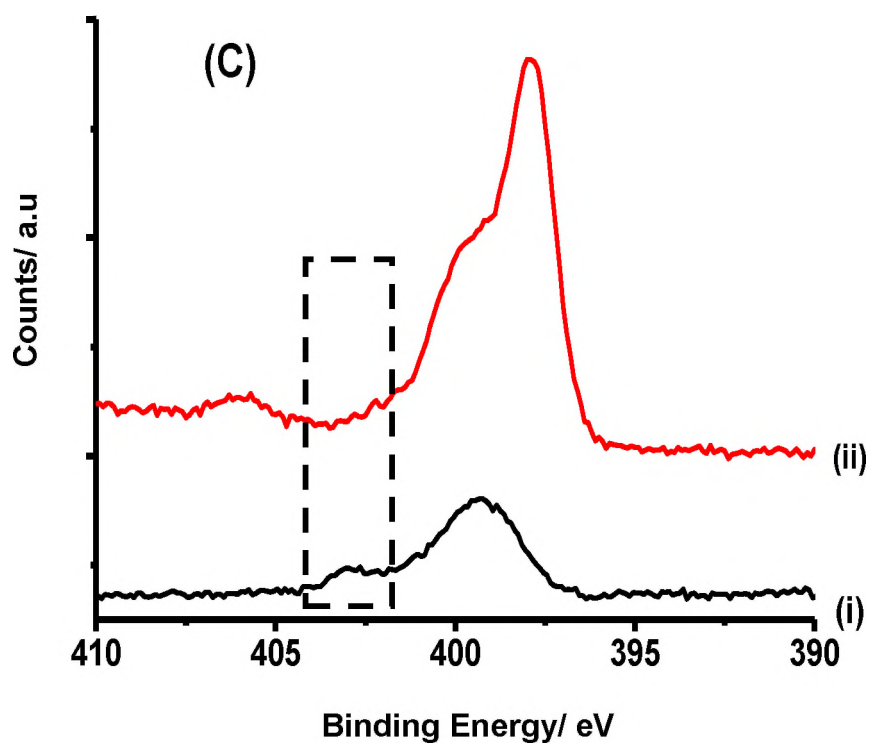
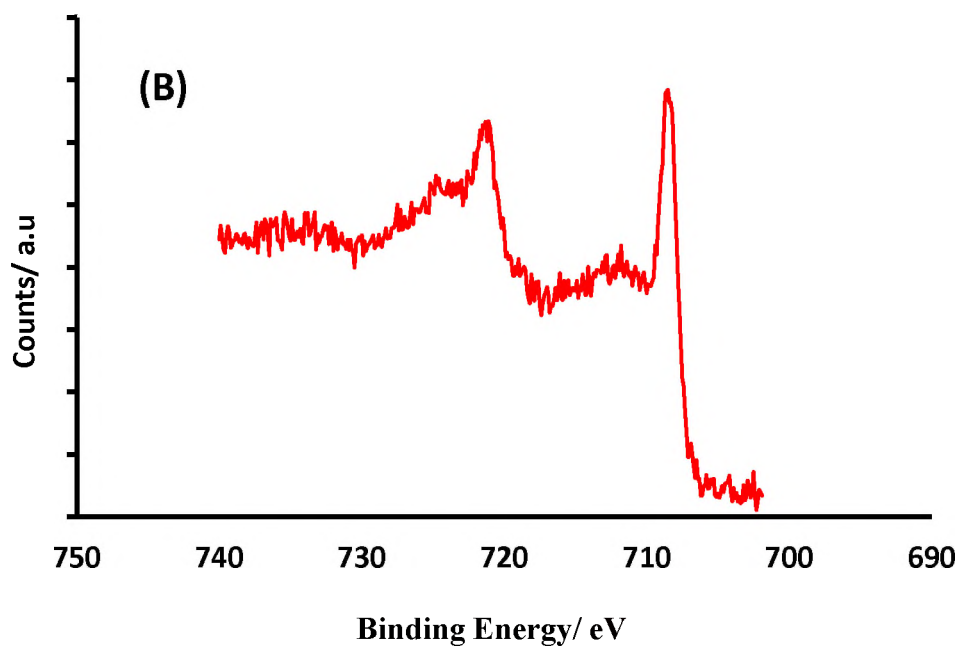
Fig. 4.5: SECM images of (A) GCE after grafting and (B) GCE after grafting and click chemistry with alkynyl FePc. Image obtained with 15 μm diameter UME Pt tip in 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M KCl at 0.15 V vs Ag/AgCl.

4.1.4 Characterization by XPS

For XPS analyses, a glassy carbon plate was modified by employing electrochemical grafting and click chemistry as carried out for the GCE and XPS was used to characterize each stage of modification. The wide scans of the bare plate and the plates with immobilized phenyl azide groups and phenyl azide groups clicked with alkynyl FePc are illustrated by Fig. 4.6A (i), (ii) and (iii) respectively. The presence of the C(1s) peak is self-explanatory and the O(1s) peak detected on the bare plate which would probably be due to adsorbed oxygen as discussed in chapter 3. The wide scan of the grafted GC plate shows the appearance of the N(1s) peak at a binding energy of 399.5 eV which confirms the success of the grafting process. However, observation of Na(1s) and F(1s) (Auger included) indicates the presence of precursors NaNO_2 and HBF_4 which were

used in the synthesis of the diazonium salt. Following the click chemistry reaction, Cu(2p_{3/2}) and Cu(2p_{1/2}) peaks are observed at binding energies of approximately 934.8 eV and 943.7 eV respectively. The observance of the Cu(2p) peak is likely a result of adsorption of copper during the immersion in the alkynyl FePc solution as it catalyzes the click reaction. The N(1s) peak is still observed at a binding energy of 399.5 eV for the clicked electrode which will be further analyzed by deconvolution of the high resolution spectra.





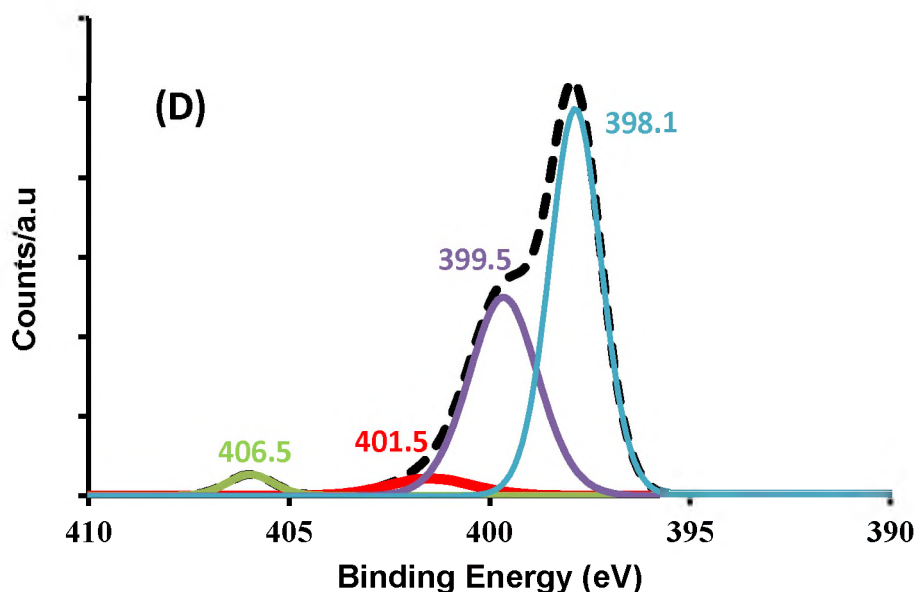


Fig. 4.6: (A) XPS wide scans of (i) bare GCE, (ii) grafted GCE and (iii) grafted GCE after click chemistry with alkynyl FePc. High resolution XPS spectrum of (B) Fe(2p), (C) N(1s) for (i) GCE after grafting and (ii) grafted GCE after click chemistry with FePc and (D) peak fitting for Fig. 4.6C(ii).

The high resolution spectrum of the Fe is illustrated by Fig. 4.6B in which two prominent peaks are observed at binding energies of 721.5 eV and 708.7 eV and are attributed to Fe(2p_{1/2}) and Fe(2p_{3/2}) respectively which is confirmed by other literature reports [99, 100]. This result confirms the presence of the alkynyl FePc after the click reaction. Fig. 4.6C shows the high resolution spectra of the N(1s) region for the grafted and clicked glassy carbon plates which proves the success of the grafting and 'click' reactions carried out. In Fig. 4.6C (i), the characteristic peak attributed to the central azide nitrogen possessing weak electron density (positively charged N; Scheme 1.1) is observed at a binding energy of 403.6 eV [99, 101-103]. Referring back to XPS results

reported in Chapter 3, the difference in the binding energy observed for this azide peak is likely due to the difference in the chemical environment of the nitrogens. The analysis involving QDs also has a contribution from the nitrogens of the GSH-capping. The peak observed at a binding energy of 399.5 eV is attributed to the azide groups and results from the overlapping signals of the nitrogen groups adjacent to the central nitrogen (N and N⁻) [39]. The N(1s) high resolution analysis results obtained after click chemistry are illustrated by Fig. 4.6C (ii) where three peaks are observed. However, after the deconvolution of Fig. 4.6C (ii), four signals were observed (Fig. 4.6D). The peak due to the central azide nitrogen on the grafted glassy carbon plate observed at a binding energy of 403.6 eV is no longer observed which confirms the success of the click reaction. The more prominent peak at a binding energy of 398.1 eV is attributed to the pyrrolic and aza-nitrogens of the FePc. The peak observed at a binding energy of 399.5 eV which is also observed in the grafted layer may be due to a combination of the nitrogen groups adjacent to the central nitrogen of the azide groups, pyrrolic and aza-nitrogen groups from the Pc and the nitrogen groups of the triazole ring [39, 55]. The peak at 406.5 eV which appears to be broader and at a higher binding energy is likely a π - π^* satellite peak resulting from the intense conjugation of the phthalocyanine ring (C-N and C=N signal). Literature reports attribute the peak at a binding energy of 401.5 eV to the unreacted aza-nitrogen groups that lie next to the central nitrogen with the weak electron density. Upon deconvolution of the spectrum, the aforementioned peak was observed with the implication that some aza-nitrogen groups had not reacted with the terminal alkyne groups of the Pc.

4.2 Adsorption of QDs-based electrocatalysts

4.2.1 Scanning electrochemical microscopy (SECM)

Fig.4.7 shows the approach curves obtained from the analysis of the different electrode surfaces in a ferricyanide solution. The GSH-capped QDs and azide-functionalized QDs demonstrated insulating behavior as expected. The bare glassy carbon plate and the ones modified with the alkynyl FePc alone and clicked FePc-QDs were, on the other hand, conducting in this solution most likely due to the presence of the FePc species. In order to compare different methods of allowing the QDs and alkynyl FePc to interact, a premixed solution of alkynyl FePc with QDs was tested in the ferricyanide solution and the conductivity was lower compared to when the two are chemically linked in clicked FePc-QDs. In addition, the alkynyl FePc alone showed almost similar conductivity to when mixed with the QDs. When comparing the SECM results obtained here for clicked FePc-QDs to that in **Fig. 4.4**, the likelihood of the differing behavior with regards to conductivity of the clicked alkynyl FePc may be a result of orientation. In this case the click reaction between the azide-QDs and the alkynyl FePc is performed before electrode modification whereas in the previous case, the alkynyl FePc was clicked directly onto the glassy carbon plate. As previously mentioned, the terminal alkyne groups of the FePc may be bonded through one or more peripheral substituents thus in this case, the Fe of the FePc may be highly exposed due to the nature of the bonding between the azide groups and the terminal alkyne groups of the FePc. The distance between the UME and the substrate has been said to possibly play a role in the currents measured [39] as well as whether or not the results obtained will suggest that the electrocatalyst is conducting or not in the ferricyanide solution.

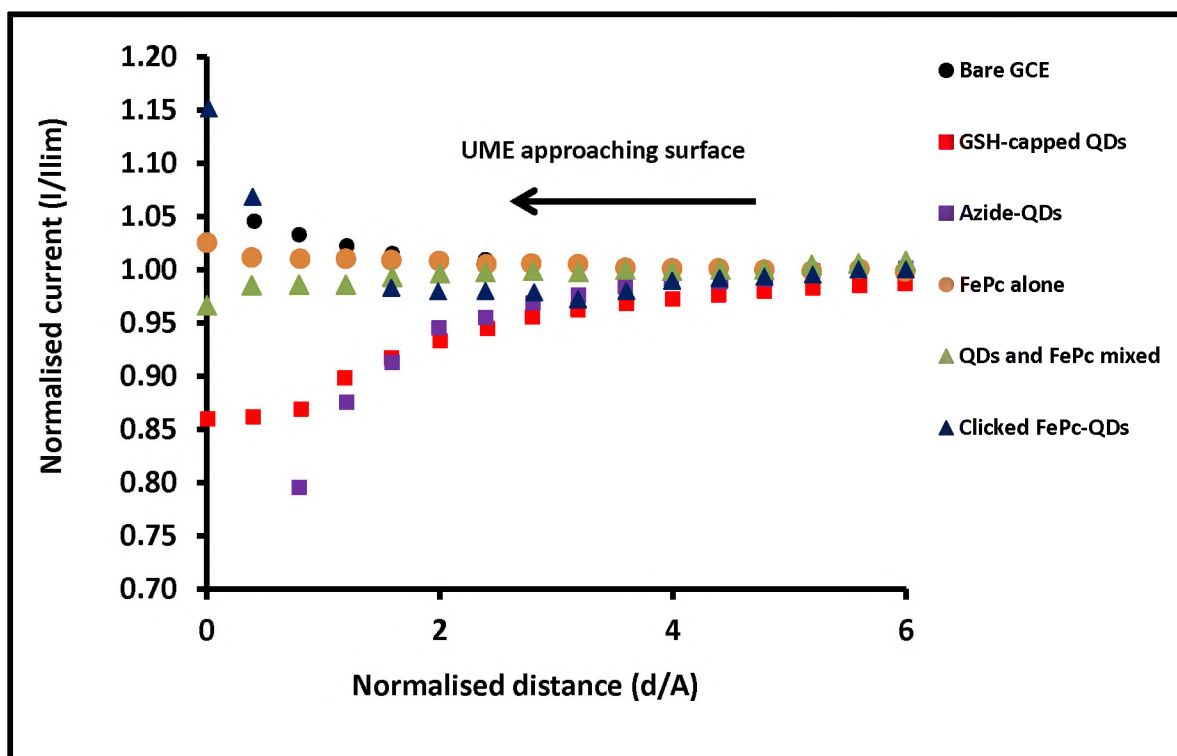


Fig.4.7: Approach curves of different electrode surfaces in 2 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at -1.2 V vs Ag/AgCl.

4.2.2 Cyclic (CV) and Differential pulse (DPV) voltammetry.

Fig. 4.8 shows the cyclic voltammograms of a glassy carbon electrode modified with QDs alone, the azide QDs, alkynyl FePc, premixed QDs-FePc and the clicked FePc-QDs as the modifiers tested in a ferricyanide solution. The electrode that demonstrated larger cathodic to anodic peak separation (ΔE) was the one modified with the azide-QDs and no peaks were observed for the premixed FePc-QDs as shown in Table 4.1. The lower the ΔE value, the more conducting the electrocatalyst is in the electrolytic solution. It was concluded that the alkynyl FePc alone was the most conducting followed by clicked FePc-QDs in the ferricyanide solution. It is important to note that this technique provides information on the changes occurring at the electrode surface. It is a method

of confirming that the nature of the electrode surface has been altered due to the differences in modifiers used. The observation made after running cyclic voltammetry analyses contradicted the results obtained in SECM analyses where the clicked FePc-QDs were more conducting than the alkynyl FePc at shorter distances between the UME and the substrate but the reverse is true at larger distances. Thus the superiority of the clicked FePc-QDs over the alkynyl FePc alone is distance dependent for SECM.

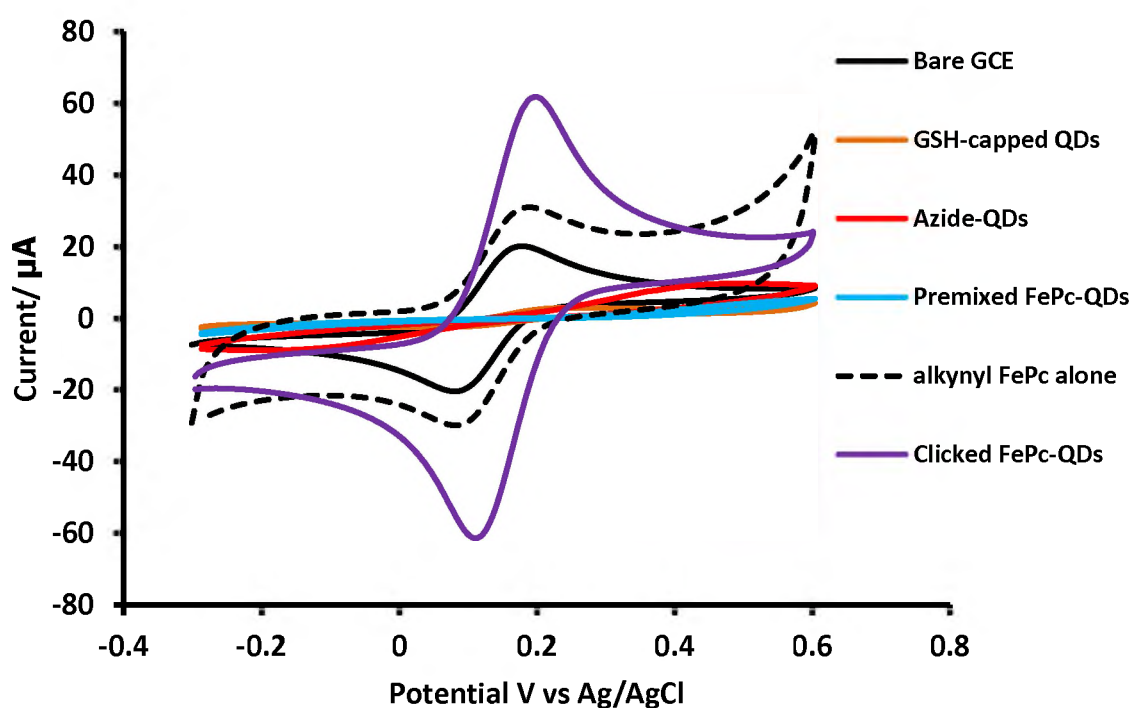


Fig. 4.8: Modified electrodes in a 2 mM ferricyanide solution with KCl as the supporting electrolyte. Scan Rate: 50 mV/s.

Table 4.1: Potential difference of each electrode tested in 2 mM $K_4[FeCN_6]$.

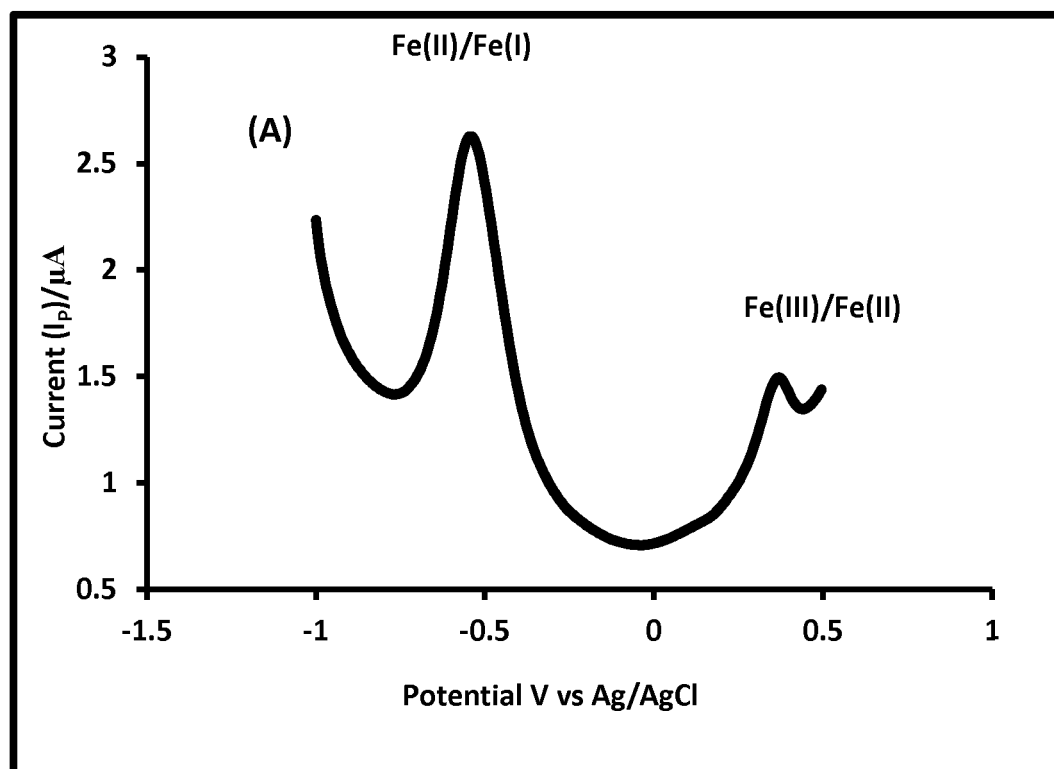
Electrode	$\Delta E/mV$ (vs Ag AgCl)
Bare	86
GSH- QDs	172
Azide-QDs	303
Alkynyl FePc alone	71
Premixed FePc-QDs	a
clicked FePc-QDs	85

a = no peaks observed

The modified electrodes were also tested in a 0.1 M NaOH solution as this solution is used to test for the analyte of interest. The peaks due to alkynyl FePc were identified using differential pulse voltammetry (**Fig.4.9**) as a result of inconclusive results obtained from cyclic voltammetric analyses.

Fig. 4.9A shows two peaks for adsorbed alkynyl FePc. The more prominent peak is observed at -0.54 V with a peak current of 2.5 μA and the other peak is observed at 0.38 V with a peak current at 1.4 μA for alkynyl FePc alone, **Fig. 4.9A**. The peak at negative potentials may be attributed to the Fe(II)/Fe(I) redox pair and the peak at positive potentials may be attributed to the Fe(III)/Fe(II) redox pair [126-128]. It can therefore be expected that the Fe(II)/Fe(I) redox pair will catalyze the reduction of paraquat. The difference in the redox potentials of the Fe(II)/Fe(I) redox pair using CV (**Fig. 4.2B (iii)**) and DPV (**Fig. 4.9A**) is likely due to the fact that DPV is more sensitive than CV. Moreover, the differences in the electrode modification may play a vital role. For **Fig. 4.2B (iii)**, the Fe(II)Pc is clicked on the electrode prior to being tested whereas in **Fig. 4.9A**, the alkynyl FePc is adsorbed onto the electrode surface. A study has shown that sensitivity of a technique (particularly with DPV compared to CV) may change the

potentials observed for a given reactant immobilized on an electrode [129] especially when strongly adsorbed onto the electrode surface.



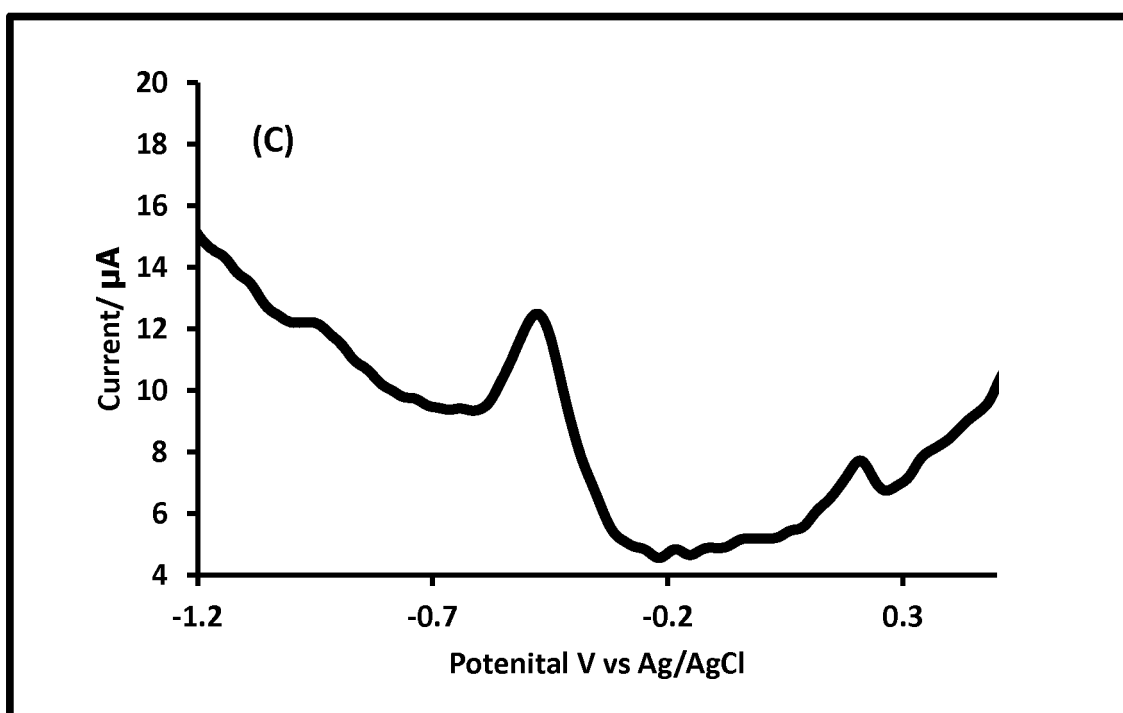
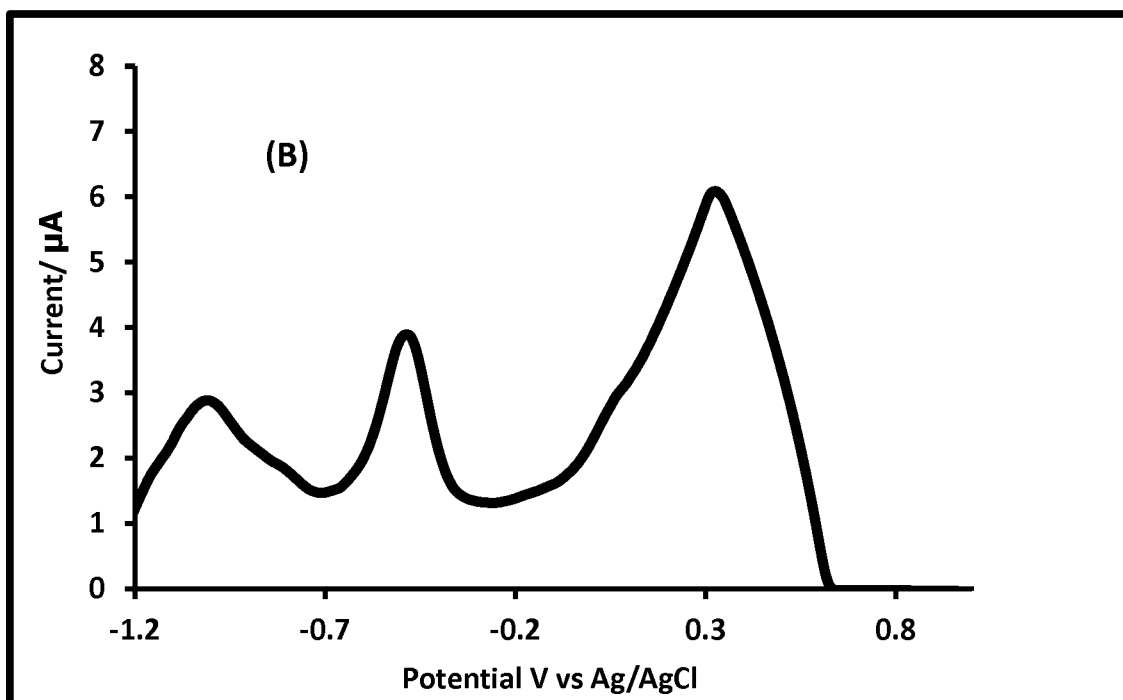


Fig. 4.9: DPV of (A) alkynyl FePc, (B) GSH-capped CdSe/ZnS QDs and (C) clicked FePc-QDs in 0.1 M NaOH.

In order to assign peaks when the alkynyl FePc and QDs are conjugated, the QDs were analyzed using differential pulse voltammetry and the results are shown in **Fig. 4.9B**. Three peaks were observed at potentials of -1.07 V, -0.52 V and +0.29 V. The peaks at -1.07 V and -0.5 V may be attributed to the reduction of the ZnS shell and the CdSe core, respectively [130]. The peak at +0.29 V can be associated with the oxidation of Cd and therefore may be assigned to the oxidation of the CdSe core [131]. **Fig. 4.9(C)** shows the results obtained from differential pulse voltammetry analysis of the clicked FePc-QDs in a 0.1 M NaOH solution. The shapes of the peaks are similar to those for alkynyl FePc alone in **Fig. 4.9(A)**, and it is possible that they are overlapping with the DPV peaks of the QDs. The peak near -0.5 V may be due to the Fe(II)/Fe(I) redox pair in comparison with alkynyl FePc alone.

4.3. Conclusion

Electrochemical techniques and XPS were used in order to characterize the modified glassy carbon electrode surfaces. It was evident from the obtained results that

CHAPTER 4: ELECTRODE MODIFICATION AND CHARACTERIZATION

modification was successful. More importantly, the click chemistry reactions proved to be successful. In addition, the behavior of the modified electrodes in the solution in which the electrocatalytic studies would be carried out provided information on the species present on the electrode surface, further confirming the success in the modification of the glassy carbon electrode made.

Chapter 5:

Electrocatalysis

This chapter will focus on the electrocatalytic ability of the electrocatalysts synthesized and characterized in this work. Click chemistry has been the main focus of producing these electrocatalysts with the aim of improving their electrocatalytic ability. The test analytes used are hydrazine and paraquat which have been described. Hydrazine was used as the test analyte when the alkynyl FePc was clicked directly onto the electrode as opposed to when clicked onto the QDs to be discussed below. Attempts to use hydrazine as a test analyte for electrodes modified with QDs were unsuccessful and an analyte which could be reduced such as paraquat was employed.

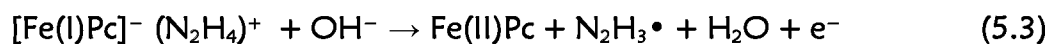
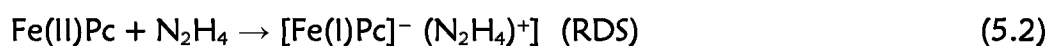
5.1. Electrooxidation of hydrazine

5.1.1. Cyclic Voltammetry

For the electrocatalysis of hydrazine, the electrode modified as shown in **Scheme 4.1** is used which involves the click chemistry reaction between immobilized phenyl-azide groups on the electrode and terminal alkyne groups on the phthalocyanine. Hydrazine has been reported as a test analyte in a few studies [39, 73, 132, 133]. **Fig. 5.1** shows comparative CVs for (i) the bare GCE, (ii) grafted GCE and (iii) grafted GCE after click chemistry with alkynyl FePc in the presence of hydrazine (5 mM in 0.1 M NaOH) at a potential window of -0.8 V to 0.8 V vs Ag/AgCl. The results showed that the bare and grafted GCE were not able to detect hydrazine. The adsorbed alkynyl FePc was able to oxidise hydrazine with double oxidation being observed at 0.3 V with a maximum peak current of 40 μ A, **Fig. 5.1A**. The grafted GCE clicked with alkynyl FePc also showed a double oxidation peak at approximately 0.1 V with a maximum peak current of 76.8 μ A. This shows evidence of improved currents and lowered potentials which was the

aim of the construction of the electrocatalysts reported. The electrooxidation of hydrazine in this work is due to the Fe(II)Pc as the active electrocatalyst [55, 73].

The involvement of the Fe^{II}/Fe^I couple in the electrochemical oxidation of hydrazine on electrodes modified with hydrazine has been proposed as shown in Eqns. 5.1-5.3 [74-77]:



The proof of the involvement of the Fe^{II}/Fe^I in this work was through the observation of the Fe^{II}/Fe^I couple in Fig. 4.2B at approximately -0.38 V. This potential differs from that observed in DPV as already explained above. The potential for the oxidation of hydrazine is in the stability range of the Fe^{II}/Fe^I couple, hence the involvement of this redox couple in the electrooxidation of hydrazine.

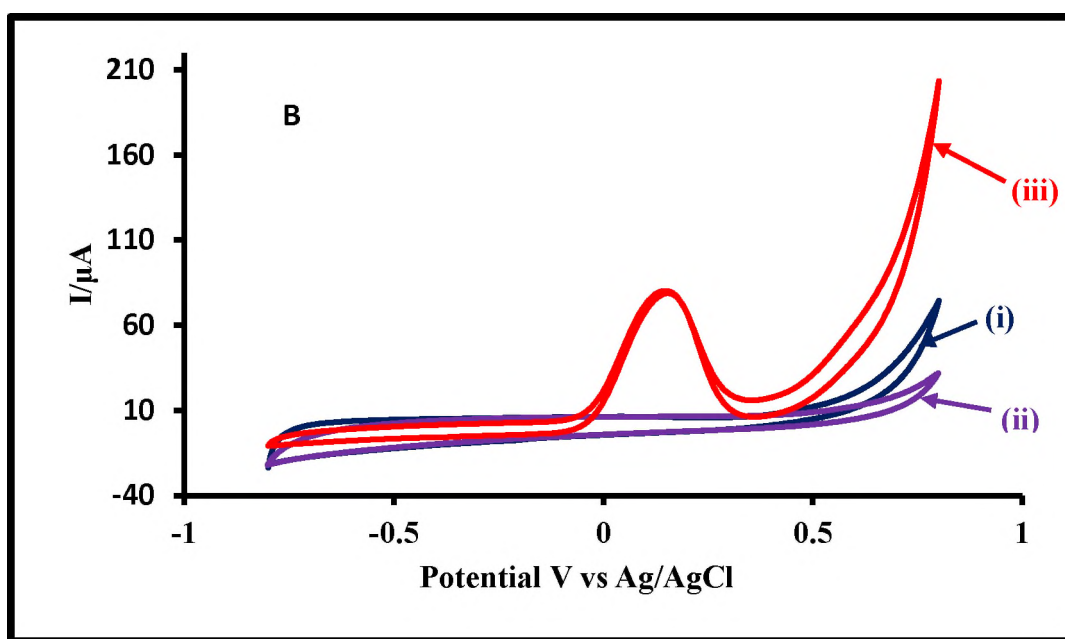
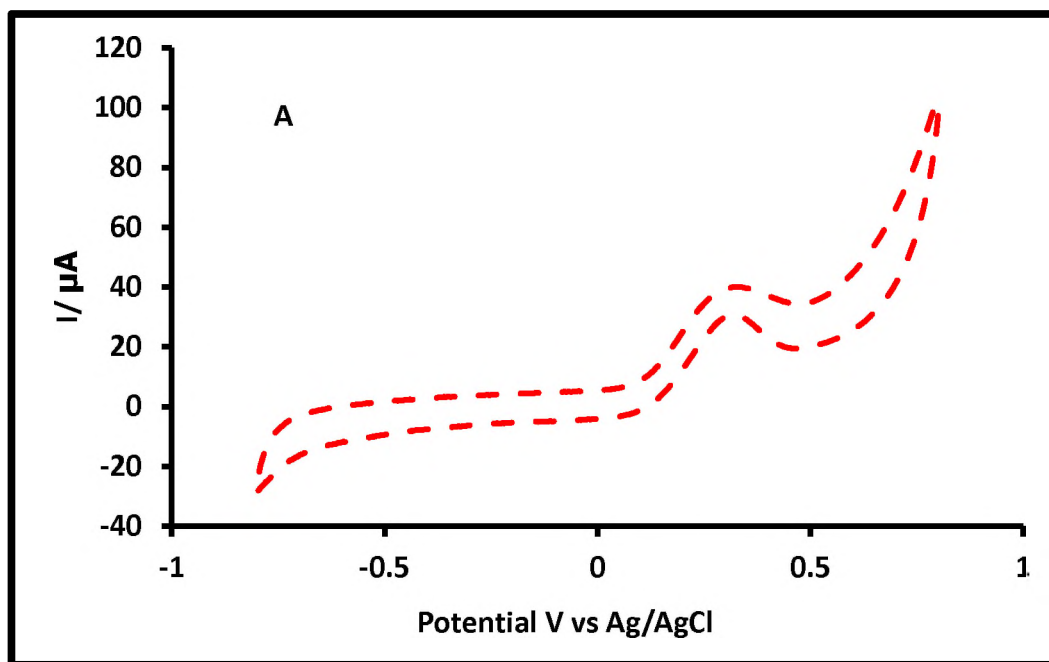
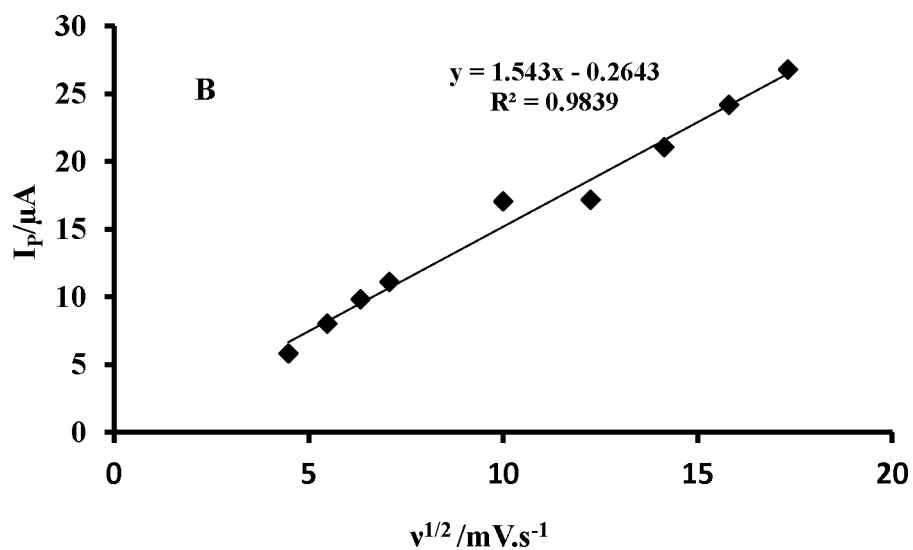
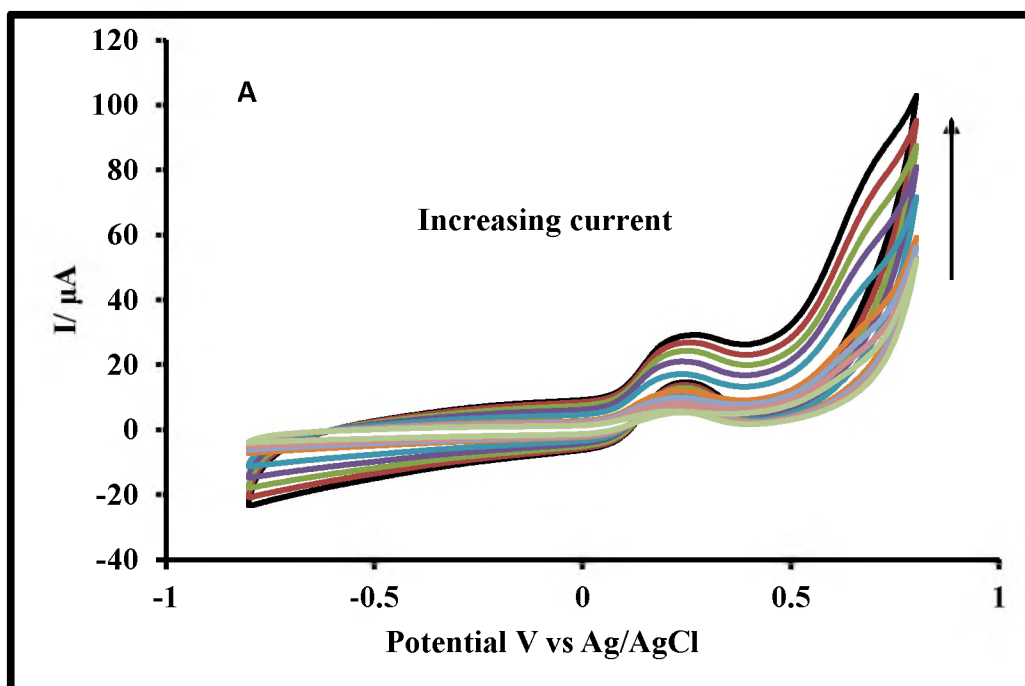


Fig. 5.1: CV of (A) FePc adsorbed onto a GCE and (B) (i) bare GCE, (ii) grafted GCE and (iii) grafted GCE after click chemistry with alkynyl FePc in 5 mM hydrazine in 0.1 M NaOH. Scan Rate = 100 mV/s.

5.1.2 Electrode kinetics



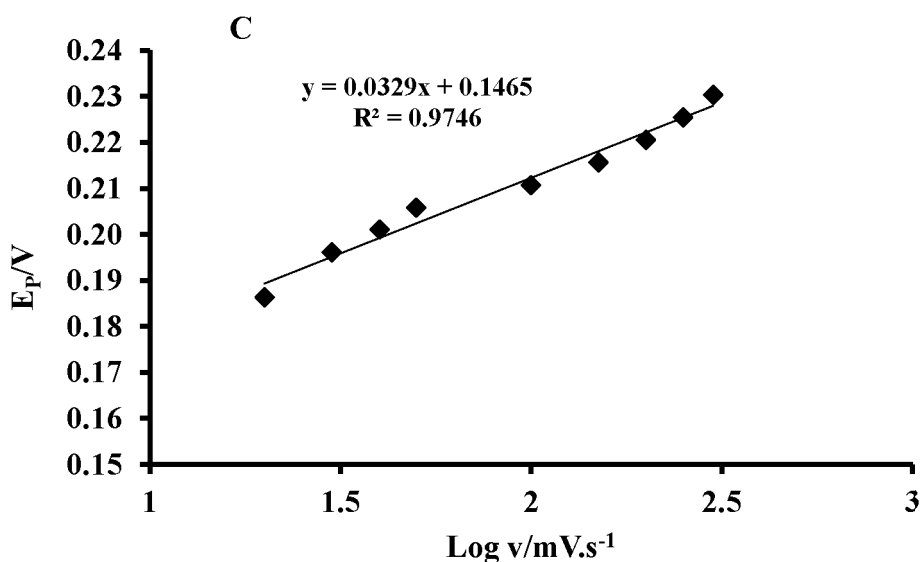


Fig. 5.2: (A) CV of current response with changing scan rate (20-50,100,150,200,250, and 300 mV.s^{-1}). (B) Plot of current ($\text{I}/\mu\text{A}$) vs square root scan rate ($v^{1/2}/\text{mV.s}^{-1}$) (C) Plot of peak potential (E/V) vs $\text{log } v/\text{mV.s}^{-1}$ vs Ag/AgCl, in 1 mM hydrazine in 0.1 M NaOH.

Here, the clicked alkynyl FePc is used to determine the electrode kinetics as it has been shown that it is a better electrocatalyst compared to the adsorbed FePc. Fig. 5.2A shows the cyclic voltammograms obtained as a result of changing scan rate. From these results, plots illustrated by Fig. 5.2B and 5.2C are obtained showing a linear relationship between current and the square root of scan rate as well as peak potential versus the log of scan rate for hydrazine oxidation, respectively. The plots in Fig. 5.2B confirm that the catalytic oxidation of hydrazine is a diffusion controlled process. The relationship between peak potential and log scan rate for an irreversible diffusion-controlled process is given by Eqn. (5.4) [134]:

$$E_p = \frac{2.3 RT}{2(1-\alpha)n_\alpha F} \log v + K \quad (5.4)$$

where α is the transfer coefficient, n_α is the number of electrons involved in the rate determining step, v is the scan rate, K is a constant, R is the universal gas constant and T is the temperature (298 K). The plot of E_p versus $\log v$ (Fig. 5.2C) gave a linear relationship and the Tafel slope was determined as 65.8 mV decade⁻¹ which is given by 2 x the slope of E_p vs $\log v$ Eqn. (5.5):

$$E_p = \frac{b}{2} \log v + K \quad (5.5)$$

A Tafel slope of near 60 mV/decade (as is the case in this work) is obtained when $\alpha = 1$, and one electron is transferred during the rate-determining step [135].

5.1.3 Chronoamperometry

Chronoamperometry allows for the determination of the relationship between concentration of solutes in solution and currents produced. The relationship determined can provide information such as the detection limits of the electrocatalyst as well as the sensitivity of detection. Low Detection limit values imply high sensor efficiency. In other words, the electrocatalyst should respond to even the lowest analyte concentrations. Fig. 5.3A shows the response of the grafted glassy carbon electrode clicked with the alkynyl FePc towards different concentrations of hydrazine. A 0.1 M NaOH solution was continuously stirred as 0.1 mM of hydrazine was added every 50 seconds for a total of 1000 seconds. The potential was held constant at 0.1 V vs Ag/AgCl. From this result, the response current (I/ μ A) was plotted against concentration (mmol) and a

linear relationship was observed (Figure 5.3B) ($R^2 = 0.9991$). The sensitivity of the sensor was determined as $15.38 \mu\text{A mM}^{-1}$ and the limit of detection (LoD) as $1.09 \mu\text{M}$ which was obtained using the $3\delta/\text{slope}$ ratio notation, where δ is the standard deviation and 3 is a recommended factor that gives a practical confidence of 90% to 99.7% [136-138]. The LOD of $1.09 \mu\text{M}$, is an improvement when compared to other electrodes modified with phthalocyanines for the electrooxidation of hydrazine which are summarized in Table 5.1. [54, 55, 73].

Table 5.1: Summary of detection limits of other phthalocyanine-based hydrazine electrocatalysts in different media compared to results obtained in this work.

Electrode	Medium	LoD/ μM	Technique	Ref.
Electro-clicked GCE with FePc	pH 8 buffer	6.4	Chronoamperometry	[54]
Axially ligated FePc with pyridine on GCE	0.1 M NaOH	10	Chronoamperometry	[55]
4-mercaptopyridine on gold	Tap water sample	5.0 & 11	OSWV & CV	[73]
Grafted GCE clicked with alkynyl FePc	0.1 M NaOH	1.09	Chronoamperometry	This work

^aOSWV = Osteryoung Square Wave Voltammetry.

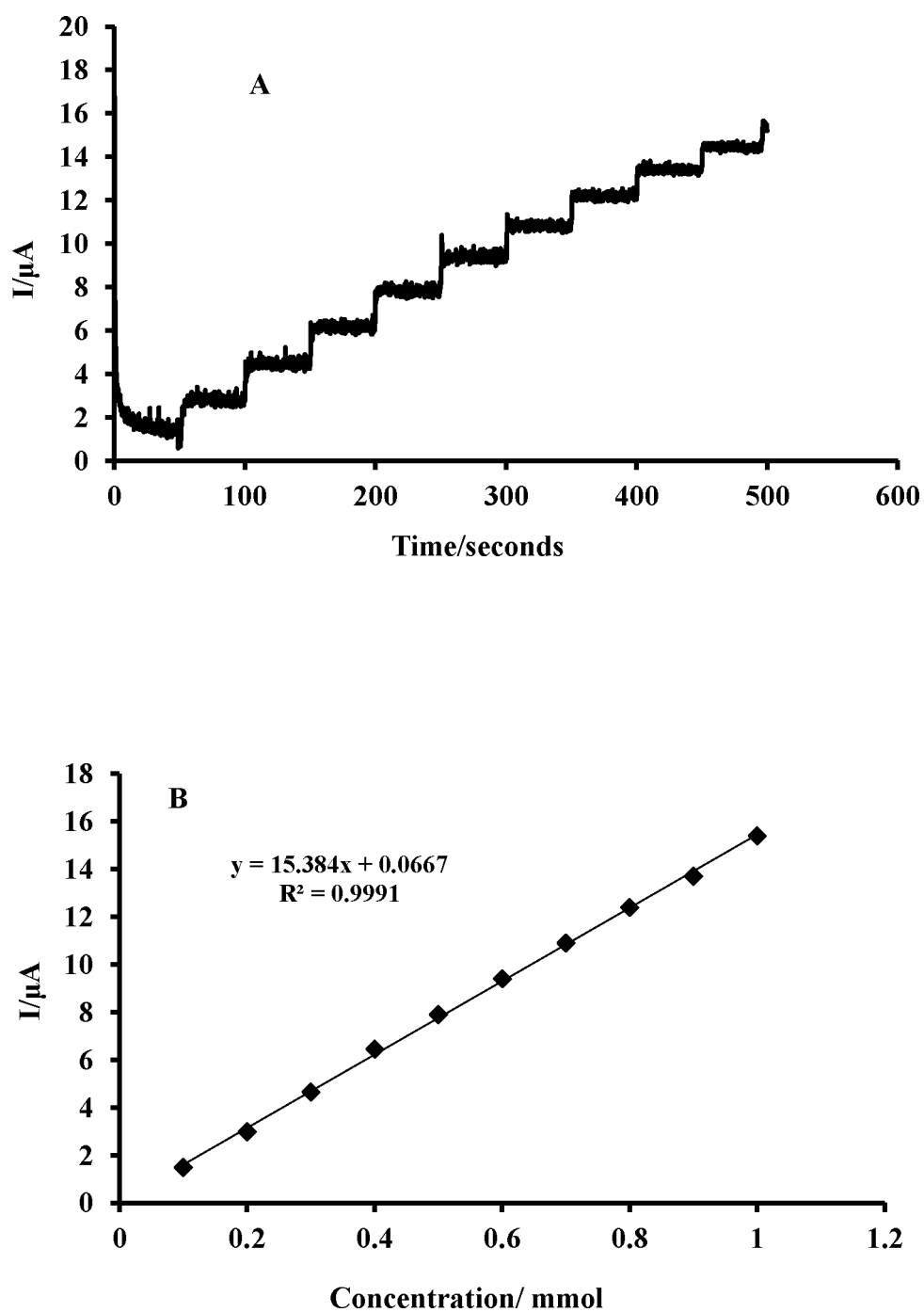


Fig. 5.3: (A) Amperometric response of grafted GCE after click chemistry in the constantly stirred 0.1 M NaOH during successive additions of 0.1 mM hydrazine into the NaOH solution at 0.1 V vs Ag/AgCl. (B) Plot of peak current (μA) vs concentration (mmol) from 0.1 mmol- 1.2 mmol.

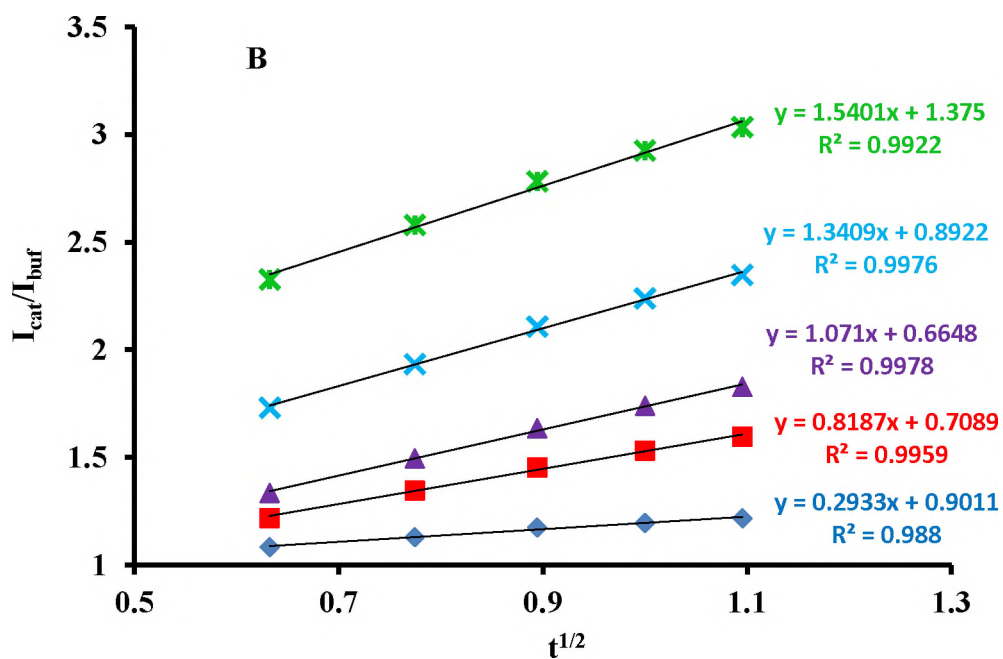
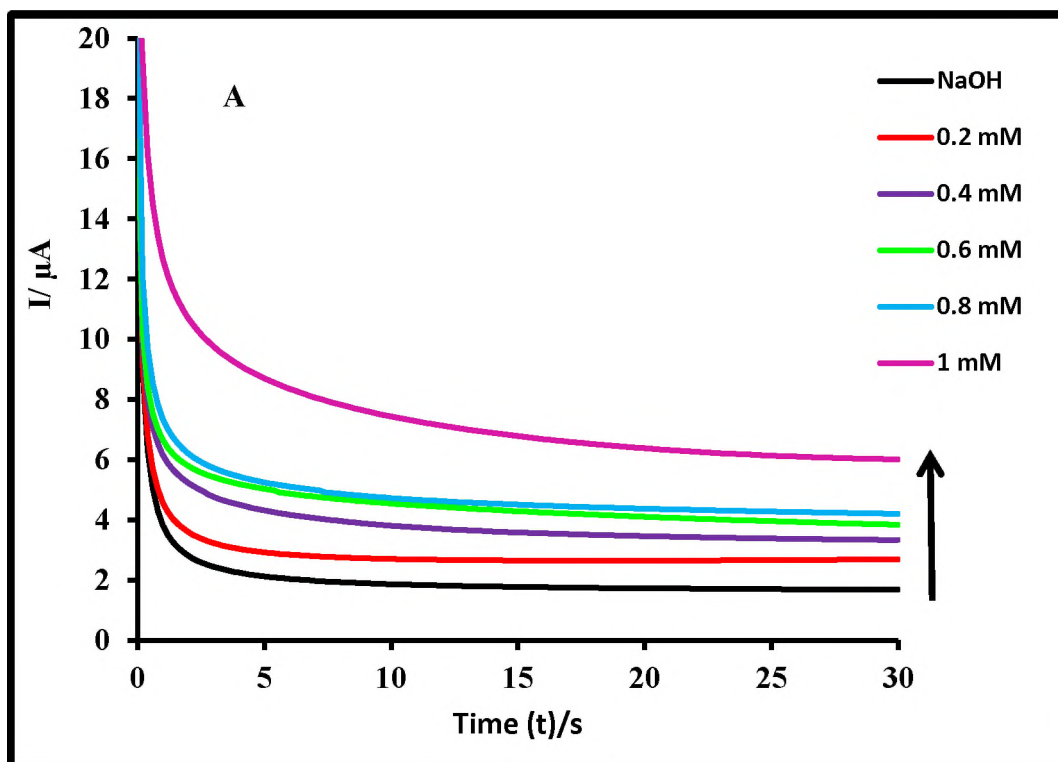
Fig. 5.4A shows chronoamperograms at different concentrations of hydrazine. The catalytic current (I_{cat}) is dominated by the rate at which hydrazine is oxidized on the modified-GCE. The slopes of the plots of (I_{cat}/I_{buf}) versus $t^{1/2}$ (Fig. 5.4B) were employed in order to determine the rate constant according to Eq. (5.6) [139].

$$\frac{I_{cat}}{I_{buf}} = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (k_{cat} C t)^{1/2} \quad (5.6)$$

where I_{cat} and I_{buf} are currents in the presence and absence of hydrazine respectively, k_{cat} is the catalytic rate constant, C is the concentration of hydrazine and t is the time elapsed in seconds. By plotting the square of the slopes obtained from Fig. 5.4B versus concentration of hydrazine, a linear relationship may be observed (Fig. 5.4C) and is represented by Eqn. (5.7):

$$y = 2,7784 [\text{hydrazine}] \left(\frac{s^{-1}}{mM} \right) - 0.4238 s^{-1}, \quad R^2 = 0.9912 \quad (5.7)$$

where the slope of this plot is equivalent to πk . The value of k_{cat} in this work was found to be $8.84 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. This value is within the range of k_{cat} values $\sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$ reported for the detection of hydrazine on phthalocyanine modified electrodes [140, 141].



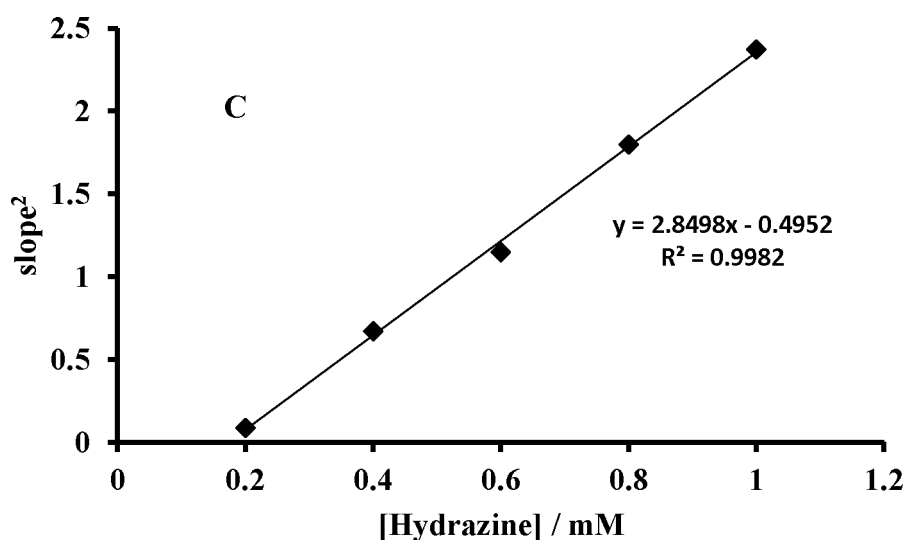


Fig. 5.4: (A) Chronoamperometric response hydrazine in 0.1 M NaOH (0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM and 1 mM). (B) Plots of $(I_{\text{cat}}/I_{\text{buf}})$ versus $t^{1/2}$ (C) Plot of the squares of the slopes from Fig. 5.3B vs [Hydrazine]. 0.1 V/s vs Ag/AgCl.

5.2. Electroreduction of paraquat

5.2.1. SECM studies

Area scans are generally used to determine how the surface topography changes due to the interaction of the solution with the electrocatalyst on the surface of the electrode. Fig. 5.5 (i)-(iii) show area scans of the QDs alone, FePc alone and azide-QDs clicked with alkynyl FePc in a paraquat solution so obtain an image of the interaction of these potential electrocatalysts with paraquat. The clicked FePc-QDs also show higher currents in paraquat than the other two surfaces tested. This gives some confidence with regards to the potential of the sensor constructed in the work reported.

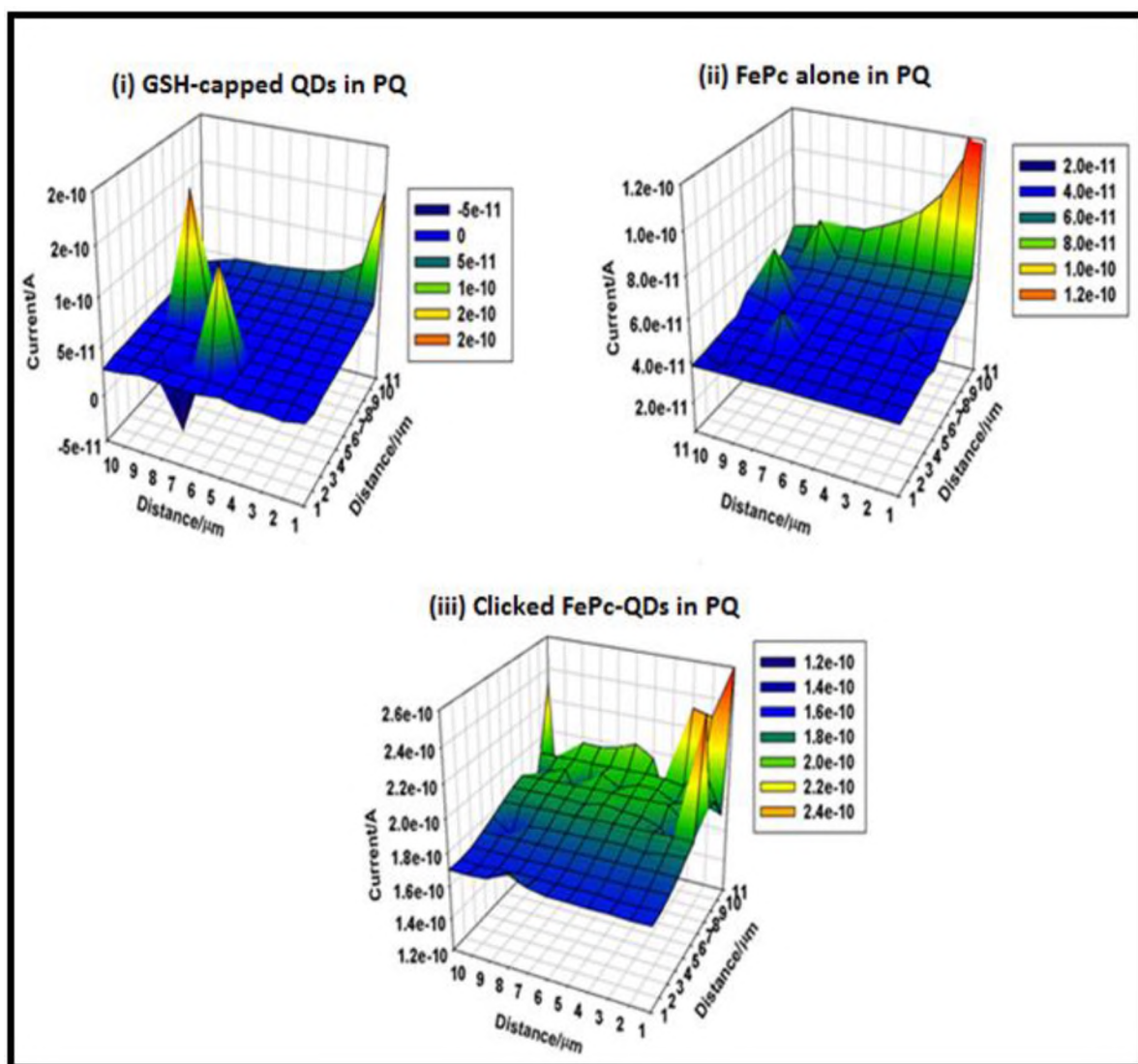


Fig. 5.5: Area scans of (i) GSH-capped QDs, (ii) alkynyl FePc alone and (iii) clicked FePc-QDs in 2 mM paraquat in 0.1 M NaOH solution using a 15 μm UME.

5.2.2. Cyclic voltammetry

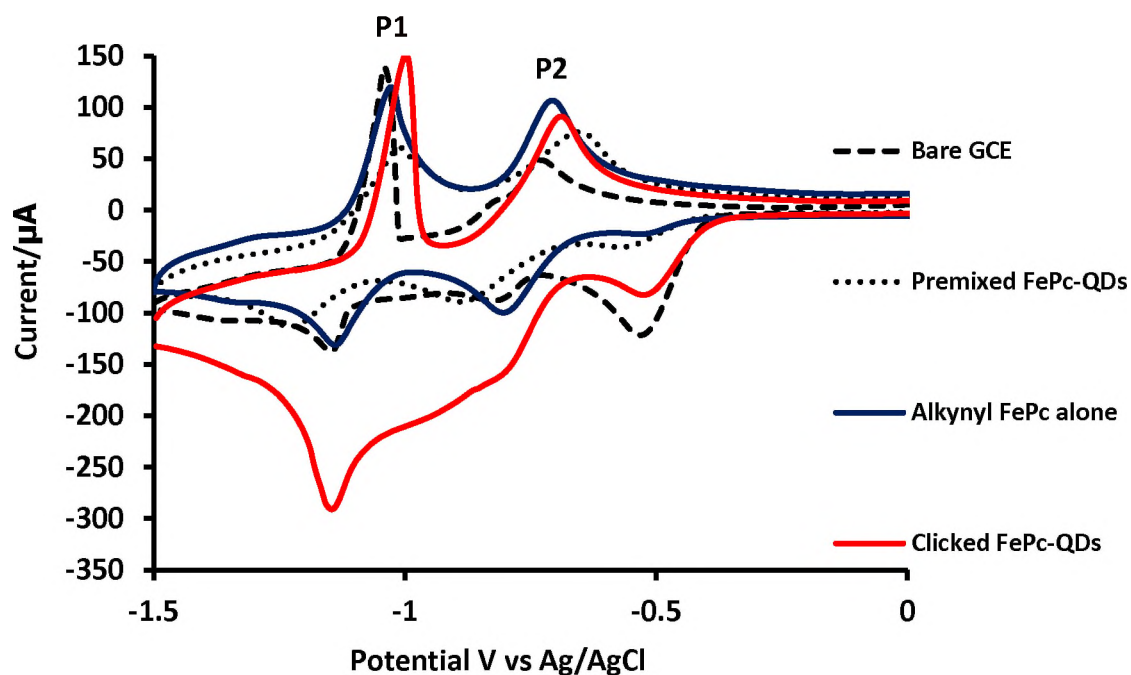


Fig. 5.6: Cyclic voltammograms of bare and modified electrodes in 2 mM paraquat in 0.1 M NaOH. Scan rate: 50 mV/s.

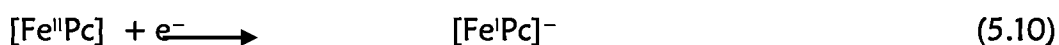
The cyclic voltammograms for the bare and modified electrodes in paraquat are shown in Fig. 5.6. Two redox processes were observed (labeled P1 and P2) on the bare electrode and on the Pc and QDs based electrodes. When the QDs and alkynyl FePc are just mixed with no conjugation reaction to achieve any formal bonding, the current response is weaker than for clicked FePc-QDs, confirming the advantage of using click chemistry as the modification route for the development of electrocatalysts for the detection of paraquat. It can also be concluded that the Fe(II)/Fe(I) redox pair (Fig. 4.2B) catalyzes the electroreduction of paraquat since it is observed in the same potential region (~ -0.3 V) as the paraquat peak P1 are observed (Fig. 5.6).

The double redox activity observed is a result of the simultaneous reduction of the two positively charged nitrogens present in the molecule. The proposed mechanism is shown by Eqns. 5.8, 5.9 [34]:



The first equation is attributed to the peak denoted as **P2** and the second equation is attributed to the peak denoted **P1** (Fig.5.6) [78].

Since it has been established that the Fe(II)/Fe(I) redox pair of the phthalocyanine catalyzes the reduction of paraquat, the mechanism may be illustrated by Eqns. (5.10)-(5.13):



where Fe(II) in Fe(II)Pc is initially reduced (5.10), followed by the adsorption of paraquat (5.11) (confirmed before [19]) and its subsequent reduction (5.12). PQ⁺ would be reduced further in the same manner.

5.2.3 Determination of detection limits

The electrodes modified with alkynyl FePc alone and clicked FePc-QDs were used to for the determination of detection limits in order to determine whether or not combining the FePc with QDs also resulted in improved detection limits. Differential pulse voltammetry was used here as cyclic voltammetry and chronoamperometry proved to be less sensitive. The results obtained are illustrated by **Fig. 5.7A** and **Fig. 5.7B** where the concentrations analyzed ranged between 0.8 and 1.3 μM . The insets show a linear relationship between the concentration and the peak currents for both redox pairs observed upon the electroreduction of paraquat. The limit of detection was determined as explained above using the 3σ -notation. The limit of detection (see **Table 5.2**) for the alkynyl FePc alone (using P2) was found to be of the same order of magnitude as some of the Pc based electrodes reported in literature for the detection of paraquat [19,142]. However, upon testing clicked FePc-QDs, the limit of detection improved compared to alkynyl Pc alone which proves the good potential of this work. The paraquat detection was the lowest for clicked FePc-QDs when compared to literature reports for Pc based electrodes [19,142] as summarized in **Table 5.2**. The Interim Maximum Acceptable Concentration (IMAC) for PQ as a dichloride in drinking water has been reported as 10 $\mu\text{g/L}$ ($3.88 \times 10^{-8} \text{ M}$) [143], which is higher than the value for clicked FePc-QDs determined in this work.

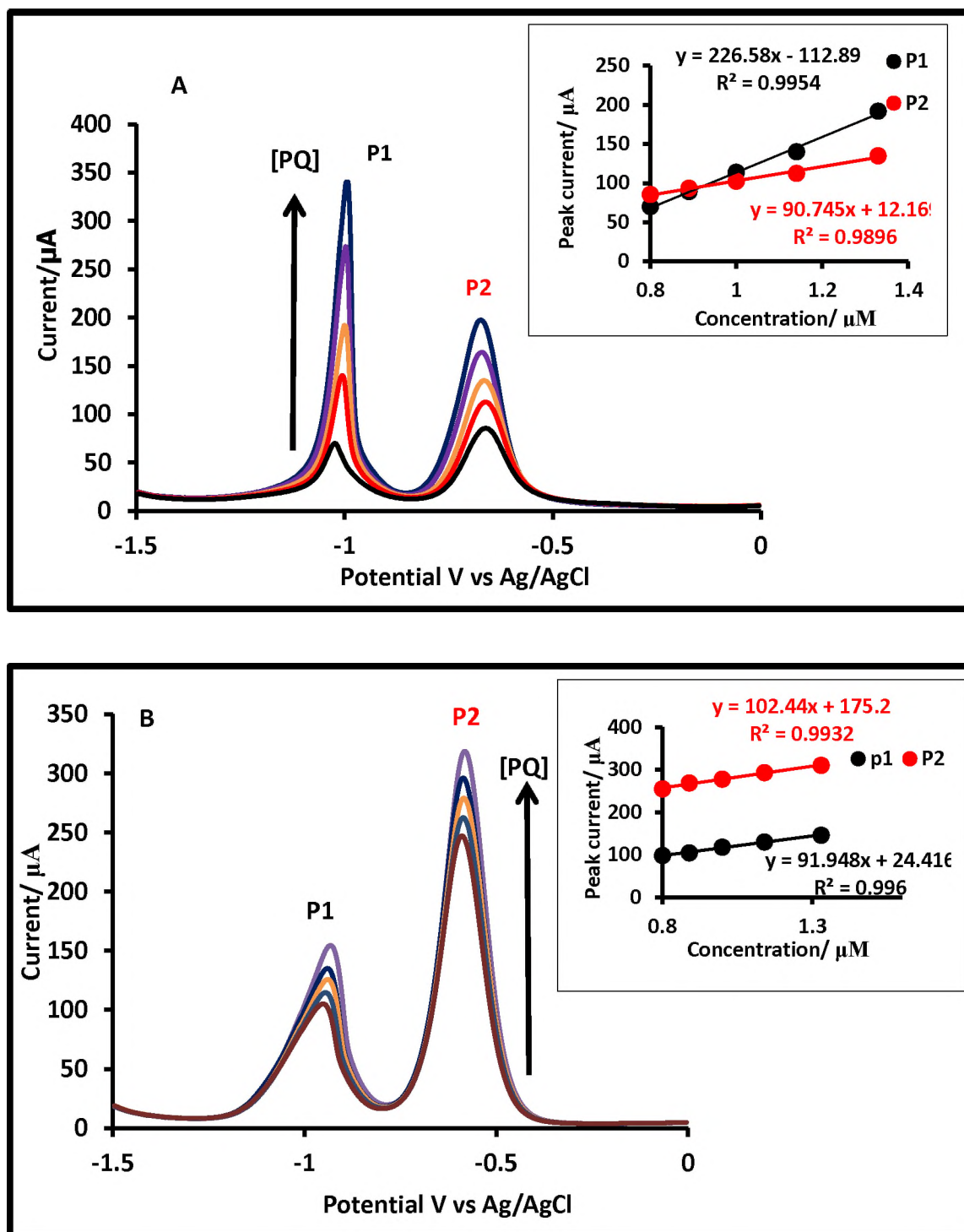


Fig. 5.7: (A) DPV of FePc adsorbed on electrode in 0.1 M NaOH with increasing paraquat concentration and (B) DPV of clicked electrode in 0.1 M NaOH with increasing paraquat concentration. Concentration range = 1.67 μM to 2 μM. Insets: Plots of concentration vs peak current for P1 and P2.

Table 5.2: Summary of results obtained with electrocatalyst using click chemistry on GCE compared with other phthalocyanine-based paraquat electrocatalyst.

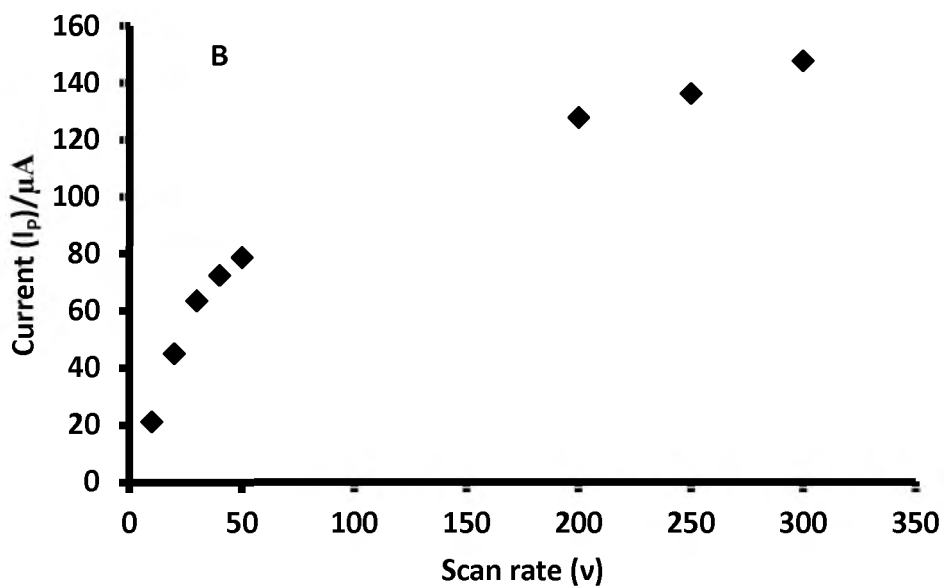
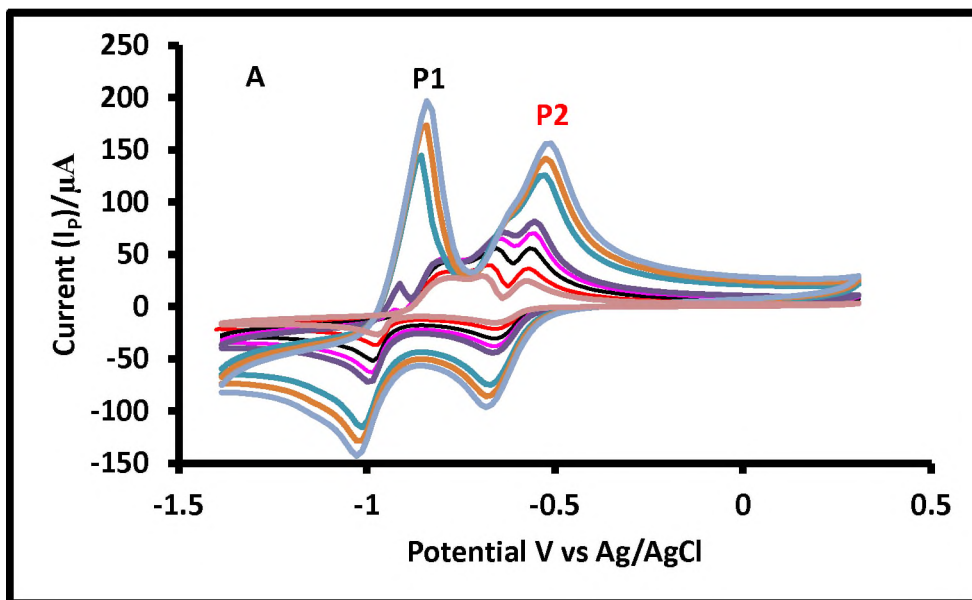
Electrode ^a	LoD/ M	Technique	Reference
rGNS-2/MWCNT/CoTAPc/GCE	3.32×10^{-8}	SWV	[19]
Pc/PGE	26.53 and 88.23×10^{-6}	SWV	[142]
FePc/GCE	P1 = 2.9×10^{-8} P2 = 4.9×10^{-8}	DPV	This work
FePc-CdSe/ZnS QDs-GCE	P 1= 7.99×10^{-9} P 2= 7.17×10^{-9}	DPV	This work

^a MWCNT= multiwalled carbon nanotubes, TAPc = tetraamino phthalocyanine, PGE = pyrolytic graphite electrode

5.2.4 Electrode Kinetics

Fig. 5.8A shows the CVs of the clicked FePc-QDs in paraquat at different scan rates. These results then provide information to plot Fig. 5.8B which shows the relationship between current and scan rate. An exponential increase is observed until a limit is reached and almost levels off from 200 mV/s. This may be a result of slow electron transfer from the electrode surface which would then limit the redox reactions at these high scan rates between the paraquat species and the electrocatalyst [55]. Fig. 5.8C is also derived from Fig. 5.8A and shows the plot of peak current versus the square root

of the scan rate which yielded a linear plot. The relationship indicates that the process is diffusion controlled [40] rather than being an adsorption process as observed in previous studies involving paraquat detection [19].



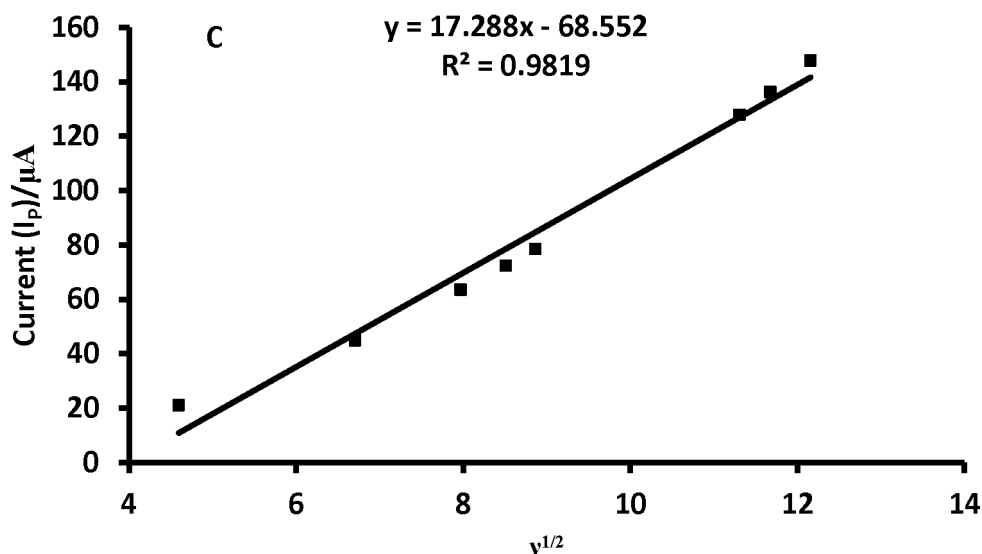


Fig.5.8: (A) Cyclic voltammograms of clicked FePc-QDs in 2 mM paraquat solution obtained with scan rates of 10, 20, 40, 60, 80, 100, 150, 200, 250 and 300 mV/s. (B) Plot of I_p vs scan rate (v) and (C) Plot of I_p vs the square root of the scan rate ($v^{1/2}$).

5.3. Conclusion

It has been proven by the results reported and discussed that click chemistry is a superior electrode modification technique as well as conjugation technique as it results in electrocatalysts with improved sensitivity and detection limits for hydrazine when compared to adsorbed alkynyl FePc. With respect to hydrazine detection, the use of covalent bonding for the immobilization of the phenyl azide groups and the phthalocyanine resulted in a reliable electrocatalyst for hydrazine electrooxidation. Similar results were obtained for the electrocatalyst produced via click chemistry for the electroreduction of paraquat where results showed an improvement compared to other phthalocyanine based paraquat electrocatalysts. It has also been demonstrated that click

chemistry may be applied for different molecules with a common goal of improvement of functionality and stability of electrocatalysts.

Chapter 6:

Final conclusions

Tetrakis(5-hexynoxy)Fe(II) phthalocyanine was successfully synthesized and characterized. In the UV spectrum specifically, the observations made were characteristic of Fe(II)phthalocyanines. The process of electrochemical grafting and click chemistry on glassy carbon electrodes was also successful and fully characterized. Compared to similar work done, the fewer steps in electrode modification using covalent attachment and directly linking the phthalocyanine to the terminated phenyl azide groups on the GCE showed an improvement in the electrooxidation of hydrazine with respect to detection limits, compared to other reported work using Fe(II)phthalocyanine and covalent attachment as a means of immobilizing the electrocatalysts on the electrode surface. It also showed an improvement in applied potentials and currents produced when compared to the detecting hydrazine in solution using the electrode with the adsorbed phthalocyanine.

For the paraquat electrocatalyst, the QDs and alkynyl phthalocyanine were characterized individually prior to conjugation and fully characterized once conjugated. The conjugation step was successful and this was mainly proven by x-ray photoelectron spectroscopy results and infrared spectroscopy results. Conjugation of the above-mentioned phthalocyanine with phenyl azide-modified QDs showed an improvement in the electrocatalytic ability towards the electroreduction of paraquat compared to the unconjugated phthalocyanine and the unconjugated QDs. This approach of conjugating the QDs and phthalocyanine via click chemistry is novel. In addition, the conjugate showed improved detection limits when compared to other phthalocyanine-based paraquat electrocatalysts.

The electrocatalysts fabricated in this work on glassy carbon electrodes showed good potential as electrocatalysts and the novel approaches proved to be a step forward in the fabrication of electrochemical sensors.

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