The Synthesis and Evaluation of Novel Core / Shell Nanoparticles Catalysts

A thesis submitted to the University of Manchester for the degree of doctor of

philosophy

in the Faculty of in the Faculty of Engineering and Physical Sciences.

2016

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Abstract

This thesis focuses on core/shell nanoparticle catalysts including preparation, characterization and testing performance using direct methanol fuel cell. Core/shell were prepared using noble and non-noble metals. Also some core/ shell nanoparticles supported on silica and different types of carbon were prepared as well in this thesis.

Non-noble core/shell nanoparticles including novel Co/Ni, SiO₂/Ni using three types of silica and novel SiO₂/CoFe were prepared by a new modified sol-gel method using hydrazine in alkali media as the reducing agent to reduce metal chloride through two steps process. Parameters such as temperature, pH of solution and reducing agents, were seen to be of great importance in deciding the morphology of the final product as well as the structure of the core/shell catalyst. Core/shell nanoparticles have been successfully prepared for Co/Ni and SiO₂/CoFe for first time by choosing the right parameters. This study presents the unique structure which has not been obtained previously for SiO₂/Ni catalyst using commercial silica as core. A novel halo shaped structure was the common feature in the catalysts prepared as indicated by TEM.

This study presents as well noble Ru/Pt core/shell nanoparticles supported on three types of carbon by a new modified polyol method for first time. The author of this work is not aware of any studies that have prepared Ru/Pt on carbon powder ≤ 50 nm and Ru/Pt on CMWNT previously. This work presents special structure (crown- jewel shaped) for Ru/Pt on Vulcan XC-72 carbon which was not obtained previously for the same catalyst. Selected catalysts were tested using a direct methanol fuel cell.

SiO₂/Pt core/shell nanoparticles were prepared for the first time by two different methods, namely a new modified sol-gel and polyol methods with novelty structures halo and crown- jewel shaped respectively. Based on the particles size obtained from TEM images, the modified polyol method seems to have a much greater impact on the particles size than the modified sol-gel method. Based on these findings Ru/Pt, Ru/Pt supported on three different types of carbon and Pt supported on CMWNT were prepared using the new modified polyol method.

Pt on CMWNT catalyst was synthesized for the first time successfully by a new modified polyol method and all the particles were found to be well dispersed with a narrow size distribution of an average particles size of 3nm. This catalyst gave promising results on DMFC.

Pt supported on CMWNT and Ru/Pt supported on Vulcan and CMWNT were used for the first time as electro-catalysts in DMFC to study the effect of the support on the catalytic activity of catalysts. The results show that Ru/Pt on CMWNT gives better performance than the unsupported Ru/Pt and Ru/Pt on Vulcan XC-72. Using Ru/Pt on CMWNT with higher methanol concentration (anode feed) improved the fuel cell power density when compared with the RuPt commercial catalyst.

Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university, or other institute of learning.

Hanan Albalwi January 2016

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Acknowledgement

I would first like to thank Dr Stuart Holmes for his guidance, support and encouragement throughout the time it has taken to complete this document.

The staff at the University of Manchester have been a great help and I would like to thank anybody who has lent me a helping hand but special thanks go out to Dr Patrick Hill for all his help with SEM and TEM analysis.

For all their understanding and continued support I would like to thank my fellow PhD students who have tried to help me out if I got stuck or too anxious; especially Mr, Sirhan Al Batty and Mr, Prabhuraj Balakrishnan.

Huge appreciation goes out to my family especially my kids and my sisters Om Fisal an Om Turky and my best friends especially Lieth Alkhafaji and Fozia Alharby, thanks all for putting up with me during the bad times and helping me enjoy the good ones. Dedicated to my kids Abdulrahman, Shaden, Lama, Wasan and Almas, my mum, my brothers and sisters.

List of Abbreviation AFC	Alkaline fuel cell
C_2H_6O	Ethanol
СНР	Carbon nanotube
CMWNT	Combined heat and power
CoCl ₂	Cobalt Chloride
CV	Cyclic voltammetry
DMFC	Direct methanol fuel cell
EG	Ethylene glycol
FeCl ₂	Iron chloride
GDL	Gas diffusion layer
IPA	Iso propanol
MCFC	Molten carbonate fuel cell
MEA	Membrane electrode assemblies
NaBH ₄	Sodium borohydride
$Na_3(C_6H_5O_7)$	Trisodium citrate
C ₆ H ₇ NaO ₇	Sodium Dihydrogen Citrate
NaOH	Sodium hydroxide
N_2H_4	Hydrazine
NH ₄ Cl	Ammonium chloride

NiCl ₂	Nickel chloride
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
PAFC	Phosphoric acid fuel cell
PtCl ₂	Platinum chloride
PEMFC	Proton-exchange membrane fuel cell
PROX	Preferential oxidation of carbon monoxide
PTFE	Polytetrafluoroethylene
PVP	Polyvinyl pyrrolidone
RuCl ₃ .nH ₂ O	Ruthenium chloride
SEM	Scanning electron microscopy
SiO ₂	Silica dioxide
SOFC	Solid oxide fuel cell
TEG	Triethylene glycol
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TOAA	Titanium oxide acethyl acetonate

Introduction and objectives

A special form of bimetallic catalysts that have been receiving great attention recently, are those having a core/shell nanostructure. These nanostructures consist of core made of inorganic materials such as metal or metal oxide or silica or organic materials surrounded by another inorganic or organic material as the shell. These structures have an abundance of applications in areas such as catalysis, electronics, sensors and optical devices.

The main problem with using precious metals such as platinum based catalyst in direct methanol fuel cell (DMFC) application is the high price. Therefore, the core/shell structure might provide an opportunity to reduce the amount of precious metal and reduce the cost of catalyst.

In general, the bimetallic core/shell nanoparticles are synthesized through the reduction of metal salts by simultaneous or successive reduction using different techniques and reducing agents.

In this thesis, we used sol-gel and polyol methods to prepare core/shell nanoparticles. It is hoped that by modifying the existing techniques for the formation of the core/shell nanostructures, this project can reduce the cost of precious metals catalyst and at the same time improve the performance of a direct methanol fuel cell (DMFC).

In the sol-gel method, hydrazine in alkali media was used as the reducing agent to reduce metal chloride through two steps process. While in polyol method, we used alcohol containing two or more hydroxyl group to act as both a solvent and reducing agent at high temperature. These processes do not need expensive equipment, something which can minimize production cost, are a simple processes to apply in the lab and they can be modified to produce different materials. For these reasons, these method was used in this research to prepare core/ shell nanoparticles catalysts.

The work reported herein has focussed on the testing the performance of catalysts prepared by using direct methanol fuel cell (DMFC) to study the effect of temperature and concentration of methanol on the performance of fuel cell. The voltage, current density and power density were used as a measure of DMFC performance under a range of methanol molarities (1M, 2M and 4M) and cell temperatures (40°C - 80°C).

Outline of Thesis

Chapter 1: Literature review of catalysts importance and their usage. This chapter is divided into four main parts: general introduction, the importance of catalysts in the chemical industry, the requirements of an industrial catalyst, classification of catalysts, forms of catalysts and the last part is dedicated for the core/shell bimetallic nanoparticles.

Chapter 2: Focuses on the processes and methods used for the synthesis of core/shell structures and applications of core/shell nanoparticles. This chapter deals with the sol-gel and polyol methods that are used in this study and discusses some studies that have used these methods in the synthesis of core/shell nanoparticles catalysts together with their applications such as in fuel cell.

Chapter 3: Focuses on the fuel cell including types of fuel cell, with special emphasis on the direct methanol fuel cell (DMFC), together with the effect of temperature, pressure, feed flow rate and concentration on the catalytic performance of DMFC.

Chapter 4: Is dedicated to the different methods used for the synthesis of core/shell bimetallic catalysts involved in this study. This chapter also includes a description of the fuel cell set up used.

Chapter 5: Shows the results obtained from characterization of the prepared catalysts. This chapter also includes the results and discussion on the performance of some core/shell catalysts prepared using the direct methanol fuel cell (DMFC).

Chapter 6: offers conclusions that can be taken from this study and offering recommendations for future work.

CHAPTER ONE

LITERATURE REVIEW

1. CHAPTER 1: CATALYST

1.1.General Introduction

1.1.1 Definition of Catalyst

A catalyst is a substance which plays an important role in a chemical reaction but is not consumed by the reaction. In order for chemicals to react, the reactants must undergo a rearrangement of chemical bonds and new bonds will form to give products. This process is done through several steps; the slowest one in the bond rearrangement produces the rate determining step. Energy is required to form the transition state called the Energy of Activation (E_a). The reactants which have energy lower than E_a cannot pass through the transition state to react and become products. A catalyst works by providing an alternative pathway with increased rate of reaction and decreased energy of activation E_a without becoming part of the product (Figure 1-1) [1].



Progress of the reaction

Figure 1-1. Graph to highlight the activation energies of uncatalysed and catalysed reactions

1.1.2 Steps Involved in Surface-Catalyzed Reaction

Surface-catalysed reactions involves physical and chemical interactions between the species in the fluid (i.e. gaseous or liquid) phase and the catalytically active surface regions or what are called as active sites. Due to these interactions the reaction is offered an alternative path which is more favourable with a lower activation energy and hence proceeds with a higher rate than in the homogenous phase.

The elementary steps involved in a heterogeneously catalysed reaction are in principle well known. These include adsorption and desorption steps and surface migration as well as reactive and nonreactive interactions between the surface species [2]. The individual steps involved in a heterogeneously catalysed reaction could be summarized as follows:

- 1. Diffusion of the reactants to the surface of the catalyst.
- 2. Adsorption of the reactants onto the surface of the catalysts, usually slow if activated.
- 3. Surface reaction between the adsorbed species.
- 4. Desorption of the products from the catalyst surface.
- 5. Diffusion of the products away from the catalyst surface.

If the mass transport (diffusion) of reactants or products is not a limiting factor for the reaction, then it can be said that for a given catalyst the rate of reaction will be only a function of temperature and of the concentrations of the species in the fluid. The steps as written, highlight the pivotal role played by the chemisorption of the reactants and products in determining the activity, selectivity and longevity of a given catalyst for a specific reaction.

1.1.3 Importance of Catalysis in Chemical Industry and the Environment

Catalysis is a very important and active area of research, which can have tremendous impact on the chemical industry. More than 90% of all chemical processes are controlled by catalysts [3]. Catalysts are made using various methods and continuous research has been carried out to search for the most efficient and cost-effective production. For example, zeolites play an important role in the petroleum industry. During the 1980s, production of fluid cracking catalysts was about 250,000 tons per year, and about 88% of these catalysts are zeolites [4]. Titanium oxide (TiO₂) is used for cleaning gaseous waste from industrial incinerators and other equipment that emits nitrogen oxides. The demand for Selective Catalytic Reduction catalysts of TiO₂ has been estimated to be 1 x 10^4 tons per year [5]. In 2005, it was estimated that the market for nanoparticle catalysts valued about US \$7.4 billion with a US \$8 to US \$68 billion projected market growth [6]. It was estimated that in 2006, products which were improved or developed through nanotechnology were worth US \$50 billion and were expected to rise to US \$2.6 trillion by 2016 [7]. However, a more recent study showed that the value to 2015 to be only US \$ 1 trillion with annual growth rate of 10.2% from 2015 to 2020 [8]. The refinery industry uses nanocatalysts in the "Platforming" of gasoline to increase its octane number, and this catalyst market is estimated to be around US \$100 million [6]. The photocatalytic properties of TiO₂ have gained much attention in research and the market is estimated to exceed US \$5 billion, in Japan alone [9].

The examples presented in Table 1-1, highlight the importance of catalysis in the fields of chemical industry and the environment.

Process	Catalyst used	Ref.
1- Partial oxidation of hydrocarbons		
• Oxidation of butane to maleic anhydride	V-P-O/SiO ₂	
• Oxidation of methanol	Fe-Mo-O	10,11
• Oxidation of ethylene	Ag-Alkali/ Al ₂ O ₃	
2- Cleaning the environment		
Automotive emission control	Pt-Rh-Ce-(Pd)-(La)/Al ₂ O ₃	
(3- way auto exhaust)		
• Dechlorination of water	Pd/Fe	10,12,13,
Hydrodesulfurisation	Mo-Co/Al ₂ O ₃	
• DeNOx	K_2CrO_4/Fe_2O_3	
3- Treatment of oil to produce better fuel		
Catalytic cracking	SiO ₂ -Al ₂ O ₃ /US-Y Zeolite	10,15,16
• Reforming	Pt/Al ₂ O ₃ , Ni/Al ₂ O ₃	
• Isomerisation	Pt/ Zeolite	
4- Synthesis of important chemicals		
Haber process (ammonia synthesis)	Fe promoted with K_2O , CaO and Al_2O_3	
Methanol synthesis process	Cu-Zn/Al ₂ O ₃	10,16
Fischer Tropsch	Fe-Co based	
Tischer Tropsen		
5- Polymerization		
Polypropylene	TiCl ₄ - MgCl ₂	7,10

Table 1-1: The importance of catalysis in chemical industry and the environment.

1.1.4 Requirements of an Industrial Catalysts

A catalyst has to meet stringent requirements before being used in an industrial process. Catalysts should be active, selective, durable and must be mass and heat transfer efficient [17]. These properties should be inherent in the catalyst so that its participation in the reaction will be significant. The surface area of the catalyst or to be more specific the surface area of the catalytically active surface regions, must be high and with minimum particle agglomeration [18]. The size of the particle is inversely proportional to its active surface, meaning, as the particle size decreases, the active surface increases and this results in more efficient reactions [19]. In general, nanoparticles, with very small size ranges (≤ 100 nm) have been attracting attention in important reactions such as the selective oxidation of carbon monoxide, due to their unique properties especially in terms of their catalytic activity and selectivity [20]. Catalysts with this particle size range for the active component/s are called nanocatalysts to distinguish them from other types of catalysts. Key to producing an efficient catalyst with desirable catalytic properties is the control of the particle size of the active component in the nano regime. The versatility and abundance of nanoparticle materials having different acid-base properties, together with their structural stability at elevated temperatures and being not cytotoxic make them good catalysts' materials [9].

1.2 Classification of Catalysts

Catalysts can be either homogeneous or heterogeneous. Homogeneous catalysts are those "dispersed in the same phase as the reactants, the dispersal being ordinarily in a gas or liquid solution" [21] while heterogeneous catalysts are in a different phase to the reactants [22]. Reactions involving gases used with solid catalysts are the most common form of heterogeneous catalysts, because these types of catalysts can be prepared more easily, more

controllably and give efficient yield. They are more convenient for commercial applications [23].

1.3 Forms of Catalysts

Table 1-1 showed that different forms of catalysts have been used in the chemical industry and/or cleaning the environment including, single oxides, binary and multi oxide systems as well as monometallic and bimetallic supported catalysts.

A special form of catalysts that have been receiving great attention those are called bimetallic catalysts due to their superior performances in terms of activities, selectivities, stabilities and resistance to poisons, when compared to their monometallic counterparts [24].

1.3.1 Bimetallic Catalysts

Bimetallic catalysts combine of two metallic elements to produce a new class of materials which have unique properties that are often different from their bulk [25]. They were first discovered in 1958; however, these kinds of catalysts started gaining commercial interest in 1960s [26]. This is when it was first used in hydrocarbon reforming in the petrochemical industry [27-29]. The most commonly used bimetallic catalysts comprise metals of group VIII and group IB and have been extensively studied e.g. Pd/Au, Ru/Au, Ru/ Mn, Ru/Cu [30,31]. In trying to interpret the mechanism by which modification of the catalytic behaviour of an active metal occurs by the addition of small amounts of another metal, two concepts have been introduced, namely, the 'ensemble' and the 'ligand' effects [24].

The 'ensemble' has been defined as the number of metal atoms present in a particular geometric orientation that are necessary for facilitating a particular catalytic process. The presence of such ensembles is thought to be necessary for the adsorption of the reactants.

Disruption of such ensembles by the addition of another metal will have an impact on the catalytic behaviour of the catalyst under investigation [24, 32].

The 'ligand' effect involves the electronic modification of the adsorptive sites or their surroundings. The addition of one metal to a second metal could bring this modification by formation of a metal-metal bonds involving charge transfer between the metals or to orbital rehybridization of one or both of the metals. The alteration of the electronic properties of the adsorptive sites would have significant effect on chemisorption, hence on the catalytic behaviour in terms of activity and selectivity [24, 33, 34].

During the past decade, bimetallic nanomaterials have attracted significant interest because of their potential application in various technologically important fields due to their unique catalytic, electrocatalytic, electronic, optical and magnetic properties [25-29].

1.3.1.1 Types of bimetallic nanoparticles

Based on the mixing pattern of two different metals, three distinct types of structures for the bimetallic nanoparticle crystals can be identified, namely, core/ shell, heterostructure, or intermetallic and alloyed structures as shown in the Figure 1-2 below.



Figure 1-2. Bimetallic nanoparticles with different types of structures: (a) core/shell; (b) heterostructure; (c) intermetallic or alloyed structures [35].

The observed morphological differences for the bimetallic in Figure 1-2, was suggested to be due to the difference in the growth process of these materials .Thus in the case of core-shell, the growth process involves the initial formation of the inner core from the reduced metal ions, to be followed by the nucleation and growth of the other metal surrounding the preformed core, hence forming the shell. Heterostructure, on the other hand forms if during the growth process, the two kinds of metal atoms share a mixed interface. Intermetallic and alloy structure is totally different from the core/shell or the heterostructure bimetallic, in that both are homogenous mixtures of the two metals in which metal-metal bonds form [35].

Over the past two years a new type of bimetallic nanoparticles has been described and called crown-jewel structure based on precious metals. These bimetallics consist of an expensive metal atom such as Au (gold) located on the top of the other metal atoms (cheaper metal) at the special position as shown in the Figure 1-3 below. There are many advantages to constructing crown-jewel structures. One of them is to improve the catalytic properties of catalyst and another consideration for using precious metal is its cost because the precious metal atoms are located on the surface of another cheaper material [36].



Figure 1-3. Crown-jewel bimetallic nanoparticles.

Generally, the bimetallic nanoparticles can be prepared by solid, gaseous, or solution state. In the solid state preparation method, heating at relatively high temperatures for a long time is needed sometimes to ensure the decomposition of the metal precursors used. Firing at high temperatures results in a low surface area product which is not usually beneficial for catalytic reactions. On the other hand, gaseous methods, requires special and dedicated equipment which renders it an expensive method. The solution state method is the most common and efficient amongst these methods. This method allows a better control of the morphology of the growing nanoparticles, through adjusting preparation variables such as, the metal precursors used, metal molar ratio, temperature, pH of solution, aging time and reducing agent used. However, it must be emphasized here that it is difficult to control the growth of two kinds of metals due to their different thermodynamic and kinetic characteristics under the same conditions [35].

A special form of bimetallic catalysts that have been receiving great attention recently, are those having a core/shell nanostructure (see Figure 1-4). These structures have an abundance of applications in areas such as catalysis, electronics, sensors and optical devices [37].



Figure 1-4. Publications per year for core/shell structure during the period 2001 to 2012. The data was collected from Web of Science Database [32].

1.4 Core/Shell Bimetallic Nanoparticles

Core/ shell nanoparticles are nanostructures that have the core and the shell which can be composed of different materials in the nanometer particle size regime ranging from 20 to 200 nm. These nanostructures consist of core made of inorganic materials such as metal or metal oxide or silica or organic materials surrounded by another inorganic or organic material as the shell as shown in Figure 1-5. In addition, the core/shell nanostructures can be composed of more than two materials. This kind of core/ shell can be defined as comprising a core, interlayer and shell [18, 39].



Figure 1-5. Types of cores and shells nanoparticles.

1.4.1 Classification of Core/Shell Nanoparticle

Depending on the nature of the materials used to make up the core and shell, core/shell nanoparticles can be divided into three groups, namely, inorganic core/shell, organic-inorganic hybrid core/shell and polymeric core/shell nanoparticles. Core/shell nanoparticles made of inorganic materials are the most commonly used in industry [18, 39].

1.4.1.1 Inorganic core/shell nanoparticles

Inorganic core/shell nanoparticles are those in which the core and the shell are made of inorganic materials. These materials could be metallic, semiconductors or lanthanides [18].

Metallic core-shell nanoparticles, are those that use metals or metal oxides or silica as the core with the shell made from metals or metal oxides [18]. Pastoriza, et al., synthesized core/shell of Ag/TiO₂ through the simultaneous reduction of silver salt and hydrolysis of titanium alkoxides [40]. Renjis, et al., reported the synthesis of Au/TiO₂, Au/ZrO₂, Ag/ TiO₂ and Ag/ ZrO₂ [41]. Tang, et al., synthesized core/shell nanostructure of SiO₂/ Ag through a one-step ultrasonic electrodeposition method [42]. Bimetallic core/shell nanoparticles that have the core and the shell made of metals are the most commonly used in heterogeneous catalysis due to their superior or favourable catalytic properties [43].

Semiconductor nanoparticles, are those that have a core made of semiconductor material or metal oxide with shell made of semiconductor material or metal oxide or silica [44]. The most common of these core and shell semiconductor nanoparticles are binary structure that alloys group 3 and group 5 metals or group 4 and group 6 metals [18]. Core/shell nanostructures of CdSe/CdS, CdSe/ZnS, ZnSe/ZnS and CdTe/CdS have fluorescent properties and used for imaging in medicine [45]. Reiss, et al., prepared core/shell semiconductor nanoparticles of CdSe/ZnSe and CdSe/ZnSe/ZnS [46].

Lanthanide nanoparticles, are those that contain lanthanide elements such as Ti, Ce, Y and Eu. These nanoparticles have applications in the field of electronics and imaging [18].

1.4.1.2 Organic/Inorganic hybrid core/shell nanoparticles

These core/shell nanoparticles are made up of organic polymers and inorganic materials. Examples of these nanoparticles are Ag/ polystyrene and SiO₂/ Polyester [47, 48].

1.4.1.3 Polymeric core/shell nanoparticles

These core/shell nanoparticles have the core and shell made of polymers, with metals embedded in either the core or the shell in order to modify or improve certain physical properties, such as strength, toughness and thermal sensitivity of polymeric materials [22].

1.4.2 Shapes of Core/Shell Nanoparticles

There are different shapes of core/shell nanoparticles passed on the synthesis techniques. New techniques make it possible to prepare a variety of shapes not only spherical core/shell but nanostructures such as cube, hexagon and tube [49-51]. These shapes have also attracted the attention of researchers because of their different novel properties [52]. Different shapes of core/shell nanoparticles are shown in Figure 1-6 below.

The most common structures of core/shell nanoparticles are spherical when the spherical core is completely coated by shell nanoparticles (Figure 1-6a) [53].



Figure 1-6. Core/shell nanostructures with different shaped nanoparticles: (a) spherical core/shell; (b) hexagonal core/shell; (c) multiple small cores coated by shell; (d) cubic core/shell; (e) movable core within hollow shell.

Since my research is focussed on the preparation, characterization and application of core/ shell bimetallic catalysts, the coming chapter will be limited to this topic.

CHAPTER TWO

LITERATURE REVIEW

2. CHAPTER 2: SYNTHESIS AND APPLICATION OF CORE/SHELL NANOPARTICLES

2.1 Synthesis of Core/Shell Nanoparticles

The majority of my thesis is focused on metallic materials rather than other types of core/shell nanoparticles. Therefore, the synthesis of metallic core/shell structures will be discussed in the following section.

In general, the bimetallic core/shell nanoparticles are synthesized through the reduction techniques of metal salts by one-step or two-step process using suitable reducing agents [1, 35].

2.1.1 One- pot or Simultaneous Reduction

In this method, core/shell nanoparticles have been prepared by simultaneous reduction where both metal precursors are reduced at the same time to present core/shell structures. In this case, one cannot control the growth of shell particles on the core. This method can be used to make core/shell structure from zirconia, titania [1, 35, 39].

2.1.2 **Two- pot or Successive Reduction**

The first step in this method is to prepare core particles and then the second metal is coated on the core by shell particles through successive reduction using a suitable agent for each step [1, 34, 38].

Generally, the main difficulties faced during synthesis of core/shell nanoparticles are: (i) agglomeration of core particles in the reaction media, (ii) incomplete coverage of the core

surface by shell particles, (iii) formation of separate shell particles rather than coating the core, (iv) control of the shell thickness [39].

Recently, various bimetallic core/shell nanoparticles have been synthesized by simultaneous and successive reduction methods. These methods are based on the chemical reduction of the metal precursors in the solution state. The method used is likely to determine the identity of the core/shell structure as well as its physical and chemical properties.

Several studies have described the synthesis of Au/Pt bimetallic core/shell nanoparticles by simultaneous or successive reduction using different reducing agents. Schmid, et al [54] synthesized core/shell of Au/Pt nanoparticles by the simultaneous reduction of H₂PtCl₆ in an aqueous gold sol with hydroxylamine and ρ -H₂NC₆H₄SO₃Na as stabilizer. A core shell structure composed of Au particles of 18 nm surrounded by Pt crystals of about 5 nm was achieved by this method. Liu, et al [55] reported the synthesis of core/shell structure consisting of Au core and Pt enriched Au/Pt alloy as a shell, through the simultaneous reduction in an aqueous solution containing tannic acid and citric acid as reducing agents. At lower Au/Pt ratios, Pt was found to grow clusters of an average diameter of 2 nm. It was suggested that this structure might possess unique catalytic properties.

The morphological differences observed in the Au/Pt core/shell systems reported in the above two investigations, could be due to the different preparation parameters used.

Fu et al [56] prepared a core/shell structure in which a Pt-rich layer coated Ni nanoparticles, with varying Ni/Pt atomic ratio from 1/10 to 2/1 via the sequential reduction method by chemical deposition of Pt on the Ni nanoparticles, these can be used as catalysts for methanol electro-oxidation in alkaline media. Ni/Pt nanoparticles size measurements showed an

increase from 8.9 nm to 1.2 nm with increasing the Ni/Pt atomic ratio from 0.1 to 2. All the prepared catalysts demonstrated superior catalytic activity, as well as better resistance to poisoning by the carbonaceous species, in comparison to that of pure Pt nanoparticles. The best electro-catalytic activity was exhibited by sample having Ni/Pt ratio of 1/10 with the thinnest Pt-rich shell layer. These results illustrate clearly the linkage between the catalytic behaviour and the morphology of the catalyst which is controlled to a great extent by the preparation method used.

In this study, we used a different way of reduction from Fu et al and others. The reduction process in this thesis depend on formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid to get a colloidal gel. The idea behind sol-gel synthesis is to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner as will be discussed in section 2.1.3.

Many studies have highlighted the dependence of the catalytic and electro-catalytic activities on the size and shape of the metal nanoparticles [57-59]. The size of particles affect the surface area available and the shape is important as the morphology exposes particular crystal faces which may have different catalytic behaviour including activity and selectivity [59,60].

Au/Pt core/shell nanostructures with varying Au/Pt atomic ratio from 1/7 to 5/1 also synthesized by successive reduction of HAuCl₄ and H₂PtCl₆ precursors by Yang et al [61]. An excess of NaBH₄ was added to ensure the complete reduction of the metals. The morphology of the Au/Pt catalysts and their electro-catalytic activity for methanol oxidation were investigated. Au/Pt nanoparticle were seen to have an average particle size of 25 nm. An average thickness of Pt shell layers of about 7 nm growing on the surface of Au nanoparticle core was observed. The presence of Au was shown to improve the electrocatalytic activity of Pt catalyst for methanol oxidation. The best performance was recorded for the sample with Au/Pt ratio of 1/2.25. Au/Pt catalysts used demonstrated a better stability when compared to that of Pt catalyst. From the previous two investigations [56, 61] it seems an optimum atomic ratio of the other metal to platinum is required to achieve the best performance in terms of the electro-activity and durability or stability.

Recently, Ti/Pt and Pd supported on carbon microspheres synthesized via chemical reduction has been shown to exhibit better catalytic activity for ethanol oxidation in alkaline media than that of platinum [62-64].

Ksar, at el [65] reported the synthesis of Au core with Pd porous shell as catalyst for ethanol oxidation. The results showed that Au/Pd has higher electrocatalytic activity for this process as well as a higher stability, when compared to that of AuPd alloy. Au/Pd core/shell nanoparticles were also synthesized via successive reduction method for the electrooxidation of formic acid at room temperature. The presence of Au was shown to enhance activity of Pd for formic acid electro-oxidation as well as improving the catalyst stability. The improvement of activity could be due to the interaction between Au core and Pd shell.

Zhang, at el [66] prepared Ag/Au core/shell nanoparticles of about 2 nm with varying Ag/Au atomic ratio by simultaneous reduction as catalyst for aerobic glucose oxidation. The best catalytic activity and long- time stability was exhibited by sample having Ag/Au atomic ratio of 1/4.

Although core/shell nanoparticles often exhibit enhanced catalytic performances in terms of activity, selectivity and stability when compared to the separate components, one should not be under the impression that this is always the case. An Au/Pt core shell nanoparticle catalyst was found to have a lower and undesirable catalytic performance when compared to that of Pt in the preferential oxidation of carbon monoxide (PROX), when a gaseous mixture of carbon
monoxide, oxygen, hydrogen and argon was introduced to the reactor. The catalytic activity and selectivity for CO oxidation were extremely low over the bimetallic Au/Pt catalyst. The lower reactivity for these catalysts compared to the monometallic Pt, was argued to be due to the strong adsorption of CO, leading to high CO saturation coverage. The strong adsorption of CO onto the Pt surface makes it difficult to remove either through oxidation or desorption, hence reducing the available free surface sites for catalytic events. In other words, CO strong adsorption poisons the Au/Pt catalyst. In fact this type of poisoning is one of the key problems facing the commercialization of the proton-exchange membrane fuel cell (PEMFC) technology [67].

In some cases the core shell nanoparticles system is supported on carbon or silica support using the methods mentioned above. Initially, the metal core is dispersed on the high surface area support before the deposition of the metal shell onto the core commences. The support in these cases, are inactive and the main purpose of using it is to give a high dispersion for the metals used and probably thermal stability for the structures prepared. High dispersion of precious metals contributes to its efficient use and cuts down the cost, through the use of lower loadings of such metals.

Yang, et al [68] synthesized core/ shell nanoparticles of Co_{1-x}/Pt_x (x= 0.33, 0.43, 0.60, 0.68, 0.82) and $Co_{1-x}/Pt_x/C$ (x = 0.60, 0.68, 0.82) by the polyol reduction process. Co/Pt and Co/Pt/C were investigated as catalysts for hydrogen generation from hydrolysis of ammonia borane (NH₃BH₃). The best catalytic performance was exhibited by $Co_{0.32}/Pt_{0.68}/C$.

Au/Pd core/shell supported on SiO_2 synthesized with various Pd thickness 0.12- 1.5 nm and Au particles of 5 nm were made using seed growth method and tested in acetylene hydrogenation [69]. A decline in the activity of Au/Pd core/ shell catalysts were observed with increasing the thickness of the Pd shell. AuPd alloyed on SiO₂ samples at 68 and 80 % Pd, formed due to the high temperature of reduction used demonstrated a higher activity than the Au/Pd core/shell on SiO_2 samples with Pd shell of 1.5 nm thickness. According to the authors, it appears that the mixed Pd-Au ensembles generated at high temperature provides better performance than the Pd regions in the thin Pd shell.

Trimetallic core/shell nanoparticles have also been prepared and studied because of their interesting electrocatalytic properties. Toshima, et al [70] synthesized core/shell nanostructure of Au core, Pt interlayer and Ru shell, for hydrogenation of methyl acrylate. The core/shell trimetallic nanoparticles of Au/Pt/Ru presented higher catalytic activity due to the sequential electronic effect between different atoms of Au, Pt and Ru nanoparticles.

To achieve success in obtaining good core/shell structures there are important parameters which affect the final morphology of core/shell and particles size such as temperature, pH of solution, reactant concentration and reducing agents [35,39]. There are various synthetic methods used by researchers as shown in Table 2-1. There are many preparation methods for core/shell nanoparticles such as sol-gel method, Stober method, polyol method, layer by layer method and polyol microwave method.

Core/shell	core	shell	method	ref
Au/SiO ₂	Au	SiO ₂	Sol-gel	71
Fe ₃ O ₄ /SiO ₄	Fe ₃ O ₄	SiO ₄	Sol-gel	72
CdS/TiO ₂	CdS	TiO ₂	Sol-gel	73
Ag/ SiO ₂	Ag	SiO ₂	Stober method	74
Ni/SiO ₂	Ni	SiO ₂	Stober method	75
Au/Co	Au	Со	Successive reduction	76
Au/Pt	Au	Pt	Successive reduction	77
Au/Pd	Au	Pd	Simultaneous reduction	78
Ni/Pt	Ni	Pt	Simultaneous reduction	79
Cu ₂ O/Au	Cu ₂ O	Au	Simultaneous reduction	80
Au/Pt	Au	Pt	Seed growth method	81
Au/Pd/ SiO ₂	Au/Pd	SiO ₂	Seed growth method	82
Au/Ag	Au	Ag	Seed growth method	83
Ag/TiO ₂	Ag	TiO ₂	Layer-by-Layer method	84
Cu/Ag	Cu	Ag	Polyol method	85
Au/Ag	Au	Ag	Polyol method	86
Fe/C	Fe	С	Polyol microwave method [*]	87

Table 2-1: Synthesis methods of core/shell nanoparticles structures.

* Polyol microwave method uses microwave oven instead of the normal heating.

A brief description about the methods mentioned in Table 2-1 is given below.

Stober method: This method is used for the preparation of silica that is used in the coating of metals or as the shell in the core/ shell nanoparticles. Silica particles were prepared by a simple one-step which involves the condensation and hydrolysis of tetraethyl orthosilicate (TEOS) in alcohol and ammonia used as the catalyst [3]. Silica has many advantages when used as the shell or core in the core/ shell system. It has a great benefit in increase the dispersion of metal due to high surface so the thickness of silica play an important role to

affect the optical property of metal [74]. It also prevents the aggregation of particles which affects the stability of the core/ shell structure [75].

Seed growth method: The seed-mediated growth method is the most common and successful method for synthesizing high-quality gold nanorods by using ascorbic acid and sodium citrate as reducing agents [81]. A typical growth method involves the addition of citrate-capped gold nanospheres as seeds to the bulk HAuCl₄ growth solution. The growth solution is obtained by the reduction of HAuCl₄ with ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB) to reduce the complex of HAuCl₄ and CTAB [82]. Using the [HAuCl₄ – CTAB] complex to reduce by ascorbic acid because it could not reduce HAuCl₄ to Au⁰ at room temperature [81-83].

Layer-by-Layer method: The layer-by-layer (LBL) is a comparatively new method of thin film deposition. In general, this method is based on the sequential adsorption of positively and negatively charged species by alternatively dipping into the solutions. Rinsing with excess solution between each adsorption step in order to get a thin layer of charged species on the surface ready for next adsorption step [3]. The major advantages of LBL are that the thickness of film can be controlled by this technique that has led to control over size nanoparticles. It also provides high-quality stratified films of nanoparticles with a long-term stability [84].

The sol- gel method and polyol method which were used in this research will be discussed in the following sections.

2.1.3 Sol-gel Method

The sol-gel process is one of the wet chemical methods used widely in research related to the preparation of materials in aqueous media, especially for synthesizing inorganic materials. The interest in sol-gel method began in 1990 by Ebelmanl and Granam. This process was originally developed by Stopber in 1968 [88].

In this process, the solution of reactants gradually turns to form colloidal suspension or sol by hydrolysis of a mixture containing both a liquid phase and solid phase. In this case, the particles density is very small compared to the volume of liquid. Centrifugation can used also to accelerate the separation process [39, 88].

In general, the sol-gel process can be divided into two main steps as described below:

1- Hydrolysis: metal oxide or metal salt are hydrolyzed in solution to produce a colloidal suspension or sol as expressed in the following equation 2-1.

$$M - OR + H_2 O \to M - OH + R - OH \tag{2-1}$$

2- Condensation and Gelation: the colloidal particles linked together to form M - O - M bonds and create a three-dimensional (3D) network with increased viscosity which finally becomes a gel as shown by the equation 2-2.

$$M - OH + HO - M \to M - O - M + H_2O$$
 (2-2)

Then the gel can be processed by various drying methods to produce materials in different forms, such as powder, films, fibers and nanoparticles as shown in Figure 2-1 (highlighted area relevance to method using in thesis).



Figure 2-1. Sol-gel Process (highlighted area relevance to method using in thesis) [89].

Several studies have described the synthesis of nanoparticle catalysts by the sol-gel method. Zhang Y, et al [90] prepared a titania (TiO₂) catalyst with different materials such as Pt, ZrO₂, MoO₃ and SiO₂ in order to improve its activity for the oxidation of formaldehyde by the sol-gel method using TiCl₄ as a precursor for TiO₂. It was reported that the TiO₂–ZrO₂ and TiO₂– SiO₂ catalysts had more activity for formaldehyde oxidation with conversion to CO₂ 52% and 94% respectively, when compared with pure TiO₂, TiO₂–Pt and TiO₂– MoO₃. It was suggested that the addition of SiO₂ and ZrO₂ increased the available surface area for the oxidation of formaldehyde. In contrast to this finding Zhang C et al [91] reported that the TiO₂–Pt catalysts had more activity than pure TiO₂ and the conversion of formaldehyde to CO₂ was 100% at room temperature. The difference observed in the two investigations, could be due to the different methods of preparation and precursors used.

Pt/SiO₂ sol- gel system has several applications in gas sensors, electrochemistry and catalysis [92]. This catalysts was synthesized for methanol oxidation through sol-gel method by Martyla et al [93] using tin (IV) acetate and $H_2PtCl_6.6H_2O$ as precursors of SiO₂ and Pt, respectively. This catalyst exhibits high electrocatalytic activity after low temperature treatment.

Much attention has been directed recently for the preparation of core/shell nanoparticles using the sol-gel method.

SiO₂/Au core/shell nanoparticles was prepared by using the modified sol-gel method using different reducing agent by Kandpal, et al [94]. This study described the growth and attachment of gold nanoparticles to the functionalized surface of silica nanoparticles. Au nanoparticles were prepared using sodium borohydride (NaBH₄) for Au nucleation on the functionalized silica particles and coating this system with Au as a shell using the same reducing agent. On the other hand, they used the same method above but using trisodium citrate Na₃ (C₆H₅O₇) for nucleation and coating silica with Au. Furthermore, they prepared SiO₂/Au core/shell structure by combination of the two method mentioned above. In this method they used Na₃ (C₆H₅O₇) to prepare Au nucleation on the functionalized silica particles which are prepared by using (NaBH₄) as reducing agent. It was found that the last method gives the best results for preparation of the SiO₂/Au core/shell nanoparticles. This study did not mention other conditions such as pH of solution which will certainly affect the final result of core/shell structure.

The core/shell nanoparticles of Au/SiO_2 was also prepared by Lu, et al [95] using sol-gel method by generating SiO_2 sols onto the surfaces of Au nanoparticles without derivatizing the surface of gold with any coupling agent. It was suggested that this process can be applied to coat precious metals cores such as silver by silica shell without using a primer.

Lu and Mulvaney [96] prepared Au/TiO₂ core/shell nanoparticles with 1 nm thickness of TiO₂ shell by the hydrolysis of titanium oxide acethylacetonate (TOAA) in a solution containing Au sol , ethanol and water. They studied the effect of precursors of TiO₂ concentration and water on the thickness of TiO₂ shell. It was found that the shell thickness at 1 mM of TOAA and 5M of water was about 1 nm, and any addition of TOAA above this limit does not increase the thickness of TiO₂ shell because more particles colloidal titania are

formed due to faster hydrolysis of TOAA when increasing the concentration of TOAA. This study did not investigate effect of the water at any other concentration on the hydrolysis rate of TOAA.

Kalel, et al [97] reported the synthesis of SiO₂ coated with uniform layer of TiO₂ to form SiO_2/TiO_2 by sol-gel method. In this study a core/shell structure composed of SiO_2 of size around 170 nm coating with TiO₂ shell thickness around 23nm. This investigation did not mention any impact of the precursor's concentration on the TiO₂ thickness shell size as in the previous study by Lu and Mulvaney.

Zinc oxide (ZnO) has attracted attention due to its unique optical and electronic properties. Many methods are used to prepare ZnO coating with different materials to form core/shell structure.

 ZnO/SiO_2 core/shell nanoparticles were synthesized by a simple sol-gel method by Han, et al [98]. It was found that the thickness of SiO_2 shell can be altered by adjusting the concentration of TEOS and hollow silica particles or film silica can be generated when the ZnO core is etched by HCl. The authors proposed that the hollow silica can be exploited in drug delivery and catalysis application.

As the above discussion shows, the sol-gel technique allows researchers to change the composition and structure of materials on the nanometer scale by changing some parameters such as pH of solution. The shell thickness can be controlled by adjusting the concentration of precursors. In addition, this process does not need expensive equipment, something which can minimize production cost, it is also a simple process to apply in the lab and it can be modified to produce different materials. For these reasons, this method was used in this research to prepare core/ shell nanoparticle catalysts.

2.1.4 Polyol Method

The polyol method has attracted considerable attention recently, because it is a simple, versatile and efficient technique to prepare different kind of materials. This method was developed in 1989 by Fievet et al [99].

The polyol process involves reduction of metal precursors by using alcohol containing two or more hydroxyl group; a diol such as ethylene glycol acts as both a solvent and reducing agent at high temperature. In this method a polymer such as PVP (vinylpyrrolidone) is used to prevent agglomeration of colloidal particles [100-102]. The steps of polyol method are shown in the diagram depicted in Figure 2-2.

Recently, the polyol method has been used to synthesise metallic and bimetallic (alloys, core/shell) nanoparticles [103-123]. However, the mechanism of this process is yet to be rationalized [121]. In general, upon heating the solution containing the metal precursor and ethylene glycol to the temperature between 150-160°C, glycolaldehyde is produced through the following oxidation reaction [124].

$$2HOCH_2CH_2OH + O_2 \rightarrow 2HOCH_2CHO + 2H_2O \qquad (2-3)$$

After that it is acting as reducing agent to reduce the metal ion to metal atom. Fievet et al [99] studied the mechanism of polyol reduction with a focus on Co and Ni hydroxide as precursors of metals. They proposed that after reaction at 197°C, diacetyl is produced then reduced to metal ion as in equations 2-4, 2-5 below.

$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O \qquad (2-4)$$

$$2M^+ + 2CH_3CHO \rightarrow CH_3COCOCH_3 + 2M + 2H^+ \qquad (2-5)$$

On the other hand, this study failed to explain the mechanism of the synthesis of metals which are prepared at temperature less than 197°C such as Pt and Pd.



Figure 2-2. Polyol Process.

The polyol method has become a popular method of preparing bimetallic nanoparticles with well-defined morphologies.

Kim et al [118] synthesized PdAg alloy catalyst nanoparticles with an average size 5.5 nm by the polyol method using ethylene glycol as both solvent and reducing agent. This catalyst was prepared also by slurry coating technique for hydrogen permeation [125]. However, this method is too expensive compared with polyol method that does not require expensive equipment and is simple to apply in the lab.

PdAg catalyst supported on γ -alumina was prepared through polyol method by Sales et al [119] for hexa-1, 5-diene hydrogenation. According to the authors this catalyst has a higher activity for hydrogenation of hexa-1, 5-diene than monometallic Pd catalyst. In the above studies, the addition of Ag improves the performance of Pd by preventing the isomerisation of hexa-1, 5-diene to hexa-2, 4-diene.

A PtCo alloy catalyst supported on C was synthesized by a modified polyol method with a small particles size of 1.9 ± 0.2 nm by Santiago et al [120]. Furthermore, PtCo catalyst was tested in a fuel cell as cathode catalyst. The results showed that, PtCo supported on C demonstrated an excellent performance as cathode in direct methanol fuel cell. Tzitzios et al [121] reported the synthesis of PtCo alloy catalyst as well using modified polyol method with nanoparticles size of 3 nm.

The two studies above, prepared PtCo catalyst using a polyol method that was developed by Sun et al [126] by using the long-chain diol alcohol hexadecanediol and polyethylene glycol-200 respectively, as solutions and reducing agents instead of ethylene glycol that is used in the conventional polyol method. However, both studies did not mention the effect of using a long- chain on the final products, and in particular on the particle size distribution of nanoparticles.

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Recently, great attention has been paid to the preparation of core/shell nanoparticles catalysts using polyol method.

The core/shell nanoparticles of AgCu core and Cu shell were prepared by polyol method using ethylene glycol by Tsuji et al [122]. They reported that, the AgCu alloy formed at molar ratio of [Ag]/[Cu] = 1 - 2 and the reaction time below 5min. In addition, the AgCu/Cu core/shell nanoparticles generated when the molar ratio of [Ag]/[Cu] between 0.25 and 0.5 and the reaction time above 15 min. The morphological differences observed in the Ag-Cu catalyst are due to the difference in the molar ratio and reaction time. At low molar ratio of [Ag]/[Cu] there are excess amounts of Cu nanoparticles. These excess nanoparticles of Cu will be deposited on the surface of Ag-Cu alloy formed AgCu alloy as core surrounded by Cu nanoparticles as a shell.

The core/shell nanoparticles of Pt/Pd have been synthesized by various modified methods to control the growth of shell on the surface of core in order to increase the catalytic activity of Pt/Pd core/shell catalyst for direct methanol fuel cells [127-130].

Long et al [123] prepared Pt/Pd core/ shell nanoparticles with different morphology cubic, tetrahedral and octahedral by modified polyol method, using silver nitrate as a modifying agent. According the study, the addition of silver nitrate effects the final morphology of Pt/Pd core/shell that could improve the performance of Pt/Pd catalyst in direct methanol fuel cells. Based on the above discussion, the polyol process is a simple and efficient synthetic route for preparing different types of bimetallic catalysts and a promising method for synthesis of core/shell structures successfully.

2.2 Applications of core/shell nanoparticles

Many applications of core/shell structure have been discussed earlier in chapter one and chapter two and the coming chapter will be dedicated for fuel cell and discussion of the application of core/shell catalysts in fuel cell.

3. CHPTER 3: FUEL CELLS AND THE DIRECT METHANOL FUEL CELL (DMFC)

3.1 General Introduction

With high energy demands, fossil fuel depletion and environment pollution, fuel cells as an alternative energy source have been attracting more and more attention in recent decades. Flexible power and low emission make the fuel cell very promising technology as a source of heat and electricity for buildings, vehicular applications and suitable for portable applications such as mobile phones and laptops [131-132].

This chapter is introduce fuel cells and the different types of fuel cells, with special emphasis on the direct methanol fuel cell which was used in this study to evaluate the performance of catalysts that were prepared in this thesis. The last part will offer an account of platinum as a catalyst in fuel cell.

3.1.1 Definition of Fuel Cells

Fuel cells are electrochemical devices that convert the energy of a chemical reaction directly into electricity, heat and water. Figure 3-1 shows that each fuel cell has two electrodes one positive and one negative namely, anode and cathode respectively, separated by solid or liquid electrolyte that carries electrically charged particles between them. A catalyst is used as well to speed up the reactions at the electrodes. A fuel cell is supplied with a source of hydrogen on one side (pure hydrogen or methanol) and a source of oxygen on the other side (usually air) which combine together to form water [131].



Figure 3-1. Basic Fuel Cell Operation [131].

The basic principle of a fuel cell is a chemical reaction between hydrogen and oxygen that produces power, heat and water. The cell consists of proton electrolyte membrane (PEM) with a catalyst layer on each side. When hydrogen is led to the first catalyst layer at anode, the hydrogen molecules are oxidized giving protons and an electrons as shown by the equation 3-1 below.

$$H_2 \to 2H^+ + 2e^-$$
 (3-1)

Then the protons migrate through the electrolyte membrane to the second catalyst layer at cathode and then react with oxygen to form water as shown by the equation 3-2 below.

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \to H_2O$$
 (3-2)

At the same time the electrons are forced to travel around the membrane to the cathode, because they cannot pass through the membrane. This movement of electrons thus creates an electrical current [131].

3.2 Types of Fuel Cell

3.2.1 General Introduction

Fuel cells are generally classified by their electrolytes or the mobile ion. The main types and the applications of fuel cells are summarized below in Table 3-1.

Туре	Electrolyte	Fuel	Mobile	Temperature	Applications
			Ion		
Phosphoric acid	Phosphoric	H ₂	H^+	150-250°C	kW scale CHP
(PAFC)	acid				
	(H ₃ PO ₄)				
Alkaline (AFC)	Aqueous	H ₂	OH	50-250°C	Used by NASA in the
	КОН				programmes.
Solid oxide	YSZ (Y ₂ O ₃	Hydrocarbons	O ²⁻	500-1000°C	All CHP (kW to MW
(SOFC)	+ ZrO ₂)	and CO			capacities)
Molten carbonate	Li, Na, K	Hydrocarbons	CO ₃ ²⁻	500-700°C	Medium to large scale
(MCFC)	carbonates	and CO			CHP (up to MW
					capacities)
Proton exchange	Sulfonated	H ₂ and	H^+	30-100°C	Vehicular, portable
membrane	polymers	Reformate gas			appliances and small
(PEMFC)	(Nafion)				scale CHP
Direct methanol	Sulfonated	Methanol	H^+	30-100°C	Portable appliances
(DMFC)	polymers				
	(Nafion)				

Table 3-1: Overview of main fuel cell types.

Each type has different kinetic behaviour depending on the operating temperature. This means that fuel cells can be characterized as high, medium and low temperature as shown in Table 3-1.

3.2.1.1 Phosphoric acid fuel cell (PAFC)

PAFC has the same principle operation as the basic hydrogen fuel cell using carbon supported platinum catalyst with efficiency range from 40 to 80%. Due to the large amount of excess heat emitted between 150 to 250°C, PAFCs are used for stationary power plants and they are already in commercial use as combined heat and power (CHP) [133].

3.2.1.2 Alkaline fuel cell (AFC)

AFC is generally fuelled with pure hydrogen and oxygen because they are very sensitive to poisoning. In this type one can use a variety of non-precious metal catalysts with efficiency of 60-70% [134].

3.2.1.3 Solid oxide fuel cell (SOFC)

SOFC is a solid state system at high temperature, this can cause the cell to rack. The efficiency is about 60%. However, the high temperature limits applications of SOFC [135].

3.2.1.4 Molten carbonate fuel cell (MCFC)

The main advantage of MCFC is using nickel as the electrode catalysts with efficiency ranging from 60 to 80%. This metal is inexpensive compared to the precious metal which are used in other cells. The high temperature operation limits the poisoning coming from carbon monoxide [136].

3.2.1.5 Proton exchange membrane (PEMFC)

This type of fuel cell is also called polymer electrolyte membrane fuel cell. The most common membrane material used in PEMFC is Nafion. This solid polymer allows only protons to pass through it [137]. Generally, PEMFC fuelled by hydrogen and operating at low temperature have an efficiency of about 40-50%. Since platinum is the most common catalyst used in PEMFC on both sides of the membrane, this makes the cost of PEMFCs much higher than other types of fuel cells. Hence, further improvements to electrode catalysts are necessary to reduce the cost of PEMFC fuel cells. The advantages of using PEMFC are low temperature operation and quick starting, these make PEMFCs suitable for vehicles and mobile applications [138].

3.2.2 The Direct Methanol Fuel Cell (DMFC)

The direct methanol fuel cell has received significant in recent years due to its relatively high performance, rapidly advancing technology and system simplicity. These beneficial features

make it suitable for portable electronic equipment and transportation systems [139]. A schematic diagram of a DMFC is shown in Figure 3-2 below.



Figure 3-2. Schematic diagram of a Direct Methanol Fuel Cell (DMFC).

DMFC is similar to PEMFC in that it uses a polymer membrane as an electrolyte but it uses methanol as fuel rather than hydrogen. DMFC operates at slightly higher temperature than PEMFC with efficiency around 40% [140]. In general, platinum is the most common catalyst used in DMFC, Platinum/Ruthenium catalyst on the anode and platinum as cathode. The principle of DMFC operation is direct electro-oxidation of methanol on the anode giving carbon dioxide and protons and electro-reduction of oxygen on the cathode as shown in equations below [138].

$$\begin{array}{ll} CH_{3} OH + H_{2} O \rightarrow CO_{2} + 6H^{+} + 6e^{-} & Anode \\ 3 - 3 \\ 3/_{2} O_{2} + 6H^{+} + 6e^{-} \rightarrow 3H_{2} O & Cathode \\ CH_{3} OH + \frac{3}_{2} O_{2} \rightarrow CO_{2} + 2H_{2} O & Overall \\ \end{array}$$

The anode reaction is in reality much more complex than indicated by equation above. The reaction consists of many different reaction steps. The mechanism of methanol oxidation on platinum alloy as anode catalyst given by Ley et al [141] is summarized as below:

$$Pt + CH_3 OH \rightarrow Pt^{\bullet}(CH_3 OH)_{ads} \qquad 3-6$$

$$Pt^{\bullet}(CH_3 OH)_{ads} \rightarrow Pt^{\bullet}(CH_3 O)_{ads} + H^+ + e^- \qquad 3-7$$

$$Pt^{\bullet}(CH_3 O)_{ads} \rightarrow Pt^{\bullet}(CH_2 O)_{ads} + H^+ + e^- \qquad 3-8$$

$$Pt^{\bullet}(CH_2 O)_{ads} \rightarrow Pt^{\bullet}(CHO)_{ads} + H^+ + e^- \qquad 3-9$$

$$Pt^{\bullet}(CHO)_{ads} \rightarrow Pt^{\bullet}(CO)_{ads} + H^+ + e^- \qquad 3-10$$

$$M + H_2 O \rightarrow M^{\bullet}(H_2 O)_{ads} \qquad 3-11$$

$$M^{\bullet}(H_2 O)_{ads} \rightarrow M^{\bullet}(OH)_{ads} + H^+ + e^- \qquad 3-12$$

 $Pt^{\bullet}(CO)_{ads} + M^{\bullet}(OH)_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^-$ 3-13

Where M is the metal alloyed with platinum. In general, PtRu catalyst is used in DMF the as anode catalyst.

There are many problems associated with the use of DMFC that have to be addressed. One of the most important problems that affects the performance of the DMFC is methanol crossover. In this case, methanol crosses from anode to cathode, and this lowers the cell performance. For this reason, many studies have been dedicated to overcoming this problem by development of a membrane that is less permeable to methanol [142]. Another serious problem in the DMFC is the poisoning of platinum catalyst due to the adsorption of carbon monoxide that is formed by the catalytic reforming of methanol on the anode which is the source of H₂ for the cell. Adsorption of carbon monoxide into the platinum surface will reduce catalyst active area and reduce the performance of the cell. This problem is usually solved by the addition of another metal like ruthenium which is active in the oxidation of carbon monoxide to carbon dioxide hence minimizing the poisoning.

In addition, there is a very important field of research that focuses on catalyst development to aiming at optimizing the anode performance. Type of catalyst used and its morphology plays an important role and one of such catalyst type that has received much attention recently is core/shell structure catalysts.

3.3 Catalysts in Fuel cell

3.3.1 Platinum Catalyst

Platinum is still the most popular catalyst used in the direct methanol fuel cell due to its high catalytic activity for the hydrogen oxidation reaction (HOR) on the anode electrode and the oxygen reduction reaction (ORR) on the cathode electrode.

Platinum can be classified into two types of catalysts; platinum supported on carbon or other kinds of supports as cathode catalyst and platinum mixed with other metals such as nickel, cobalt and ruthenium to form alloyed catalyst or core/shell catalyst in order to enhance the catalytic activity and also reduce the cost of platinum [138].

Recently, platinum has attracted much research interest as a shell with different nobel or nonnobel metals such as Au, Ir, Ru, Rh, Pd, Ni, Cu and Co as cores in order to reduce the cost and improve its performance for the different reactions [67, 143-145].

A 1-2 monolayer thick of Pt was deposited on the variety of nobel metals including Ir, Au, Ru, Rh and Pd [67, 143-145]. It was reported that the core/ shell of Ru/Pt, Rh/Pt, Ir/Pt and Pd/Pt nanostructures were more active for preferential CO oxidation (PROX) than bulk Pt and nanoalloys of RuPt, RhPt, PdPt, IrPt and AuPt. They also observed that among the core/ shell nanostructures studied, Ru/Pt core/shell nanostructure has the highest PROX activity and selectivity, with complete CO oxidation achieved at 30°C. It was suggested that this enhanced catalytic activity for the core shell nanoparticles is due to a combination of two factors namely, the increased availability of the CO-free Pt surface sites on the Ru/Pt

nanoparticles as well as the hydrogen-mediated low temperature CO oxidation on these surfaces.

Several studies were also carried out in which Pt shell was deposited onto the surface of the non-noble metals such as Ni and Cu [145,146]. Wang, et al [146] synthesized a core/ shell of Ni/Pt with an atomic ratio of Ni:Pt= 5:1 via chemical reduction and sequential chemical deposition as catalyst for oxygen reduction reaction(ORR). From the X-ray diffraction, it was suggested that the thin layer of Pt is deposited on Ni. Ni/Pt was found to exhibit enhanced catalytic activity compared to the commercial E-TEK pure Pt catalyst. It was suggested that the presence of Ni increases the available surface active sites for ORR by preventing the strong adsorption of hydroxyl species onto the surface of catalyst, which is responsible for poisoning the catalyst and inhibition of oxygen reduction.

The core/shell nanoparticles of Cu/Pt on a porous carbon electrode for polymer electrolyte membrane fuel cells (PEMFCs) were synthesized through two- step electrochemical method by Wei, et al [147]. The electrodes with Cu/Pt core- shell nanostructures exhibited much higher activity for the ORR than that of the commercial Pt/C even though the Pt loadings in the core-shell of Cu/Pt are lower.

In the past few years, numerous papers have been published that focus on improving the catalytic performance of platinum in direct methanol fuel cell (DMFC). Some of these studies are summarized in Table 3-2.

Catalyst	Method/	Precursor	Measurement	Activity	Ref.
	Reducing		Method		
	agent				
Pt ₇₅ Ru ₂₅ (alloy) on C	Chemical reduction using HCOOH	H ₂ PtCl ₆ , RuCl ₃	A single cell test DMFC, 2M CH ₃ OH at 70°C	$\frac{300 \text{mA/cm}^2}{400 \text{mV/s}}$ at	148
Pt ₅₀ Ru ₅₀ (alloy) on C	Chemical reduction Using NaBH ₄	H ₂ PtCl ₆ , RuCl ₃	Cyclic voltammetry (CV), 1M H ₂ SO ₄ + 2M CH ₃ OH	4mA/cm ² at 400mV/s, 1mg/cm ²	149
Pt ₅₀ Ru ₅₀ (alloy) on C	Chemical reduction Using H ₂ +N ₂	Pt(NH ₃) ₂ (NO ₂) ₂ , RuNO(NO ₃) _x	Polarization (glassy carbon), 0.5M H ₂ SO ₄ + 1M CH ₃ OH, 60°C	$\frac{8\text{mA/cm}^2}{400\text{mV/s}}$ at $\frac{400\text{mV/s}}{0.06\text{mg/cm}^2}$	150
Pt ₆₇ Ru ₃₃ (alloy) on C	Chemical reduction Using H ₂ H ₆ O ₂	H ₂ PtCl ₆ , RuCl ₃	A single cell test, 1M CH ₃ OH, 90°C	$\begin{array}{c} 300 \text{mA/cm}^2 \text{at} \\ 400 \text{mV/s}, \\ 2 \text{mg/cm}^2 \end{array}$	151
Pt ₅₀ Ru ₅₀ (alloy) on C	Chemical reduction using NaBH ₄ /AOT	H ₂ PtCl ₆ , RuCl ₃	A single cell test, 3M CH ₃ OH, 90°C	$\begin{array}{c} 50 \text{mA/cm}^2 & \text{at} \\ 400 \text{mV/s}, \\ 1 \text{mg/cm}^2 \end{array}$	152
Pt ₅₀ Ru ₅₀ (alloy) on C	Chemical reduction Using N ₂ H ₄	H ₂ PtCl ₆ , Ru((NO)(NO) ₃) ₃	Cyclic voltammetry (CV), $0.5M$ HClO ₄ + 1M CH ₃ OH, 25°C	0.02mA/cm ² at 400mV/s, 0.01mg/cm ²	153
Pt ₅₃ Ru ₄₇ (alloy) on C nanotube	Chemical reduction Using H ₂ H ₆ O ₂	K ₂ PtCl ₄ , K ₂ RuCl ₅	Cyclic voltammetry (CV), 1M H ₂ SO ₄ + 2M CH ₃ OH, 25°C	0.20mA/cm ² at 20 mV/s	154
Ni/Pt (1:10) Core/Shell	Successive reduction Using NaOH+N ₂ H ₄	NiCl ₂ , H ₂ PtCl ₆	Cyclic voltammetry (CV), 1M KOH + 1M CH ₃ OH	4.38 mA/mg at 50 mV/s,	56
PtPd/Pt Core/Shell on C	Deposition Pt shell on PdPt alloy using C ₆ H ₇ NaO ₇	PdCl ₂ , H ₂ PtCl ₆	Cyclic voltammetry (CV), $0.5M$ $H_2SO_4 + 0.5M$ CH ₃ OH, room temperature	2.81 A/mg at 50 mV/s, 0.02mg/cm ²	155
PdCu/PtRu Core/Shell on C	Successive reduction Using C ₆ H ₇ NaO ₇	PdCl ₂ , CuCl ₂ , H ₂ PtCl ₆ , RuCl ₃	Cyclic voltammetry (CV), 0.5M H ₂ SO ₄ + 0.5M CH ₃ OH, 25°C	6.15 A/mg at 50mV/s about 15 times larger than Pt on C (0.41A/mg) and 3.4 times larger than PtRu on C (1.84 A/mg)	156

Table 3-2: Summary of the Pt based catalyst synthesized by different methods for DMFC.

Au/Pt Core/Shell	Successive reduction Using NaBH ₄	HAuCl ₄ , H ₂ PtCl ₆	Cyclic voltammetry (CV), 1M H ₂ SO ₄ + 1M CH ₃ OH	410 mA/mg at 50 mV/s about 1.52 times larger than Pt catalyst (270 mA/mg) and Au/Pt shows excellent long- term cycle stability	157
Au/Pt Core/Shell on C	Successive reduction Using Na ₃ C ₆ H ₅ O ₇ and NaBH ₄	HAuCl ₄ , H ₂ PtCl ₆	Cyclic voltammetry (CV), 1M HClO ₄	10 μA at 20 mV/s	158
Au/Pt Core/Shell on C	Successive reduction Using Na ₃ C ₆ H ₅ O ₇	HAuCl ₄ , H ₂ PtCl ₆	Cyclic Voltammetry (CV), IM HClO ₄	0.16 mA/µg at 10 mV/s	159
Cu/Pt Core/Shell	Electro- deposition	$\begin{array}{l} CuSO_4.5H_2O,\\ H_2PtCl_6 \end{array}$	A single cell test at 70°C	Power density = 0.9 W/cm^2 , Pt loading 0.24 mg/cm ²	147
Ni/Pt Core/Shell	Sequential chemical deposition	Ni(OCOCH ₃) ₂ .4H ₂ O H ₂ PtCl ₆	Cyclic voltammetry (CV), 0.5M H ₂ SO ₄	0.75 mA/mg at 50 mV/s	146
PdCu/Pt Core/Shell on C	Successive reduction Using C ₆ H ₇ NaO ₇ and KOH	PdCl ₂ , CuCl ₂	Cyclic voltammetry (CV), $0.5M$ H_2SO_4 , room temperature	0.025 A/mg at 50 mV/s	160

Observation of Table 3-2 reveals that there are limited studies on the performance of catalysts using a direct methanol fuel cell (DMFC), this work aimed to investigate the direct methanol fuel cell efficiency using new structure of catalyst core/shell nanoparticles.

CHAPTER FOUR

4. CHAPTER 4: EXPERIMENTAL AND CHARACTERIZATION

4.1 Synthesis of Core/Shell Nanoparticle Catalysts

All chemicals used are listed in Appendix A.

4.1.1 Synthesis of Novel Co/Ni Core/Shell Nanoparticles by a New Modified Sol-gel Methode

The nickel coated cobalt nanoparticles were prepared by a new modified sol-gel method using N₂H₄ (hydrazine) as reducing agent for CoCl₂ (cobalt chloride) and NiCl₂ (nickel chloride) in ethanol solution, as shown in Figure 4-1 below. The Co nanoparticles as seeds were prepared first by adding 40 ml of 0.5 M N₂H₄ (hydrazine) and 80 ml of 1 M NaOH (sodium hydroxide) aqueous solution to 40 ml of 0.1M CoCl₂ in ethanol solution. After the addition, the mixture was continuously stirred and heated to 60°C for 0.5 h. After cooling, 40 ml of 0.1M NiCl₂ in ethanol solution was added drop by drop to the formed Co colloid with continuous stirring. This was followed by the dropwise addition of 40 ml of 0.5 M N₂H₄ and 80 ml of 1 M NaOH to achieve the reduction and deposition of Ni nanoparticles onto the surface of Co seeds. The mixture was then heated under reflux at 60°C for 0.5 h. An excess of N₂H₄ and NaOH were added to the mixture to ensure the complete reduction of the Co and Ni ions. The product was filtered and washed with ethanol and then dried in an oven at 100°C for 24 h.



Figure 4-1. Schematic diagram showing preparation and the expected structure of Co/Ni core/ shell nanoparticle.

4.1.2 Synthesis of SiO₂/Ni Core/Shell Nanoparticles by a New Modified Sol-gel Method Three kinds of silica are used for preparation of SiO₂/Ni core/shell nanoparticles, silica suspension, prepared silica dried powder and commercial silica.

4.1.2.1 Preparation of SiO₂ particles

5ml of TEOS (Tetraethyl orthosilicate) was added to 30 ml CH₃CH₂OH under sonication. After 10 min 50 ml of 25% ammonium hydroxide solution and 50 ml of CH₃CH₂OH (ethanol) were added to the reaction mixture. Sonication was continued at 24°C under reflux for 50 min to get a white turbid suspension. 10 ml of this suspension was removed to be used in the preparation silica suspension with Ni (This type of silica is going to be referred as liquid silica in the preparation to follow to distinguish it from other type of silica). The rest of the reaction mixture was centrifuged. The separated silica particles were washed with water and ethanol respectively. The washed silica was collected and dried under vacuum at 50°C for 4h [161]. (This type of silica is going to be referred as dried silica in the preparation to follow).

4.1.2.2 Synthesis of SiO₂/Ni core/shell nanoparticles using liquid silica

SiO₂/Ni core/ shell nanoparticles were prepared by a new modified sol- gel method. At first 10 ml of the liquid silica prepared by the above method (4.1.2.1) was ultrasonicated for 30 min. 40 ml of 10% NiCl₂ in ethanol solution was then added slowly to the silica suspension with continuous stirring. 35 ml of 0.5 M N₂H₄ (hydrazine) and 80 ml of 1 M NaOH (sodium hydroxide) were added drop by drop to the previous mixture, which was then heated under reflux at 60°C for 90 min to complete the sol–gel process. Thereafter, the product suspension was filtered and washed with pure ethanol. During the washing, the produced sample was ultrasonicated to prevent any particle aggregation. Finally, the sample was dried in an oven at 100° C for 24 h.

4.1.2.3 Synthesis of SiO₂/Ni core/shell nanoparticles using dried silica

SiO₂/Ni core/ shell nanoparticles were prepared by a new modified sol- gel method. At first 1.0 g of the SiO₂ prepared by the above method (4.1.2.1) was added to 60 ml of an aqueous solution of ethanol (2:8). The mixture was ultrasonicated for 30 min. 40 ml of 10% NiCl₂ in ethanol solution was then added slowly to the silica colloid with continuous stirring. 35 ml of 0.5 M N₂H₄ (hydrazine) and 80 ml of 1 M NaOH (sodium hydroxide) were added drop by drop to the previous mixture, which was then heated under reflux at 60°C for 90 min to complete the sol–gel process. Thereafter, the product suspension was filtered and washed with pure ethanol. During the washing, the produced sample was ultrasonicated to prevent any particle aggregation. Finally, the sample was dried in an oven at 100° C for 24 h.

4.1.2.4 Synthesis of SiO₂/Ni core/shell nanoparticles using commercial silica

The method discussed in section 4.1.2.3 was followed to prepare SiO_2/Ni core/shell nanostructure using commercial silica with 10 nm particle size.

4.1.3 Synthesis of Novel SiO₂/CoFe Core/Shell Nanoparticles by a New Modified Solgel Method

The Co/Fe shell coated SiO₂ (commercial silica) nanoparticles were prepared through a new modified sol-gel process of CoCl₂ (cobalt chloride) and FeCl₂ (iron chloride), as shown in Figure 4-2. 1.0 g of SiO₂ powder was added to 60 ml of aqueous ethanol solution (2:8) and the mixture was ultrasonicated for 30 min. 60 ml of 0.1 M CoCl₂ in ethanol solution was then slowly added to the silica colloid. This was followed by the slow addition of 60 ml of 0.5 M N₂H₄ (hydrazine) and 120 ml of 1 M NaOH (sodium hydroxide) to the mixture. Then 60 ml of 0.1M FeCl₂ in ethanol solution was added drop by drop, and a further 60 ml of 0.5 M N₂H₄ (hydrazine) and 120 ml of 1 M NaOH were added slowly to the mixture before the commencement of heating the mixture under reflux at 60°C for 2 h. The suspension was then

filtered and washed with pure ethanol. During the washing, the produced sample was ultrasonicated to prevent any particle aggregation. Finally, the sample was dried in an oven at 100° C for 24 h.



Figure 4-2. Schematic diagram showing preparation and the expected structure of $SiO_2/CoFe$ core/shell nanoparticles.

4.1.4 Synthesis of Novel SiO₂/Pt Monometallic Core/Shell Nanoparticles by Two Different Methods

4.1.4.1 Synthesis of SiO₂/Pt monometallic core/shell nanoparticles by a new modified sol-gel method

First 0.5g of the SiO₂ (commercial silica) was added to 60 ml of an aqueous solution of ethanol (2:8). The mixture was ultrasonicated for 30 min. The next step, 1.87 mmol of PtCl₂ (platinum chloride) in 18 mL of ethylene glycol was added to the above suspension. This was followed by the slow addition of 60 ml of 0.5 M N₂H₄ (hydrazine) and 120 ml of 1 M NaOH (sodium hydroxide) to the mixture. After that, the mixture was continuously stirred and heated under reflux at 160°C for 1.5 h to achieve the reduction and deposition of Pt nanoparticles onto the surface of SiO₂. The sample was separated from the solution by centrifuging at 11000 rpm for 30 min. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

4.1.4.2 Synthesis of SiO₂/Pt monometallic core/shell nanoparticles by a new modified polyol method

0.5g of the SiO₂ (commercial silica) was added to 60 ml of an aqueous solution of ethanol (2:8). The mixture was ultrasonicated for 30 min. the next step, 1.87mmol of PtCl₂ was dissolved in 18 mL of ethylene glycol (EG) then added slowly drop by drop to the above suspension. After that, the mixture was continuously stirred and heated under reflux at 160°C for 1.5 h to achieve the reduction and deposition of Pt nanoparticles on the surface carbon nanotubes. The sample was separated from the solution by centrifuging at 11000 rpm for 30 min. The product was filtered and washed with deionized water and then dried in an oven at 100° C for 24 h.

4.1.5 Synthesis of Ru/Pt Core/ Shell Nanoparticles by a New Modified Polyol Method

Ru/Pt core/shell bimetallic nanoparticles were prepared by a new modified polyol reduction method via three steps as follows:

- Preparation of Ru nanoparticles: in a 50 mL flask, 57.1 mg of PVP and 0.4 mmol of RuCl₃.nH₂O (ruthenium chloride) dissolved in 12 mL of triethylene glycol (TEG). After that, the mixture was continuously stirred and heated under reflux at 285°C for 3 h to achieve the reduction and preparation of homogeneous colloidal solution of Ru nanoclusters.
- Preparation of Pt nanoparticles: in a 50 mL flask, 0.25 mmol of PtCl₂ (platinum chloride) dissolved in 18 mL of ethylene glycol (EG). After that, the mixture was continuously stirred and heated under reflux at 160°C for 1.5 h to generate Pt-complex solution containing Pt²⁺ ions.

3. Preparation of Ru/Pt bimetallic nanoparticles: The Pt solution obtained at step 2 was added slowly to the formed Ru colloid with continuous stirring for 4h to achieve the deposition of Pt nanoparticles on the surface of Ru nanoparticles. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

4.1.6 Synthesis of Ru/Pt Core/Shell Nanoparticles Supported on Various Types of Carbon by a New Modified Polyol Method

Three kinds of carbon are used for preparation of Ru/Pt core/ shell nanoparticles vulcan C-X72 carbon, nanocarbon powder ≤ 50 nm and multi-walled carbon nanotubes (CMWNT) as described below.

4.1.6.1 Synthesis of Ru/Pt core/shell nanoparticles supported on Vulcan C-X72 carbon

For the first step, 108 mg of Vulcan XC-72 (50 mg) was dispersed in 200 ml of water. The mixture was ultrasonicated for 30 min. 12 mM RuCl₃.nH₂O was dissolved in 12 mL of triethylene glycol (TEG) then added slowly to the above suspension. The mixture was continuously stirred and heated under reflux at 285°C for 3 h in order to ensure the reduction and deposition of Ru onto the support. The next step, 36 mM of PtCl₂ in 18 mL of ethylene glycol (EG) was added drop by drop to the above mixture. After that, the mixture was continuously stirred and heated under reflux at 160°C for 1.5 h to achieve the reduction and deposition of Pt nanoparticles onto the surface of Ru seeds. The sample was separated from

the solution by centrifuging at 11000 rpm for 30 min. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

4.1.6.2 Synthesis of novel Ru/Pt Core/shell nanoparticles supported on nanocarbon powder ≤ 50 nm

The method discussed in section 4.1.6.1 was followed to prepare Ru/Pt core/shell nanoparticles using nanocarbon powder ≤ 50 nm.

4.1.6.3 Synthesis of novel Ru/Pt Core/Shell Nanoparticles Supported on Multi-Walled carbon Nanotubes (CMWNT)

The same method described in section 4.1.6.1 was followed to prepare Ru/Pt core/shell nanoparticles using carbon nanotube as support.

4.1.7 Synthesis of Novel Pt Supported on Multi-walled Carbon Nanotubes by a New Modified Polyol Method

0.5 mg of multi walled carbon nanotubes were dispersed in 100 ml of water. The mixture was ultrasonicated for 30 min. 2mmol of $PtCl_2$ was dissolved in 18 mL of ethylene glycol (EG) then added slowly drop by drop to the above suspension. After that, the mixture was continuously stirred and heated under reflux at 160°C for 2 h to achieve the reduction and deposition of Pt nanoparticles onto the surface carbon nanotubes. The sample was separated from the solution by centrifuging at 11000 rpm for 30 min. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

4.2 Testing the Performance of Catalysts Preparing Using the Direct Methanol Fuel Cell (DMFC).

The performance of the Pt based core/ shell nanoparticles catalysts which were prepared in section 4.1.5, 4.2.6 and 4.1.7 and the effect of different kinds of carbon support on the catalytic activity of Ru/Pt core/shell catalysts were tested in a DMFC. Catalysts that have been selected are summarized in the following Table (4-1).

Table 4-1: Summary of the Pt based core/shell catalyst synthesized by modified polyol method for DMFC.

]		
Catalyst	Anode	Cathode	Platinum
			loading
Commercial PtRu	Commercial PtRu	Commercial Pt Supported on	1mg/cm ²
Supported on Vulcan	Supported on Vulcan	Vulcan C-X72 Carbon	
C-X72 Carbon	C-X72 Carbon		
Ru/Pt core/shell	Ru/Pt core/ shell	Commercial Pt Supported on	1mg/cm ²
nanoparticles without	nanoparticles	Vulcan C-X72 Carbon	
support			
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt Supported on	1mg/cm ²
nanoparticles	nanoparticles	Vulcan C-X72 Carbon	
supported on Vulcan	supported on Vulcan		
C-X72 Carbon	C-X72 Carbon		
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt Supported on	1mg/cm ²
nanoparticles	nanoparticles	Vulcan C-X72 Carbon	
supported on Carbon	supported on Carbon		
nanotube	nanotube		
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt Supported on	0.5mg/cm ²
nanoparticles	nanoparticles	Vulcan C-X72 Carbon	
supported on Carbon	supported on Carbon		
nanotube	nanotube		
Pt supported on	Commercial PtRu	Pt supported on Carbon	1mg/cm ²
Carbon nanotube	Supported on Vulcan	nanotube	
	C-X72 Carbon		

To test samples in Table 4-1 need to prepare MEA.

4.2.1 Membrane Electrode Assemblies (MEA)

In general, MEA contains a uniform catalyst layer applied to a gas diffusion layer (GDL) and polymer electrolyte membrane (Nafion membrane). After the fabrication all the necessary components (anode, cathode, membrane) they are hot pressed together to form the MEA [162] as shown in Figure 4-3 below.



Figure 4-3. Membrane electrode assemblies (MEA): (1) bipolar plate, (2) gasket, (3) gas diffusion layer, (4) catalyst layer and (5) polymer electrolyte membrane [163].

4.2.1.1 Nafion 117 membrane activation

As shown in Figure 4-4 [162].



Figure 4-4. Procedure for preconditioning Nafion membrane.

4.2.1.2 Preparation of gas diffusion layer (GDL)

The GDL was prepared by spraying 1mg/cm^2 carbon ink onto (9.0 cm x4.5 cm) carbon paper then applied catalyst layer (1mg/cm^2) by spraying catalyst ink onto GDL using an airbrush and 2bar N₂ feed to spray carbon ink and catalyst ink, respectively. Figures 4-5 and 4-7 shown the procedure for preparation of carbon ink and catalyst ink, respectively.

Preparing Carbon Ink [161]

Polytetrafluoroethylen (PTFE 60%W, 0.06g) + Propa-2-ol (IPA, 5ml) Sonicate for 10 After that, Adding Ketjen Black (0.324g) Sonicate for 30-60 Then adding IPA (55 ml) gradually over 24-48 h with sonication for 30 minutes between additions Carbon ink Figure 4-5. Method for preparing carbon ink.

Spraying Carbon ink on Carbon Paper:

- A carbon paper (20.25 cm2) was weight. Since the optimum amount of carbon ink on the GDL is 1mg per cm2, the target weight of ink added into carbon paper was 0.02025g.
- 2- The carbon paper was placed on a hotplate surface to maintain 60°C and enhance evaporation of IPA.
- 3- Airbrush was used to spry the carbon ink on the carbon paper. Before spraying, the airbrush was cleaned and connected to nitrogen gas at one psi.
- 4- 5ml of IPA was sprayed to wet the carbon paper.

- 5- After wetting the carbon paper, the airbrush was placed perpendicularly at a 2cm distance from the carbon paper.
- 6- 2ml of the ink was placed in the airbrush and sprayed back and forth in straight lines to maintain a uniform layers.
- 7- The carbon paper was dried at 120°C in oven for ten minutes and weighted to obtain the required weight of ink on the paper.
- 8- Finally, the GDL was sintered at 360°C for one hour with a ramping temperature of 1°C per minute.

Preparing Catalyst Ink

Anode Catalyst Layer Preparation (figure 4-6)

- 1- 1.429g of Nafion 5% solution was placed in into vial.
- 2- 15ml of Acetone was added into the vial and sonicated for ten minutes until the mixture was clear.
- 3- 0.405g of catalyst was added to the mixture and sonicated for one hour.

Cathode Catalyst Layer Preparation (figure 4-6)

- 1- 1.429g of Nafion 5% solution was placed in into vial.
- 2- 15ml of Acetone was added into the vial and sonicated for ten minutes until the mixture was clear.
- 3- 0.27g of catalyst (Pt: 60%) was added to the mixture and sonicated for one hour.



Figure 4-6. Method for catalyst ink (anode and cathode) preparation.

Spraying catalyst ink on GDL

- The GDL was weighted and the number of grams of catalyst was needed for loading (one electrode) on the GDL was 0.0506g for anode and 0.03375g for cathode.
- 2- The catalyst was sprayed without using a hotplate and starting number of ml of catalyst ink was 0.5ml.
- 3- The solvent that has been used in spraying catalyst was acetone instead of IPA.
- 4- After spraying the catalyst via airbrush, the GDL was dried in an oven at120°C for ten minutes and weighted.
- 5- The spraying steps were repeated to achieve the target catalyst loading on the GDL.

Preparation of Nafion Coating Anode and Cathode

These steps were used for coating electrodes, anode and cathode, for MEA.

1- 0.972g of Nafion 5% solution was placed in a vial.
- 2- 10ml of acetone was added into the vial and sonicated for 30 minutes.
- 3- 5ml of the solution was sprayed on the anode electrode using the airbrush at room temperature in the fume hood.
- 4- The anode electrode was dried in an oven at 120°C for 15 minutes.
- 5- The same procedures for Nafion coating were followed for the cathode electrode.

4.2.1.3 MEA fabrication and thermal compression

Fabrication the MEA was homemade in the University of Manchester by following steps:

- Anode electrode was placed on one of the stainless steel plate facing the top as shown in Figure 4-7.
- 2- Activated membrane was placed on the top of the anode and centered.
- 3- On top of activated membrane, cathode electrode was placed facing on the bottom, where both electrodes were facing each other and the activated membrane comes in between.
- 4- The other stainless steel plate was to place on the cathode to sandwich the MEA.
- 5- The stainless steel plates were wrapped with an aluminum foil and placed in th thermal press equipment.
- 6- Two stages of press were preformed; the first stage was accomplished be thermal pressing the MEA at temperature and pressure of 137°C and 3 bar for 3 minutes.
- 7- The second stage was made by flipping the stainless steel plate and cools it down by applying a pressure of 3 bar for 30 minutes.
- 8- Once the compression was done, the MEA was taken out from the equipment, kept on the bench, and cools down to naturally to room temperature.
- 9- The MEA was placed in the fuel cell and kept under hydration, by circulating DI water for overnight.



Figure 4-7. The anode placed on the stainless steel.

4.3 Characterization of Core/Shell Nanoparticles

Characterization of core/ shell nanoparticles was carried out by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.3.1 General Principles of Electron Microscopy

In both of these electron microscopes a highly energetic monochromatic beam of electrons is allowed to interact with the specimen under investigation. These interactions are detected and converted into an image by the image recording system. The interaction of the electron beam with the specimen gives information concerning its morphology, topography, crystallographic arrangement, elemental composition and particle size. The electron microscope consists of an electron source, anode, magnetic lenses, apertures, specimen stage and image recording system all of which operate in a high vacuum. The electron source can be made of various types of materials. The most common is the tungsten filament which, when heated, produces electrons which are attracted by the anode and are accelerated down the column and interact with the specimen. The electrons so the resulting beam is monochromatic. This monochromatic beam is focused and interacts with the specimen in different ways, depending on the type of electron microscope. These interactions are detected and converted into an image by the image recording system. This system converts the radiation into a permanent image either onto photographic film, or into a digital image [164,165].

4.3.2 The Transmission Electron Microscope (TEM)

In the TEM, the focused, monochromatic electron beam interacts with and is transmitted through the sample, focused into an image and projected onto a phosphor coated screen which emits visible light. The brighter areas of the image represent areas where more electrons have passed through the sample. The darker areas represent areas where fewer electrons have passed through as a result of higher specimen density. A TEM can magnify up to about 500,000x [164].

The transmission electron microscope (TEM) works much like a light microscope, transmitting a beam of electrons through a thin specimen and then focusing the electrons to form an image on a screen or on film. This is the most common form of electron microscope and has the best resolution. Figure 4-8 (a) shows a schematic of TEM column. The TEM was carried out with a JEM-100SX microscope to determine the structure and particle size in the samples investigated.

4.3.3 The Scanning Electron Microscope (SEM)

Figure 4-8 (b) shows a schematic of an SEM column. The scanning electron microscope (SEM) scans a fine beam of electrons onto a specimen and collects the electrons scattered by the surface. This has poorer resolution, but gives excellent 3-dimentional images of surfaces [165].

In the SEM, a set of scan coils moves the electron beam across the specimen in a 2 dimensional grid fashion. When the electron beam scans across the specimens, different interactions take place. These interactions are decoded with various detectors situated in

the chamber above the specimen. Some electrons from the surface material are knocked out of their orbitals by the electron beam, and are called secondary electrons. These electrons are detected by the secondary electron detector. Different interactions give images based on topography, elemental composition or density of the sample. A SEM can magnify up to about 100,000x.

Scanning electron microscopy (SEM) in these studies was carried out with a "Quanta instrument from the FEI Company with an accelerating voltage of 100 kV. SEM instrument was equipped with energy dispersive X-Ray analysis (EDX) facility allowing elemental identification as well as compositional analysis on specimens used.



Figure 4-8. (a) Schematic of TEM column [166] and (b) schematic diagram of SEM column [167].

CHAPTER FIVE

5. CHAPTER 5: RESULTS AND DISCUSSION

5.1 Synthesis of Core/Shell Nanostructure

Although the major work in this study is dedicated to synthesizing catalysts based on the use of Pt and Ru compounds, it was thought to be more appropriate to star with cheaper substances with the aim of gaining experience in the synthesis procedures.

Co, Ni and Fe compounds used here were readily available in the market and much cheaper than the precious metal compounds which were used later on in this study to prepare the targeted core/ shell catalysts.

5.1.1 Synthesis of Novel Co/Ni Core/Shell Nanoparticles

Core/shell nanoparticles have been successfully prepared for novel Co/Ni catalyst for first time with extremely small particles size 1.96 nm. The formation of the metals can be monitored by observing the colour changes associated with the mixing of the solutions prepared. In this study, the colour turned from light blue to dark blue immediately after the addition of the reducing agent to $CoCl_2$ in CH_3CH_2OH solution, indicating the formation of Co nanoparticles. This was followed by the addition of the NiCl₂ in CH_3CH_2OH solution. At this stage the colour of the solution turned dark green, indicating the reduction of Ni ions to Ni. In a recent study Libor et al [168] reported the reduction of the [Ni $(N_2H_4)_3$]²⁺ complex in an alkaline media as expressed in the following equation:

$$Ni^{2+} + 3N_2H_4 \leftrightarrow [Ni(N_2H_4)_3]^{2+}$$
 5-1

Then $[Ni(N_2H_4)_3]^{2+}$ reacts with OH^- in alkali system as follows:

$$2[Ni(N_2H_4)_3]^{2+} + 40H^- \rightarrow 2Ni \downarrow + N_{2+}4H_2 \ 0 + 5N_2H_4 \qquad 5-2$$

A similar reduction process could be envisaged to the Co, N_2H_4 complex in this case. It is suggested that that Co/Ni nanoparticles formed in the reduction are not simply a physical mixture of individual metallic nanoparticles.

The SEM images obtained indicated that the sample investigated has hollow building blocks core/shell shaped structure which has never been reported previously for Co/Ni, as shown in Figure 5-1. By observing Figure 5-1 it could be assumed that the hollow structure is formed by self-assembly of particles giving Co/Ni core/shell in the form of building blocks.

However, it must be emphasized in this study that the TEM images recorded are supposed to be more reliable and better in revealing the actual structure obtained. This will be presented in the TEM section.



Figure 5-1. SEM micrograph of Co/Ni showing hollow core/shell structure.

Here is a similar morphology from literature [169], they reported the synthesis of $CoSnO_2/C$ hollow nanostructure by fast growth of Co porous shell around Sn in alkaline medium as shown in Figure 5-2 below.



Figure 5-2. SEM image of CoSnO₂/C hollow shell nanostructure [169].

Many studies have indicated the effect of parameters such as temperature, pH of solution and aging on the morphology of the resulting metal nanoparticles formed [168, 170-171]. In this study, the use of a high pH solution around 11 results in the formation of hollow building blocks core/shell instead of spherical core/shell nanostructure.

EDX was used for elemental identification and composition of the core/ shell bimetallic material prepared. Results obtained showed an atomic ratio of nearly 1:1 (Table 5-1) as expected from the calculations based on the amounts of the precursors used. The EDX results obtained from three spots for the sample investigated.

Element	Weight %	Atomic %	
СоК	55.57	55.48	
NiK	44.43	44.52	
Total	100	100	

Table 5-1: Elemental composition for Co/Ni as shown by EDX.

A typical TEM images of the prepared Co/Ni nanoparticles is shown in Figures 5-3 and 5-4. The following Table 5-2 reports on the diameter of Co/Ni nanoparticles measured manually from the TEM micrograph (Figure 5-3). Results obtained revealed that an average particle size around 1.96 nm has been achieved, using sol-gel method by reduction of CoCl₂ and NiCl₂ in $C_2H_6O_2$ solution.

Number of particles	Diameter nm
7	3± 0.5 nm
13	2 ± 0.5 nm
10	1 ± 0.05 nm
5	$0.5 \pm 0.05 \text{ nm}$
$\sum n = 35$	$\sum d = 69.1835$

Table 5-2: The particles size of Co/Ni core/Shell catalyst.

Total average particle size = $\sum n / \sum d \approx 1.96 \text{ nm}$



Figure 5-3.TEM micrograph of Co/Ni bimetallic nanoparticles.



Figure 5-4. TEM micrograph of Co/Ni core/shell nanoparticles.

The objective of this preparation was to obtain a core/ shell structure for the Co/Ni bimetallic nanoparticles. SEM micrographs gave a clear evidence that a core/shell hollow shaped which is considered as one of the forms of the core/shell nanostructure has been obtained. This study presents a new catalyst with extremely small particle size and halo shaped of Co/Ni catalyst which has not been obtained previously.

Hollow core/shell has a high porosity and good electronic conductivity because it could be used in several applications as energy storage.

5.1.2 Synthesis of SiO₂/Ni Core/Shell Nanoparticles Using Three Types of Silica

The results indicated in SEM and TEM images (figures 5-5 and 5-6) confirmed the successful preparation of core/shell nanoparticles for SiO_2/Ni through a new modified sol-gel method with novelty structure for SiO_2/Ni (commercial silica) which has not been obtained previously. NiCl₂ in CH₃CH₂OH solution was added drop by drop to a solution of SiO₂ in

(1:1) H₂O:CH₃CH₂OH as mentioned earlier in chapter four (4.1.2). The reduction of Ni ions to Ni nanoparticles was indicated by the change in colour of solution from light green to dark after the addition of the reducing agent, as expressed previously in equations 5-1 and 5-2. Figure 5-5 (a-c), show the SEM images obtained for the SiO₂/Ni core / shell nanoparticles prepared using (a) commercial silica, (b) liquid silica and (c) dried silica, respectively.

The SEM images obtained (figure 5-5 a-c) show an interesting feature in the images presented, although with varying degrees of clarity. The commercial SiO_2 sample gave the clearest image for cubic core/shell nanostructure as shown in figure 5-5 (a) below. The relative homogeneity in the particle size of commercial SiO_2 could have played a role in that.



Figure 5-5 (a-c). (a) SEM micrograph of SiO₂/Ni core/ shell nanoparticles using commercial silica, (b) SEM micrograph of SiO₂/Ni core/ shell nanoparticles using liquid silica and (c) SEM micrograph of SiO₂/Ni core/ shell nanoparticles using dried silica.

EDX also was used to determine the composition of SiO_2 core and Ni shell nanoparticles as shown in Table 5-3.

SiO ₂ /Ni using commercial silica		SiO ₂ /Ni using dried silica			
Element	Weight %	Atomic %	Element	Weight %	Atomic %
SiK	13.89	25.22	SiK	37.04	55.15
NiK	86.11	74.78	NiK	62.96	44.85
Total	100	100	Total	100	100

Table 5-3: Elemental composition for SiO₂/Ni as shown by EDX.

By observing Table 5-3, there is a big difference when using commercial silica and dried silica. This difference could be due with the particles size of the types of silica used. Further work is needed to explore this difference.

TEM was carried out on the sample prepared by using the commercial silica only. Figure 5-6 show the TEM image obtained. The halo shaped structure is the common feature in these TEM images. Similar images for Pd/ Au core/shell bimetallic nanocrystals have been observed, where the Au in the halo represented the shell, while the inner part of the structure constituted the Pd core, in the core/ shell nanocrystal prepared (figure 5-7) [172].



Figure 5-6. TEM micrographs of SiO₂/Ni showing halo core/shell nanoparticles.



Figure 5-7. TEM images of Pd/Au core/ shell nanoparticles [172].

It is suggested that the halo structure observed in the TEM images in the samples in this study demonstrates the existence of cubic core /shell nanostructure, in which the halo represents Ni, while the inner part forming the core is the SiO₂. Particle size analysis based on the TEM images yields an average diameter of about 60 nm for SiO₂/Ni core/ shell nanoparticles with thin Ni shell thickness as shown in Figure 5-6.

The results indicated in SEM and TEM images (figures 5-5(a) and 5-6) confirmed the successful preparation of core/shell nanoparticles for SiO_2/Ni through a new modified sol-gel method. In this study, we present the special structure which was not obtained previously for SiO_2 (commercial)/Ni catalyst. This structure may possess unique catalytic properties.

5.1.3 Synthesis of Novel SiO₂/CoFe Core/Shell Nanoparticles

 SiO_2 nanoparticles homogeneously coated with CoFe halo shell were prepared for the first time by a new modified sol-gel method with an average size of 39 nm with novelty halo shaped as shown in Figure 5-9. To deposit CoFe shell on the surface of SiO₂, hydrazine in alkali media was chosen as the reducing agent. The halo core/shell of SiO₂ /CoFe nanostructure is characterized by SEM and TEM spectroscopy. The data derived from SEM and TEM confirmed that the halo shell CoFe successfully coated the SiO₂ core nanoparticles. Figure 5-8 shows SEM images of the SiO₂/CoFe core/shell nanoparticles. Based on the SEM, it is concluded that the nanoparticles has halo shaped and hollow building blocks well dispersed on the silica surface as shown in Figure 5-8.



Figure 5-8. SEM micrographs of SiO₂/CoFe core/ shell nanoparticles.

The TEM images in Figure 5-9 show conformal overgrowth of CoFe on the SiO_2 layer generating SiO_2 / CoFe halo core/ shell nanostructure.



Figure 5-9. TEM micrograph of SiO $_2$ /CoFe core/ shell nanoparticles showing halo core/shell nanostructure.

From the TEM image in Figure 5-9, the thin CoFe shell can be observed as a white halo around each SiO_2 core nanoparticles with a clear core/shell structure. In addition, it was found that SiO_2 core surrounded by uniform halo shell, suggesting that the CoFe nanoparticles growth together as alloy on the multiple nucleation sites of SiO_2 nanoparticles during the synthesis or Co nanoparticles coated SiO_2 first as interlayer then the Co interlayer surrounded by Fe nanoparticles as outer layer to form halo sandwich core/ shell nanostructure.

Several studies have described the synthesis of core/shell halo structure with different materials and similar images have been observed in Pd/Au (figure 5-7), Au/Pt and Au/Pd nanoparticles which have been attributed to the formation of a core/ shell nanostructure [173,174] as shown in Figures 5-10 and 5-11 below.



Figure 5-10. TEM images of Au/Pt core/ shell nanoparticles [173].



Figure 5-11. TEM images of Au/Pd core/ shell nanoparticles [174].

EDX was also used as well to determine the composition of material prepared as shown in Table 5-4.

Element	Weight %	Atomic %	
SiK	16.95	29.33	
FeK	48.12	41.87	
СоК	34.93	28.81	
Total	100	100	

Table 5-4: Elemental composition for SiO₂/CoFe core/ shell nanoparticles by EDX.

Based on the SEM and TEM results which are discussed above, the core/shell nanostructure for SiO₂/CoFe has been achieved using the modified sol-gel method. This catalyst with new structure has not been prepared before. We suggest that, SiO₂/CoFe core/shell nanoparticles could be promising catalyst in the Fischer-Tropsch process, since Fe is known to be an essential metal in FT synthesis catalyst that is responsible for the production of unsaturated hydrocarbons [16].

5.1.4 Synthesis of Novel SiO₂/Pt Monometallic Core/Shell Nanoparticles

 SiO_2/Pt core/shell nanoparticles were prepared by two different methods namely a new modified sol-gel method, and a new modified polyol method for first time with novel structures halo and crown- jewel shaped respectively to investigate the effect of the preparation on the obtained catalysts structure.

5.1.4.1 Synthesis of novel SiO₂/Pt monometallic core/shell nanoparticles by a new modified sol-gel method

Since the sol- gel method has been proven in non-noble metals with core/ shell nanostructures (sections 5.1.1, 5.1.2 and 5.1.3), this method was then applied to prepare noble metals as core/ shell structures in this project. The platinum nanoparticles (Pt) coated commercial silica

 (SiO_2) were prepared by a modified sol-gel method for first time (particles size around 75 nm) with a high yield of product comparing to polyol method. In this case, ethylene glycol (EG) was added to platinum chloride (PtCl₂) with increasing reaction temperature at 160°C to modify sol- gel method in order to be more suitable for the preparation of noble metals with a core/shell structure. We suggest the mechanism of reduction platinum chloride (PtCl₂) to platinum particles (Pt) using the modified sol- gel method, as shown in Figure 5-12.



Figure 5-12. The mechanisms of reducing platinum chloride (PtCl₂) to platinum particles.

The morphology of the SiO₂/Pt core/shell nanoparticles was investigated by SEM and TEM microscopy. Figures 5-13 show the SEM images of SiO₂/Pt monometallic core/shell, the results obtained revealed that SiO₂/Pt catalyst is shaped like a cube with well distributed.



Figure 5-13. SEM micrograph of SiO₂/Pt core/ shell nanoparticles using a new modified solgel method.

From TEM micrograph (Figure 5-14) it can be concluded that SiO_2/Pt core/shell structure is obtained at 160°C and pH around 12. Micrographs reveal conformal overgrowth of Pt particles on the SiO₂ surface with thin Pt halo shell surrounding the SiO₂ core. This a unique symmetric structure could be due to the reaction temperature and high pH. TEM images confirm that there are almost no Pt nanoparticles aggregation and well distributed on the SiO₂ surface, this confirms the effect of high temperature and pH on the structure of SiO₂/Pt obtained in this study. In addition, TEM images obtained indicate as well different morphology for the particles in the sample investigated, namely needle shaped structure.



Figure 5-14. TEM micrographs of SiO₂/Pt core/ shell nanoparticles using a new modified sol-gel method.

As can be seen from the results of SEM and TEM spectroscopy, SiO_2/Pt core/shell nanoparticles were synthesized successfully through modified sol-gel method with clear halo shell structure. It is suggested that high temperature and high pH are suitable parameters to form noble metal as shell in core/shell structures. This fact proved the modified sol-gel method is a suitable for preparation SiO_2/Pt monometallic core/shell structure.

The core/shell structure of SiO_2/Pt nanoparticles obtained in this study is similar to the SiO_2/Ag core/shell commercial catalyst (10-12 nm) from Sky Spring Nanomaterials (SSNano) [175] as shown in its TEM micrograph in Figure 5-15.



Figure 5-15. TEM micrograph of SiO₂/Ag core/shell commercial catalyst [175].

5.1.4.2 Synthesis of SiO₂/Pt monometallic core/shell nanoparticles by a new modified polyol method

Another method was used here to prepare SiO_2/Pt core/shell monometallic nanoparticles. In this case, SiO_2/Pt core/shell catalyst was prepared without addition of any other reducing agent apart from ethylene glycol with pH around 10 to reduce Pt^{2+} ions to Pt particles.

SEM and TEM were used to investigate the morphology and homogeneity of the produced catalyst.

The SEM images obtained show the Pt particles distribution as bright spots on the SiO_2 surface as shown in Figure 5-16.



Figure 5-16. SEM micrograph of SiO₂/Pt core/ shell nanoparticles using a new modified polyol method.

TEM was carried out to determine the shapes and size of SiO₂/Pt core/shell particles. It was found that the Pt nanoparticles distribution as very small dark dots on the spherical shape core of SiO₂ to form crown- jewel core/shell structure when the Pt nanoparticles located on the top of the SiO₂ core with an average size of 3 nm which has never been reported previously for SiO₂/Pt as shown in Figure 5-17.



Figure 5-17. TEM micrograph of SiO_2/Pt core/ shell nanoparticles using a new modified polyol method.

From previous discussions in sections 5.1.4.1 and 5.1.4.2, the results can be summarized as follow: SEM and TEM results revealed considerable difference between the morphologies of SiO₂/Pt monometallic catalysts were prepared using different methods namely a new modified sol-gel method and a new modified polyol method.

What is noticeable in SiO₂/Pt catalyst prepared by polyol method is the absence of clear halo shell observed in the TEM micrograph of SiO₂/Pt catalyst prepared by modified sol-gel method (figure 5-17). It is suggested that this halo shell structure could be attributed to the effect of modified sol-gel parameters (pH and temperature) on the growth of Pt particles on the SiO₂ surface. It was found that SiO₂/Pt catalyst prepared by modified sol-gel technique has halo structure while SiO₂/Pt catalyst prepared by using modified polyol method has crown- jewel core/shell structure. These structures never been reported previously.

Based on the particles size obtained from TEM images (Figures 5-14 and 5-17), the new modified polyol method seem to have a much greater impact on the particles size (3nm) than the modified sol-gel method (75 nm).

It was also noted that that the sol-gel method is given a high yield of product comparing to polyol method.

5.1.5 Synthesis of Ru/Pt Core/Shell Nanoparticles

Ru/Pt core/shell nanoparticles were prepared by a new modified polyol method for the first time through reduction of RuCl₃.nH₂O and PtCl₂. The formation of the metals can be monitored by observing the colour changes during the heating of solution. The colour of the solution of RuCl₃.nH₂O in TEG (triethylene glycol) changed from dark red to light yellow then turned to dark brown during heating at 285°C for 3 h , indicating the formation of Ru nanoparticles. During heating of PtCl₂ in ethylene glycol (EG), the colour of the solution changed from light brown to dark brown at 160°C for 1.5 h indicating the reduction of Pt²⁺ ions to Pt nanoparticles. To deposit Pt nanoparticles on the surface of Ru, the Pt solution added slowly to the formed Ru colloid with continuous stirring for 4h to achieve the deposition of Pt nanoparticles on the surface of Ru nanoparticles. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

The catalytic activity of Ru/Pt core/shell catalyst was tested using direct methanol fuel cell (DMFC) as will be discussed in section (5.2.2).

SEM images for Ru/Pt obtained at low and high resolution are shown in Figure 5-18. SEM image taken at high resolution has clearer structural details.



Figure 5-18. (a) SEM micrograph at low resolution of Ru/Pt core/shell nanoparticles and (b) SEM micrographs at high resolution of Ru/Pt core/shell nanoparticles.

SEM micrographs gave a clear evidence that a spherical shape which is considered as one of the possible forms of the core/shell nanostructure has been obtained as shown in Figure 5-18 (b).

TEM was carried out to determine the shapes and size of Ru/Pt core/shell particles. It was found that the Ru/Pt nanoparticles have spherical shape grey circles as core attributed to Ru containing a large dark spots as shell attributed to Pt particles with an average size of 6 nm. TEM images of the Ru/Pt core/shell nanoparticles is shown in Figure 5-19.



Figure 5-19. TEM micrograph of Ru/Pt core/ shell nanoparticles.

5.1.6 Synthesis of Novel Ru/Pt Core/Shell Nanoparticles Supported on Various Types of Carbon

The preparation of highly dispersed Ru/Pt catalysts on a support such as carbon with lower Pt is one of the goals of this research. The RuPt bimetallic nanoparticles were coated on three kinds of carbon [(Vulcan XC-72, carbon powder \leq 50 nm and multi- walled nanotube carbon (CMWNT)] and were prepared by the new modified polyol method. The author of this work is not aware of any studies that have prepared Ru/Pt on carbon powder \leq 50 nm and carbon multi-walled nanotube previously. In this method we used triethylene glycol and ethylene

glycol as solvents and reducing agents. To prepare Ru/Pt core/shell on carbon support, first the carbon was dispersed in 200 ml of water. The mixture was ultrasonicated for 30 min. 12 mM RuCl₃.nH₂O was dissolved in 12 mL of triethylene glycol (TEG) then added slowly to the above suspension. The mixture was continuously stirred and heated under reflux at 285°C for 3 h in order to ensure the reduction and deposition of Ru onto the support. The next step, 36 mM of PtCl₂ in 18 mL of ethylene glycol (EG) was added drop by drop to the above mixture. After that, the mixture was continuously stirred and heated under reflux at 160°C for 1.5 h to achieve the reduction and deposition of Pt nanoparticles onto the surface of Ru seeds. The sample was separated from the solution by centrifuging at 11000 rpm for 30 min. The product was filtered and washed with deionized water and then dried in an oven at 100°C for 24 h.

The performance of the Ru/Pt core/shell catalysts prepared were tested using a direct methanol fuel cell (DMFC) to study the effect of the support on the catalytic activity of catalysts as will be discussed in sections (5.2.3).

The morphologies of Ru/Pt core/shell on different kind of carbon were examined using SEM, EDX and TEM.

The morphologies of the Ru/Pt core/shell supported on carbon are shown in the SEM images in Figure 5-20 (a-c). SEM images clearly depict the effect of different carbon morphologies on the types of structures shown in the coming discussion. All samples appeared with well dispersed and fairly narrow size distribution of the bimetallic nanoparticles as revealed by the SEM micrographs.

For Ru/Pt core/shell supported on Vulcan XC-72 in Figure 5-20 (a), Ru/Pt nanoparticles appeared as bright dots coating carbon particles and under higher magnification it can be observed that bright spots is most likely to be Pt particles dispersed on the grey areas these

could be attributed to the presence of Ru particles. Since the Ru being lighter than Pt is expected to produce less electron scattering hence it is supposed to produce areas of lower brightness. Moreover, it could be assumed that the Ru nanoparticles deposited on the Vulcan carbon first as interlayer then the Ru interlayer coated by Pt nanoparticles as outer layer to form sandwich core/ shell nanostructure Ru/Pt/C or the RuPt nanoparticles growth together as alloy on the carbon surface during the synthesis to form RuPt as alloy shell and C as core.

SEM image of Ru/Pt on carbon powder \leq 50 nm in Figure 5-20 (b) revealed that some Ru/Pt nanoparticles aggregate as big bright specks on some part of carbon surface to produce a cluster type network.





Figure 5-20. (a) SEM micrograph of Ru/Pt core/ shell nanoparticles supported on Vulcan XC-72, (b) SEM micrograph of Ru/Pt core/ shell nanoparticles supported on carbon powder \leq 50 nm and (c) SEM micrograph of Ru/Pt core/ shell nanoparticles supported on CMWNT.

The SEM image of Ru/Pt on carbon nanotube (CMWNT) in Figure 5-20 (c) obtained indicated that the Ru/Pt nanoparticles with good size distribution are located on the nanotube surface and no catalyst particles are observed off the bundles of CMWNT.

Structural characterizations of the Ru/Pt nanoparticles supported on Vulcan XC-72, carbon powder \leq 50 nm and carbon multi- walled nanotube (CMWNT) were carried out using TEM as shown in Figures 5-21, 5-22 and 5-23, respectively.





Figure 5-21 (a) and (b). TEM micrographs of Ru/Pt core/shell nanoparticles supported on Vulcan XC-72.

By observing TEM images of Ru/Pt bimetallic on Vulcan carbon in Figures 5-21 (a, b) it is assumed that the Ru/Pt nanoparticles distribution as dark dots shell on the spherical shape core of Vulcan carbon to form what is referred to crown-jewel bimetallic core/ shell nanostructure. These bimetallics consist of an expensive metal atom such as Pt located on the top of the other metal atoms (cheaper metal) or cheaper materials such as C or SiO₂. The particles size of Ru/Pt catalyst was estimated to be 4 nm according to the TEM images.

Moreover, TEM result of Ru/Pt on Vulcan carbon is similar to the one obtained by Zhu et al [176] for Cu/Pt on Vulcan XC-72 as shown in Figure 5-22. Zhang et al [177] reported the preparation of Co/Pt nanoparticle catalyst on Vulcan carbon and the results obtained from TEM images of catalyst (figure 5-23) was similar to the results we have obtained for the Ru/Pt on Vulcan carbon.



Figure 5-22. HRTEM images of Cu/ Pt/C core/shell catalyst [176].



Figure 5-23 . TEM micrograph of Co/Pt core/ shell nanoparticles supported on Vulcan XC-72 [177].

For the nanocarbon supported Ru/Pt bimetallic catalyst in Figure 5-24, the Ru/Pt nanoparticles dispersion on nanocarbon surface was homogeneous with a narrow particles size distribution around 3 nm. Here, it is suggested that a core/ shell structure is obtained of crown-jewel type (these bimetallics consist of an expensive metal atom such as Pt located on the top of the other metal atoms (cheaper metal) at the special position) where the Ru/Pt has taken a crown shape as indicated in the Figure 5-24.



Figure 5-24. TEM micrograph of Ru/Pt core/ shell nanoparticles supported on nanocarbon ≤ 50 nm.

The morphology and particles size of Ru/Pt nanoparticles on carbon nanotube were analysed by TEM as well. The results obtained confirm that the configuration of the Ru/Pt nanoparticles along the nanotube structure and located as black specks on the bundles of multi-walled carbon nanotube without any separate nanoparticles present off the nanotube structure, as shown in Figures 5-25 (a, b).



Figure 5-25 (a). TEM micrographs of Ru/Pt core/ shell nanoparticles supported on carbon multi –walled nanotube (CMWNT).



Figure 5-25 (b). TEM micrographs of Ru/Pt core/ shell nanoparticles supported on carbon multi –walled nanotube (CMWNT).

It has been mentioned that the most common problems when depositing metal on carbon nanotube surface is controlling the size and distribution of nanometal particles. Functionalization of surface carbon nanotube by addition of functional group such as with (HO⁻) or (NH_4^+) was found to essential requirement for a achieving deposition metal nanoparticles on the carbon nanotube surface. However, this makes the preparation more complex and increases the cost [178]. In this project, we describe a simple method for depositing nanoparticles on the carbon nanotube surface to form Ru/Pt core/shell supported on carbon nanotube, without the need of functionalization.

Table 5-5 show the compositions of Ru/Pt bimetallic nanoparticles on three kinds of carbon were measured by EDX spectra. The EDX results indicated that Ru:Pt atomic ratio of nearly 1:1 for all samples.

Ru/Pt on Vulcan XC-72		Ru/Pt on nanocarbon ≤50		Ru/Pt on carbon nanotube		
Element	Weight	Atomic	Weight	Atomic	Weight	Atomic
	%	%	%	%	%	%
СК	60.40	94.52	74.10	96.94	74.29	96.89
PtM	21.03	2.03	12.92	1.04	11.65	0.94
RuL	18.57	3.45	12.98	2.02	14.06	2.18
Total	100	100	100	100	100	100

Table 5-5: Elemental composition for Ru/Pt core/ shell on three types of carbon as shown by EDX.

On the basis of the investigation of the Ru/Pt core/shell bimetallic catalysts supported on Vulcan XC-72, carbon powder \leq 50 nm and carbon multi- walled nanotube (CMWNT) by SEM, TEM and EDX, the following can be concluded.

- 1- High and homogeneous dispersion of spherical Ru/Pt bimetallic on the carbon surface with a narrow particles size distribution is revealed.
- 2- There are almost no Ru/Pt nanoparticles aggregation except in the Ru/Pt on carbon powder ≤ 50 nm observed some nanoparticles aggregate as big bright specks on some part of carbon s powder ≤ 50 surface as shown in Figure 5-20 (b).

- 3- The average size according to the TEM images for the Ru/Pt bimetallic nanoparticles supported on Vulcan XC-72, carbon powder ≤ 50 nm and carbon multi- walled nanotube (CMWN) was estimated to be 4 nm, 3 nm and 2.5 nm, respectively.
- 4- These small particle sizes have not been reported before for similar materials which enhances the novelty of the work reported in this thesis.
- 5- For Ru/Pt on CMWN no catalyst nanoparticles off the bundles of carbon nanotube.
- 6- For Ru/Pt on Vulcan carbon core/ shell structure appeared as a bright spherical shapes of Vulcan carbon cores coated by dark dots of Ru/Pt nanoparticles as shell.
- 7- Good results obtained without need to functionalization of carbon surface before coated by Ru/Pt nanoparticles, this means less cost for the preparation of catalysts especially for Ru/Pt on carbon nanotube.
- 8- This project present sample, fast and reliable method to prepare Ru/Pt core/shell on C where by choosing the right parameters of preparation which again highlight novelty of this study.

5.1.7 Synthesis of Novel Pt Monometallic Nanoparticles on Carbon Nanotubes

Platinum nanoparticles supported on carbon multi-walled nanotube (CMWNT) were obtained by a new modified polyol method using ethylene glycol as reducing agent and solvent. The nucleation of Pt particles occurred at about 160°C based on the solution colour change.

The catalytic activity of Pt on CMWNT catalyst was examined as cathode catalyst in a direct methanol fuel cell (DMFC) as will be discussed in section (5.2.4).

The morphology of Pt/CMWNT nanoparticles was investigated by SEM and TEM.

A SEM micrograph of the Pt/CMWNT is shown in Figure 5-26. As can be seen, the Pt nanoparticles dispersed on CMWNT surface as bright dots. Some Pt nanoparticles aggregate as big bright specks on some part of carbon surface to produce a cluster type of Pt particles.



Figure 5-26. SEM micrograph of Pt nanoparticles supported on carbon multi-walled nanotube (CMWNT).

From the TEM images of Pt/CMWNT in Figure 5-27, it can be concluded that there are no particles located off the bundles of CMWNT with limited agglomeration. All the particles are well dispersed with a narrow size distribution and reveal that an average particles size of 3nm has been achieved which was not obtained previously.



Figure 5-27. TEM micrograph of Pt nanoparticles supported on carbon multi-walled nanotube (CMWNT).

EDX was also used for elemental identification of composition of Pt nanoparticles supported on CMWNT prepared as shown in Figure 5-28 and Table 5-6.



Figure 5-28. EDX shows the composition of Pt/CMWNT monometallic nanoparticles.

Element	Weight %	Atomic %
СК	71.62	97.62
PtM	28.38	2.38
Total	100	100

Table 5-6: Elemental composition for C nanotube/Pt core/ shell nanoparticles as shown by EDX.

From Table 5-6 the amount of Pt was 28% this amount gave power density on DMFC about 21 mV/Cm^2 with 1 mg/cm^2 Pt loading at 1 M. This result gives a highly promising catalyst as cathode in DMFC comparing with commercial Pt on Vulcan C-X72 carbon catalyst which has 60% Pt as will show in next discussion (5.2.4). The catalyst performance have 28% Pt as good as the commercial catalyst which has 60% Pt.

5.2 Performance of Catalysts in Direct Methanol Fuel Cell (DMFC)

Ru/Pt core/shell without support, Ru/Pt on Vulcan XC-72 support, and Ru/Pt on carbon multi-walled nanotube (CMWNT) support catalysts were prepared and tested in a direct methanol fuel cell (DMFC), to study the effect of the support on the catalytic activity of catalysts using different parameters including temperature and methanol concentration.

All the catalysts were prepared by the polyol preparation method in which ethylene glycol and tri ethylene glycol were used as reducing agents. The reduction process was carried out at around 170° C. All catalysts were dried, filtered and washed with deionized water several times to maintain neutral pH value. Catalyst ink preparation was followed by spraying it on the electrodes (as a catalyst layer) of the fuel cell by using an airbrush with a nitrogen as carrier gas at 2 bars. Both catalyst layers were coated with nafion glue (1.2mg/cm^2) to
enhance the triple phase boundary between the gas diffusion layer, catalyst layer and membrane. Nafion 117 membrane was sandwiched between the electrodes and hot pressed for 3min at 130°C to form the membrane electrode assembly (MEA). Due to the hot press process, the MEA was placed in DMFC and hydrated overnight. After MEA preparation, compressing, and overnight hydration, the MEA was taken for conditioning. The fuel cell was operated by passing methanol at the anode and air at the cathode. Anode feed was maintained by mechanical pump whereas cathode flow rate was controlled by a flow meter. The fuel cell temperature was controlled by a hot plate attached to the surface of the graphite blocks. The temperature sensor element used was a thermocouple attached to the temperature controller.

5.2.1 Performance of Commercial RuPt Catalyst as Anode in DMFC

Commercial 60% RuPt on 40% on Vulcan XC-72 support was tested first in the DMFC as standard catalyst. Table 5-7 shows the standard condition parameters for catalysts testing. Table 5-7: The standard condition parameters for catalysts testing.

Fuel cell operating temperature	40°C	50°C	60°C	70°C	80°C
Methanol concentration	1M	1 M	1 M	1M, 2M and 4M	1M
Methanol feed flow rate	5ml/min	5ml/min	5ml/min	5ml/min	5ml/min
Air flow rate	1L/min	1L/min	1L/min	1L/min	1L/min
Fuel cell pressure	1 bar	1 bar	1 bar	1 bar	1 bar

The methanol feed flow rate was tested manually in the lab to make sure that the fuel cell was receiving the desired amount of methanol at the anode. The air flow rate at the cathode was delivered by supply tank. The fuel cell operating temperature (40 - 80°C) was reached by

using the temperature controller and the open circuit voltage (OCV) were watched by the multi-meter. The fuel cell kept running for 30 minutes at same conditions listed in table 5-7 to reach study state condition. The maximum OCV was reached when no load current was applied. The test was made by applying a current from DC power supply and the recording the produced voltage.

Fuel cell voltage was recorded at different current loadings during the fuel cell operation as shown in Figure 5-29. The maximum cell voltage was 0.621V at open circuit voltage (OCV) without applying a load at 80°C. The moment current was applied; the voltage was starting to drop. Figure 5-30 depicts the variation in the power density as a function of temperature for the same catalyst. The maximum power density was obtained in this test was 37 mW/cm². The fuel cell performance increased by increasing the operating temperature excepting at 60°C and 70°C, this is due to the influence of temperature on the reaction rate.



Figure 5-29. Polarization curve of DMFC vs current density at the different temperature investigated using commercial RuPt catalyst.



Figure 5-30. Power density of DMFC vs current density at different temperatures investigated using commercial RuPt catalyst.

The performance of the fuel cell using Ru/Pt on carbon nanotube with varying concentration of the methanol (1M, 2M and 4M) fed at the anode, while keeping the temperature and the flow rate constant at 70°C and 5ml/min respectively. The results obtained are depicted in figures 5-31 and 5-32.



Figure 5-31. Polarization curve of DMFC vs current density at the different methanol concentrations investigated using commercial RuPt catalyst.



Figure 5-32. Power density of DMFC vs current density at the different methanol concentrations investigated using commercial RuPt catalyst.

The results in Figures 5-31 and 5-32 indicate that the concentration of the methanol feed affects the performance of the fuel cell when the power density is considered. A maximum power density of 37 mW/cm² is achieved when using 1M of methanol. Moreover, the performance at 4M methanol concentration decreased by increasing concentration of methanol, where a decrease of about 50% in the performance as observed at this concentration.

5.2.2 Performance of Ru/Pt Catalyst Unsupported as Anode in DMFC

In this study, the Ru/Pt core/shell bimetallic without carbon support was used as catalyst ink for the anode electrode of the DMFC. The catalyst ink was coated on carbon paper to form the catalyst layer. The run was carried out by using 1M of methanol as an anode feed with flow rate of 5ml/min. The fuel cell temperature was varied between 60-90°C. Figure 5-33 shows the polarization curve (voltage versus current density) of the fuel cell. The maximum cell voltage was 0.719V at open circuit voltage (OCV) without applying a load at 90°C.



Figure 5-33. Polarization curve of DMFC vs current density at the different temperatures investigated using Ru/Pt catalyst without carbon support.

Figure 5-34 depicts the variation in the power density as a function of temperature for the same catalyst.

Observation of Figure 5-34 reveals that the maximum power density was around 4.5 mW/cm^2 . Ru/Pt catalyst has a much lower power density compared to the RuPt standard catalyst which was around 37 mW/cm^2 as shown in Figure 5-30. Standard catalyst usually contains 40% of carbon as a support which gives a higher surface active metal area for the reaction, whereas prepared Ru/Pt core/ shell bimetallic catalyst contains no carbon.



Figure 5-34. Power density of DMFC vs current density at different temperatures investigated using Ru/Pt catalyst without carbon support.

The results obtained from Figure 5-33 and 5-34 revealed that the fuel cell performance when using Ru/Pt core/shell without carbon support not good enough compared with the performance of commercial RuPt on C catalyst, this is due to the influence of carbon support on the catalytic activity.

5.2.3 Performance of Ru/Pt Catalysts on Vulcan XC-72 and Carbon Multi- walled Nanotube (CMWNT) as Anode in DMFC and the Effect of the Support on the Performance of Fuel Cell

As there are limited studies on the effect of the support on the performance of direct methanol fuel cell, this work aimed to investigate the impact of different types of carbon support on the direct methanol fuel cell efficiency using a new structure of catalyst core/shell nanoparticles.

Ru/Pt core/shell catalysts on Vulcan XC-72

Ru/Pt on Vulcan XC-72 as a support was used as a catalyst for this study. The catalyst was coated at the anode electrode by airbrush to maintain a uniform layer and thickness. The platinum loading was 1mg/cm². This run was made by passing 1M methanol with flow rate of 5ml/min to the anode side while air was fed to the cathode side at flow rate of 1L/min. Initially, the fuel cell temperature was kept at 25°C to maintain steady state anode /cathode feed flow rate. The fuel cell temperature was then set at 70°C for activation of the catalyst. Several runs at this temperature were carried out to condition the fuel cell, before starting to vary the temperature to collect the results at each temperature investigated. The fuel cell temperature was varied from 40°C to 80°C, at 10⁰C increments. The results obtained showed that fuel cell performance increased by increasing the temperature. Figures 5-35 shows the fuel cell power density as a function of current density. The maximum power density of the fuel cell with Ru/Pt catalyst supported on Vulcan XC-72 was 14.5 mW/Cm² at 80°C. The catalyst with the carbon support did boost the fuel cell efficiency by around 50%, when

compared with Ru/Pt without carbon. The maximum cell voltage was 0.46 V at open circuit voltage (OCV) without applying a load at 80°C as shown in Figure 5-36.



Figure 5-35. Power density of DMFC vs current density at different temperatures investigated using Ru/Pt on Vulcan XC-72 catalyst.



Figure 5-36. Polarization curve of DMFC vs current density at different temperatures investigated using Ru/Pt on Vulcan XC-72 catalyst.

Figures 5-35 and 5-36 revealed the promising results of Ru/Pt core/shell catalyst supported on Vulcan XC-72 as anode in DMFC. It seems that the better performance was due to the dispersion of Ru/Pt catalyst on the carbon support, which increases the available active metal surface area for methanol reaction.

Ru/Pt core/shell catalysts on carbon multi- walled nanotube (CMWNT)

Another catalyst was prepared by using carbon multi- walled nanotube (CMWNT) supported Ru/Pt. The study was made to test the effect of this type of carbon support on the catalyst performance using DMFC. The fuel cell was fed by using 1M methanol at anode and flow rate of 5ml/min with platinum loading 1 mg/cm².

The maximum power density obtained was $\approx 18.7 \text{ mW/cm}^2$ and the maximum cell voltage was 0.528 volt at 80°C as shown in Figures 5-37 and 5-38.



Figure 5-37. Power density of DMFC vs current at the different temperatures investigated using Ru/Pt on CMWNT catalyst.



Figure 5-38. Polarization curve of DMFC vs current density at the different temperatures investigated using Ru/Pt on CMWNT catalyst.

Considering figures 5-34, 5-35 and 5-37 reveal clearly that catalyst Ru/Pt on carbon nanotube exhibit better performance than Ru/Pt on Vulcan XC-72 and Ru/Pt without support.

The performance of the fuel cell using Ru/Pt on carbon nanotube with varying concentration of the methanol (1M, 2M and 4M) fed at the anode, while keeping the temperature and the flow rate constant at 70°C and 5ml/min respectively. The results obtained are depicted in figures 5-39 and 5-40.

The results in Figures 5-39 and 5-40 indicate that the concentration of the methanol feed affects the performance of the fuel cell when the power density is considered. A maximum power density of 20.3 mW/cm² is achieved when using 4M of methanol. Moreover, compared to the fuel cell using Ru/Pt commercial the performance decreased by increasing concentration of methanol as shown in Figures 5-31 and 5-32.



Figure 5-39. Power density of DMFC vs current density at the different methanol concentration investigated using Ru/Pt on CMWNT catalyst.



Figure 5-40. Polarization curve of DMFC vs current density at the different methanol concentration investigated using Ru/Pt on CMWNT catalyst.

The anode feed concentration was reported to have an affect the efficiency of the fuel cell. The performance decreased by increasing concentration of methanol. In DMFC, the higher the methanol concentration the more methanol crossover takes place through the membrane leading to a mix potential at the cathode which leads to a drop in the fuel cell power density. Using Ru/Pt on CMWNT support as anode catalyst with higher methanol concentration (anode feed) improved the fuel cell power density when compared with the standard catalyst on Vulcan XC-72 support. At 4M methanol concentration the performance of Ru/Pt on CMWNT is better than that of the RuPt standard catalyst, where a decrease of about 50% in the performance is observed at this concentration, as can be seen from figure 5-31. It seems that the number of active sites in CMWNT is much higher than that in Vulcan XC-72, and this could reduce the crossover of methanol in the fuel cell, as more methanol reacts.

Since the Ru/Pt on carbon nanotube catalyst has better performance in DMFC with platinum loading 1mg/cm² this following test was carried out using the same catalyst but with less loading of platinum 0.5mg/cm². In both experiments, the catalyst inks were prepared by the same stoichiometric ratio to maintain the same viscosities in both inks. The catalyst was coated on the electrode by using airbrush maintaining a distance of 2cm. Platinum loading

was different in both experiments. This difference was made by observing the weight of platinum on the electrodes.

Table 5-8: Summarizing the different Pt loadings on both electrodes in DMFC, together with the flow rates of methanol and air.

Exp. No	Catalyst support	Pt anode loading g/cm2	Pt Cathode loading g/cm2	Anode flow rate (ml/min)	Cathode flow rate (L/min)
1	Carbon Nanotube	1	1	5	1
2	Carbon Nanotube	0.5	1	5	1

The results obtained on the performance of the fuel cell using this catalyst is shown in Figures 5-41 and 5-42.

The temperature was varied from 40°C to 80°C after several runs at 70°C to activate the fuel cell. Figure 5-41 showed the power density as a function of the fuel cell temperatures investigated for this catalyst. An increase in temperature in the range investigated increases the power density of the fuel cell. This is to be expected as an increase in temperature can drive the kinetics of the reaction between platinum and methanol at the surface of the electrode.



Figure 5-41. Power density of DMFC vs current density at the different temperatures investigated using 0.5 mg/cm² Ru/Pt on CMWNT catalyst at 1M of methanol.



Figure 5-42. Polarization curve of DMFC vs current density at the different temperatures investigated using 0.5 mg/ cm^2 Ru/Pt on CMWNT catalyst at 1M of methanol.

Table 5-9 summarize the results obtained from the previous discussion. Ru/Pt core/shell unsupported, Ru/Pt on Vulcan XC-72 support and Ru/Pt on carbon multi-walled nanotube (CMWNT) support were prepared and tested as anode in a direct methanol fuel cell (DMFC) and compering with commercial RuPt catalyst as standard.

- 1- The results obtained reveal that Ru/Pt on CMWNT exhibit better performance than Ru/Pt on Vulcan XC-72 and Ru/Pt unsupported. At 4M methanol concentration the performance of Ru/Pt on CMWNT is better than that of the RuPt commercial catalyst, where a decrease of about 50% in the performance at the same methanol concentration.
- 2- The results obtained from table 5-9 revealed that the fuel cell performance when using Ru/Pt core/shell without carbon support not good enough compared with the performance of commercial RuPt on C catalyst, this is due to the influence of carbon support on the catalytic activity.
- 3- The fuel cell efficiency using 0.5mg/cm^2 platinum loading still showed a better performance where it gave power density $\approx 16 \text{ mW/cm}^2$ at 80°C than Ru/Pt and Ru/Pt on Vulcan XC-72.
- 4- The results obtained here demonstrates clearly the effect of the different types of carbon used as a support on the performance of the catalyst in the fuel cell. This could be due to the different physical and electrical properties of these types of carbon.

5- Since the Ru/Pt on carbon nanotube catalyst has better performance in DMFC with platinum loading 1mg/cm² and with less loading of platinum 0.5mg/cm² which was not reported by other before, we recommend that more work is required to improve the performance of Ru/Pt on carbon nanotube.

Table 5-9: Summary of the results using Pt based core/shell catalyst synthesized by the modified polyol method for anode in DMFC.

	Electrodes		Platinum	Maximum power
Catalyst	Anode	Cathode	loading	density
Commercial	Commercial	Commercial Pt	1mg/cm ²	37 mV/cm^2 at 1M
PtRu Supported	PtRu Supported	Supported on Vulcan C-X72		16 mV/cm^2 at 4M
on Vulcan C-	on Vulcan C-	Carbon		
X72 Carbon	X72 Carbon			
Ru/Pt core/shell	Ru/Pt core/ shell	Commercial Pt	1mg/cm ²	4.5 mV/cm^2 at 1M
nanoparticles	nanoparticles	Supported on		
unsupported		Vulcan C-X72		
		Carbon		
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt	1mg/cm ²	14.5 mV/cm^2 at
nanoparticles	nanoparticles	Supported on		1M
supported on	supported on	Vulcan C-X72		
Vulcan C-X72	Vulcan C-X72	Carbon		
Carbon	Carbon			
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt	1mg/cm ²	18.7 mV/cm^2 at
nanoparticles	nanoparticles	Supported on		1 M
supported on	supported on	Vulcan C-X72		20.2 mV/am^2 at
Carbon nanotube	Carbon nanotube	Carbon		20.5 mv/cm at
				4111
Ru/Pt core/shell	Ru/Pt core/shell	Commercial Pt	0.5mg/cm ^{2*}	$16 \text{ mV/cm}^2 \text{ at } 1\text{M}$
nanoparticles	nanoparticles	supported on		
supported on	supported on	Vulcan C-X72		
Carbon nanotube	Carbon nanotube	carbon		

* Notice: Ru/Pt core/shell nanoparticles including only 0.5 mg/cm²

5.2.4 Performance of Pt on MWNT Catalyst as Cathode in DMFC

In this experiment, Platinum chloride was used as a precursor to prepare cathode electrode catalyst on MWNT Carbon. The catalyst was washed deionized water, followed by centrifuging, after which it was dried in an oven set at 100 C. then dried in oven.

0.14g of the powdered catalyst was used to prepare the catalyst ink. Electrode catalyst layer was made of 85% catalyst and 15% nafion (diluted solution in water). The cathode catalyst was applied on a carbon paper by an airbrush maintaining 1 mg per cm². The MEA was placed in the fuel cell and was hydrated by water over night. The fuel cell was operated by using 1M methanol at a flow rate of 5 ml/min as anode feed at 70°C. The cathode side was fed with air at flow rate of 1L /min. During the operation, the fuel cell was activated at 70°C to reach the maximum fuel cell efficiency.

The fuel cell was operated at different temperature and anode feed concentration to study the catalytic behavior of the cathode electrode using Pt on MWNT carbon.

Effect of Temperature in DMFC

This study was made by varying the fuel cell temperature to study the behavior of the fuel cell using Pt on MWNT carbon support as a cathode electrode catalyst. Fuel cell temperature was varied from 40° C to 80° C by a temperature controller attached to the graphite blocks. Figure 5-43 shows the fuel cell behavior at different operating temperature.

Effect of methanol concentration on DMFC

The Pt on C MWNT cathode catalyst was test at different methanol concentration as an anode feed. Three different methanol concentration were prepared to feed the anode side of the fuel cell. Methanol was fed to the fuel cell via a pump, in each test, the methanol flow rate was

maintained at 5ml/min. Figure 5-44 shows the fuel cell power density as a function of methanol concentration at 70°C.



Figure 5-43. Power density of DMFC vs current density at the different temperatures investigated using Pt on CMWNT catalyst.



Figure 5-44. Power density of DMFC vs current density at the different methanol concentrations investigated using Pt on CMWNT catalyst.

The results obtained on the performance of the fuel cell using Pt on CMWNT showed in Figures 5-43 and 5-44 indicated the best results obtained at 70°C and 1M methanol concentration with 5 ml/min anode flow rate where the maximum power density was around 21 mV/cm^2 . This result is promising compared with commercial RuPt catalyst.

Summary

Core/shell nanostructures have been successfully prepared for Co/Ni by a modified sol-gel method with average sizes of 1.96 nm. The TEM micrographs gave a clear evidence to obtain core/shell halo shaped which is considered as one of the forms of the core/shell nanostructure shaped which has not been obtained previously.

The results indicated in SEM and TEM images (figures 5-5 and 5-6) confirmed the successful preparation of core/shell nanoparticles for SiO₂/Ni through a new modified sol-gel method for first time with a high yield of product. It is suggested that the halo structure observed in the TEM images in the samples in this study demonstrates the existence of cubic core /shell nanostructure, in which the halo represents Ni, while the inner part forming the core is the SiO₂. Particle size analysis based on the TEM images yields an average diameter of about 60 nm for SiO₂/Ni core/ shell nanoparticles with thin Ni shell thickness as shown in Figure 5-6.

The SiO_2 nanoparticles homogeneously coated with CoFe halo shell to create new catalyst core/shell were prepared by a new modified sol-gel method with an average size of 39 nm. The halo shaped structure was the common feature in this sample prepared as indicated by TEM and SEM. From the TEM images in Figures 5-9, the thin CoFe shell can be observed as a white halo around each SiO₂ core nanoparticles with a clear core/shell structure.

SiO₂/Pt core/shell nanoparticles were prepared by two different methods namely a new modified sol-gel and polyol methods for first time to study the effect of preparation on the catalysts structure were obtained from these methods. The results can be summarized as follow: SEM and TEM results revealed considerable difference between the morphologies of SiO₂/Pt monometallic catalysts were prepared using different methods namely modified sol-gel method and polyol method. What is noticeable in SiO₂/Pt catalyst prepared by polyol method is the absence of clear halo shell observed in the TEM micrograph of SiO₂/Pt catalyst

prepared by the new modified sol-gel method (figures 5-14). It is suggested that this halo shell structure could be attributed to the effect of modified sol-gel parameters (pH and temperature) on the growth of Pt particles on the SiO₂ surface. The modified sol-gel method has a very important effect on the catalyst structure. It was found that SiO₂/Pt catalyst prepared by modified sol-gel technique has higher uniform structure and distribution than SiO₂/Pt catalyst prepared by using polyol method. Based on the particles size obtained from TEM images (Figures 5-14 and 5-17), the polyol method seem to have a much greater impact on the particles size (5nm) than the modified sol-gel method (75nm).

Ru/Pt catalyst has been successfully prepared using the new modified polyol reduction method. The average particles size estimated were 5nm by manually measuring. TEM was carried out to determine the shapes and size of Ru/Pt core/shell particles. It was found that the Ru/Pt nanoparticles have spherical shape grey circles as core attributed to Ru coating with a dark spots as shell attributed to Pt.

The preparation of highly dispersed Ru/Pt catalysts on support such as carbon with less Pt particles loading is one of the goals of this research. Ru/Pt core/shell catalysts supported on three types of carbon [Vulcan XC-72, carbon powder ≤ 50 nm and carbon multi- walled nanotube (CMWNT)] with different shapes and size were prepared by the new polyol method using ethylene glycol and triethylene glycol as reducing agents for PtCl₂ and RuCl₃, respectively. Moreover, the performance of the Ru/Pt core/shell catalysts prepared were tested using direct methanol fuel cell (DMFC) to study the effect of the support on the catalytic activity of catalysts. On the basis of the investigation of the Ru/Pt core/shell bimetallic catalysts supported on Vulcan XC-72, carbon powder ≤ 50 nm and carbon multi-walled nanotube (CMWNT) by SEM, TEM and EDX, the following can be concluded.

- 1- High and homogeneous dispersion of spherical Ru/Pt bimetallic on the carbon surface with a narrow particles size distribution is revealed.
- 2- There are almost no Ru/Pt nanoparticles aggregation except in the Ru/Pt on carbon powder ≤ 50 nm observed some nanoparticles aggregate as big bright specks on some part of carbon s powder ≤ 50 surface as shown in Figure 5-20 (b).
- 3- The average size according to the TEM images for the Ru/Pt bimetallic nanoparticles supported on Vulcan XC-72, carbon powder ≤ 50 nm and carbon multi- walled nanotube (CMWN) was estimated to be 4 nm, 3 nm and 2.5 nm, respectively. These small particle sizes have not been reported before for similar materials.
- 4- For Ru/Pt on CMWN no catalyst nanoparticles off the bundles of carbon nanotube.
- 5- For Ru/Pt on Vulcan carbon core/ shell structure appeared as a bright spherical shapes of Vulcan carbon cores coated by dark dots of Ru/Pt nanoparticles as shell.
- 6- Good results obtained without need to functionalization of carbon surface before coated by Ru/Pt nanoparticles, this mean less cost for the preparation of catalysts especially for Ru/Pt on carbon nanotube.
- 7- This project present sample, fast and reliable method to prepare Ru/Pt core/shell on C where by choosing the right parameters of preparation.

Platinum nanoparticles supported on carbon multi-walled nanotube (CMWNT) were obtained by the new modified polyol method using ethylene glycol as reducing agent and solvent. The nucleation of Pt particles occurred at about 160°C based on the solution colour change. The catalytic activity of Pt on CMWNT catalyst was examined as cathode catalyst in a direct methanol fuel cell (DMFC). The Pt nanoparticles dispersed on CMWNT surface as bright dots with good size distribution as shown in SEM micrograph. From the TEM images of Pt/CMWNT in Figure 5-27, it can be concluded that there is no particles located off the bundles of CMWNT with limited agglomeration. All the particles are well dispersed with a narrow size distribution and reveal that an average particles size of 3nm has been achieved.

Ru/Pt core/shell unsupported, Ru/Pt on Vulcan XC-72 support and Ru/Pt on carbon multiwalled nanotube (CMWNT) support were prepared and tested as anode in a direct methanol fuel cell (DMFC). The results obtained reveal that Ru/Pt on CMWNT exhibit better performance than Ru/Pt on Vulcan XC-72 and Ru/Pt unsupported. At 4M methanol concentration the performance of Ru/Pt on CMWNT is better than that of the RuPt standard catalyst, where a decrease of about 50% in the performance at the same methanol concentration.

Pt nanoparticles on CMWNT was prepared and tested as cathode catalyst in the direct methanol fuel cell (DMFC) as well. The best results was obtained at 70°C and 1M methanol concentration with 5 ml/min anode flow rate where the maximum power density was around 21 mV/cm^2 .

CHAPTER SIX

6. CHAPTER 6: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1 Conclusions

6.1.1 Synthesis of Catalysts

Core/shell nanostructures have been successfully prepared with various shapes for noble and non-noble metals by a new modified sol-gel and polyol methods. The halo shaped structure was the common feature in the Co/Ni, SiO₂/Ni and SiO₂/CoFe core/shell nanoparticles which were prepared by the new modified sol-gel method.

The effect of preparation method on the shape and particles size of SiO_2/Pt core/shell was investigated by preparation of catalyst through two methods, namely the new modified solgel method and the new modified polyol method. For the sample prepared by the new modified sol-gel method it was found that SiO_2/Pt has halo shaped core/shell structure, while SiO_2/Pt catalyst prepared by using the new modified polyol method has crown- jewel core/shell structure. The modified polyol method seem to have a much greater impact on the particles size (3nm) than the modified sol-gel method (75 nm).

Ru/Pt core/shell unsupported and with three different types of carbon Vulcan XC-72, carbon powder ≤ 50 nm and multi- walled nanotube carbon (CMWNT) as supports were prepared by the new modified polyol method. The performance of the Ru/Pt core/shell catalysts prepared were tested using direct methanol fuel cell (DMFC) to study the effect of the support on the catalytic activity of the catalysts. For the Ru/Pt core/shell unsupported and Ru/Pt core/shell on CMWNT the TEM indicated the existence of spherical shaped morphological structure, with an average particle size of around 6 and 2.5 nm, respectively. For the Ru/Pt support on Vulcan XC-72 and carbon powder ≤ 50 nm have crown- jewel core/shell structure with a narrow particles size distribution of around 4 and 3 nm respectively. These small particle sizes have not been reported previously. Pt nanoparticles supported on carbon multi-walled nanotube (CMWNT) were prepared by polyol method. All the particles are well dispersed without any particles located off the bundles of CMWNT and an average particles size of 3nm has been achieved. The author is not aware of any study that has achieved this small particle size for Pt on CMWNT. All core/shell catalysts prepared in this study and its particulars are summarised in Table 6-1 below.

Catalyst	Preparation	Reducing agent	Particles	Shapes of
	method		size	core/shell
Novel Co/Ni	Modified sol-gel	Hydrazine in an alkaline	1.9 nm	halo shaped
		media		
SiO ₂ /Ni	Modified sol-gel	Hydrazine in an alkaline	60 nm	halo shaped
		media		
Novel	Modified sol-gel	Hydrazine in an alkaline	39 nm	halo shaped
SiO ₂ /CoFe		media		
Novel SiO ₂ /Pt	Modified sol-gel	Hydrazine in an alkaline	75 nm	halo shaped
		media		
Novel SiO ₂ /Pt	Modified polyol	Ethylene glycol	3 nm	crown- jewel
				shaped
Ru/Pt	Modified polyol	Triethylene glycol,	6 nm	spherical
		ethylene glycol		shaped
Ru/Pt on Vulcan	Modified polyol	Triethylene glycol,	4 nm	crown- jewel
XC-72 carbon		ethylene glycol		shaped
Novel Ru/Pt on	Modified polyol	Triethylene glycol,	3 nm	crown- jewel
carbon powder \leq		ethylene glycol		shaped
50 nm				
Novel Ru/Pt on	Modified polyol	Triethylene glycol,	2.5 nm	spherical
carbon multi-		ethylene glycol		shaped
walled nanotube				
Novel Pt on	Modified polyol	Ethylene glycol	3 nm	Dark spots on
carbon multi-				CMWNT
walled nanotube				surface

Table 6-1: Summary of	of the	core/shell	catalysts	synthesized.
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6.1.1.1 Overview of core/shell catalysts which in this thesis

In this work, we report the synthesis of Co/Ni, SiO₂/Ni, SiO₂/CoFe, SiO₂/Pt, Ru/Pt and Ru/Pt supported on three kinds of carbon bimetallic nanoparticles with core/ shell structures and investigate catalytic activity of Ru/Pt unsupported, Ru/Pt supported on Vulcan XC-72 carbon, Ru/Pt on carbon multi-walled nanotube and Pt on carbon multi-walled nanotube using DMFC. The novelty of this work lies with the synthetic approach to prepare new catalysts with novel shapes and size of particles as indicated by the following:

- The author of this work is not aware of any studies that have prepared Co/Ni (1.96 nm particle size) and SiO₂/CoFe (39 nm particle size) core/shell nanoparticles with halo shaped using the method described here.
- 2. In this study, we present the unique structure which has not been obtained previously for SiO₂/Ni catalyst and using commercial silica as core for the first time.
- 3. SiO₂/Pt core/shell nanoparticles were synthesized successfully by two different methods; a new modified sol-gel and a new modified polyol methods with novelty structures halo and crown- jewel shaped respectively using commercial silica as core in this study.
- This study reported for the first time a new method for preparing Ru/Pt core/shell with 6 nm particle size by a new modified polyol method.
- 5. Ru/Pt supported on three kinds of carbon were synthesized successfully by a new modified polyol method. The author is not aware of any studies that have prepared Ru/Pt on carbon powder ≤ 50 nm and carbon multi-walled nanotube previously with extremely small particles size 3 and 2.5 nm respectively. This work presents as well special structure (crown- jewel shaped) with 4 nm particle size for Ru/Pt on Vulcan XC-72 carbon which was not obtained previously for the same catalyst.

 Pt on carbon multi-walled nanotube catalyst was synthesized for the first time successfully by a new modified polyol method with extremely small particles size 3nm.

6.1.2 Testing the Performance of Catalysts Using the Direct Methanol Fuel Cell (DMFC)

Ru/Pt core/shell unsupported, Ru/Pt on Vulcan XC-72 support and Ru/Pt on carbon multiwalled nanotube (CMWNT) support were prepared and tested as anode in a direct methanol fuel cell (DMFC). The results obtained reveal that Ru/Pt on CMWNT exhibit better performance than Ru/Pt on Vulcan XC-72 and Ru/Pt unsupported. At 4M methanol concentration the performance of Ru/Pt on CMWNT is better than that of the RuPt commercial catalyst, where a decrease of about 50% in the performance at the same methanol concentration.

Pt nanoparticles on CMWNT were prepared and tested as cathode catalyst in the direct methanol fuel cell (DMFC) as well. The best results was obtained at 70°C and 1M methanol concentration with 5 ml/min anode flow rate where the maximum power density was around 21 mV/cm^2 . The catalyst performance have 28% Pt as good as the commercial catalyst which has 60% Pt.

Table 6-2 shows the results we are obtained for Ru/Pt without support and Ru/Pt on Vulcan X and multi- walled nanotube carbon (CMWNT) as anode and Pt support on CMWNT as cathode in the DMFC.

Table 6-2: Summary of the results using Pt based core/shell synthesized by modified polyol method for DMFC.

	Electrodes		Platinum	Maximum power
			loading	density
Catalyst	Anode	Cathode		
Commercial PtRu Supported on	Commercial PtRu Supported on	Commercial	1mg/cm ²	37 mV/cm^2 at 1M
Vulcan C-X72 Carbon	Vulcan C-X72 Carbon	Pt Supported on Vulcan C-X72 Carbon		16 mV/cm ² at 4M
Ru/Pt core/shell nanoparticles unsupported	Ru/Pt core/ shell nanoparticles	Commercial Pt Supported on Vulcan C-X72 Carbon	1mg/cm ²	4.5 mV/cm ² at 1M
Ru/Pt core/shell	Ru/Pt core/shell	Commercial	1mg/cm ²	14.5 mV/cm ² at 1M
nanoparticles supported on Vulcan C-X72 Carbon	nanoparticles supported on Vulcan C-X72 Carbon	Pt Supported on Vulcan C-X72 Carbon		
Ru/Pt core/shell	Ru/Pt core/shell	Commercial	1mg/cm ²	18.7 mV/cm ² at 1M
nanoparticles supported on Carbon nanotube	nanoparticles supported on Carbon nanotube	Pt Supported on Vulcan C-X72 Carbon		20.3 mV/cm ² at 4M
Ru/Pt core/shell nanoparticles	Ru/Pt core/shell nanoparticles	Commercial Pt Supported on	0.5mg/cm ²	16 mV/cm ² at 1M
supported on Carbon nanotube	supported on Carbon nanotube	Vulcan C-X72 Carbon		
Pt supported on Carbon nanotube	Commercial PtRu Supported on Vulcan C-X72 Carbon	Pt supported on Carbon nanotube	1mg/cm ²	21 V/cm ² at 1M

6.1.2.1 Overview of Pt based catalysts for DMFC

The results obtained from Table 6-2 demonstrate clearly the effect of the different types of carbon used as a support on the performance of the catalyst in the fuel cell. This could be due to the different physical and electrical properties of these types of carbon.

Observation of Table 3-2 in chapter 3 revealed that there are limited studies on the performance of catalysts using a direct methanol fuel cell (DMFC). Hence this work aimed to investigate the direct methanol fuel cell efficiency using catalysts of different structure namely core/shell nanoparticles structure.

- 1. This thesis presents for the first time the testing of catalytic activity of Ru/Pt core/shell on different types of carbon and Pt on carbon nanotube using DMFC.
- 2. The best results obtained at 4M methanol concentration for Ru/Pt on CMWNT was 20.3 mV/cm^2 , which is better than that of the RuPt commercial catalyst, where a power density of 16 mV/cm² was obtained at the same methanol concentration.
- 3. Promising results were obtained at 70°C and 1M methanol concentration with 5 ml/min anode flow rate where the maximum power density was around 21 mV/cm² for Pt on Carbon nanotube as cathode in DMFC, compared to 37 mV/cm² for the commercial catalyst. The catalyst performance have 28% Pt as good as the commercial catalyst which has 60% Pt.

6.2 Suggestions for Future Work

Based on the previous discussion, future work will include the following:

- SiO₂/CoFe core/ shell catalyst has a unique structure never reported before. Future work should consider testing the catalytic activity of the catalyst in the Fischer-Tropsch process, since catalysts based on Co and Fe is used for this process.
- 2. Ru/Pt on CMWNT gave good result on DMFC at 4M methanol concentration compared to the commercial catalyst. Future work should focus on optimizing and improving the system to give better results may be by improving the synthesis method. Further investigation into the effect of Pt loading on the performance of the catalyst is recommended for future work.
- 3. Pt on CMWNT seems to give promising result as cathode in DMFC. Future work should include preparation of the catalyst using sol-gel method in order to compare with the results obtained here.
- 4. Testing Ru/Pt on CMWNT as anode and Pt on CMWNT as cathode prepared in this study together on DMFC.

As stated there is further novel work for the scientific literature from this thesis, including:

- The synthesis and characterization of SiO₂/Ni by a new modified sol-gel method.
- The synthesis of novel SiO₂/CoFe core/shell nanoparticles by a new modified sol-gel method.
- The synthesis of novel Ru/Pt on CMWNT core/shell nanoparticles using a new polyol method and testing its performance using DMFC.

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Appendix A: Chemicals used

Ammonium chloride (NH₄Cl, 25%, Aldrich), Carbon nanotube (multi-walled, Aldrich), carbon powder (\leq 50 nm, Aldrich), Carbon Vulcan XC-72, Cobalt Chloride (CoCl₂, anhydrous, Aldrich), Ethanol (C₂H₆O, 95%, Aldrich), Ethylene glycol (EG, C₂H₆O₂, 99.8% anhydrous, Aldrich), Hydrazine (N₂H₄, 64%, Aldrich), Iron chloride (FeCl₂, 98%, Aldrich), Nafion, Nickel chloride (NiCl₂, 98%, Aldrich), Platinum chloride (PtCl₂, anhydrous, Aldrich), Polyvinyl pyrrolidone (PVP, Aldrich), Polytetrafluoroethylen (PTFE 60%W), Propa-2-ol (IPA), Ruthenium chloride (RuCl₃.nH₂O, Aldrich), Silica dioxide powder (SiO₂, 99.5%, Aldrich), Sodium hydroxide (NaOH, 98%, Aldrich), Tetraethyl orthosilicate (TEOS, 99.99%, Aldrich), Triethylene glycol (TEG, C₆H₁₄O₄, Aldrich).