Electrode modification by diazonium chemistry : studies on the effect of steric bulk on film thickness, and modified activated carbon cloths for energy storage

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**ELECTRODE MODIFICATION BY DIAZONIUM
CHEMISTRY: STUDIES ON THE EFFECT OF STERIC BULK
ON FILM THICKNESS, AND MODIFIED ACTIVATED
CARBON CLOTHS FOR ENERGY STORAGE**

ARNOLD SUBRATA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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ARNOLD SUBRATA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Richard D. Webster

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as A. Subrata, A. Veksha, Z.Y. Pong, G. Lisak, and R.D. Webster. Electrografting of Sterically Bulky Tetramethylaniline Groups on Glassy Carbon Electrodes through Aryldiazonium Chemistry: Reasons for the Formation of Multilayers. *ChemElectroChem* **2020**, 7, 3368–3380. DOI: 10.1002/celec.202000796.

The contributions of the co-authors are as follows:

- I conceived the initial project direction and co-designed the study with Prof. Webster.
- I prepared the manuscript drafts, which were revised by Prof. Webster.
- I performed all the laboratory work at the School of Physical and Mathematical Sciences, and analyzed all collected data with guidance from Prof. Webster.
- Dr. Veksha and Prof. Lisak assisted with the use of the tube furnace for the preparation of pyrolyzed photoresist films.
- Mr. Pong assisted with the collection of cyclic voltammetry data during the early stages of the project.

Chapter 4 is published as A. Subrata and R.D. Webster. Comparing diazonium modified and unmodified activated carbon cloths for energy storage in supercapacitors. *Electrochemical Science Advances* **2021**, e2100084. DOI: 10.1002/elsa.202100084.

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Arnold Subrata

Abstract

The chemical modification of electrode surfaces with organic molecules is an important reaction in electrochemistry. Of the multiple methods which exist for this purpose, aryl diazonium cation reduction is widely considered to be the most popular, due to the high stability of the grafted layer on the surface, as well as the relative ease of the modification procedure.

One key disadvantage of grafting by diazonium chemistry is the inherent tendency of the grafted film to bear multilayers of organic molecules, which is not desired in most applications requiring modified electrodes. The side reactions forming these polymeric multilayers are known to occur at vacant, unsubstituted carbons on the aryl ring of the grafted layer. In the first of two broad parts of this thesis, studies were carried out on a glassy carbon (GC) electrode modified with bulky 2,3,5,6-tetramethylaniline (TMA) groups (i.e. **GC-TMA**), using the precursor to the diazonium salt, 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD). Chapter 2 focuses on the formation of **GC-TMA** and its extensive characterization using electrochemical and spectroscopic techniques, with the aim of addressing the above problem of multilayer formation since TMPD bears a fully substituted aryl ring, thus preventing the multilayer-forming side reactions due to steric hindrance. The results show that sparse multilayers of TMA groups were observed on **GC-TMA** instead of the expected monolayer, with an investigation of the possible reasons for the unexpected formation of TMA multilayers. Chapter 3 then explores the same modified electrode further through additional coupling experiments performed on **GC-TMA**. Various small molecules were conjugated onto the TMA layer of **GC-TMA** with the intent of ascertaining the feasibility of such coupling, especially given the presence of outward-protruding methyl groups on each TMA moiety. Among these molecules were single-walled carbon nanotubes (SWCNTs), which allowed for

the formation of **GC–TMA–SWCNT** and an assessment of the ability of the tethered SWCNTs to function as molecular wires for both solution-phase and SWCNT-bound species.

The second part of the thesis puts the focus on the modification of activated carbon cloth (ACC) electrodes for their use in supercapacitors, such as electric double layer capacitors (EDLCs). Although ACCs have inherently lower porosity and specific surface area than other more commonly preferred carbonaceous materials for EDLCs, they were chosen for the study due to their mechanical stability and flexibility (and hence great potential for use in wearable electronics) while being electrically conductive. In Chapter 4, electrochemically-active anthraquinone (AQ) molecules were attached to predominantly-capacitive ACCs by diazonium chemistry with the aim of increasing the total amount of charge stored and released through faradaic redox reactions. The resulting AQ-modified ACCs saw an increase in the total charge compared to unmodified ACCs, but only at lower scan rates and charge densities in cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) experiments, respectively. This was found to be due to a combination of the high resistance of the three-electrode cell setups used in our experiments, and the complicated proton-coupled electron transfer (PCET) reactions which AQ molecules undergo.

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List of Abbreviations and Symbols

A	Ampere(s)
a.c.	Alternating current
AFM	Atomic force microscopy
Ag/AgCl	Silver/silver chloride redox couple
AQ	Anthraquinone
AQ2S	Anthraquinone-2-sulfonic acid
BET	Brunauer-Emmett-Teller
C	Coulomb(s)
ca.	Circa
C_{DL}	Double layer capacitance
cm	Centimeter(s)
CNTs	Carbon nanotubes
CPE	Controlled-potential electrolysis
c.p.s.	Counts per second
CV	Cyclic voltammetry
DA	Dopamine
DCC	<i>N,N'</i> -Dicyclohexylcarbodiimide
DPPH	2,2-Diphenyl-1-picrylhydrazyl
DMAP	4-Dimethylaminopyridine
DMSO	Dimethylsulfoxide
e^-	Electron(s)
E	Potential
$E_{1/2}$	Half-wave potential
E_p^{ox}	Oxidative peak potential

E_p^{red}	Reductive peak potential
EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
EDLC	Electric double-layer capacitor
EIS	Electrochemical impedance spectroscopy
ESR; R	Equivalent series resistance
eV	Electron-volt(s)
Fc	Ferrocene
FcNH ₂	Aminoferrocene
$\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$	Ferricyanide/ferrocyanide redox couple
FMN	Flavin mononucleotide
g	Gram(s)
GC	Glassy carbon
h	Hour(s)
HER	Hydrogen evolution reaction
HOPG	Highly oriented pyrolytic graphite
Hz	Hertz
i	Current
i_p	Peak current
i_p^{ox}	Oxidative peak current
i_p^{red}	Reductive peak current
K	Kelvin
kHz	Kilohertz
M	Molar(s)
mA	Milliampere(s)
mAh	Milliampere hour(s)

mg	Milligram(s)
min	Minute(s)
mL	Milliliter(s)
mM	Millimolar(s)
mm	Millimeter(s)
mV	Millivolt(s)
NHS	<i>N</i> -Hydroxysuccinimide
nm	Nanometer(s)
OCP	Open circuit potential
<i>P</i>	Power delivered
PBS	Phosphate buffered saline
PCET	Proton-coupled electron transfer
PD	<i>para</i> -Phenylenediamine
PPF	Pyrolyzed photoresist film
R_{CT}	Charge-transfer resistance
r.p.m.	Rotations per minute
R_q	Root mean square roughness
R_s	Uncompensated solution resistance
s	Seconds
SAM	Self-assembled monolayer
SWCNTs	Single-walled carbon nanotubes
TMA	2,3,5,6-Tetramethylaniline
TMPD	2,3,5,6-Tetramethyl- <i>para</i> -phenylenediamine
V	Volt(s)
<i>V</i>	Cell voltage

XPS	X-ray photoelectron spectroscopy
Z'	Real component of impedance
Z''	Imaginary component of impedance
Z_w	Warburg impedance
ΔE_p	Peak-to-peak separation
Γ	Surface coverage
μA	Microampere(s)
μm	Micrometer(s)
ν	Scan rate
Ω	Ohm(s)

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1.1 Background (Electrode modification by diazonium chemistry)

1.1.1 Carbon electrodes and carbonaceous materials

For decades, carbon electrodes have been widely used in electrochemistry due to their versatility in facilitating a myriad of redox reactions. A number of its advantages include a wide potential window, inertness, excellent electrical conductivity, and relatively low cost.^[1-2] The attractiveness of carbon as a conduit for electron transfer reactions has thus spawned a variety of carbonaceous materials with different chemical properties; some examples of the different forms of carbon used in electrochemistry include glassy carbon (GC), highly oriented pyrolytic graphite (HOPG),^[3] pyrolyzed photoresist film (PPF)^[4] and carbon nanomaterials such as single-/multi-walled carbon nanotubes (CNTs)^[5] and carbon nanowires^[6].

Amongst the various types of carbon electrodes, GC is one of the most commonly used for electrochemistry. Structurally, it is a complex, randomly oriented network of ribbon-like graphite,^[7-8] consisting of a mixture of sp^2 carbons and oxygen-containing functional groups including ketones, carboxylic acids and phenols (Figure 1.1).^[9] GC electrodes are often used in their bare, non-functionalized state, whereby they are able to catalyze many electrochemical reactions. In order to maintain this bare state, they are often mechanically polished with fine alumina prior to (as well as in between) experiments and subsequently washed and sonicated to physically remove any adsorbed material which could adversely affect electrochemical measurements.^[10]

Figure 1.1 Partial structure of polished glassy carbon (GC) surface. Reprinted (adapted) with permission from Chen, P.; McCreery, R. L., *Anal. Chem.* **1996**, 68, 3958–3965. Copyright 1996 American Chemical Society

PPF, on the other hand, is much less commonly found in the electrochemist's laboratory. As its name suggests, PPF is a form of carbon that is made from a photoresist solution heated to very high temperatures in a tube furnace (up to 1300 K), which results in a conductive film that is nearly atomically flat (root mean square roughness of <0.5 nm) and has minimal defects (Figure 1.2).^[11] These characteristics of PPF allow it to act a replacement for GC in experiments where its flatness is required, such as atomic force spectroscopy (AFM). Unfortunately, PPF is

not commercially available, and its resource-intensive preparation procedure means that not all laboratories have immediate access to its use.

Figure 1.2 Photograph of pyrolyzed photoresist film (PPF) plates

CNTs are a class of nanomaterials which has seen tremendous growth in their use and research across various fields. Individually, they exist as cylindrical graphitic sheets, and have diameters in the nanometer range and lengths of up to a few micrometers.^[1, 6] Much like GC, they possess very good electrical conductivity, mechanical strength, and inertness in many aqueous and organic electrolyte solutions. Additionally, their small size and large specific surface area (ca. 200–300 m² g⁻¹) confers excellent properties for electrochemistry, especially for applications like (bio)sensing where a high signal-to-noise ratio for analyte sensing is required.^[12] CNTs rarely function on their own, and so are usually attached to an electrode through physical means (e.g. dropcasting) or covalently via chemical bonds.

More recently, numerous studies have been carried out on the modification of electrode surfaces in order to confer additional properties to them, such as improved affinity for specific target molecules, or increased rates of heterogeneous electron transfer. Particularly for GC, a

number of modification methods which take advantage of its surface functionality have been thoroughly explored.^[2, 13-14] Some of these include amine and carboxylate oxidation,^[15-16] photochemical and thermal modification,^[17] and aryldiazonium reduction.^[14]

1.1.2 Aryldiazonium salts

Aryldiazonium (or, simply, diazonium) ions consist of the diazonium (N_2^+) functional group bonded to an aryl moiety (Figure 1.3), and often exist as salts with an accompanying counter anion. Before their active use as precursors for surface modification, aryldiazonium ions were more commonly used as adducts for various organic synthetic reactions including addition reactions to olefins (the Meerwein reaction)^[18] and the Sandmeyer reaction.^[19]

Figure 1.3 Structure of an aryldiazonium cation, bearing the diazonium group

In a process called diazotization, diazonium salts are formed from primary amines (more commonly aryl amines) through a series of steps, requiring a diazotization agent such as HNO_2 (generated by adding NaNO_2 to aqueous HCl) in aqueous media^[20-21] or $t\text{BuNO}_2$ in organic media^[22-23] for the conversion (Scheme 1.1). The diazonium salt formed can then be purified and isolated at low temperatures, or they can be used immediately for subsequent reactions.^[24-26] The latter (*in situ* diazotization) is an attractive option owing to the inherent instability of most diazonium compounds under ambient conditions.^[17]

Scheme 1.1 Diazotization of a primary amine to its diazonium cation, its reduction to the aryl radical, and subsequent attachment to an electrode surface

One of such uses for diazonium salts is its reduction to form the corresponding aryl radical (Scheme 1.1). This reduction may be performed either chemically^[17, 27] or electrochemically,^[28] both result in the loss of dinitrogen, providing the driving force for the reaction. Particularly, when aryldiazonium compounds are electrochemically reduced at a carbon electrode, the highly reactive aryl radical produced forms a covalent bond with a carbon atom on the electrode in a concerted manner, thereby grafting itself onto the surface of the electrode (Scheme 1.1). Effectively, the electrode is modified with the chemically-bound aryl compound, and it has been shown that this layer is stable enough to withstand ultrasonication in various solvents, and extreme potentials and temperatures.^[13, 20] Due to the highly stable nature of the layer grafted by diazonium chemistry, as well as its versatility in accommodating various aryl compounds, this method of electrografting has been well exploited by many for various applications such as sensing^[14, 29-30] and energy storage.^[31-33]

1.1.3 *Electrografting by diazonium chemistry*

The first known reports of electrografting by diazonium chemistry was by Savéant and co-workers in 1992.^[34] Before then, methods for the modification of electrode surfaces were largely limited to their electrochemical oxidation, which would produce a mixture of carboxylic, hydroxylic, and phenolic groups (among other oxygenated functional groups) on the surface to act as attachment points for subsequent conjugation of further molecules.^[35-36] However, there is little control over the extent of formation of these surface oxides during such oxidative

treatment, and unwanted large background currents would arise due to irreversible corrosion of the carbon surface with harsher oxidative treatment.^[37] The need for a more reproducible and noncorrosive electrode modification method thus prompted an investigation into the use of diazonium salts as viable electrografting precursors.

To perform electrografting with a diazonium salt, it has to be reduced at a sufficiently negative potential before covalent grafting can occur. As such, the reduction potential of the diazonium group needs to be determined first, typically by cyclic voltammetry (CV). Diazonium reduction is a chemically irreversible process and can thus be easily identified on a cyclic voltammogram as an irreversible cathodic peak.^[25, 38-39] Another feature that distinguishes this reduction process from most other redox reactions on the voltammogram is the large decrease in the cathodic peak current beyond the first CV cycle (Figure 1.4). This occurs for most aryldiazonium compounds studied thus far, and was found to be due to the formation of an insulating layer which physically covers the electrode surface during the first CV cycle at sufficiently negative potentials, effectively blocking access to anymore diazonium compounds in solution reaching the electrode surface for reduction.^[40-41] In the example shown in Figure 1.4, the reduction potential of the commonly studied 4-nitrobenzene diazonium tetrafluoroborate salt was identified to be at 0.30 V vs. Ag/AgCl in 3 M KCl, and this peak disappears from the second cycle onwards. (The reduction peak at -0.50 V is thought to belong to the uncatalyzed diazonium reduction reaction,^[42] but is not pertinent to the present discussion.)

Figure 1.4 Cyclic voltammogram of 3 mM 4-nitrobenzene diazonium tetrafluoroborate salt with 0.1 M $n\text{Bu}_4\text{NPF}_6$ in acetonitrile at $\nu = 0.1 \text{ V s}^{-1}$ with a 3 mm diameter GC working electrode

The result of the above CV experiment is a GC electrode that is modified with 4-nitrobenzene groups, with carbon-carbon covalent bonds being formed between the GC surface and C-1 of the benzene group of 4-nitrobenzene.

The attractiveness of aryldiazonium reduction as a grafting method lies in its versatility; in most cases, if a compound bears an aniline group which can be converted to the aryldiazonium group, it becomes a viable candidate for reduction and subsequent grafting onto an electrode surface, leading to electrode modification.^[14]

1.1.4 Factors affecting extent of electrografting

Electrografting can either be carried out by CV or by controlled-potential electrolysis (CPE). For each method, the amount of electrodeposition by diazonium chemistry on an electrode surface is affected by multiple factors.

In CV, the main parameters which can be changed are the number of CV cycles and scan rate. Although there is no universal rule for the minimum number of CV cycles required for electrografting to be deemed “complete”, a common recommendation is to perform CV up until the diazonium reduction peak is no longer visible on the last cycle, as explained in the previous Section. As for scan rate, in most cases involving electrografting onto planar surfaces such as GC, the scan rate is set at a value between 50 and 100 mV s⁻¹,^[43-45] with 100 mV s⁻¹ being the most common (deviations away from this range are rare).

As for CPE, the set potential and electrolysis duration are the key factors in question. Clearly, the potential should be set at a value that is slightly more negative (e.g. 100 mV) than the reduction potential of the diazonium salt for facile reduction and subsequent electrografting. As such, during a first attempt of electrografting a diazonium salt with an unknown reduction potential, a CV scan is usually carried out first to identify the diazonium reduction peak, before performing CPE proper on another fresh electrode. The duration of electrolysis has, on the other hand, greater room for variation, ranging from a short 10 s^[46] up to 100 min.^[47] Intuitively, a longer electrolysis duration leads to greater coverage of the film on the electrode, but only up to a certain threshold (that is dependent on the identity of the diazonium salt itself) beyond which no further electrografting occurs.^[47] This is referred to as the self-limiting nature of the grafted film, and is the reason why CPE durations typically do not exceed 10 min which is when electrografting may be considered complete.

A common factor shared between CV and CPE (or any other electrografting method) is the concentration of the diazonium salt, with most studies perform electrografting with 1 mM of the compound. Though higher concentrations (e.g. 5 mM)^[48-49] can be used, increasing the number of CV cycles or CPE duration instead would still achieve the same goal of complete electrografting, while using less of the reagent.

1.1.5 Spontaneous grafting by diazonium chemistry

As mentioned earlier, a reducing agent is required to reduce the aryldiazonium cation to the corresponding aryl radical. For electrografting, the potentiostat may be considered as the “reducing agent” as it directly supplies electrons to the diazonium cation through the electrode. On the other hand, the use of chemical reductants for surface modification^[17, 50] is much less common, since electrografting does the same but with greater convenience and fewer by-products.

Vautrin-UI and co-workers discovered in 2005 that various surfaces or substrates (including GC, copper and iron) could be spontaneously grafted with diazonium salts in the absence of electrochemical induction and chemical reductants, simply by immersion of the bare surface into a solution of the diazonium salt.^[51] A number of other papers on spontaneous grafting subsequently followed,^[2, 17, 52] and it is generally agreed that the layers formed by such “electroless” grafting produced thinner layers than those formed by conventional electrografting under the same grafting duration due to slower grafting rates. It was also found that substrates with more negative open circuit potentials (OCPs) or are more reducing in nature, such as metals, can better facilitate spontaneous grafting than less reducing substrates like carbon. It was thus inferred that electrons were donated from the substrate itself to the diazonium salt, hence the increased spontaneous grafting rates on substrates with highly negative OCPs.

Spontaneous grafting is the method of choice for the modification of materials for which electrochemical grafting is practically not feasible, such as CNTs and activated carbon powders.^[53]

1.1.6 Monolayer and multilayer film formation

Films grafted onto electrode surfaces by diazonium chemistry are often compared to self-assembled monolayers (SAMs) of thiols on gold surfaces, with each having their own advantages and drawbacks. The covalent bond formed between the electrode surface and the diazonium-grafted aryl group imparts excellent stability to the electrografted layer, whereas the thiol-gold bond on the SAMs are comparatively weaker and are prone to breakdown when exposed to relatively milder conditions and/or ultrasonication in some solvents.^[54-56] However, unlike the latter case whereby the thiol molecules always form an ordered monolayer on the surface, the grafted film produced by diazonium chemistry are, more often than not, polymeric in nature (Scheme 1.2).

Scheme 1.2 (a) Multilayer film on electrode surface produced by diazonium chemistry, and
(b) SAM on Au surface produced by thiol-gold chemistry

Due to the highly labile aryl radicals formed through diazonium reduction, they may attack vacant sites (aryl carbons bearing hydrogen) on the already grafted film to form a multilayer linked by carbon-carbon bonds (Scheme 1.3a).^[57-58] Aryldiazonium compounds yet to be reduced may also be attacked by cyclohexadienyl radicals which may be present on the

growing layer through azo bonds (Scheme 1.3b), providing yet another alternative for thick multilayers to form.^[53]

Scheme 1.3 Multilayer-forming side reactions from electrografting by diazonium chemistry:

- (a) an aryl radical attacks an unsubstituted carbon on the grafted film, and (b) a cyclohexadienyl radical attacks a diazonium cation in solution

The distinction between a monolayered and multilayered film is important because the thickness of the grafted film is known to affect the rate of heterogeneous electron transfer across the modified electrode.^[59-60] In situations or applications where a fast electron transfer rate is to be prioritized without compromising the function of the modified electrode, the grafted film is usually made to be as thin as possible. For example, in an investigation performed by Brozik and co-workers on the application of electrodes modified with pyrroloquinoline quinone (PQQ) molecules for electrochemical β -nicotinamide adenine dinucleotide (NADH) detection, it was found that the heterogeneous electron transfer coefficient for the PQQ-modified electrodes (determined by simulations) decrease with

increasing thickness of the PQQ film (which was varied by changing the diazonium electrografting conditions).^[30]

Studies on monolayer formation from aryldiazonium salts have increased in interest over the past decade. Combining the best of both electrografting by diazonium chemistry (stability) and SAM formation by thiol-gold chemistry (monolayer formation) is a promising area of research, with various methods of monolayer formation being discovered over the year differing in methodology and mechanism. In one example, a redox mediator (e.g. chloranil, 2,2-diphenyl-1-picrylhydrazyl) with a lower reduction potential than that of the diazonium cation is added to the usual diazonium-containing grafting solution.^[61] Once a suitable potential is applied, multilayer growth is inhibited through a redox cross-reaction between the reduced mediator and the diazonium cation which occurs in the diffusion layer, far away from the electrode surface. In another series of examples, the bulky nature of some aryl substituents (e.g. *tert*-butyl) were utilized to prevent multilayer-forming side reactions (in Scheme 1.3) from occurring merely by steric hindrance.^[62-63] Upon further investigation, the same authors found that the alkyl side chains on diazonium cations such as 2-ethylbenzenediazonium and 2,6-dimethylbenzenediazonium (Figure 1.5) were of sufficient bulk to prevent their reaction with (and hence, grafting onto) the electrode surface.^[39]

Figure 1.5 Chemical structures of 2-ethylbenzenediazonium and 2,6-dimethylbenzenediazonium cations

1.1.7 Film characterization

Various methods exist for the characterization of the grafted film on a surface. Here, the methods which have been employed for the projects covered in this thesis will be described.

1.1.7.1 Cyclic voltammetry

Besides being used as a technique for electrografting, CV can also be used for film characterization. If the film on the electrode surface contains electrochemically-active molecules, a suitable CV of a blank solution using the modified electrode will produce a voltammogram with the redox peak(s) of the molecules. In the example shown in Figure 1.6, a reversible pair of redox peaks corresponding to anthraquinone (AQ) reduction and oxidation in blank 0.1 M KOH solution (reaction scheme^[64] shown in Scheme 1.4) were observed on the CV curve of a GC electrode which has been chemically modified with AQ groups. This method of characterization is often used after thorough washing and sonication of the modified electrode, in order to ascertain that the grafting has been successfully performed (as opposed to just physical adsorption of the molecules to be grafted). It should also be noted that, unlike the typical “duck”-shaped voltammograms of solution-phase analytes,^[65] the redox peaks of species adsorbed onto the electrode each has a symmetrical appearance instead due to the inability of the species to diffuse away from the grafted film, as is the case for the AQ-modified GC shown in Figure 1.6.

Figure 1.6 Cyclic voltammogram of a blank solution of aqueous 0.1 M KOH with a 3 mm diameter GC electrode chemically modified with anthraquinone (AQ) groups at $\nu = 0.1 \text{ V s}^{-1}$

Scheme 1.4 Reversible reduction reaction of GC-bound AQ to its singly-protonated, reduced form in 0.1 M KOH

The relationship between the peak current, i_p (in A), and scan rate, ν (in V s^{-1}), on the cyclic voltammogram of an electrochemically reversible system which is adsorbed on an electrode surface is given by Equation 1.1:^[66]

$$i_p = \frac{n^2 F^2 \Gamma A \nu}{4RT} \quad (1.1)$$

where n = number of electrons per redox reaction; F = Faraday constant (96485 C mol^{-1}); Γ = surface coverage of the film (in mol cm^{-2}); A = geometric surface area of the electrode (in cm^2);

R = ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); and T = temperature (in K). Thus, in most electrochemical systems involving adsorbed species, i_p is directly proportional to v .

The above may be regarded as a variant of the Randles–Ševčík equation (Equation 1.2), which also relates peak current to scan rate but for electrochemically reversible systems in solution at 298 K instead.^[66]

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A C D^{\frac{1}{2}} v^{\frac{1}{2}} \quad (1.2)$$

where C = bulk concentration of the electroactive species; and D = diffusion coefficient of the same species. Such species under diffusion control would thus exhibit linearity between i_p and the square root of v ; this behavior can generally be used to distinguish diffusion-controlled species from adsorbed species.

Based on the area under the redox peaks, the surface coverage of the film can be calculated using Equation 1.3:

$$\Gamma = \frac{Q}{nFA} \quad (1.3)$$

where Q = charge integrated under the peak on the cyclic voltammogram (in C). Surface coverage values may be useful as they can provide a rough estimate for the number of layers containing electroactive molecules that are grafted onto the electrode surface, when compared against known values for the surface coverage of a monolayer for a particular molecular species.^[67] However, these calculations are underestimates at best, as it is uncertain whether all of the electroactive material within the grafted film underwent the redox reaction or not (i.e. electro-addressable) during the CV procedure.^[68-69] Moreover, CV provides little information on the presence of pinholes or defects on the film, which limits their usefulness if used as the sole method of characterization.

On the other hand, even if the grafted film contains electrochemically-inactive material, CV can still be employed for its characterization by comparing the CV profile of the modified

electrode in a solution containing another suitable electroactive species (or redox probe) with that of an unmodified GC electrode. A voltammogram showing the absence of any redox peaks corresponding to the redox probe indicates the presence of a film that is capable of completely blocking contact between the species and the electrode surface. The most common redox probes used for this purpose include the ferricyanide/ferrocyanide ($\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$) couple, and dopamine.

The $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ couple is a useful tool for studying modified electrodes as it is an inner-sphere redox system, which means that its electron transfer kinetics are sensitive to the nature of the electrode surface.^[70] This is as opposed to outer-sphere redox systems such as $\text{Ru(NH}_3)_6^{2/3+}$ which are largely unaffected by such modified surfaces and so undergo relatively fast electron transfer kinetics regardless of the presence of deposited material on the electrode.^[71] Similarly, an aqueous acidic solution of dopamine can also be used to determine the presence of a grafted film, while showing greater sensitivity towards the presence of film defects which $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ may fail to reveal.^[72] Dopamine undergoes a reversible two-proton, two-electron oxidation in aqueous acidic media to form dopamine-*o*-quinone, as shown in Scheme 1.5. For example, when comparing the CV profiles of a bare, unmodified GC electrode and one modified with aniline groups in a 1 mM solution of dopamine in 0.1 M H_2SO_4 (Figure 1.7), it is clear that the aniline film has an adverse effect on the heterogeneous electron transfer rate, evident by the marked widening of the peak-to-peak separation of the voltammogram compared to unmodified GC.

Scheme 1.5 Reversible oxidation reaction of dopamine to dopamine-*o*-quinone in aqueous 0.1 M H_2SO_4

Figure 1.7 Cyclic voltammograms of dopamine (1 mM) in aqueous 0.1 M H₂SO₄ with unmodified GC, and aniline-modified GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$

1.1.7.2 Electrochemical impedance spectroscopy

EIS is a non-destructive technique capable of measuring various parameters of an electrochemical cell which cannot otherwise be easily measured through other electrochemical methods, including double layer capacitance, uncompensated solution resistance, and charge transfer resistance across the electrode surface.^[73] EIS functions by measuring the change in current to a small amplitude perturbation of the potential, or vice versa, in the frequency domain, followed by a calculation of the electrochemical impedance, Z_{cell} , at each frequency (in Ω).^[74-75] In conventional electrical circuits, this is given by Equation 1.4:

$$Z_{\text{cell}} = \frac{E_{\text{cell}}}{i_{\text{cell}}} \quad (1.4)$$

where E_{cell} = voltage across the cell (in V), and i_{cell} = current passing through the cell (in A). The sinusoidal nature of the potential/current perturbation allows impedance values (which have a phase shift and an amplitude) to be expressed as a complex number, and these values are in turn presented most commonly as a Nyquist plot for ease of interpretation.^[74] Shown in

Figure 1.8 is an example of a Nyquist plot of a GC electrode modified with tetramethylaniline groups.

Figure 1.8 Nyquist plot of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in aqueous 0.1 M KCl using a 3 mm diameter GC modified with tetramethylaniline groups

In a Nyquist plot, the real component of the impedance (Z_{Re} or Z') is plotted against the negative of its imaginary component ($-Z_{\text{Im}}$ or $-Z''$). Higher frequency measurements are displayed on the left, and lower frequencies on the right of the plot, with measurements performed in order of decreasing frequency. In the context of EIS measurements of electrodes modified with a film, the plot would generally appear like the one in Figure 1.8, with a semicircle on the high-frequency region and a 45° line on the low-frequency region.

For EIS experiments to be meaningful, some prior knowledge is required of the electrochemist; an equivalent circuit that best fits the electrochemical behavior of the cell has to be constructed using circuit components (e.g. capacitors, resistors), which in the case of a simple reversible electron transfer is shown in Figure 1.9.^[75] The electrolyte solution between

the electrodes in an electrochemical cell behaves as an ionic conductor with a certain solution resistance, R_s . The capacitor represents the double layer capacitance, C_{DL} , on the electrode-solution interface where electrolyte ions are present to balance the charge with the electrode. Parallel to the capacitor, there are two resistors in series: one represents the kinetics of the charge-transfer process (with resistance, R_{CT}) between a redox species in solution and the electrode, and the other represents the rate of mass transport of the redox species, signified by the Warburg impedance element with impedance, Z_W .

Figure 1.9 Equivalent circuit diagram of a simple reversible electron transfer. R_s : uncompensated solution resistance; R_{CT} : charge-transfer resistance; Z_W : Warburg impedance; and C_{DL} : double layer capacitance

Going back to the Nyquist plot in Figure 1.8, the example electrochemical cell can be modelled by the equivalent circuit constructed in Figure 1.9. The relevant parameters which can be extrapolated from the EIS data include R_s from the intercept of the high-frequency end of the semicircle, and R_{CT} from the diameter of the semicircle. Particularly, the value of R_{CT} is useful as it typically gives an indication of the extent of grafting on the electrode surface, especially when compared with an unmodified electrode. Additionally, the 45° line at the low-frequency end is also known as the Warburg line, representing the Warburg diffusion element.

1.1.7.3 X-ray photoelectron spectroscopy

XPS is a surface technique which gives information on the elemental composition of the surface (ca. 10 nm) of the sample. This is done by firing X-ray photons (from a radiation source) onto the surface, and then measuring the kinetic energy and number of photoelectrons emitted by the surface resulting from absorption of the X-ray photons.

XPS is an excellent technique for film characterization. It provides qualitative analysis (elemental identification) through measurement of the kinetic energy of the ejected photoelectrons, since each element has a unique binding energy associated with it. The technique also provides quantitative analysis through measurement of the number of photoelectrons ejected, which is related to the atomic concentration of elements on the sample surface. If the film possesses a unique element that cannot be present on a negative control (unmodified electrode), the presence of the said element provides confirmation of successful grafting of the film. Much less commonly, treatment of the results from XPS experiments can give an estimation of the extent of grafting. This involves calculation of the R/C_{1s} atomic concentration ratio (where R = sum of atomic concentrations of the substituent on the phenyl group and the N_{1s} peak), then multiplication with a factor representing the surface density of carbon atoms on GC, to obtain a value for the surface coverage, Γ .^[20, 76-77] Like CV, the calculated surface coverage has to be compared to a theoretical value for meaningful deduction of the monolayer or multilayer nature of the film.

Knowing the above, there are situations where XPS may not be suitable for film characterization. In cases where the grafted film is expected to be thicker than 10 nm and is nonuniform in composition, the user has to be wary of employing XPS as the sole or key characterization method lest erroneous conclusions on the elemental makeup of the film be drawn from the results. Likewise, XPS is of little help in characterizing thin films where its elemental composition is largely similar to the underlying substrate, such as a thin polyphenyl

film on a GC surface. Lastly, although rare, degradation of the film may also occur under X-ray irradiation during the analysis,^[78] which may interfere with accurate measurements.

1.1.7.4 Atomic force microscopy scratching

The current gold standard for the quantification of grafted film thickness is by a rather specific technique known as atomic force microscopy (AFM) scratching, which was first discovered in 2003 by McCreery and co-workers.^[79] It was with this method that they were able to conclude how high concentrations of diazonium salts and/or longer electrolysis durations led to more extensive multilayer formation. The process is illustrated in Scheme 1.6.

Scheme 1.6 The AFM scratching technique in sequence: (a) probe approach; (b) initial scratching of film; (c) area-defined scratching; (d) area/line profiling; and (e) line profile output (figures are not drawn to scale)

First, the substrate with the grafted film is set in contact mode under an AFM probe with a low force constant, and “scratching” — the deliberate physical removal of the film, is performed with the tip of the probe. The technique works because the grafted film is much softer than the underlying substrate and can thus be mechanically removed by a suitable instrument.^[67] This is done with the intention of creating a (usually rectangular) trench that is as deep as the actual height of the film, which can then be profiled by regular AFM in non-contact or tapping mode using a probe with a higher force constant. The difference in height measured between the film and substrate thus corresponds to the thickness of the film.

As the AFM scratching technique is highly sensitive down to the nanometer range, regular substrates such as GC (which may seem flat) are less suitable to be used for scratching experiments as they are microscopically rough,^[1] and may potentially cause problems when attempting to scratch thinner films. PPF substrates make for excellent GC replacements due to their very low roughness, while sharing similarities in electrochemical reactivity with GC.^[1, 80] Hence, PPF is the most suitable substrate for purposes of AFM scratching and subsequent topological profiling of a grafted film.

1.1.8 Conjugation of secondary molecules onto existing films

Beyond just the film formed from the grafting process, it is also possible to further conjugate additional secondary molecules, typically with some useful functionality, onto the film as illustrated in Scheme 1.7.^[81] This method is particularly useful if the secondary molecule is unable to attach itself directly onto the surface (due to structural limitations, for example), and can only do so through an intermediate bridge (i.e. the grafted film) linking the electrode and the molecule together. In a couple of examples where the grafted film on the electrode comprises aniline or aminophenyl groups, the lingering amine group is converted to

a diazonium group for further reaction with another molecule, such as hydroxymethylferrocene^[82] and *N,N*-dimethylaniline.^[81] In another clever example, click chemistry was employed between 4-phenylazide groups on the grafted film and the alkyne groups of ethynylcobaltocenium, ensuring strong coupling between the two moieties.^[83]

Scheme 1.7 Electrode surface modified with an aryl film, which is subsequently conjugated with an outer layer of secondary molecules (round objects)

Besides the attachment of regular small molecules onto existing films, researchers have sought to restore the electrical conductivity of the electrode by tethering CNTs onto the otherwise insulating film to form molecular wires (Scheme 1.8).^[26, 84-85] In doing so, they were able to capitalize on the excellent electrochemical properties of CNTs for the restoration of electron transfer rates to solution species compared to modified electrodes without CNT attachment. This method of covalently bonding CNTs with the existing film produces a much more robust modified electrode than the simpler but less recommended alternative of dropcasting, which not only produces weaker physical bonds between the electrode surface and CNTs, but was also found not to completely exclude the base electrode from contributing to the voltammetric response.^[86]

Scheme 1.8 Examples of strategies for assembling vertically-aligned CNTs on amine-terminated films. Reprinted (adapted) with permission from Garrett, D. J.; Flavel, B. S.; Shapter, J. G.; Baronian, K. H.; Downard, A. J., *Langmuir* **2010**, 26, 1848–1854. Copyright 2010 American Chemical Society

1.2 Objectives (Electrode modification by diazonium chemistry)

The above background bears relevance to Chapters 2 and 3 of this thesis.

One particular study which merited further examination was that of Podvorica and co-workers' (*vide supra*, Section 1.1.6), where they concluded after a series of experiments that aryl diazonium cations bearing at least an ethyl group, or two methyl groups, *ortho* to the diazonium group were poor electrografting candidates.^[39] Furthermore, we were cognizant of the availability of many reports which showed the successful formation of aniline or aminophenyl films by diazonium chemistry, using the common *p*-phenylenediamine (PD) precursor.^[81, 87-89] These findings led us to investigate the feasibility of modifying electrodes with the diazonium cation of 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD) (Figure 1.10), which is the bulkier counterpart of PD. Essentially, we were interested in studying the feasibility of electrografting its diazonium cation onto an electrode surface, and in case of its success, whether the resulting film would be a monolayer or otherwise.

In Chapter 2 (Electrografting of sterically bulky tetramethylaniline groups on glassy carbon electrodes by aryl diazonium chemistry: Reasons for the formation of multilayers), the

objective was to characterize the properties of GC electrodes modified with bulky 2,3,5,6-tetramethylaniline (TMA) groups, along with a thorough exploration of the possible reasons for unexpected multilayer formation on the electrode.

Figure 1.10 Chemical structures of 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD) and *p*-phenylenediamine (PD)

Having drawn parallels between the aniline-modified electrodes from past studies and our own TMA-modified GC, we were naturally inclined to perform the conjugation of various secondary molecules onto the TMA film. These include electroactive small molecules such as anthraquinone-2-sulfonate (AQ2S), which has been previously used for the electrochemical reduction of oxygen,^[25] and flavin mononucleotide (FMN), which has potential applications in energy storage (Figure 1.11).^[90] The covalent conjugation of activated CNTs onto the TMA film was also explored, so as to explore the possibility of using the resulting CNT-terminated electrode as a conduit for transducing molecules.

In Chapter 3 (Covalent tethering of small molecules and carbon nanotubes to glassy carbon electrodes through a tetramethylaniline film), the aim was to ascertain the feasibility of conjugating small molecules and CNTs onto TMA-modified GC electrodes as prepared from the preceding Chapter. Further, the capability of tethered CNTs in restoring the fast electron transfer rates to solution species as molecular wires was investigated.

Figure 1.11 Chemical structures of anthraquinone-2-sulfonate (AQ2S) and flavin mononucleotide (FMN)

1.3 Background (Modified activated carbon cloths for energy storage)

1.3.1 *Energy storage systems*

In the face of rising energy requirements to suit the ever-changing consumption patterns of people worldwide, the need for suitable energy storage devices and technologies to meet these demands grows. Naturally, so too has research into these areas increased, as evidenced in Figure 1.12 by a steady rise in the number of papers published on “energy storage” in the Web of Science database. (The lower-than-expected increase for Year 2020 is possibly due to the COVID-19 pandemic which slowed down overall research output.)

Figure 1.12 Bar chart illustrating the growth in research publication output containing the term “energy storage” on the Web of Science database

While there has been noticeable advocacy in the use of renewable energy sources such as wind and solar energy, their rates of energy generation fluctuate, which is undesirable for applications requiring energy on demand.^[91-93] Electrochemical energy storage systems thus allow for the efficient storage of energy generated to meet this need.^[93-94] Of the myriad of energy storage devices which exist in electrochemical space, two of the most common types are batteries and electrochemical capacitors.

Between the two, batteries have been in existence longer than supercapacitors, and are more widely recognized by the layperson. The most prevalent type of battery is the Li-ion battery, which are still very actively researched and used.^[95] Batteries are very generally characterized by their high energy density, but low power density.^[96] In other words, they are capable of storing a large amount of energy per unit weight, but undergo inherently slow charging (energy storage) and discharging (energy release) processes. In the case of Li-ion batteries, which function based on the intercalation of Li^+ within the fine structures of the electrode material, the relatively low power density is attributed to the sluggish diffusion of Li^+

within the graphite layers of the anode and the crystalline lattices of the cathode.^[97-98] As such, they are commonly found in devices where higher power densities are not as critical to the functioning of the device, such as light-duty vehicles and consumer electronics.^[99]

Electrochemical capacitors (also known as supercapacitors) have a similar configuration with that of a conventional battery, with the main components being two electrodes, separated by an ion-permeable membrane, in an electrolyte solution (Figure 1.13). Highly conductive current collectors are often necessary to ensure intimate electrical contact between the electrode and the external circuit. Compared to batteries, supercapacitors have lower energy densities, but exhibit a wider range of power densities.^[96] This is illustrated in Figure 1.14 as a Ragone plot, which is a common way of depicting the main differences in specific energy and power between various energy storage systems. In essence, much of current research into energy storage systems seeks to engineer current technologies (or discover new ones) such that they lie on the upper-right corner of the Ragone plot.

Figure 1.13 Simplified schematic representation of a supercapacitor cell (connected to an external power source)

Figure 1.14 Ragone plot of specific power against specific energy for various energy storage systems. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, *Nature Materials*, Materials for electrochemical capacitors, Simon, P.; Gogotsi, Y., Copyright 2008

Supercapacitors are so-called because they have higher specific energies than conventional capacitors by several orders of magnitude, while exhibiting the same fundamental charge-storage mechanism of building up a potential difference between two thinly separated materials.^[100] During their infancy, supercapacitors consisted of electrodes which operated solely on the mechanism of electric double layer capacitance; these devices are aptly called electric double layer capacitors (EDLCs).^[32] However, in light of the discovery of new mechanisms for energy storage over the years, supercapacitor devices have grown to include

electrodes operating on other mechanisms such as pseudocapacitance^[101-102] and faradaic redox reactions;^[103-104] each of these are further described in the following Sections, and references will be made to certain parts of Figure 1.15 below for ease of comparison.

Figure 1.15 Representative cyclic voltammograms and galvanostatic discharge curves for various energy-storage materials. Reprinted (adapted) with permission from Gogotsi, Y.; Penner, R. M., *ACS Nano*. **2018**, *12*, 2081–2083. Copyright 2018 American Chemical Society

1.3.2 Electric double layer capacitance

When an electrode is immersed into an electrolyte solution and charged by an external power source, a build-up of charge occurs at the electrode-electrolyte interface, which results in the presence of a double layer capacitance.^[100, 105] This way, charge is stored electrostatically by the accumulation of electrolyte ions of opposite charge to that on the electrode surface while maintaining electrical neutrality. Particularly, in an EDLC, this effect is amplified manifold since the electrodes used are of much high specific surface area (e.g. activated carbon powders,

carbon cloths), allowing for a significant increase in the amount of charge stored per unit volume (Figure 1.16).^[100, 105] Furthermore, in a pure EDLC, energy-storage is entirely capacitive in nature without any redox processes taking place (i.e. non-faradaic), and is best characterized by a cyclic voltammogram with a constant current over the whole potential window (Figure 1.15a). The ability of EDLCs to undergo fast charging and discharging is thus attributed to the processes involving only the movement of ions to and from the electrode surface, as opposed to batteries where slower steps such as electron transfer, intercalation and phase-changes are involved.^[106]

Figure 1.16 Schematic representation of an electric double layer capacitor (EDLC) under charge. Reprinted from *Journal of Power Sources*, 157, Pandolfo, A. G.; Hollenkamp, A. F., Carbon properties and their role in supercapacitors, 11–27, Copyright 2006, with permission from Elsevier

The key components of an EDLC are the electrodes, which in most cases are carbonaceous in nature. Carbon stands out as an excellent choice for EDLCs due to a combination of factors including high conductivity, high specific surface area (for certain forms) and resistance to corrosion in most common electrolytes.^[106] Examples of the most common forms of carbon materials used for EDLC devices include activated carbons and carbon cloths.

Carbon activation is a process that is employed on a carbon precursor to greatly increase its specific surface area, resulting in a form of carbon that is highly porous (specific surface area: $\sim 1000\text{--}3500\text{ m}^2\text{ g}^{-1}$)^[105] with excellent specific capacitance ($\sim 200\text{--}400\text{ F g}^{-1}$).^[106] The extensive microporosity of activated carbon lends itself well to its use as an electrode material for EDLCs, due to the linear increase of specific capacitance with specific surface area (up to the point where electrolyte access into smaller pores become limited).^[107] As a catch-all term for materials of this nature, activated carbons exist in various sizes and forms, but are often processed into fine granules and powders. (Carbon blacks, though similar in appearance to activated carbon powders and also find use in EDLCs,^[108] are produced differently and generally have lower specific surface areas than activated carbon.) Activated carbons are rarely used on their own, and thus form part of a group of other components (e.g. conducting binder, carbon black) which make up a composite electrode.^[32, 109]

Carbon cloths or fibers, on the other hand, generally work well on their own as standalone electrodes in an EDLC setup. Individually composed of flexible fibers with diameters ranging in the tens of micrometers, carbon cloths are formed by weaving or knitting these fibers to form a piece of fabric,^[110] not unlike how a cotton cloth is made from individual cotton fibers. Where used, carbon cloths are chosen for their structural flexibility and mechanical strength, especially in applications such as wearable electronics.^[111-112] However, this is counterbalanced by them having an innately low specific surface area ($< 10\text{ m}^2\text{ g}^{-1}$)^[112] and capacitance ($< 5\text{ F g}^{-1}$)^[110]. These disadvantages can be remedied to some extent by the

carbon cloths undergoing an activation procedure to improve their porosity and charge-carrying capacity, thus forming activated carbon cloths (ACCs). Because such activation procedures vary within the academic^[113-116] and commercial sectors, the resulting ACCs themselves will differ in terms of their electrochemical properties and performance, but it suffices to say that they generally show marked improvements in their specific surface area ($\sim 1000\text{--}3000\text{ m}^2\text{ g}^{-1}$)^[105] and capacitance ($180\text{--}210\text{ F g}^{-1}$) over their untreated counterparts,^[100] thus making them good electrodes for EDLCs.

1.3.3 Faradaic redox reactions

Compared to the purely capacitive (i.e. electrostatic) nature of electrodes in EDLCs, electrodes utilizing redox reactions are said to be faradaic electrodes, though exceptions exist (*vide infra*, Section 1.3.4). Examples of such electrodes are activated carbons or carbon cloths chemically modified with quinones.^[104, 109, 117-118] As can be observed from their representative cyclic voltammogram (Figure 1.15g), electrodes of this kind combine characteristics from both battery-type systems as well as EDLCs, possessing the conspicuous faradaic oxidation and reduction peaks of the former and the increased capacitive background current of the latter. Researchers who study energy-storage materials of this kind, do so with the goal of producing modified electrodes which outperform those in EDLCs: where an additional faradaic component can be introduced without significantly decreasing the overall contribution by electric double layer capacitance. This is exemplified in Figure 1.17, which illustrates the above possibility in CV.

Figure 1.17 Cyclic voltammograms of a blank solution of aqueous 1 M H_2SO_4 using unmodified ACC, and ACC modified with AQ groups at 1 mV s^{-1}

When choosing which electroactive molecule to modify supercapacitor electrodes with, the key factor to consider is its redox potential, and how close it is to the upper or lower limits of the potential window of a given electrolyte solution. This importance arises out of the need to maximize the total energy stored in a supercapacitor, which transpires if the faradaic redox reaction occurs at potentials near to (but not exceeding) the ends of the suitable potential window.^[117] For example, given that the undesirable hydrogen evolution reaction (HER) occurs at ca. $-0.50 \text{ V vs. Ag/AgCl (3 M KCl)}$ in aqueous acidic solution^[119], the AQ-modified ACC electrode in Figure 1.17 would make for a suitable negative electrode in an aqueous supercapacitor. However, some authors have considered the redox potential of AQ to be too close to that of the HER, noting the apparent merging of AQ redox waves with those of HER at higher CV scan rates.^[120]

1.3.4 Pseudocapacitance

It should be mentioned at the outset that the modified electrodes studied in this thesis do not exhibit pseudocapacitance. However, a discussion of energy-storage systems is incomplete without a simple introduction to pseudocapacitance.

By definition, pseudocapacitance refers to “the behavior of electrode materials (RuO_2 , MnO_2) that have the electrochemical signature of a capacitive electrode, i.e. a linear dependence of the charge stored with changing potential within the window of interest, but in which charge storage originates from electron-transfer mechanisms, rather than simply relying on the accumulation of ions in the electrochemical double layer.”^[121] The precise definition is invoked here because there was some confusion within the research community about the proper usage of the term “pseudocapacitance”, whereby it was erroneously used to describe materials which do not exhibit the abovementioned characteristics.^[121-122] The CV profile of an electrode bearing pseudocapacitive material would look like that of Figure 1.15b.

Pseudocapacitive materials have been known to bridge the EDLC-battery gap quite effectively; it has been touted that the most promising types of materials which can bring both high power and energy densities to supercapacitors are pseudocapacitive in nature.^[97-98] Their faradaic redox reactions occur much faster than those of batteries due to them occurring at the surface and are hence not diffusion-limited, and charging rates have been shown to exceed even those of conventional EDLCs.^[107] The earliest known materials under this category include amorphous, hydrated $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ discovered in 1999,^[123] and hydrated $\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ further back in 1971,^[124] which to date are still actively being researched upon. The detailed mechanisms behind pseudocapacitance and its variations shall not be covered here as they are not the focus of this thesis. However, it is apparent that a simple combination of materials individually bearing double layer capacitance and redox characteristics (as is the case of the modified electrodes studied in Chapter 4) does not make the system pseudocapacitive.

1.3.5 Experiments in energy storage

1.3.5.1 Variables measured

The energy-storage performance of an electrode material is most typically quantified by measurement of its capacitance, C (in F), which is its ability store electric charge electrostatically.^[125] Otherwise, the measure of capacity (in C or mAh) is used for electrodes which do not fall under those categories. For ease of comparison with other electrode materials, specific capacitance, C_{sp} , is used whereby normalization is usually gravimetric (g^{-1}).

At the supercapacitor (i.e. full device) level, the energy stored and power delivered, E and P , respectively, of the entire device becomes relevant. These are respectively given by Equations 1.5 and 1.6:

$$E = \frac{1}{2} CV^2 \quad (1.5)$$

$$P = \frac{V^2}{4R} \quad (1.6)$$

where V = cell voltage (in V); and R = equivalent series resistance, or ESR (in Ω).^[105] The mass-specific energy (in W h kg^{-1}) and power (in W kg^{-1}) values of a full supercapacitor device are useful for comparison with other supercapacitors and batteries across laboratories (especially in a Ragone plot), though normalization by area (cm^{-2}) or volume (cm^{-3}) are not uncommon.

The total resistance of a two-electrode cell, or ESR, is an important variable in determining the overall performance of an energy storage device, as can be seen from the formula for P . ESR is the function of a sum of multiple sources of resistance, including resistance of the electrode material, resistance at the electrode-current collector interface, resistance of ionic movement through the porous membrane/separator, solution resistance, and

charge-transfer resistance.^[106] The ESR of a supercapacitor cell can be determined by dividing the pre-discharge iR drop by the change in the applied current.^[126]

The primary technique used to quantify the relevant variables mentioned above, directly or otherwise, is the galvanostatic charge-discharge (GCD) test. A GCD experiment involves multiple repeated cycles of charging and discharging of the system, with the total capacitance (or capacity) being measured during each charging and discharging process. The coulombic efficiency, which is the ratio of capacitance released on discharge to capacitance stored during charge, can then be calculated to determine how much charge is retained (or lost) during each complete cycle. Likewise, the similar metric of energy efficiency (energy released divided by energy stored) can be calculated. When plotted, a single charge-discharge cycle of a GCD experiment would look similar to Figure 1.18. As previously alluded to, the iR drop is represented by the vertical jump in potential immediately prior to the charging or discharging process; a larger jump indicates a higher resistance value within the cell.^[126]

Figure 1.18 GCD plot of a single charge-discharge cycle of unmodified ACC in aqueous 1 M H_2SO_4 at a current density of $1 A g^{-1}$, in three-electrode mode

GCD tests are oftentimes known as long-term cycling experiments, as they involve subjecting the electrode to thousands of charging and discharging cycles to determine the long-term stability and usability of the electrode material.^[97] As such, when used in a two-electrode setup, prolonged GCD experiments give valuable information not only on the capacitance of the full supercapacitor device, but also the cycling stability of the device through changes in its coulombic and energy efficiencies over time.

As an alternative, CV can also be used for measuring the capacitance or capacity of an electrode or supercapacitor,^[126] although GCD testing is still the primary technique most researchers use for testing of energy storage systems.

1.3.5.2 Cell configuration

Capacitance measurements of single electrodes are performed with a three-electrode setup, with the material to be measured as the working electrode. Single-compartment cells typically used for conventional electrochemical experiments can be used for single-electrode capacitance measurements, though specialized cells exist which mimic the compact spatial configuration in a packaged supercapacitor cell, while providing an extra compartment for the reference electrode. The T-type Swagelok cell shown in Figure 1.19 is an example of such a cell that is suitable for three-electrode experiments.^[127-128]

Figure 1.19 (A) Schematic cross-section diagram, and (B) photograph of a T-type Swagelok cell. Reprinted (adapted) with permission from Garcia, G.; Schuhmann, W.; Ventosa, E. *ChemElectroChem*. **2016**, 3, 592–597. Copyright 2016 John Wiley and Sons

On the other hand, two-electrode setups are best used for simulating the actual conditions of a packaged supercapacitor (in the absence of a reference electrode), where contact between the current collectors, electrodes and membrane/separator is made very tight, as can be seen from the test cell shown in Figure 1.20. Other variations of two-electrode cells exist, such as the two-way Swagelok cell.^[107]

Figure 1.20 (top) Schematic cross-section diagram of an assembled supercapacitor test cell, reprinted (adapted) with permission from Stoller, M. D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R. S., *Nano Lett.* **2008**, 8, 3498–3502. Copyright 2008 American Chemical Society; (middle) photograph of the assembled test cell; and (bottom) disassembled test cell

Three-electrode setups are most suitable for determining the electrochemical characteristics of a single electrode, such as faradaic reactions. Through CV, it is also used for identifying the maximum possible electrochemical potential window of an electrolyte solution, beyond which unwanted electrolyte decomposition occurs.^[129] While single-electrode capacitance measurements are also possible in a three-electrode cell by performing GCD experiments, care should be exercised in the values obtained; the specific capacitance values, C_{sp} , obtained from three-electrode GCD experiments are often twice as much (or more) than those obtained using a two-electrode setup, due to differences in the charge transfer behavior and voltage applied between the two.^[130]

On the other hand, a researcher looking to evaluate the performance of a full supercapacitor device should employ a two-electrode setup instead, especially if they have an electrode well-suited to be the positive electrode and another to be the negative electrode each. Results obtained from experiments run using two-electrode setups will reflect contributions from all parts of the cell, including resistances from the separator, leads, and electrode-current collector interface, some of which may be significant and are often overlooked. Moreover, in the case of asymmetric supercapacitors (i.e. different anode and cathode materials), an important consideration to be made is the need to achieve charge balance between the two electrodes, in order to split the voltage equally between the two during charging and discharging processes.^[131] This is done by adjusting the mass ratio between the positive and negative electrode until the theoretical maximum charge stored at each electrode is calculated to be the same.^[132-133] Lastly, as cautioned in the previous paragraph, prudence should be exercised when comparing capacitance data between two- and three-electrode setups. Where necessary, single-electrode specific capacitance can be derived from the total capacitance of a *symmetric* supercapacitor by using Equation 1.7 as follows:

$$C_{sp} = 4 \times \frac{C}{m} \quad (1.7)$$

where C = total measured capacitance of the two-electrode cell; and m = total mass of the active material in both electrodes.^[126] It should be noted that the above equation is only applicable for symmetric supercapacitors bearing identical cathode and anode electrode materials.

1.3.5.3 Other considerations

The electrolyte solution used in a supercapacitor cell is an important contributor of its energy storage performance. Each electrolyte solution is electrochemically stable within a certain potential window, beyond which degradation occurs. Given that both energy and power are directly proportional to the cell voltage squared (Equations 1.5 and 1.6), the choice of electrolyte is thus a key determinant of the theoretical maximum energy stored for the device. Electrolytes are generally categorized as being either aqueous or nonaqueous, though certain exotic classes such as ionic liquids have begun to surface in recent years.^[100] Aqueous electrolytes (e.g. KCl, H₂SO₄, KOH) are cheap, abundant, and have few concerns with regards to safe use, but suffer from a relatively narrow theoretical potential window of 1.23 V. Nonaqueous electrolytes (e.g. propylene carbonate, acetonitrile), on the other hand, exhibit much wider potential windows ranging between 2.5 and 2.8 V, and thus see greater commercial use. However, some nonaqueous solvents like acetonitrile are flammable and toxic, which may raise safety concerns in the case of accidental solvent leakages due to mishandling, or during cell manufacturing and recycling.^[105, 134]

The current collector is, as its name implies, a highly conductive medium or conduit through which electrical current is passed to and from the electrodes and the external load, with heat dissipation as the secondary function.^[100] The presence of a current collector reduces the overall resistance of the cell by increasing the electrical contact between the electrode and

external load. Some examples of current collectors include aluminium, stainless steel, titanium, and even carbon fibers and papers.^[99-100, 134]

1.4 Objectives (Modified activated carbon cloths for energy storage)

In the ever-expanding field of energy storage systems, the modification of electrodes by diazonium chemistry is one of many efforts which aim at increasing their capacity to store and release charge.^[31, 33, 135] Given the attractive properties of activated carbon powders as earlier mentioned, much research has gone into the chemical modification of these materials with redox-active molecules by diazonium chemistry.^[118, 136-138] For example, Bélanger's group found a doubling of the capacitance upon attachment of AQ groups onto activated carbon powders, which was tested through the use of a composite electrode in a supercapacitor setup.^[137] Elsewhere, Cougnon and co-workers showed an increased specific capacity of nitrobenzene-modified activated carbon powders compared to their unmodified versions, while demonstrating the ability of 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavengers in limiting multilayer formation of the nitrobenzene film.^[139]

We were thus interested to investigate the modification of ACCs instead, of which only few studies have been performed, to the best of our knowledge.^[104, 127] In those studies, the attached molecules (catechol^[127] and 2-anthraquinone^[104]) were indeed found to provide additional capacity to the carbon cloths through experiments run under aqueous acidic conditions.

In Chapter 4 (Comparing modified and unmodified activated carbon cloths for energy storage in supercapacitors) of this thesis, the energy-storage capability of AQ-modified ACCs was compared with that of unmodified ACCs, with the aim of optimizing the carbon cloth electrodes for use in supercapacitors. The study then evaluates the conditions under which

chemical modification of ACCs with redox-active AQ groups does not lead to improved electrode capacities.

1.5 References

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CHAPTER 2 ELECTROGRAFTING OF STERICALLY BULKY TETRAMETHYLANILINE GROUPS ON GLASSY CARBON ELECTRODES BY ARYLDIAZONIUM CHEMISTRY: REASONS FOR THE FORMATION OF MULTILAYERS

2.1 Abstract

Within the field of electrografting with aryldiazonium cations, there are various methods available to graft a monolayer of organic groups onto electrode surfaces. One of these relies on the presence of steric groups or constraints on the aryldiazonium cation itself, which prevent multilayers from being formed by blocking access of the free aryl carbons on the grafted layer to the diazonium cations. Here, we investigate the nature of the layer formed from the electrochemical reduction of bulky 2,3,5,6-tetramethylaniline monodiazonium cations on glassy carbon electrodes, to form 2,3,5,6-tetramethylaniline-modified glassy carbon (**GC–TMA**), which was subsequently characterized by atomic force microscopy scratching, cyclic voltammetry, electrochemical impedance spectroscopy, and X-ray photoelectron spectroscopy. Despite the bulky structure of the TMA group, **GC–TMA** was found to exhibit sparsely distributed multilayers, owing to the ability of the precursor to undergo a competing electropolymerization reaction under the experimental conditions used.

2.2 Introduction

Electrografting by diazonium chemistry as a surface modification method has been widely explored since it was first reported by Savéant and co-workers in 1992.^[1] Briefly, the procedure involves the electrochemical reduction of an aryldiazonium group to yield the corresponding aryl radical in a homolytic fashion, which subsequently forms a covalent bond with surface atoms of the electrode to form the layer-grafted electrode. Heterolytic cleavage of

the diazonium cation, which gives an aryl carbocation instead, is also possible though less likely in the presence of a reducing agent. Compared to the self-assembled monolayers (SAMs) formed by thiol-on-gold chemistry, the layers formed from the reduction of aryldiazonium salts are more stable to a wider range of temperatures, pH, and electrode potentials.^[2-3] However, unlike the thin monolayers of SAMs, films formed by diazonium chemistry tend to be polymeric in nature. These covalently linked multilayers arise from the side reactions of the highly reactive aryl radicals with the existing film on the surface or other aryldiazonium cations in solution, forming carbon-carbon and azo bonds respectively (Scheme 2.1).^[4-5]

With modified electrodes finding use in various applications including (bio)sensors^[6-7] and cathodes/anodes for energy storage systems,^[8-9] it is desired that heterogeneous electron transfer between the electrode and the redox species in solution be as fast as possible, which may be achieved with a thin layer of the grafted film on the electrode surface. Conversely, the thicker the film, the slower the through-bond electron transfer across the modified electrode.^[10-11] Particularly for electrochemical sensors, there is an inherent trade-off between having a high density of active recognition sites on the surface (achieved by having a thicker film to accommodate more active molecules), and fast electron-transfer kinetics from having thin layers.^[7]

Scheme 2.1 Electrografting side reactions which form multilayers: (a) attack of an aryl radical on a vacant ortho carbon on the grafted layer; and (b) attack of a cyclohexadienyl radical on a diazonium cation

Limiting the thickness of the film thus grafted onto the surface (by diazonium chemistry) to a thin monolayer has been explored before by several groups, with various approaches being taken to limit multilayer formation. This topic is covered in excellent depth by Downard in her review paper,^[12] with a few of these methods being mentioned here. One of these approaches, developed by Breton et al., involves the use of redox mediators in the grafting solution which react with diazonium cations before they can diffuse towards the electrode surface.^[13] By extension, the same authors were able to elegantly utilize the reductive ability of superoxide ions generated from dissolved oxygen in the grafting solution; similar to the redox mediators, the superoxide ions react with diazonium cations before they can reach the electrode, thereby resulting in ultrathin films being formed.^[14]

Another commonly studied method is the protection-deprotection strategy developed by Hapiot and Downard et al. It involves the grafting of diazonium cations bearing generally bulky protecting groups (e.g. triisopropylsilyl for aryl alkynes,^[15] Boc and Fmoc for amines)^[16]

onto the electrode, then their subsequent deprotection to afford a monolayered film. This approach has the added advantage of the resulting film possessing functional groups which allow for further conjugation of secondary molecules via known coupling reactions (e.g. click coupling for alkyne-terminated films,^[15] and amide coupling for amine-terminated films.)^[16] A similar method by Daasbjerg et al. is the formation-degradation procedure using cleavable disulfide bonds formed within multilayers, to ultimately form a monolayer of grafted thiophenolate groups.^[17]

Yet another approach also involves the use of bulky substituents, albeit not as protecting groups. Podvorica et al. discovered that having *tert*-butyl substituents *meta* to the diazonium group on the aryl ring result in monolayer formation on metal surfaces, since they prevent the side reactions of the aryl radicals (as in Scheme 2.1) from occurring on those positions due to steric hindrance.^[18] They then significantly expanded the scope of the study to include more substituted aryldiazonium species, and (among other findings) concluded that the presence of at least an ethyl group on the *ortho* position (as in 2-ethylbenzenediazonium), or two methyl groups on the *ortho* position (as in 2,6-dimethylbenzenediazonium) would prevent any reaction with the surface.^[5] Separately, De Feyter et al. successfully applied the same techniques for the modification of graphitic substrates with *tert*-butyl substituted diazonium species to afford monolayers.^[19]

The findings of the experiments in the above studies on bulky diazonium cations led us to explore the possibility of modifying electrode surfaces using 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD), which belongs to the commonly studied class of phenylenediamine compounds. The electrografting of conductive surfaces with the diazonium cation produced from the structurally simpler *p*-phenylenediamine (PD) to produce surfaces decorated with aniline groups has been performed previously,^[8, 20-23] which led us to explore this possibility with TMPD. Here, we selectively diazotized only one amine group of TMPD

to generate (*in situ*) the monodiazonium cation of 2,3,5,6-tetramethylaniline (TMA), and performed electrografting with glassy carbon electrodes in the resultant solution, as shown in Scheme 2.2, to form 2,3,5,6-tetramethylaniline-modified GC (**GC-TMA**). Given its relatively bulkier molecular structure which may aid in limiting multilayer growth, we were interested in the properties of electrodes modified with the diazonium compound of TMPD which, to the best of the authors' knowledge, has not been studied yet. Height data of the TMA film formed on **GC-TMA** was obtained by the atomic force microscopy (AFM) scratching method,^[24] which revealed the presence of multilayers on the modified electrode. Further characterization of **GC-TMA** was also performed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). Comparisons of the properties of **GC-TMA** with another related modified electrode, aniline-grafted GC (**GC-A**), were also made. In this paper, we explore the reasons for multilayer formation on **GC-TMA**, despite the use of a sterically bulky precursor.

Scheme 2.2 Mechanism for electrografting TMA groups onto a GC electrode from TMPD by diazonium chemistry to form **GC-TMA**

2.3 Results and Discussion

2.3.1 Electrochemical behavior of TMA monodiazonium cations

Modification of the GC electrode to form **GC-TMA** was first performed by a CV of the monodiazonium cation of TMA, which was formed *in situ* by the addition of one equivalent of NaNO₂ to an acidic solution of TMPD. It has previously been shown that the monodiazonium cation formed from PD (produced *in situ*) is preferentially formed over its bis-diazonium form due to the former being thermodynamically more stable and, hence, less reactive to a second diazotization.^[22] As seen in Figure 2.1, a chemically irreversible reduction peak is present at -0.22 V whose current decreases sharply from the second cycle onwards. This decrease in current is typically observed for electrode modification with diazonium salts by CV, which occurs due to passivation of the electrode surface by the grafted film. The reduction peak was assigned to the reduction of the aryldiazonium group to the aryl radical, since the highly donating amine and methyl groups on the monodiazonium cation of TMA necessitate a more negative potential for its reduction to the aryl radical, as predicted by the relationship between the reduction peak potential of substituted aryldiazonium salts and the Hammett constant of the substituent group.^[25] Henceforth, **GC-TMA** was prepared through chronoamperometric CPE with the potential set at -0.47 V vs. Ag/AgCl (see **Experimental Section**) for 3 min.

Figure 2.1 5-cycle cyclic voltammogram of *in situ* generated monodiazonium cation of TMA (1 mM) in aqueous 0.5 M HCl with a bare GC electrode at $\nu = 0.1 \text{ V s}^{-1}$

However, at the chosen starting potential of 0 V, there is already a reductive current (ca. $-7.0 \text{ } \mu\text{A}$) present, which indicates that another moiety is being reduced even before the irreversible diazonium reduction at -0.22 V . When CV was carried out from a higher (more positive) potential instead (Figure 2.2, black trace), the voltammogram observed is unlike that of a typical voltammogram for grafting by diazonium chemistry. Besides the shallow reduction peak at -0.22 V , two pairs of peaks with much larger currents are present at $E_{1/2} = 0.22 \text{ V}$ and 0.35 V , which account for the initial negative current seen in Figure 2.1. Since the reduction processes are at least partially chemically reversible, and occur at much more positive potentials, it is highly unlikely that they correspond to TMA diazonium cation reduction.

Figure 2.2 Cyclic voltammograms of grafting by two different methods in aqueous 0.5 M HCl with a bare GC electrode at $\nu = 0.1 \text{ V s}^{-1}$; arrows indicate initial direction of the CV

Separately, in an experiment involving the 10-cycle CV of solution-phase TMPD (*not* its diazonium cation) in aqueous 0.5 M HCl from 0.00 V to 0.60 V on bare GC (Figure 2.2, blue trace), two redox couples with $E_{1/2} = 0.21 \text{ V}$ and 0.35 V are seen to increase in current with increasing CV scans, indicating an electropolymerization process. These redox pairs do not appear if the potential scan is limited to potentials below 0.40 V (Figure 2.2, red trace), which is the onset potential for the oxidation of TMPD to its radical cation. Assuming that TMPD follows a similar oxidative electropolymerization process as PD in aqueous acidic solution,^[26] the polymer from TMPD (i.e. poly(TMA)) is proposed to be formed via the mechanism shown in Scheme 2.3. It should be noted that, upon washing and sonication of this poly(TMA)-modified GC in acetonitrile, a CV of the resulting GC electrode in blank aqueous solution did not show any discernible peaks in the potential window studied, indicating that poly(TMA) was only weakly bound to the GC surface by physical adsorption.

Scheme 2.3 Proposed electropolymerization mechanism to form poly(TMA)

Drawing a comparison between the voltammograms in Figure 2.2 (black and blue traces), it is very likely that these redox pairs correspond to the same processes, given that their half-wave potentials match closely. It follows that the resulting films formed from both grafting methods could be structurally similar to each other, despite their precursors being different. This might imply that, in the formation **GC-TMA** by diazonium chemistry, electropolymerization of TMPD (to form poly(TMA)) occurs well before the required potential

for the reduction of its monodiazonium cation, which would impede monolayer formation. To investigate this possibility further, the spontaneous grafting of GC with the monodiazonium cation of TMA was performed in the absence of an applied potential to minimize diazonium reduction. The resulting modified GC (hereby termed **s-GC-TMA**) was then studied by measuring its cyclic voltammogram in a blank solution of aqueous 0.5 M HCl, and the results compared with that of **GC-TMA** as shown in Figure 2.3.

Figure 2.3 Cyclic voltammogram of a blank solution of aqueous 0.5 M HCl with **GC-TMA** (GC electrode electrochemically modified with TMA groups), **s-GC-TMA** (GC spontaneously modified with TMA groups) and bare GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$. All modified electrodes have been sonicated in fresh acetonitrile prior to CV measurements

Both methods of electrode grafting result in modified GC electrodes with an oxidation step with an onset potential of 0.17 V, which indicates that spontaneous grafting did indeed occur. A plot of anodic peak current against scan rate (varied from 0.1 to 1.0 V s^{-1} , not shown) for each modified electrode yields a good linear relationship ($R^2 = 0.998$ and 0.992 for **GC-TMA** and **s-GC-TMA**, respectively), consistent with the films being surface-bound, and the peaks appear reproducibly when scanned three times consecutively. It should be noted that

these modified electrodes have been sonicated in fresh acetonitrile for 5 min prior to CV measurements.

We tentatively assign these redox pairs to the reversible redox reactions of the poly(TMA) film, given that their half wave potentials match the pair of peaks with the same $E_{1/2}$ of 0.22 V in Figure 2.2. The redox couple at $E_{1/2} = 0.35$ V seen in Figure 2.2 does not seem to be present in the modified electrodes in Figure 2.3, which is indicative of the removal of weakly-bound intermediates of the electropolymerization process. Being analogous to polyaniline in structure, poly(TMA) is proposed to be able to undergo reversible oxidation from the leucoemeraldine to the emeraldine form of the polymer^[27] at $E = 0.20$ V as illustrated in Scheme 2.4. The much broader appearance of the peaks on **GC-TMA** is likely due to the film being a mixture of poly(TMA) and TMA groups bonded to the GC surface through diazonium chemistry. Further, the presence of the initial reductive current in Figure 2.1 can be ascribed to the reduction of poly(TMA) from the emeraldine to leucoemeraldine form. Given that the open circuit potential of the GC electrode in a solution of 1 mM TMPD in aqueous 0.5 M HCl was measured to be 0.37 V, it follows that poly(TMA) just formed on the electrode surface is in the oxidized state. More interestingly, the presence of a redox pair (and hence an electroactive film) on **s-GC-TMA** was unexpected since there was no reducing potential or agent present, especially given the highly negative potential required for the reduction of the TMA monodiazonium cation. Some other mechanism must be responsible for the formation of the film on **s-GC-TMA**.

Scheme 2.4 Mechanism for the reversible oxidation of poly(TMA) from the leucoemeraldine to emeraldine forms

At this point, the alternative heterolytic pathway for diazonium cleavage to form the aryl carbocation becomes relevant, as it could account for the above findings. We propose that the electrografting is preceded by heterolytic dediazonation to initiate the polymerization steps, thus producing a multilayered film on **GC-TMA**, explained as follows. In the presence of a reducing reagent or electron-rich substrate, homolytic diazonium cleavage is usually preferred over its heterolytic counterpart.^[28] In the case of TMPD, however, the electron-donating methyl groups would confer additional stability on its aryl carbocation by the inductive effect, thereby increasing the likelihood of its monodiazonium cation undergoing the heterolytic pathway before it gets reduced at $E_{\text{red}} = -0.22$ V (Figure 2.1). The resulting aryl carbocation is then able to polymerize (Scheme 2.3) to form the electroactive poly(TMA) chain, which occurs in the presence or absence of an applied potential (as in **GC-TMA** and **s-GC-TMA**, respectively). Given that poly(TMA) exists as a chain of multiple TMA groups linked together, it follows that the resulting film formed from any of the above grafting processes is multilayer in nature. The entire process of **GC-TMA** and **s-GC-TMA** formation is depicted in Scheme 2.5. The

washing and sonication steps performed at the end of each grafting procedure ensures the removal of any stray poly(TMPD) chains bound by physical adsorption.

Scheme 2.5 Proposed mechanisms for **GC-TMA** and **s-GC-TMA** formation

Assuming a one-electron oxidation per TMA moiety in the film, the experimental surface coverage (Γ) of the films on the modified GC electrodes can be calculated based on the anodic peak on the cyclic voltammograms in Figure 2.3: $(6.13 \pm 0.10) \times 10^{-11} \text{ mol cm}^{-2}$ and $(4.98 \pm 0.25) \times 10^{-11} \text{ mol cm}^{-2}$ for **GC-TMA** and **s-GC-TMA**, respectively. However, these values are only valid if all the TMA moieties on the TMA film undergo oxidation, which is not likely. Moreover, the values do not give much information on how sparsely or densely distributed the film is (e.g. presence of pinholes), especially since Γ was found to be below

typical monolayer values ($(2.5 \pm 0.5) \times 10^{-10}$ mol cm⁻² for 4-nitrophenyl groups on a flat surface).^[29]

As for the formation of aniline-grafted GC (i.e. **GC-A**) from PD, the reduction potential of its aniline monodiazonium cation was determined to be -0.12 V from its CV in acidic solution (Figure S2.1), which is notably less negative than that of the monodiazonium cation of TMA due to the absence of electron-donating methyl groups on PD. Interestingly, the profile of the voltammogram of aniline monodiazonium cation reduction (which resembles that of a typical diazonium reduction) differs largely from that of TMA monodiazonium cation reduction, despite this difference being attributable “only” to the additional steric bulk on TMA groups. Moreover, the relative decrease in the current from the second cycle onwards is larger (i.e. greater electrode passivation) than that for the reduction of the monodiazonium cation of TMA in Figure 2.1, which could point to the formation of thicker and/or more tightly-packed aniline layers than TMA layers. As with **GC-TMA**, subsequent preparation of **GC-A** was also prepared through chronoamperometric CPE, except at a potential of -0.37 V for 3 min.

Unlike **GC-TMA**, the cyclic voltammogram of **GC-A** in blank acidic solution did not show any discernible redox peaks in the potential window studied, hence disallowing the calculation of surface coverage by similar means. However, due to the absence of substituted groups on the phenyl moiety of PD which allows for electrografting side reactions (Scheme 2.1) to occur, it is expected that **GC-A** also forms multilayered films on the GC surface,^[21-23] though not via an electropolymerization route.

2.3.2 *AFM scratching experiments on PPF-TMA and PPF-A*

In order to ascertain the thickness of the layers formed, AFM scratching was used.^[24] The technique involves physically removing a portion of the film (hence “scratching”) using a probe with a low force constant under contact mode, then imaging the topography of the

resulting film with a probe with a higher force constant under tapping mode. The technique relies on the observation that the underlying substrate is not removed by the scratching process, and so the difference in height measured from the film removal would correspond to its thickness. PPF substrates were used as the conductive substrates as they have low roughness (<0.5 nm) and are hence suitable for the topographical measurements of nanometer-thick films. These are shown in Figure 2.4 for **PPF-TMA** and Figure 2.5 for **PPF-A**.

Figure 2.4 AFM image ($4.5 \times 0.9 \mu\text{m}$) of **PPF-TMA** with film partly removed (left), and corresponding sample line profile (right); the red line corresponds to the part of the sample profiled

Figure 2.5 AFM image ($3.0 \times 0.7 \mu\text{m}$) of **PPF-A** with film partly removed (left), and corresponding sample line profile (right); the red line corresponds to the part of the sample profiled

The thicknesses of the films of **PPF-TMA** and **PPF-A** were found to be $15.5 \pm 4.0 \text{ nm}$ and $17.1 \pm 0.7 \text{ nm}$, respectively. Considering that monolayer-thin films have thicknesses which are typically less than 1 nm , **GC-TMA** can thus be expected to form multilayers of TMA groups as well. As explained earlier, the multilayers observed by AFM are likely to be poly(TMA) chains formed from electropolymerization. Unsurprisingly, **PPF-A** (and **GC-A**, by extension) was found to possess a multilayered aniline film.

One difference between the two films is their packing density, indicated by the root mean square roughness (R_q) values also obtainable by AFM. The TMA film of **PPF-TMA** ($R_q = 5.11 \pm 0.31 \text{ nm}$) was found to be rougher than the aniline film of **PPF-A** ($R_q = 2.01 \pm 0.10 \text{ nm}$), which may indicate the presence of a greater number of pinholes and defects on the former. This may be explained with reference to the mechanism of **GC-TMA** formation (Scheme 2.5): any physically adsorbed poly(TMA) chains which remain after the electrografting step would be removed by the final washing and sonication steps, leaving behind pinholes on the resulting

film. Such desorption is not likely in the case of **GC-A** since the immediate first layer of the aniline film is covalently bonded to the electrode surface.

2.3.3 XPS spectra of GC-TMA and GC-A

The survey spectra of both grafted electrodes (Figure 2.6a–b) show that the major signals of interest are contributed by the GC surface and its adventitious contaminants (C_{1s} and O_{1s} peaks) and the organic layer (C_{1s} and N_{1s} peaks). The N_{1s} peak of **GC-TMA** is significantly less intense than that of **GC-A** under similar electrografting conditions, which indicates that the TMA film of **GC-TMA** is either thinner or sparser than that of the aniline film of **GC-A**.

Further information on the organic films can be gleaned from the high-resolution XPS spectra of the N_{1s} region of both modified GC surfaces (Figure 2.6c–d). The peaks at 399.4 and 399.3 eV from **GC-TMA** and **GC-A**, respectively, can be assigned to the amine group present in both organic films.^[8, 22] Another peak at 400.1 eV on **GC-A** is assigned to the azo group,^[22] which is likely formed from the multilayer-forming side reaction involving an attack of a cyclohexadienyl radical on a diazonium cation of PD (Scheme 2.1), giving evidence of the multilayer nature of the aniline film on **GC-A**. As for **GC-TMA**, the presence of two signals at 400.9 eV and 402.6 eV corresponds to the film having the amino radical cation ($-NH_2^{*+}$) and quinone imine cation ($-NH^+=$) functionalities,^[30] contributed by the emeraldine forms of poly(TMA).

Figure 2.6 XPS survey spectra of (a) **GC-TMA** and (b) **GC-A**; and high-resolution XPS spectra of the N_{1s} core level regions of (c) **GC-TMA** and (d) **GC-A**

2.3.4 Further electrochemical characterization of GC-TMA and GC-A

The blocking ability of **GC-TMA** was compared against that of **GC-A** by CV experiments of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple in aqueous buffered solutions from pH 3 to 10 (Figure 2.7). This inner-sphere redox-active couple is a useful probe for studying amine-terminated modified electrode surfaces as these probes are negatively charged, therefore exhibiting varying levels of electrostatic interactions with TMA groups at their protonated state (below their pK_a) and deprotonated state (above their pK_a), depending on the pH of the medium.

Figure 2.7. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ (1 mM) in Britton-Robinson buffer from pH 3 (red trace) to 10 (violet trace) with (a) **GC-TMA** and (b) **GC-A** at $\nu = 0.1 \text{ V s}^{-1}$

At a sufficiently low pH, **GC-TMA** is protonated at the amine groups, which forms electrostatic interactions with the negatively-charged $\text{Fe}(\text{CN})_6^{3-}$ molecules in the acidic medium. These interactions compensate for any increase in electron transfer resistance due to physical blocking effects, thus exhibiting electrochemically reversible behavior on **GC-TMA**. At a much higher pH, however, there are little electrostatic interactions between the neutral deprotonated film and the $\text{Fe}(\text{CN})_6^{3-}$ molecules, which then slows down the electron transfer of the probe molecules across the **GC-TMA** surface, increasing the peak-to-peak separation (ΔE_p) of the reaction. Since such changes in ΔE_p do not occur on a bare, unmodified GC (Figure S2.2), the observations made from Figure 2.7a point to the successful electrografting of the GC electrode with an amine-containing film.

Figure 2.8 Plots of peak current and peak-to-peak separation of $\text{Fe}(\text{CN})_6^{3-}$ (1 mM) on **GC-TMA** and **GC-A** against pH of Britton-Robinson buffer

From the results obtained, the pK_a of the TMA film can be estimated from the inflection points of the pH-dependent plots in Figure 2.8, which reflects the point at which half of the molecules on the film are in the protonated state (and the other half is not). Using reductive peak current (i_p^{red}) as the dependent variable gives a rough value of $\text{pK}_a \approx 7.0$, while using ΔE_p gives $\text{pK}_a \approx 7.5$. Given that the pK_a of protonated TMA (i.e. the protonated 2,3,5,6-tetramethylaniline *molecule*) was previously found to be 4.3,^[31] there is an increase in the pK_a going from solution-phase TMA to its immobilized form on **GC-TMA**. This increase in pK_a was also noted in another study which compared solution-phase *N,N*-diethylaniline ($\text{pK}_a = 6.6$) with its surface-immobilized counterpart ($\text{pK}_a \approx 10.0$).^[25] On the other hand, a decrease in pK_a was found in the comparison between benzoic acid in solution ($\text{pK}_a = 4.2$) and a 4-carboxyphenyl film on a GC surface ($\text{pK}_a \approx 2.8$).^[32] Though such comparison studies are not uncommon in the literature, it is still not yet clear how these trends can be explained.

Separately, the CV experiment with the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple was carried out using **GC-A** instead (Figure 2.7b), which is expected to bear multilayers of aniline groups.

The results for **GC-A** (pK_a of protonated aniline = 4.6)^[33-34] follow a similar trend as those for **GC-TMA** across the pH range studied, with fast electron transfer kinetics at low pH and slower electron transfer at higher pH. However, the increase in ΔE_p and decrease in i_p^{red} with increasing pH is much greater on **GC-A**. Since the pK_a values of the protonated forms of both molecular TMA and aniline are quite similar, the large difference in ΔE_p could be attributed to **GC-TMA** having more pinholes than **GC-A**, with the latter exhibiting a greater blocking effect to $\text{Fe}(\text{CN})_6^{3-}$ molecules at high pH. Interestingly, the results imply that the greater packing density on the film of **GC-A** has little effect, if any, on the slowing down of electron transfer kinetics at low pH when compared to **GC-TMA**. This could imply that pinholes are still not completely absent from the aniline film of **GC-A**, which would allow passage of probe molecules to the electrode surface for electron transfer.

On the other hand, in the case where the same CV experiments on **GC-TMA** are carried out with the $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$ redox couple instead, the results show that ΔE_p and i_p^{red} do not change significantly throughout the entire pH range studied (Figure S2.3). Since $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$ is an outer-sphere redox system that is largely insensitive to the presence of defects or modifications on an electrode surface, it exhibits fast electron transfer across the TMA film regardless of its state of protonation at various pH. It is also worth noting that repulsion effects from like charges between the positively charged probes and protonated TMA groups at low pH were not observed from the CV results, likely due to the associated slowing of electron transfer kinetics being masked over by the outer-sphere property of the redox couple.

Similar experiments were carried out using dopamine in aqueous 0.1 M H_2SO_4 (Figure 2.9), which is usually considered to be a more sensitive inner-sphere redox probe towards pinholes on the grafted film. Here, differences in ΔE_p of the reversible two-electron oxidation of dopamine to dopamine-*o*-quinone for the various electrodes are compared. The ΔE_p on **GC-**

TMA (63 mV) was found to be only slightly greater than on bare GC (42 mV), which indicates that there are many pinholes present within the TMA film for dopamine to diffuse through to the electrode surface. On the other hand, the much greater ΔE_p on **GC-A** (258 mV) is due to there being much fewer pinholes on the multilayered aniline film.

Figure 2.9 Cyclic voltammograms of dopamine (1 mM) in aqueous 0.1 M H₂SO₄ with **GC-TMA**, **GC-A** and bare GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$

Measurements of the blocking abilities of both **GC-TMA** and **GC-A** were also carried out by EIS experiments using the same $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ redox couple in buffer solutions of varying pH, and are displayed as Nyquist plots (Figure 2.10). Here, additional buffer solutions in the more basic region (up to pH ~12) were also used.

Figure 2.10 Nyquist plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in buffer solutions from pH 3 (red trace) to 12 (pink trace) using (a) **GC-TMA** and (b) **GC-A**

The results from these EIS experiments mirror those from the CV experiments previously discussed; similar conclusions can be made on the blocking behavior of **GC-TMA** and **GC-A** towards the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple at various pH, whereby R_{CT} becomes greater with increasingly basic pH. Moreover, the R_{CT} of **GC-TMA** was found to be smaller than that of **GC-A** at more basic pH, which further supports the finding that the sparser film on **GC-TMA** allows for faster electron transfer across the modified GC surface.

In earlier studies on sterically hindered diazonium salts, Podvorica et al. found that grafting is highly unlikely in the case of the *ortho*-substituted 2,6-dimethylbenzenediazonium salt, due to the high kinetic barrier imposed by the methyl substituents on covalent bond formation between the aryl carbon and the electrode surface.^[5] Having thoroughly characterized **GC–TMA**, we are inclined to agree with their conclusion, especially given the low surface coverages obtained. However, that is not to say that such grafting is impossible; indeed, cyclic voltammograms of the GC electrode after treatment with 2,6-dimethylbenzenediazonium tetrafluoroborate compared to that of bare GC in aqueous ferricyanide solution show a slight widening of the peak-to-peak separation for the ferricyanide couple, indicating that at the very least, some electrografting has occurred.^[5]

There is also the possibility that some of the TMA film may comprise TMPD molecules bonded to the GC surface through the amine group (i.e. C–N bonded). This normally occurs under oxidative conditions (in organic or aqueous media), where removal of an electron from an amine-bearing molecule first produces its radical cation, followed by deprotonation to give its aminyl radical, then subsequent attack of the radical on the substrate to give the modified surface.^[35-36] In one example, PD in acetonitrile solution was immobilized onto a GC electrode by continuous cycling around its oxidation peak potential ($E_p^{ox} = 0.66$ V), until the irreversible oxidation peak no longer decreases with increasing cycles.^[37] The resultant electrode was then found, by CV peak integration, to possess a monolayer of PD groups. Though we do not completely discount the above possibility in our study of **GC–TMA** (due to the high kinetic barrier to be overcome for C–C bonding to occur, as discussed earlier), C–N bonded TMPD groups are not likely to form the majority of **GC–TMA** as no oxidizing potential was applied during the electrografting procedure to form the necessary aminyl radicals.

In any case, it is apparent that the resulting **GC–TMA** produced is not without defects. This may be attributed to TMPD having two amine groups, which may present several

problems in the electrografting process such as the presence of free (“non-diazotized”) TMPD in the grafting solution (as a result of being limited to the use of one equivalent of NaNO_2), which in turn leads to undesired electropolymerization. The use of diazonium precursors with a single amine group (as is the case for most studies in the field) would allow for the use of an excess of the diazotizing agent, which considerably decreases the potential for side reactions to occur.

2.4 Conclusion

Electrografting was performed on GC electrodes using the monodiazonium cation produced *in situ* from TMPD. The resulting modified electrode (**GC-TMA**), which was characterized through electrochemical and spectroscopic means, was found to exhibit sparse multilayers along with pinholes. The ability of TMPD to electropolymerize both in its native and monodiazonium forms disfavors its use as a precursor for the formation of low-defect modified surfaces, much less one with a monolayer. Outside of the concerns of electropolymerization (to form poly(TMPD)), while the methyl substituents of TMPD may serve to prevent multilayer-forming side reactions, they also limit efficient attachment of their aryl radicals onto the electrode surface due to the high repulsive forces to be overcome. Fortunately, many alternatives for stable monolayer formation exist. Researchers looking to utilize the usefulness of bulky groups to limit unwanted multilayer formation may consider the protection-deprotection strategy, a research area where there is much potential for growth. With more being understood about the mechanisms of aryldiazonium and other electrografting methods, care should be taken in choosing the appropriate technique and precursor for the intended purpose or application.

2.5 Experimental Section

2.5.1 Chemicals

The following chemicals were used as received from their respective commercial sources: *p*-phenylenediamine (PD, $\geq 98\%$, Tokyo Chemical Industry), 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD, $\geq 98\%$, Tokyo Chemical Industry), sodium nitrite (98%, Alfa Aesar), potassium hexacyanoferrate (II) trihydrate ($\geq 99\%$, Merck), potassium hexacyanoferrate (III) ($\geq 99\%$, Merck), hexaammineruthenium (III) chloride (98%, Sigma-Aldrich), dopamine hydrochloride ($\geq 99\%$, Merck), acetic acid (99%, Alfa Aesar), boric acid (99.9%, Sinopharm), phosphoric acid (85%, Sigma-Aldrich), sodium hydrogen phosphate ($\geq 98\%$, Alfa Aesar), sodium hydroxide (99%, Merck), hydrochloric acid (37%, VWR Chemicals), hydrofluoric acid (40%, Fisher Scientific), potassium chloride ($\geq 99\%$, Fischer Scientific), acetonitrile (HPLC grade, Fulltime), AZ P4620 positive photoresist (MicroChemicals GmbH, Germany).

Britton-Robinson buffer solutions of pH 3 to 10 were prepared according to established procedures^[38], using 0.04 M stock solutions of CH_3COOH , H_3BO_3 and H_3PO_4 , with the pH adjusted using aqueous 0.1 M NaOH solution and the ionic strength brought to 0.1 M using KCl. Buffer solutions of pH 11 to 12 were prepared with mixtures of aqueous 0.05 M Na_2HPO_4 and 0.1 M NaOH solution, and their ionic strengths were calculated to be 0.077 M and 0.084 M, respectively. Ultrapure water (18.2 M Ω cm resistivity) used was generated by a Pure Lab ELGA water-purification system (PURELAB Option-Q, UK). pH measurements were performed with a glass pH probe (Metrohm 827 Lab), which was calibrated with standard IUPAC buffer solutions of pH 4, 7 and 10 prior to its use.

2.5.2 Surfaces

3 mm diameter planar glassy carbon (GC) disk (Metrohm) working electrodes were used for cyclic voltammetry (CV), controlled-potential electrolysis (CPE) and electrochemical impedance spectroscopy (EIS) experiments. 1 cm $\times$ 1 cm GC plates (SIGRADUR® HTW, Germany) were used for X-ray photoelectron spectroscopy (XPS) experiments. Pyrolyzed photoresist films (PPF) were used for AFM scratching experiments, and were prepared with slight modifications from a known procedure^[29] as follows: A Si(100) wafer with thermal oxide was first cut into 1 cm $\times$ 1 cm pieces before wet etching with 10% HF for 10 min to remove the oxide layer, followed by washing with ultrapure water and drying under a 120°C oven for another 10 min. The dried Si pieces were then brought to room temperature, onto which AZ P4620 photoresist was spin-coated at 6,000 r.p.m. for 30 s (three drops per piece), followed by a soft-baking step at 110°C for 20 min. An additional layer of photoresist was spin-coated and soft-baked for a total of two coatings. The samples were then pyrolyzed in a quartz tube furnace under 100% N₂ throughout all phases: an initial 20 min flushing phase at room temperature, then heating at 5°C min⁻¹ up to 950°C, then holding at 950°C for 60 min, followed by gradual cooling to room temperature within the furnace.

2.5.3 Electrochemical measurements

CV, CPE, and EIS experiments were performed with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat, with a three-electrode setup, using a 3 mm diameter planar GC disk WE, a platinum wire (Metrohm) counter electrode, and a silver/silver chloride (Metrohm) in 3.0 M KCl reference electrode with double junction system. Prior to the start of each experiment where a bare (unmodified) working electrode is required, the GC electrode was successively polished with 0.3 μ m and 0.05 μ m alumina slurry on an Ultra-Pad polishing cloth (Buehler), then sonicated with fresh acetonitrile for 5 min, followed by blow-

drying with a stream of N₂. In order to minimize electromagnetic noise, all electrochemistry experiments were performed in a Faraday cage at room temperature (298 ± 2 K). Deoxygenation was carried out by bubbling N₂ into the electrochemical solution for 5 min prior to each measurement. EIS experiments with a frequency response analyzer (FRA) used an a.c. voltage of 10 mV in sine-wave amplitude with a frequency range from 10 kHz to 0.1 Hz, and were performed in buffer solutions of varying pH containing 5 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ at the open circuit potential.

The surface coverage of the modified GC electrodes (Γ) was calculated using Equation 2.1:

$$\Gamma = \frac{Q}{nFA} \quad (2.1)$$

where Q = charge integrated under the peak on the cyclic voltammogram; n = number of electrons per redox reaction; F = Faraday constant (96485 C mol⁻¹); and A = geometric surface area of the electrode (0.071 cm²). Uncertainties listed are the standard deviation of three replicate experiments.

2.5.4 AFM measurements

AFM measurements were performed on a MultiMode V8 scanning probe microscope (Bruker, Singapore) along with the Nanoscope Analysis v1.90 software for data processing. The AFM scratching technique^[24] involves removal of a section of film under contact mode with silicon nitride probes (Bruker) at a setpoint voltage of 1.0 V and tip velocity of 1 μm s⁻¹, and subsequent imaging under tapping mode with rotated tapping mode etched silicon probes (Bruker) at resonant frequencies of ca. 350 kHz. Before analysis, the resulting images were plane-fitted under a first order polynomial. For film thicknesses, the average height of the films on both sides of the scratch were first calculated, then subtracted with the average height of the underlying PPF substrate. This was performed a total of three times at separate line profiles

across the scratch, from which the mean and standard deviation were obtained. Root mean square roughness (R_q) measurements were found from five separate $0.5 \times 0.5 \mu\text{m}$ boxed regions, from which the mean and standard deviation were obtained.

2.5.5 XPS measurements

High resolution XPS experiments were performed on an ESCAProbeP (Omicron Nanotechnology Ltd., Taunusstein, Germany) spectrometer equipped with a monochromatic magnesium X-ray radiation source (1253.6 eV). Three survey scans and 15 high-resolution C_{1s} , N_{1s} , and O_{1s} core-level scans were performed for each sample. For the calibration of all spectra, the binding energy of the C_{1s} peak was taken to be 284.6 eV. The relative sensitivity factors used in the determination of atomic concentrations from the survey spectra for the three elements mentioned are 1, 1.77, and 2.85, respectively. Peak deconvolution was performed using CasaXPS software (ver. 2.3.16).

2.5.6 Modification of electrodes by diazonium chemistry

A solution of the monodiazonium cations of the phenylenediamine compounds was prepared *in situ* as follows: The phenylenediamine was dissolved in aqueous 0.5 M HCl (4.9 mL, final concentration of 1 mM), and the solution was bubbled under N_2 for 5 min. A chilled solution of NaNO_2 (0.1 mL, final concentration of 1 mM) was then added dropwise into the above solution, followed by another 1 min of bubbling under N_2 . Electrografting (by CV or CPE) was performed as soon as the GC electrode was immersed into the above grafting solution in the three-electrode setup. Where electrografting was performed by CPE, the duration of electrolysis was 3 min, with the grafting potential set at an overpotential of -0.25 V more negative than the aryldiazonium reduction potential as established from prior CV experiments. After each electrografting procedure, the modified GC electrode was first washed with

ultrapure water, and then sonicated in fresh acetonitrile for 5 min, followed by blow-drying with a stream of N₂. Spontaneous modification of electrodes was also carried out in a similar manner as above; except in the absence of an applied potential, all other conditions remained the same, with the duration of exposure of the electrode to the diazonium cation solution being 3 min.

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CHAPTER 3 COVALENT TETHERING OF SMALL MOLECULES AND CARBON NANOTUBES TO GLASSY CARBON ELECTRODES THROUGH A TETRAMETHYLANILINE FILM

3.1 Introduction

Electrode modification is often performed with the intent of its subsequent use for certain applications, such as biosensing^[1] and environmental sensing.^[2] These usually involve the transducing molecules being in close electrical contact with the electrode surface, either through a thin intermediate film which still allows for through-bond electron transfer, or through a longer conductive pathway (i.e. molecular wires). The latter phenomenon is especially valuable for biomolecular transducers such as proteins, where their redox active centers can be located deep within the molecule.^[3-4] In one example, the authors were able to demonstrate successful electrical contact between a gold electrode surface and the glucose oxidase enzymes which were connected to the surface through vertically-aligned single-walled carbon nanotubes (SWCNTs).^[3] As such, an important part of electrochemical research on modified electrodes is ensuring effective electrical communication between the electrode and the tethered molecule.

In the previous chapter, **GC-TMA** was thoroughly characterized on the nature of the grafted TMA film. Despite the film having multiple layers, it is believed that **GC-TMA** can still function as a suitable tether point for a variety of secondary molecules, by virtue of the exposed amine groups present on the TMA film. Of particular interest was the feasibility of such conjugation of secondary molecules, as the methyl substituents of the TMA moiety may hinder the conjugation step by steric hindrance.

This chapter details the attempts made to conjugate various secondary molecules onto **GC-TMA**. These molecules include anthraquinone-2-sulfonate (AQ2S), which has been

previously used for the electrochemical reduction of oxygen,^[5] and flavin mononucleotide (FMN), which has potential applications in energy storage.^[6] Further, SWCNTs were conjugated onto **GC-TMA** as a possible way of forming molecular wires, with the intent of restoring fast electron transfer rates to solution species. This was facilitated by prior acid-cutting of SWCNTs to form carboxylic acid-terminated SWCNTs (hereby termed SWCNT-COOH), followed by activation with a carbodiimide crosslinker to allow for facile coupling with amine-terminated surfaces through amide coupling,^[7-10] ultimately forming the modified electrode **GC-TMA-SWCNT**. Finally, the ability of **GC-TMA-SWCNT** to further couple with other molecules is investigated, with the motivation of studying the electrical communication between the electrode and the tethered molecule through the SWCNTs.

3.2 Results and Discussion

3.2.1 Conjugation by diazotization of TMA film

Knowing that **GC-TMA** is formed through diazotization and dediazonation of the amine-containing precursor, it is natural to consider the same possibility for the TMA film on **GC-TMA** itself: that is, the exposed amine groups on **GC-TMA** can be converted to the diazonium group, followed by its removal to form the aryl radical, which in turn may react with a suitable species in solution to complete the coupling step. The presence of the diazonium group on the electrode upon conversion is illustrated in Figure S3.1 where a noticeable decrease in current is observed from the second CV cycle onwards at potentials below 0.20 V, indicating the reduction of the diazonium group during the first cycle.

As electroactive small molecules, AQ2S and FMN were chosen for their ease of identification by CV. Scheme 3.1 shows the conjugation of these molecules onto **GC-TMA** to form **GC-TMA-AQ2S** and **GC-TMA-FMN**, which is proposed to go through an azo coupling mechanism as in Scheme 1.3b; such coupling to diazonium-terminated surfaces has

previously been demonstrated before, whereby the secondary molecule used was horseradish peroxidase.^[11]

Scheme 3.1 Diazotization of **GC-TMA**, and subsequent conjugation of **AQ2S** or **FMN** to form **GC-TMA-AQ2S** and **GC-TMA-FMN**, respectively. TMA films are depicted as monolayers for illustration purposes only

As shown in Scheme 3.2, both **AQ2S** and **FMN** undergo a chemically reversible two-electron, two-proton reduction reaction in aqueous acidic solution to form doubly-protonated species. It can thus be expected that these molecules in their surface-bound forms can undergo similar redox reactions in the same medium, as observed from the cyclic voltammograms of **GC-TMA-AQ2S** and **GC-TMA-FMN** in Figure 3.1. It should be noted that there is very little physically adsorbed **AQ2S** or **FMN**, if any, on **GC-TMA-AQ2S** and **GC-TMA-FMN** as these electrodes were sonicated in fresh acetonitrile before CV was carried out.

Scheme 3.2 Chemically reversible reduction reactions of AQ2S and FMN to their respective doubly-protonated reduced versions in aqueous acidic solution

Figure 3.1 Cyclic voltammogram of a blank solution of 0.5 M HCl with **GC-TMA**, **GC-TMA-AQ2S**, and **GC-TMA-FMN** at $\nu = 0.1 \text{ V s}^{-1}$

The voltammograms of **GC-TMA-AQ2S** and **GC-TMA-FMN** show that the reduction reaction of the tethered molecules occurs at their respective potentials ($E_{1/2}^{\text{AQ2S}} = -0.08 \text{ V}$; $E_{1/2}^{\text{FMN}} = -0.05 \text{ V}$), together with the redox reaction of the TMA moieties ($E_{1/2} = 0.25 \text{ V}$), which appears at a potential slightly more positive than that belonging to **GC-TMA** ($E_{1/2} = 0.21 \text{ V}$). The electroaddressable surface coverage of the TMA groups on both **GC-TMA-AQ2S** ($\Gamma = 2.30 \times 10^{-11} \text{ mol cm}^{-2}$) and **GC-TMA-FMN** ($\Gamma = 4.75 \times 10^{-11} \text{ mol cm}^{-2}$) have decreased relative to those on the voltammogram of **GC-TMA** ($\Gamma = 9.54 \times 10^{-11} \text{ mol cm}^{-2}$), along with the concomitant appearance of the AQ2S ($\Gamma = 6.15 \times 10^{-11} \text{ mol cm}^{-2}$) and FMN

reduction peaks ($\Gamma = 5.23 \times 10^{-11} \text{ mol cm}^{-2}$) on their respective voltammograms. Due to the presence of the TMA redox peaks on the voltammograms of **GC–TMA–AQ2S** and **GC–TMA–FMN**, it is likely that not all of the TMA groups were converted to their diazonium forms. However, the surface coverage values only account for the electroaddressable TMA groups, and likely do not account for those which are further away from the electrode surface and are hence more likely to be converted to either AQ2S or FMN. Because of this limitation of voltammetry, it is difficult to attempt an accurate quantification of the extent of coverage of the various electroactive groups on the modified electrodes.

Scan rate studies were also performed on the three modified electrodes to ascertain that the peaks observed in Figure 3.1 belong to adsorbed species (as opposed to diffusion-controlled, solution-phase species). As plotted in Figure S3.2, within the range of $\nu = 0.05$ to 1.0 V s^{-1} , the current heights of all the peaks observed show excellent linearity ($R^2 > 0.99$) with scan rate, indeed confirming that electrografting of TMPD and subsequent conjugation with AQ2S and FMN were carried out successfully to form adsorbed species in a diffusion-less system.

3.2.2 Conjugation by amide coupling with SWCNTs

Molecular wires are molecules which are conduits for long-range electron transfer along its length, thus allowing for electronic coupling to occur between an electron donor and acceptor at either end of the “wire”.^[13-14] They are useful in cases where unwanted analyte adsorption to the electrode surface (e.g. protein corona-surface interactions)^[15-16] occurs, and so have found much use in the fields of biosensing^[1] and environmental sensing.^[2]

Because of their good electronic properties, SWCNTs make for excellent molecular wires. Here, SWCNTs were conjugated onto **GC–TMA** through amide coupling to form the modified electrode **GC–TMA–SWCNT** (Scheme 3.3). The SWCNT precursors were first functionalized with carboxylic acid groups on their ends by acid-cutting with mixed

concentrated acid, and then activated using *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) before it can be tethered onto **GC-TMA**. A series of CV experiments in dopamine were then carried out to compare the rates of electron transfer across the various modified electrodes, as shown in Figure 3.2.

Scheme 3.3 Reaction scheme of SWCNT functionalization to SWCNT-COOH, followed by conjugation onto **GC-TMA** by amide coupling to form **GC-TMA-SWCNT**

Figure 3.2 Cyclic voltammogram of dopamine (1 mM) in aqueous 0.1 M H_2SO_4 with **GC-TMA**, **GC-TMA-SWCNT**, and bare GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$

Upon conjugation of the SWCNTs, the peak-to-peak separation of the dopamine redox reaction saw a 13 mV decrease from $\Delta E_p = 78$ mV on **GC-TMA** to $\Delta E_p = 65$ mV on **GC-TMA-SWCNT**, thus suggesting an increase in the heterogeneous electron transfer rate. Although it can be said that the above change in ΔE_p was not dramatic, this is because of the already small difference in ΔE_p between bare GC and **GC-TMA**.

Indeed, the effect of a SWCNT-attachment regime on the electron transfer kinetics of modified electrodes was much more conspicuous for Downard et al., who observed more than a 700 mV decrease in ΔE_p in the CV of 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (in 1 M KCl) between aminophenyl-modified PPF and the same after 24 h of reaction with SWCNTs.^[17] Curiously, in our hands, a similar CV experiment in 1 mM $\text{Fe}(\text{CN})_6^{3-}$ using **GC-TMA**, **GC-TMA-SWCNT**, and bare GC electrodes showed very little difference in ΔE_p between them ($\Delta E_p = 83$ mV, 77 mV, and 71 mV, respectively) as observed from Figure 3.3. Again, this is likely due to the TMA film being not nearly as insulating as other more commonly studied organic films like an aminophenyl film. Nevertheless, the Nyquist plots of these electrodes (Figure 3.4) clearly show a decrease in the charge-transfer resistance upon SWCNT conjugation from $R_{CT} = 447 \Omega$ on **GC-TMA** to $R_{CT} = 105 \Omega$ on **GC-TMA-SWCNT**, which similarly shows the positive effect the SWCNT molecular wires have on electron transfer rates across the electrode.

Figure 3.3 Cyclic voltammogram of $\text{Fe}(\text{CN})_6^{3-}$ (1 mM) in aqueous 0.1 M KCl with **GC-TMA**, **GC-TMA-SWCNT**, and bare GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$

Figure 3.4 Nyquist plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in aqueous 0.1 M KCl with **GC-TMA**, **GC-TMA-SWCNT**, and bare GC electrodes

3.2.3 Further conjugation onto GC-TMA-SWCNT by amide coupling

Besides being an electronic conduit for solution-phase analytes, we were interested to explore the feasibility of electron transfer to and from molecules covalently attached to the

exposed ends of the SWCNTs (facing away from the electrode surface). This was shown by a few authors to be possible, with various proteins (e.g. enzymes) being used as the molecules to be conjugated.^[3-4, 18] Moreover, these authors were able to conclude from their experiments that electrical communication between the protein molecules and electrode through the SWCNT molecular wires was possible.

With **GC-TMA-SWCNT**, aminoferrocene (FcNH_2) was first chosen as the tether molecule as it bears both the Fc moiety known for its electrochemical reversibility, and the amine group for amide coupling with the exposed carboxylic acid groups of **SWCNT-COOH**. However, attempts made to tether FcNH_2 onto **GC-TMA-SWCNT** were not successful, as the cyclic voltammogram of the resulting electrode in blank solution returned with no Faradaic peaks belonging to Fc. The results were the same whether the activation reagents DCC and DMAP or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) were employed for amide coupling, although FcNH_2 has previously been shown to be able to couple with COOH-terminated alkylthiol SAMs by EDC/NHS chemistry elsewhere.^[19]

Dopamine (DA) was then used as an alternative molecule for the above purpose, as it also contains an amine group as well as an electroactive catechol moiety, albeit with less reversible behavior. Based on the presence of the pair of redox peaks belonging to DA in the cyclic voltammogram of the resulting electrode in blank phosphate buffered saline (PBS) as shown in Figure 3.5 ($\Delta E_p = 103 \text{ mV}$), the covalent attachment of DA to form **GC-TMA-SWCNT-DA** (using the EDC/NHS coupling method) was deemed to be successful.

Figure 3.5 Cyclic voltammogram of blank PBS (pH 7.4) with **GC-TMA-SWCNT-DA**, and bare GC electrodes at $\nu = 0.1 \text{ V s}^{-1}$

However, scan rate studies within the range of $\nu = 0.05$ to 1.0 V s^{-1} point to a nonlinear relationship between the oxidative peak currents of DA and the scan rate (Figure 3.6a), which is not usually the case for surface-confined species. Instead, good linearity was observed on the plot with respect to the square root of the scan rate (Figure 3.6b), which seemingly indicates that DA oxidation in **GC-TMA-SWCNT-DA** was under diffusion control. A possible explanation for this could be the presence of solution-phase (i.e. untethered) DA molecules within the SWCNT forest, despite our best attempts to remove as much physically-adsorbed DA as possible through sonication in ultrapure water. Nevertheless, this would still require a degree of free movement of DA molecules within the pores or channels of the tethered SWCNTs, which is unlikely.

Figure 3.6 Plot of (a) peak current vs. scan rate, and (b) peak current vs. square root of scan rate for **GC-TMA-SWCNT-DA**

Conversely, if indeed a large majority of the DA moieties in **GC-TMA-SWCNT-DA** are tethered to SWCNTs, it could then be possible that the Randles–Ševčík equation (*vide supra*, Section 1.1.7.1) should not be invoked in this case. In other words, a link cannot be made between the observation of $i\text{-}\nu^{1/2}$ linearity in Figure 3.6b and the conclusion that DA is under diffusion control, because **GC-TMA-SWCNT-DA** does not meet the requirements for the Randles–Ševčík equation in the first place. In the strictest sense, the Randles–Ševčík equation

is applicable only to electrochemical reactions which are not coupled to any other chemical reactions (e.g. Fc oxidation and reduction), since the terms in the equation are associated with electron transfer between an electrode and one solution-phase species.^[20] This should not be the case for DA, which bears a catechol moiety and thus undergoes proton-coupled electron transfer (PCET) reactions in buffered aqueous solutions (Scheme 3.4).^[21] The forward oxidation processes occur in sequential electron transfer steps to first form the cation radical ($\text{DA}^{\bullet+}$), which deprotonates to form the neutral radical ($\text{DA}^\bullet$), which is then oxidized to form a cation (DA^+) that immediately deprotonates to form the dopamine *o*-quinone (DAQ) (Scheme 3.4, yellow pathway). The reverse reduction pathway also occurs sequentially but by a different route (Scheme 3.4, blue pathway). Therefore, the complicated PCET reaction means that the process may not follow the Randles–Ševčík equation, even for a purely diffusional controlled reaction. Curiously, despite the restriction of the Randles–Ševčík equation only to uncoupled electrochemical reactions, it has previously been used for the study of DA in other experiments,^[22-23] presumably because in those cases the PCET reactions had little effect on the linear i - $\nu^{1/2}$ relationship.

Scheme 3.4 Proton-coupled electron transfer reactions for the two-electron oxidation of dopamine (DA) to dopamine *o*-quinone (DAQ)

Given the results of these experiments, it could be said that there is utility in the attachment of SWCNTs onto **GC-TMA** for electrical communication between the electrode surface and solution-phase analytes. However, this utility does not seem to extend beyond the SWCNT layer, as evidenced both by the inability of **GC-TMA-SWCNT** to couple to FcNH₂, as well as the deviation of attached DA on **GC-TMA-SWCNT-DA** away from the expected adsorption-type behavior.

3.3 Conclusion

Experiments were performed to investigate the feasibility of conjugating secondary molecules onto **GC-TMA** through the amine groups of the TMA film. Conjugation by diazotization of the TMA film, followed by introduction of the secondary molecule was shown to be successful for a couple of molecules: AQ2S and FMN, ascertained through CV of the resulting modified electrodes. Conjugation by amide coupling was also demonstrated by coupling with carboxylic acid-terminated SWCNTs to form **GC-TMA-SWCNT** modified electrodes, which was subsequently characterized by CV and EIS. The above experiments illustrate the potential viability of **GC-TMA** as a less insulating alternative to other similar modified electrodes (e.g. aminophenyl-modified GC) for decoration with secondary molecules.

Subsequently, further attempts were made to tether other molecules onto **GC-TMA-SWCNT** through amide coupling with the carboxylic acid ends of the SWCNTs, with the aim of determining the usefulness of SWCNTs as molecular wires for electronic transmission to and from these tethered molecules. However, failure in the coupling attempts with FcNH₂ as well as a lack of understanding of the unusual behavior observed with DA-coupled **GC-TMA-SWCNT** (i.e. **GC-TMA-SWCNT-DA**) point to this particular modified electrode being less suited for the abovementioned purpose.

3.4 Experimental Section

3.4.1 Chemicals

These commercially-sourced chemicals were used as received: sodium nitrite (98%, Alfa Aesar), 2,3,5,6-tetramethyl-*p*-phenylenediamine ($\geq 98\%$, Tokyo Chemical Industry), 9,10-anthraquinone-2-sulfonic acid sodium salt monohydrate (97%, Alfa Aesar), riboflavin-5'-phosphate sodium salt monohydrate (analytical reagent grade, Alfa Aesar), *N,N'*-dicyclohexylcarbodiimide (99%, Fluka Analytical), 4-dimethylaminopyridine (99%, Sigma-

Aldrich), potassium hexacyanoferrate (III) ($\geq 99\%$, Merck), potassium hexacyanoferrate (II) trihydrate ($\geq 99\%$, Merck), dopamine hydrochloride ($\geq 99\%$, Merck), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride ($\geq 98\%$, Fluka Analytical), *N*-hydroxysuccinimide ($\geq 99\%$, Merck), sodium hydrogen phosphate ($\geq 98\%$, Alfa Aesar), sodium hydroxide (99%, Merck), hydrochloric acid (37%, VWR Chemicals), potassium chloride ($\geq 99\%$, Fischer Scientific), potassium dihydrogen phosphate ($\geq 98\%$, Alfa Aesar), acetone (GC grade, 99.5%, Tedia), acetonitrile (HPLC grade, Fulltime), dimethylsulfoxide (HPLC grade, Tedia). Single-walled carbon nanotubes (90%, 1–2 nm diameter, 5–30 μm length) were from Nanostructured and Amorphous Materials Inc. (Texas, USA).

Ultrapure water was produced by a Pure Lab ELGA water-purification system (PURELAB Option-Q, UK), and had resistivity of 18.2 M Ω cm. Measurements of pH were performed using a glass pH probe (Metrohm 827 Lab), which was prior calibrated with standard IUPAC buffer solutions of pH 4, 7, and 10. PBS (pH 7.4) was prepared with 137 mM NaCl, 2.7 mM KCl, 10 mM Na₂HPO₄, and 1.76 mM KH₂PO₄.

3.4.2 *Electrochemical measurements*

Please refer to Section 2.5.3.

3.4.3 *SWCNT functionalization*

The procedure for the functionalization of SWCNTs with carboxylic acid groups was adapted from Downard and co-workers:^[17] SWCNTs (10 mg) were acid-cut by sonication in a concentrated H₂SO₄:HNO₃ solution (3:1, 10 mL) for 10 h at 20°C, after which the mixture was poured into 200 mL ultrapure water and left to stand overnight. The mixture was then filtered through a 0.22 μm polyvinylidene fluoride (PVDF) filter and washed with ultrapure water, following which the SWCNT cake was peeled off and resuspended in dimethylsulfoxide

(DMSO) to afford a 1 mg mL⁻¹ stock solution of COOH-functionalized SWCNTs (i.e. SWCNT-COOH).

3.4.4 GC-TMA formation and conjugation with secondary molecules

As previously laid out in Section 2.5.6, **GC-TMA** formation was performed as follows: a 1 mM solution of TMPD in aqueous 0.5 M HCl was first bubbled under N₂ for 5 min, followed by dropwise addition of a chilled solution of NaNO₂ (final concentration of 1 mM) and an additional 1 min of bubbling. CPE was then performed (applied potential = -0.47 V for 3 min) immediately upon immersion of the GC electrode into the above solution. After the electrografting procedure, the resulting electrode was washed with ultrapure water, then sonicated in acetonitrile for 5 min, and lastly blow-dried with N₂.

Conjugation of secondary molecules onto **GC-TMA** by further diazonium chemistry was performed as follows: **GC-TMA** was first diazotized by immersion into a deoxygenated solution of NaNO₂ (0.1 mL, final concentration of 1 mM) in 0.5 M HCl (4.9 mL) for 15 min. Afterwards, the electrode was quickly washed with ultrapure water before immersion for 30 min into a separate cell containing a saturated solution of the desired compound to be conjugated. The solution contains either AQ2S (10 mM), or FMN (1 mM), thoroughly dissolved in 0.5 M HCl. The fully modified and conjugated electrode was then washed with ultrapure water, sonicated in fresh acetonitrile for 5 min, then blow-dried with a stream of N₂.

3.4.5 Amide coupling

Amide coupling was performed by either one of two ways: DCC/DMAP or EDC/NHS chemistry.

With the use of DCC/DMAP chemistry for coupling SWCNT-COOH onto **GC-TMA**, the method employed by Moore et al. was used:^[24] a solution of 0.2 mg mL⁻¹ SWCNT-COOH,

0.25 mg mL⁻¹ DCC, and 0.14 mg mL⁻¹ DMAP was first sonicated for 1 h, before immersion of **GC-TMA** into the same solution for 24 h. For the attempted coupling of FcNH₂ onto **GC-TMA-SWCNT**, the modified electrode was first immersed into a solution of 40 mM DCC and 40 mM DMAP in DMSO for 30 min, followed by addition of FcNH₂ (final concentration of 5 mM) before being left to react for 24 h.

Where EDC/NHS chemistry was used also for coupling FcNH₂ onto **GC-TMA-SWCNT**, a modified version of the procedure by Booth et al. was adapted:^[19] in a solution of 5 mM EDC and 5 mM NHS in PBS was immersed the modified electrode for 1 h, followed by a transfer of the resulting electrode into a solution of PBS/DMSO (9:1) containing 250 µM FcNH₂, which was left to react for either 10 min or 1 h. With DA as the tether molecule instead, **GC-TMA-SWCNT** was immersed into a solution of 20 mM EDC and 20 mM NHS for 1 h, followed by addition of dopamine hydrochloride (final concentration of 5 mM) into the solution, after which the mixture was left to react for 6 h.

3.5 References

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CHAPTER 4 COMPARING DIAZONIUM MODIFIED AND UNMODIFIED ACTIVATED CARBON CLOTHS FOR ENERGY STORAGE IN SUPERCAPACITORS

4.1 Abstract

Activated carbon cloths (ACCs) were chemically modified with anthraquinone (AQ) groups and the resulting AQ-modified ACCs were characterized and tested for their potential use in supercapacitors. At modest scan rates and current densities, AQ-modified ACCs were found to store and release less charge than unmodified ACCs, under conditions where equivalent series resistance (ESR) is not minimized.

4.2 Introduction

Electrochemical capacitors (ECs), also known as supercapacitors, are a class of energy storage systems which typically exhibit quick energy storage and release capabilities, especially when compared alongside batteries. The ability of ECs to store electrical charge comes from one of two main phenomena: electrical double-layer capacitance, or pseudocapacitance. Electrical double-layer capacitors (EDLCs) function by accumulating electrostatic charge at the electrode-electrolyte interface.^[1] Pseudocapacitors, on the other hand, rely on fast and reversible faradaic reactions occurring across electrodes containing specific materials (most typically RuO₂ or MnO₂) despite its electrochemical behavior resembling that of a true capacitor.^[2]

Various carbonaceous materials have been used for EDLCs, including (but not limited to) activated carbon powders,^[3-5] activated carbon cloths/fibers,^[6-8] and graphene hydrogels.^[9-10] A common characteristic of these materials is their relatively high porosity. This translates into a large specific surface area, which allows EDLCs to achieve high capacitance values. In

particular, activated carbon cloths (ACCs) also have the added advantage of being mechanically stable and highly flexible, and thus see potential use in wearable devices.^[11] Unfortunately, when compared alongside materials like activated carbon powders, ACCs still fall short in terms of their specific surface area, porosity, and electrolyte wettability,^[12] prompting researchers to investigate ways to improve their overall performance in EDLCs.

One method of improving performance involves attaching electroactive molecules onto the electrode, which serves to introduce a faradaic component to its charge-storage mechanism. If the molecules are electroactive within the potential window used, the total capacity stored in one charge should increase, assuming that the attachment of the molecules has a negligible effect on the capacitance of the electrode. Grafting by diazonium chemistry is a popular method for the covalent attachment of molecules on carbon surfaces, and can be performed in the presence or absence of an applied potential,^[13] making it an attractive option for modifying materials in discrete forms (e.g. powders). Various research groups have successfully modified carbon materials in this way, with the most common electrode material being commercial activated carbon powder.^[4, 14-16] On the other hand, to the best of the authors' knowledge, there have been few studies which have examined the covalent attachment of molecules on ACCs for energy storage in supercapacitors.^[17-18] In those studies, the attached molecules (catechol^[18] and 2-anthraquinone^[17]) were indeed found to provide additional capacity to the carbon cloths through experiments run under aqueous acidic conditions.

In this study, anthraquinone (AQ) groups were first grafted onto ACCs through diazonium chemistry,^[19] then the energy-storage capability of AQ-modified ACCs were tested by galvanostatic charge-discharge (GCD) experiments in aqueous acidic electrolyte. As shown in Scheme 4.1, two aminoanthraquinone precursors were used for the modification: 1-aminoanthraquinone (1AQ) and 2-aminoanthraquinone (2AQ), each resulting in different points of attachment onto the ACC surface, forming ACC-1AQ and ACC-2AQ, respectively.

Here, we report the conditions under which modification of ACCs with AQ groups does not translate to increased charged storage, in the context of their use for supercapacitors.

Scheme 4.1 Mechanism for spontaneous grafting of AQ groups on an ACC surface to form AQ-modified ACC

4.3 Results and Discussion

Results from Brunauer-Emmett-Teller (BET) porosimetry and electrochemical measurements performed on pristine AQ-modified ACCs, shown in Table 4.1, highlight the changes which occur on the electrode upon grafting. The decrease in both specific surface area and pore volume upon modification are the result of the attached AQ groups blocking the entrances to micropores present on the carbon cloth surface. Thus, a smaller area of the ACC–AQ surface is accessible to the N_2 adsorbent, and by extension, the electrolyte molecules. Similarly, the Nyquist plots (Figure 4.1) derived from electrochemical impedance spectroscopy (EIS) data reveal a slight increase in charge-transfer resistance, R_{CT} , across the electrode surface upon modification, which confirm the attachment of AQ groups on the ACC surface. The components of the equivalent circuit (Scheme S4.1) used to fit the Nyquist plots are described in the Experimental Section.

Table 4.1 BET porosimetry and electrochemical data for pristine and AQ-modified ACCs

Electrode	Surface characteristics		Electrochemical data		
	BET surface area / $\text{m}^2 \text{g}^{-1}$	Pore volume / $\text{cm}^3 \text{g}^{-1}$	Charge-transfer resistance, R_{CT} / Ω	Surface coverage ^a / mol cm^{-2}	iR drop ^b / mV
Pristine ACC	1007	0.518	2.26	N/A	221
ACC-1AQ	745	0.342	3.14	1.85×10^{-11}	354
ACC-2AQ	746	0.342	6.10	1.41×10^{-11}	272

^aCalculated using CV experiments at 1 mV s^{-1} ; ^bMeasured using GCD experiments at 1 A g^{-1}

Figure 4.1 Nyquist plots of pristine and AQ-modified ACCs in aqueous $1 \text{ M H}_2\text{SO}_4$

Cyclic voltammetry (CV) experiments of pristine and AQ-modified ACCs were performed at 1 mV s^{-1} , and the results are shown in Figure 4.2a. While the CV curve of pristine ACC shows the rectangular shape typical of an EDLC, those of ACC-1AQ and ACC-2AQ show an additional pair of redox peaks centered at $E_{1/2} = -0.12 \text{ V}$ and -0.09 V , respectively. These correspond to the reversible 2-electron reduction of the grafted AQ to its reduced hydroquinone form in aqueous acidic media (Scheme 4.2) which was proposed to increase the total charge that can be stored and released by the electrode. The calculated surface coverages of AQ molecules on both AQ-modified ACCs, shown in Table 4.1, indicate sub-monolayer coverage and are comparable to those of 1AQ-modified carbon blacks.^[19] Taking the approximation that the maximum surface coverage of a monolayer of AQ on a high-surface area carbon is $5.6 \times 10^{-11} \text{ mol cm}^{-2}$,^[19] the percentage coverages of ACC-1AQ and ACC-2AQ are calculated to be 33% and 25%, respectively. Such sub-monolayer percentage coverages are to be expected, since it is unlikely for the AQ molecules to cover the entire microporous network of the ACCs. Furthermore, since the BET surface area was determined from BET porosimetry using N_2 as the adsorbent, the above calculations on the surface coverage of AQ molecules (which rely on the BET surface area) are estimations at best.

Notably, the capacitive charge attributable to EDLC does not change significantly upon modification (at least for ACC-2AQ), as shown by the quasi-rectangular portions of the CV curves of pristine and ACC-2AQ having similar areas. In our hands, we consistently found ACC-1AQ to possess a slightly lower capacitive charge than the other two electrodes. Also, the redox peaks on the CV curve of ACC-1AQ are broader than those of ACC-2AQ, which is in agreement with a previous report which studied 1AQ- and 2AQ-modified carbon blacks.^[3]

Figure 4.2 Cyclic voltammograms of aqueous 1 M H_2SO_4 using pristine ACC (dashed line), ACC-1AQ (solid line) and ACC-2AQ (dotted line) at (a) 1 mV s^{-1} , (b) 2 mV s^{-1} , and (c) 5 mV s^{-1}

Scheme 4.2 Reversible reduction of ACC–AQ to its reduced form in aqueous acidic electrolyte

At the slow scan rate of 1 mV s^{-1} , the AQ redox reaction contributes to a significant portion of the total charge passed. However, when the scan rate is increased (Figure 4.2b and c), the shape of the voltammograms changed significantly, such that the faradaic charge as a proportion of total charge decreases with increasing scan rate (i.e. redox peaks become shallower). In particular, at 5 mV s^{-1} , the AQ redox peaks almost disappear completely, and the areas under the CV curves of both AQ-modified ACCs become smaller than that of pristine ACC, with ACC–1AQ showing a more significant decrease than ACC–2AQ. At the highest scan rate, pristine ACC outperforms both AQ-modified ACCs in terms of total charge stored.

Scheme 4.3 Electrochemical square-scheme mechanism for reduction of quinones (Q) and oxidation of hydroquinones (QH_2) in acidic environments. Counterions for the charged molecules are provided by the electrolyte

Although the redox reaction between the oxidized and reduced form of the quinone is written as a reversible $2\text{e}^-/2\text{H}^+$ process in Scheme 4.2, the reaction actually occurs through consecutive electron transfer and proton transfer steps, i.e. proton-coupled electron transfer (PCET) as drawn in Scheme 4.3.^[20] The reduction of the quinone to the hydroquinone follows the yellow pathway (left to right) while the oxidation of the hydroquinone to the quinone follows the blue pathway (right to left) in Scheme 4.3. Typically, the homogeneous and heterogeneous PCET reactions for Q/ QH_2 systems are sufficiently fast such that cyclic voltammograms of solution phase molecules at a scan rate of 0.1 V s^{-1} appear chemically

reversible with closely spaced oxidation and reduction peaks. Therefore, the complete absence of Faradaic peaks at a relatively slow scan rate of only 5 mV s^{-1} in Figure 4.2c indicates kinetic constraints to the PCET reactions within the pores.

GCD experiments were also performed to observe the impact of longer-term cycling on the performance of the electrodes. Here, it should be noted that charging involves applying a negative current (to reduce AQ groups), while discharging is the reverse. The average specific capacities of pristine ACC, ACC-1AQ and ACC-2AQ over 1000 cycles at 1 A g^{-1} were found to be 32.2, 30.0 and 29.4 A g^{-1} respectively, with pristine ACC showing consistently higher capacities than both modified ACCs (Figure 4.3). Likewise, it can also be observed from the GCD plots shown in Figure 4.4 that pristine ACC exhibits a lower iR drop (221 mV) than ACC-1AQ (354 mV) and ACC-2AQ (272 mV) prior to the charging and discharging steps. When the current density was increased from 1 A g^{-1} to just 2 A g^{-1} , all the electrodes saw large increases in their iR -drops to values from 300 mV (for pristine ACC) up to over 600 mV (for ACC-1AQ); the resistance values at this current density were considered too high for us to perform meaningful long-term cycling experiments at 2 A g^{-1} .

Figure 4.3 Cycling performance of pristine and AQ-modified ACCs in aqueous $1 \text{ M H}_2\text{SO}_4$ at 1 A g^{-1}

Figure 4.4 Representative galvanostatic charge-discharge plots of pristine and AQ-modified ACCs in aqueous 1 M H₂SO₄ at 1 A g⁻¹ (thick lines) and 2 A g⁻¹ (thin lines)

The results above seem to illustrate that electrodes modified with AQ groups store less charge than unmodified electrodes at higher scan rates and current densities. However, there are a number of examples in the literature which show otherwise. Pickup's group showed that, at the scan rate of 20 mV s⁻¹, their AQ-modified ACC (Spectracarb 2225) still showed significantly greater specific capacitance over unmodified ACC.^[21-22] Similarly, Bélanger's group showed, in separate studies, improved performance of AQ-modified ACC (Kynol)^[17] and activated carbon powders (Black Pearls 2000)^[4] at a range of scan rates and current densities. Here, we explain the apparent discrepancy between the results of our experiments shown here, and those of similarly modified electrodes found in the literature.

It is generally known that an increase in current density (or scan rate) decreases the capacitance of an energy storage system due to increased cell resistance, or equivalent series resistance (ESR). This decrease in capacitance is more apparent on highly porous electrodes such as ACC, where penetration of the electrolyte into the pores of the electrode may be incomplete during a given charge-discharge cycle.^[23-24] The gradual disappearance of the AQ

redox peaks going from Figure 4.2a to 4.2c can be rationalized in the following way: as the scan rate increases, ion diffusion into the pores of the ACC (where some of the AQ groups reside) becomes increasingly difficult.^[23] At a high-enough scan rate, the reduction of AQ to its reduced form becomes nearly absent from the CV curve as there is insufficient time for the reduction to occur before the scan is reversed, likely due to the proton transfer reactions (Scheme 4.3) being restricted by the porosity of the ACCs. Furthermore, the capacitive (non-Faradaic) portion of the CV curves of both AQ-modified ACCs also decreased in area with increasing scan rate, likely because access of the electrolyte to the inner pores (to maintain charge neutrality) is hampered by the blockage of these pores by the attached AQ moieties. This observation is not commonly shared with other studies of AQ-modified electrodes, which found that the porous texture of the carbonaceous material was unaffected upon modification.^[3, 17]

Likewise, the shapes of the GCD plots in Figure 4.4 also tell a similar story. The sloped portions of the GCD plot of pristine ACC are straight due to the fully capacitive nature of the charging and discharging steps, while those of ACC-1AQ and ACC-2AQ vary due to the occurrence of both capacitive charging/discharging as well as faradaic reactions. It can be observed that, even at the low current density of 1 A g^{-1} , the slopes of the curves of both AQ-modified ACCs did not “return” back to the steeper gradient (which characterizes capacitive charging) before reaching the lower potential of -0.4 V , indicating that AQ reduction was incomplete during charging. Consequently, the discharge step releases less charge than it is capable of releasing. Coupled with the higher iR drops of both AQ-modified ACCs, it can thus be understood how pristine ACC was still able to outperform ACC-1AQ and ACC-2AQ under these conditions. This is exacerbated in the case of the experiments carried out at 2 A g^{-1} , whereby the electrodes see a large decrease in charge stored and released.

It should be noted that our experiments were conducted in a single-compartment cell, where the ESR is inherently larger than that of specialized cells which are more suited for supercapacitors.^[25] These cells (e.g. T-cells^[17]) typically lower resistance by being compact, as they are built to minimize inter-electrode distance and maximize contact between the electrode and current collector. Composite electrodes which use (modified) activated carbon powders also benefit from an even more intimate electrode-current collector contact, which is why carbon powders,^[3, 5] as opposed to carbon cloths,^[11] are often the material of choice for EDLCs. Lastly, the activated carbon cloths used in our experiments (Chemviron) were also sourced from a different manufacturer than those we found in the literature;^[17, 21-22] these cloths may have varying propensities towards being functionalized with organic molecules such as AQ, which in turn affects their performance in an EDLC. For example, the ACC used in our study had a pore volume of $0.518 \text{ cm}^3 \text{ g}^{-1}$, which decreased by 34% to $0.342 \text{ cm}^3 \text{ g}^{-1}$ upon modification with AQ. However, from a similar study of AQ-modified ACCs elsewhere which used a largely similar modification method, the ACC used (Kynol) had a pore volume of $0.708 \text{ cm}^3 \text{ g}^{-1}$ which decreased by 66% to $0.244 \text{ cm}^3 \text{ g}^{-1}$. The larger and more extensive microporous network of Kynol ACC is likely to have contributed to its better energy storage performance upon modification compared to Chemviron ACC.

In spite of the results obtained, the use of ACCs for supercapacitors should not be dismissed altogether. For example, Yu and co-workers capitalized the strengths of activated carbon fiber tows by assembling and sewing them into a glove, and each fiber was able to retain its capacitance after multiple GCD cycles under bending and knotting deformation conditions, illustrating their feasibility for use in wearable and flexible electronics.^[26] Though their actual energy storage capabilities still fall short when compared against materials with innately higher capacitance, ACCs still have their place in the ever-expanding field of wearable electronics, where their mechanical stability and flexibility are valued.

4.4 Conclusion

ACCs covalently attached with electroactive AQ groups by diazonium chemistry were found to exhibit increased capacities compared to their unmodified counterparts, but only at very low scan rates when measured with cyclic voltammetry. At modest scan rates and current densities (in GCD experiments), modification of ACC with AQ groups may serve to worsen their charge-storage performance, depending on the ESR of the cell used. Noting that the recommended conditions for supercapacitor testing are in the order of 5 to 60 seconds for GCD charge/discharge times and 20 to 40 mV s⁻¹ for CV experiments,^[25] researchers seeking to utilize ACCs as electrodes for potential charge storage applications should be wary of their shortcomings in spite of their attractiveness in other areas (e.g. mechanical stability, flexibility).

4.5 Experimental Section

4.5.1 Chemicals and materials

The following chemicals were used as received from their respective commercial sources: 1-aminoanthraquinone (98%, Alfa Aesar), 2-aminoanthraquinone (>86%, Tokyo Chemical Industry), *tert*-butyl nitrite (>90%, Tokyo Chemical Industry), hydrochloric acid (37%, VWR Chemicals), acetonitrile (HPLC grade, Fulltime), acetone (GC grade, Tedia), *N,N*-dimethylformamide (HPLC grade, Tedia). Flexzorb® ACC (FM10) was obtained without cost from Chemviron.

4.5.2 Activated carbon cloth modification

A portion of ACC was first washed with ultrapure water and acetone, and dried in a vacuum oven at 60°C. Separately, a solution of the diazonium cation of aminoanthraquinone was prepared *in situ* as follows: The aminoanthraquinone was fully dissolved in acetonitrile (1

mM, 20 mL) and the solution was bubbled under Ar for 15 min. *tert*-Butyl nitrite (5 eqv.) was then added to the solution, which was further bubbled for another 20 min, followed by addition of the washed ACC (0.1 eqv.) with continuous stirring. After 30 min, another portion of *tert*-butyl nitrite (5 eqv.) was added to the mixture, which was left to stir overnight. The resulting modified ACC was washed thoroughly with dimethylformamide, acetonitrile and acetone, and then dried at 60°C in a vacuum oven before use.

4.5.3 *Electrochemical measurements*

CV, EIS and GCD experiments were performed with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat, with a three-electrode setup. The ACC working electrode used is typically weighed at 10–13 mg (ca. 8×11 mm), with the counter electrode being a pristine ACC (8×13 mm), and a silver/silver chloride (3 M KCl) reference electrode spaced ca. 6 mm away from the working electrode. All electrochemistry experiments were performed in a Faraday cage at room temperature (298 ± 2 K), with aqueous sulfuric acid (1 M) being used as the electrolyte. Electrodes were first immersed into the electrolyte solution for 15 min before the commencement of electrochemical measurements. Results obtained from GCD experiments are expressed here in terms of capacity (mAh) instead of capacitance (F), in accordance with the guidelines laid out by Brousse et al.^[27]

EIS experiments with a frequency response analyzer (FRA) used an a.c. voltage of 10 mV in sine-wave amplitude from 10 kHz to 10 mHz and were performed at open circuit potential. From the equivalent Randles circuit in Scheme S4.1, R_s is the internal resistance; R_{CT} is the charge-transfer resistance; Z_W is the Warburg impedance; C_{DL} is the double layer capacitance; C_L is the low-frequency mass capacitance; and R_{leak} is the low-frequency leakage resistance.

The surface coverage (Γ) of the AQ-modified ACCs were calculated using Equation 4.1:

$$\Gamma = \frac{Q}{nFA} \quad (4.1)$$

where Q = charge integrated under the faradaic peak on the cyclic voltammogram; n = number of electrons per redox reaction; F = Faraday constant; and A = surface area of pristine ACC calculated from its BET surface area.

4.5.4 Surface analysis

Surface area and pore volume measurements were carried out with a Micromeritics ASAP2460 surface area and porosity analyzer with N₂ as the adsorbent, and the BET method was used for the calculation of the specific surface area.

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5.1 Summary and future work

Aryldiazonium salts have seen much use in electrochemistry and materials science for surface modification since their discovery nearly three decades ago. This thesis seeks to add to the growing body of knowledge in this field of study, by investigating two particular aspects of diazonium chemistry: its inherent tendency to form multilayered films upon electrografting, and the effectiveness of modified activated carbon cloths (ACCs) for energy storage in supercapacitors.

The inherent tendency of films grafted by diazonium chemistry to be multilayered is one of the main problems which the technique has. Chapter 2 detailed the study which aimed at addressing this problem by investigating the potential for bulky 2,3,5,6-tetramethylaniline (TMA) groups to limit multilayer formation by steric hindrance. The results of the study showed otherwise: instead, sparse multilayers were observed on electrodes modified with TMA groups (**GC-TMA**). Possible reasons for the unexpected formation of TMA multilayers were also posited, with most reasons stemming from the fact that the precursor to the diazonium salt, 2,3,5,6-tetramethyl-*p*-phenylenediamine (TMPD), contains two amine groups.

Chapter 3 covered additional coupling experiments performed on the same **GC-TMA** electrode as prepared from the previous Chapter. Various small molecules and single-walled carbon nanotubes (SWCNTs) were tethered onto the TMA layer of **GC-TMA** with the intent of ascertaining the feasibility of such coupling, especially given the presence of outward-protruding methyl groups on each TMA moiety. The molecules used in the experiments were found to have coupled to **GC-TMA** successfully. Particularly, **GC-TMA** electrodes modified with SWCNTs (**GC-TMA-SWCNT**) were investigated further, as the tethered SWCNTs were identified to be potentially suitable for use as molecular wires for restoring fast heterogeneous

electron transfer to solution species. Experimental results point to a small increase in the electron transfer rates with **GC–TMA–SWCNT**. However, attempts made to couple other molecules onto the protruding ends of the SWCNTs (as is commonly seen in studies with functional proteins attached to molecular wires) were less successful.

In essence, these two chapters detailed studies on the novel **GC–TMA** electrode per se, as well as its potential base for further applications requiring further modified electrodes. While **GC–TMA** may not compare as favorably to similar, more common counterparts such as aminophenyl-modified GC, much has been gleaned about the chemistry behind grafting sterically-bulky diazonium molecules on GC electrodes.

Finally, Chapter 4 looked at how modification of activated carbon cloths (ACCs) with anthraquinone (AQ) molecules affects their energy-storage capabilities for their use in supercapacitors. Although the electrochemically-active AQ moieties add a faradaic component to the predominantly-capacitive ACCs, an improvement in the total charge stored and released relative to unmodified ACC was only observed at lower scan rates and charge densities. Given the high-resistance nature of three-electrode cell setups used in our experiments, as well as how AQ undergoes complicated proton-coupled electron transfer (PCET) reactions, this same improvement was not observed at moderate scan rates and charge densities. A recommendation is given to exercise caution in utilizing modified ACCs as electrodes for charge storage.

Although grafting by diazonium chemistry is not an entirely new field of study, there is still much to be discovered from this surface modification method. On the topic of monolayer formation, researchers may look to other properties of the diazonium precursors besides their steric bulk, such as electrostatic interactions/repulsions between the grafted film and diazonium cations. Electrografting under typical atmospheric conditions is also an avenue that is worth consideration. As for energy storage in supercapacitors, an improvement in the capacity of ACCs could be investigated through chemical modification of the ACCs per se, as opposed to

simple addition of electroactive molecules onto them. These may include thermal or chemical modifications aimed at expanding the native double layer capacitance of the microporous network of the ACCs.

In summary, this thesis details three studies relating to electrode modification by diazonium chemistry. The ability to chemically modify surfaces is a fundamentally important reaction in electrochemistry and materials science, and aryl diazonium cation reduction most commonly being the surface modification method of choice is a testament to its popularity among the scientific community. It is hoped that the findings laid out in this thesis may aid fellow researchers involved in this active field of study.

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Figure S2.1 Cyclic voltammogram (5 cycles) of aniline monodiazonium cation (1 mM) in aqueous 0.5 M HCl with a bare GC electrode at $\nu = 0.1 \text{ V s}^{-1}$

Figure S2.2 Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ (1 mM) in Britton-Robinson buffers from pH 3 to 10 with a bare GC electrode at $\nu = 0.1 \text{ V s}^{-1}$

Figure S2.3 Cyclic voltammograms of $\text{Ru}(\text{NH}_3)_6^{3+}$ (1 mM) in Britton-Robinson buffers from pH 3 to 10 with **GC-TMA** electrode at $\nu = 0.1 \text{ V s}^{-1}$

Figure S2.4. CPE plots of **GC-TMA** formation by electrografting

Figure S2.5 CPE plots of **GC-A** formation by electrografting

Figure S2.6 Bode plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in pH 3 buffer solution using **GC-TMA**

Figure S2.7 Bode plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in pH 12 buffer solution using **GC-TMA**

Figure S2.8 Bode plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in pH 3 buffer solution using **GC-A**

Figure S2.9 Bode plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in pH 12 buffer solution using **GC-A**

Figure S3.1 Cyclic voltammogram of a blank solution of aqueous 0.5 M HCl with **GC-TMA** that has been immersed (for 15 min) in a deoxygenated solution of NaNO_2 in HCl at $\nu = 0.1 \text{ V s}^{-1}$

Figure S3.2 Plots of peak current vs. scan rate for (a) **GC-TMA**, (b) **GC-TMA-AQ2S**, and (c) **GC-TMA-FMN**

Figure S3.3 Bode plots of $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ (5 mM) in aqueous 0.1 M KCl with a bare GC electrode

Figure S3.4 Bode plots of $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ (5 mM) in aqueous 0.1 M KCl solution using GC-TMA

Figure S3.5 Bode plots of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (5 mM) in aqueous 0.1 M KCl solution using **GC-TMA-SWCNT**

Scheme S4.1 Equivalent circuit used to fit the Nyquist plots in Figure 4.1

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