

Synthesis of Catalyst Nanoparticles Encapsulated in Mesoporous Carbon Spheres and their Subsequent use as Catalysts for the Oxygen Reduction Reaction

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DECLARATION

I declare that the dissertation, which I hereby submit for the degree of Master of Science at the Faculty of Science, University of the Witwatersrand, Johannesburg, is my own work and has not previously been submitted by me to any institution.



Evah Ramokone Phago

On this _____ day of September 2016

DEDICATION

To my parents; Martha Magano and Jacob Phago;
my nephew Bathabile Segopotso Phago;
and to my late cousin Thabiso Masilo

*“Courage allows the successful woman to fail and learn powerful lessons from the failure, so
that in the end, she didn’t fail at all”*

Maya Angelou

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PRESENTATIONS AND PUBLICATIONS

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Table of Contents

DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGMENTS	iv
PRESENTATIONS AND PUBLICATIONS	v
ABSTRACT	x
LIST OF FIGURES AND SCHEMES	xii
LIST OF TABLES	xv
LIST OF ABBREVIATIONS	xvi

CHAPTER 1: INTRODUCTION TO STUDY, RESEARCH QUESTIONS AND HYPOTHESES 1

1.1 Introduction	1
1.2 Motivation	5
1.3 Aim	6
1.4 Objectives	6
1.5 Dissertation Outline	7
References	8

CHAPTER 2: LITERATURE REVIEW 10

2.1 Introduction	10
2.1.1 Carbon Spheres	10
2.2 Carbon in Fuel Cells:	13
2.2 Oxygen Reduction Reaction (ORR)	15
2.3.1 Review of Literature of ORR Catalysts	15
2.4 Core-Shell Nanomaterials (CSNMs)	19

2.4.1	Synthesis of Core-Shell Nanomaterials	20
2.4.1.1	Pre-Decoration.....	20
2.4.1.2	Post-Decoration	21
2.5	Core-Shell Nanomaterials in Catalysis	22
2.5.1	Oxidation Reactions.....	23
2.5.2	Hydrogenation Reactions:.....	24
2.5.3	Carbon-Carbon Coupling Reactions	25
2.5.4	Integrated Multiple Catalytic Reactions	27
	References.....	28
	CHAPTER 3: EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES.....	37
3.1	Pt@mC catalyst synthesis	37
3.1.1	Materials	38
3.1.2	Template Synthesis	38
3.1.3	Pt@hmC Synthesis	39
3.2	Structural Characterization	41
3.2.1	Transmission Electron Microscopy (TEM)	41
3.2.2	Brunauer-Emmet and Teller (BET)	42
3.2.3	X-ray Diffraction (XRD)	42
3.2.4	Raman Spectroscopy.....	42
3.2.5	Thermogravimetric Analysis (TGA).....	42
3.3	Electrochemical Characterization	43
3.3.1	Materials	43
3.3.2	Electrochemical Cell Setup.....	43
3.3.3	Cyclic Voltammetry (CV).....	44
3.3.4	Linear Sweep Voltammetry	46
3.3.5	Chronoamperometry Measurements	46
	References.....	47

CHAPTER 4: SYNTHESIS OF PLATINUM LOADED ON MESOPOROUS SILICA SPHERES	49
4.1 Introduction.....	49
4.2 Synthesis of mesoporous silica spheres (<i>mSiO₂</i>)	50
4.2.1 Effect of surfactant on <i>mSiO₂</i> synthesis.....	50
4.2.2 Particle size and yield relationship	53
4.3 Platinum deposition on <i>mSiO₂</i>	56
4.3.1 Effect of different loading procedures	57
4.3.2 Effect of Pt precursor type	61
References	64
CHAPTER 5: CARBONIZATION	66
5.1 Introduction.....	66
5.2 Bubbling Method for Carbonization	68
5.2.1 Experimental	69
5.2.2 Results and Discussions.....	69
5.2.2.1 TEM Analysis	70
5.2.2.2. Thermogravimetric Analysis.....	71
5.3 Nanocasting Method for carbonization.....	73
5.3.1 Experimental.....	73
5.3.2 Results and discussion	74
5.3.2.1 TEM Analysis	74
5.3.2.2 Thermogravimetric analysis.....	76
5.4 Hollow Carbon Spheres	77
5.4.1 Experimental	78
5.4.2 Results and discussion	78
5.4.2.1 TEM analysis.....	78

5.4.2.2 TGA Analysis.....	81
5.4.2.3 Raman analysis.....	82
5.4.2.4 Surface Area Measurements.....	84
5.5 Electrochemical Measurements	85
5.5.1 Experimental.....	85
5.5.2 Results and Discussion	86
References.....	88
CHAPTER 6: APPLICATION – ELECTROCATALYTIC TESTS.....	92
6.1 Introduction.....	92
6.2 Experimental	94
6.2.1 Pt-Carbon Composite Synthesis	94
6.2.2 Electrochemical Measurements	95
6.3 Results and Discussion	96
6.3.1 TEM Analysis	96
6.3.2 Electrochemical Measurements	99
6.3.2.1 Effect of Deposition Technique	100
6.3.2.2 Effect of Hollow Carbon Sphere (HCS) Size	102
6.3.2.3 Effect of Platinum Precursor	104
6.3.2.4 Effect of Platinum Location	105
6.3.2.5 Effect of Scan Rate.....	108
6.4 Activity Comparisons with a Commercial Catalyst.....	110
References.....	114
CHAPTER 7: OVERALL CONCLUSIONS AND RECOMMENDATIONS.....	117
7.1 Conclusions.....	117
7.2 Recommendations.....	118

ABSTRACT

In the current study, different platinum-hollow carbon sphere catalysts were synthesized for use as electrocatalysts in low temperature fuel cells such as proton exchange membrane fuel cells (PEMFCs). The support material was synthesized via a hard templating method using mesoporous silica (synthesized using a modified Stöber method) as a sacrificial template. In fuel cells, one aim is to ensure that as much platinum as possible is present on a given electrode while keeping the entirety of the catalytic layer as thin as possible (i.e. with the minimum amount of carbon). One approach to achieving this was to make the hollow carbon spheres as small as possible, starting of course with the templating material. It was found that tailoring the molar ratios between the two co-solvents (that is water and ethanol) during Stöber synthesis was the key to achieving particles as small as approximately 150 nm with a uniform shape, size, and significant yields of up to 5.00 g.

Another focal point in terms of the template material was achieving a silica structure that consisted of a solid core, and a distinctly mesoporous shell. Two different surfactants were explored in order to fabricate these structures; namely octadecyltrimethoxysilane ($C_{18}TMS$) and cetyltrimethylammonium bromide (CTAB). It was found that of the two, the $C_{18}TMS$ resulted in more distinctly formed mesoporous silica layers with higher measured specific surface areas.

Because the type of support material greatly influences the catalytic behaviour of the loaded catalysts, two different carbonization techniques were explored; namely the bubbling method using toluene as a carbon source, and a nanocasting method where resorcinol formaldehyde (RF) was the carbon source. The toluene-synthesized hollow carbon spheres had advantages over their RF-synthesized counterparts in that they were more thermally stable and had a more graphitic crystalline carbon framework. The RF-synthesized carbon, however, possessed a pseudo-capacitance due to surface carbon-oxygen groups, as well as a higher specific surface area, which resulted in the RF-carbon cyclic voltammetry profile spanning a larger current range in microampere per square centimetre.

The effect of the size of the support materials was also explored; comparing 350 nm and 150 nm hollow carbon spheres. Besides the type of carbon, the metal precursor used to synthesize the catalyst nanoparticles was also explored, with either platinum(II)chloride (PtCl_2) or platinum(II)acetylacetonate [$\text{Pt}(\text{acac})_2$] being used as the platinum source. It is also known that achieving high metal yields using conventional methods is quite difficult, and so an easier, quicker and less wasteful method was also explored; comparing the traditional wet-impregnation (WI) method with a chemical vapour deposition (CVD) method. Ultimately, it was found that platinum loaded on top of small-sized toluene-synthesized hollow carbon spheres using the CVD method and $\text{Pt}(\text{acac})_2$ as the metal precursor was the better catalyst in terms of oxygen reduction (determined using linear sweep voltammetry measurements); outperforming even commercial Pt/C catalysts as a result of improved mass transfer afforded by the voided cores of the hollow carbon spheres.

The ability of a catalyst to withstand the reaction conditions present in a PEM fuel cell (i.e. oxygen-rich environments) was also considered. The stability of the catalysts was tested using chronoamperometry measurements in an oxygen-saturated perchloric acid solution. It was evident that the platinum loaded on the inner shells of the hollow carbon spheres showed far superior stability to those loaded on the outside surface. This was attributed to the qualities bestowed by the carbon shell around the platinum nanoparticles, protecting said platinum against the consequences of support corrosion due to the oxygenated environment; consequences such as metal sintering and interaction with surrounding carbon supports for example. These encapsulated catalysts, however, displayed a decrease in electrocatalytic activity compared to the catalysts with top-loaded platinum.

In conclusion, the study of different platinum-carbon catalysts studied in the current work revealed that (a) loading platinum on top of small sized toluene-synthesized hollow carbon spheres using a CVD method and $\text{Pt}(\text{acac})_2$ as a metal precursor resulted in a highly active oxygen reduction catalyst, while (b) loading platinum on the inside surface of the hollow carbon spheres under the same conditions resulted in a more electrocatalytically stable catalyst.

LIST OF FIGURES AND SCHEMES

Chapter 1

Figure 1.1: General structure of a fuel cell	2
Figure 1.2: Overview of PEM fuel cell structure.....	3
Figure 1.3: The electrode of a PEM fuel cell	4
Figure 1.4: (a) Triphasic system with catalyst particles physically separated by SiO ₂ layer ²³ , (b) Pt nanoparticle encapsulated in a carbon shell	6

Chapter 2

Figure 2.1: Representation of (a) solid, (b) core-shell, and (c) hollow carbon spheres...	11
Figure 2.2: Au@ZrO ₂ structures (a) before and (b) after heat treatment at 800 °C ²²	12
Figure 2.3: (a) TEM and (b) SEM images of the ordered mesoporous carbon spheres (OMCSs) ³⁷	16
Figure 2.4: Au/Pt/C catalyst's (a) LSV and (b) CV measurements; commercial Pt/C (c) LSV and (d) CV measurements before and after cycling tests ⁵⁰	18
Figure 2.5: Preparation steps for Au@ZrO ₂ yolk-shell catalyst: (I) gold colloid, (II) silica covered gold nanoparticle, (III) silica-covered Au with reduced particle size, (IV) zirconia covered spheres, and (V) Au@ZrO ₂ yolk-shell structures ⁷¹	21
Scheme 2.1: Process of the immobilization of active metal nanoparticles on the interior surface of a shell ⁶⁸	21
Figure 2.6: Illustrations of particle encapsulation using post-decoration approaches to form (Top) Multi yolk@shell, and (Bottom) Multi core@shell structures ⁶⁸	22
Figure 2.7: TEM images of Pd nanoparticles (a) inside (Pd@hmC) and (b) on top of (Pd/hmC) hollow mesoporous carbon spheres ⁸⁰	24
Scheme 2.2: Representation of the hydrogenation of an olefin to form an alkane	25
Scheme 2.3: Representation of coupling reaction catalysed by palladium nanoparticles encapsulated in hollow porous silica nanoshells	26
Scheme 2.4: Multistep cascade-type catalysis with core@shell nanoreactor, which sequentially combines cyclization and Pd-catalyzed hydrogenation reactions ⁹³ ..	27

Chapter 3

Scheme 3.1: Synthesis of Pt encapsulated in hollow carbon spheres	38
Scheme 3.2: Carbonization process via (a) bubbling and (b) nanocasting methods.....	40
Figure 3.1: Illustration of the three electrode electrochemical cell. The reference electrode is Ag/AgCl, the counter electrode is a Pt rod, and the working electrode is a polished glassy carbon electrode attached to a rotor and modified with a catalyst ink	44
Figure 3.2: Typical voltammogram of a Pt-catalyst with labels for appropriate peaks ¹⁵	45
Figure 3.3: Illustration of (a) typical LSV profile ¹⁶ , and (b) bottom view of the working electrode during linear sweep voltammetry measurements ¹⁷	46

Chapter 4

Figure 4.1: Silica spheres fabricated using (a) and (b) CTAB, and (c) and (d) C18-TMS as surfactants.....	51
Figure 4.2: CTAB-synthesized silica spheres forming necklace-like structures on increasing the amount of CTAB	52
Figure 4.3: Surface Areas as a function of the amount of surfactant added when the surfactant is either (a) CTAB or (b) C ₁₈ TMS.....	53
Figure 4.4: Silica spheres. (a) From Stöber method, (b) increasing amount of TEOS.....	55
Figure 4.5: (a) – (d): Silica spheres synthesized using methods 2 – 5 respectively.....	56
Figure 4.6: (a) and (b) Pt-CVD synthesized, (c) and (d) Pt-WI synthesized loaded TMS-synthesized silica spheres.....	58
Figure 4.7: Platinum size distribution for (a) Pt-WI and (b) Pt-CVD methods.....	59
Figure 4.8: X-ray diffraction patterns of (a) plain mesoporous silica, and Pt deposited on mesoporous silica via the (b) CVD, (c) wet impregnation methods	60
Figure 4.9: Pt loaded on CTAB-synthesized silica spheres.....	61
Figure 4.10: TEM images and size distributions for (a) and (b) Pt(acac) ₂ 150 nm, (c) and (d) Pt(acac) ₂ 350 nm, (e) and (f) PtCl ₂ 350 nm structures.....	62

Chapter 5

Figure 5.1: Illustration of (left) horizontal and (right) vertical CVD setups ²³	68
Figure 5.2: TEM images illustrating carbonization as a function of template size: (a) 350 nm, (b) 150 nm	71
Figure 5.3: (a) TEM image illustrating carbonization of 350 nm template at gas flow rate of 150 sccm, (b) Zoomed in section of (a)	71
Figure 5.4: (a) TGA and (b) derivative plots of toluene-carbonized 150 nm and 350 nm silica templates. Carbonization conditions: Carrier gas = Argon, Flow rate = 100 sccm, Temperature = 900 °C	72
Figure 5.5: Polymerization of the resorcinol formaldehyde (RF) polymer from resorcinol salt and formaldehyde solution ²⁵	74
Figure 5.6: TEM images of (a) SiO ₂ @RF and (b) RF-SiO ₂ @C composite structures from 150 nm silica template, and (c) & (d) RF-SiO ₂ @C composite structure from 350 nm silica template	75
Figure 5.7: (a) TGA and (b) derivative plots of the 150 nm and 350 nm RF-carbonized silica. Carbonization conditions: Carrier gas = Argon, Flow rate = 100 sccm, Temperature = 900 °C	76
Figure 5.8: TEM images of hollow carbon spheres fabricated from (a) - (b) the bubbling method, and (c) - (d) the nanocasting method. (a) And (c) are the 150 nm HCSs, (b) and (d) are the 350 nm HCSs	79
Figure 5.9: TEM images illustrating defects in 150 nm HCSs synthesized using the nanocasting method	80
Figure 5.10: (a) TGA and (b) derivative plots of the 150 and 350 nm hollow carbon spheres synthesized using RF and Toluene and carbon sources	81
Figure 5.11: Raman plots for the four hollow carbon spheres: (a) Small toluene-synthesized (Tol-HCS-s) (b) Small RF-synthesized (RF-HCS-s) (c) Large toluene-synthesized (Tol-HCS-b) (d) Large RF-synthesized (RF-HCS-b)	83
Figure 5.12: N ₂ sorption isotherms for (a) 150 nm, and (b) 350 nm RF- and Toluene-synthesized Hollow Carbon Spheres	84
Figure 5.13: CV curves obtained for 150 nm plain Toluene-synthesized and RF-synthesized mesoporous hollow carbon spheres	87

Chapter 6

Figure 6.1: TEM images and size distributions for: (a) and (b) tol-Pt(ac)_top, (c) and (d) tol-PtCl ₂ _top, (e) and (f) tol-PtCl ₂ _top-b, (g) and (h) tol-PtCl ₂ _inside, (i), (j) and (k) RF-PtCl ₂ _top, (l) and (m) RF-Pt(ac)_top, (n) and (o) WI catalysts	97
Figure 6.2: (a) CV profiles, (b) XRD spectra, (c) LSV scans, and (d) chrono-amperometric measurements for WI- and CVD-deposited platinum	101
Figure 6.3: (a) CV profiles, (b) XRD spectra, (c) LSV and (d) chrono-amperometric measurements of various catalysts as a function of carbon support size..	103
Figure 6.4: (a) CV profiles, (b) XRD spectra (c) LSV and (d) chrono-amperometric measurements of different catalysts as a function of Pt-precursor type ...	105
Figure 6.5: (a) CV profiles, (b) XRD spectra, (c) LSV and (d) chrono-amperometric measurements of varies catalysts as a function of Pt location.....	108
Figure 6.6: CV profiles of various catalysts as a function of scan rate and Pt precursor; scan taken at (a) 10 mV/s, and (b) 100 mV/s	109
Figure 6.7: (a) CV scans and (b) LSV measurements comparing the synthesized tol-Pt(ac)_top, tol-Pt(ac)_inside, and the commercial Vulcan Pt/C catalysts.....	110

LIST OF TABLES

Chapter 1

Table 1.1: Description of the different types of fuel cells	2
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Chapter 2

Table 2.1: Physical features of commercially available carbon blacks used in fuel cells...	14
Table 2.2: Comparison of the catalytic activity of platinum encapsulated in hollow mesoporous carbon spheres (Pt@hmC) compared to platinum on PVP (Pt-PVP)	

and activated carbon (Pt/AC) ²⁰	25
Table 2.3: Summary of results for cross coupling reactions catalyzed by Pd@SiO ₂ core@shell catalysts ⁹⁵	26

Chapter 4

Table 4.1: Effect of surfactant for synthesizing mesoporous silica shell for 450 nm spheres.....	51
Table 4.2: Conditions for decreasing <i>m</i> SiO ₂ particle size	54
Table 4.3: Summary of Pt nanoparticle sizes on different sized silica spheres	63

Chapter 5

Table 5.1: Reaction parameters used during the CVD carbonization process.....	69
Table 5.2: Summary of data for percentage of carbon deposited during carbonization ...	82
Table 5.3: Summary of Raman Results.....	83
Table 5.4: Sorption Data for RF- and Toluene-synthesized Hollow carbon Spheres.....	85

Chapter 6

Table 6.1: Denotations and descriptions of tested catalysts.....	95
Table 6.2: Summary of Cyclic Voltammetry Measurements	111
Table 6.3: Summary of Linear Sweep Voltammetry Measurements.....	112
Table 6.4: Summary of Chronoamperometric Measurements	112

LIST OF ABBREVIATIONS

ABBREVIATION	DEFINITION
BET	Brunauer-Teller-Emmett
CSCS	Core-shell Carbon Sphere
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition

ECSA	Electrochemically Surface Area
GC	Glassy carbon
HCS	Hollow Carbon Sphere
LSV	Linear Sweep Voltammetry
<i>m</i>	Mesoporous
mA	Miliampere
ORR	Oxygen Reduction Reaction
PEMFC	Proton Exchange Membrane fuel cell
RDE	Rotating Disk Electrode
RPM	Rotations per minute
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
V	Volts
WE	Working Electrode
WI	Wet Impregnation
wt%	Weight percent metal loading
XRD	X-ray Diffraction

CHAPTER 1:

INTRODUCTION TO STUDY, RESEARCH QUESTIONS AND HYPOTHESES

1.1 Introduction

Given the world's finite fossil fuel resources, as well as the ever-growing population, it is clear that the total power consumption by humans is currently such that energy supply and usage are unsustainable. Besides the supply and demand limitations of fossil fuels, there is also their contribution to various pollution-related issues that make it even more imperative that alternative energy technologies be developed.

One such technology that has since been developed as a means of supplying a clean alternative power source that will reduce dependency on fossil fuels is the fuel cell.¹ Fuel cells are energy conversion devices that cleanly, quietly, and efficiently convert chemical energy into electrical energy,² using relatively renewable sources of fuel and producing significantly less harmful by-products than technologies that utilise fossil fuels.³ Another advantage fuel cells have over conventional energy technologies is that they have high energy-conversion efficiencies, whereby under favourable circumstances this efficiency can reach about 60%. Conversely, a car engine at low power can achieve only 30% efficiency, becoming more efficient only at higher powers, whereas fuel cells are more efficient at low power loads.⁴

Although there are a variety of different fuel cells, they all have the same general principle of functioning.⁵ In general, these cells are made up of three main components: the anode, electrolyte, and cathode (*figure 1.1*). At the anode a fuel, which is continuously supplied from an external source, is oxidized by a catalyst to produce a positively charged ion and electrons. The positive ion travels through the electrolyte to the cathode, while the electrons travel through an external wire, thus creating an electric current, to the cathode. At the cathode,

oxygen reacts with the positively charged ions and consumes the electrons, producing water or carbon dioxide depending on the fuel used.⁶

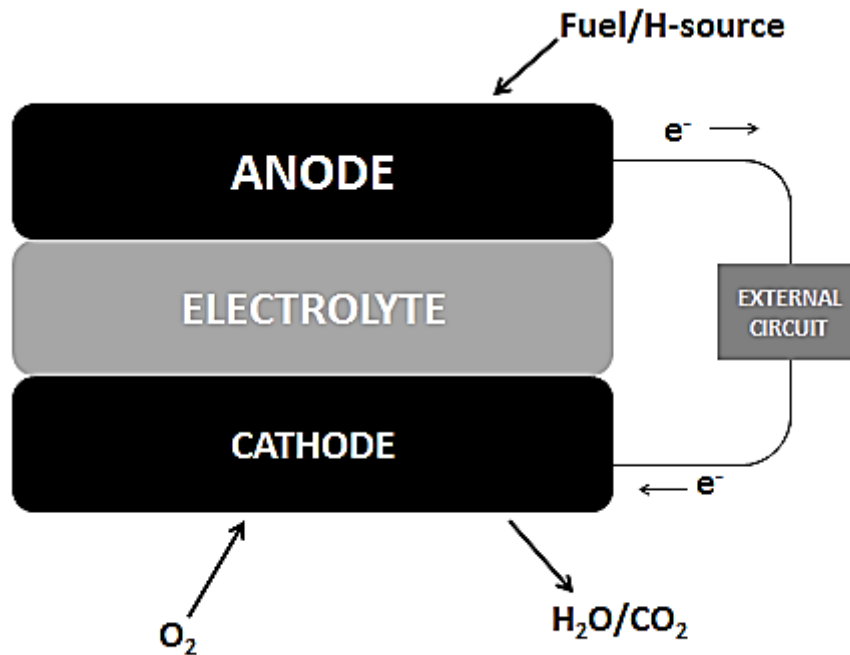


Figure 1.1: General structure of a fuel cell

The classification of fuel cells usually depends on the type of electrolyte, and they can be further categorized into low-temperature (< 200 °C) and high-temperature (> 450 °C) fuel cells.⁷ There are six main types of fuel cells: alkaline (AFC), direct methanol (DMFC), phosphoric acid (PAFC), molten carbonate (MCFC), solid oxide (SOFC), and proton exchange membrane (PEMFC) fuel cells (*table 1.1*). The different fuel cell types have their weak and strong attributes, and as a result have different applications.

Table 1.1: Description of the different types of fuel cells

Type	Electrolyte	Operating Temperature
AFC	Potassium hydroxide	RT – 90 °C
DMFC	Proton exchange membrane	60 °C – 130 °C
PAFC	Phosphoric acid	180 °C – 220 °C
MCFC	Molten alkali metal carbonates	400 °C – 650 °C
SOFC	Oxide ion conducting ceramic	800 °C – 1000 °C
PEMFC	Proton exchange membrane	RT – 90 °C (up to 200 °C)

The PEM fuel cell, because of its high power density and relatively low operating temperatures, has been recognized as a promising candidate for future power generating systems and is especially ideal for portable systems.⁸ Generally speaking, PEM fuel cells adhere to the structure shown in *figure 1.1*, but in their case the electrolyte layer separating the two electrodes is a polymer (*figure 1.2*) which has been prepared so that it conducts protons but not electrons.⁴ In a PEM fuel cell, hydrogen gas enters the cell and is carried to the anode where it is split into two protons, which cross the proton exchange membrane to the cathode, and two electrons, which travel via an external circuit to the cathode. This process is known as the hydrogen oxidation reaction (HOR):



At the opposite side of the cell, oxygen enters and travels to the cathode. At the cathode, this oxygen is reduced by the protons from the anode, a process termed the oxygen reduction reaction (ORR). This reaction consumes electrons, producing water, which then leaves the fuel cell⁹:

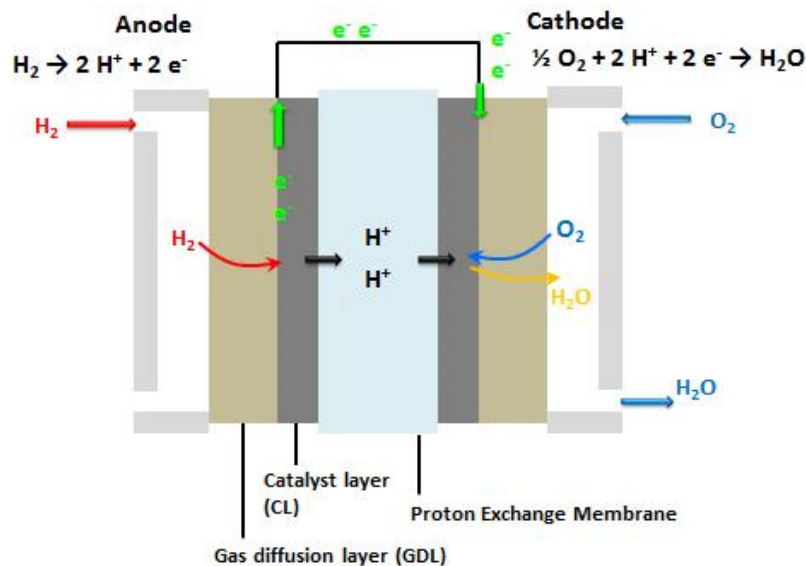
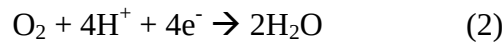


Figure 1.2: Overview of PEM fuel cell structure and functioning

The electrode in a PEMFC (*figure 1.3*) comprises of three components: (1) the proton conducting media, (2) the catalyst layer, and (3) the gas diffusion layer. Of these three, the catalyst layer is considered the most important because it is in essence the “active layer” where the two half-reactions essential for the functioning of the cell (the HOR and ORR) take place. After extensive research into the catalysis of the HOR and ORR, platinum and platinum-based alloys have been found to be amongst the most active catalysts for these reactions.¹⁰

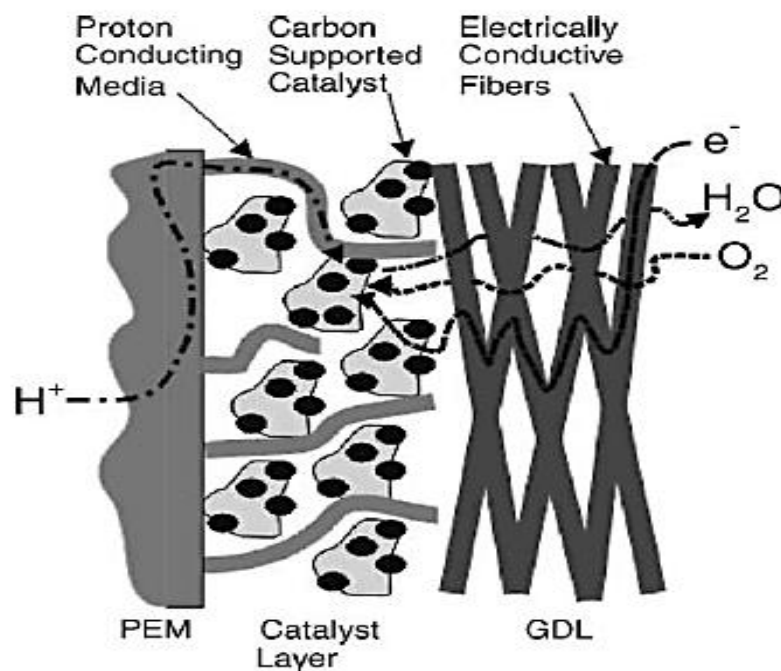


Figure 1.3: The electrode of a PEM fuel cell⁹

If the amount of desired product retrieved is dependent upon the amount of catalyst, then an obvious approach for increasing the catalytic efficiency of a system would be to increase the amount of catalyst; an economically unviable approach when dealing with expensive metals such as platinum.¹¹ A way to decrease the catalyst loading in a system would be to develop a fabrication method which maximizes the utilization of the platinum present in the system,¹² which can be achieved by decreasing the rate at which the catalyst deactivates.

There are five main causes of deactivation, namely: (1) Poisoning, which is defined as deactivation by strong adsorption of impurities to the catalyst surface,¹³ which decreases the catalyst active surface. (2) Fouling, which describes any phenomenon where a surface is

covered by an unwanted deposit, such as dust, and this affects how a chemical process proceeds.¹⁴ (3) Mechanical deactivation, which can be caused by the crushing of the catalyst particles, breaking up of catalyst particles to produce fines, and erosion of catalyst particles due to high fluid velocities.¹³ (4) Corrosion or leaching also causes catalyst particles to deactivate, especially if the reaction medium has a very high or very low pH value.¹⁵ (5) Thermal degradation is a physical process that causes deactivation because of resultant processes such as sintering, evaporation, etc.¹⁶

1.2 Motivation

Sintering comes about when catalyst particles migrate towards each other in the desire to lower their increased surface free energies as a result of either elevated temperatures or pressures.^{17,18} When it occurs, sintering causes a decrease in the number of surface metal atoms per unit mass of metal and therefore decreases the number of active catalyst sites.^{18,19} Because sintering is one of the most common methods by which catalyst deactivation occurs, extensive research has been done, and is undergoing, into developing sinter-resistant systems. One such approach is to enhance the interaction between the catalyst nanoparticles and the supporting material,²⁰ thus slowing down the migration of particles across the support surface. Theoretically, introducing a physical barrier between catalyst particles should retard, if not eliminate, the sintering phenomenon.²¹

In the past this has been done by the deposition of a thin, porous layer of an oxide over the supported catalyst particles, physically separating the nanoparticles from each other (*figure 1.4a*).²² Another means of physical separation is to encapsulate the catalyst in a porous shell (*figure 1.4b*); a method that results in a vast increase in thermal stability, but in the past also resulted in decreased catalytic activity due to the barrier between reactants and the catalyst's surface.²¹

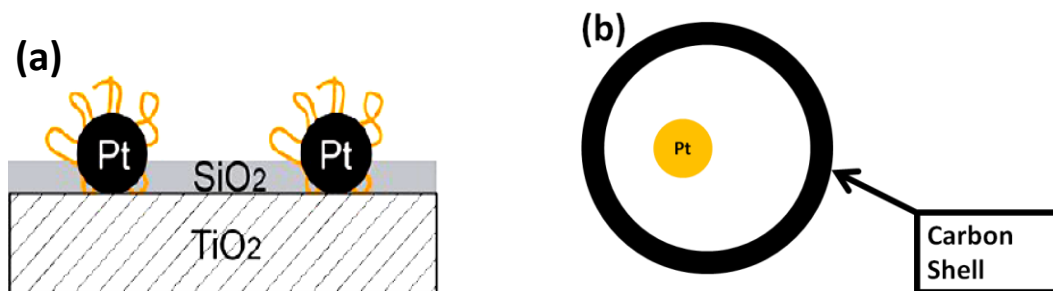


Figure 1.4: (a) Triphasic system with catalyst particles physically separated by SiO₂ layer,²³ (b) Pt nanoparticle encapsulated in a carbon shell

1.3 Aim

The aim of the current study was:

To synthesize a catalyst layer for a Proton Exchange Membrane fuel cell consisting of platinum nanoparticles encapsulated in mesoporous carbon shells

1.4 Objectives

The individual objectives were:

- To synthesise silica spheres with a distinctive mesoporous layer using a modified Stöber method
- To load platinum nanoparticles onto these mesoporous silica spheres
- Investigate the effects of using two different carbonization methods to deposit a carbon layer on the platinum-silica composite structures
- To remove the template using chemical etching with hydrofluoric acid

- To characterize these structures using techniques which include transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), thermogravimetric analysis (TGA), and Raman spectroscopy
- To estimate the electrochemically active surface area (ECSA) of the catalyst using cyclic voltammetry (CV)
- To estimate the catalyst's activity for the oxygen reduction reaction (ORR) using linear sweep voltammetry (LSV)

1.5 Dissertation Outline

The content of the current dissertation is as follows:

- Chapter 1: Gives the research hypothesis, motivation, aim and objectives of the current study
- Chapter 2: Reviews in detail the literature focused on the use of different types of electrocatalytic systems in proton exchange membrane fuel cells (PEMFCs)
- Chapter 3: Explains the experimental procedures involved in synthesizing platinum nanoparticles encapsulated in hollow mesoporous carbon spheres (Pt@hmC), and the experimental parameters for catalyst electrochemical testing
- Chapter 4: Reports the results for the synthesis of small size silica spheres with distinctive mesoporous shells
- Chapter 5: Reports the results for the carbonization and chemical etching processes
- Chapter 6: Reports the results for the electrochemical testing using cyclic voltammetry, linear sweep voltammetry, and chronoamperometric measurements
- Chapter 7: Provides the overall conclusions for the current study as well as recommendations for future studies

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CHAPTER 2:

LITERATURE REVIEW

Alternative sustainable energies have been a research topic for many years now, with the world attempting to find “green” alternatives to the fossil fuels we have come to rely on. To this end, alternative energy conversion devices are being studied worldwide, with fuel cells at the fore-front. This chapter reviews the literature on fuel cell studies; specifically the Proton Exchange Membrane fuel cells, the reactions involved and the catalysts, and catalyst support materials used.

2.1 Introduction

2.1.1 Carbon Spheres

For a very long time, diamond and graphite were thought to be the only ways that pure carbon atoms arranged themselves. However, today we know that carbon can exist in many allotropic forms, each with extreme variations in physical and chemical behavior. These allotropes include carbon nano-tubes and –fibres,¹ onions,² horns,³ calabashes,⁴ flasks,⁵ and more relevant to the current dissertation, carbon spheres.⁶ The unique subtlety in bonding configurations that result from carbons ability to employ almost any conceivable combination of sp , sp^2 , and sp^3 hybridization is the main reason for this wide range of materials found with an immensely diverse range of properties and morphologies.⁷

Spherically shaped carbon materials have been studied for decades, and have garnered particular interest in such industries as the tyre, battery, and printer ink industries.⁸ There are three main types of spherical carbon materials; namely solid carbon spheres (SCSs), core-shell carbon spheres (CSCSs), and hollow carbon spheres (HCSs)⁹ (*figure 2.1*).

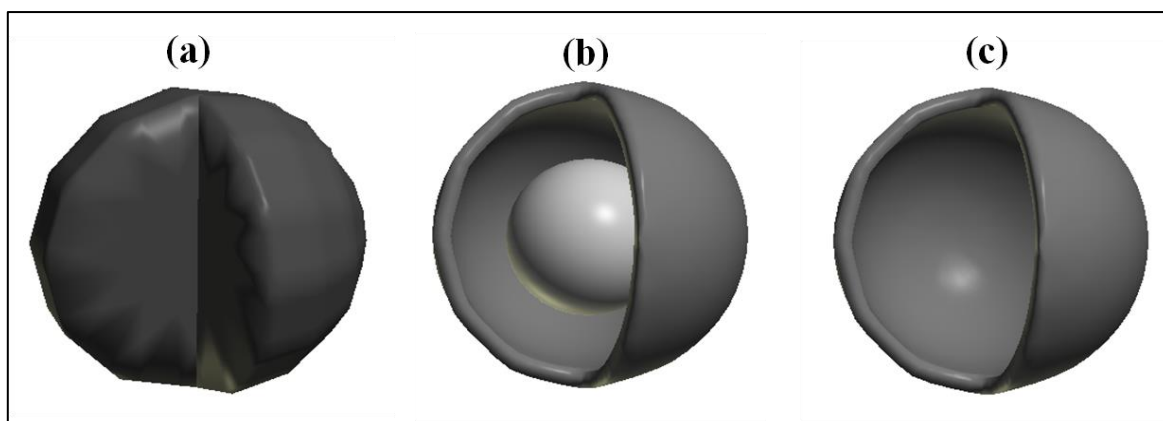


Figure 2.1: Representation of (a) solid, (b) core-shell, and (c) hollow carbon spheres

Solid carbon spheres, as the name suggests, are nanospheres with a completely dense carbon structure. These structures have over the years been synthesized via different mechanisms; both catalyzed and non-catalyzed pathways have been researched.^{10,11} Of these synthetic routes, the direct pyrolysis of various hydrocarbons at relatively high temperatures (that is chemical vapor deposition without a catalyst) has been reported as one of the best methods for SCS synthesis.¹² These solid spheres have found use in a variety of applications as reinforcement materials for rubber, lubricating materials, and of course as catalyst support materials.¹³

Since CSCSs and HCSs are very closely related, in that HCSs are essentially the “shell” portion of core-shell carbon spheres, the two will be discussed simultaneously.

Core-shell structured nanomaterials are described as those having different materials with different functionalities in both their cores and their shells, consequently making these materials excellent candidates in applications such as drug delivery, energy conversion, and storage systems.¹⁴ There have been numerous reports on core-shell structures composed of metal nanoparticles encapsulated in silica spheres ($M@SiO_2$) being researched for their potential in applications in the electronics, magnetic, optics, and catalysis fields.^{15–17} The traditional catalysts in which metal nanoparticles are loaded on top of a carbon support material have been reported to exhibit metal leaching and aggregation.¹⁸ For these reasons, carbon-encapsulated metal nanoparticles ($M@Carbon$) have piqued the interest of many research groups for their potential uses in catalysis.¹⁹

The successful fabrication of these M@Carbon composite structures has been reported in the literature. One such report was published by Ikeda *et al.*,²⁰ where a platinum nanoparticle was encapsulated inside hollow porous carbon Pt@hmC) via a hard-templating route. During the procedure, synthesized Pt nanoparticles were coated first with a silica layer, and this M@SiO₂ was subsequently coated with a carbon layer. The silica was then removed, resulting in the Pt@hmC structure which proved to be effective in the prevention of Pt particle aggregation during olefin hydrogenation reactions. They then further tested this hypothesis by replacing platinum with rhodium, and found that similar results were observed whereby metals were stabilized against aggregation while still maintaining their catalytic activity.²¹ A similar hard-templating synthetic method was applied by Arnal *et al.*,²² who proved the thermal stability of gold nanoparticles encapsulated in zirconium dioxide shells (Au@ZrO₂) by exposing these structures to temperatures as high as 800 °C (*figure 2.2*), and having the encapsulated gold particles retaining their shape and size.

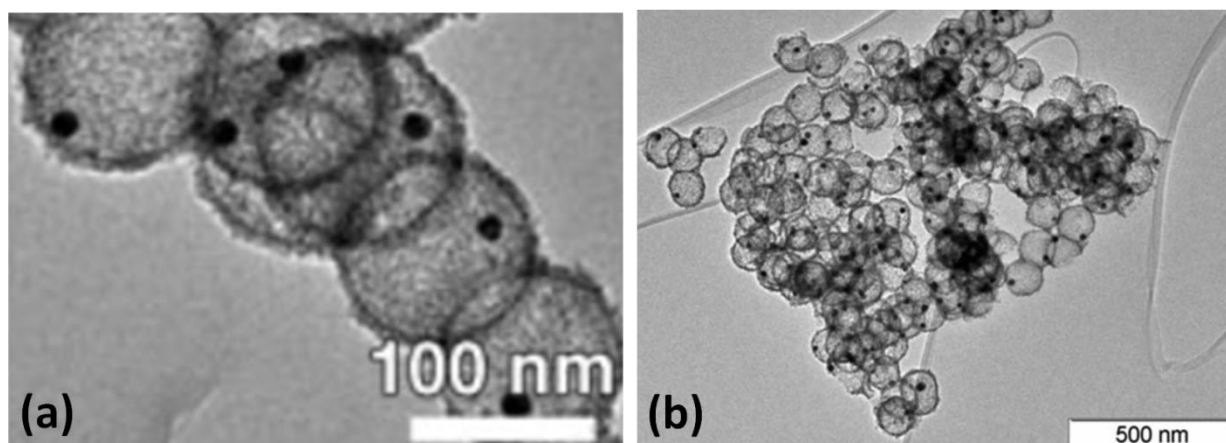


Figure 2.2: Au@ZrO₂ structures (a) before and (b) after heat treatment at 800 °C²²

Apart from the prevention of particle agglomeration due to reaction conditions, encapsulating active metal particles in hollow carbon spheres can also serve to keep the consequences of physical changes to said metal particles isolated from all other particles in a given catalyst sample. An example of this was demonstrated by Lee *et al.*,²³ who encapsulated tin (Sn) nanoparticles in hollow carbon spheres (Sn@HCSs) for use as catalysts in lithium secondary batteries. Agglomeration in these batteries came about due to the volume changes to the Sn metal due to alloying and dealloying with lithium ions during operation, causing the metal to lose its ability to store said lithium ions. The encapsulation of the Sn effectively isolated these alloying reactions, allowing for the volume changes to take place without coagulation of

metal particles, and the voided space of the HCSs was able to experience these expansions/contractions without collapsing; an advantage in terms of the cycling of the batteries.

2.2 Carbon in Fuel Cells:

Grouped according to the type of fuel they utilize, low temperature fuel cells that use hydrogen include the phosphoric acid fuel cell (PAFC)²⁴ and polymer electrolyte membrane fuel cell (PEMFC),²⁵ and those that use either methanol or ethanol include the direct methanol fuel cells (DMFC)²⁶ and direct ethanol fuel cells (DEFC)²⁷ respectively. Over the years, these fuel cells have gained popularity in the research of environmentally friendly alternative energy devices which directly convert the fuels listed above into electrochemical energy.²⁸

Platinum and its different alloys have been found to be the best catalysts for the reactions taking place in these different fuel cells.²⁴ The catalytic activity of a given catalyst will depend on the active surface area of said catalyst, and, not taking into account the particle size effect,²⁹ it is generally observed that the smaller a given catalyst particle is, the larger its reactive surface area.³⁰ To keep sizes of the catalysts in the smaller nm range, catalysts are deposited on a high surface area support material which possesses sufficient electrical conductivity which will allow the support to act as a path for the flow of electrons during the electrochemical reactions.³¹ It is imperative that the best material possible be used as the support because the support greatly influences the activity of the catalyst as there is an interaction between the two.³²

The support has two main effects on the catalyst material. Firstly, it can change the electronic character of the catalyst; consequently modifying the reaction characteristics of the catalyst's active sites. Secondly, it can modify the geometric shape of the loaded catalyst particles. A combination of these two effects has the potential to dramatically alter the electrochemical activity of the catalyst.³³ To this effect, an important issue when it comes to research based on low temperature fuel cells is to look at improving properties of supports, and developing new carbon (as well as non-carbon) supports.

In recent years, there has been a considerable amount of interest in developing new types of carbon materials to act as supports for electrocatalysts. Carbon blacks have been the usual electrocatalyst support of choice for fuel cells. These include the commercially available options Vulcan XC-72, Black pearl 2000, Denka Black, Shawinigan Black, Conductex 975 Ultra, Ketjen EC-300 J, and Ketjen EC-600 JD. The physical properties and synthesis techniques of these different carbons are listed in *table 2.1*. The most widely used of these carbon blacks (both commercially and for research purposes) is the Vulcan XC-72 carbon which is synthesized via the furnace method using oil fracture as the carbon source.³⁴ The disadvantages facing most of these commercial catalysts is that they have poorly defined porous structures because their particle sizes and pore widths have very wide distribution ranges. An example to this effect is that only half of Vulcan's total BET pore volume is attributed to macro- or mesopores; the rest of the pores are micropores of diameters which are mostly less than 1 nm,³⁵ which is problematic because these small pores contribute very little to the catalytic performance because they are inaccessible to fuels.³⁶ It has been found that it is much more advantageous to have a carbon that is mainly macro- and mesoporous, as this makes for a more electrocatalytically stable catalyst that is less susceptible to dissolution and agglomeration.³⁷

Table 2.1: Physical features of commercially available carbon blacks used in fuel cells

Carbon Black	Supplier	Synthesis Route	Surface Area (m²/g)	Particle Size (nm)	Refs
Vulcan XC-72	Cabot	Furnace Black	250-260	20-50	38
Black Pearl 2000	Cabot	Furnace Black	1475-1500	15	34,39
Denka Black	Denka	Acetylene Black	58-65	40	34,39
Shawinigan Black	Chevron	Acetylene Black	70-90	40-50	34,40
Conductex 975 Ultra	Columbian	Furnace Black	250	24	39
Ketjen EC-300 J	Akzo Nobel	Furnace Black	800	30	41
Ketjen EC600 JD	Akzo Nobel	Furnace Black	1270	30	42

2.2 Oxygen Reduction Reaction (ORR)

2.3.1 Review of Literature of ORR Catalysts

Besides the commercial catalysts mentioned earlier in this chapter, there has been extensive research conducted in the search for alternative catalysts for the cathodic reduction of oxygen in fuel cells. In this section, the research that has already been conducted towards finding an alternative catalyst for this reaction is reviewed. Even though it is the general consensus that platinum supported on carbon is the usual catalyst for the ORR, other types of catalysts have been researched over the years. These catalysts can very broadly be placed in the following categories:

- i. Platinum catalysts: this category includes unsupported platinum nanoparticles, hollow platinum catalysts, platinum on carbon, etc.
- ii. Platinum Alloys: in this category are catalysts that consist of platinum alloyed with various metals, and can be either supported or unsupported
- iii. Non-Platinum catalysts: metals other than platinum have been explored for the reduction of oxygen
- iv. Metal-free: these catalysts include carbon structures with different functionalities

One of the ways to decrease the amount of precious metal needed in order to synthesize an efficient ORR electrocatalyst is to stabilize small platinum nanoparticles against sintering, and one of the ways to do this is to load the platinum on a high surface area carbon support. There are many types of carbon that can act as supports for these platinum electrocatalysts, each with its own advantages and drawbacks. One type of carbon support that has been studied is the three-dimensionally ordered mesoporous carbon sphere (OMCS) shown in *figure 2.3*. The activity of platinum loaded on these structures (Pt/OMCS) has been studied

by Zhang *et al.*³⁷ They found that the OMCS-supported catalyst was more active than the commercial catalyst for the ORR reaction, and attributed this to the unique hierarchical structure of the OMCSs with ordered macro- and meso-pores that are able to better facilitate mass transfer and improve the platinum particle dispersion. Another study by Yan *et al.*⁴³ compared the activities for the ORR of the commercial Pt/Vulcan XC-72 (Pt/C) catalyst with that of platinum loaded on mesoporous hollow carbon spheres (Pt/HCSs) synthesized using glucose as a carbon precursor. They found that the platinum loaded on the hollow carbon spheres was not only smaller in size, but also better dispersed and more electrocatalytically stable, mostly due to the very high surface area of the carbon support provided by its hollow structure. As a result, the mass current density for the Pt/HCS catalyst was found to be 1.7 times higher than for the commercial catalyst, and this was partly attributed to the improved mass transfer for the Pt/HCS catalyst.

Keeping with the idea that hollow structures, with their low densities and high surface areas, allow for improved mass transport, and therefore improved ORR catalytic activity, some researchers have opted to study the effect of synthesizing unsupported hollow platinum structures as electrocatalysts for the reduction of oxygen. One such study was reported by Chen *et al.*,⁴⁴ where hollow platinum nanostructures were synthesized using a modified galvanic replacement reaction. The study further proved the point that upon a change from the solid counterparts to a hollow structure, the catalytic activity of the catalyst is improved.

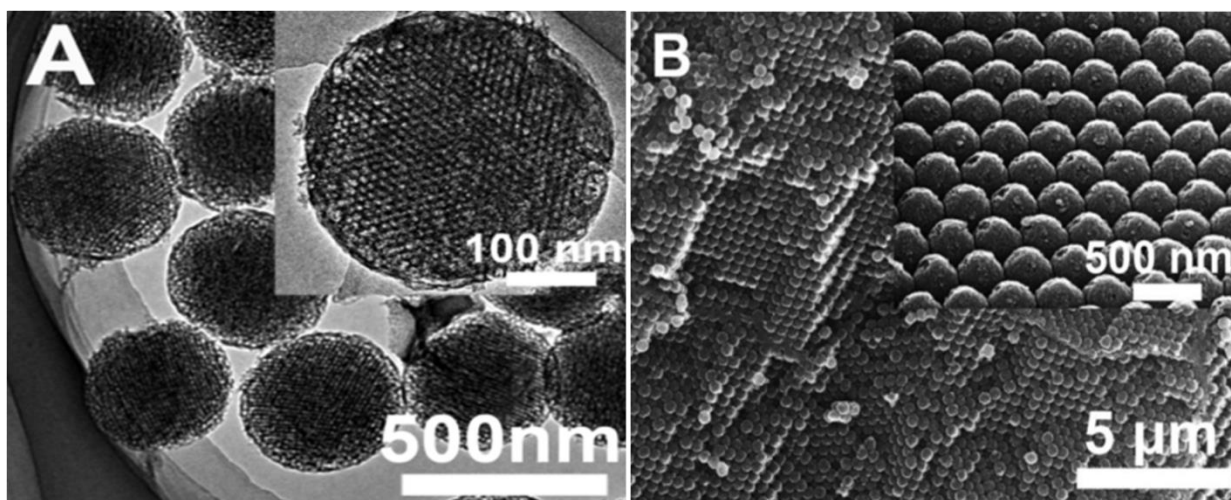


Figure 2.3: (a) TEM and (b) SEM images of the ordered mesoporous carbon spheres (OMCSs)³⁷

Another way to stabilize the platinum nanoparticles is to form bimetallic catalysts where platinum is alloyed with another metal that will improve the catalysts overall activity by either stabilizing the platinum within the catalyst, or itself participating in the oxygen reduction reaction. Many reports in the literature are aimed at showing that the incorporation of an additional active-metal to carbon-supported platinum can improve the configuration between platinum and the carbon support,⁴⁵ which would in turn improve reaction activity of the catalyst. Carbon-supported Pt-Co alloys have been shown to improve the durability of the catalysts in PEM fuel cells by reducing platinum dissolution and migration during operation,^{46,47} while carbon-supported Pt-Ru alloys improve carbon dioxide tolerance of the catalysts in these fuel cells.⁴⁸ Fıçıcılar *et al*⁴⁹ studied how the extent of alloying affected catalytic activity of Pt-Pd/C catalysts. They found that adding only small amounts of Pd increased the stability of the proposed electrocatalyst, as well as assist in the reconfiguration of Pt-C interaction compared to plain Pt-C catalysts.

An alternative to the alloying approach could be to introduce a second metal onto a pre-existing platinum-carbon catalyst, in the hopes that this will stabilize the platinum metal. This approach was studied by Zhang *et al*⁵⁰ who aimed to test the stability of platinum stabilized by gold clusters. Stability tests were performed using an accelerated stability test where linear potential sweeps were continuously applied in order to cause the surface oxidation/reduction cycles of the platinum. They found that even after 30 000 cycles, the platinum was still as active as it was before the cycling tests, unlike the commercial Pt-carbon catalyst used for comparison (*figure 2.4*); thus attesting to the stabilizing effect of adding a second metal to the catalyst. The downside of the alloying/second-metal approach, of course, is that it does nothing to alleviate the costs involved in commercializing such a catalyst.

Even though the Pt-carbon catalysts are still currently the top contenders as ORR electrocatalysts, it is worth mentioning the variety of research concentrating on non-platinum-based catalysts for the reduction of oxygen.

Platinum is one of the most expensive precious metals on the market, as a result making Pt-based electrocatalysts difficult to commercialize.⁵¹ Many researchers have attempted to find alternative metals to act as electrocatalysts for the reduction of oxygen, thus replacing platinum altogether.^{52,53} One approach has been to synthesize heteroatom-doped

nanostructured carbon materials that exhibit ORR performance comparable to the more traditional Pt/C catalysts, and then adding certain transition metals (such as iron and cobalt) to the doped carbon frameworks thus forming nonprecious metal (NPM) catalyst systems.⁵⁴ To this effect, Liang *et al*⁵⁵ developed a variety of mesoporous carbon-nitrogen-cobalt (C-N-Co) and carbon-nitrogen-iron (C-N-Fe) catalysts which exhibited high ORR activity, high selectivity, and excellent electrochemical stability in acidic medium. These desirable characteristics were attributed to their well-defined mesoporous structures, high BET surface areas, and the homogeneous distribution of many metal-nitrogen active sites. In another study, Mabena *et al*⁵⁶ compared the ORR activity of ruthenium deposited on nitrogen-doped carbon nanotubes (Ru/N-CNTs) with Ru content of 2.0, 5.0, and 10 wt%. The ruthenium was found to be very well distributed on the N-CNT surface, and that the smallest Ru loading resulted in the best ORR catalytic activity.

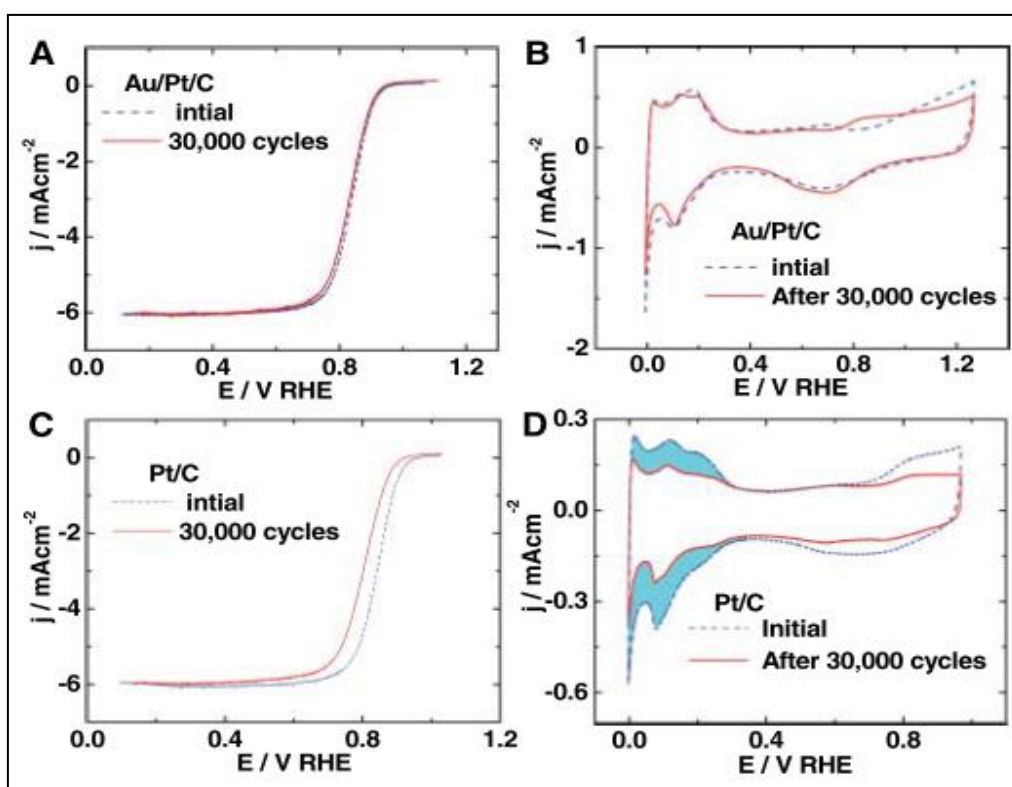


Figure 2.4: Au/Pt/C catalyst's (a) LSV and (b) CV measurements; commercial Pt/C (c) LSV and (d) CV measurements before and after cycling tests⁵⁰

Some researchers have taken the replacement of platinum to the next level, by attempting to synthesize ORR electrocatalysts that are completely free of any metals. Yu *et al*⁵⁷ have reviewed the activities of metal-free carbon-based catalysts for a variety of reactions,

including oxidative dehydration (ODH) and oxygen reduction reactions. They have suggested that modified carbon nanomaterials (for example by heteroatom doping) can be comparable in terms of activity with traditional metal-based catalysts, are more durable than said catalysts, and furthermore are much more cost efficient. An example of this type of carbon-framework modification was reported by Lu *et al.*,⁵⁸ where the ORR activity of boron-doped hollow carbon spheres (BHCSs) was tested. These catalysts showed outstanding ORR activity, and better long-term stability than the commercial Pt/C catalyst, and overall these structures were shown to be promising metal-free alternatives for catalysing the ORR in fuel cells. Li *et al.*⁵⁹ opted to synthesize CNT-graphene complexes, and modify them by introducing various defects into the surface of each carbon; defects which were ultimately responsible for the ORR activity. These catalysts were found to be quite stable in both alkaline and acidic media, showing high ORR activity and durability, which was attributed to the novel carbon-based structure of the CNTs.

2.4 Core-Shell Nanomaterials (CSNMs)

This section aims to review the literature reporting on the concept of the nanoreactor composed of catalytic species encapsulated within a cavity that is enclosed by a porous shell; essentially core-shell nanomaterials. This cavity or void is a feature that has seen these structures become research topics for various applications such as drug delivery vehicles,^{60,61} contrast agents for molecular imaging,^{62,63} and energy- and gas-storage materials.^{64,65} When a catalytic species is incorporated in the voided space of a hollow nanosphere, these structures become very attractive candidates as nanoreactors.^{66,67} This, of course, would eliminate one of the weakest points of conventional nanoparticle-based catalysts; that is catalyst deactivation due to agglomeration of the active nanoparticles. Another attractive feature of these nanoreactors is that because the active metal is trapped within the voided space in a surfactant-free state, the catalyst can exert high catalytic activity without interference from surface-capping ligands.⁶⁸

2.4.1 Synthesis of Core-Shell Nanomaterials

In order to apply hollow nanomaterials as nanoreactors, the interior voided space needs to first be functionalized with catalytically active particles thus allowing chemical reactions to take place in the core protected by the porous shell. The different functionalisation methods can be characterized according to the sequence of the hollowing, then functionalisation processes: the decoration of the hollow materials with the active metals can be either (i) before the structure is hollowed out (pre-decoration), or (ii) after hollowing (post-decoration).

2.4.1.1 Pre-Decoration

As mentioned before, this approach involves introducing the active metal catalyst particles before any hollowing procedures are employed. The most reported method for carrying out this approach is by the use of a sacrificial template. There are many reports in the literature that describe the fabrication of yolk@shell structures consisting of a single metal particle in the core^{69,70}; that is, rattle-type structures where the core moves about within the hollowed space. For example, Güttel *et al*⁷¹ suggested a method to encapsulate a gold particle in a zirconium dioxide shell (Au@ZrO₂) using silica as the sacrificial template. The process is summarized in *figure 2.5*. However, to make these nanoreactors practical for catalytic use, they would have to be modified to multiple-core yolk-shell structures, whereby the metal nanoparticles within the hollow core are not moving about. The problem with this being that the multiple cores would end up agglomerating in a bid to decrease their surface energies, thus forming large metal particles within the core which would not be very catalytically active.

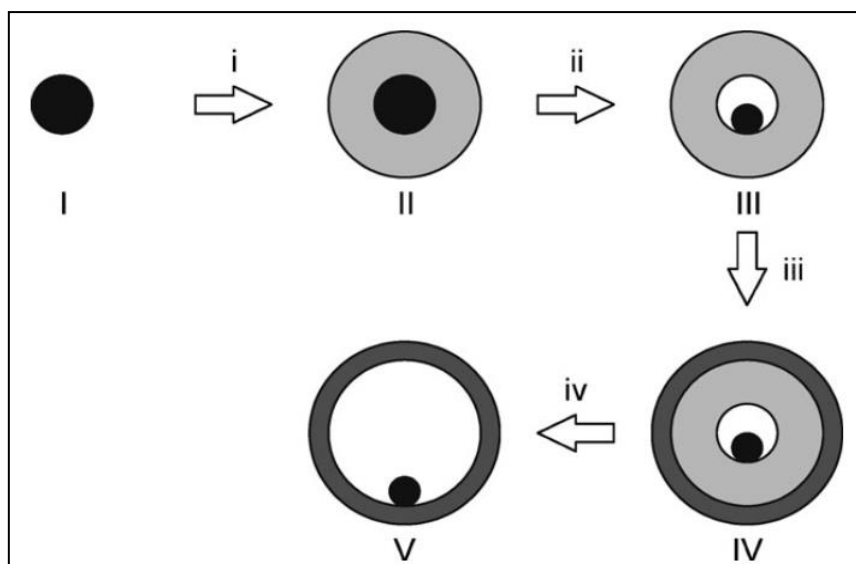
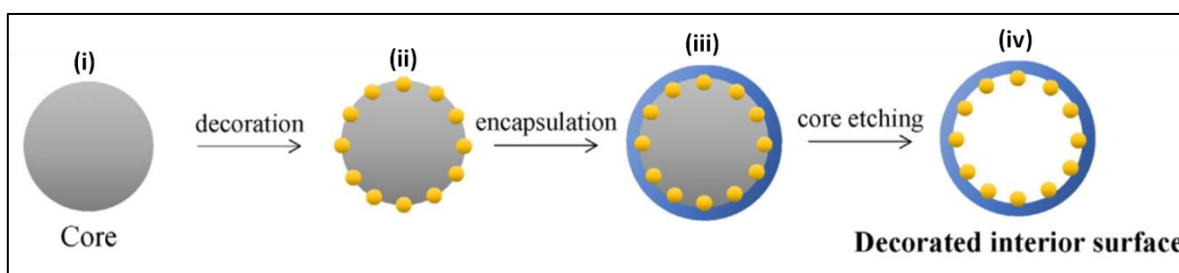


Figure 2.5: Preparation steps for Au@ZrO₂ yolk-shell catalyst: (I) gold colloid, (II) silica covered gold nanoparticle, (III) silica-covered Au with reduced particle size, (IV) zirconia covered spheres, and (V) Au@ZrO₂ yolk-shell structures⁷¹

A solution to this would be to immobilize the metal particles on the inside surface of the shell by transferring the active metal from the sacrificial template to the interior shell wall. The steps involved in this process are illustrated in *scheme 2.1*, and proceed as follows: (i) the template (core) is synthesized; (ii) the template is decorated with the active metal particles, (iii) coating with the shell material, (iv) the template material is completely removed, leaving the active metal particles on the shell's interior wall.



Scheme 2.1: Process of the immobilization of active metal nanoparticles on the interior surface of a shell⁶⁸

2.4.1.2 Post-Decoration

As the name suggests, this method involves first synthesizing the completely hollow material, and subsequently introducing the active metal particles. One approach to this method is the “ship-in-a-bottle” technique; which involves encapsulating metal particles via reduction or

assembly of a metal precursor solution.⁷² The resultant structures from this method are synonymous to the multiple-core yolk@shell structures, and so are catalytically unfavourable. Alternately, there have been some reports on the post-decoration of the interior wall surface of preformed hollow nanomaterials, where the active metal is immobilised on the inside surface. This has been demonstrated by Kim *et al*,⁷³ who employed a galvanic replacement reaction⁷⁴ to ultimately encapsulate different metal nanoparticles inside preformed hollow silica nanospheres. These processes are summarized in *figure 2.6*.

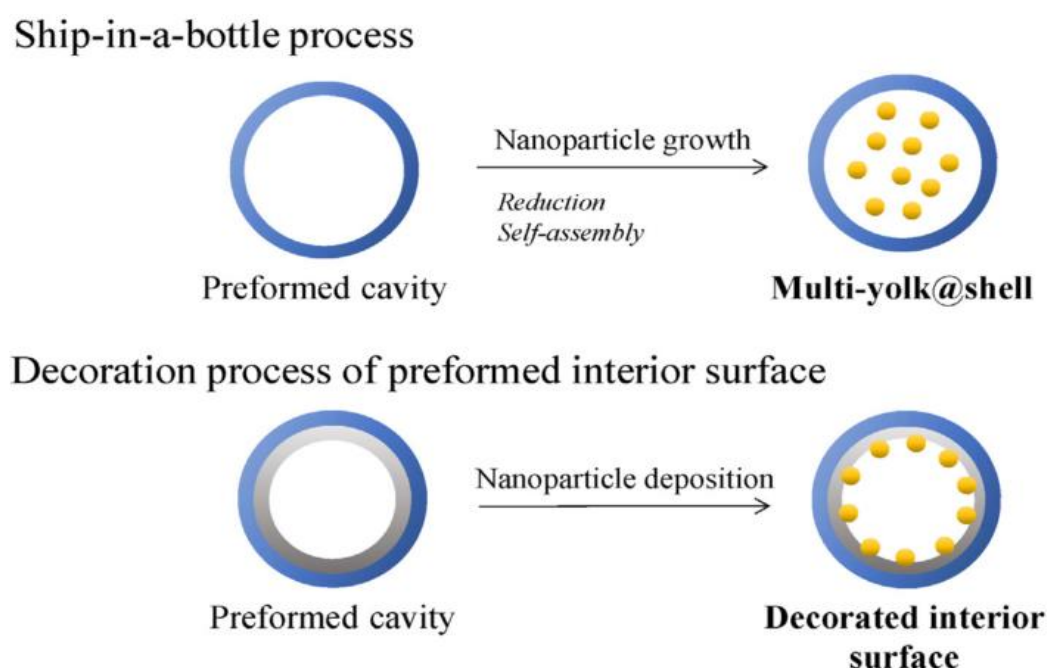


Figure 2.6: Illustrations of particle encapsulation using post-decoration approaches to form (Top) Multi yolk@shell, and (Bottom) Multi core@shell structures⁶⁸

2.5 Core-Shell Nanomaterials in Catalysis

There have been a multitude of different chemical reactions catalyzed using core@shell/yolk@shell structures. The nanoreactors described in this section are composed of single- or multi-cores of active metal nanoparticles and their alloys, while the hollow shells are composed of oxide materials, carbon-based materials, and organic polymers. In this regard, this section aims to give an overview of some of the reactions that have been performed using these nanoreactor catalytic systems. We, of course, cannot be exhaustive in our review of the literature, so the reactions discussed here are some of many examples of (i)

oxidation, (ii) hydrogenation, (iii) nitroarene reduction, (iv) carbon-carbon coupling, and (v) the integration of multiple catalytic reactions.

2.5.1 Oxidation Reactions

Many oxidation reactions have been catalyzed using core-shell nanoreactors, and one such reaction is the oxidation of carbon monoxide (CO). Many reports are available in the literature ^{75–77} attest to the thermal stability that the core@shell structure introduces to a catalyst, improving the amount of CO conversion at more favourable reaction conditions. For example, Huang *et al* ⁷⁸ encapsulated gold nanoparticles in hollow titania and zirconium dioxide shells to form yolk@shell structures (Au@TiO₂ or Au@ZrO₂), prepared from monodispersed hydrophobic gold nanoparticles via an assembly approach, for use as a catalyst for CO oxidation. They found that the Au active metal maintained its catalytic activity even after heat treatment at 800 °C; maintaining a 50% CO conversion at 200 °C. Another reaction reported is the oxidation of methane. Park *et al* ⁷⁹ encapsulated a single nickel nanoparticle in a silica nanoshell (Ni@SiO₂) and used it in the steam reforming process for methane oxidation. Not only were the metal nanoparticles found to be more thermally stable, but the conversion yields of hydrogen and methane were found to be preserved above 70 and 90% respectively.

The above-mentioned examples are reactions taking place with substrates in the gaseous phase, but these nanoreactors have also been shown to be viable for oxidation reactions with reactants in solution. For example, the oxidation of alcohols is a very important process in organic synthesis, but is often carried out at elevated temperatures; meaning a thermally stable catalyst is very desirable in this field. Harada *et al* ⁸⁰ synthesized a core@shell composite by encapsulating palladium nanoparticles in a hollow carbon shell (Pd@hmC) via the pre-decoration process described in section 2.4.1.1, and compared the activity for primary alcohol oxidation of this catalyst with one where the Pd nanoparticles were loaded on top of the said hollow carbon spheres (Pd/hmC) (figure 2.7). This Pd@hmC core@shell nanoreactor was found to have great activity for the oxidation of the primary alcohols, and when the mechanistic aspects of these reactions were compared to those occurring on the Pd/hmC

catalyst; they were found to be the same, thus implying that the superior activity of the Pd@hmC catalyst is mainly due to its core@shell structure.

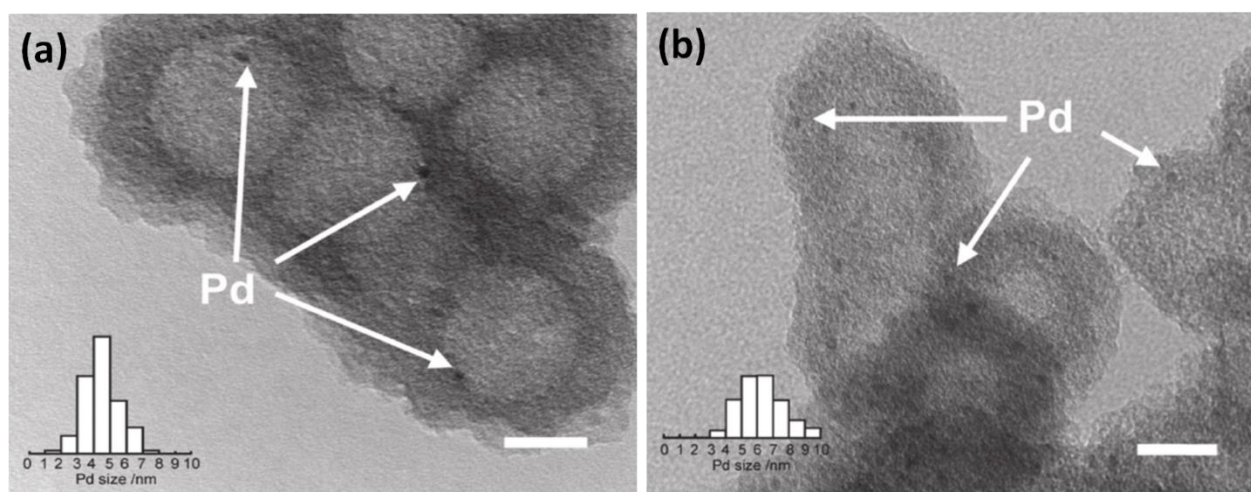
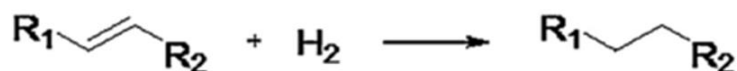


Figure 2.7: TEM images of Pd nanoparticles (a) inside (Pd@hmC) and (b) on top of (Pd/hmC) hollow mesoporous carbon spheres⁸⁰

A similar observation was made by Chen *et al*⁷⁶ where Pd@hmCeO₂ catalysts were found to have superior catalytic activity and stability to not only their Pd/hmCeO₂ counterparts, but also to Pd/C catalysts for the oxidation of cinnamyl alcohol.

2.5.2 Hydrogenation Reactions:

In 2004, Alivisatos *et al*⁸¹ reported on the hydrogenation of ethylene using a yolk@shell catalyst composed of platinum encapsulated in a hollow cobalt oxide nanoshell (Pt@CoO) that was prepared via the Kirkendall hollowing process. This started many research groups down the path of investigating different core@shell catalysts for different hydrogenation reactions using various active metals such as Pt,⁸² Rh²¹ and Ni.⁸³ For example, Ikeda *et al*²⁰ encapsulated platinum in hollow mesoporous carbon spheres (Pt@hmC) and applied this catalyst in the hydrogenation of various olefins (*scheme 2.2* and *table 2.2*). They found that these structures had superior activity to platinum supported using polyvinyl propylene (PVP) and activated carbon (Pt-PVP and Pt/AC).



Scheme 2.2: Representation of the hydrogenation of an olefin to form an alkane

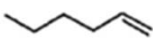
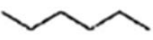
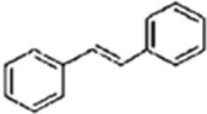
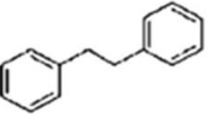
Substrate	Catalyst	Product	<i>t</i> [h] ^[b]	Conv. [%] ^[c]
	Pt@hmC		2	> 99
	Pt-PVP		2	91
	Pt/AC		2	7
	Pt@hmC		2	96
	Pt-PVP		2	70
	Pt/AC		2	16
	Pt@hmC		1	91
	Pt-PVP		1	42
	Pt/AC		1	3
	Pt@hmC		15	72
	Pt-PVP		15	46
	Pt/AC		15	16

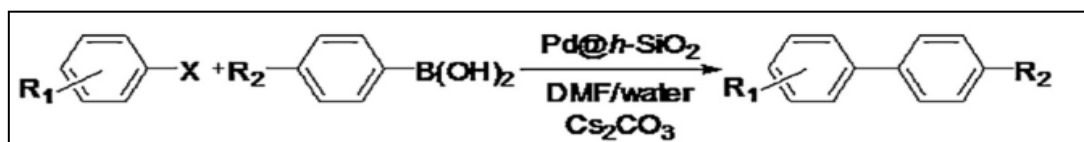
Table 2.2: Comparison of the catalytic activity of platinum encapsulated in hollow mesoporous carbon spheres (Pt@hmC) compared to platinum on PVP (Pt-PVP) and activated carbon (Pt/AC)²⁰

It was concluded from this study that the hollow structure of the carbon nanoshell was definitely contributing to the enhanced catalytic activity observed by (i) protecting the platinum nanoparticles from aggregation and ultimately coalescence, and (ii) rendering the internal void where the reactions take place hydrophobic, thus allowing for the enrichment of the organic substrates near the surfactant-free nanoparticle surface.

2.5.3 Carbon-Carbon Coupling Reactions

Because these reactions are extremely important reactions, particularly in organic synthesis (particularly pharmaceuticals) and the electronics industry, many catalysts have been developed for them.⁸⁴ Since Bellar *et al*⁸⁵ reported on the success of their Pd-based catalyst

for the Heck coupling reaction in 1996, most catalyst development studies since have focused in Pd-based nanoparticles for coupling reactions. Although there have been note-worthy advances in this respect, the use of the catalysts still faces many challenges. To try and overcome some of these challenges, many Pd-containing hollow nanoreactors have been evaluated, mostly for the Suzuki coupling reactions.⁸⁶ These studies involved, for the most part, encapsulating Pd or Pd-alloys in cavities protected by porous silica nanoshells.^{87,88} Song *et al*⁸⁹ encapsulated Pd nanoparticles in hollow porous silica nanoshells (Pd@SiO₂) and applied these structures as catalysts for coupling reactions between bromobenzene and phenylboronic acid. Their findings are summarized in *table 2.3*, where it evident that these nanoreactors showcased excellent activities for these coupling reactions, where many of the reactions produced yields as high as 100%.



Scheme 2.3: Representation of coupling reaction catalysed by palladium nanoparticles encapsulated in hollow porous silica nanoshells

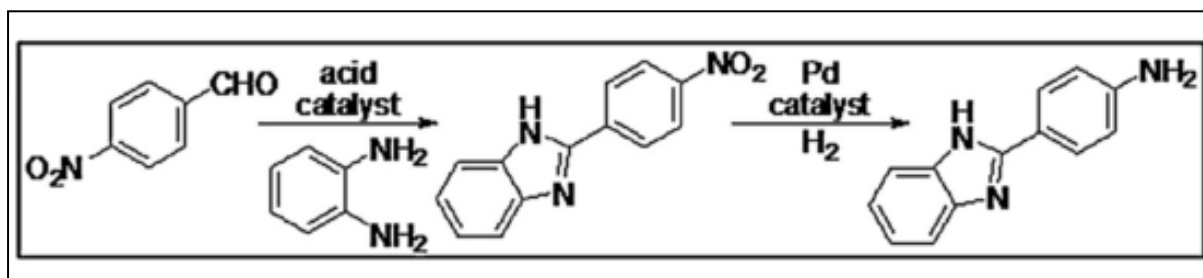
entry	R ₁	R ₂	X	t (h)	yield (%) ^b
1	H	H	Cl	3	100
2	4-OCH ₃	H	Br	3	64
3	4-CHO	H	Br	3	64
4	2-CHO	H	Br	3	100
5	4-CF ₃	H	Br	3	61
6	4-CHO	H	Cl	3	68
7	2-CHO	H	Cl	3	100
8	H	OMe	Br	3	100
9	H	Me	Br	3	87

Table 2.3: Summary of results for cross coupling reactions catalysed by Pd@SiO₂ core@shell catalysts⁸⁹

2.5.4 Integrated Multiple Catalytic Reactions

The integration of multiple reactions (i.e. multistep cascade reactions) are a way to solve issues such as efficiency and atom economy during organic synthesis.⁹⁰ The idea is to perform syntheses of complex products in a single reaction vessel, which would effectively decrease the number of separation and purification steps involved.⁹¹ In this regard, hollow nanoreactors are promising candidates for these reactions because they have the potential to integrate several catalytic species within a narrow confine.⁹² These nanoreactors would catalyze reactions of incoming substrates sequentially at the shell, and then at the active core within the void.

A good example of this concept was reported by Zheng *et al*⁹³ who employed this concept using a Pt/Au alloy encapsulated in an aluminosilicate nanoshell to catalyze first a condensation and then a hydrogenation reaction. During the first reaction, 4-nitrobenzaldehyde and 1,2-phenylenediamine were condensed to 2-(4-nitrophenyl)-1H-benzimidazole at the shell. This was followed by the sequential hydrogenation of this product to 2-(4-aminophenyl)-1H-benzimidazole performed by the catalyst in the core. This reaction gave a yield of 92% of the desired product, proving this a successful concept. These processes are summarized in *scheme 2.4*.



Scheme 2.4: Multistep cascade-type catalysis with core@shell nanoreactor, which sequentially combines cyclization and Pd-catalyzed hydrogenation reactions⁹³

To conclude, this chapter has shown that the concept of using core@shell nanoreactors in catalysis is quite a valid one. These structures have proven to be very effective at improving the activity and selectivity of catalyst particles for many types of reactions in a diverse variety of fields, mostly owing to the fact that the encapsulation of these active metal particles inside hollow mesoporous nanoshells endows catalysts with many desirable

features, such as increased stability and improved selectivity. In terms of the use of these core@shell structures as a catalyst in fuel cells, not much work has been reported, and there is therefore a need for more research in this regard.

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CHAPTER 3:

EXPERIMENTAL AND CHARACTERIZATION

TECHNIQUES

This chapter describes the general experimental procedures used for the synthesis of the platinum nanoparticles encapsulated in mesoporous hollow carbon spheres (HCSs), including the morphological and electrochemical characterization of the Pt-HCSs.

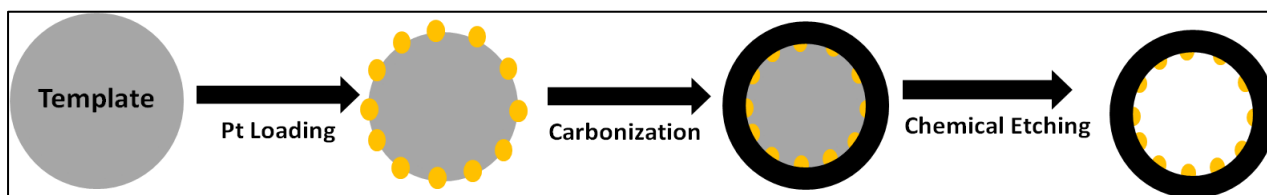
3.1 Pt@mC catalyst synthesis

Nanosize metal particles have the capacity to be used in a variety of applications, including catalysis, because of their large surface areas and size-dependent properties which differ from their bulk counterparts.¹ It has been found that dispersing these metal nanoparticles by immobilizing them on support materials has greatly improved their catalytic activity by stabilizing the catalytic particles.² It has, however, also been pointed out that in these types of systems leaching of the catalyst into the reaction solution, as well as aggregation of said catalyst particles, has been observed.³ These observations have opened up a need for the development of new approaches for the synthesis of catalytic systems that are more stable towards sintering and leaching, and are catalytically active.

One such approach is to immobilize catalyst particles inside the framework of mesoporous carbons. It has been reported in literature that these types of systems not only prevent movement of catalyst particles, but also allows for the accessibility of reactants to the catalyst's active sites, and the removal of products from the system.⁴

Currently, the most popular method for fabricating these structures is based on a template-assisted synthesis,⁵ with solid silica spheres being the most widely used template material.⁶ The general schematic of this procedure is summarized in *figure 3.1*. From left to right, the process involves synthesizing the templating material, loading the metal nanoparticles on the template surface, adding a layer of carbon over this metal-template composite, and removing

the template by way of chemical etching to leave the metal nanoparticles encapsulated inside the hollow carbon spheres.



Schematic 3.1: The synthesis of Pt encapsulated in hollow carbon spheres

3.1.1 Materials

The bulk of the chemicals used were purchased from Sigma-Aldrich. They included the silica precursor material, 98% tetraethyl orthosilicate (TEOS), absolute ethanol used as a co-solvent along with distilled water, and 25% ammonia solution. The two surfactants that were analysed in the study are 90% trimethoxy(octadecyl)silane (C_{18} -TMS) and $\geq 98\%$ hexadecyl trimethylammonium bromide (CTAB). The reducing agent used was sodium borohydride ($NaBH_4$). The carbon precursors that were used were toluene and a resorcinol formaldehyde polymer synthesized from the resorcinol salt and a formaldehyde solution. For chemical etching, a solution of 48% hydrofluoric acid (HF) diluted using distilled water was used.

3.1.2 Template Synthesis

In the current study, the template used was mesoporous silica spheres ($mSiO_2$), synthesized by a modified Stöber method. The first step was to synthesize the solid silica core. This was done by hydrolysis of the silica precursor (TEOS), followed by nucleation and growth described in more detail in the literature.^{7–11} The reaction times and reagent conditions were varied accordingly in order to tailor the diameter of the particles. In general, the ammonia solution was added to the co-solvents (ethanol and distilled water) and the resultant mixture was stirred for 10 minutes to ensure homogenous mixing. The TEOS was then added to this mixture, and the resultant solution stirred at room temperature for 4 hours.

The next step in the synthesis was to add the mesoporous silica layer. The variations of the reactants and reaction conditions used to tailor the shell thickness and pore behaviour of the mesoporous shells are summarized in *table 4.1* (see *chapter 4*). Generally, the surfactant, and in some cases, together with TEOS, was added to the above mentioned reaction mixture, and the resultant solution was stirred for 24 hours. The resulting solutions were centrifuged at 3500 rpm for 15 minutes to separate the precipitated product from the liquid reagents. The precipitate was then washed three times with a 50/50 distilled water/ethanol mixture and centrifuged three times to remove any unreacted reactants. The collected solid was then dried in an oven overnight at 80 °C. The silica powder was then calcined in air at 500 °C for 4 hours.

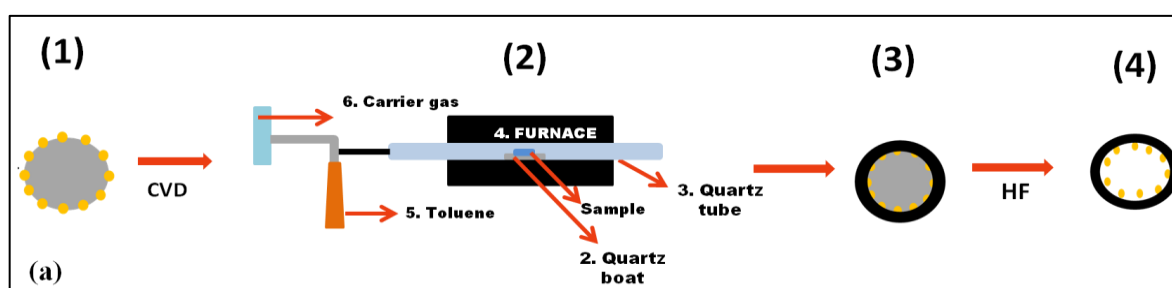
3.1.3 Pt@hmC Synthesis

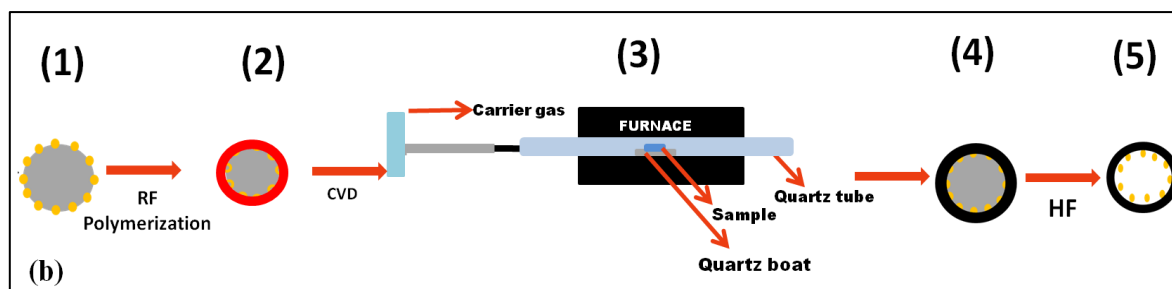
The carbonization of the silica spheres was performed either by way of a bubbling or a nanocasting method. Explained below is the bubbling method, illustrated in *figure 3.2 (a)*:

- (1) This is the as-synthesized template, either the Pt-silica composite or plain silica, synthesized as per *section 3.1.2*.
- (2) The as-synthesized template was placed in a quartz boat, and this was placed in a quartz tube which was then placed inside a horizontal furnace. In the furnace, the template was preheated under an inert atmosphere provided by the carrier gas. Thereafter, the toluene together with this carrier gas was then bubbled through the reactor, following which the reactor was allowed to cool to room temperature.
- (3) The product obtained after the reaction was a black powder consisting spheres made up of a template core covered by a carbon layer.
- (4) The template core was etched out using a 10% hydrofluoric acid solution for 24 hours, after which a hollow carbon shell was obtained. The product was washed 3 times with a water/ethanol 50/50 mixture, and dried at 70 °C overnight.

The nanocasting method (illustrated in *figure 3.2 (b)*) proceeded as follows:

- (1) Again, this is the as synthesized template to be used in the synthesis of the hollow carbon spheres
- (2) During this step, a layer of the carbon source (that is resorcinol formaldehyde (RF)) is allowed to polymerize around the template at room temperature for 20 hours, resulting in a red powder which consisted of a template core covered by a RF polymer layer.
- (3) The RF was carbonized by placing this red powder in a quartz boat, placing this in a quartz tube, and then placing the tube in a horizontal furnace. The reactor was then heated under an inert atmosphere provided by an inert gas. The reactor was then allowed to gradually cool down to room temperature.
- (4) The product from the above reaction was a black powder which consisted of a template core covered by a layer of carbon; a different type of carbon layer as was obtained using toluene as a carbon source.
- (5) The template core was then again removed using a 10% HF solution for 24 hours, resulting in hollow carbon spheres. The product was again washed 3 times with a water/ethanol 50/50 mixture, and dried at 70 °C overnight.





Scheme 3.2: Carbonization process via (a) bubbling and (b) nanocasting methods

Loading the platinum nanoparticles on top of the hollow carbon spheres involved simply mixing the platinum salt with the black HCS powder, and slightly grinding in a pestle-mortar to achieve a homogenous mixing. The mixture was then heated in a horizontal furnace enough to vaporize the platinum salt. Following cooling, the platinum nanoparticles were then deposited on top of the hollow carbon spheres.

3.2 Structural Characterization

Transmission electron microscopy (TEM) was used in order to assess the size, morphology, and shell thickness of the silica particles. Brunauer-Emmet and Teller (BET) measurements were used to determine the adsorption behaviour of the mesoporous shells, as well as the surface area, pore sizes and pore volumes of the shells. X-ray diffraction (XRD) was used to assess the behaviour of the crystallites making up the different particles. Raman spectroscopy was used to assess the graphitic nature of the carbon materials, and thermogravimetric analysis (TGA) was used to assess the thermal stability, purity, and the catalyst loading, of the synthesized catalysts. A brief description of each process is given below.

3.2.1 Transmission Electron Microscopy (TEM)

The two dimensional images were taken with a FEI Tecnai Spirit G2 transmission electron microscope operating at 120 kV. Sample preparation involved ultrasonically suspending powders to be examined in methanol for 30 minutes. A drop of this suspension was then dropped onto a copper grid, and the grid dried before analysis.

3.2.2 Brunauer-Emmet and Teller (BET)

The surface area measurements, as well as the porosity characteristics of the different materials, were analysed using a Micromeritics TRISTAR 3000 analyser using the BET method.¹² Prior to analysis ± 0.2 g of sample was first degassed in nitrogen gas using a Micromeritics Flow Prep 060 sample degasser at 150 °C overnight to ensure complete vacation of the pores.

3.2.3 X-ray Diffraction (XRD)

The nature of the crystallites making up the different structures was assessed using a Pan'Analytical X-ray diffractometer, using Cu K α wavelength (1.5405 Å). The X-rays were scanned from $2\theta = 20 - 80^\circ$ at a scan rate of 0.0445°/s. Before analysis, the sample was ground until fine, and then mounted onto a sample holder, ensuring an evenly flat surface.

3.2.4 Raman Spectroscopy

The ratio between the crystallinity and the disorder of the carbon framework of the synthesized catalyst were analysed by Raman spectroscopy. Measurements were conducted using a Bruker Senterra Raman Spectrophotometer driven by Opus 7.1 software. The catalyst powder was placed on a glass slide for analysis, and the sample was run in dark field under ambient conditions.

3.2.5 Thermogravimetric Analysis (TGA)

The thermal behaviour of the catalyst was assessed using a Perkin Elmer TGA 4000. For the analysis, ± 10 mg of sample was placed in a ceramic pan, which was then placed in the furnace of the instrument. The sample was heated at 10 °C/min under air or nitrogen gas, at a

flow rate of 20 ml/min, from 30-900 °C. Data collection and retrieval was from a PC connected to the instrument.

3.3 Electrochemical Characterization

The electrocatalytic activity of the catalysts was tested using a three-electrode electrochemical setup (*section 3.3.2*). The activity was tested in an acid electrolyte under inert (*section 3.3.3*) as well as oxygenated (*section 3.3.4*) environments. Electrochemical results were reported according to the current density (J); that is the amount of electric current flowing per unit cross-sectional area of a material.

3.3.1 Materials

The chemicals used for electrochemical characterization were purchased from Sigma-Aldrich. They included 70% perchloric acid (HClO_4), 5 wt% Nafion ionomer, and isopropanol. Alumina powder was used for electrode polishing.

3.3.2 Electrochemical Cell Setup

The cyclic voltammetry measurements were performed to determine the electrochemical surface area of the catalyst using a Metrohm Autolab single cell system (*figure 3.3*) driven by General Purpose Electrochemical Systems (GPES) data processing software. The cell consisted of an Ag/AgCl reference electrode, a platinum rod counter electrode, and a polished glassy carbon (GC) working electrode with an area of 0.0314 cm^2 . The working electrode was modified by depositing the catalyst on the GC, and was prepared as follows: 1 mg of catalyst was dispersed in a solution of 2.0 ml of isopropanol and 2.0 μl of Nafion by ultrasonication for 30 minutes to form a catalyst ink. A 2.0 μl aliquot of this ink was

deposited onto the polished GC electrode, which was then dried at room temperature for 30 minutes.

The electrolyte used for electrochemical characterization was a 0.1 M solution of perchloric acid (HClO_4). Prior to analysis, the electrolytic cell, equipped with electrodes and electrolyte, was purged with nitrogen (section 3.3.3) or oxygen (section 3.3.4). All voltammograms were recorded for the 15th scan.

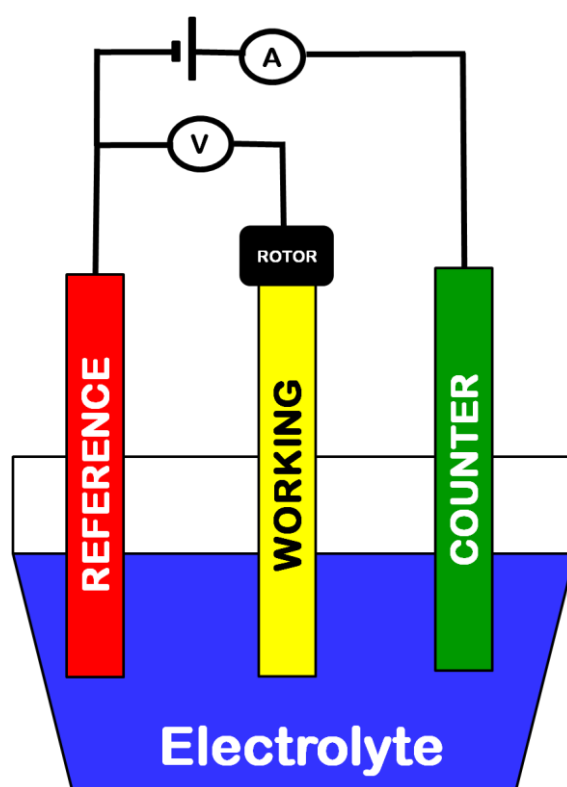


Figure 3.1: Illustration of the three electrode electrochemical cell. The reference electrode is Ag/AgCl, the counter electrode is a Pt rod, and the working electrode is a polished glassy carbon electrode attached to a rotor and modified with a catalyst ink

3.3.3 Cyclic Voltammetry (CV)

In order to determine the electrochemical surface area (ECSA), as well as the H_2 adsorption/desorption behaviour of the catalyst, cyclic voltammetry (CV) was used.¹³ The ECSA was calculated using equation 3.2¹⁴:

$$ECSA = \frac{Q_H}{[Pt] \times 0.21 \text{ mC/cm}^2} \quad 3.2.$$

where Q_H is the charge of hydrogen desorption in mC/cm^2 , $[Pt]$ is the total Pt loading in g/cm^2 , and 0.21 mC/cm^2 is the charge required to oxidize one monolayer of hydrogen on platinum.¹⁴

The voltammetry measurements were performed at scan rates of 10 and 100 mV/s between the scan potentials $-0.245 - 0.945 \text{ V}$ vs. Ag/AgCl . The profile of a typical voltammogram of a Pt catalyst in an acid electrolyte is illustrated in *figure 3.4*. The figure shows Pt-oxide formation/reduction at 0.65 V and 0.50 V , hydrogen adsorption/desorption at $-0.20 - 0.10 \text{ V}$, and a capacitive region at $0.80 - 1.1 \text{ V}$.

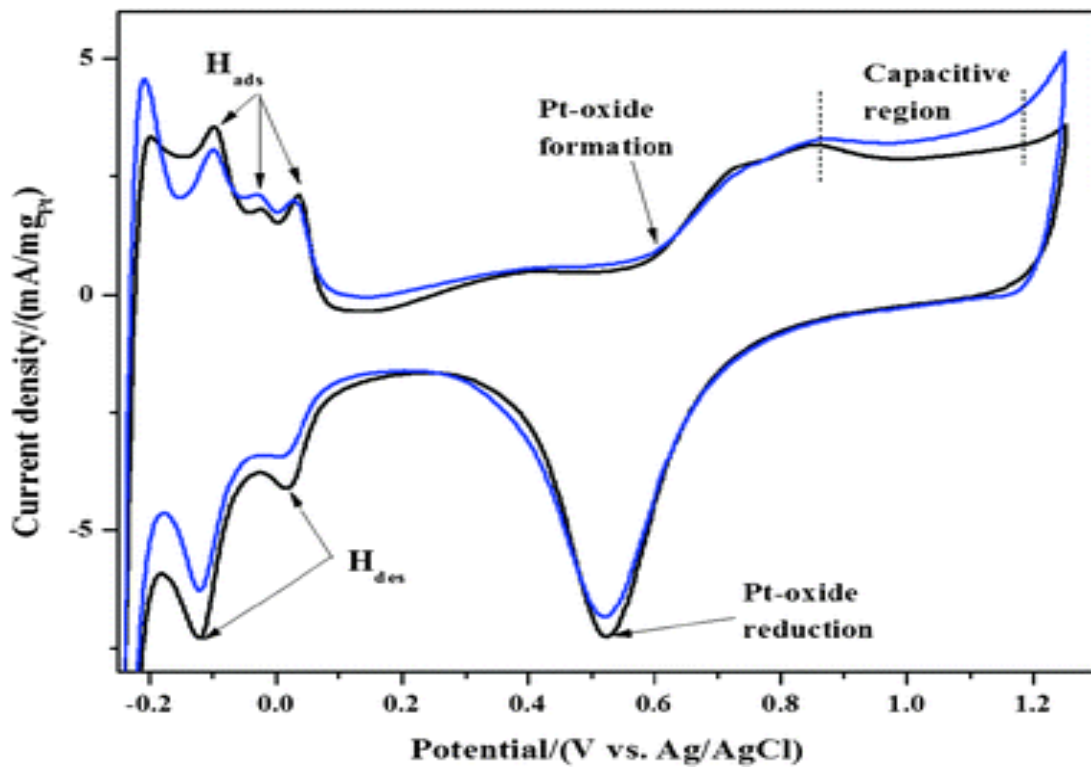


Figure 3.2: Typical voltammogram of a Pt-catalyst with labels for appropriate peaks¹⁵

3.3.4 Linear Sweep Voltammetry

In order to assess the catalyst's activity towards the oxygen reduction reaction (ORR), linear sweep voltammetry (LSV) was employed. Briefly, LSV involves introducing movement of the working electrode. This has the effect of (i) agitating the electrolyte solution, (ii) changing the hydrodynamics of the systems, and therefore (iii) changing the diffusion rates of the reactants towards the working electrode surface. A typical LSV profile in acid media, with appropriate labels, is illustrated in *figure 3.5*. The electroactivity of the catalyst was assessed using a rotating disk electrode (RDE) (*see Chapter 6*). Prior to analysis, the electrolyte was saturated with oxygen (99.99%, Air Liquide).

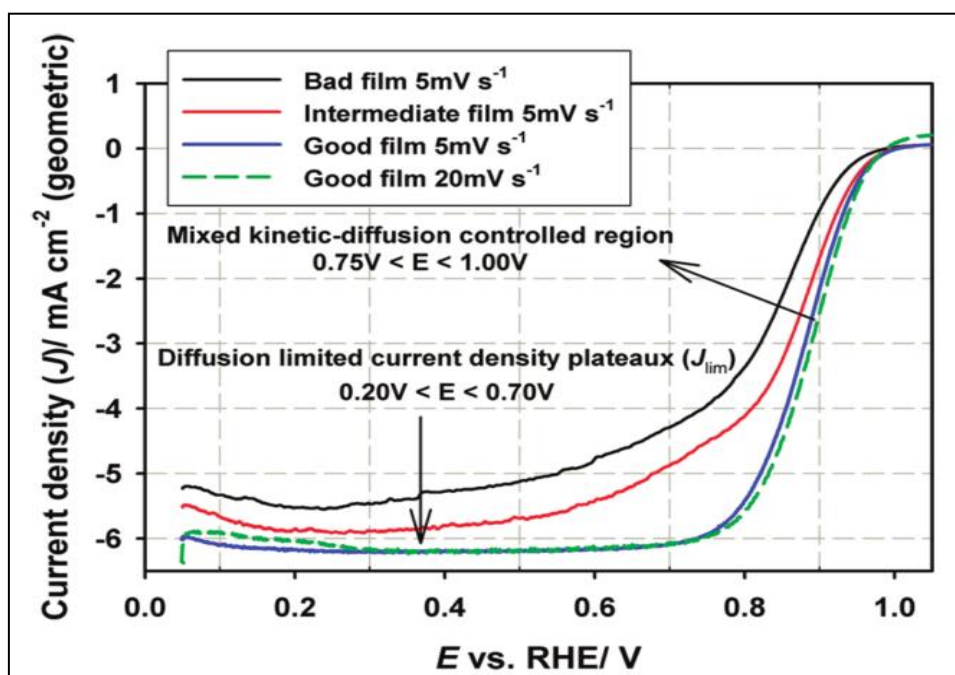


Figure 3.3: Illustration of (a) typical LSV profile of the working electrode during linear sweep voltammetry measurements¹⁶

3.3.5 Chronoamperometry Measurements

Chronoamperometry measurements are current vs. time measurements used to determine the time dependence of the current.¹⁸ These measurements were used to determine the stability of

the supported platinum electrocatalysts. The measurements were carried out at room temperature in oxygen-saturated HClO₄ at a steady current of 0.70 V for 1800 seconds.

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CHAPTER 4:

SYNTHESIS OF PLATINUM LOADED ON MESOPOROUS SILICA SPHERES

The following sections describe the methods and results for the assessment of the size, morphology and uniformity of mesoporous silica spheres to be used as templates in the synthesis of hollow carbon spheres. The effects of different surfactants on the mesoporous silica layer as well as reactant conditions on the size and yield of the particles are also discussed. Also, the influence that the above-mentioned parameters have on platinum deposition on the silica spheres is discussed.

4.1 Introduction

There are many studies in the literature that emphasize the importance of the silica spheres fabrication which possess both particle monodispersity and a specific mesopore orientation. However, the synthesis of monodispersed nanoparticles that possess highly tuned mesopores poses a challenge in the field of materials science.¹ Since the discovery of M4IS silica in 1992, inorganic materials with uniform mesopores have been of great interest to researchers.² A way of controlling the behaviour of these mesopores is by tailoring the surfactant used during synthesis.

The Stöber method is employed in the synthesis of silica spheres through the hydrolysis and condensation of silicon alkoxides, such as tetraethyl orthosilicate (TEOS). The reaction is carried out in basic aqueous solutions which comprise of ammonia and different alcohols such as methanol, ethanol, or isopropanol.³ Silica spheres synthesized via the Stöber method are, by convention, considered to be non-porous. However, it has been found that metal nanoparticles embedded in these silica spheres can be leached out, for example during chemical etching, thus suggesting that these structures must possess some porosity; the porosity of these Stöber-type silica spheres depends on certain experimental parameters.⁴

4.2 Synthesis of mesoporous silica spheres ($m\text{SiO}_2$)

The mesoporous silica spheres to be used as templates in the synthesis of hollow carbon spheres were fabricated using a modified Stöber method as described in *section 3.1.2*. The method involved tailoring certain experimental parameters in order to achieve the desired final $m\text{SiO}_2$ structures composed of a solid silica core covered by a distinctive mesoporous silica shell. The individual aspects are discussed in detail in the following sections.

4.2.1 Effect of surfactant on $m\text{SiO}_2$ synthesis

The following section reports the synthesis of monodispersed core-shell silica particles composed of a solid silica core and a distinctive mesoporous silica shell. The characteristics of the mesoporous shell were controlled by using different surfactants, namely octadecyltrimethoxysilane ($\text{C}_{18}\text{-TMS}$) or cetyltrimethylammonium bromide (CTAB); these porogens were chosen specifically to compare the nature of the mesoporous shell obtained from each.

Attaining silica spheres that are surrounded by a very distinctive mesoporous layer is imperative in ensuring a very porous layer with controllable shell thickness and tunable pores.⁵ The surfactant that is used to generate this distinctive layer will certainly have an effect on the features of said layer. To this effect, the surfactants CTAB and $\text{C}_{18}\text{-TMS}$ were investigated by tailoring experimental conditions as summarized by *table 4.1*. The table summarizes the effect the two surfactants have on a variety of the mesoporous shell's properties.

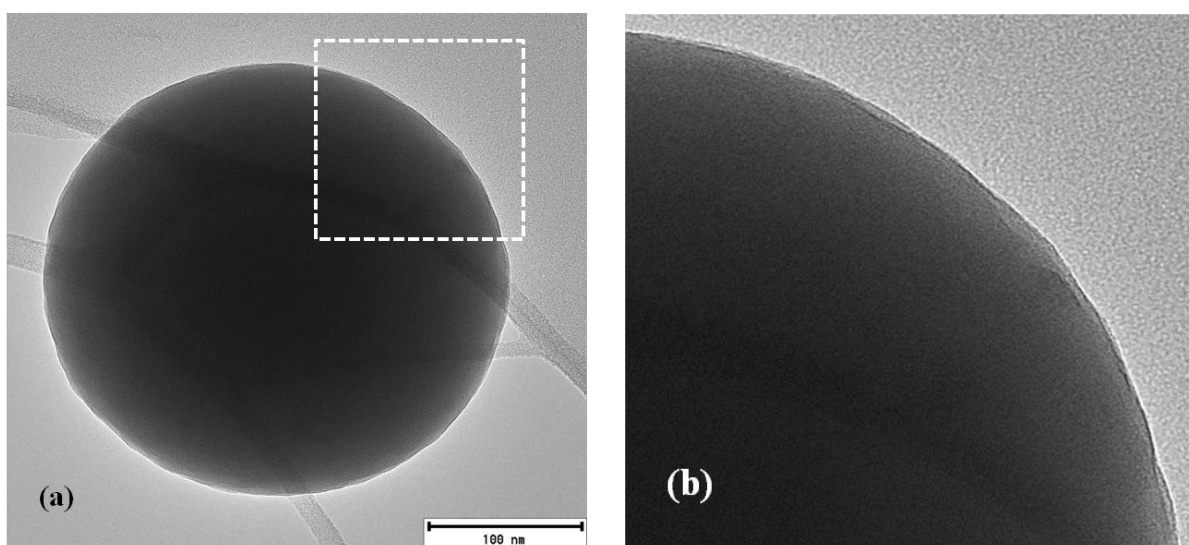
As seen from *figure 4.1(a)* and *(b)*, the CTAB-synthesized silica spheres had no observable mesoporous shell. This fact is reiterated in the low specific surface areas that are observed for these samples (*table 4.1*). A non-linear trend was observed whereby the surface area increased as the amount of CTAB was increased (*figure 4.3a*). However, there seemed to be a threshold that was reached whereby as the surfactant was increased, the silica spheres began to coagulate and form necklace-like structures (*figure 4.2*), and consequently the surface area

measured began to decrease as a result of there being less available adsorption sites on the particle surfaces. On the other hand, increasing the amount of C₁₈TMS systematically results in a more linear increase in surface area (*figure 4.3b*).

Table 4.1: Effect of surfactant for synthesizing mesoporous silica shell for 450 nm spheres

Reagent	Amount	Shell Thickness (nm)	BET Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)
CTAB	50.0 mg	-	8.1	14.3	0.029
	100 mg	-	11.3	11.8	0.116
	150 mg	-	78.3	5.93	0.044
	250 mg	-	10.4	16.8	0.034
C18-TMS	0.2 ml	10	42.2	6.49	0.071
	1.0 ml	20	71.8	4.93	0.090
	2.0 ml	25	95.0	5.22	0.124

Another trend observed was that generally there was an inverse relationship between the measured surface area and the pore sizes (i.e. the bigger the pores, the smaller the surface area). This observation comes about because the bigger the pores on a given surface, the fewer pores there will actually be on said surface, and so the overall porosity of the surface (and therefore its surface area) will be lower.



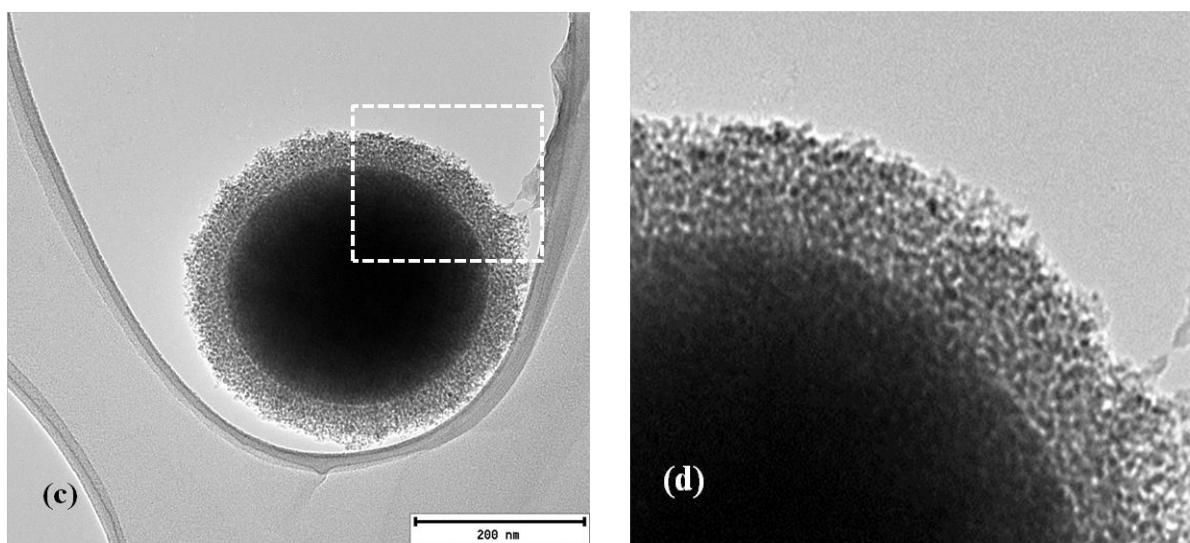


Figure 4.1: Silica spheres fabricated using (a) and (b) CTAB, and (c) and (d) C18-TMS as surfactants

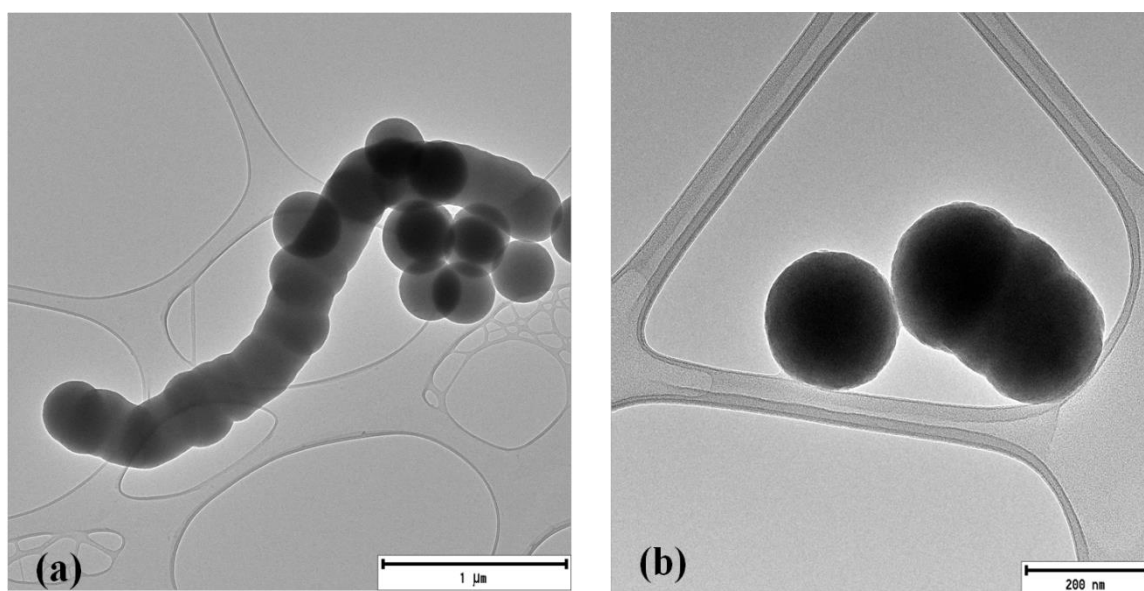


Figure 4.2: CTAB-synthesized silica spheres forming necklace-like structures on increasing the amount of CTAB

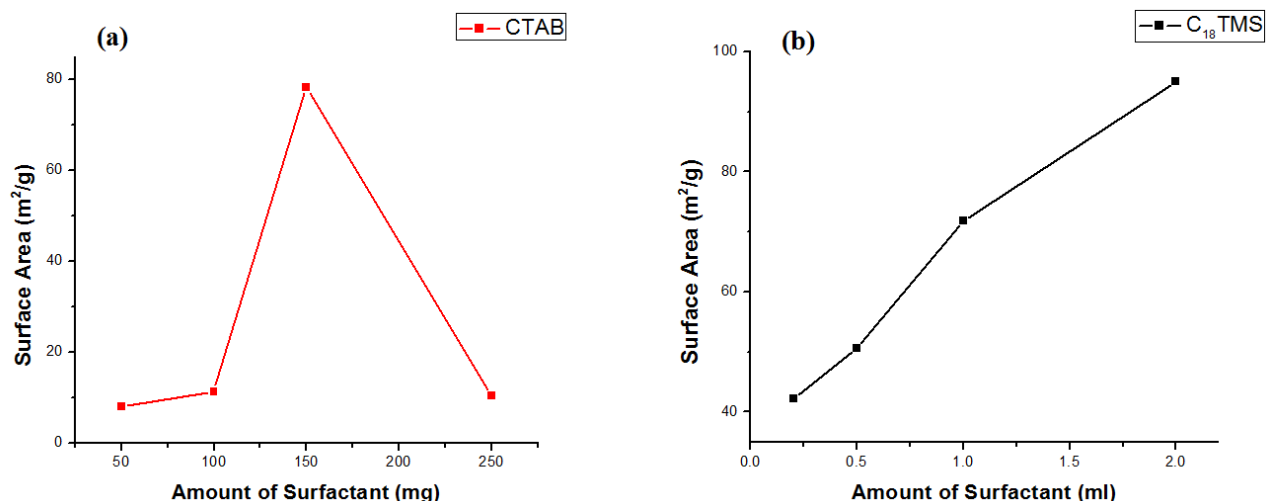


Figure 4.3: Surface Areas as a function of the amount of surfactant added when the surfactant is either (a) CTAB or (b) C₁₈TMS

Conclusion: We observed an increase in surface area as the amount of the respective surfactants was increased. Also the CTAB surfactant did not form the desired mesoporous shell, and of the two surfactants, resulted in a much lower surface area. Furthermore, increasing the amount of CTAB added resulted in coagulation of the silica spheres, forming necklace-like structures.

4.2.2 Particle size and yield relationship

It has been shown that catalytic reactions become more effective when the size distribution of not only the catalyst particles, but also of the catalyst supports, is uniform. The uniformity of the final support material (i.e. the hollow carbon spheres) will depend on the uniformity of the template material because, as previously stated elsewhere in this dissertation, the features bestowed upon the templating material during synthesis will be taken on by the final carbon product. Besides being uniform in size and morphology, another aspect considered was the actual size of the support materials. If the support size is too large, more catalyst powder will be needed at the electrodes of the fuel cells in order to get the desired loading, and this will result in very thick catalyst layers within the cell, which is undesired.

All this considered the issue of the yield that would be obtained from the synthesis method of choice had to be addressed. There is sufficient literature available on methods for decreasing

the particle sizes of silica spheres.⁶⁻¹⁰ These reports, however, do not emphasize the effect of the method on the yield. A decision was taken to make this a point of focus because the amount of catalyst needed at the catalyst layer for a fuel cell far exceeded the yields that were being achieved in trying to minimize the size of the silica particles. It would be more desirable to achieve the desired yield in a single synthesis batch rather than by mixing many batches together, to keep reaction conditions, as well as the obtained results, as identical as possible. Also, achieving the desired yield in a single batch is a much less time-consuming exercise.

Therefore, this section reports on three aspects of the synthesis of mesoporous silica spheres: (1) synthesizing mesoporous silica spheres of a uniform morphology and size, (2) a high yield, and (3) a decreased size. It is worth mentioning that while numerous methods were attempted, *table 4.2* only summarizes the methods which yielded the most relevant results.

Table 4.2: Conditions for decreasing $m\text{SiO}_2$ particle size

	Reagent (ml)						
Method	TEOS	NH ₃	Ethanol	H ₂ O	C ₁₈ -TMS	Particle Size (nm)	Yield (g)
1	44.8	15.4	120	18.0	-	± 950	± 5.00
2	15.0	10.0	200	10.0	2.00	± 600	± 5.00
3	15.0	10.0	100	10.0	2.00	± 350	± 5.00
4	15.0	10.0	100	-	2.00	± 150	± 5.00
5	15.0	10.0	50.0	10.0	2.00	-	± 5.00

It is also worth noting that all methods ran for a total time of 24 hours. *Method 1* from *table 4.2* represents the well-known Stöber method as it was originally reported in 1968.³ In this method, the silica precursor (TEOS) was added in two stages; half in the beginning, then the other half after the first part of the reaction. This method resulted in a satisfactory amount of product (5.00 g). However, the size of spheres was much too large (at approximately 950 nm, *figure 4.4a*). Modifications were therefore made to this method in an attempt to decrease the particle size without tampering with the amount of product obtained.

Each reagent in the Stöber method was altered individually. Firstly, decreasing the amount of TEOS used resulted in spheres of the same large size, but with a smaller product yield. It was also observed that upon increasing the amount of TEOS, the spheres began to lose their uniform size distribution (*figure 4.4b*). Secondly, increasing or decreasing the morphological catalyst (NH_3) resulted in increased and decreased product yields respectively. Because we were after a method that would keep the yield the same and decrease the particle sizes, the methods in *table 4.2* in where the TEOS and NH_3 amounts were left constant, while changing the molar ratios of the two co-solvents used. The $\text{C}_{18}\text{-TMS}$ was kept constant because of the results obtained from earlier studies.

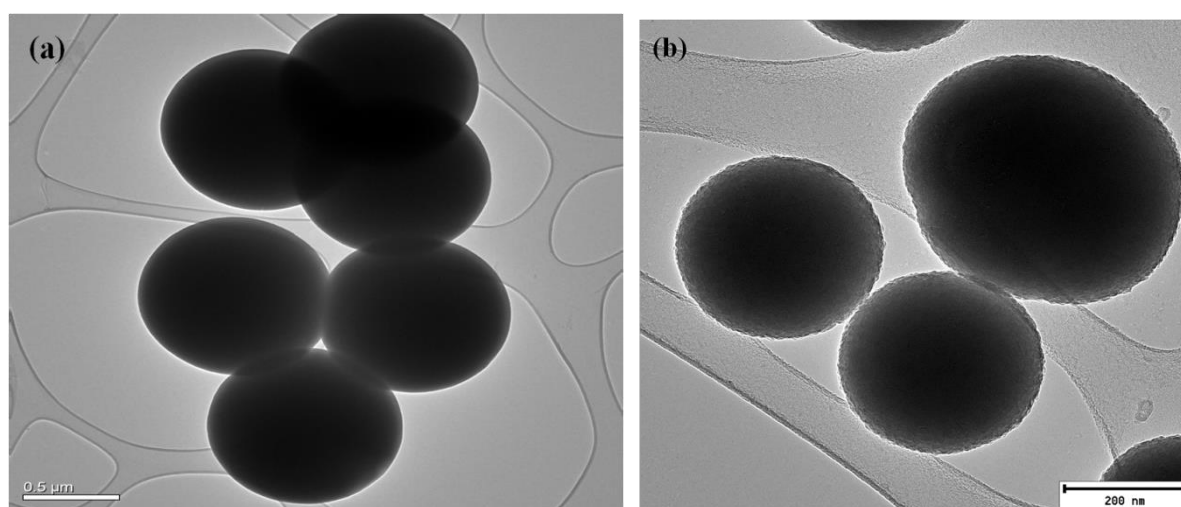


Figure 4.4: Silica spheres. (a) From Stöber method, (b) increasing amount of TEOS

Method 2 was the first of the modified methods to give the desired result; giving a product with the distinctive mesoporous silica layer, uniform size distribution, and with high yield. However, the size of the silica particles, at approximately 600 nm, was still too large for our studies. Subsequent methods were carried out by varying the ratio of the alcohol to water according to *table 4.2*. From *figure 4.5* and *table 4.2*, it is evident that the smallest SiO_2 particle size is achieved by decreasing the amount of alcohol and removing the water from the system all together (*Method 4*). We suspect that the reason for this is that upon decreasing the amount of total solvent in the solution, the concentration of the TEOS and, more importantly, the NH_3 , is consequently increased. The result is that most of the TEOS was used for the formation of nucleation sites, and therefore less precursor was available for particle growth.^{11,12} The end result is that the particle size decreased, but the amount of product remained the same.

Upon continuing to decrease the amount of solvent present, it seems a threshold was reached, whereby too many nucleation sites were being formed without sufficient particle growth (*figure 4.5d*). This resulted in the formation of silica clumps consisting of particles which had lost their uniformity with no distinctive shape.

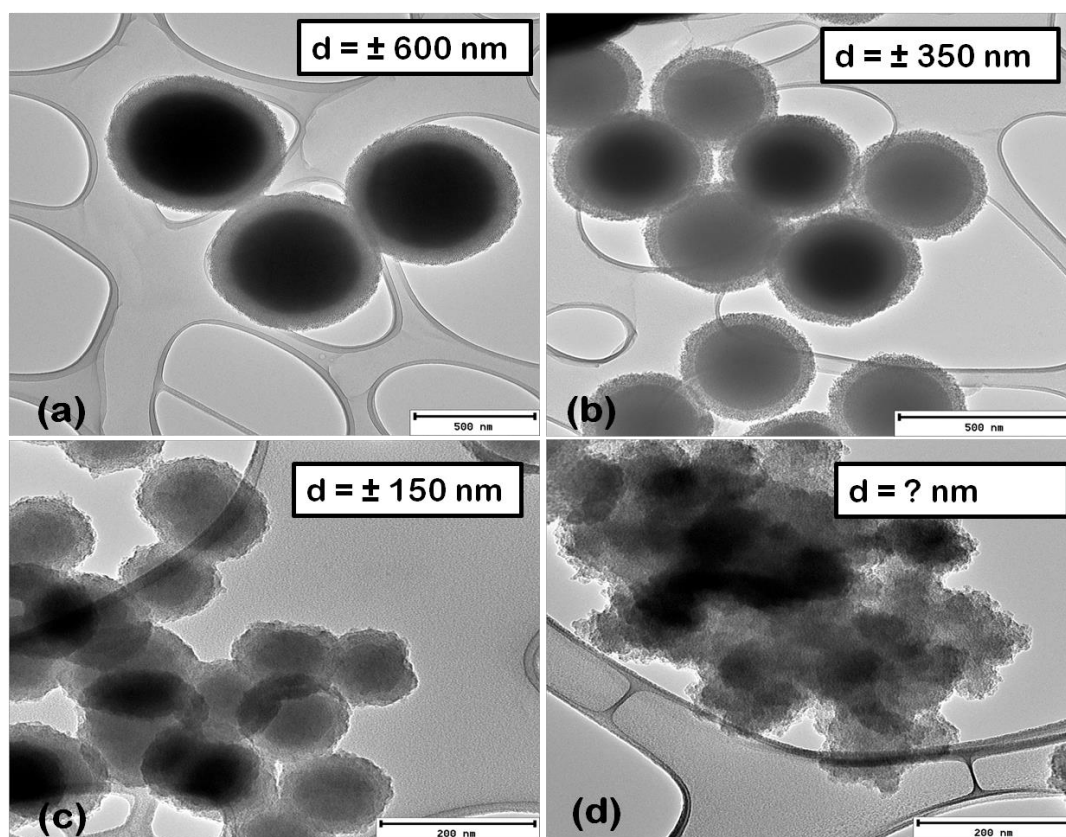


Figure 4.5: (a) – (d): Silica spheres synthesized using methods 2 – 5 respectively

Conclusion: The key to obtaining the smaller SiO_2 sizes without affecting either the yield or particle uniformity was to tailor the water: ethanol co-solvent molar ratios in order to allow for maximum nucleation sites and minimum particle growth.

4.3 Platinum deposition on $m\text{SiO}_2$

Amongst the noble metals, platinum has been found to have the highest catalytic activity for the oxygen reduction reaction,¹³ a reaction that is problematic within PEM fuel cells for reasons previously stated in this dissertation. Although platinum may be very efficient, there are still problems associated with this metal; the biggest being its cost. One way of tackling

this problem is by lowering the catalyst loading required to maintain sufficient catalytic activity by ensuring homogeneous deposition of the platinum nanoparticles on high surface area supports.¹⁴ The factors that influence the catalytic activity of these Pt nanoparticles include particle shape and size, and the size distribution.¹⁵

Currently PEMFCs require quite high loadings of catalyst (c.a. 40 wt % and above) in order to sustain satisfactory performance, and achieving these high metal loadings is quite difficult using conventional synthetic methods, such as the wet impregnation method, while still maintaining small sizes and narrow size distributions.¹⁶ It has also been reported in the literature that the particle size of the Pt catalyst seems to increase drastically (from 2.0 – 8.8 nm) upon increasing the loading (from 10 – 60 wt %).¹⁷

The challenges addressed in this section are (1) synthesizing catalysts with a high metal loading (>10 wt %), and (2) ensuring that these catalyst particles are well distributed with a small size and a narrow size distribution.

4.3.1 Effect of different loading procedures

In this section, two different types of loading procedures are reported; namely the wet impregnation (denoted Pt-WI) and the chemical vapor deposition (denoted Pt-CVD) methods. The CVD method is generally advantageous over the wet method because it allows one to circumvent processes such as washing, drying, and reduction. It also helps to avoid the change in catalyst dispersion of the metal that can take place during the reduction process. Another drawback of the wet method is the number of steps involved, and the fact that a slight deviation in one of the steps could result in a drastic effect on the resultant final catalyst.¹⁸ Furthermore, compared to the Pt-WI method, the Pt-CVD method is simpler in that it comprises of just one step, whereby the Pt-WI method includes multiple intricate steps that, if carried out incorrectly, result in an undesired product after days of synthesis. Also, controlling the wt% of Pt loading is much easier using the Pt-CVD method, as it simply entails using the mass of each component directly.

The difference between the two methods is that the wet impregnation method involves dissolving the metal precursor salt in an aqueous solution and depositing the metal on a support using a reducing agent. The CVD method on the other hand involves directly

mixing the metal salt with the support and placing the mixture in a CVD furnace where the ligands attached to the metal are vaporized as the metal is deposited onto the support as it cools. The effects on the well-dispersed deposition of the platinum on the silica with two different types of surfaces (TMS- and CTAB-synthesized) are also reported. In both the methods reported in this section, the Pt precursor salt used was PtCl_2 .

In *Figure 4.6* below, (a) and (b) illustrate platinum nanoparticles loaded onto the TMS-synthesized silica using the CVD loading method, while (c) and (d) illustrate loading using the wet impregnation method. The most evident difference between the two experiments is that the Pt-CVD method results in Pt nanoparticles that are much more dispersed on the silica surface. From *figure 4.7*, it is also evident that the WI- and CVD-loaded platinum are generally the same size. The two methods yield Pt nanoparticles with an average size of approx. 5 nm.

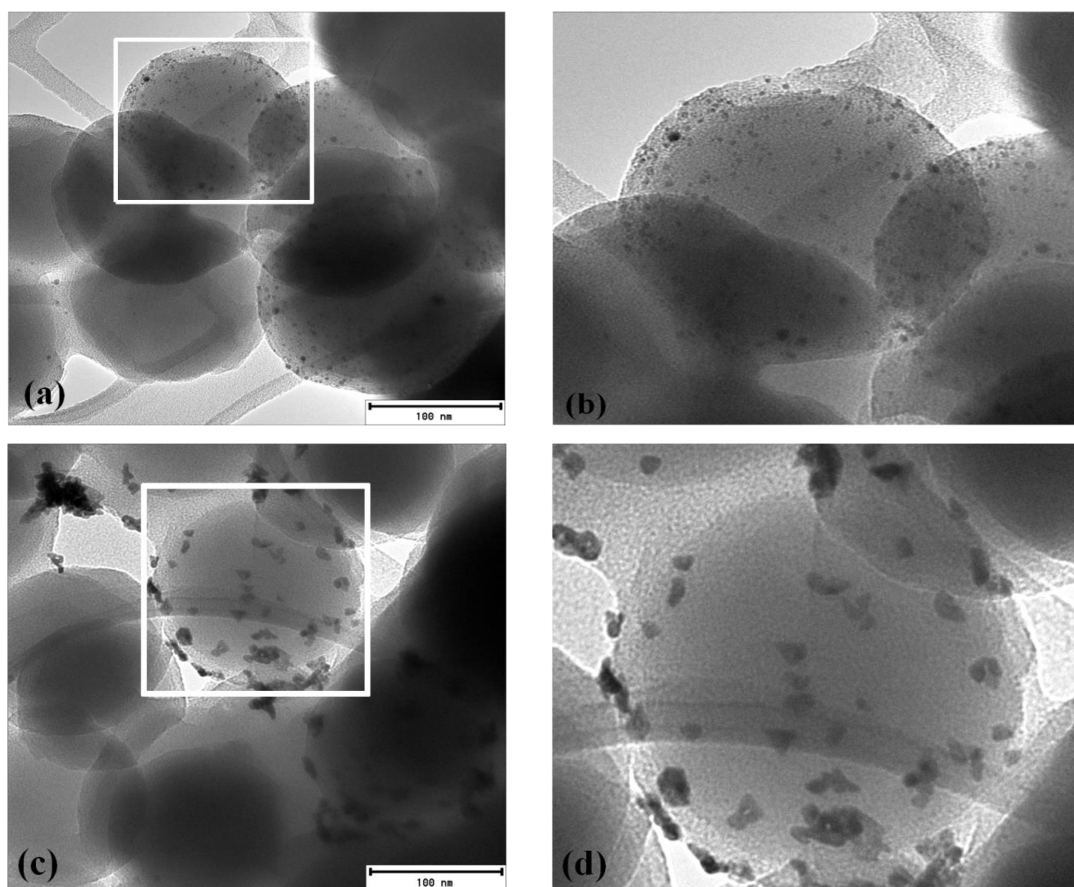


Figure 4.6: (a) and (b) Pt-CVD synthesized, (c) and (d) Pt-WI synthesized loaded TMS-synthesized silica spheres

Another advantage of the CVD method has over the WI method is that the CVD method wastes less platinum than the WI method; the latter results in loss of platinum during processes such as washing, centrifugation, etc. Seeing as the main objective is to decrease the amount of platinum needed during catalyst synthesis, the CVD method is more desirable in this regard, and loading methods reported from this point forward refer exclusively to the CVD method.

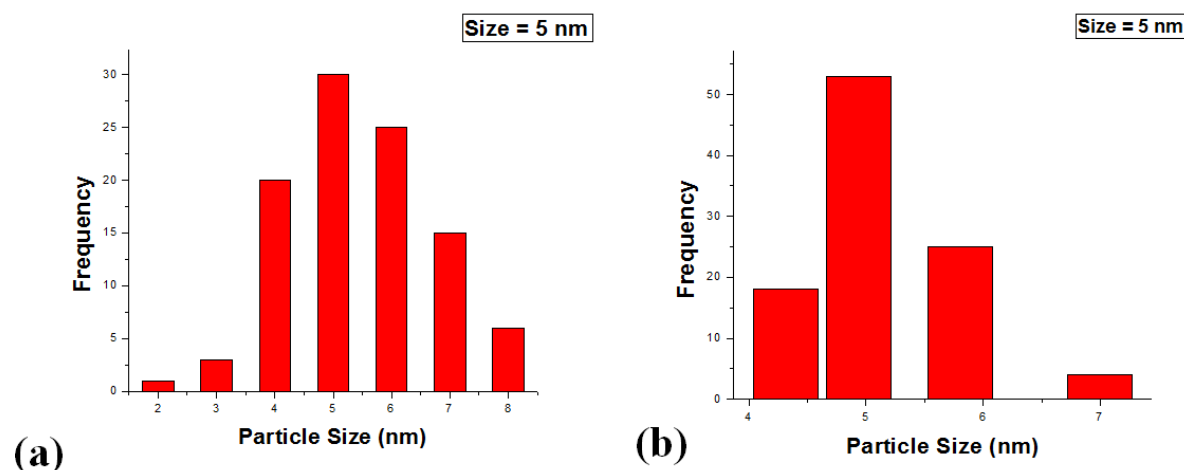


Figure 4.7: Platinum size distribution for (a) Pt-WI and (b) Pt-CVD methods

Illustrated in *figure 4.8* are the X-ray diffractograms of plain silica (*figure 4.8a*) as well as platinum deposited on mesoporous silica by either the chemical vapor deposition (*figure 4.8b*) or the wet impregnation method (*figure 4.8c*). The XRD patterns show that the platinum was successfully loaded onto the silica template because of the appearance of certain peaks from *figure 4.8(a)* to (c). In all three X-ray diffractograms, the broad peak at 26° corresponds to diffraction of the silica template. In (b) and (c), the peaks downfield of the broad silica peak correspond to different crystalline planes of the deposited Pt nanoparticles. In *figure 4.8(b)*, the peaks at $2\Theta = 39.6^\circ$, 47.4° , and 73.9° correspond to the (111), (200), and (220) crystallite planes of platinum. In *figure 4.8(c)*, the above mentioned planes are found at $2\Theta = 39.4^\circ$, 47.2° , and 73.9° ; indicating that there is a very slight, if any, difference between the WI and the CVD deposited platinum. The particle sizes calculated from the Scherrer equation correspond to those calculated from the TEM images. Said particles are comparable in size, corresponding to the size distribution plots in *figure 4.7*.

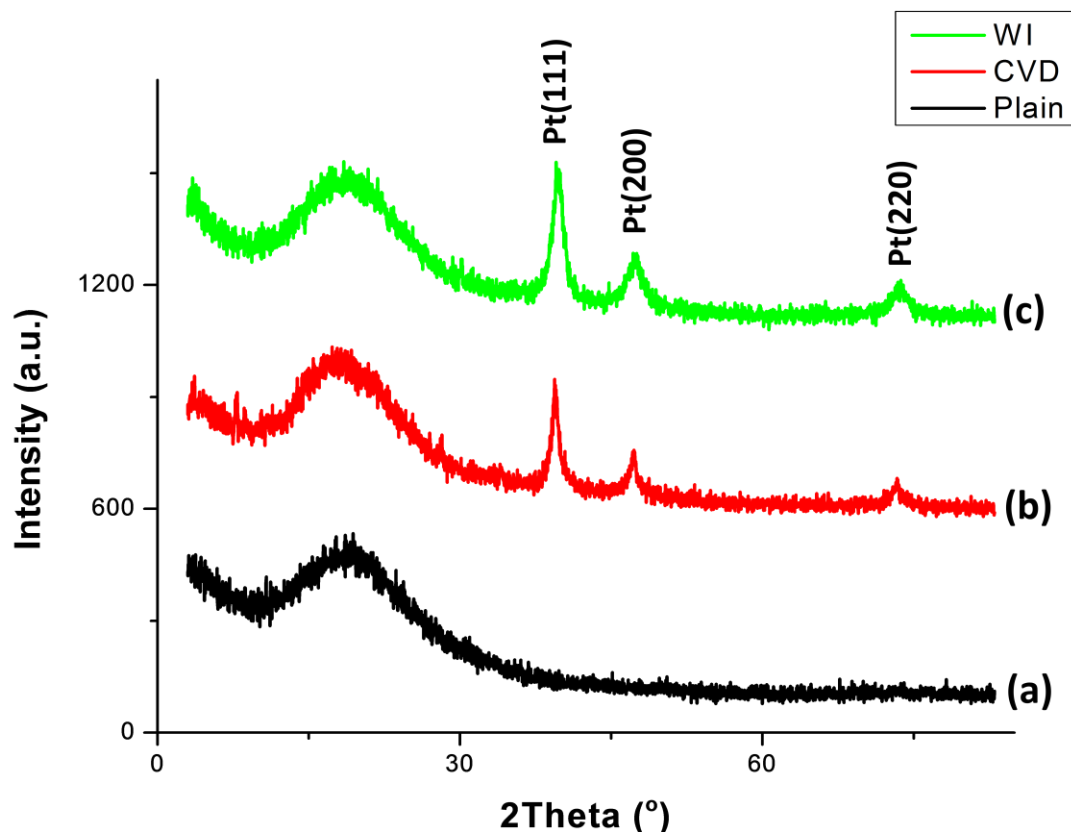


Figure 4.8: X-ray diffraction patterns of (a) plain mesoporous silica, and Pt deposited on mesoporous silica via the (b) CVD, (c) wet impregnation methods

Earlier in this chapter, two types of silica particles were introduced; the TMS-synthesized and CTAB-synthesized silica spheres, with the two types of surfactants resulting in silica particles with differing surfaces. It is evident that the support that has the more distinct mesoporous layer (*figure 4.6*), and thus higher surface area, results in a very well dispersed catalyst with a size of approximately 5 nm. Even though there is some aggregation present, it is not to a significant degree, and the platinum nanoparticles are still discrete. Conversely, the platinum nanoparticles loaded on the CTAB-synthesized silica (*figure 4.9*) tend to aggregate, even at room temperature, and form nanoparticle clusters of differing sizes. These results can be explained by the fact that the TMS-synthesized silica is better able to physically interact with the metal nanoparticles, therefore preventing the particles from easily aggregating on the support surface.

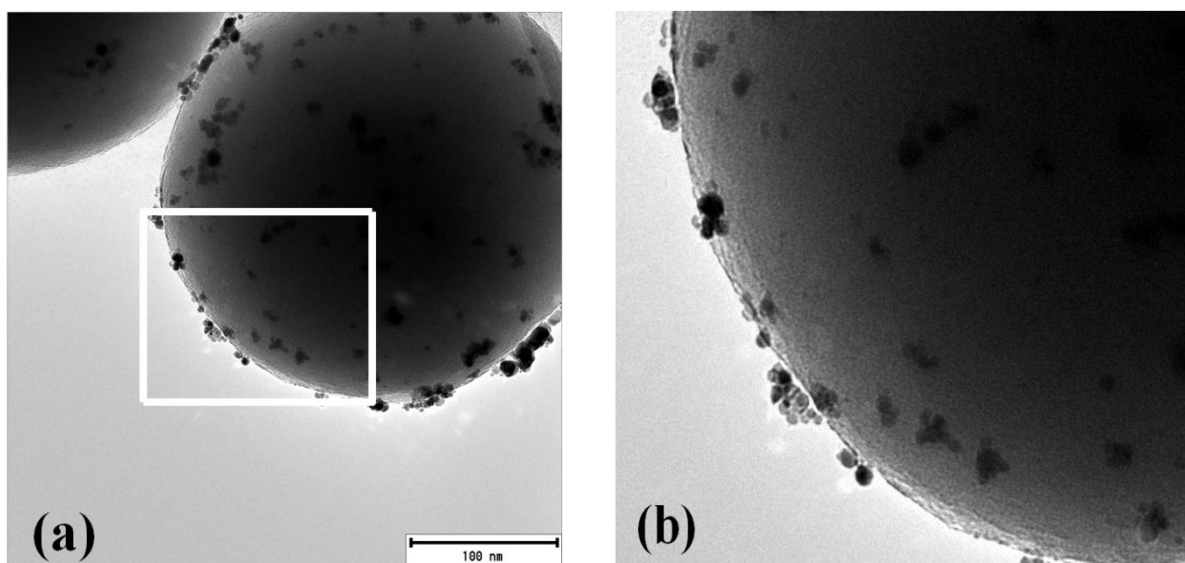


Figure 4.9: Pt loaded on CTAB-synthesized silica spheres

Conclusions: The CVD method is the preferred method because (i) it results in better dispersion on the silica surface, and (ii) the CVD method results in less platinum wastage than the WI method during synthesis. Also, the TMS-synthesized silica makes for a better support, and thus results in better Pt dispersion than the CTAB-synthesized silica.

4.3.2 Effect of Pt precursor type

The type of platinum precursor used to synthesize platinum nanoparticles plays an important role in the catalytic activity of the final catalyst system, as well as in how well the platinum catalyst is dispersed on the support material and the size of the nanoparticles.¹⁹ To this end, the effect of using either one of two different platinum salts; namely Platinum(II)Chloride (PtCl_2) and platinum(II)acetylacetonate ($\text{Pt}(\text{acac})_2$), on dispersion and particle size was investigated. The platinum was loaded on the silica using the CVD method.

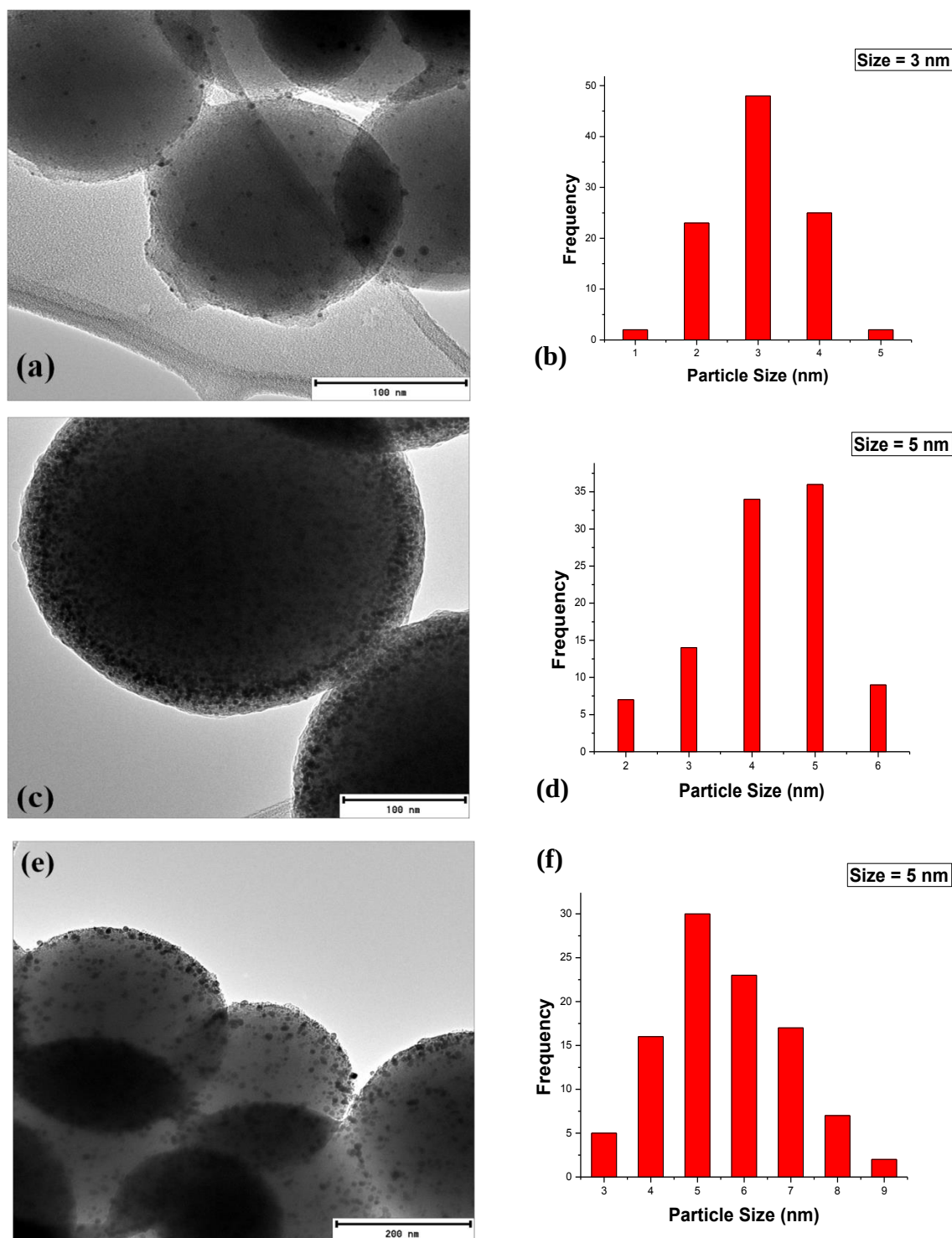


Figure 4.10: TEM images and size distributions for (a) and (b) Pt(acac)₂ 150 nm, (c) and (d) Pt(acac)₂ 350 nm, (e) and (f) PtCl₂ 350 nm structures

The results comparing the two different precursors and two different support sizes are shown in *figure 4.10* and summarized in *table 4.3*. When comparing the dispersion of the Pt nanoparticles synthesized using Pt(acac)₂ (*figure 4.10 (a)*) with those from the PtCl₂ precursor (*figure 4.10 (e)*), it is evident that both these methods result in well dispersed

catalyst particles. However, the $\text{Pt}(\text{acac})_2$ precursor resulted in the formation of smaller nanoparticles. Another observation made was that the $\text{Pt}(\text{acac})_2$ nanoparticles have a narrower size distribution (*figure 4.10(b)*), whereas the PtCl_2 resulted in nanoparticles that had sizes spread over a wider range (*figure 4.10(b)*).

Loading Pt using the two different precursors on larger silica spheres (*figure 4.10(c)-(f)*) yielded some interesting results as well. Firstly, the use of $\text{Pt}(\text{acac})_2$ again resulted in better dispersion of the catalyst particles. From the size distribution charts (*figure 4.10 (d) and (f)*), even though the approximate sizes of the nanoparticles are the same at 5 nm, most of the particles from $\text{Pt}(\text{acac})_2$ are between 4-5 nm, while the PtCl_2 range between 5-6 nm. Another observation made was that the $\text{Pt}(\text{acac})_2$ resulted in platinum nanoparticles that seem to be embedded inside the pores of the mesoporous silica layer. The pores of the 350 nm silica spheres is approximately 5.2 nm (*table 4.1*), which is big enough to allow for the presence of the 4-5 nm Pt nanoparticles within the pores.

Comparing the Pt loaded from $\text{Pt}(\text{acac})_2$ on the bigger and smaller silica spheres shows that the Pt nanoparticles loaded on the smaller spheres are themselves smaller, with a narrower size distribution. There is also a more even distribution of the Pt nanoparticles on the smaller silica spheres. In contrast to the Pt loaded on the larger spheres results in high Pt-loadings on some spheres, and no Pt whatsoever on others. This has implications for the final hollow carbon spheres formed from the larger silica spheres, whereby some of the spheres will be empty, while others will have a large loading of platinum within them.

Table 4.3: Summary of Pt nanoparticle sizes on different sized silica spheres

Pt Precursor	mSiO ₂ Size (nm)	Pt Size (nm)
PtCl ₂	350	5
PtCl ₂	150	5
Pt(acac) ₂	350	5
Pt(acac) ₂	150	3

Conclusions: To make Pt/silica spheres, it was observed that the $\text{Pt}(\text{acac})_2$ precursor is a better platinum precursor than the PtCl_2 as it resulted in metal nanoparticles that are smaller

with better dispersion and with an even distribution on the silica support. It was also observed that the smaller the support material, the smaller the loaded platinum particles when $\text{Pt}(\text{acac})_2$ was the metal precursor.

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CHAPTER 5:

CARBONIZATION

The following sections report on the process of fabricating the Pt@hmC catalyst. More specifically, on the effect of different experimental conditions on producing this final product; conditions such as different carbonization techniques, reaction temperature, and carrier gas flow rate.

5.1 Introduction

Hollow nanomaterials which have been physically and chemically tailored have, in the past, been applied in controlled release, confined synthesis, optics and electronics, energy storage, environmental protection, and, more relevant to the current study, catalysis.¹ Amongst these nanomaterials, hollow carbon spheres have become of particular interest because these structures have been found to not only exhibit the desirable catalyst support traits of high surface areas and low densities, but these structures have also been found to be superior to polymer- and metal-based hollow nanostructures in that they exhibit excellent chemical and thermal stabilities.² The encapsulation of functional nanoparticles in hollow materials has been shown to enhance the stability of the nanoparticles, as well as introduce new functionalities to said hollow materials.³ Furthermore, metal nanoparticles encapsulated by carbon exhibit a very high conductivity and are very attractive in applications such as energy storage and electro-catalysis.⁴

The characteristics of these hollow carbon supports are quite crucial to the catalytic performance of the proposed catalyst systems; characteristics such as the morphology, porosity, and durability of the support.⁵ These characteristics are more often than not determined by the way in which the catalyst has been synthesized. There are many methods reported for the fabrication of hollow carbon spheres, including hydrothermal,⁶ and more relevant to the current dissertation, the template method,² which is based on the pyrolysis of a carbon source.⁵ The success of a catalyst support will depend firstly on the catalyst's intended applications, then, amongst others, on the morphology, size, chemical, physical and electrical attributes of the support material.⁷

The hydrothermal method, or hydrothermal carbonization, involves the hydrothermal decomposition of an organic substance (such as starch, glucose, or sucrose) or simpler compounds such as furfural in water in the presence of a template at low temperatures (ranging from 150-350 °C).⁸ This method results in the formation of water-soluble organic substances along with a carbon-rich solid product.⁹ The process is typically carried out in an autoclave at pressures higher than under ambient conditions (c.a. 10 - 40 bar) in order to keep water in its liquid phase at the elevated temperatures.¹⁰

The templating method can either be carried by a soft or a hard templating approach. The soft templating method allows for the synthesis of hollow nanospheres without the need for a solid template.¹¹ The method involves making use of relatively flexible structures such as emulsion droplets, supramolecular micelles, polymer aggregates/vesicles, and gas bubbles as templates for the formation of hollow structures.¹² The shell growth of the target structure then takes place during the removal of the template along the interfacial region.¹³ However, these flexible structures do have some disadvantages as templates. For instance, reaction conditions have to completely comply with a certain range of conditions for a particular template because these templates are thermodynamically metastable and sensitive to various parameters; parameters such as pH, temperature, solvent, ionic strength, concentration of the organic templates and inorganic additives.¹⁴

Conversely, the hard templating approach involves using a “rigid” material as a template, and removing the template by different chemical means, thus leaving behind the desired hollow structure.¹² One of the advantages this method has over the soft template alternative is the easy control of the size, morphology, and structure of the resultant hollow carbon spheres,¹⁵ because the templates themselves can be manipulated in these regards as was shown in the previous chapter. The general procedure for this method involves coating the template’s surface with a precursor material, forming a core-shell structure composed of the template as the core and the target material as the outer shell, and removal of the template at the core by a suitable etching process results in the desired hollow structure.^{16–18}

The before-mentioned Stöber method (described in *section 4.1*) has been extended to the synthesis of monodispersed RF-resin polymer colloidal spheres, followed by the synthesis of carbon spheres via the carbonization of the RF spheres.¹⁹

In the current study, two different carbonization techniques were explored: (1) a bubbling method that uses toluene (*section 5.2*), and (2) a nanocasting method that uses a resorcinol formaldehyde polymer (*section 5.3*) as a carbon source. The hollow structures were obtained by leaching of the silica template from the core-shell structure using hydrofluoric acid (*section 5.4*). The electrochemical properties of the two different types of carbon was then tested using cyclic voltammetry (*section 5.5*).

5.2 Bubbling Method for Carbonization

This procedure involves the decomposition of a carbon source at high temperatures in an inert atmosphere. There are a number of methods available in this regard such as arc-discharge,²⁰ shock compression techniques,²¹ laser ablation and plasma processes,²² and chemical vapor deposition (CVD); a process involving the conversion of a volatile carbon source into a non-volatile solid carbon product.²³

In general, the CVD process is carried out by the direct pyrolysis of a carbon source. The reaction is carried out in a quartz tube which is placed in an electronically-controlled furnace, which can be either vertical or horizontal (*figure 5.1*), and include a catalyst or not.

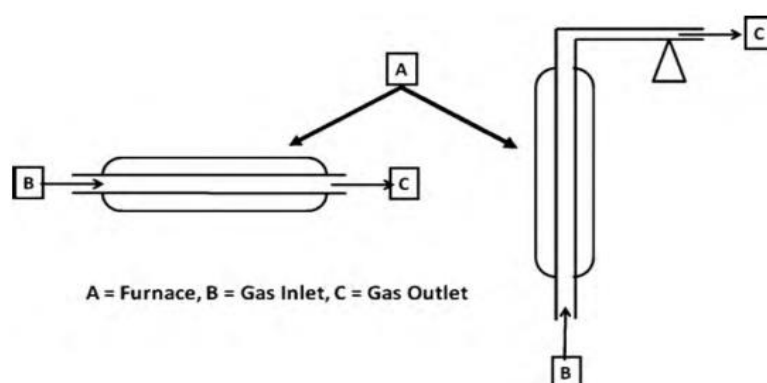


Figure 5.1: Illustration of (left) horizontal and (right) vertical CVD setups²³

5.2.1 Experimental

The template-carbon core-shell composite structures were synthesized by a chemical vapor method. The template material used was mesoporous silica (*chapter 4*). The template powder was firstly placed in a quartz boat, which was subsequently placed in a quartz tube. The tube together with the boat was placed in a horizontal CVD furnace, taking care to ensure that the quartz boat was in the middle of the furnace. The carrier gas and the carbon source (toluene) were connected to the quartz tube in a confirmation shown previously (*figure 3.2a*).

Initially, the furnace was ramped up at a rate of 10°C/min to the desired temperature under a flow of the carrier gas. Once the temperature was reached, the carrier gas was bubbled through the carbon source, carrying it into the quartz tube where it was vaporized and subsequently deposited onto the surface of the template material under a constant temperature. The reaction was then allowed to cool to room temperature, after which the black product was collected.

The biggest determinants for how well the carbonization process is carried out will depend on (1) the carrier and the flow rate, (2) the reaction temperature, and (3) the reaction time. To this effect, the reaction parameters studied, namely the carrier gas, flow rates, temperatures, and reaction times, were used as shown in *table 5.1*.

Table 5.1: Reaction parameters used during the CVD carbonization process

Reaction Parameter	Reaction 1	Reaction 2
Temperature (°C)	900	900
Flow rate (sccm)	100	200
Reaction Times (hours)	4	4
Template Size (nm)	± 150	± 350

5.2.2 Results and Discussions

Described in the following sections are the results of the template-carbon structures fabricated by methods described in *section 5.2.1*. The sections systematically describe the

results obtained from the characterization techniques, explaining the information gauged from each, in detail.

5.2.2.1 TEM Analysis

Illustrated in *figure 5.2* are the TEM images obtained from the carbonization process as a function of the size of the template material used, with *figure 5.2a* showing the bigger particles. The carbonization process was carried out at a flow rate of 100 sccm. It is evident from the images that the size of the template in this instance is not playing a significant role in how well the carbon is deposited on said template. The carbon completely covered the silica template in both cases, and took on the shape of said template, with only a few carbon flakes visible on the particles' surfaces.

Illustrated in *figure 5.3* is carbonization as a function of gas flow rate for 350 and 150 nm templates. The gas flow rates were 100 and 200 sccm for the images in *figures 5.2 and 5.3* respectively. Recall, during carbonization using the bubbling method, the carbon source as a vapor flows over the template material in the quartz tube and deposits on the template's surface. It is imperative that the gas flow rate allow the carbon source to have sufficient time to deposit evenly on the silica spheres in order for this deposition to be successful. If the flow rate is too fast, not all the silica spheres will be evenly covered by the carbon source, because the carbon source does not have sufficient time to properly deposit on the silica surface. This phenomenon is illustrated in *figure 5.3*, where it is evident that some mesoporous silica was still uncovered by a carbon layer at the end of the carbonization experiment.

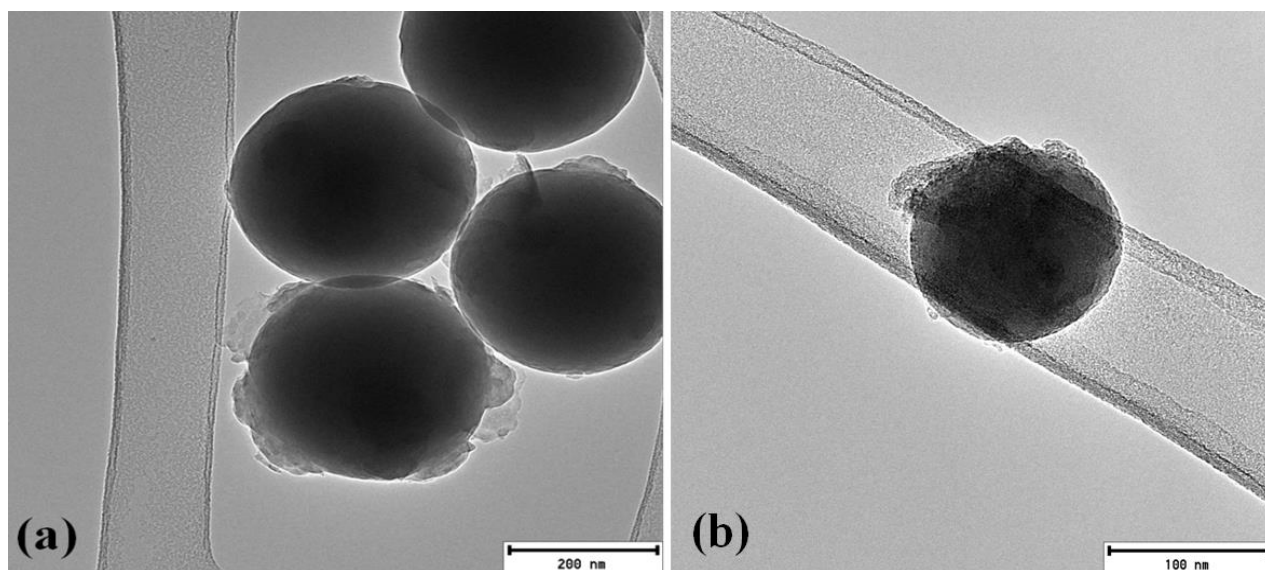


Figure 5.2: TEM images illustrating carbonization as a function of template size: (a) 350 nm, (b) 150 nm

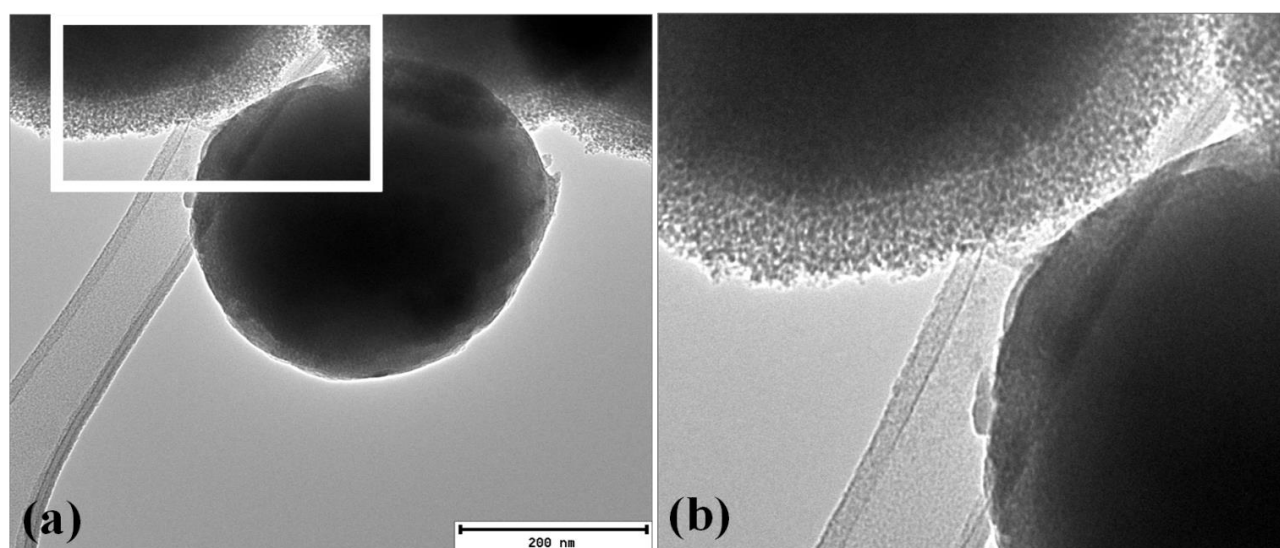


Figure 5.3: (a) TEM image illustrating carbonization of 350 nm template at gas flow rate of 200 sccm, (b) Zoomed in section of (a)

5.2.2.2. Thermogravimetric Analysis

Illustrated in *figure 5.4* are the TGA and derivative plots of the 150 nm and 350 nm silica-carbon core-shell structure (denoted as Tol-SiO₂@C-s and Tol-SiO₂@C-b respectively) fabricated using toluene as the carbon source. The first observation made from the TGA plots (*figure 5.4 (a)*) is that the larger spheres contained more carbon than the smaller spheres. The lower the weight % observed during the TGA measurements, the less silica (and therefore

more carbon) present in the structure. Therefore, the fact that the TGA plot for the larger spheres is at a lower weight % at 900 °C than the smaller spheres means that more carbon was present in the larger spheres compared to the smaller spheres.

According to the TGA plots, the Tol-SiO₂@C-s and Tol-SiO₂@C-b composite structures are composed of approx. 26 and 37% of carbon by weight (summarized in *table 5.2*). From the previous chapter, it was found that the mesoporous silica layer in the SiO₂@mSiO₂ structures made up approx. 11% of the sphere's diameter, and since the carbon deposits by conforming to this mesoporous layer, we expect the carbon to make up about 11% of the SiO₂@C composite as well. However, from *figure 5.4*, the carbon yields were higher than expected, implying that the method of carbonization in this case indeed involves nanocasting, but is mainly due to carbon deposition on the surface.

Another observation made was that the larger spheres were more thermally stable than their smaller counterparts; where the decomposition temperatures were measured at 780 and 700 °C for the big and smaller spheres respectively. This is seen from the inflection points in the derivative plots shown in *figure 5.4 (b)*. A hypothesis for this observation is that because there is less curvature present in the carbon flakes making up the larger spheres, these spheres are harder to oxidize.

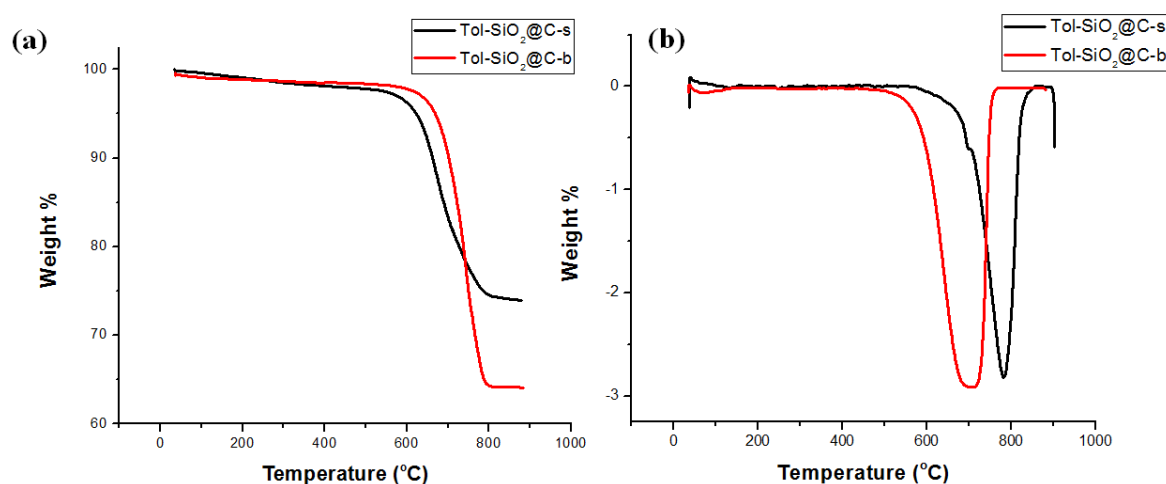


Figure 5.4: (a) TGA and (b) derivative plots of toluene-carbonized 150 nm and 350 nm silica templates. Carbonization conditions: Carrier gas = Argon, Flow rate = 100 sccm, Temperature = 900 °C

5.3 Nanocasting Method for carbonization

The nanocasting method is more often than not used in order to synthesize materials with very high surface areas. This method implies that the material is synthesized within the nanospaces or pores of the template being used. Following the synthesis of the framework material (carbon in the current study), the template is then selectively removed. The general synthesis procedure can be summarized in three steps: (i) a solution containing the framework precursor material infiltrates the pores of the porous template, (ii) this composite material is heat treated in a controlled atmosphere to convert this infiltrated precursor into the framework material, and (iii) removal of the template by dissolution.²⁴

5.3.1 Experimental

In this case, the silica-carbon composite core-shell structures were synthesized via a nanocasting method. The first step was to polymerize the carbon source around the template material. This was done by dispersing 2.00 g of silica (150 and 350 nm templates) in a solution of 2.00 ml NH_3 25% solution and absolute ethanol by ultrasonication. The carbon precursor solution was made by dissolving 0.750 g of resorcinol salt and 1.00 g of CTAB in 1.50 ml of formaldehyde, 1.00 ml of TEOS, and 50.0 ml of absolute ethanol. The polymerization process is illustrated in *figure 5.5*. This second solution was then added to the first solution, and the mixture was stirred at 30 °C for 20 hours. The mesoporous silica product covered by a layer of resorcinol formaldehyde (RF) (denoted $\text{SiO}_2\text{@RF}$), was obtained by centrifugation, and washed with a 50/50 water/ethanol solution. The red product was then dried at 100 °C overnight. Carbonization of the carbon precursor was performed in a horizontal CVD furnace under an inert atmosphere at 900 °C for 2 hours to give the silica-carbon composite structure ($\text{RF-SiO}_2\text{@C}$). A schematic of this process is outlined by *figure 3.2b* (see *chapter 3*).

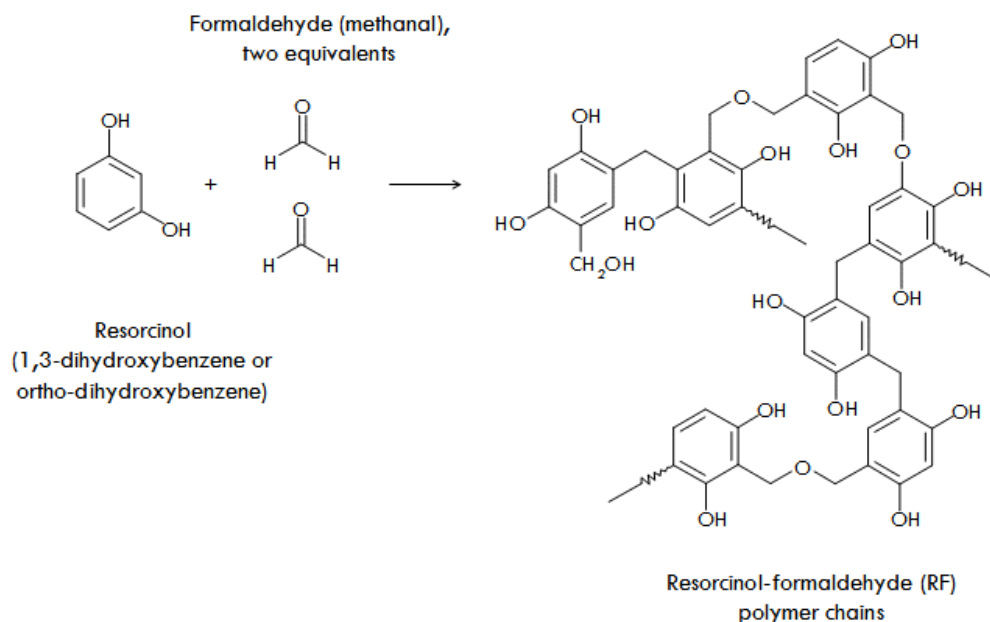


Figure 5.5: Polymerization of the resorcinol formaldehyde (RF) polymer from resorcinol salt and formaldehyde solution ²⁵

5.3.2 Results and discussion

Described in the following sections are the results for the process described in *section 5.3.1*. The sections also explain the problems that were encountered when attempting to synthesize the silica-carbon composite structures using the nanocasting method.

5.3.2.1 TEM Analysis

Illustrated in *figure 5.6* are the composite structures before and after RF carbonization of the (a)-(b) 150 and (c)-(d) 350 nm silica templates; as explained in *section 5.2.1*. *Figure 5.6a* shows the $m\text{SiO}_2@\text{RF}$ sandwich-like structure, similar to that reported by Fang *et al.*²⁶ Upon carbonization at 900 °C under Ar gas with a flow rate of 100 sccm, the RF-SiO₂@C composite structure was obtained (*figure 5.6 b-d*).

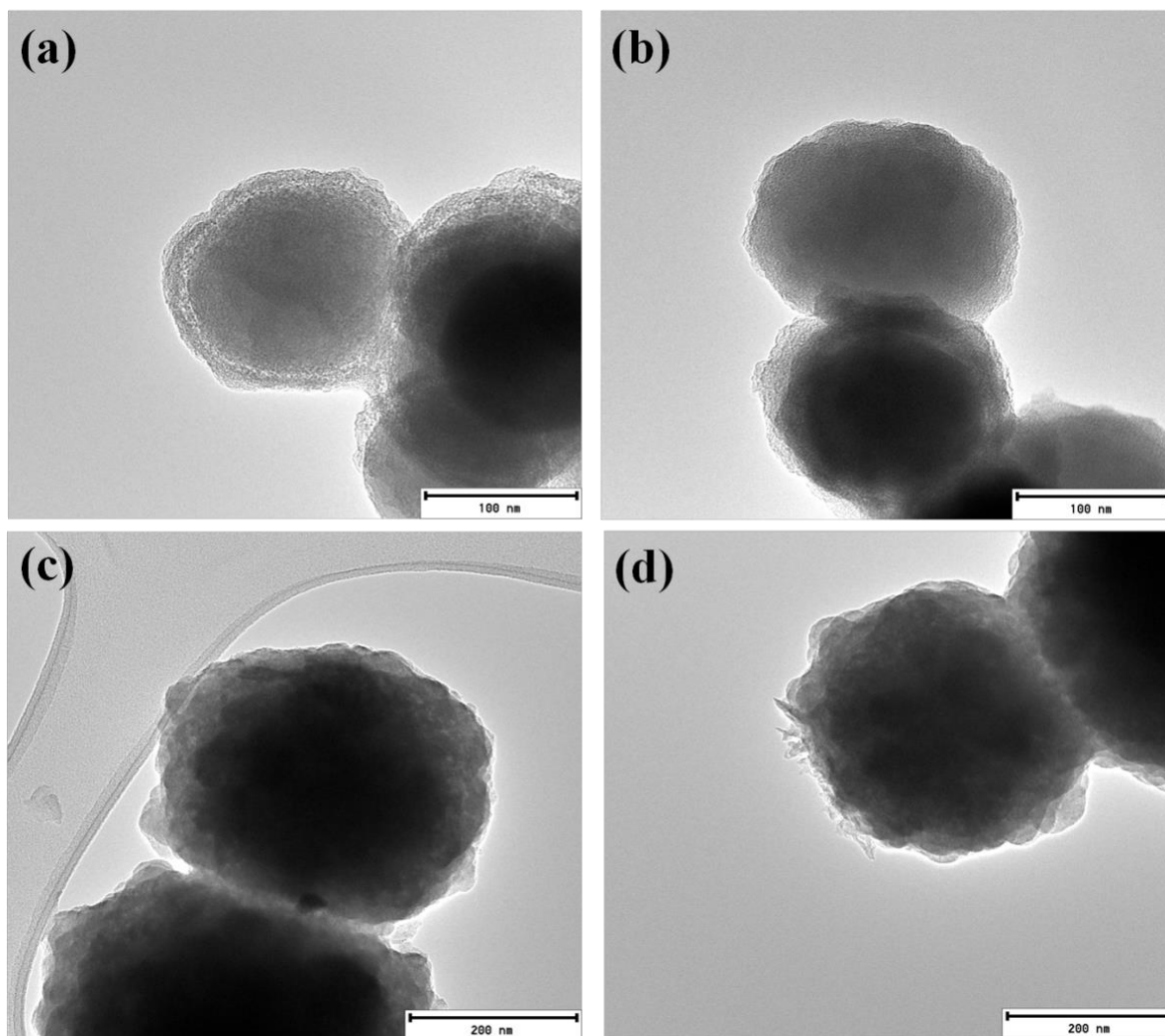


Figure 5.6: TEM images of (a) $\text{SiO}_2@\text{RF}$ and (b) $\text{RF-SiO}_2@\text{C}$ composite structures from 150 nm silica template, and (c) & (d) $\text{RF-SiO}_2@\text{C}$ composite structure from 350 nm silica template

Similar to the results for the toluene carbonized silica (*section 5.2*), the size of the template does not seem to make a significant difference to the deposition of the carbon; as evidenced by the fact that both sizes of silica are evenly covered by carbon. Compared to the toluene-synthesized structures, the carbon layer that results from the RF appears to have a more irregular spherical structure whereby the shell is quite jagged, whereas the toluene-synthesized carbon layer is smoother. In other words, the toluene precursor better emulates the silica's shape, almost perfectly conforming to the template's shape.

5.3.2.2 Thermogravimetric analysis

Depicted in *figure 5.7* are the TGA and derivative plots of the RF-SiO₂@C material. Just as observed for the Tol-SiO₂@C samples, the larger RF-synthesized spheres were found to contain more carbon than the smaller spheres; with the RF-SiO₂@C-b and RF-SiO₂@C-s samples containing 22 and 16% respectively (*figure 5.7 (a)*). As stated in *section 5.2.2.2*, we expect the carbon to make up about 11% of the SiO₂@C composite. The carbon yields obtained from using RF as a carbon source were closer to this expected percentage, implying that the method of carbonization in this case mainly involves nanocasting, as opposed to carbon deposition on the surface.

As with the toluene-synthesized spheres, the larger composites were found to be more thermally stable than their smaller counterparts; where the decomposition temperatures were found to be 680 and 650 °C for the RF-SiO₂@C-b and RF-SiO₂@C-s structures respectively (*figure 5.7 (b)*). Because these inflection points are lower than those of the Tol-SiO₂@C structures (780 °C and 700 °C for the large and small spheres respectively), it can be concluded that when RF is used as a carbon source under the given conditions, the result is a product that is less thermally stable than when toluene is used as a carbon source under the same conditions.

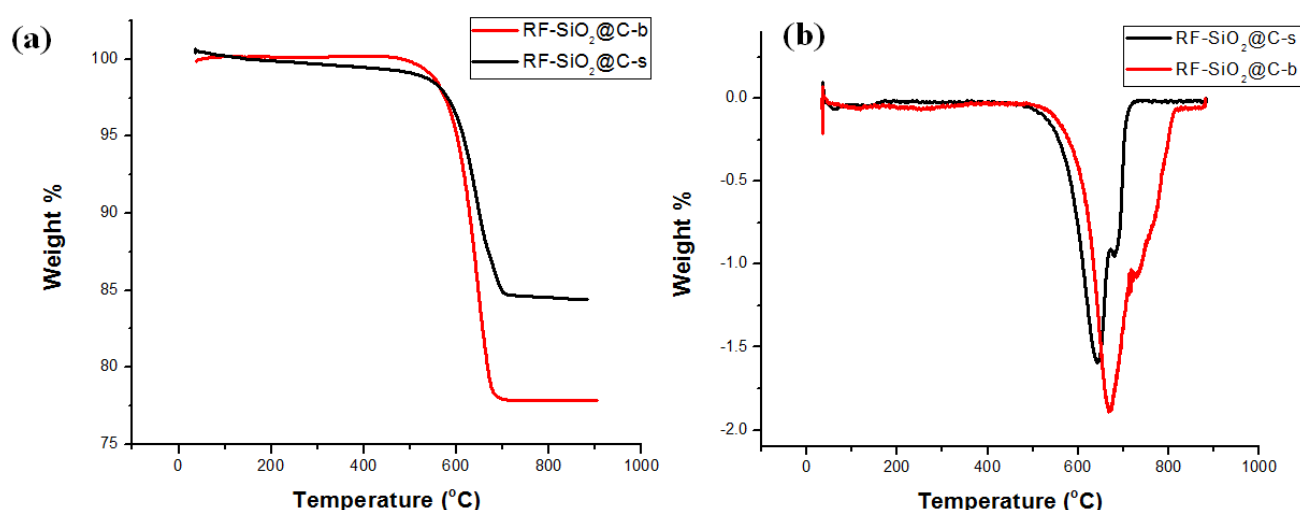


Figure 5.7: (a) TGA and (b) derivative plots of the 150 nm and 350 nm RF-carbonized silica. Carbonization conditions: Carrier gas = Argon, Flow rate = 100 sccm, Temperature = 900 °C

Conclusions:

The conclusions that can be drawn from the carbonization sections are that firstly, the successful deposition using both carbonization techniques is independent of the size of the template used. However, thermal analyses revealed that for both techniques the larger spheres not only contained more carbon, but were also more thermally stable than their smaller counterparts. Toluene as a carbon precursor seems to better emulate the shape of the silica template, and toluene-synthesized carbon was also found to be more thermally stable than carbon synthesized from RF. Furthermore, using toluene as a carbon source also resulted in higher carbon yields compared to when RF is used.

5.4 Hollow Carbon Spheres

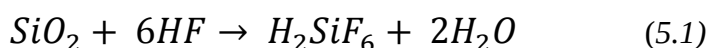
When employing the hard-templating method (described in *section 5.1*) to synthesize hollow nanomaterials, a selective etching chemical procedure is often used in order to get rid of the sacrificial template and to leave behind the desired hollow framework. This technique is selective and the sacrificial core to be etched need not be compositionally different from the shell.²⁷ An example of this has been found in the literature where Chen *et al* have reported on the synthesis of mesoporous hollow silica spheres by selectively etching away the solid silica core using a sodium carbonate (Na_2CO_3) solution.²⁸

The current study describes a method for the removal of the silica template from the above-mentioned silica-carbon composite structures using an aqueous hydrofluoric acid (HF) solution to obtain the hollow carbon sphere. The reaction takes place between the silica template and the etching agent, leaving the carbon shell intact and void of the silica core by the end of the process. One challenge faced during this stage of synthesis is making sure that the acid was strong enough to remove all the silica in a single etching cycle but not so strong as to cause carbon flaking. Another issue related to etching involved etching to form Pt encapsulated in HCSs. A challenge faced in this case was ensuring that the encapsulated platinum nanoparticles do not escape the carbon framework during etching.

5.4.1 Experimental

It is important to note that the apparatus used during this part of the synthesis should be resistant to corrosion by hydrofluoric acid. As a result, all beakers, measuring cylinders, etc. used were made of either plastic (e.g. polypropylene) or a metal.

The first step was to dilute the as-purchased 48% HF solution to 10% using distilled water. This solution, along with the catalyst powder, was placed into a plastic beaker with a magnetic stirrer bar (approximately 100 ml HF solution per every 1.00 g catalyst). The beaker was then covered with perforated parafilm, and the reaction left stirring at a moderate speed at room temperature for 24 hours. The product was collected by decanting, washing with distilled water until neutral, and drying. The reaction that takes place during the etching process is described in *equation (5.1)*.



5.4.2 Results and discussion

The following sections report the results for the process described in *section 5.4.1*. The sections compare the plain hollow carbon spheres obtained from using either toluene or resorcinol formaldehyde as a carbon source.

5.4.2.1 TEM analysis

Illustrated in *figure 5.8* are the TEM images of the hollow carbon spheres (HCSs) obtained from methods described in *section 5.4.1*. *Figure 5.8 a-b* show HCSs fabricated via the bubbling method and *c-d* via the nanocasting method. Illustrated in *(a)* and *(c)* are HCSs of diameters of approximately 150 nm (denoted tol-HCS-s and RF-HCS-s respectively), and in *(b)* and *(d)* HCSs of diameters of approximately 300 nm (denoted tol-HCS-b and RF-HCS-b respectively). From the TEM images, it is evident that the spheres are composed of a carbon

framework with a hollow core. The spheres are still intact, i.e. there are no broken spheres, showing that the HCS structures stayed intact during HF treatment.

The toluene-synthesized HCSs (*figure 5.8 a-b*) have a thicker carbon framework than the RF-synthesized HCSs (*figure 5.8 c-d*). These results were expected based on the results obtained in *sections 5.2* and *5.3*. Furthermore, the toluene-synthesized HCSs have a better-defined carbon framework which emulates the silica sphere templates. The RF-synthesized spheres on the other hand have a jagged framework.

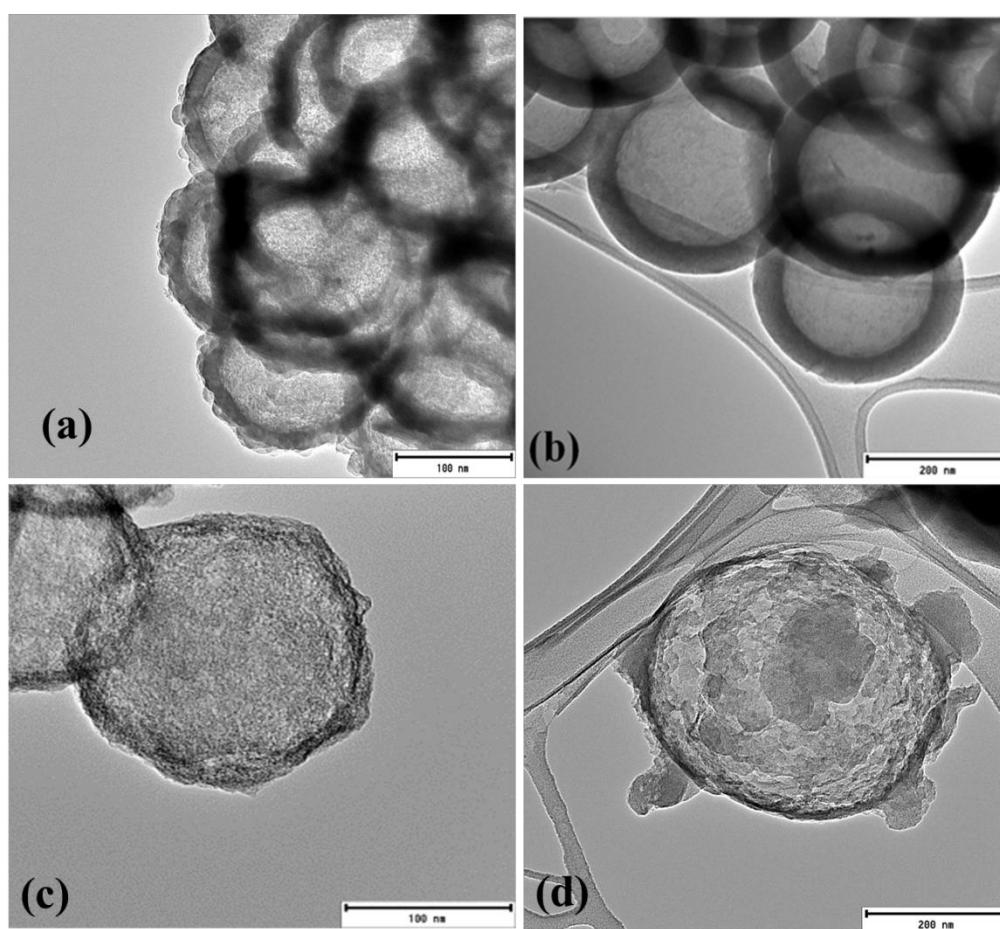


Figure 5.8: TEM images of hollow carbon spheres fabricated from (a) - (b) the bubbling method, and (c) - (d) the nanocasting method. (a) And (c) are the 150 nm HCSs, (b) and (d) are the 350 nm HCSs

An observation made from the RF-synthesized spheres was that a large percentage of the HCSs possessed some or other morphological defect. These defects are illustrated in *figure 5.9*. The spheres seen in (a) represents spheres that have partially collapsed on one side, (b) and (c) show the formation of hemispheres (i.e. incomplete or collapsed hollow carbon

spheres), and (d) represents spheres that have coagulated to form clusters of conjoined spheres. This last defect is particularly undesired because the aim when synthesizing hollow carbon spheres is to ensure that the spheres are not only discrete with tailorable shell thickness and cavity size, but also to ensure that the spheres do not end up coagulating to form large masses of indistinguishable spheres; a phenomenon particularly found when the nanospheres are less than 200 nm in diameter.²⁹

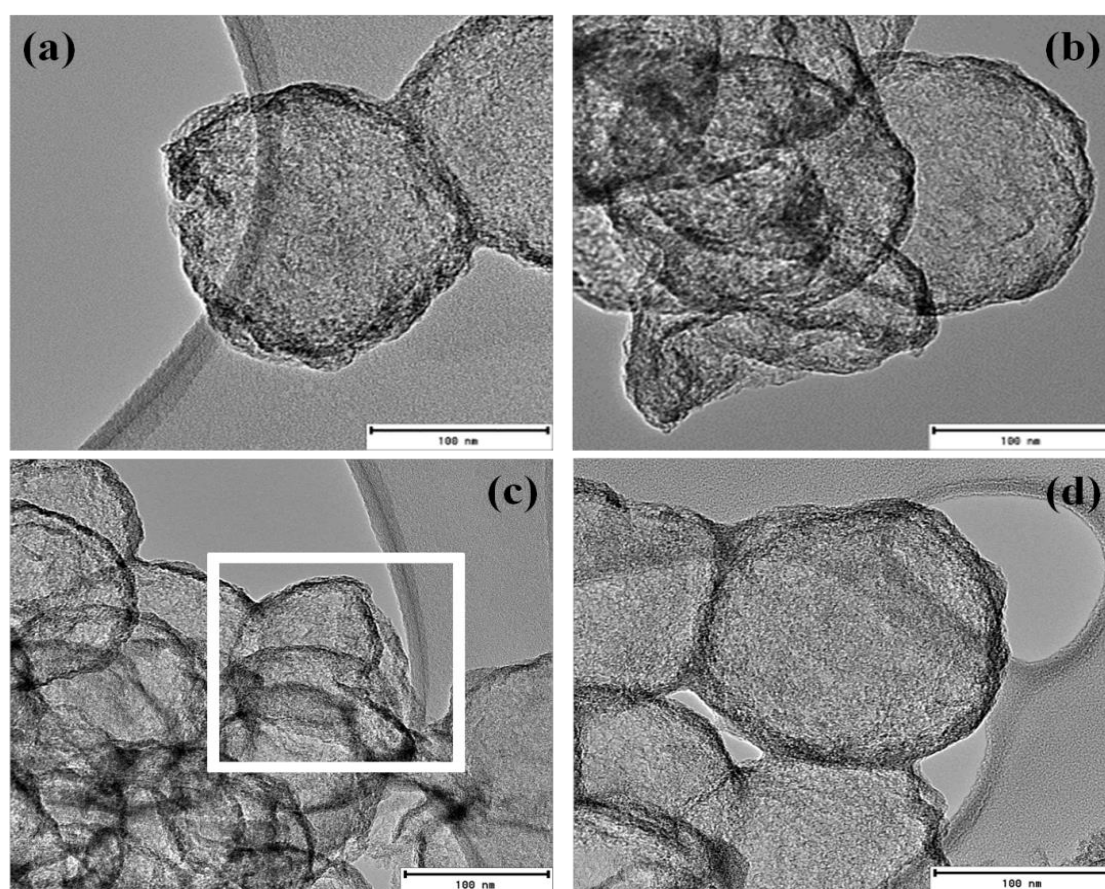


Figure 5.9: TEM images illustrating defects in 150 nm HCSs synthesized using the nanocasting method

A hypothesis for these observations is based on the nanocasting method itself. It is hypothesized that these effects are mostly observed in the smaller size spheres because during the RF polymerization process the smaller spheres are able to pack more closely, i.e. they may not disperse as well as the larger spheres. This results in the RF polymer not covering each sphere individually. Consequently, during carbonization, the carbon framework would not be covering the silica spheres sufficiently, and as the silica is removed from the structures, the resultant hollow carbon spheres possess a variety of defects.

5.4.2.2 TGA Analysis

Illustrated in *figure 5.10* are the TGA and derivative plots as a function of carbonization method and HCS size. The key message from the TGA profiles (*figure 5.12 (a)*) is that the silica template was completely removed from the carbon's core by the HF, seen by the negligible residue at 900 °C. This emphasizes the efficiency of silica removal by the aqueous HF solution, as well as the quality of the carbon sample.

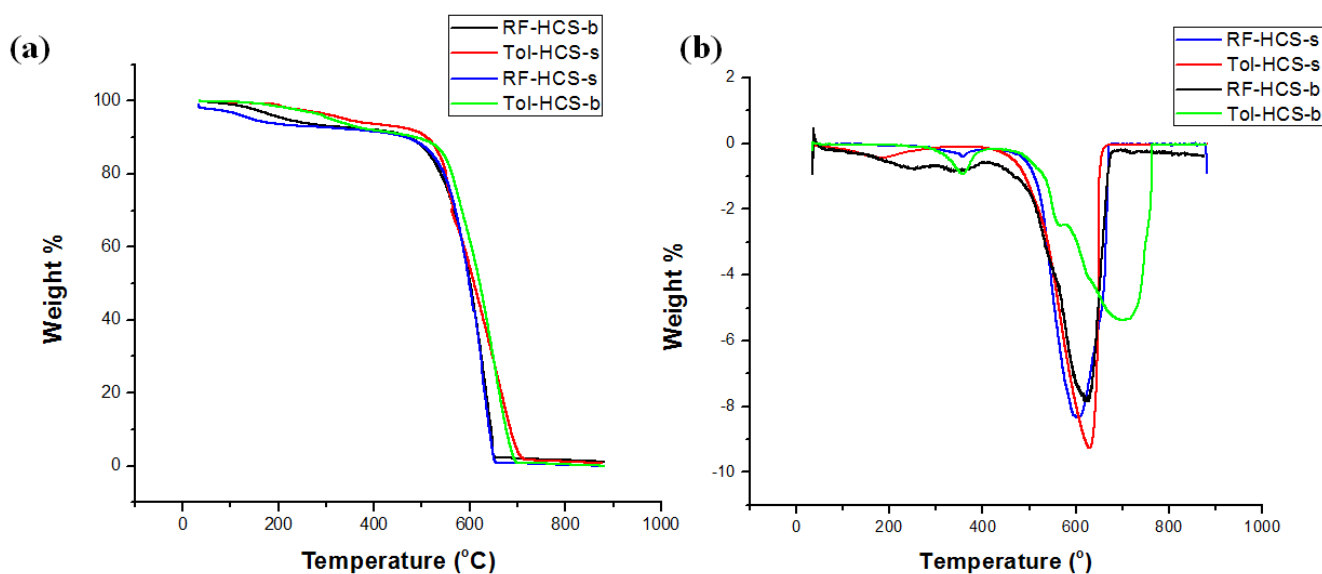


Figure 5.10: (a) TGA and (b) derivative plots of the 150 and 350 nm hollow carbon spheres synthesized using RF and Toluene and carbon sources

An observation made from the derivative plots (*figure 5.10 (b)*) was that upon treatment with HF, there was a decrease in thermal stability for both the toluene- and RF-synthesized HCSs. The Tol-HCS-s and Tol-HCS-b spheres decompose at approx. 650 and 700 °C, while the RF-HCS-s and RF-HCS-b samples decompose at approx. 600 and 650 °C respectively. Recall from *sections 5.2* and *5.3* that the decomposition temperatures for the Tol-SiO₂@C-s, Tol-SiO₂@C-b, RF-SiO₂@C-s and RF-SiO₂@C-b composite structures were approx. 700, 780, 680 and 650 °C respectively. This trend observed is in agreement with the trend observed for the silica-carbon composite structures. The observation also shows that the carbon framework of the respective spheres is not significantly diminished even after a harsh acid (hydrofluoric acid) treatment under mechanical stirring; which speaks to the maintained integrity of the carbon framework.

Furthermore, it is evident from the derivative plots that upon treatment with aqueous HF, there was an introduction of small decomposition peaks in the plots for the various samples. The introduction of these peaks could be as a result of the addition of more volatile substances or moisture into the carbon framework during the removal of the silica from the core with HF.³⁰

Illustrated in *table 5.2* below is a summary of the amount of carbon added in each of the samples described in the current chapter. It is clear from the table that overall, the bubbling method deposits more carbon onto the silica template than the nanocasting method.

Table 5.2: Summary of data for percentage of carbon deposited during carbonization

Sample	Diameter/Shell Thickness (nm)	TGA Peaks (% Weight)	% Carbon Added
tol-Si@C-s	150	74	26
tol-HCS-s	25	0	
RF-Si@C-s	15	84	16
RF-HCS-s	15	0	
tol-Si@C-b	350	63	37
tol-HCS-b	40	0	
RF-Si@C-b	350	78	22
RF-HCS-b	20	0	

5.4.2.3 Raman analysis

Raman spectroscopy was used in order to gauge the crystallinity and level of graphitization of the as-synthesized hollow carbon spheres as a function of carbonization technique. Each Raman spectrum consists of two bands; the D and G bands, which are found at approximately 1330 cm^{-1} and 1580 cm^{-1} respectively. The D-band originates from lattice distortions which are induced by disorder, while the G-band is a result of the in-plane stretching vibration mode (the E_{2g} mode) of a single crystal of graphite.³¹ The Raman spectra of the HCSs are given in *figure 5.11*, and a summary of these Raman results is given in *table 5.3*.

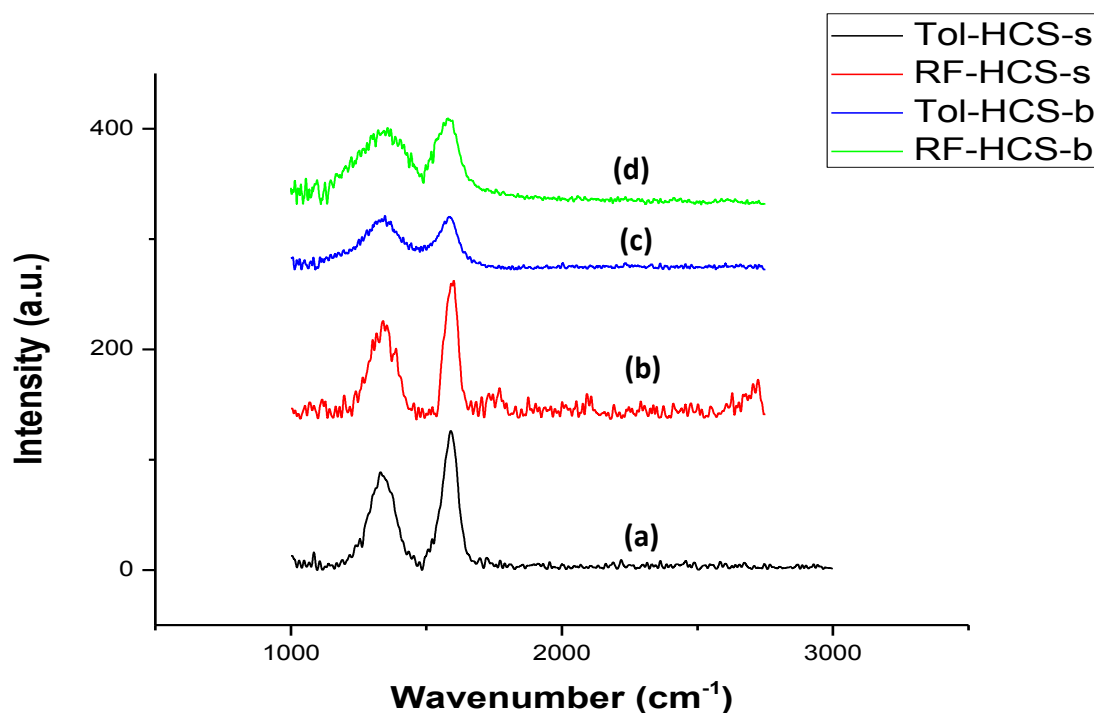


Figure 5.11: Raman plots for the four hollow carbon spheres: (a) Small toluene-synthesized (Tol-HCS-s) (b) Small RF-synthesized (RF-HCS-s) (c) Large toluene-synthesized (Tol-HCS-b) (d) Large RF-synthesized (RF-HCS-b)

The I_D/I_G ratios for the tol-HCS-s and tol-HCS-b are 0.69 and 0.64 respectively, while for the RF-HCS-s and -b are both 0.99. It is evident from these values that using toluene as a carbon source resulted in a more graphitic carbon framework, while the carbon framework synthesized using RF as a carbon source appears to be more disordered. Another observation made is that the size of the carbon spheres does have a significant impact on the level of crystallinity of the carbon. These results are in agreement with TGA data, in which the toluene-synthesized carbon is more thermally stable; a trait synonymous with a higher level of graphitization.

Table 5.3: Summary of Raman Results

	Sample	D-peak Position (cm ⁻¹)	G-peak Position (cm ⁻¹)	I_D/I_G
(a)	Tol-HCS- s	1336	1588	0.69
(b)	RF-HCS- s	1334	1580	0.99
(c)	Tol-HCS- b	1338	1593	0.64
(d)	RF-HCS-b	1334	1581	0.99

5.4.2.4 Surface Area Measurements

Brunauer-Teller-Emmet (BET) measurements were used to determine the porosity characteristics of the as-synthesized hollow carbon spheres. *Table 5.4* gives a summary of the information attained from these measurements, while *figure 5.12* illustrates the adsorption/desorption characteristics of the material.

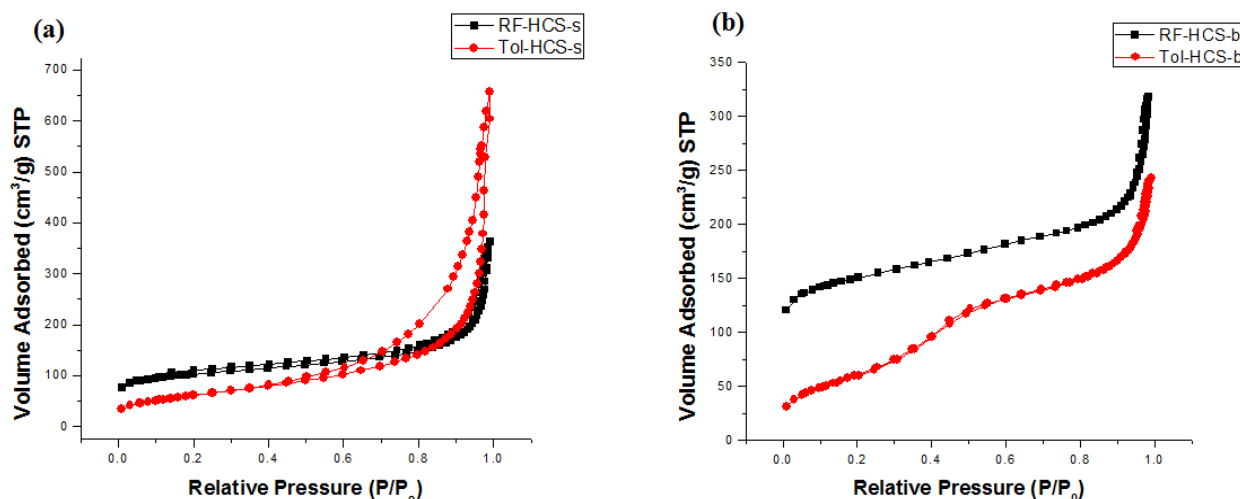


Figure 5.12: N₂ sorption isotherms for (a) 150 nm, and (b) 350 nm RF- and Toluene-synthesized Hollow Carbon Spheres

Both the 150 nm HCSs and the 350 nm RF-synthesized HCSs display a typical type II isotherm, while 350 nm toluene-synthesized 350 nm HCSs displays a type IV isotherm.^{32,33} In the type II isotherms, there is a steep adsorption observed at relative pressures between 0.60 – 0.80 which can be attributed to the mesopores in the carbon framework. Furthermore, a pronounced type H4 hysteresis loop is present in the Tol-HCS-s isotherm, which typically indicates the presence of a large number of mesopores.^{3,34} Conversely, the other three isotherms show very little hysteresis between the adsorption and desorption peaks, indicating a decreased number of mesopores within their carbon frameworks. The type IV isotherm displays a sharper adsorption increase at a relative pressure of approx. 0.4 which is caused by capillary condensation of nitrogen in the mesoporous.^{35,36} In all four isotherms, a steep adsorption is observed at P/P_0 close to 1.0, which is attributed to the large hollow volume of the HCSs.³⁷

Table 5.4: Sorption Data for RF- and Toluene-synthesized Hollow carbon Spheres

Sample	BET surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Width (nm)
RF-HCS-s	340.1	0.52	6.2
Tol-HCS-s	214.1	0.37	6.5
RF-HCS-b	489.4	0.48	4.0
Tol-HCS-b	230.6	0.36	6.5

The data given in *table 5.4* illustrates some trends that would be expected according to previous results illustrated within this dissertation (see *section 4.1.1*). It is expected that the measured surface area for each type of carbon would increase as (i) the number of pores increase, (ii) the pore volume increases, and (iii) the pore width decreases. For both HCS sizes, the RF-synthesized carbon, with its more disordered nature as shown by Raman data, has a larger amount of available surface area, and a larger pore volume, according to the BET data. The implications of these sorption features on the capacitance of each type of carbon are explored in the following electrochemical measurements section.

5.5 Electrochemical Measurements

Porous carbon materials have attracted great attention in electrochemical applications because they possess a variety of desirable properties which include, but are not limited to, support materials for electrocatalysts.³⁸ Of these porous carbon materials, hollow carbon spheres have gained huge popularity for electrochemical applications in super capacitors,³⁹ lithium-ion batteries,⁴⁰ drug delivery systems,⁴¹ and, more relevant to the current study, in fuel cells.⁴² Taking the results reported in this chapter into consideration, the hypothesis that the toluene-synthesized HCSs will perform better electrochemically than the RF-synthesized HCSs was made. The following section reports the results of the study.

5.5.1 Experimental

The electrochemical measurements were carried out in the aqueous electrolyte perchloric acid (0.100 M HClO₄). The first step in each experiment was to polish the glassy carbon (GC)

working electrode using alumina powder, rinse the electrode with isopropanol and ultra-pure water, and to allow it to dry at room temperature. The catalyst ink was prepared as per *section 3.2.2*, after which 2.00 μl was dropped onto the clean GC electrode. The electrode was then allowed to dry at room temperature, leaving an evenly-coated dry catalyst on the GC electrode. After placing this modified working electrode (WE) in the system (*figure 3.3*; see *chapter 3*), the electrolyte was purged with N_2 gas for 30 minutes prior to measurements being taken. The measurements were taken at room temperature at a scan rate of 100 mV/s.

5.5.2 Results and Discussion

Cyclic voltammetry measurements were used to assess the electrochemical performance of the mesoporous hollow carbon spheres synthesized using two different carbon sources; toluene and resorcinol-formaldehyde (RF); the results of which are illustrated in *figure 5.13*. The CV curves firstly illustrate that the RF-synthesized HCSs exhibit superior capacitance resistance to their toluene-synthesized counterparts. This can be attributed to the fact that the RF-synthesized HCSs have a larger pore volume and higher specific surface area than the toluene-synthesized HCSs.^{38,43} The CV curves also exhibit a quasi-rectangular “box-like” shape. It is worth mentioning that this feature is characteristic of well-performing double-layer supercapacitors.^{44,45}

It is also observed that the CV curve for the RF-synthesized HCSs possesses large redox peaks. It can be assumed that these peaks are as a result of charging of the electrical double layer due to a pseudo-Faradic contribution (or pseudo-capacitance) of some surface functionality, most likely oxygen-containing groups, on the carbon’s surface.^{43,45} It is also worth noting that these peaks are completely absent from the toluene-synthesized HCSs, suggesting that the surfaces of these HCSs do not possess oxygen-containing groups. This might have an impact on the performance of the platinum catalysts once they are loaded onto the support, which is discussed in *chapter 6*.

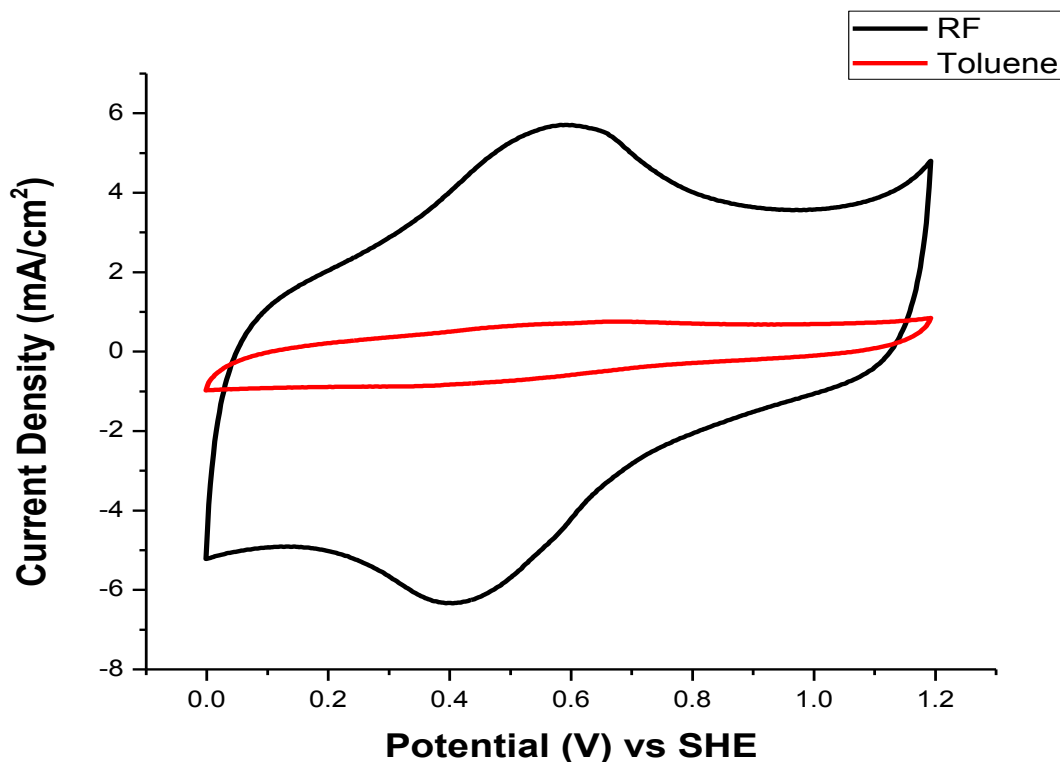


Figure 5.13: CV curves obtained for 150 nm plain Toluene-synthesized and RF-synthesized mesoporous hollow carbon spheres

Conclusions: Hollow carbon spheres with generally conserved structural integrity were successfully synthesized by removing the silica template via chemical etching using hydrofluoric acid. It was found that the toluene-synthesized HCSs had a thicker, more well-defined carbon framework which was more thermally stable and showed a more graphitic crystalline structure than the RF-synthesized counterparts, which possessed more morphological defects.

On the other hand, the electrochemical measurements show that in terms of capacitance, the RF-synthesized carbon framework is superior to the toluene-synthesized carbon. This is attributed to the presence of oxygen-containing groups on the surface of the RF-carbon, as well as to the higher specific surface area observed for the RF-synthesized HCSs. The effect that these observations will have on the catalytic activity of the loaded platinum catalyst nanoparticles is investigated in the following chapter.

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CHAPTER 6:

APPLICATION – ELECTROCATALYTIC TESTS

The following sections report the results for the electrochemical testing of the hollow carbon spheres obtained from the two different carbonization methods. Also reported are the electrocatalysis results for the carbon-encapsulated platinum catalysts and these are compared to the results for platinum placed on top of said hollow carbon spheres. The effects of using two different platinum precursors and deposition methods are also studied.

6.1 Introduction

Over the years, much research has gone into the catalysts utilized in PEM fuel cells, and the results have been extensively reported in the literature. However, not as much research has gone into the catalyst support materials. In PEMFCs, the electrocatalytic activity depends largely on a number of factors which include metal particle shape and size, particle size distribution, the catalyst preparation technique used, the structure of the catalyst support, the properties of the metal precursors, and the accessibility of the metal on the support.¹

For the purposes of PEMFC applications, platinum deposited on carbon has been reported as a very effective electrocatalyst,² when compared to the unsupported platinum counterparts.³ This is due in part to the fact that carbon possesses electronically conductive properties that allow this support material to facilitate the interaction at the three phase boundary; that is between the electrode-electrolyte-reactant interface; thus resulting in an increase in the efficiency of the fuel cell.⁴ Even though Vulcan XC-72 is the most widely used commercial carbon support material used, it does have its disadvantages. For example, it has random pores with varying sizes that could lead to an ineffective multiphase transfer of the reactants and products during fuel cell operation.⁵ Another disadvantage of this carbon is that it contains a large number of micropores with diameters of less than 1 nm, which results in many of the Pt nanoparticles being trapped within said pores, and thus not participating in the electrochemical reactions due to the absence of the triple phase boundary.⁶

Thus, many alternative types of carbon have been synthesized,⁷ and it has been found that mesoporous hollow carbon spheres are a great alternative because they are able to facilitate the diffusion of hydrogen, oxygen, and water within the fuel cell.⁸ Of the two reactions that take place within the PEMFCs, the reaction at the cathode, which is the oxygen reduction reaction (ORR), is a particular focal point for researchers, as this reaction is the less kinetically-favourable of the two. Due to said poor kinetics, the cathode reaction is usually the source of poor performance of PEM fuel cells.⁹

Currently, platinum-based metals have been found to be the top performers as electrocatalysts for the reduction of oxygen, especially in acidic media,¹⁰ because it provides the lowest overpotential and highest stability.¹¹ However, commercializing these catalysts has proved to be problematic for numerous reasons, including the cost of synthesizing platinum-based electrocatalysts on a large scale.¹² Strategies to lower platinum catalyst loadings, and therefore costs, include improving the dispersion of the catalyst on the support, and it has been shown by Liu *et al* that ordered mesoporous carbon supports were better in this respect than the commercial Vulcan XC-72 carbon.¹³ In addition, Yan *et al* have shown that hollow carbon spheres not only improve the dispersion of the platinum catalysts, but also improve the mass transfer and stability of the electrocatalysts in catalysing the ORR.¹⁴

In the current study, the effects of varying the following parameters were tested: (i) the platinum-deposition technique (CVD or wet impregnation), (ii) location of the platinum nanoparticles (i.e. either on top or inside HCSs), (iii) carbon source (RF or toluene), (iv) platinum precursor (PtCl_2 or $\text{Pt}(\text{acac})_2$), and (v) size of the carbon support. The sections that follow report the results for the activity of these electrocatalysts synthesized as per *chapter 3*. The electrochemical surface area (ECSA) of the supported platinum nanoparticles was determined. Galvanostatic measurements were used to determine (1) the stability of the HCSs from the different synthesis techniques, and (2) the effect of introducing platinum on the stability of the carbon. Linear sweep voltammetry (LSV) measurements were used to compare the activity of the different catalysts for the oxygen reduction reaction. And lastly, the stability of the platinum particles in the different catalysts was tested using chronoamperometry measurements.

6.2 Experimental

This section describes in detail how the Pt-carbon composite structures were synthesized, using either the wet impregnation (WI) or chemical vapour deposition (CVD) techniques. Also described are the methods used for the electrochemical characterization.

6.2.1 Pt-Carbon Composite Synthesis

Wet Impregnation (WI) Method

This method involved loading the platinum nanoparticles onto the mesoporous silica template. This was achieved by mixing the silica template (1.00 g) with distilled water (62.5 ml) and the platinum precursor (0.100 M H_2PtCl_6 , 10 ml) by ultrasonication for 15 minutes. The reducing agent (0.100 M NaBH_4 , 10.0 ml) was then added drop wise under moderate stirring. The yellow-orange solution was then stirred for 4 hours at room temperature. The resulting dark brown product was then collected by centrifugation and washing, and dried in an oven at 50 °C overnight.

Chemical Vapour Deposition (CVD) method

During this method, the platinum salt ($\text{Pt}(\text{acac})_2$ or PtCl_2) and the silica powder were mixed using a pestle-mortar to ensure homogeneous mixing. The mixture, in a quartz boat, was then placed in a quartz tube and this placed in a horizontal furnace. The mixture was then heated (PtCl_2 at 300°C, $\text{Pt}(\text{acac})_2$ at 320 °C) for 2 hours under an inert gas atmosphere. Upon cooling, the dark brown powder was then collected.

Following both methods, carbonization was carried out as per *chapter 5* by either the bubbling or nanocasting method. For the top-loaded platinum nanoparticles, the CVD method was carried out using as-synthesized hollow carbon spheres instead of silica.

For simplicity, the denotations of the different catalysts along with their descriptions are given in the table below.

Table 6.1: Denotations and descriptions of tested catalysts

	Denotation	Description
1	tol-Pt(ac)_top	Pt loaded on top of small toluene-synthesized HCSs via CVD method using Pt(acac) ₂ as the metal precursor
2	tol-PtCl ₂ _top	Pt loaded on top of small toluene-synthesized HCSs via CVD method using PtCl ₂ as the metal precursor
3	tol-PtCl ₂ _top-b	Pt loaded on top of big toluene-synthesized HCSs via CVD method using PtCl ₂ as the metal precursor
4	tol-Pt(ac)_inside	Pt loaded inside small toluene-synthesized HCSs via CVD method using Pt(acac) ₂ as the metal precursor
5	RF-PtCl ₂ _top	Pt loaded on small RF-synthesized HCSs via CVD method using PtCl ₂ as the metal precursor
6	RF-Pt(ac)_top	Pt loaded on small RF-synthesized HCSs via CVD method using Pt(acac) ₂ as the metal precursor
7	WI	Pt loaded inside small toluene-synthesized HCSs via wet impregnation method using PtCl ₂ as the metal precursor

6.2.2 Electrochemical Measurements

For the electrochemical testing of the different Pt-HCS catalysts, the cleaning and modification of the working electrode, as well as the electrochemical setup were as described in *section 5.5.1*. The measurements were taken at room temperature, at scan rates of 5.00 mV/s and rotation speeds of 2500 rpm for LSV measurements, and the scan rates were varied between 10.0 mV/s and 100 mV/s for CV measurements. These two scan rates for CV measurements were chosen as they fell at extremes to each other, and the aim was to gauge

the different levels of information one could extract from the two different scan rates. Chronoamperometry measurements were carried out at a steady potential of 0.70 V for 1800 seconds at a scan rate of 10 mV/s.

6.3 Results and Discussion

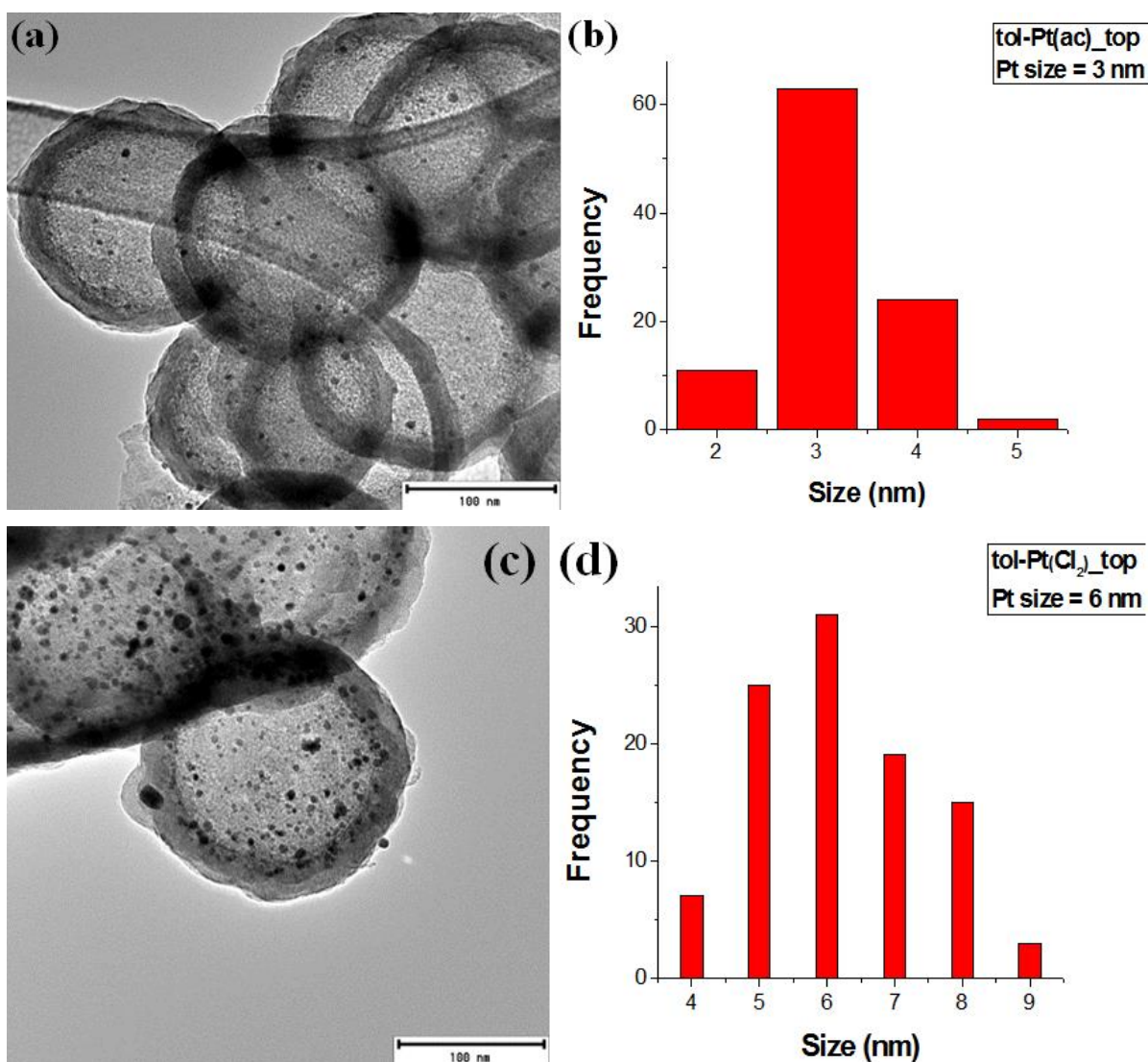
6.3.1 TEM Analysis

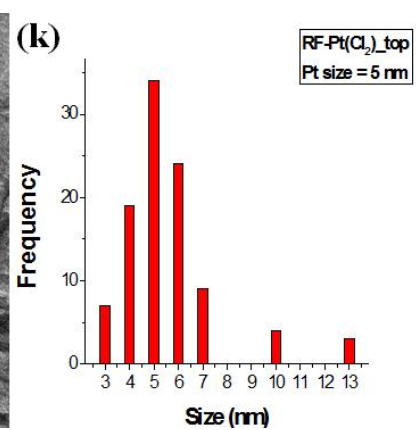
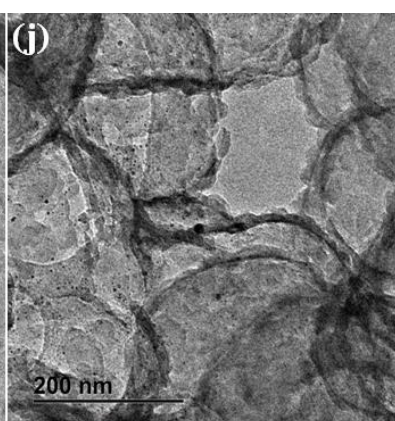
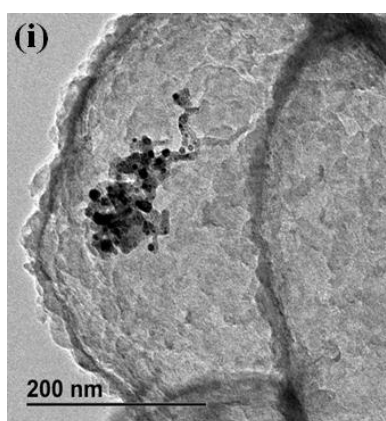
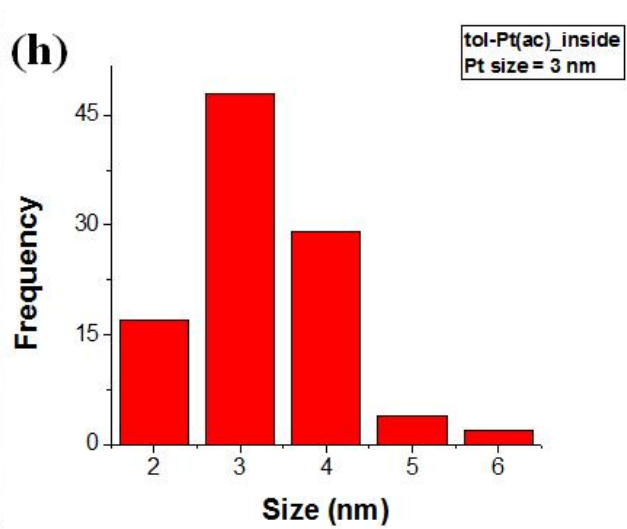
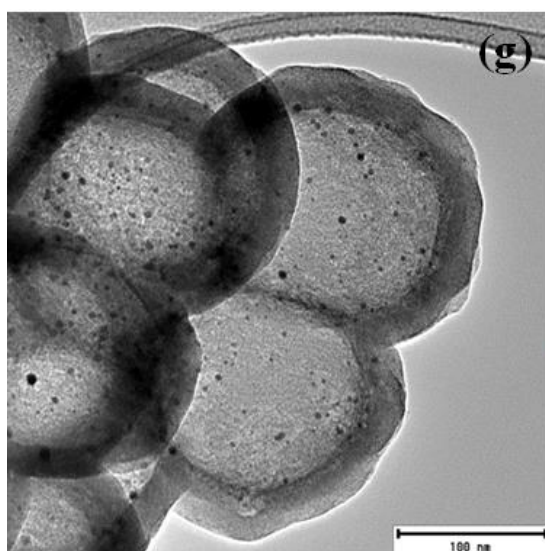
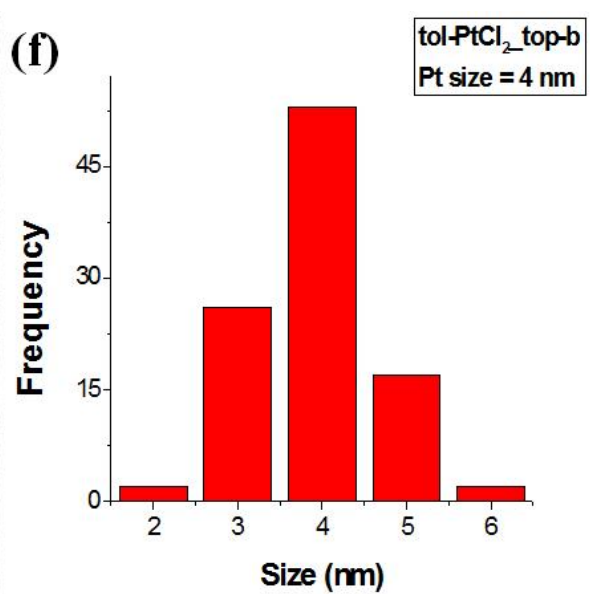
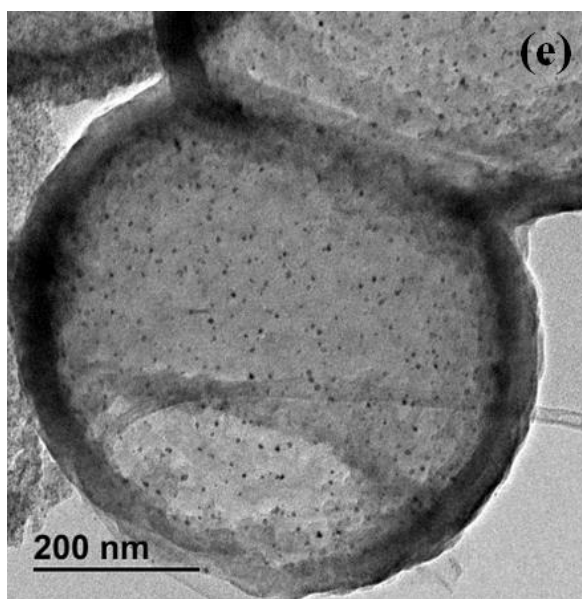
Reported in this section are the TEM images, as well as size distributions, of the catalysts tested for their activity for the ORR reaction which were synthesized as per section 6.2.1. The platinum loading for the “WI” catalyst, as well as the “CVD” catalyst, was 10 wt%, while loadings for all other catalysts were 20 wt%.

The first observation made was that when $\text{Pt}(\text{acac})_2$ was used as a platinum precursor for Pt deposition via the CVD method, the metal particles all had an average diameter of 3 nm, irrespective of the type of support (*figure 6.1 (a)-(b), (g)-(h), (l)-(m)*), ; while Pt loaded using PtCl_2 salt as the precursor resulted in larger particles ranging from averages diameters of 4 – 6 nm (*figure 6.1 (c)-(d), (e)-(f), (i)-(k)*), with the Pt loaded on the tol-synthesized carbon (*figure 6.1 (c)-(d)*) being the largest at an average diameter of 6 nm. This demonstrates that for the CVD method, $\text{Pt}(\text{acac})_2$ salt is better suited to deposit smaller sized metal particles. An interesting observation made was that even though the Pt was loaded on the inside surface of the HCSs (*figure 6.1 (g)-(h)*) was subjected to temperatures as high as 900 °C during carbonization, the platinum nanoparticles also had an average diameter of 3 nm; thus demonstrating the stabilizing effect of encapsulating the metal particles inside the spheres.

Another general observation made was that using $\text{Pt}(\text{acac})_2$ as the metal precursor allowed for the preparation of better dispersed particles on the support materials; again irrespective of the type of support material used. Exceptions to this observation occurred, when PtCl_2 was the metal precursor, were when Pt was loaded (1) on the larger HCS support, and (2) when the WI method was employed for deposition. The first observation could be due to the fact that the metal has a larger space to distribute particles more evenly (possibly due to higher surface energies of the larger carbon spheres), and so less agglomeration is observed, as is the case when the support material is half the size. The second observation could be that the PtCl_2

more evenly distributes when it is reduced using a low concentration of reducing agent over a longer period in an aqueous environment, as opposed to being decomposed more rapidly using heat treatment, and then cooled. It was also observed that Pt from PtCl_2 loaded onto RF-synthesized HCSs using the CVD method resulted in severe agglomeration on some spheres, as opposed to when $\text{Pt}(\text{acac})_2$ was the Pt precursor. This reiterates the point previously made that PtCl_2 decomposed using heat treatment makes for a relatively unstable metal on the support surface; possibly indicating that the interaction between the carbon and the Pt is relatively weak; perhaps due to the presence of the chloride ion. The platinum particle sizes are summarized in *table 6.2* at the end of the chapter.





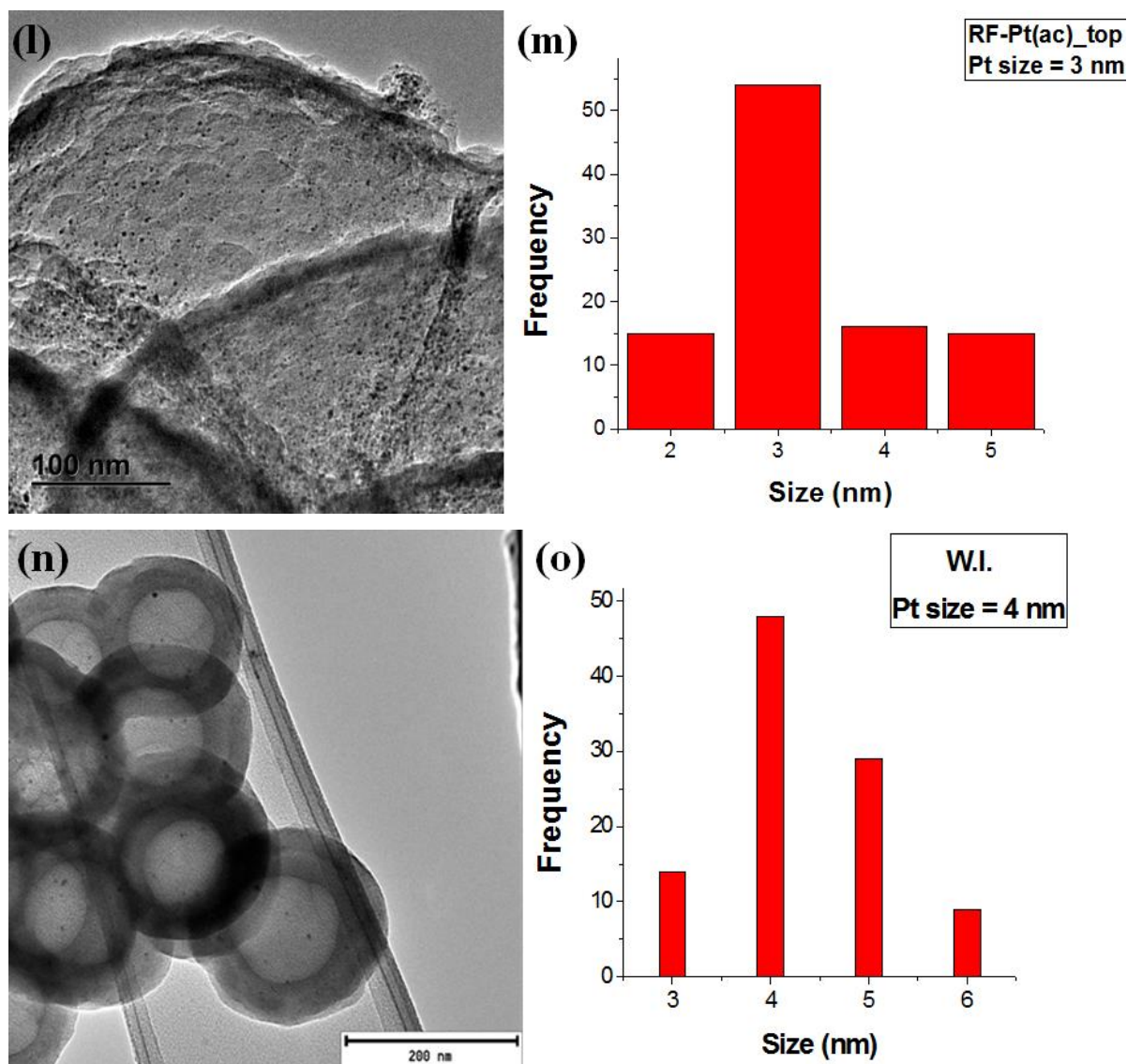


Figure 6.1: TEM images and size distributions for: (a) and (b) tol-Pt(ac)_{top}, (c) and (d) tol-PtCl₂_{top}, (e) and (f) tol-PtCl₂_{top-b}, (g) and (h) tol-PtCl₂_{inside}, (i), (j) and (k) RF-PtCl₂_{top}, (l) and (m) RF-Pt(ac)_{top}, (n) and (o) WI catalysts

6.3.2 Electrochemical Measurements

The effect on the catalytic activity and catalyst stability when the active metal placed on either the inner or outer surface of the HCSs was explored. These experiments were performed to determine whether or not the catalyst is more active and/or more stable when placed in either location. In a previous chapter, it was shown that the type of platinum precursor used for the deposition of the metal onto a support plays a significant role in the deposition behaviour of the platinum nanoparticles (see *chapter 4*). The effect of using

different metal precursors on the electrocatalytic activity of the final catalyst systems was also studied. The electrocatalytic activity of platinum deposited using different deposition techniques (i.e. wet impregnation (WI) and chemical vapour deposition (CVD)) is also reported here.

The results for the CV measurements of the different electrocatalysts are given below as a function of platinum deposition technique (*section 6.3.2.1*), HCS size (*section 6.3.2.2*), platinum precursor (*section 6.3.2.3*), and platinum location (*section 6.3.2.4*). The effect the scan rate has on the CV curve profiles is also reported (*section 6.3.2.5*). The corresponding XRD patterns of the catalysts before the reactions are also given to better understand the platinum behaviour in each catalyst system. The LSV and chronoamperometric measurements are given to compare the catalyst activities for the oxygen reduction and the catalyst stabilities respectively. The results for the CV, LSV, and chronoamperometry measurements are summarized in *table 6.2*, *6.3*, and *6.4* respectively at the end of the chapter.

6.3.2.1 Effect of Deposition Technique

10wt% Platinum was loaded via either the chemical vapour deposition (CVD) or wet-impregnation (WI) methods using PtCl_2 and H_2PtCl_6 as platinum precursors. Measurements were taken at 100 mV/s. The chosen potential ranges for the WI and the CVD catalysts were 0 – 1.0 and 0 – 1.1 V respectively. The slightly smaller range for the WI catalyst serves to reveal more information about the H_2 adsorption-desorption features of the catalyst. The results are given in *figure 6.2*.

Neither of the two CV curves (*figure 6.2a*) reveals the typical, expected CV profile. However, the CVD-deposited catalyst is closer to the typical shape, with more prominent characteristic H_2 adsorption-desorption peaks, while the shape of the WI-deposited catalyst tends towards the typical “box-like” shape of electrical double layer capacitors.^{15,16} The XRD patterns are those typical of FCC platinum,¹⁴ and show platinum diffraction peaks at $2\theta = 39.6^\circ$, 47.2° , and 73.4° corresponding to the (111), (200) and (220) crystallite faces respectively; as well as a carbon (002) diffraction peak at 22.5° . These diffraction peaks are observed for all samples discussed in this chapter. The spectra also reveal stronger peaks for the CVD-deposited platinum, indicating that the CVD method results in more platinum being directly deposited onto the support material, while there is loss of platinum using the WI

method, probably due to less of the precursor being reduced by the reducing agent. The measured ECSA values for the CVD- and WI-deposited platinum are 19.0 and 1.55 m²/g respectively; values in agreement with the CV profiles.

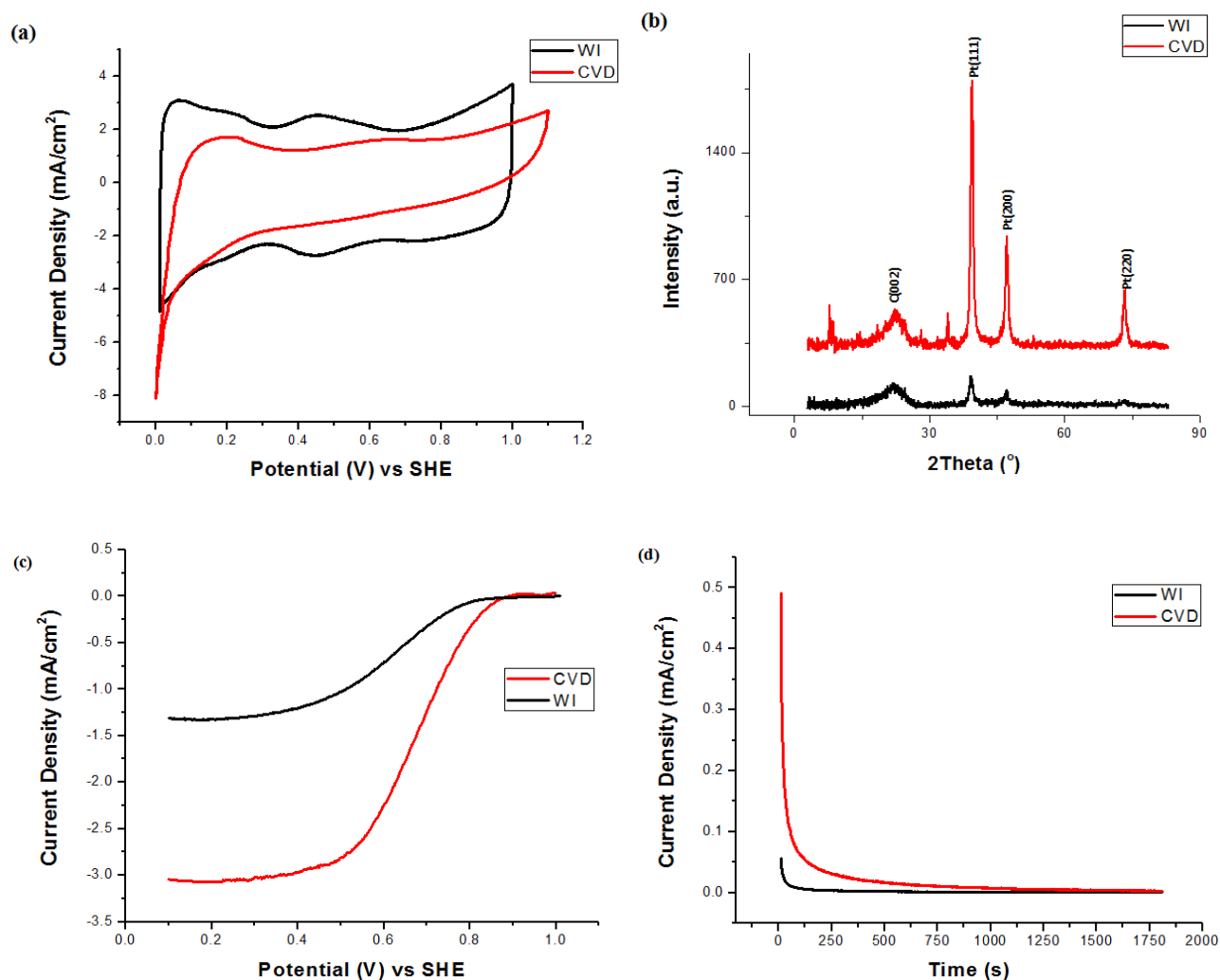


Figure 6.2: (a) CV profiles, (b) XRD spectra, (c) LSV scans, and (d) chronoamperometry measurements for WI- and CVD-deposited platinum

The LSV scans conform to the observed trend as per the calculated ECSA values. Firstly, the observed onset of the reduction reaction are at approx. 0.85 and 0.80 V for the CVD- and WI-synthesized catalysts respectively, but the diffusion limited current densities are quite different at -3.10 and -1.30 mA/cm² for the respective catalysts. From the chronoamperometric measurements (*figure 6.2d*) the CVD-synthesized catalyst exhibits a much higher initial current density (0.5 mA/cm²) than the WI-synthesized catalyst (0.05 mA/cm²); a trend in agreement with the calculated ECSA as well as LSV data. The

chronoamperometric curve for the WI-synthesized material is steeper than for the CVD-synthesized, indicating that the current decay for the CVD-synthesized catalyst is slower, and the Pt within this catalyst more electrochemically stable. Despite these observations, by the end of the measurements (after 1800s), the current for both catalysts have completely decayed (final current density = 0 mA/cm²).

6.3.2.2 Effect of Hollow Carbon Sphere (HCS) Size

The catalysts were loaded on top of hollow carbon spheres synthesized using either RF or toluene as a carbon source. The metal nanoparticles were loaded using the CVD method, and PtCl₂ was used as a platinum source. The results are illustrated in *figure 6.3*. The profiles of the CV curves of the different catalysts (*figure 6.3.a*) show the typical Pt-C CV profile. It is, however, evident that the RF-supported catalyst shows a greater capacitance; a result which is expected as per *section 5.5*. As mentioned earlier in this dissertation, the motivation for decreasing the size of the carbon supports was to reduce the amount of carbon present on the electrode. Therefore, the catalyst powder (1.00 mg) used to make the catalyst ink, would contain more platinum in the smaller spheres than in the powder with the bigger spheres, resulting in a larger ECSA being measured for the small HCS-supported platinum. The ECSA values are 43.8, 14.9, and 6.48 m²/g for the tol-PtCl₂_top-s, tol-PtCl₂_top-b, and RF-PtCl₂_top-s catalysts respectively. This HCS size effect is reiterated by the fact that although the Pt on the larger toluene-synthesized HCSs is smaller in size (4 nm) than on the smaller ones (6 nm), the platinum on the smaller spheres is still more active; emphasizing that in this case the size of the support takes precedent over the size of the platinum.

The XRD patterns for these catalysts (*figure 6.3.b*) are in agreement with the CV data, where it is evident that compared to the other two catalysts, the peaks for platinum supported on the bigger HCSs are less intense. The XRD spectrum for the RF-PtCl₂_top-s catalyst shows an extremely weak peak for carbon (002), thus making the peak appear to be absent, and leading to a very low intensity compared to the other two catalysts. According to the LSV scans the diffusion limited current density values are approx. -3.10, -3.50, and -2.35 mA/cm² for the tol-PtCl₂_top-s, RF-PtCl₂_top-s, and tol-PtCl₂_top-b catalysts respectively. The reaction onset potential (indicated by the potential at which the LSV curve begins its descent) for the RF-PtCl₂_top-s catalyst is not only closer to the theoretical value of 0.900 mA/cm², it also

occurred earlier than the other two catalysts, indicating that the reaction kinetics on the RF-carbon appear to be better, which could be as a result of the RF-carbon being more porous than the toluene counterpart.

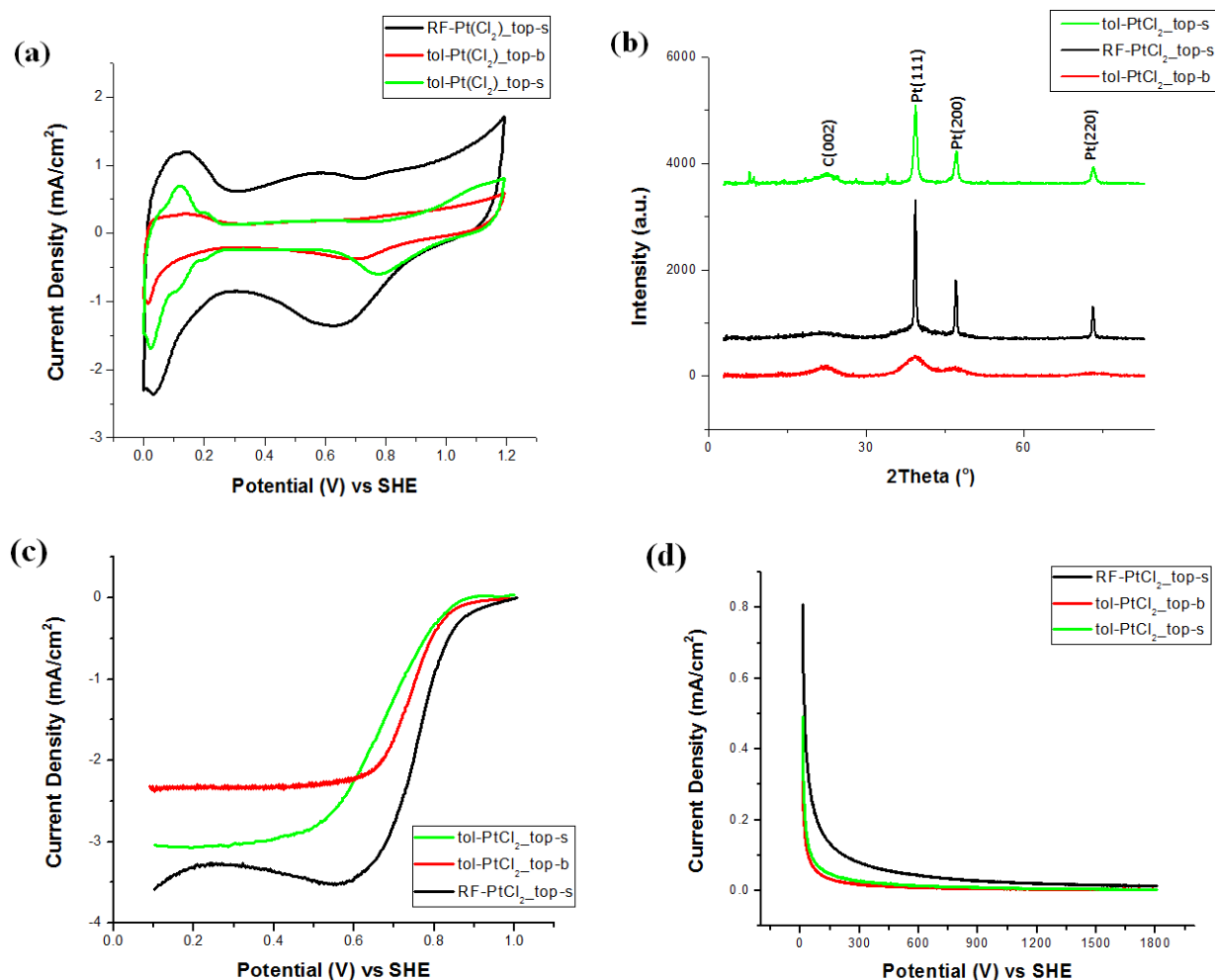


Figure 6.3: (a) CV profiles, (b) XRD spectra, (c) LSV and (d) chronoamperometric measurements of various catalysts as a function of carbon support size

The chronoamperometric measurements indicate that the RF-synthesized catalyst has the highest initial current (0.80 mA/cm²), and has a final current of 0.020 mA/cm²; which is 1.25% of the initial current. The tol-PtCl₂_top-s and tol-PtCl₂_top-b catalysts have initial current densities of 0.50 and 0.32 mA/cm² respectively, and they have both decayed completely by the end of the measurements. From the slopes of the chronoamperometry scans, the order of Pt stability follows the expected order: RF-PtCl₂_top-s > tol-PtCl₂_top-s > tol-PtCl₂_top-b.

6.3.2.3 Effect of Platinum Precursor

The platinum from the two different sources was loaded on top of the small RF- or toluene-synthesized HCSs using the CVD method. *Figure 6.4* illustrates the results. As before, the RF-supported catalysts exhibit superior capacitance to the toluene-supported counterparts. All the CV curves possess the typical CV profile for Pt-carbon catalysts, with only slight differences in the ECSA values between the Pt(acac)₂ and the PtCl₂-synthesized catalysts. It does, however, appear that the RF-supported PtCl₂ synthesized catalyst has a slightly higher ECSA value with more pronounced H₂ adsorption-desorption peaks than for the toluene-synthesized catalysts. The ECSA values for the tol-Pt(ac)_top, tol-Pt(Cl₂)_top, RF-Pt(ac)_top and RF-Pt(Cl₂)_top are 54.6, 43.8, 7.75, and 6.48 m²/g respectively.

Another interesting observation was made for the tol-Pt(ac)_top catalyst. In this CV profile, a small anodic peak in the double layer region (at approx. 0.60 V) is present. This peak has also been reported by Zhan *et al* in a paper that reviewed H₂ adsorption/desorption on platinum electrodes.¹⁷ The explanation given for the presence of this additional H₂ desorption peak is suggested to be the spillover of hydrogen atoms from the Pt surface to the surrounding material, which in the current study is the carbon support. The desorption of these hydrogen atoms from this surrounding material is what causes the additional desorption peaks.¹⁷ This observation has implications for hydrogen storage capabilities of materials¹⁸ as well Pt-stability during the ORR reaction.¹⁹

The XRD spectra for all four catalysts show that although the platinum peaks seem to be identical, the RF-carbon peaks are slightly weaker than the toluene-carbon peaks. This speaks to the fact that the toluene-carbon is more crystalline in nature than the RF-carbon; which is in agreement with Raman data (see *section 5.4.2.3*). The onset potentials for the ORR measured using LSV for the tol-Pt(ac)_top, tol-PtCl₂_top, the RF-Pt(ac)_top, and RF-PtCl₂_top are 0.90, 0.85, 0.88 and 0.88 V; while the diffusion limited currents are -7.5, -3.1, -3.5 and -3.7 respectively. The tol-Pt(ac)_top catalyst, which has the highest ECSA value appears to be the best performing catalyst for the ORR. The chronoamperometry measurements show that the overall current decays for the tol-Pt(ac)_top, tol-PtCl₂_top, RF-Pt(ac)_top, and RF-PtCl₂_top catalysts are 100, 100, 87, and 98.8%; showing that the platinum in the RF-Pt(ac)_top catalyst is the most electrochemically stable; although not by a great margin.

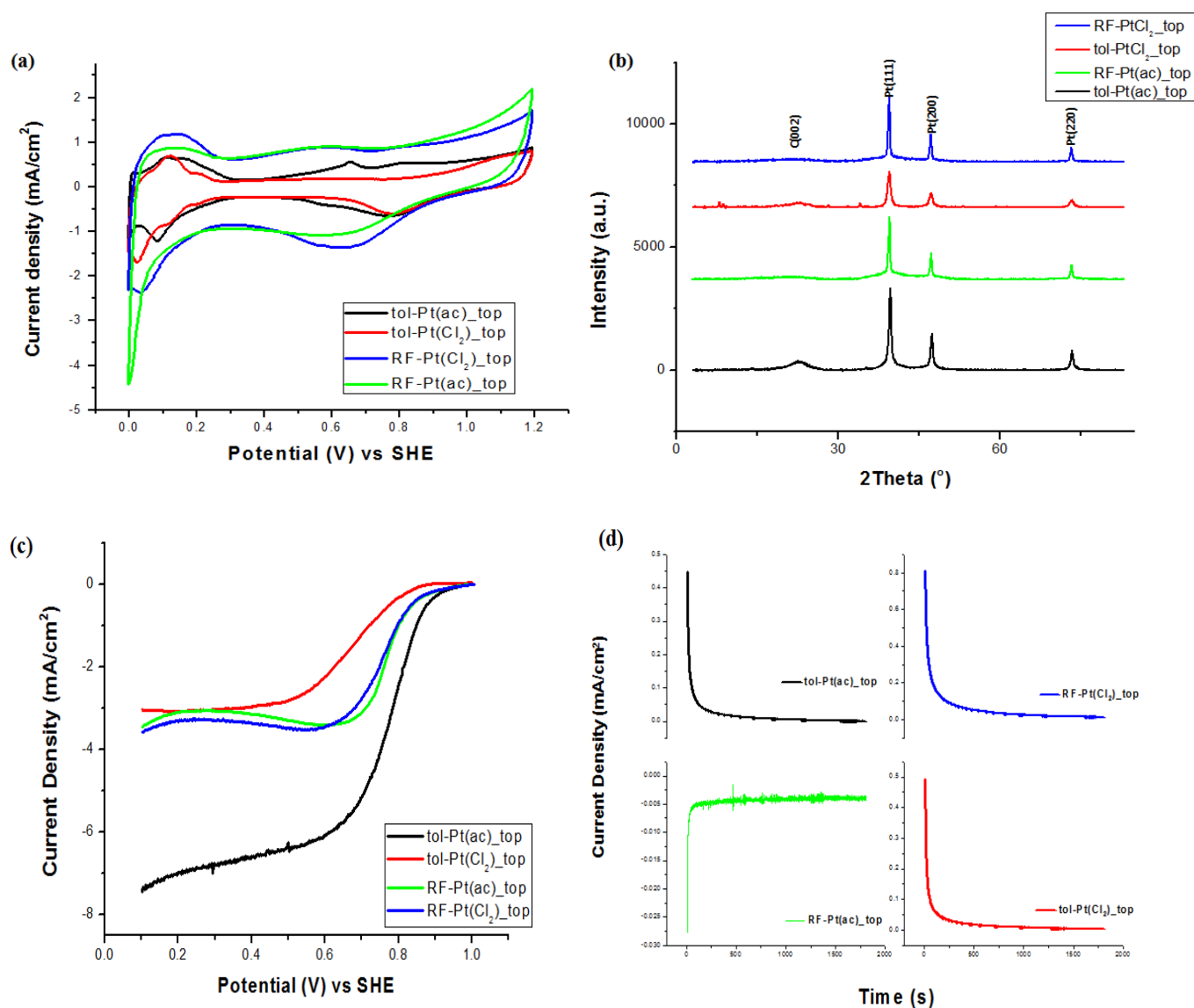


Figure 6.4: (a) CV profiles, (b) XRD spectra (c) LSV and (d) chronoamperometric measurements of different catalysts as a function of Pt-precursor type

6.3.2.4 Effect of Platinum Location

The platinum was loaded via the CVD deposition method using Pt(acac)₂ as the platinum precursor. The CV curves for all the catalysts adhere to the typical Pt-carbon CV profile, with the tol-Pt(ac)_top catalyst having the most pronounced H₂ adsorption-desorption peaks. The results are illustrated in *figure 6.5*.

In this case, the tol-Pt(ac)_inside catalyst has a larger capacitance than even the tol-Pt(ac)_top catalyst. A hypothesis for this is that because the platinum is on the inside of the HCS, during

CV measurements more of the carbon's capacitance, rather than the Pt's electrochemically active surface, is being detected. The XRD spectra reiterate this fact, whereby the tol-Pt(ac)_inside catalyst has a stronger carbon peak than the RF-Pt(ac)_top catalyst, but weaker Pt diffraction peaks than both the "top" catalysts. The measured ECSA values for the tol-Pt(ac)_top, tol-Pt(ac)_inside, and RF-Pt(ac)_top catalysts are 54.6, 38.6, and 7.75 m²/g respectively; values in agreement with the CV curves.

As per the LSV measurements, the reaction onset potentials for the tol-Pt(ac)_inside, tol-Pt(ac)_top, and the RF-Pt(ac)_top catalysts are 0.90, 0.90, and 0.88 V respectively; while the diffusion limited currents for each respective catalyst is -6.20, -7.50, and -3.50 mA/cm², confirming that in terms of activity for oxygen reduction, the tol-Pt(ac)_top catalyst is the best performer. In this case, all the Pt nanoparticles have an average diameter of 3 nm, and yet the catalysts loaded on toluene-synthesized HCSs show higher activity; reiterating that here it is the type of carbon rather than the size of the Pt that is determinant of the catalysts' activity. The top-loaded platinum is more electrocatalytically active than the platinum loaded on the inside surface of the HCSs. This could be as a result of some of the active sites of the platinum loaded on the inside being blocked by carbon during the carbonization process, thus resulting in less available reaction sites during oxygen reduction.

The chronoamperometric measurements reveal that the platinum supported on the inside of the HCS is the most stable, with a total current decay of 59%, while the other two catalysts show 100% decay by the end of the 1800 seconds. This of course can be attributed to the core@shell structure of the catalyst. There are a few possible explanations as to why the platinum loaded on the outside of the HCSs is less stable:

Firstly, corrosion of the carbon support could be occurring during chronoamperometry measurements. That is, the carbon support on which the platinum nanoparticles could be deteriorating as a result of the oxidizing conditions of the reaction environment. When the platinum is on top of the corroding support, this would in turn result in the instability of said supported catalysts.²⁰ This is an observation that was observed by Arenz *et al*,²¹ where carbon support corroded when held at a constant potential under oxidizing conditions. The platinum on the inside surface of the HCSs would be affected by this to a lesser extent, because

corrosion would occur from the outside shell, and so the platinum on the inside would stay stable for longer.

Another possibility is that particle agglomeration could be taking place. The corrosion of the carbon support would force the platinum particles closer together on the surface of the support, and thus result in the coalescence of the platinum nanoparticles.²² Again the platinum on the inside surface would agglomerate at a much slower rate, remaining disperse for a longer period of time.

Lastly, the detachment of the particle nanoparticles could be taking place, also as a result of the corrosion of the carbon support. As the support deteriorates, this would result in the weakening of the interaction between the carbon and the loaded platinum. As this interaction is weakened, the platinum becomes rather unstable and detaches from the support altogether.²³ This itself could lead to particle agglomeration. The platinum on the inside shell would stay attached to the support longer, thus benefiting from the supports stabilizing effects for a longer period of time.

The chronoamperometry profiles for the tol-Pt(ac)_inside and RF-Pt(ac)_top (*figure 6.5 (d)*) show a sharp increase at the beginning of the experiments. This initial increase could be due to the adsorption of intermediates during produced during the reaction. These intermediates could potentially poison the catalyst explaining any decline in electrocatalytic activity,²⁴ and this behaviour has been reported for chronoamperometric measurements performed in alcohol electrolytes.²⁵

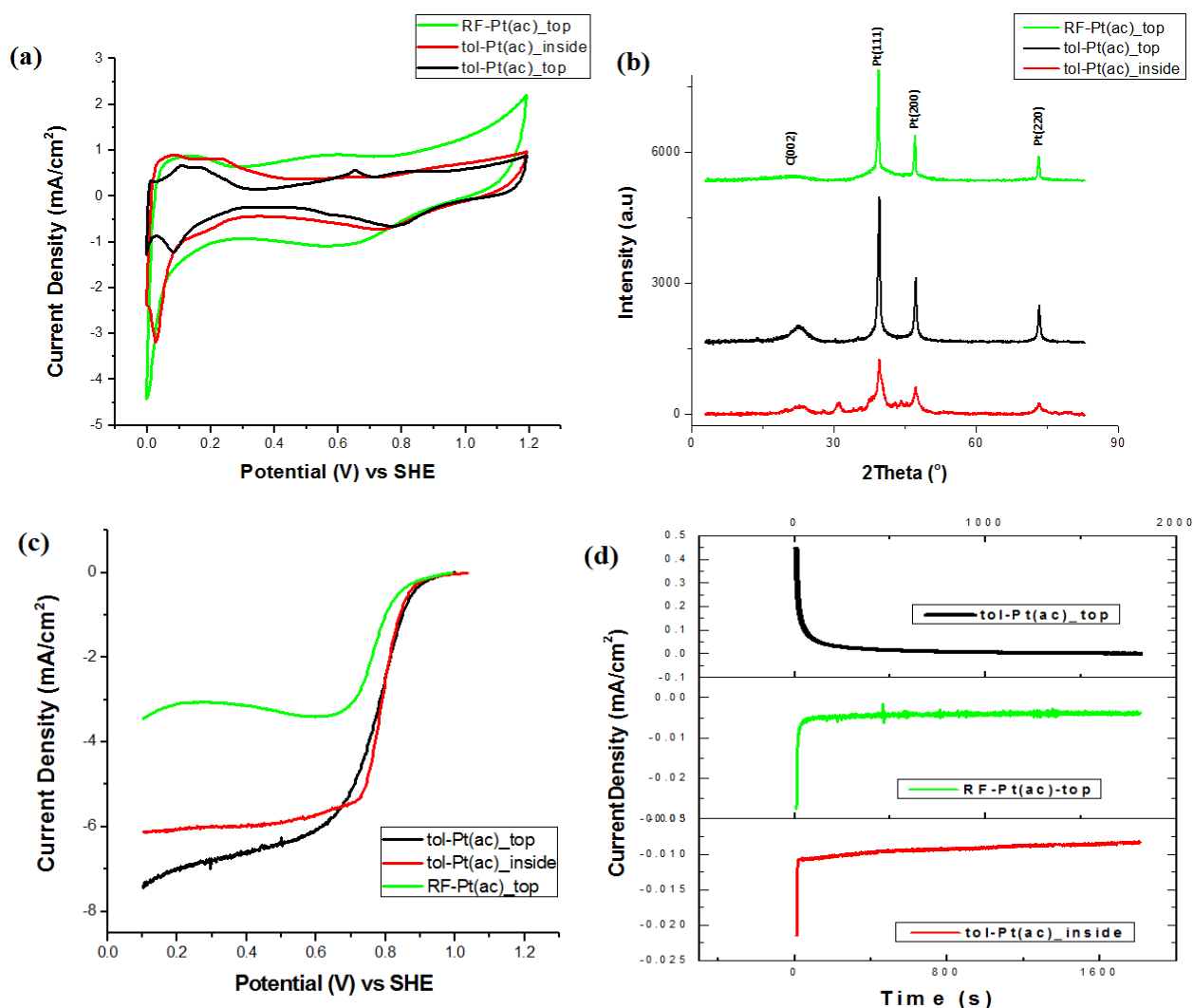


Figure 6.5: (a) CV profiles, (b) XRD spectra, (c) LSV and (d) chronoamperometric measurements of various catalysts as a function of Pt location

6.3.2.5 Effect of Scan Rate

At higher scan rates, charging current may hide important information that would otherwise be present in the CV curves if a slower scan rate were to be used. The aim in this section was to discover whether or not the scan rate used has an effect on not only the features present in a given CV profile, but also on the current density range that the CV would span. Measurements were taken at 10 and 100 mV/s, comparing catalysts loaded via the CVD method on small size toluene-synthesized HCSs using either PtCl₂ or Pt(acac)₂ as the Pt precursor. The results are shown in figure 6.6.

It is quite noticeable from the CV profiles that the scans recorded at the slower rate possess more information than those recorded at the faster scan rates. This is evidenced by the fact that there are peaks present in the slow rate scans that are absent from the faster counterparts. The peaks for the slower scans are also noticeably more refined.

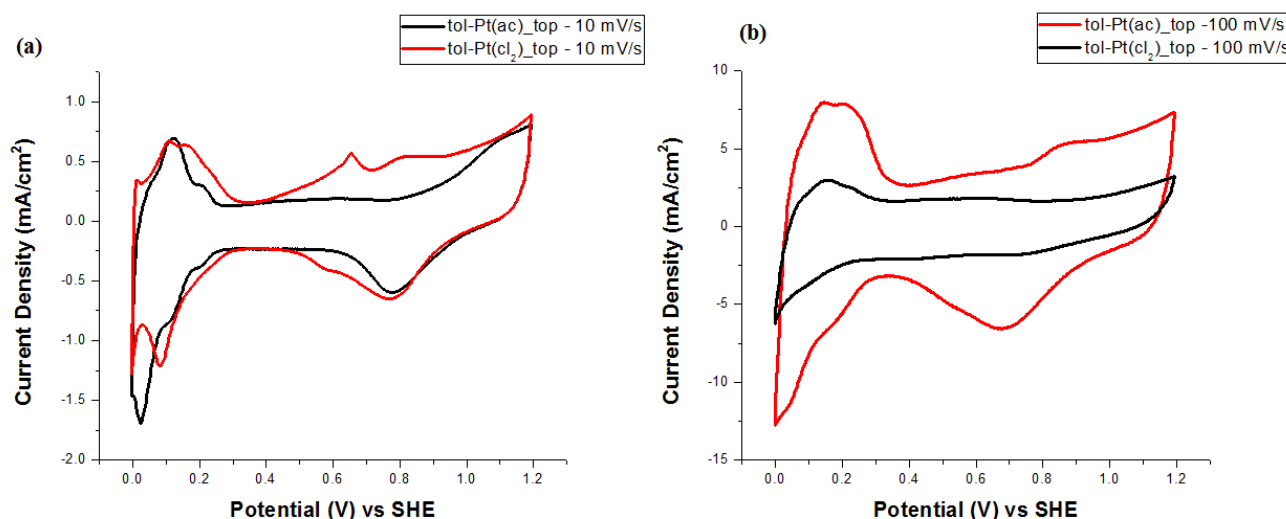


Figure 6.6: CV profiles of various catalysts as a function of scan rate and Pt precursor; scan taken at (a) 10 mV/s, and (b) 100 mV/s

Some factors that influence the profile of a cyclic voltammogram include the size of the diffusion layer above the electrode's surface, and the time taken to record a given scan. The slower the scan rate, the further away from the electrode the diffusion layer grows, and the smaller the flux of reactants to the electrode's surface. Since the current is proportional to this flux, the current density range which the CV scan spans will consequently be smaller. From *figure 6.6*, it is evident that the CVs recorded at the faster rate (*6.6b*) span a larger current density. A general observation was also made whereby the Pt(acac)₂-catalyst seems to perform better than the PtCl₂ catalyst; an observation which has been the consensus throughout the current chapter.

It can, therefore, be concluded that the voltage scan rates, and therefore the time taken to record a given voltammogram, strongly effects the profile of a CV; more specifically the current density range the CV profile will span.

6.5 Activity Comparisons with a Commercial Catalyst

The following section compares the catalytic activity for the oxygen reduction reaction of the best performing synthesized catalysts from the previous sections with a commercial catalyst typically used in fuel cells. The synthesized catalysts are the tol-Pt(ac)_top and the tol-Pt(ac)_inside catalysts; chosen because they far surpassed all the other synthesized catalysts in the oxygen reduction reaction; and the commercial catalyst is a 40 wt% Pt/C catalyst composed of platinum loaded on a Vulcan XC-72 carbon. Although there are differences in electrocatalytic activity between the three catalysts, these differences are not large.

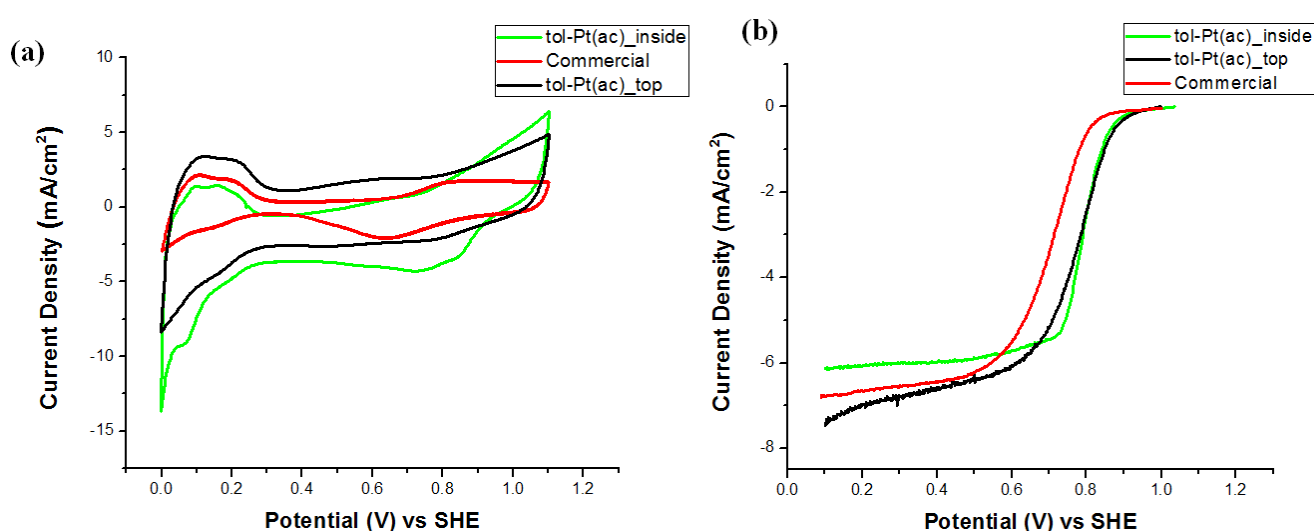


Figure 6.7: (a) CV scans and (b) LSV measurements comparing the synthesized tol-Pt(ac)_top, tol-Pt(ac)_inside, and the commercial Vulcan Pt/C catalysts

The ECSA values calculated from the CV curves for the tol-Pt(ac)_top, tol-Pt(ac)_inside, and commercial catalysts are 54.6, 38.6 and 42.6 m²/g respectively. A similar ECSA value (42.5 m²/g) for the commercial catalyst has been reported in the literature.²⁶ From the LSV scans, the onset potentials are 0.90, 0.90 and 0.80 V for the tol-Pt(ac)-top, tol-Pt(ac)_inside, and commercial catalysts respectively; while the diffusion current densities for the respective currents are -7.5, -6.2 and -6.8 mA/cm². It is clear that the platinum loaded on the toluene-synthesized hollow carbon spheres using the CVD method and Pt(acac)₂ as a Pt precursor is a better catalyst for the reduction of oxygen, than even the typical commercial catalyst. A possible explanation for the superior limiting current density could be improved mass transfer when hollow carbon spheres are used as a support.^{14,27} Our results resemble those obtained by

Yan *et al*¹⁴ who measured diffusion limited current of *c.a.* -7.2 mA/cm², a result comparable to that of the current study (-7.5 mA/cm²) and also better than a Pt/C catalyst where platinum was loaded onto Vulcan XC-72.

The platinum in the core@shell structure is the worst performing catalyst of the three. As stated earlier in this chapter, the carbon shell could be blocking active sites on the catalyst, or acting as a barrier for reactants; both of which would result in an overall decreased activity of the platinum.

Found below are tables summarizing all the electrochemical data discussed in all the above sections:

Table 6.2: Summary of Cyclic Voltammetry Measurements

	Sample	Pt Average Particle Size (nm)	Electrochemical Surface Area (m²/g)
1	tol-Pt(ac)_inside	3.0	38.6
2	tol-Pt(ac)_top	3.0	54.6
3	tol-PtCl ₂ _top	6.0	43.8
4	RF-Pt(ac)_top	3.0	7.75
5	RF-PtCl ₂ _top	5.0	6.48
6	tol-PtCl ₂ _top-b	4.0	14.9
7	WI	4.0	0.25
8	Commercial	3.0	42.6

Table 6.3: Summary of Linear Sweep Voltammetry Measurements

	Sample	Onset Potential (V) vs. SHE	Diffusion Limited Current Density (mA/cm ²)
1	tol-Pt(ac)_inside	0.90	-6.20
2	tol-Pt(ac)_top	0.90	-7.50
3	tol-PtCl ₂ _top	0.85	-3.10
4	tol-PtCl ₂ _top-b	0.84	-2.35
5	RF-PtCl ₂ _top	0.88	-3.70
6	RF-Pt(ac)_top	0.88	-3.50
7	WI	0.80	-1.30
8	Commercial	0.80	-6.80

Table 6.4: Summary of Chronoamperometric Measurements

	Sample	Initial Current Density (I ₀) (mA/cm ²)	Final Current Density (I _f) (mA/cm ²)	Overall Current Decay (%)
1	tol-Pt(ac)_inside	-0.022	-0.009	59
2	tol-Pt(ac)_top	0.30	0	100
3	tol-PtCl ₂ _top	0.50	0	100
4	tol-PtCl ₂ _top-b	0.32	0	100
5	RF-PtCl ₂ _top	0.80	0.02	98.8
6	RF-Pt(ac)_top	-0.028	0.004	87
7	WI	0.05	0	100

Overall conclusions noted from this chapter are that:

- When deposition of Pt is carried out using the CVD method, $\text{Pt}(\text{acac})_2$ allowed for better dispersed Pt nanoparticles with smaller size, irrespective of the kind of support used.
- The CVD method resulted in more electrocatalytically active platinum.
- RF-synthesized HCSs still showed higher capacitance as per *chapter 5*; this is evident in their CVs which spanned greater current density ranges.
- Using the CVD method to load platinum using $\text{Pt}(\text{acac})_2$ on the inside surface of the small size toluene-synthesized hollow carbon spheres makes for a more stable catalyst.
- Placing the catalyst on top under the same conditions makes for a more active catalyst; even more active than the commercial catalyst. This catalyst, however, does not possess very good long term stability.
- The determinant factor for high catalyst activity appears to be the type of carbon used, as well as the size of the HCSs rather than the size of the Pt nanoparticles.

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CHAPTER 7:

OVERALL CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The aim of the study was to synthesize platinum-carbon catalysts using different carbonization and metal-deposition techniques, with platinum loaded either on the inside or outside surface of hollow carbon spheres. These platinum-carbon composite structures were applied as electrocatalysts for the oxygen reduction reaction. TEM, TGA, Raman, BET, XRD, and various electrochemical techniques were employed in order to draw the following conclusions:

In attempting to form solid-core/mesoporous-shell silica spheres, C18-TMS was found to be the preferred surfactant as it formed more distinct mesoporous layers than the CTAB surfactant. C18-TMS also allowed for deposition of better dispersed platinum on the silica templates.

The CVD method was found to be an easier method for depositing high loadings of Pt using less platinum/mg with better dispersion compared to the WI deposition method. Also, $\text{Pt}(\text{acac})_2$ as a metal precursor resulted in smaller and better dispersed Pt nanoparticles compared to PtCl_2 as the precursor when the CVD method was used for Pt deposition. These findings were observed when Pt was deposited on either the silica template or directly onto the HCSs.

Comparing the bubbling and nanocasting methods for carbonization of the silica templates revealed that both methods are successful, irrespective of the template size. It was, however, found that the bubbling method allowed for better emulation of the template's shape. It was further found that toluene as a carbon source made for a more thermally stable and more graphitic carbon framework, due to the fact that the carbon framework of the RF-synthesized

HCSs possessed more defects. Furthermore, the toluene-synthesized HCSs had thicker more well-defined carbon shells.

The resorcinol RF carbon, on the other hand, showed superior capacitance to their toluene-synthesized counterparts due the higher specific surface area of the RF-carbon. This feature was retained following the loading of Pt onto the HCSs. Loading Pt using the CVD method on the inside surface of toluene-synthesized HCSs using $\text{Pt}(\text{acac})_2$ as the metal precursor resulted in the most electrocatalytically stable catalyst, while Pt loaded on top of HCSs under the same conditions gave the best performance; better even than the commercial catalyst.

7.2 Recommendations

Since Pt loaded inside toluene-synthesized HCSs showed such great electrocatalytic stability, attempts to make this catalyst more active are of primary interest. One method to achieve this could be to place the metal on both the inside and the outside of the HCSs simultaneously.

In our laboratories, nitrogen-doped carbon nanospheres have been synthesized, and show increased photocatalytic activity. To this effect, another approach could be to introduce heteroatoms, such as nitrogen or boron, into the HCS framework themselves (i.e. heteroatom doping). This would effectively make the carbon shells more electronically active (in terms of electron transfer), and hopefully add enhance the activity of the encapsulated Pt.

The application of the catalysts from this study in PEM fuel cells still requires a better understanding of their *ex situ* electrocatalytic behaviour. The current study reported extensively on the procedures involved in synthesizing the different catalysts. It will be beneficial in future to concentrate largely on studying mainly the electrochemical aspects (i.e. employ more advanced electrochemical analyses) of the catalyst in order to synthesize a catalyst best suited for application in low temperature fuel cells. Once these catalysts have been extensively studied *ex situ*, *in situ* tests then need to be completed in order to confirm the validity of the catalysts.