Nanostructured electrocatalysts for proton exchange membrane fuel cells (PEMFCS)

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**NANOSTRUCTURED ELECTROCATALYSTS FOR
PROTON EXCHANGE MEMBRANE FUEL CELLS
(PEMFCs)**

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ABSTRACT

The research work presented in this thesis is focused on the synthesis and characterization of nanostructured electrocatalysts for fuel cell reactions. “Firstly, a novel noncovalent functionalization method has been successfully developed to modify carbon nanotubes (CNTs) as electrocatalyst supports. The physicochemical characterizations and activity testing for methanol electrooxidation have been performed. We found the noncovalent functionalization method could significantly improve the dispersion and distribution of Pt (or PtRu) nanoparticles (NPs) supported on CNTs while preserving the perfect structure of CNTs, which resulted in the increased electrochemical active surface area and improved catalytic activity for methanol electrooxidation of Pt nano-electrocatalysts.

Secondly, the as-developed noncovalent functionalization method could effectively equip carbon nanotubes with the specified surface functional groups. By choosing some characteristic polyelectrolytes, four given functional groups were introduced on the CNT surface, followed by the deposition of Pt NPs. The spectroscopic characterization, DFT calculation, and electrochemical testing demonstrated that the four different functional groups on CNTs as Pt supports had significantly different effect on the electronic properties and electrocatalytic activity for methanol oxidation on Pt NPs. It is proposed that the negatively charged functional groups could donate electrons to Pt surface, leading to weakened chemical adsorption energy with carbon monoxide (CO, a poisonous intermediate generated during the methanol electrooxidation), and thus improve catalytic performance for methanol

electrooxidation.

Thirdly, the combination of the polyol reduction method and the seed-mediated growth method could effectively load Pt NPs on CNTs with a wide range of Pt loadings (10 wt% ~ 93 wt %). As Pt loading on CNTs increases, both the interconnectivity and the electrocatalytic activity of Pt NPs increase gradually. The correlation between the electrocatalytic activity and the interconnectivity of Pt NPs is proposed. Our results illustrated that interconnected Pt NPs as electrocatalysts are more electrochemically active than the isolated Pt NPs.

Finally, we designed novel approaches to synthesize Pt and Pd nanowire networks (NWNs) with controlled nanostructured morphology. The as-synthesized nanowire network structure of Pt and Pd NWNs shows improved electrocatalytic activities as compared to the NPs-shaped electrocatalysts. The enhanced activities are attributed to the unique two-dimensional structures.”

Keyword: “Proton exchange membrane fuel cells; Electrocatalysts; Carbon nanotubes; Methanol oxidation; Formic acid oxidation, Nanomaterials.”

List of Abbreviations

PEMFC: proton exchange membrane fuel cell

DMFC: direct methanol fuel cell

DFAFC: Direct Formic acid fuel cell

CNT: carbon nanotube

MWCNT: multi-walled carbon nanotube

SWCNT: single-walled carbon nanotube

DWCNT: double-walled carbon nanotube

NP: nanoparticle

MOR: methanol oxidation reaction

ORR: oxygen reduction reaction

1-AP: 1-aminopyrene

PDDA: poly (diallyldimethylammonium chloride)

PDDA-CNT: PDDA wrapped CNT

AO-CNT: acid oxidized CNT

Pt/PDDA-CNT: Pt NPs supported on PDDA-wrapped CNT

Pt/AO-CNT Pt NPs: supported on acid oxidized CNT

NWN: nanowire network

SOM: small organic molecule

CO₂: carbon dioxide

CO: carbon monoxide

S: sulfur

OCP: open-circuit-potential

FAOR: formic acid oxidation reaction

AAO: anodized aluminum oxide

PSS: poly (sodium 4-styrenesulfonate)

1-AP-MWCNTs: 1-AP functionalized MWCNTs

PtRu/1-AP-MWCNTs: PtRu NPs on 1-AP-MWCNTs

PtRu/AO-MWCNTs: PtRu NPs on acid-oxidized MWCNTs

EG: ethylene glycol

TEM: transmission electron microscopy

XPS: X-ray photoelectronic spectroscopy

GCE: glass carbon electrode

CV: cyclic voltammogram

XRD: X-ray diffraction

TGA: thermal gravity analysis

ECSA: electrochemical active surface area

SCE: saturated calomel electrode

PAH: Poly (allylamine hydrochloride)

PAA: Poly (acrylic acid sodium)

PSS-CNT: PSS wrapped CNT

PAA-CNT: PAA wrapped CNT

PAH-CNT: PAH wrapped CNT

DFT: density functional theory

MeOH: methanol

CTAB: cetyltrimethylammonium bromide

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- [1] Shuangyin Wang, San Ping Jiang*, Xin Wang*, “Polyelectrolyte Functionalized Carbon Nanotubes as a Support for Noble Metal Electrocatalysts and Their Activity for Methanol Oxidation”, *Nanotechnology*, 2008, 19, 265601
- [2] Shuangyin Wang, Xin Wang*, San Ping Jiang*, “PtRu NPs Supported on 1-Aminopyrene Functionalized MWCNTs and Their Electrocatalytic Activity for Methanol Oxidation”, *Langmuir*, 2008, 24, 10505
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- [4] Shuangyin Wang, Noel Kristian, San Ping Jiang*, Xin Wang*, “Controlled Synthesis of Dendritic Au@Pt Core-Shell Nanomaterials as Effective Fuel Cell Electrocatalyst”, *Nanotechnology*, 2009, 20, 25605
- [5] Shuangyin Wang, San Ping Jiang*, T. J. White, Jun Guo, Xin Wang*, “Electrocatalytic Activity and Interconnectivity of Pt NPs on Multi-Walled Carbon Nanotubes for Fuel Cells”, *The Journal of Physical Chemistry C*, 2009, 113, 18935
- [6] Shuangyin Wang, San Ping Jiang*, T. J. White, Jun Guo, Xin Wang*, “Assembling Interconnected Pt NPs on Multi-walled Carbon Nanotubes and Their Electrocatalytic Activity for Fuel Cells”, *Advanced Functional Materials*, DOI:

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[7] **Shuangyin Wang**, San Ping Jiang*, Xin Wang*, "Synthesis of Pt and Pd nanosheaths on Multi-Walled Carbon Nanotubes as Potential Electrocatalysts of Low Temperature Fuel Cells", *Electrochimica Acta*, DOI:10.1016/j.electacta.2009.09.003

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- [1] Shuangyin Wang, San Ping Jiang*, Xin Wang*, “Polyelectrolyte Functionalized Carbon Nanotubes as a Support for Noble Metal Electrocatalysts and Their Activity for Methanol Oxidation”, *Nanotechnology*, 2008, 19, 265601
- [2] Shuangyin Wang, Noel Kristian, San Ping Jiang*, Xin Wang*, “Controlled Deposition of Pt on Au Nanrods and Their Catalytic Activity towards Formic Acid Oxidation”, *Electrochemistry Communications*, 2008, 10, 961
- [3] Shuangyin Wang, Xin Wang*, San Ping Jiang*, “PtRu NPs Supported on 1-Aminopyrene Functionalized MWCNTs and Their Electrocatalytic Activity for Methanol Oxidation”, *Langmuir*, 2008, 24, 10505
- [4] Shuangyin Wang, Xin Wang*, San Ping Jiang*, “Controllable Self-assembly of Pd Nanowire Networks as Highly Active Electrocatalysts for Direct Formic Acid Fuel Cells”, *Nanotechnology*, 2008, 19, 455606
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Chapter 1 Introduction and Scope of the Thesis

1.1. Introduction

Energy as the driving force of the economic growth for the current society is one of the most urgent issues for the world today. The excessive consumption of fossil fuels in the past has caused a quick depletion of them and resulted in various environmental problems. People are searching for alternative and sustainable energy sources or technologies with high energy efficiency and low pollutant emission. Among them, fuel cell, a device converting chemical energy directly to electrical energy, has been extensively investigated for both stationary and portable applications.[1, 2] Fuel cell has high energy efficiency and low emission compared to the conventional internal combustion engine. As an active member of the fuel cell family, proton exchange membrane fuel cell (PEMFC) is attracting more and more attention as a leading technology for various applications including portable electronic devices, military communications, and automobiles.[3]

In a PEMFC, a solid polymer (typically, Nafion membrane) is used as the electrolyte with the capability of proton conductivity. Oxygen or air is supplied to the cathode side of PEMFC. At the early stage of the development of PEMFC, hydrogen is mainly employed as the fuel at the anode side. However, the generation, storage and transportation of hydrogen source are the main bottleneck for hydrogen-fueled PEMFCs. Subsequently, small organic molecules (SOMs) including methanol and formic acid as the fuels of PEMFCs were developed extensively, especially for

portable applications. However, the slow kinetics of these SOMs still impedes the large-scale commercialization of PEMFCs. To improve the anode kinetics of SOMs-fueled PEMFCs, a great deal of research work has been performed on the development of electrocatalysts with improved activity and durability.[3, 4]

“Nano-sized noble metal electrocatalysts are mainly used in PEMFCs to catalyze both the anode and cathode reactions. Currently, the most commonly used electrocatalyst for PEMFCs is Pt or its alloy NPs which are supported on porous carbon support (Pt/C or PtRu/C).[1, 5] The porous carbon materials have high surface area. However, such electrocatalysts suffer from serious slow kinetics and poor durability. Meanwhile, the expensive cost of the precious Pt and Pt alloy electrocatalysts, as well as their low utilization efficiency in the catalyst layers seriously render the large-scale commercialization of PEMFCs. Thus the reduction in the amount of precious metal electrocatalysts is important to lower the overall cost of fuel cells. In order to reduce the Pt usage and increase the fuel cell performance, both mass and specific activity of Pt-based electrocatalysts should be enhanced.”

1.2. Objectives of the Research

As described above, “the electrocatalyst is the main and critically important component of PEMFCs. The electrocatalytic activity and durability of PEMFC catalysts strongly depend on their interaction with catalyst supports and their morphology. In this thesis, we will focus on these two aspects to improve the activity and durability of electrocatalysts for PEMFCs. On one hand, we use a more

corrosion-resistant carbon material, carbon nanotube (CNT), as a novel electrocatalyst support. CNTs with excellent mechanical properties, good electrical conductivity, and chemical and thermal stability improve both the activity and durability of Pt-based electrocatalysts. We develop a non-covalent functionalization method to modify the CNT surface to support Pt-based NPs as electrocatalysts for PEMFCs. Fundamentally, the further detailed study about the influence of Pt loadings and various different functional groups (interlinkers) on CNTs on the catalytic activity of Pt NPs gives some interesting conclusions. On the other hand, the enhanced activity of metal electrocatalysts can be obtained through the morphology control to prepare multi-dimensional nanowire network structures. In this case, various nanostructured electrocatalysts such as Pt and Pd nanowire networks are designed and synthesized for methanol oxidation and formic acid oxidation, respectively.”

1.3. Scope of the Thesis

The thesis consists of 9 chapters. Chapter 1 outlines the background of the study and provides a scope of the thesis. Chapter 2 gives a literature review on the fundamental aspects of fuel cells and summarizes the advanced development of electrocatalysts for PEMFCs. In the following chapters, the research results of the study are presented. As described in the previous section, the research work here focuses on the development of nanostructured electrocatalysts for PEMFC applications in two aspects:

1.3.1. Investigation of CNTs as Electrocatalyst Supports.

“Carbon nanotubes have attracted much attention as the supporting materials of metal electrocatalysts in PEMFCs.[6-10] Due to the inert nature of their surface, CNTs should be pre-functionalized before the successful deposition of metal nanoparticles (NPs).[11] Conventionally, a harsh acid covalent method was frequently utilized to realize this goal. However, this approach will damage the perfect CNT structure and reduce its mechanical properties and chemical and thermal stability.[10, 11] In order to overcome this drawback, we develop two non-covalent methods to functionalize CNTs: bifunctional molecule stacking and polyelectrolyte wrapping techniques. Both of the two methods can lead to charged surface of CNTs, on which metal precursors having opposite charge can be attracted onto the as-functionalized CNT surface uniformly. After being reduced, metal NPs are uniformly deposited on the CNTs with good dispersion and without aggregate formation. Chapter 3 presents the work on the non-covalent functionalization of CNTs with a bifunctional molecule, 1-aminopyrene (1-AP), to stack CNTs and their application as PtRu NP supports for methanol oxidation in acid medium.[12] PtRu NP is used as a model electrocatalyst to study their electrocatalytic performance for methanol oxidation. Under weak-acid condition, 1-AP molecule stacked on CNT trends to be protonated and thus positively charged. The positive charge on 1-AP-stacked CNTs would attract negatively charged Pt precursor (PtCl_6^{2-}) via electrostatic interaction followed by the electrostatic attraction of positive Ru^{3+} on PtCl_6^{2-} to form complex. The subsequent reduction by a microwave-heated polyol reduction method results in the formation of PtRu NPs on 1-AP-stacked CNTs. It has been found that such 1-AP functionalized CNTs lead to

more uniform deposition of PtRu NPs with smaller average particle size, compared to the conventional harsh acid functionalized CNTs as PtRu NP supports. The as-synthesized PtRu/1-AP-CNTs used as electrocatalyst show significantly enhanced activity and durability.”

“Chapter 4 presents the work on a polyelectrolyte wrapping approach to noncovalently functionalize CNTs as Pt electrocatalyst supports. Pt NPs are used as model electrocatalysts for methanol oxidation.[13] Polymer wrapping is a facile approach to functionalize CNTs and it can be realized by just simply dispersing CNTs in aqueous solution containing a small amount of polymer. As an example, in chapter 4, a polycation, poly (diallyldimethylammonium chloride) (PDDA), is used to wrap CNTs. The PDDA wrapping around CNTs leads to the uniform distribution of positive charges on CNTs, which thus results in the well-dispersed Pt NPs on PDDA-CNTs. The electrochemical characterization shows that Pt NPs supported on PDDA-wrapped CNTs (Pt/PDDA-CNTs) are more active for methanol electrooxidation than those supported on acid oxidized CNTs (Pt/AO-CNTs) and commercial E-TEK electrocatalysts: Pt/C.”

Chapter 5 as a continuation of chapter 4 presents the work on the study of the effect of different functional groups introduced by the polymer wrapping approach on the catalytic activity of Pt NPs for methanol electrooxidation. In this work, by selecting the characteristic polyelectrolytes with specific functional groups (positive or negative), various expected functional groups can be facilely introduced onto the surface of CNTs. These functional groups having different charge natures would show

different effects on the electronic properties and thus the electrocatalytic behavior of the subsequently deposited Pt NPs. It has been found that negatively charged functional groups can shift the d-band center of Pt NPs downwards by donating electrons from the functional groups to Pt surface. The downshifted d-band center would weaken the chemisorption energy of CO (a poisonous intermediate of methanol electrooxidation) and thus enhance the electrocatalytic activity for methanol electrooxidation. This work provides a novel principle for the design of electrocatalysts.

“Chapter 6 as a continuation of chapter 4 presents the combination of a polyol reduction method and a seed-mediated growth method to synthesize Pt/PDDA-CNT electrocatalysts with varied Pt loadings on CNTs from 10 wt% to 93 wt%. It should be pointed out that it’s a huge challenge to prepare Pt/CNT electrocatalysts with high Pt loading (above 50 wt %). In this chapter, besides the advantageous PDDA wrapping technique, a seed-mediated growth method is also adopted to grow additional Pt atoms/clusters on the pre-synthesized Pt/PDDA-CNTs by the polyol reduction method. We have investigated the electrocatalytic performance for CO and methanol electrooxidation and oxygen reduction reactions and have found that there is a close correlation between the electrocatalytic activity and interconnectivity of Pt NPs on CNTs. The definition and quantitative calculation of the interconnectivity of Pt NPs have been proposed. The reasons behind this correlation are also discussed in details.”

1.3.2. Morphology Control of Metal Electrocatalysts.

“The electrocatalytic activity is also significantly dependent on the morphology metal electrocatalysts.[14-22] The bounding facets, number of low coordinated atoms, and surface-to-volume ratios of metal electrocatalysts can lead to unique surface properties. The above chapter 6 has concluded that there is a close correlation between the electrocatalytic activity and interconnectivity of Pt NPs on CNTs and the increased activity is partially attributed to the formation of grain boundaries. This conclusion motivates us to investigate the electrocatalytic activity of metal nanowire networks, because amounts of grain boundaries may exist in metal nanowire networks. These studies are presented in Chapter 7 and 8.

Chapter 7 presents the synthesis of Pt nanowire networks (Pt NWN) in a micelle environment and their comparison with commercial Pt/C electrocatalysts for carbon monoxide and methanol oxidation. It has been found that Pt NWN shows enhanced electrocatalytic activity for all of the above reactions.

Chapter 8 presents the synthesis of Pd nanowire networks (NWNs) with a novel self-assembly method and their application for formic acid electrooxidation in acid medium. A polyanion, PSS, functions as a soft template for the formation of Pd NWN. The mixing of PSS and Pd^{2+} produces a complex by the electrostatic interaction. The subsequent fast reduction leads to the formation of Pd nanowire network following the network structure of PSS. By contrast, the slow reduction would lead to the formation of Pd NPs instead of nanowire network structure. The interconnectivity of Pd NWNs

can be tuned by controlling the PSS/Pd molar ratios. It has also been found that the increase of the interconnectivity of Pd NWNs also results in the increase of their catalytic activity for formic acid electrooxidation.”

Chapter 9 gives the conclusion of this thesis and outlines the recommendations for the future studies.

Chapter 2 Literature Review

2.1. Basics of Fuel Cell

Fuel cell as a “zero emission” technology has attracted more and more attention. Fuel cell, a promising device converting chemical energy directly into electrical energy, involves the electrochemical reactions like the conventional battery.[1, 4, 23, 24] The difference is that fuel cell has an externally continuous supply of fuels and does not store the energy in chemicals. This continuous supply of fuels ensures the long lifetime of a fuel cell without the concerns of the degradations of electrolytes and electrocatalysts, while batteries are limited by their energy capabilities. On the other hand, fuel cell eliminates the pollutant problem that more and more people care about nowadays.

The electrochemical reactions in a fuel cell are divided into two half-reactions by the electrolyte. The anode reaction of a fuel cell involves the oxidation of fuels such as hydrogen and small organic molecules (SOMs, including methanol and formic acid). The cathode reaction involves the electrochemical reduction of oxygen. The electrolytes used may be different depending on the type of fuel cells. The electrons generated from the electrochemical reactions are collected by an external circuit.[1, 4]

In the fuel cell family, PEMFC has been proposed as the leading technology for various applications, including electronic devices, military communication, and automobiles etc. PEMFCs use a solid polymer membrane as the electrolyte. Protons can flow through this solid polymer membrane from anode to cathode when it is

saturated with water, but electrons can not flow through it. The PEMFCs rely upon the oxidation of fuels within an electrocatalyst layer to generate carbon dioxide (CO_2). Water is consumed and produced at the anode and cathode side, respectively. Depending on the fuels used, PEMFCs can be categorized as hydrogen/oxygen fuel cells, direct methanol fuel cells (DMFCs) and direct formic acid fuel cells (DFAFC) etc.[1, 4, 23, 25-29]

2.2. Types of Proton Exchange Membrane Fuel Cells

2.2.1. Hydrogen/Oxygen Fuel Cells:

Hydrogen/oxygen fuel cells use hydrogen as the fuel. The electrooxidation of hydrogen occurs at the anode side and the kinetics of this reaction is very fast on Pt-based electrocatalysts. Unfortunately, however, for the practical hydrogen/oxygen fuel cells, the hydrogen source always contains some impurities such as carbon monoxide (CO) and sulfur (S), which could seriously poison the catalyst and decrease its catalytic performance. Much research work has been focused on the CO removal for this kind of fuel cell. Two strategies have been extensively used: 1) external control systems are set up to minimize the CO contamination, but this method increases the complexity of the fuel cell system; 2) CO-tolerant electrocatalysts, like PtRu alloy electrocatalysts, are developed to remove the adsorbed CO species. On the other hand, the generation, storage, and transportation of hydrogen also increase the difficulty of commercializing the hydrogen/oxygen fuel cells. Therefore, alternatively, other small organic molecules should be explored as fuels for PEMFCs.[4]

2.2.2. Direct Methanol Fuel Cells (DMFCs)

The liquid small organic molecules, which can be easily produced, stored, and transported, have lots advantages to be used as fuels in proton exchange membrane fuel cells, compared to hydrogen as fuels.[1]

When methanol is used as the fuel, DMFCs are named. DMFCs are the promising power sources for various portable applications because of their high power density, quick start-up, and low operating temperature.[1, 30] The anode and cathode sides involve the methanol oxidation reaction (MOR) and oxygen reduction reactions (ORR), respectively.

The half-reactions in DMFCs are:[1]

Overall reaction in DMFCs is:

At the anode side, during methanol oxidation catalyzed by Pt-based electrocatalysts, CO is always formed as poisonous intermediate due to the incomplete oxidation. This CO species can block the active surface of the catalyst and hinder any further reaction. For this reason, lots of research has been focused on the modification of the Pt electrocatalyst to facilitate the CO removal.[1] This can be achieved by forming Pt

alloy with a second metal element (M) that has a strong capability of water activation to form M-OH. The OH on M could facilitate the CO removal by their reaction to CO₂. The most commonly used bimetallic electrocatalysts for methanol electrooxidation is PtRu/C.[8, 31-36] The classical bifunctional mechanism has been proposed to illustrate the good CO tolerance of PtRu/C. Alternatively, it should be pointed out that another bimetallic alloy electrocatalysts, PtSn/C, could also significantly enhance the electrocatalytic activity of methanol oxidation. However, the promotion mechanism is different from that on PtRu/C. It has been demonstrated that the enhanced electrocatalytic activity of MOR on PtSn/C is due to the electronic effect, namely, Sn tends to donate electrons to Pt surface because of their different electro-negativity values.[37-41] On the other hand, much research is also being performed on improving the electrocatalytic activity of carbon-supported Pt-based NPs by modifying the carbon supports, which can affect the particle size, dispersion on carbon support, and even the electronic properties of Pt NPs, and by proper nanostructure design.[6, 42, 43]

Another serious barrier for DMFCs is methanol cross-over through the membrane from anode to cathode.[44] In order to equip it with good proton conductivity for DMFCs, the membrane must have some water content. The methanol at the anode would partially cross-over through the membrane driven by the electro-osmotic drag and diffusion to the cathode of DMFCs, which leads to a mixed potential because of the interference of MOR with ORR and thus a decreased fuel cell performance. To solve this problem, researchers are focusing on two aspects: 1) developing novel or modified membranes with improved methanol cross-over resistance; 2) designing

methanol-tolerant cathode electrocatalysts.[45]

2.2.3. Direct Formic Acid Fuel Cells (DFAFCs)

“Recently, DFAFCs, in which formic acid is used as fuel, have also been the focus of research attention, due to their advantages over DMFCs. Compared to DMFCs, DFAFCs have lower fuel cross-over through the membrane and higher theoretical open-circuit-potential (OCP). Similar to methanol, formic acid as a small organic molecule is directly fed into the cell. It has been reported that formic acid shows a smaller crossover through the electrolyte membrane than methanol, which allows using concentrated fuels and thinner membranes in DFAFCs. At the anode, formic acid electrooxidation (FAOR) produces two electrons per formic acid molecule. The reactions involved in a DFAFC are described as:[46-51]”

The half-reactions in DFAFCs are:

Overall reaction in DFAFCs is:

“The most commonly accepted reaction mechanism for the formic acid electrooxidation on Pt electrocatalysts is the parallel pathway mechanism. The first reaction pathway is the direct oxidation via dehydrogenation reaction, through which

no CO poisonous intermediate is produced.”

However, the second pathway involves the formation of adsorbed poisonous intermediate: CO, by dehydration:

“In the dehydration pathway, formic acid would first adsorb on Pt surface with generating CO species, and then CO is oxidized to CO₂. For DFAFCs, the dehydrogenation reaction pathway is desired to enhance the overall fuel cell performance and to prevent poisoning the catalyst. Therefore, the design of anode electrocatalysts always aims at directing the formic acid electrooxidation to occur via the dehydrogenation pathway.[50-52]”

2.2.4. Oxygen Reduction Reaction in Fuel Cells

For any type of the above PEMFCs, ORR always occurs at the cathode.[45] The ORR can proceed by two overall pathways in aqueous electrolytes, a direct 4-electron pathway or an indirect 2-electron pathway. The direct 4-electron pathway is preferable as it does not form peroxide species and the cell efficiency of the reaction is greater. Pt-based electrocatalysts are also usually used for ORR. Due to the high cell potential at which ORR occurs, the ORR electrocatalysts suffer from serious corrosion degradation. Therefore, the study of ORR electrocatalysts always aims at improving both electrocatalytic activity and durability. Under the electrochemical environment,

Pt surface is partially oxidized to form Pt oxide (Pt-OH). The presence of OH on Pt surface blocks the active sites for the ORR. Thus, the design of cathode electrocatalysts always aims at decreasing the chemisorption energy of Pt nano-electrocatalysts with oxygen-containing species. Besides, as stated above in the DMFC section, developing methanol-tolerant electrocatalysts is another aspect to eliminate the influence of methanol cross-over.

2.3. Electrocatalysts

“Nanosized metal NPs supported on carbon supports are the most commonly used and important electrocatalysts for all of these fuel cells. However, the unaffordable high cost of the precious metal electrocatalysts as well as their low utilization efficiency seriously blocks the large-scale commercialization of PEMFCs. In order to reduce the Pt usage, which thus reduce the overall cost of fuel cells, while still preserving the cell performance of PEMFCs, a great deal of effort must be devoted to improving the electrocatalyst utilization efficiency and enhancing the intrinsic catalytic activity of electrocatalysts. This goal could be achieved by using high surface area porous carbon materials (e.g., carbon nanotube, carbon black) as supports to enhance the dispersion and distribution of metal electrocatalyst NPs and to improve their utilization efficiency.[53] The dispersion of metal electrocatalyst NPs on carbon supports strongly depends on the interaction between metal electrocatalysts and their supports, and intrinsic properties of carbon supports. On the other hand, the electrocatalytic activity is also highly dependent on the morphology and particle size of metal electrocatalysts. Metal electrocatalysts exhibit shape-, size- and

dimension-dependent catalytic properties, which lead the morphology control of metal electrocatalysts to become an active and prolific research area.”

2.3.1. Synthesis Methods for Metal Electrocatalysts

To date, various synthetic approaches have been extensively investigated to prepare supported metal electrocatalysts, such as impregnation, potential step electrodeposition, colloid route, and microwave-assisted polyol methods.[5] The impregnation method, which is also named as the electroless deposition method, is widely used to prepare highly dispersed metal NPs supported on carbon supports. This approach involves the pre-mixing of carbon supports and metal precursors followed by the addition of reducing agents (i.e., sodium borohydride, ethylene glycol, and formic acid.) The average particle size, dispersion and distribution of the as-produced metal NPs strongly depend on the properties of carbon supports and reducing agents. The synthesis and deposition of Pt NPs by the electrodeposition could be realized by pulse deposition in 1.0 M H₂SO₄ electrolyte containing metal precursors, while the carbon supports are pasted on the working electrode. However, such an electrodeposition method is not suitable for the large-scale production of electrocatalysts. The colloidal route for the synthesis of supported metal electrocatalysts involves the pre-formation of metal NPs followed by the deposition on carbon supports. In this case, colloid precursors are used to stabilize metal NPs to avoid aggregation and obtain fine NPs. More recently, the microwave-assisted polyol reduction method has been developed to synthesize highly-dispersed metal NPs deposited on carbon supports with much smaller particle size. The microwave

irradiation facilitates the fast reduction of metal precursors to metal atoms and the uniform distribution of the heat in the reaction solution leads to the fine particle size.[54]

2.3.2. Carbon Nanotubes as Electrocatalyst Supports

2.3.2.1. General

“Platinum-based electrocatalysts, most commonly used in PEMFCs, always exist in the form of nano-scaled particles with highly exposed surface for electrocatalytic reactions. However, Pt NPs tend to aggregate to form bigger Pt nanoclusters in order to realize the minimum surface energy of NPs, especially under electrochemical conditions. Therefore, in order to improve their utilization efficiency, electrocatalytic performance, and durability, Pt (or Pt-based alloy) NPs should be supported on some catalyst supports with high surface area.[55] The catalyst supports not only prevent the nano-scaled electrocatalyst particles from aggregation, but also play a significant role in transporting the electrons generated from and consumed for the electrochemical reactions.”

It has been demonstrated that catalyst supports have great influence on the performance and durability of electrocatalysts as well as the cost of the fuel cells. An ideal catalyst support should meet the following requirements: 1) high surface area to improve the catalyst dispersion, 2) low combustive reactivity, 3) high conductivity, and 4) high electrochemical and thermal stability. Currently, the most popular support material is porous carbon black (XC-72) with high surface area, which leads to

well-dispersed electrocatalyst NPs.[55] A high dispersion is the pre-requisite to produce high-performance electrocatalysts. Recently, developing novel catalyst supports for PEMFC application has attracted much attention. Of them, much effort has been devoted to investigating carbon nanotubes (CNTs) as catalyst supports.[7, 8, 10, 55-57]

“CNTs have attracted increasing attention due to their promising physical and chemical properties, since their discovery in 1990s by Ijima in Japan. Nowadays, the synthesis of carbon nanotubes could be realized by three main approaches: chemical vapour deposition, laser vaporization, and arc-discharge evaporation.[5, 55] CNTs are categorized as multi-walled carbon nanotubes (MWCNTs), double-walled carbon nanotubes (DWCNTs), and single-walled carbon nanotubes (SWCNTs) on the basis of the number of graphitic layer, as illustrated in Scheme 2.1. CNTs have attracted increasing interest in both fundamental and applications such as mechanically reinforced composites, field-effect transistors, chemical/electrochemical sensors, hydrogen storage, catalysis, and electronic nano-devices.[58-61]”

Scheme 2. 1 Illustration of MWCNTs, DWCNTs, and SWCNTs.

“CNTs are widely investigated as support materials for Pt and Pt alloy catalysts in fuel cells due to their high surface area, good electronic conductivity, and high chemical and thermal stability.[7, 24, 57, 62] It is believed that the unique electrical and structural properties ensure CNTs to be an excellent candidate as supporting materials of metal electrocatalysts. The high electrical conductivity of CNTs and the unique interaction between metal electrocatalysts and CNTs (the π -electrons of carbon nanotubes and d-electrons of metal (i.e., platinum)) would lead to the enhanced electrocatalytic activity.[55] The deposition, dispersion, and size of metal NPs supported on CNTs strongly depend on the surface properties of CNTs.[54] The electrocatalytic activity of metal NPs is significantly affected by the nature of their interaction with CNTs and the intrinsic properties of CNTs. Since pristine CNTs are chemically inert, it is necessary to activate the graphitic surface of the nanotubes in order to efficiently deposit catalyst NPs.[11] Therefore, the pre-functionalization process is the pre-requisite for CNTs to support metal electrocatalyst NPs.”

2.3.2.2. Functionalization of Carbon Nanotubes

Usually, the synthesis process of CNTs always generates CNT bundles composed of amounts of single nanotubes, especially for single-walled CNTs, which limits their efficient applications.[55] The individual CNTs are preferred usually and the functionalization strategy of CNTs can extend their applications. At the early development stage of CNT functionalization, the chemical oxidation of CNTs is most commonly used. Typically, this method involves the ultrasonication or refluxing in a harsh acid mixture: sulfuric and nitric acid, resulting in the formation of

oxygen-containing functional groups (i.e., carboxyl groups) on the ends and side-walls of CNTs.[10] Such a vigorous functionalization process leads to the damage of the perfect CNT structure, namely, opening the nanotube caps and generating holes in the CNT side-walls. In addition, the introduced functional groups prefer to locate at the defect sites of CNTs, and thus the distribution of functional groups is not uniform. The presence of carboxyl groups introduced by the chemical oxidation enables the further functionalization of CNTs *via* the covalent coupling. Various expected functional groups could be obtained on CNTs through the synthetic chemistry design. However, this manner is too complexed.[11]

“Alternatively, a gentler and more facile noncovalent functionalization method has been extensively developed recently. Surfactant aggregating, bifunctional molecule stacking, macromolecule immobilization, and polymer wrapping on CNTs are the four main strategies to noncovalently functionalize CNTs. Surfactants are of amphiphile molecules, in which the hydrophobic ends direct to the hydrophobic CNT surface and the hydrophilic ends direct to the solvent (aqueous solution) forming aggregates on CNTs. For a bifunctional molecule containing aromatic groups could be efficiently stacked on CNT surface *via* the π - π interactions.[63] For macromolecules like proteins, the hydrophobic regions in the proteins could be responsible for the adsorption on CNTs. CNTs could be effectively functionalized by most of water-soluble polymers *via* a polymer wrapping technique. These noncovalent functionalization methods can effectively and uniformly introduce specified molecules/functional groups on CNT surface without any damage on their structures. Compared to the covalent method, the noncovalent method is more facile and effective for the functionalization of CNTs.”

2.3.3. Morphology Control of Nanostructured Electrocatalysts

“Recently, extensive effort has been directed toward the synthesis of morphology-controlled nanomaterials because of their extraordinary morphology-dependent properties and their wide applications in the field of catalysis, optoelectronics, biolabeling, chemical sensors, and fuel cells. [20, 64–67] To date, various forms of nanostructures have been developed from highly monodispersed spherical and cubic NPs to various anisotropic nanostructures such as nanowires, nanorods, and nanotubes. Usually, metal electrocatalysts are used in the form of small NPs, as smaller particle size would exhibit higher exposed surface area which is especially essential for the surface catalysis applications.[42] Recently, however, a lot of attention has been attracted to the branched metal nanomaterials such as porous NPs, multipods, nanowire networks, and dendritic NPs. Among these nanostructures, metal nanowire arrays or networks (NWNs) have attracted much attention and have been fabricated using a variety of approaches including chemical vapor deposition, laser assisted synthesis, electrochemical deposition, and structural templating.[68–73] Wang et al.[74] electrochemically synthesized platinum NWNs using mesoporous silica as a hard template. However, the hard template method generally produces low metallic interconnectivity due to the poor continuity of precursors in mesoporous silica templates. In order to remove the silica template, hydrofluoric acid needs to be used, which is a serious concern for the environment and safety. The template method based on the anodized aluminum oxide (AAO) is also limited by the channel diameter of the AAO available. The diameter of the nanowires using the AAO template method

is typically in the range of 80 ~120 nm.[74] On the other hand, templateless low-temperature wet-chemical approaches offer enormous process flexibility to assemble nanoscale building blocks into variety of nano-architectures. For example, metal nanowires can be synthesized using micelles, polymer-mediated NP assembly, and surfactant-stabilized water-in-oil microemulsions.[75-77]”

Chapter 3 “PtRu Nanoparticles Supported on 1-Aminopyrene-Functionalized Multiwalled Carbon Nanotubes and Their Electrocatalytic Activity for Methanol Oxidation”

3.1. Introduction

“The poisoning of the Pt electrocatalysts by CO is a very serious problem for methanol oxidation in DMFCs.[78] Pure Pt electrocatalysts are prone to being poisoned by CO since CO can strongly adsorb onto the Pt surface and block the active sites for any further reaction. As a result, Pt electrocatalysts rapidly deactivate during the electrooxidation of methanol. Bimetallic PtRu alloy nanoparticles (NPs) have been studied as the most effective CO-tolerant electrocatalysts to alleviate this problem. It has been demonstrated that the adsorption of hydroxyls on the oxophilic Ru facilitates the removal of CO species adsorbed on the Pt and thus releases the occupied active sites for the further reactions.

Carbon nanotubes (CNTs) are extensively studied as support materials in fuel cells. The deposition, distribution, and size of Pt or Pt alloy NPs supported on CNTs depend strongly on the surface properties of CNTs.[54] The activity of Pt NPs is also significantly affected by the nature of their interaction with CNTs and the intrinsic properties of CNTs. Since the surface of pristine CNTs are chemically inert, it is necessary to activate the surface of the nanotubes in order to deposit catalytic NPs. CNTs are usually functionalized by harsh oxidative processes, such as refluxing in the concentrated mixture of HNO₃ and H₂SO₄ to generate functional groups on CNTs[8,

54, 79] However, due to the introduction of a large number of defects, such a chemical oxidation method reduces the electrical conductivity and corrosion resistance of CNTs. Corrosion of carbon black or CNT supports has been identified as one of the main reasons for the reduced durability during fuel cell operation.[57] Therefore, development of a better and more effective functionalization method that can not only introduce homogeneous surface functional groups but also has little or even no structural damage to the structure and properties of CNTs remains a major challenge.

Recently, the noncovalent functionalization of CNTs has attracted particular attention because it enables the properties of the hybrids of NPs and CNTs to be tailored while still preserving nearly all the intrinsic properties of CNTs. Correa-Duarte et al.[80] used multilayer assembled CNTs of poly(sodium 4-styrenesulfonate) (PSS) and PDDA as templates to support silica-coated Au NPs. Ou et al.[63] assembled semiconductor and metal NPs on MWCNTs by use of pyrene-containing molecules as interlinkers, but in this case, the dispersion of NPs on carbon nanotubes is not satisfactory, as indicated by the formation of NP aggregates.

In this chapter, we present a study on the functionalization of MWCNTs by a bifunctional molecule, 1-aminopyrene (1-AP), and the synthesis of bimetallic PtRu electrocatalysts on 1-AP-functionalized MWCNTs (denoted as 1-AP-MWCNTs) by a microwave-assisted polyol reduction process. Our work represents a new synthesis method of PtRu/MWCNT electrocatalysts with many benefits as compared to the synthesis of PtRu electrocatalysts on the conventional acid-oxidized MWCNTs (denoted as AO-MWCNTs). One of the most important advantages is that, in contrast

to the AO-MWCNTs, where the harsh chemical acids are used to produce carboxylic acid sites on the surface, the 1-AP-functionalization treatment preserves the integrity and the electronic structure of MWCNTs. The distribution of PtRu NPs on 1-AP-MWCNTs (PtRu/1-AP-MWCNTs) is much more uniform, as compared with that deposited on the conventional acid-oxidized MWCNTs (PtRu/AO-MWCNTs). PtRu NPs on 1-AP-MWCNTs have higher electrochemical surface area and better activity for methanol electrochemical oxidation than that supported on AO-MWCNTs and XC-72 carbon black. In addition, the significantly enhanced stability for the methanol electrooxidation was also observed for the PtRu NPs supported on 1-AP-MWCNTs.

3.2. Experimental and Characterization Methods

3.2.1. Materials

Materials used in the present work include DI water (resistivity $>18.0 \text{ M}\Omega \text{ cm}$), sulfuric acid (99.5%, Fluka), nitric acid (65%, Fluka), ethanol (Fluka), methanol (Fluka), multiwalled carbon nanotubes (Shenzhen Nano Port, China), hexachloroplatinic(IV) acid (Sigma-Aldrich), ruthenium chloride (Sigma-Aldrich), ethylene glycol (EG, Fluka), 1-aminopyrene (Sigma-Aldrich), Nafion solution (5 wt % in isopropanol and water), and carbon black (XC-72, Gashub). All the chemicals and powders were used as received without further purification.

3.2.2. 1-AP- and Acid-Functionalization of MWCNTs

The procedure for the noncovalent functionalization of MWCNTs using 1-AP is as follows. First, 200 mg of pristine MWCNTs was sonicated in 100 mL of ethanol containing 20 mg of 1-AP for 1 h and stored at room temperature overnight. Then the above solution was filtered using a nylon filter membrane and washed, and the filtration was repeated several times. The as-functionalized MWCNTs were dried in a vacuum oven at 70 °C for 10 h and collected. As a comparison, MWCNTs were also functionalized by a conventional acid treatment. In this treatment, 200 mg of MWCNTs was treated in 200 mL of a mixed strong acid solution ($\text{H}_2\text{SO}_4\text{:HNO}_3$ in 1:1 v/v ratio), followed by refluxing at 140 °C for 4 h. The obtained solution was then diluted with 2 L of DI water to reduce the acidity of the solution, followed by filtration. The acid-treated MWCNTs were washed for several times and dried in a vacuum oven at 70 °C for 24 h. The acid-treated MWCNTs are denoted as AO-MWCNTs.

3.2.3. Synthesis of PtRu/MWCNT Electrocatalysts

To deposit the PtRu NPs on 1-AP-functionalized MWCNTs, 30 mg of 1-AP-MWCNTs was mixed with approximate amount of H_2PtCl_6 and RuCl_3 with a molar ratio of $\text{Pt/Ru} = 1:1$ in ethylene glycol (EG) solution under ultrasonication in a beaker. The solution was controlled at a pH of slightly less than 7 (e.g., pH 6.5) to maintain a weak acidity. The beaker was then placed in a microwave oven and heated for 2 min. The solution changed from light yellow to dark brown, indicating the reduction and formation of PtRu NPs on MWCNTs. The solution was then filtered

using a nylon filter membrane and washed, and the filtration was repeated several times. The obtained PtRu electrocatalysts on 1-AP-functionalized MWCNTs were dried in a vacuum oven at 70 °C for 24 h. PtRu electrocatalysts on acid-functionalized MWCNTs and XC-72 carbon black (PtRu/C) were prepared using similar procedures as described above. PtRu NPs with different total metal loading (20 and 40 wt %) were obtained on 1-AP-MWCNTs and AO-MWCNTs through controlling the concentration of H_2PtCl_6 and RuCl_3 .

3.2.4. Characterization and electrochemical measurements

UV–visible spectroscopy was used to confirm the existence of 1-AP after 1-AP functionalization of MWCNTs. The samples were dissolved in tetrahydrofuran prior to the UV–visible spectroscopy measurement. The effect of 1-AP and acid functionalization methods on the surface structure of MWCNTs was also examined by Raman spectroscopy (Renishaw), using He/Ne laser with a wavelength of 633 nm. The transmission electron microscopy (TEM, JEOL 2010) was performed on PtRu/MWCNT and PtRu/C electrocatalysts using the acceleration voltage of 160 kV. An X-ray diffractometer, using Cu $\text{K}\alpha_1$ ($\lambda = 1.54056 \text{ \AA}$) as the radiation source was used for identification of the crystalline structure and average crystallite size of Pt particles. The tube current and voltage were 25 mA and 35 kV, respectively. The average crystallite size of Pt particles was estimated from the diffraction peak of Pt (220) using the Scherrer equation.

The electrochemical activity of the as-synthesized electrocatalysts was measured for

the electrooxidation of methanol. Generally, 4 mg of the electrocatalyst sample was ultrasonically mixed in 4 mL of ethanol to form a homogeneous ink followed by dropping 20 μL of the electrocatalyst ink onto the surface of a glass carbon electrode (GCE). The diameter of GCE is 4 mm. Then, 1 μL of Nafion solution of 0.5 wt% in 2-propanol was added to fix the electrocatalysts on the GCE surface. Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials in the present study were given *versus* Ag/AgCl reference electrode. The electrochemical active surface area (ECSA) of PtRu/MWCNT and PtRu/C electrocatalysts was measured in a nitrogen-saturated 0.5 M H_2SO_4 solution at a scan rate of 50 mV/s and the electrocatalytic activity for the methanol oxidation reaction was measured in a nitrogen-saturated 0.5 H_2SO_4 + 1.0 M CH_3OH solution at a scan rate of 50 mV/s. For the electrochemical tests for PtRu/1-AP-MWCNTs-40 wt % and PtRu/AO-MWCNTs-40 wt %, 10 μL of the as-prepared electrocatalyst ink using the above procedure was placed on the GCE. The Pt metal loading was kept at 2.68 μg . The tests were conducted at room temperature.

3.3. Results and Discussion

Scheme 3.1 illustrates the principle of the synthesis of PtRu NPs on 1-AP-MWCNTs. The noncovalent functionalization involves a bifunctional molecule, 1-AP, adsorbed onto the surface of MWCNTs. 1-AP is a bifunctional molecule with a pyrenyl group and an amino functional group. The pyrenyl group, being highly aromatic in nature, is known to interact strongly with the basal plane of graphite via π -stacking.[81, 82] In a similar manner, the pyrenyl group of 1-AP could also strongly

interact with the sidewalls of MWCNTs, immobilizing 1-AP on the MWCNTs. When the pH of the solution is controlled at slight acidity (e.g., pH 6.5), the amino groups of 1-AP immobilized on the MWCNT surface are protonated and become weakly positively charged.[83] This leads to the electrostatic attraction of the negatively charged PtCl_6^{2-} , followed by the subsequent self-assembly of positively charged Ru^{3+} , on the 1-AP-MWCNTs. The microwave-assisted polyol treatment in the presence of ethylene glycol as a reducing agent reduces the PtRu precursors, forming PtRu NPs on MWCNTs.

Scheme 3. 1 Schematic diagram of the synthesis of PtRu electrocatalysts on 1-AP-functionalized MWCNTs.

3.3.1. UV-vis characterization

Figure 3.1 is the UV-visible spectra of 1-AP, 1-AP-MWCNTs, and pristine MWCNTs, confirming the successful noncovalent stacking between 1-AP and MWCNTs. The pristine MWCNTs show a typical featureless spectrum (curve c in Figure 3.1A). 1-AP-MWCNTs show additional peaks around 355 and 290 nm (curve b in Figure 3.1A). This corresponds to the characteristic peaks of 1-AP at around ca. 285 and 365 nm (curve a in Figure 3.1A).[84] The appearance of the additional peaks in the differential UV-vis curves (Figure 3.1B) also indicates the successful functionalization of MWCNTs by 1-AP via the π - π interaction between the pyrenyl groups of 1-AP and the six-membered rings of the sidewalls of MWCNTs. This is similar to the immobilization of 1-pyrenebutanoic acid succinimidyl ester on the sidewalls of single-walled carbon nanotubes *via* π -stacking.[85]

Figure 3. 1 UV-vis spectra (A) and differential UV-vis spectra (B) of (a) 1-AP, (b) 1-AP-functionalized MWCNTs, and (c) pristine MWCNTs.

3.3.2. Raman Characterization

Figure 3. 2 Raman spectra of pristine MWCNTs, 1-AP-MWCNTs, and AO-MWCNTs.

The Raman spectroscopy was used to study the surface structure of 1-AP-MWCNTs, AO-MWCNTs, and pristine MWCNTs, and the results are shown in Figure 3.2. MWCNTs with and without functionalization treatment have similar Raman scattering patterns. The peak near 1328 cm⁻¹ is assigned to the disordered graphite structure (*D*-band), and the high frequency peak at near 1577 cm⁻¹ (*G*-band) corresponds to a splitting of the E_{2g} stretching mode of graphite, which reflects the structural intensity of the sp²-hybridized carbon atoms.[86] Thus the extent of the modification or defects in MWCNTs can be evaluated by the intensity ratio of the *D*- and *G*-bands. The intensity ratios of I_D/I_G are 1.34, 1.01, and 1.77 for pristine-MWCNTs, 1-AP-functionalized MWCNTs, and acid-oxidized MWCNTs, respectively. The slightly decreased I_D/I_G ratio for 1-AP-MWCNTs as compared to that of pristine

MWCNTs indicates that the immobilization of 1-AP on the sidewalls of MWCNTs *via* π -stacking has no detrimental effect on the surface structure of carbon nanotubes. Rather, the decreased ratio suggests the coverage of the original defect sites by the 1-AP molecules. On the other hand, the intensity of the I_D/I_G ratio of AO-MWCNTs is 1.77, much higher than 1.34 of the pristine MWCNTs, consistent with that reported previously.[54] This indicates that the harsh chemical acid treatment produces carboxylic acid sites on the surface, causing significant structural damage of MWCNTs. This would decrease the electrical conductivity of MWCNTs and lower the corrosion resistance. In contrast, the 1-AP functionalization method preserves the integrity and electronic structure of carbon nanotubes and provides highly effective functional groups on the surface of MWCNTs for the subsequent deposition of PtRu NPs.

3.3.3. TEM Characterization

The TEM micrographs of the PtRu NPs deposited on AO-MWCNTs, 1-AP-MWCNTs, and carbon black are shown in Figure 3.3. The PtRu loading is 20 wt %. In the case of 20 wt% PtRu/AO-MWCNTs, the dispersion of PtRu NPs on AO-MWCNTs is characterized by a poor distribution with a large number of aggregates (Figure 3.3a). The average particle size of PtRu NPs is 3 ± 0.4 nm. For the MWCNTs functionalized by the acid oxidation treatment, the defects generated are usually not uniform. When PtRu NPs are deposited on the MWCNTs, the particles tend to deposit on these localized defect sites, leading to poor dispersion and extensive aggregation.[54, 62] The extensive aggregation of PtRu electrocatalysts would lead to

the reduced electrocatalytic activity of the PtRu electrocatalysts. In contrast, PtRu NPs are evenly deposited on the 1-AP-MWCNTs with no agglomeration (Figure 3.3b). The average particle size is 2 ± 0.2 nm, much smaller than that on the AO-MWCNTs. This clearly indicates that immobilization of 1-AP on the sidewalls of MWCNTs produces a uniform distribution of the amino groups, which serve as functional groups for the self-assembly of Pt and Ru precursors on the surface of MWCNTs. Therefore, a much more uniform distribution of PtRu NPs would be expected. The distribution of PtRu NPs supported XC-72 carbon black is reasonable (Figure 3.3c). This suggests that the good distribution and nanosized PtRu NPs can be obtained by the microwave-assisted polyol method. The EDX spectrum of PtRu/1-AP-MWCNT electrocatalysts confirms that both Pt and Ru elements were successfully deposited on 1-AP-functionalized MWCNTs (Figure 3.3d).

Figure 3. 3 TEM images of (a) PtRu/AO-MWCNTs, (b) PtRu/1-AP-MWCNTs, and (c) PtRu/C. The EDX spectrum of PtRu/1-AP-MWCNTs is shown in panel (d). The PtRu loading on carbon support is 20 wt %.

Figure 3. 4 TEM images and distribution histograms of PtRu NPs on 1-AP-MWCNTs (a and b) and AO-MWCNTs (c and d). The PtRu loading was 40 wt %.

The PtRu loading on MWCNTs can be increased by proper control of the amount of Pt and Ru precursors. Figure 3.4a shows an example of a TEM micrograph of 40 wt% PtRu/1-AP-MWCNTs. With the increase in the PtRu loading, a good dispersion is still maintained on the 1-AP-MWCNTs without agglomeration (Figure 3.4a). The histogram indicates that the distribution of the PtRu NPs is very narrow and the average particle size is 2 nm, similar to that for 20 wt% PtRu/1-AP-MWCNTs (Figure 3.3b). On the other hand, for PtRu/AO-MWCNTs with 40 wt % PtRu loading, the agglomeration problem became more serious (Figure 3.4c). The histogram indicates

that the distribution of the particle size is broad and the average diameter is about 4.3 nm (Figure 3.4d), which is larger than that with 20 wt % PtRu loading. The results are significant as not only uniformly distributed PtRu NPs but also a high PtRu loading can be obtained on 1-AP-MWCNTs. The high loading and uniformity of PtRu NPs on 1-AP-MWCNTs are clearly due to the immobilization of bifunctional molecules, 1-AP, which offers large and uniform distributed active sites for anchoring metal ions and metal NPs. Thus, 1-AP-functionalized MWCNTs are far more effective supports than the conventional acid-oxidized MWCNTs.

3.3.4. XRD Characterization

Figure 3.5 shows the XRD patterns of PtRu/AO-MWCNTs and PtRu/1-AP-MWCNTs with the 20 wt % PtRu loading. The XRD results show the presence of diffraction peaks at 39.6° , 46.3° , 67.4° , which can be assigned to Pt (111), Pt (200), and Pt (220), consistent with the face-centered cubic (fcc) structure of platinum. PtRu alloys would take the face-centered cubic (fcc) structure of Pt if the Ru content is below 60 wt %. The peak near 2θ of 26° originates from the graphitic carbon of MWCNTs. The Pt (220) bands at 67.4° are broader and weaker for PtRu/1-AP-MWCNTs-20 wt % than that for PtRu/AO-MWCNTs-20 wt %, indicating the smaller size of PtRu NPs on 1-AP-MWCNTs. On the basis of Sherrer's equation through line broadening of the Pt (220) peak, the average size of Pt NPs for PtRu/1-AP-MWCNTs and PtRu/AO-MWCNTs was calculated as 2 and 3 nm, respectively. These values agree quite well with the TEM results.

Figure 3. 5 XRD patterns of PtRu/AO-MWCNTs and PtRu/1-AP-MWCNTs.

3.3.5. Electrochemical Characterization

The electrocatalytic activity of the PtRu/1-AP-MWCNTs as potential electrocatalysts for the low-temperature fuel cells was examined. Figure 3.6 shows the cyclic voltammograms (CVs) of PtRu/1-AP-MWCNTs and PtRu/AO-MWCNTs with different PtRu loadings measured in a nitrogen-saturated 0.5 M H_2SO_4 solution in the absence and presence of 1.0 M CH_3OH . For the purpose of comparison, the catalytic activity of carbon black (XC-72) supported PtRu catalysts was also investigated. In the CV curves measured in 0.5 M H_2SO_4 solutions (Figure 3.6a, c), the hydrogen adsorption/desorption area could be used to roughly evaluate the electrochemical active surface area (ECSA), even though the incorporation of Ru may make the calculation not accurate. The roughly estimated ECSA values are summarized in Table 3.1.

Figure 3. 6 Mass-normalized cyclic voltammograms of PtRu catalysts supported on 1-AP-MWCNTs, AO-MWCNTs, and carbon black with the 20 wt % PtRu loading in (A) nitrogen-saturated 0.5 M H_2SO_4 and (B) nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH and with the 40 wt % PtRu loading in (C) nitrogen-saturated 0.5 M H_2SO_4 and (D) nitrogen-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH . The scan rate is 50 mV/s.

The ECSA for the PtRu/1-AP-MWCNTs-20 wt % is higher than PtRu/AO-MWCNTs-20 wt % and PtRu/C-20 wt %, most likely due to the smaller size and much better dispersion of the PtRu NPs on 1-AP-MWCNTs. This also demonstrates that the PtRu NPs deposited on 1-AP-MWCNTs are more electrochemically accessible, which is very important for electrocatalyst applications in fuel cells. With further increase of PtRu loading to 40 wt %, the ECSA for

PtRu/AO-MWCNTs is decreased by 51% as compared with the 20 wt % PtRu/AO-MWCNTs. This can be attributed to the more serious agglomeration of PtRu on MWCNTs due to the increase of PtRu loading, which is also confirmed by the increase in the size of PtRu NPs as the loading increased from 20 to 40 wt % (Table 3.1). This observation is consistent with the results reported by Cho et al.[87] that the ECSA decreases with the increase of the metal loading on carbon black. On the other hand, for PtRu/1-AP-MWCNTs with 40 wt % loading, the ECSA is very close to that for 20 wt % PtRu/1-AP-MWCNTs. This is because the uniform distribution of PtRu NPs on 1-AP-MWCNTs is still maintained, even at a high loading.

Table 3. 1 Particle Size, Electrochemical Active Surface Area, Onset Potential, and Forward Peak Current of Different PtRu Electrocatalysts on 1-AP-MWCNTs, AO-MWCNTs, and XC-72 Carbon

Catalyst	Particle size (nm)	ECSA (cm ² /mg Pt)	Onset potential (V)	Forward peak current (mA/mg Pt)
PtRu/1-AP-MWCNTs-20wt%	2	423	0.37	295.04
PtRu/AO-MWCNTs-20wt%	3	370.6	0.38	247.43
PtRu/1-AP-MWCNTs-40wt%	2	416	0.38	283.89
PtRu/AO-MWCNTs-40wt%	4.3	182	0.385	178.47
PtRu/C-20wt%	2	164.9	0.405	98.32

The high electrochemical active surface area for the PtRu/1-AP-MWCNTs is also supported by the high electrocatalytic activity for the electrooxidation reaction of

methanol (Figure 3.6B, D). The CV curves for the methanol oxidation in 0.5 M H₂SO₄ + 1.0 M CH₃OH exhibit the well-known features of methanol oxidation on Pt-based electrocatalysts. For the CV on PtRu/1-AP-MWCNTs, the forward oxidation current peak occurs at 0.65 V and the backward oxidation current peak at 0.46 V, which are close to that reported in the literature.[8, 34, 88] The activity of PtRu electrocatalysts for the methanol oxidation can be represented by the magnitude of the forward anodic current peak. The forward peak current density normalized by Pt loading on GCE for the methanol oxidation reaction on MWCNTs with different PtRu loadings and carbon black are also given in Table 3.1. In the case of 20 wt % PtRu loading, as shown in Figure 3.6B, the significantly higher anodic current for the reaction on PtRu/1-AP-MWCNTs and PtRu/AO-MWCNTs indicates a much higher electrocatalytic activity of MWCNT-supported PtRu electrocatalysts than the carbon-supported PtRu electrocatalysts, consistent with that reported by Prabburam et al.[8] The higher electrocatalytic activity for the methanol oxidation on PtRu/1-AP-MWCNTs-20 wt % than that on PtRu/AO-MWCNTs-20 wt % again shows the importance of the distribution and dispersion of PtRu electrocatalysts on MWCNT supports, in agreement with the high electrochemically active surface area of PtRu/1-AP-MWCNTs.

With the increase of PtRu loading to 40 wt % on MWCNTs, the forward peak current density for the PtRu/AO-MWCNTs is 178.5 mA/mg Pt, a decrease by 28% in comparison with 247.4 mA/mg Pt for the reaction on 20 wt% PtRu/AO-MWCNTs. The significant decrease in anodic current density is most likely due to the increased size of PtRu NPs on AO-MWCNTs with the increase of the PtRu loading. For

PtRu/1-AP-MWCNTs-40 wt %, the decrease in the anodic current density is only 3.8% as compared to that on 20% PtRu/1-AP-MWCNTs, which is significantly smaller than the 28% in the case of AO-MWCNTs supports. This is consistent with the ECSA results. For practical fuel cells applications, in order to reduce the thickness of the catalytic layer and thus facilitate the mass transport within catalytic layer, the high PtRu loading on supports is essential. At the same high PtRu loading (40 wt %), PtRu/1-AP-MWCNTs shows much higher electrochemical surface area than PtRu/AO-MWCNTs. On the other hand, the onset potentials for methanol oxidation on PtRu/1-AP-MWCNTs and PtRu/AO-MWCNTs are similar, but slightly lower than that on PtRu/C (Table 1). The values of the onset potential for PtRu/MWCNTs are close to the reported by Prabhum et al.[8]

Figure 3. 7 Stability of PtRu/1-AP-MWCNTs-40 wt % and PtRu/AO-MWCNTs-40 wt % electrocatalysts in 0.5 M H₂SO₄ + 1.0 M CH₃OH. The potential scan was performed from -0.2

to 1.0 V vs Ag/AgCl and the scan rate was 50 mV/s.

3.3.6. Durability Evaluation of Electrocatalysts

The long-term stability of the PtRu electrocatalysts is very important for the development of commercially viable DMFCs. The forward peak currents on PtRu/1-AP-MWCNTs and PtRu/AO-MWCNTs were measured as a function of the number of cycles performed from -0.2 to 1.0 V in 0.5 M H₂SO₄ + 1.0 M MeOH, and the results are shown in Figure 3.7. For PtRu electrocatalysts on MWCNTs, the forward peak density increases initially. In the case of PtRu/1-AP-MWCNTs, the peak current remains almost constant from the 40th cycle to the 350th cycle after the initial increase. The peak current starts to decrease gradually after the 350 cycles of potential scan. Using the current density measured after the 20th cycle as the reference, the anodic peak current of the 600th cycle is about 82% of that measured at the 20th cycle. The reduction in the electrocatalytic activity for the methanol electrooxidation on PtRu/1-AP-MWCNTs is around 18%. In the case of PtRu/AO-MWCNTs, a poorer stability was observed. The peak current starts to decrease quickly after about 50 cycles. The peak current of the 600th cycle is around 59% of the current density measured at the 20th cycle. In general, the gradual decrease of the catalytic activity after successive cycles of potential scan could result from the consumption of methanol during the electrochemical oxidation reaction. However, the effect of the microstructural change of the PtRu NPs caused by the perturbation of the potentials on the electrocatalytic activity can be substantial. The high anodic peak currents and much slower degradation in the anodic peak currents for the reaction on

PtRu/1-AP-MWCNTs as compared to that on PtRu/AO-MWCNTs demonstrate the significantly enhanced activity and stability of PtRu electrocatalysts on 1-AP-MWCNTs. The increased stability also indicates that the attachment of PtRu on MWCNTs via 1-AP as interlinkers is strong. The results in this study demonstrate the promising potential of noncovalent functionalization of MWCNTs by 1-AP as highly efficient and effective catalyst supports, especially for the development of PtRu electrocatalysts with high loading for the methanol electrooxidation in DMFCs.

3.4. Conclusion

The synthesis of PtRu electrocatalysts on 1-aminopyrene (1-AP)-functionalized MWCNT supports assisted by a microwave polyol process was studied in detail. The work represents a new synthesis method of PtRu/MWCNT electrocatalysts with many benefits. First, the synthesis process is simple and can be carried out at room temperature without the use of expensive chemicals or corrosive acids. Second, different from the acid-oxidized MWCNTs, where the harsh chemical acids are used to produce carboxylic acid sites on the surface, the 1-AP-functionalization treatment preserves the integrity and the electronic structure of MWCNTs. Third, the density of PtRu electrocatalysts could be effectively controlled by adjusting the feed amount of the metal precursors. PtRu electrocatalysts on 1-AP-MWCNTs are characterized by uniform distribution and dispersion with narrow particle size distribution. The average particle size is 2 nm, and no aggregation occurs, even at high PtRu loading. The distribution and dispersion is significantly better than that on the conventional acid oxidized MWCNTs. PtRu NPs on 1-AP-MWCNTs have higher electrochemical

surface area, much better activity, and enhanced stability for the methanol electrochemical oxidation in acid solution than those on AO-MWCNTs and XC-72 carbon black.”

In this chapter, a bifunctional molecule is used to non-covalently functionalize CNTs leading to enhanced electrocatalytic activity of PtRu NPs for methanol oxidation. As another strategy, in the following chapter 4, we adopt a polymer wrapping technique to non-covalently functionalize CNTs and use them to support Pt NPs as model electrocatalysts for methanol oxidation.

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Chapter 4 “Poly (diallyldimethylammonium chloride) Functionalized Carbon Nanotube as a Support for Pt Nano-Electrocatalysts and Their Activity for Methanol Oxidation”

4.1. Introduction

“In this chapter as a continuation of chapter 3 in which a non-covalent functionalization method, bifunctional molecule stacking, was used to modify CNTs as PtRu electrocatalyst supports, we develop another strategy to non-covalently functionalize CNT surface, namely, polyelectrolyte wrapping technique. It is demonstrated that polyelectrolyte wrapping is also a facile and efficient functionalization method for MWCNTs as Pt electrocatalyst supports.

Specifically, we use poly (diallyldimethylammonium chloride) (PDDA) to wrap CNTs in aqueous solution. PDDA, the chemical structure of which is given in Scheme 4.1 is a water-soluble quaternary ammonium with positive charge. During the functionalization process, sodium chloride salt is added to allow the PDDA chain to adopt a random configuration, thus leading to a high coverage of PDDA chains on MWCNTs (denoted as PDDA-MWCNTs). The strong adsorption of the positively charged PDDA on MWCNTs is believed due to the π - π interaction between PDDA and the basal plane of graphite of MWCNTs.[81, 89] This noncovalent functionalization not only leads to high density and homogeneous surface functional groups on MWCNTs, but also preserves the intrinsic properties of MWCNTs without damaging their perfect surface structure. As illustrated in Scheme 4.2, because of the

positive surface charge on MWCNTs, a large amount of negatively charged Pt precursor can be anchored onto MWCNT surface *via* electrostatic interaction. The subsequent reduction by ethylene glycol (EG) gives Pt NPs with uniform distribution and high density.

Scheme 4. 1 The chemical structure of PDDA.

Scheme 4. 2 Illustration of the synthesis of Pt NPs on PDDA wrapped CNTs

4.2. Experimental and Characterization Methods

4.2.1. Materials

Deionized water (DI water), sulfuric acid (99.5%, Fluka), nitric acid (65%, Fluka), methanol (Fluka), MWCNTs (Shenzhen nano, port), hexachloroplatinic (IV) acid (Sigma-Aldrich), ethylene glycol (Fluka), sodium hydroxide (Fluka), sodium chloride (Fluka), hydrogen chloride (Sigma-Aldrich), poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, MW=5000–40 000, Aldrich), Nafion solution (5% in isopropanol and water) and 50 wt% E-TEK Pt/C catalysts (PEMEAS Fuel Cell Technologies, NJ).

4.2.2. Functionalization of MWCNTs

The procedure for the polyelectrolyte functionalization of MWCNTs with PDDA is described as follows. Briefly, 100 mg of MWCNTs were initially suspended in 400 ml of DI water by ultrasonication in the presence of 0.5 wt% PDDA, which acted as the functionalization polyelectrolyte, and yielded a stable dispersion of individual MWCNTs. PDDA has positively charged ammonium groups, which serve as primers for the homogeneous deposition of Pt NPs. During the functionalization process, NaCl was added to give a concentration of 0.5 wt%. The presence of NaCl drastically affects the polymeric chains' configuration in polyelectrolyte solutions and promotes the functionalization. In the presence of NaCl salt, the counter ions partially screen the charges, allowing the PDDA chain to adopt a random configuration, thus leading to a high coverage of PDDA chains on MWCNTs. The solution was then filtrated and

washed several times to remove the excess PDDA in the solution followed by drying in a vacuum oven at 70 °C for 24 h. For a comparison, deposition of Pt NPs on conventional acid-oxidized MWCNTs (denoted as AO-MWCNTs) was also investigated. Acid-oxidized MWCNTs were prepared according to the same procedure as described in Chapter 3.

4.2.3. Deposition of Pt NPs on Functionalized MWCNTs

To deposit Pt NPs on PDDA-MWCNTs with different Pt loadings, 30 mg of PDDA-wrapped MWCNTs was mixed with a stoichiometric amount of H_2PtCl_6 in ethylene glycol solution under ultrasonication. The pH of the solution was then adjusted to 12.5 by adding 2.5 M of NaOH solution in EG dropwise, followed by refluxing the solution at 130 °C for 3 h. After the reduction, the pH was adjusted back to 3~4. During the whole reaction process, PDDA-MWCNTs first form complexes with PtCl_6^{2-} ions, followed by reduction of metal precursors forming metal NPs on MWCNTs. In the case of deposition of Pt NPs on AO-MWCNTs, the procedure is similar. MWCNTs-supported Pt catalysts were collected by filtrating the resultant solution and washing for several times using a Nylon filter membrane followed by drying in a vacuum oven at 70 °C for 24 h.

4.2.4. Characterization

The zeta potentials of the samples were measured using a zeta potential analyzer (Brookhaven Instruments Co., USA). The weight percentage of surface wrapped PDDA on MWCNTs was determined using a thermal gravity analyzer (TGA) at an

increasing temperature rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 100 to $800\text{ }^{\circ}\text{C}$ under a continuous nitrogen gas flow with a flow rate of 100 sccm. The effect of different surface functionalization methods on the surface structure of MWCNTs was examined by Raman spectroscopy (Renishaw), using a He/Ne laser with a wavelength of 633 nm. X-ray diffraction (XRD) measurements were performed on a D8 Bruker AXS X-ray diffractometer with a continuous scanning at a scan rate of $0.025\text{ }^{\circ}/\text{s}$. The transmission electron microscopy (TEM, JEOL 2010) was performed at an acceleration voltage of 160 keV.

4.2.5. Electrochemical Measurement

As a typical process, about 4 mg of catalyst samples was ultrasonically mixed in 4 ml ethanol to form homogeneous ink followed by dropping 30 μl of ink onto the surface of the glass carbon electrode (GCE), and then 1 μl of Nafion solution of 0.5 wt% in 2-propanol was dropped to fix the catalysts on the electrode. Pt wire and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All potentials in the present study are quoted versus SCE. The electrochemically active surface area (ECSA) of Pt/MWCNTs composites was measured in a nitrogen saturated 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1} and the activity for methanol oxidation reaction in a nitrogen saturated 0.5 M H_2SO_4 +1.0 M CH_3OH solution at a scan rate of 20 mV s^{-1} . All the tests were conducted at room temperature.

4.3. Results and Discussion

4.3.1. Zeta Potential Measurement of the As-prepared Carbon Nanomaterials

The zeta potential is the electrical potential that exists at the shear plane of a NP. It is widely used for the quantification of the magnitude of the electrical charge at the double layer. Herein we performed the zeta potential measurement to confirm the successful functionalization or wrapping of MWCNTs by PDDA. During the measurement, the samples were suspended in DI water in very low concentrations to make sure of a constant pH among different samples. Therefore, the change of zeta potential can only be ascribed to the surface properties of different CNTs. From Figure 4.1, we can see that the zeta potential of AO-MWCNTs is more negative than that of the as-received MWCNTs (raw-MWCNTs). This indicates that there are more negative functional groups on the surface of AO-MWCNTs, because of the introduction of carboxyl and hydroxyl groups by the acid treatment. The zeta potential changed to a positive value for PDDA-MWCNTs, confirming that the positively charged PDDA molecules were indeed wrapped on the MWCNT surface. As a result of the cationic and hydrophilic PDDA functionalization, a better dispersion of MWCNT in aqueous solution was obtained due to the MWCNT–MWCNT electrostatic repulsion and the improved CNT hydrophilicity. The cationic charges in the PDDA chains subsequently served as anchor sites to form complexes with PtCl_6^{2-} by electrostatic attraction, which can facilitate a uniform deposition of Pt NPs during

the *in situ* reduction. After deposition of Pt NPs, the zeta potential changed to a negative value. Such results indicate that the Pt NPs are negatively charged. Thus, we can conclude that the positive ammonium cationic groups of PDDA function in two ways: one is to adsorb PtCl_6^{2-} and form complexes to allow for a uniform reduction, and the other is to adsorb the negatively charged Pt NPs which are reduced from either complex PtCl_6^{2-} or free PtCl_6^{2-} .

Figure 4. 1 Zeta potential of Raw-MWCNTs, AO-MWCNTs, PDDA-MWCNTs and Pt-PDDA-MWCNTs

4.3.2. Thermal Gravimetric Analysis (TGA) Measurement of the Functionalized MWCNTs

The weight percentage of wrapped PDDA moieties around MWCNTs was determined by using thermal gravimetric analysis (TGA). Before TGA measurement, all the samples were dried in a vacuum oven at 80 °C overnight. From Figure 4.2, the

weight loss for PDDA-MWCNTs in the temperature range of 200–600 °C is due to the decomposition of surface-wrapped PDDA moieties. For AO-MWCNTs, the much smaller weight loss in this temperature range is due to the decomposition of functional groups, such as carboxylic groups, introduced by the acid oxidation. The weight loss occurring in the higher temperature region of 600–800 °C is induced by the thermal decomposition of MWCNTs themselves. As shown in Figure 4.2, the weight loss is about 4 wt % in the case of PDDA-wrapped MWCNTs. This means the loading of PDDA on this kind of composite is about 4 wt %. The TGA results again indicate successful functionalization of MWCNTs by PDDA, consistent with that indicated by zeta potential analysis.

Figure 4. 2 TGA analysis of surface modified MWCNTs

4.3.3. Raman Characterization of MWCNTs

Raman spectroscopy has been used to study the surface structure of PDDA-MWCNTs, AO-MWCNTs, and raw-MWCNTs, as shown in Figure 4.3. All three kinds of MWCNTs have similar Raman scattering patterns. The peak near 1328 cm^{-1} is assigned to the disordered graphite structure (*D*-band) and the high frequency peak near 1577 cm^{-1} (*G*-band) corresponds to a splitting of the E_{2g} stretching mode of graphite, which reflects the structural intensity of the sp^2 -hybridized carbon atoms. Thus the extent of the modification or defects in MWCNTs can be evaluated by the intensity ratio of the *D*- and *G*-bands. The intensity ratios of I_D/I_G are 1.34, 1.10 and 1.77 for raw-MWCNTs, PDDA-functionalized MWCNTs and acid-oxidized MWCNTs, respectively. As the PDDA polymeric chains are wrapped around MWCNTs, the intensity ratio of the *D*-band to the *G*-band is slightly decreased, suggesting the coverage of the defect sites by the PDDA chains.[90] On the other hand, the intensity ratios of I_D/I_G of AO-MWCNTs are much higher than that of raw-MWCNTs, consistent with that reported in the literature.[54] This result indicates that the acid-oxidation method causes significant structural damage on MWCNTs which would potentially decrease the electrical conductivity of MWCNTs and lower the corrosion resistance. In contrast, the PDDA functionalization method does not cause any structural damage, and furthermore, it provides highly effective functional groups on the surface of MWCNTs.

Figure 4. 3 The Raman spectra of Raw-MWCNTs, PDDA-MWCNTs and AO-MWCNTs

4.3.4. TEM Characterization

Figure 4. 4 TEM images of (A). Pt/AO-MWCNTs-20 wt%, and Pt/PDDA-MWCNTs with the Pt loadings of 20 wt%, (B), 50 wt% (C), and 60 wt% (D).

Figure 4.4 shows the TEM images of Pt NPs deposited on AO-MWCNTs and PDDA-MWCNTs with different Pt loadings. In the case of 20 wt% Pt-AO-MWCNTs, a poor dispersion of Pt NPs on MWCNTs with a large number of aggregates was found (Figure 4.4a). The average particle size of Pt NPs was 5 ± 2 nm. For the MWCNTs functionalized by the acid-oxidation treatment, the defects generated are usually not uniform. When Pt NPs are deposited on the MWCNTs, the particles tend to deposit on these localized defect sites. This may be the reason for the poor

dispersion and extensive aggregation observed. In contrast, Pt NPs were evenly deposited on the PDDA-MWCNTs and the average particle size was 1.8 ± 0.4 nm, much smaller than that on AO-MWCNTs (Figure 4.4b). When the Pt loading is increased to 50 wt% and 60 wt%, a very good dispersion can still be achieved on the PDDA-MWCNTs without agglomeration (Figures 4.4c and d). The results are significant as not only uniformly distributed Pt NPs but also a very high Pt loading can be obtained on PDDA-functionalized MWCNTs. The high loading and uniformity of Pt NPs on MWCNTs is clearly due to the PDDA, which offers large and uniform distributed active sites for anchoring metal ions and metal NPs. In this regard, PDDA-functionalized MWCNTs are more effective supports than the conventional acid-oxidized MWCNTs.

Figure 4. 5 XRD patterns of Pt/AO-MWCNTs-20 wt% and Pt/PDDA-MWCNTs-20 wt%

4.3.5. XRD Characterization

Figure 4.5 shows the XRD patterns of Pt NPs deposited on AO-MWCNTs and PDDA-MWCNTs. The face-centered cubic (fcc) structure of Pt was confirmed by the presence of diffraction peaks at 39.6° , 46.3° and 67.4° , which are assigned to Pt (111), Pt (200), and Pt (220), respectively. Compared with Pt/AO-MWCNTs, the peak intensities of Pt/PDDA-MWCNTs are lower and the full width at half-maximum (FWHM) for all three peaks are bigger, indicating a smaller average size of Pt NPs on PDDA-MWCNTs on the basis of Scherrer's equation, the average sizes of Pt NPs for Pt-PDDA-MWCNTs and Pt-AO-MWCNTs are calculated at 1.9 nm and 6 nm, respectively. These values agree quite well with the TEM results. Herein, the reason for choosing the Pt (220) peak but not others is that the Pt (111) peak is interfered with by the neighboring Pt (200) due to their closeness.

Figure 4. 6 Cyclic voltammetrys of Pt catalysts supported on PDDA-MWCNTs and AO-MWCNTs in (a) nitrogen saturated 0.5 M H_2SO_4 and (b) nitrogen saturated 0.5 M $\text{H}_2\text{SO}_4 + 1.0 \text{ M CH}_3\text{OH}$

4.3.6. Electrochemical Characterization

Finally the electro-catalytic activity of the Pt-PDDA-MWCNTs as potential electrocatalysts for low temperature fuel cells was examined. Figure 4.6a shows the cyclic voltammograms (CVs) of Pt-PDDA-MWCNTs and Pt-AO-MWCNTs measured in nitrogen purged 0.5 M H_2SO_4 solutions. The electrochemically active surface area of Pt NPs on MWCNTs can be obtained from the area of the hydrogen desorption peak after correcting for the double layer charging current from the CVs measured in 0.5 M H_2SO_4 solutions. It can be seen that Pt-PDDA-MWCNTs exhibit a

larger electrochemically active surface area than Pt-AO-MWCNTs, apparently due to the smaller size and better dispersion of the Pt NPs on PDDA-MWCNTs. This is consistent with the TEM and XRD observations. This also demonstrates that the Pt NPs deposited on PDDA-MWCNTs are more electrochemically accessible, which is very important for fuel cell reactions. Taking the methanol electro-oxidation reaction as an example, the catalytic properties of Pt-PDDA-MWCNTs and Pt-AO-MWCNTs were characterized by CVs in a nitrogen purged 0.5 M H₂SO₄+1.0 M CH₃OH solution, as shown in Figure 4.6b. As a kinetically controlled reaction, the activity of methanol oxidation on Pt can be represented by the magnitude of the anodic peak. The higher anodic current indicates a higher electro-catalytic activity on Pt-PDDA-MWCNTs, in agreement with the observation of a larger electrochemically active surface area. The maximum current density of Pt-PDDA-MWCNTs reaches 104.5 mA cm⁻² mg Pt⁻¹, which is comparable to the value of 106.7 mA cm⁻² mg Pt⁻¹ as reported by Hsin.[42]

4.4. Conclusion

In summary, noncovalently functionalized MWCNTs by PDDA were prepared and employed as support materials for the *in situ* deposition of Pt NPs. Pt NPs with an average size of 1.8 nm were successfully deposited and well distributed on the PDDA-functionalized MWCNTs. As compared to the conventional acid-oxidation method, PDDA functionalization causes no structural damage to the CNT surface and provides much higher density and homogeneity of surface functional groups. The

electrochemically active surface area and the electro-catalytic activity for methanol oxidation of Pt/PDDA-MWCNTs are significantly higher than that of Pt/AO-MWCNTs, indicating that such deposited Pt NPs on PDDA-MWCNTs are electrochemically accessible and highly active. It is also believed that increased durability can be expected when the Pt/PDDA-MWCNT electrocatalyst is used in fuel cells, because of the reservation of the structural integrity and subsequent high corrosion resistance of the MWCNT supports. The newly developed polyelectrolyte functionalization method as described here shows a promise for the facile and efficient surface functionalization of CNTs as Pt electrocatalyst supports.”

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Chapter 5 Effect of Interlinkers between Pt Nanoparticles and Carbon Nanotubes on Their Electrocatalytic Activity for Methanol Oxidation

5.1. Introduction

In Chapter 4, we successfully functionalize PDDA on MWCNTs by use of a polymer wrapping technique. It's believed that some expected characteristic functional groups could be efficiently introduced on MWCNTs through this method. In this chapter, we will experimentally introduce various characteristic functional groups on MWCNTs and discuss their influence on the catalytic activity of Pt nanoparticles (NPs) for methanol electrooxidation.

The fundamental concern of electrocatalysis study involves the chemical adsorption energy of electrocatalysts with reactants, intermediates, and products. During an electrocatalytic reaction, both pre-adsorption of reactants and prompt release of intermediates and products on and from the electrocatalyst surface determine the catalytic activity of the electrocatalyst. Specifically, Pt-based electrocatalysts are mainly utilized at both anode and cathode sides of proton exchange membrane fuel cells (PEMFCs).[12, 14, 37, 91] The electrooxidation reaction at the anode side gives rise to the formation of poisonous strongly adsorbed CO species resulting in poor catalytic activity; on the other hand, the adsorbed hydroxyl species (OH) on the electrocatalyst surface blocks the available active reaction sites for the oxygen reduction reaction (ORR) at the cathode. Therefore, the chemical adsorption energy with adsorbents on metal electrocatalysts significantly influences their catalytic

activity.

Recently, Norskov et al.[92, 93] developed a d-band center theory that correlates the d-band center of a metal with its adsorption energy. On the basis of this theory, strong bonding occurs if the d-band center shifts upwards; in contrast, weak bonding occurs if d-band center shifts downwards.[94] Following this theory, lots of researchers have designed some novel electrocatalysts with modified electronic structures and thus enhanced electrocatalytic activity.[1, 37, 95] Typically, alloying Pt with another metal is the most commonly used approach. For examples, PtSn alloy NPs have been demonstrated with significantly improved electrocatalytic activity for methanol oxidation.[1] Due to their different electronegativity values, Sn trends to donate electrons to Pt element leading to downshifted d-band center of Pt, which thus would weaken the chemisorption energy with the poisonous CO intermediates. Similarly, Markovic et al.[95-97] designed PtCo and PtNi alloy electrocatalysts for ORR with the downshifted d-band center of Pt caused by the addition of Co or Ni, and the weakened chemisorption with hydroxyl species provides more available active sites for ORR. To date, although lots of strategies have been developed to improve the electrocatalytic activity of metal electrocatalyst with the modification of their electronic structure (d-band center), to the best of our knowledge, there is no report on tuning the electronic structure of electrocatalysts with specified functional groups on catalyst supports.

In this chapter, we introduced four charged functional groups (two polyanions and two polycations) on MWCNTs as electrocatalyst supports *via* the polymer wrapping

technique developed in Chapter 4. The electronic properties of Pt NPs were modified with the four charged functional groups on MWCNTs. We combined spectroscopic techniques, electrochemical tools, and density functional theory (DFT) calculation to prove the shift of d-band center (change of electronic structure) caused by the above functional groups. The electrochemical results for the methanol oxidation indicated that Pt NPs with downshifted d-band center caused by the electron donation from polyanions on MWCNTs are more active, relative to those supported on polycations functionalized MWCNTs.

“5.2. Experimental and Characterization Methods

5.2.1. Materials

Materials used in the present work include deionized water (DI water), methanol (Fluka), multi-walled carbon nanotubes (MWCNT diameter: 20-30 nm, SYST Integration PTE LTD), hexachloroplatinic(IV) acid (Sigma-aldrich), sodium chloride, ethylene glycol (Fluka), Nafion solution (5% in isopropanol and water), poly(diallyldimethylammonium chloride), Poly(allylamine hydrochloride) (PAH), Poly(styrenesulfonic acid) (PSS), and Poly(acrylic acid sodium) (PAA)).

5.2.2. Noncovalent Functionalization of MWCNTs

The procedure for the noncovalent functionalization of MWCNTs using the four polyelectrolytes is similar with that described in Chapter 4. Briefly, MWCNTs (100 mg) were first ultrasonically suspended in deionized water (400 ml) in the presence of

polyelectrolyte (0.5 wt %) and NaCl (1 wt %) for 1 h to yield a stable nanotube suspension, and then keep the stirring for overnight. The suspension was filtrated using a nylon filter membrane and washed, and the filtration was repeated several times to remove excess polyelectrolyte and NaCl, then dried in vacuum oven (70 °C / 24 h). The as-prepared MWCNTs were denoted as PDDA-CNT, PAH-CNT, PSS-CNT, and PAA-CNT.”

5.2.3. Synthesis of Pt NPs and Deposition on the As-functionalized MWCNTs.

In order to alleviate the particle size effect on their electronic structure and electrocatalytic activity, the Pt NPs were pre-synthesized under the exactly same conditions, followed by the deposition on the four different polyelectrolytes functionalized CNTs. The synthesis and deposition of Pt NPs on MWCNTs were performed as follows: “Briefly, 1.55 ml H_2PtCl_6 (11 mM) was mixed with ethylene glycol (EG) under vigorous stirring followed by the pH adjustment to ~ 12 by adding NaOH (2.5 M) dropwise. The above solution was placed and heated in a house-hold microwave oven for 60 seconds followed by cooling down to room temperature. To deposit the as-synthesized Pt NPs on CNTs, 30 mg of the as-functionalized CNTs were ultrasonically suspended in the above solution followed by the pH adjustment to 3 $\sim$ 4. The suspension was placed at room temperature overnight under vigourous stirring. The product was collected by filtration using a nylon membrane and washed several times with water before vacuum drying at 70 °C for 24 h. The Pt loading on CNTs was designed to be 10 wt%. The as-deposited Pt NPs on CNTs functionalized by the four polyelectrolytes were denoted as Pt/PDDA-CNT, Pt/PAH-CNT, Pt/PSS-CNT, and

Pt/PAA-CNT.”

5.2.4. Characterization.

“The zeta potentials of the samples were measured using a zeta potential analyzer (Brookhaven Instruments Co., USA). The transmission electron microscopy (TEM, JEOL 2010) was performed using the acceleration voltage of 200 kV. The XPS characterization was carried out on using Kratos, AXIS Ultra system with a 150 W, 15 kV Monochromatic Alumina K α source. The powder samples are made into pellets. For spectra analysis, the background correction was made using Shirley’s method. All the binding energies were corrected for the signal for C1s at 284.6 eV as an internal standard. Deconvolutions of the XPS spectra were carried out using the software XPSPeak 4.1. The relative concentrations of the surface species are equal to the corresponding deconvoluted peak areas divided by the total XPS signal area extracted from the experimental XPS core level regions of Pt 4f.

The electrochemical measurements were performed in a conventional three electrode cell, using glassy carbon electrode (GCE, 4 mm in diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and Pt foil as the counter electrode at room temperature. To load electrocatalyst suspension onto GCE, the electrocatalyst powder was ultrasonically mixed in water to form a homogeneous ink with the catalyst concentration of 2 mg/mL, followed by dropping 10 μ L of the electrocatalyst ink onto the surface of GCE. Then, 1 μ L of Nafion solution of 0.5 wt% in isopropanol was added to fix the electrocatalysts on GCE

surface. All potentials reported in the present study were given versus SCE reference electrode. The electrochemical surface area of Pt/CNTs was measured by collecting cyclic voltammograms (CVs) in a nitrogen-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mV/s, and the electrocatalytic activity for methanol oxidation was characterized by collecting CVs in 0.5 M H₂SO₄ + 0.5 M MeOH at a scan rate of 50 mV/s.”

5.2.5 DFT Calculation Method

All the DFT calculations are performed with PWscf program[98], which uses periodic super-cells. The Kohn-Sham one-electron wave function is expanded based on the plane waves.[99] Ultrasoft pseudopotentials are employed for nuclei and core electrons,[100] and the exchange and correlation are involved by using generalized gradient approximation along with the Perdew-Burke-Ernzerhof function.[101] Spin-polarization is also taken into account. The Pt(111) surface was modeled as a (2×2) three-layer slabs with equilibrium lattice constant of 3.993 Å for Pt unit cells, and the topmost layer is relaxed with the adsorbed group, whereas the two substrate layers are fixed in their bulk positions (Scheme 5.1). The accuracy of this structure is tested using a five-layer slab with its uppermost two layers relaxed and shows that the change of adsorption energy is negligible. A vacuum layer of 20 Å in thickness is added above the top layer of slabs in order to avoid interactions between slabs. Sampling of the Brillouin zones was performed through the summation over Monkhorst-pack meshes [102] with dimensions of (5 x 5 x 1) for a 0.25 monolayer surface coverage. Structural optimization was performed until the Cartesian force

components acting on each atom were brought below 10^{-3} Ry/Bohr and the total energy converged to within 10^{-5} Ry.

Scheme 5. 1 Optimized structures for Pt slab with different charged groups

Scheme 5. 2 Optimized structures for Pt slab with different charged groups and O

The d-band center of bottom atoms are also calculated by taking the first moment of

the normalized projected local density of states about the Fermi level.

The adsorption energy of O was computed by

$$E_{ads} = E_{O/slab+group}^{total} - (E_{slab+group} + E_O^{free})$$

where $E_{O/slab+group}^{total}$ and $E_{slab+group}$ refers to the total energy of a system in the presence and absence of O, respectively. E_O^{free} was computed by placing a single O atom in a cubic cell with length of 20 Å. Note that the optimized structures of slab with charged groups were used as initial configurations, and both O and the bottom layer Pt atoms were allowed to relax while other atoms were fixed in this calculation (Scheme 5.2.). In addition, only the fcc-hollow site of the bottom layer atoms was investigated, since this is the most stable site.

5.3. Results and Discussion

In Chapter 4, we have developed a non-covalent method to functionalize CNTs as electrocatalyst supports.[12, 13] With this method, some specified/expected functional groups could be uniformly introduced on CNTs. However, the traditional harsh acid covalent functionalization method always introduces impure functional groups, and it is not suitable for the investigation of the effect of the given functional groups. In this chapter, four different polyelectrolytes (two positively charged: PDDA and PAH; and two negatively charged: PSS and PAA) were employed to functionalize CNTs and to equip characteristic functional groups on CNTs by the polymer wrapping technique. The nature of polyelectrolytes ensures that the as-functionalized CNTs hold differently

charged surfaces, which would significantly affect the electronic properties of Pt NPs subsequently deposited on CNTs.

Scheme 5. 3 The molecule structures of the four polyelectrolytes and the illustration of electron donation models with Pt NPs.

5.3.1. Zeta Potential Characterization

The chemical structures of PDDA, PAH, PSS, and PAA with characteristic functional quaternary ammonium, amine, sulfonic, and carboxyl groups, respectively, are demonstrated in Scheme 5.3. PDDA and PAH are representative polycations, while PSS and PAA are typical polyanions. Zeta potential measurement confirmed the successful functionalization by the four polyelectrolytes, as shown in Figure 5.1. The change of the zeta potential could be ascribed to the surface properties of the as-functionalized CNTs. From Figure 5.1, we can see that the zeta potential of raw

CNTs is slightly negative, indicating the existence of small amount of negatively charged functional groups probably generated by the purification step of the fabrication process of CNTs. After wrapping/functionalizing negatively charged polyanions, PSS and PAA, on CNTs, the zeta potentials became more negative indicating that more negative functional groups (sulfonic and carboxyl groups from PSS and PAA, respectively) were successfully functionalized around CNTs. However, after wrapping positively charged polycations, PDDA and PAH, on CNTs, the zeta potentials changed to positive values proving the existence of positive charged functional groups (quaternary ammonium and amine groups from PDDA and PAH, respectively), which confirmed the successful functionalization of CNTs by PDDA and PAH. No matter what kinds of surface charges exist on CNTs, the zeta potentials changed to negative values once Pt NPs were deposited on the as-functionalized CNTs, indicating the negative nature of Pt NPs obtained in the reduction process by ethylene glycol. For Pt/PDDA-CNT and Pt/PAH-CNT, The as-modified positive functional groups by PDDA and PAH function as anchors to electrostaticly attract negatively charged Pt NPs, therefore, the deposition of Pt NPs on them are quite facile. However, for Pt/PSS-CNT and Pt/PAA-CNT, due to the negative nature of both CNTs and Pt NPs, no electrostatic forces exist between them, but the deposition of Pt NP on them still succeeded, as evidenced by the TEM images shown in Figure 5.2 below. It's experimentally noteworthy that filtrate is colorless after mixing Pt NPs with PDDA-CNT or PAH-CNT for as short as 2 h followed by the filtration. However, to deposit Pt NPs on PSS-CNT or PAA-CNT, it took longer time (overnight) to get colorless filtrate. If the deposition was stopped after mixing Pt NPs with PSS-CNT or

PAA-CNT for only 2 h, the filtrate was still dark brown, the color of Pt NP solution. In despite of the difficulty of the deposition, Pt NPs were still finally successful deposited on PSS- and PAA-CNT, as evidenced by the TEM images in Figure 5.2. It's believed that the functional groups on the surface of PSS-CNT and PAA-CNT function as the active sites attaching Pt NPs. This experimental phenomenon indicates that the deposition of Pt NPs on PDDA- and PAH-CNT is relatively easier than that on PSS- and PAA-CNT.

Figure 5. 1 Zeta potential Measurements.

5.3.2. TEM Characterization

The TEM images in Figure 5.2 show that Pt NPs were uniformly deposited on the polycations and polyanions functionalized CNTs. The designed Pt loading on CNTs was 10 wt%, which is relatively lower than most cases previously reported.[13] The

consideration behind this low loading is to get more obvious contribution from polyelectrolytes to Pt NPs (e.g., electronic structure) and their catalytic activity. In order to alleviate the particle size effect, the synthesis of Pt NPs by the microwave-assisted polyol method was exactly controlled under the same condition to ensure the same particle size for all the four samples. As shown by the particle size distribution histogram in Figure 5.3, Pt NPs on PDDA-CNT, PAH-CNT, PSS-CNT, and PAA-CNT have the same average particle size (i.e., ~ 1.5 nm).

Figure 5. 2 TEM images of Pt/PDDA-CNT (A), Pt/PAH-CNT (B), Pt/PSS-CNT (C), and

Pt/PAA-CNT (D).

Figure 5. 3 The distribution histogram of the particle size of Pt NPs on PDDA-CNT (A), PAH-CNT (B), PSS-CNT (C), and PAA-CNT (D).

Figure 5. 4 XPS spectra of the Pt 4f photoemission from Pt/PDDA-CNT (A), Pt/PAH-CNT (B), Pt/PSS-CNT (C), and Pt/PAA-CNT (D).

5.3.3. XPS Characterization

The different surface charge properties of CNTs functionalized by different polyelectrolytes would definitely contribute different effects to the electronic structure of Pt NPs.[103, 104] The charge states of Pt cores supported on different CNTs which were functionalized by different polyelectrolytes were probed utilizing XPS. XPS is a useful spectroscopic tool to study the electronic properties of metal electrocatalysts and it has been extensively utilized to prove the electrochemical analysis on various electrocatalysts.[105] Figure 5.4 displays the XPS spectra of the Pt 4f region of Pt/CNTs. The Pt 4f spectra show a doublet containing a low energy band (Pt 4f_{7/2}) and a high energy band (Pt 4f_{5/2}). All the binding energies were corrected for the signal for

C1s at 284.6 eV as an internal standard. In order to identify the different chemical states of Pt, the spectra were deconvoluted into three components, as labeled by Pt (0), Pt (II), and Pt (IV), which could be ascribed to Pt-metal, PtO, and PtO₂, respectively.[105] The binding energies at the Pt 4f_{7/2} signal for the different components are given in Table 5.1 along with their relative intensities. We could find that the binding energies of Pt (0) for Pt/PAA-CNT and Pt/PSS-CNT are relatively more negative than that for Pt/PDDA-CNT and Pt/PAH-CNT. Although the difference in binding energies is relatively small, the XPS results are reproducible. The change in the binding energies (BE) of metal core level reflects the shift of its d-band center relative to Fermi level, that is, the negative shift of BE represents the downshift of d-band center.[94] The shift of d-band center reflects the change in the electron density around metal core.[104] Recently, Liu et al.[103] and Tsukuda et al.[104] studied the effect of poly (*N*-vinyl-2-pyrrolidone) (PVP) as the stabilizer of Au and Pt NPs on their electronic structures. Their results both revealed that PVP functions as electron donors to small Pt or Au NPs, reflected by the lower Pt 4f_{7/2} BE, which indicates the higher electron density in the vicinity of the Pt or Au atoms due to the electron donation from PVP molecules to the Pt or Au atoms. It's believed that the C=O group in PVP may be in charge of the electron donation because of its electron-rich property. Similarly, in our case, two polyanions, as demonstrated in Scheme 5.3, PSS and PAA, on CNTs may function as electron-donors to increase the electron density around Pt atoms *via* the negatively charged (electron-rich) characteristic functional groups to small Pt NPs. However, for PDDA and PAH, they have no electron-rich functional groups; by contrast, the positive charge nature

probably leads to the partial back-donation of electrons from Pt NPs to polycations. The increased electron density around Pt sites by PSS- and PAA-CNTs would cause partial filling of Pt 5*d*-bands, resulting in the down-shift of the *d*-band center and weaker chemisorption with oxygen-containing species, such as OH_{ad} and CO_{ad}. [95, 103, 104] However, PDDA- and PAH-CNTs would have a contrary effect on the electronic structure and chemisorption properties of Pt NPs. Therefore, we could predict that negatively charged polyanions-functionalized CNTs as supports modifying the electronic structure (increase the electron density and downshift the *d*-band center) of Pt NPs and thus leading to the weaker chemisorption with poisonous CO intermediates generated in the methanol electrooxidation would facilitate the methanol oxidation in fuel cells.

Table 5. 1 Distribution of Pt species and their relative intensities from the XPS analysis in the four electrocatalysts: Pt/PDDA-CNT, Pt/PAH-CNT, Pt/PSS-CNT, and Pt/PAA-CNT.

Sample	Pt surface	Binding Energy of Pt	Relative
	species	4f _{7/2} /eV	intensities
Pt/PDDA-CNT	Pt(0)	71.79	39.20%
	Pt(II)	72.75	35.80%

	Pt(IV)	73.73	25.00%
	Pt(0)	71.82	41.30%
Pt/PAH-CNT	Pt(II)	72.75	33.69%
	Pt(IV)	73.69	25.01%
	Pt(0)	71.73	41.50%
Pt/PSS-CNT	Pt(II)	72.55	31.70%
	Pt(IV)	73.55	26.80%
	Pt(0)	71.72	41.60%
Pt/PAA-CNT	Pt(II)	72.58	35.10%
	Pt(IV)	73.70	23.30%

5.3.4. DFT Calculation Result

Furthermore, the d-band center and adsorption energy with oxygen of Pt slabs with and without the four interacted polyelectrolytes were obtained from the DFT calculation. To simplify the calculation process, we did not involve the CNT support. Figure 5.5 shows the correlation between the d-band center and the oxygen adsorption energy of Pt slabs. As we can see, Pt + PDDA and Pt + PAH have high-lying d-band centers relative to the pure Pt slab caused by the electron withdrawing from Pt NPs to PDDA and PAH; while Pt + PAA and Pt + PSS have low-lying d-band centers relative to the pure Pt slab due to the electron donation from PAA and PSS to Pt NPs. Consequently, based on the d-band theory, Pt + PDDA and Pt + PAH would have stronger oxygen adsorption energy than Pt + PAA and Pt + PSS.[94] The oxygen adsorption energy could serve as a good descriptor for the catalytic activity of the

corresponding electrocatalyst surface. The calculation result is consistent with the above XPS characterizations. It should be pointed out that the adsorption energy of Pt+PDDA deviates slightly from the would-be linear trend and the reason for this deviation is unclear yet.

Figure 5. 5 Correlation between the adsorption energy of O and d-band center of Pt slabs.

5.3.5. Electrochemical Characterization

Figure 5. 6 (A) ECSA-normalized CVs of the four electrocatalysts obtained in 0.5 M H₂SO₄; (B) Mass-normalized CVs of the four electrocatalysts obtained in 0.5 M H₂SO₄ + 0.5 M MeOH solution.

The electrochemical technique is another effective tool to study the surface properties of metal NPs.[91] The different effect of polyanions and polycations on the electronic structure and chemisorption properties of Pt NPs would definitely lead to different electrochemical behaviors. We investigated their cyclic voltammogram (CV)

features on the four Pt/CNT catalysts in the supporting 0.5 M H₂SO₄ electrolyte. Figure 5.6A shows CV results for the Pt/PDDA-CNT, Pt/PAH-CNT, Pt/PSS-CNT, and Pt/PAA-CNT measured in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mVs⁻¹, in which the current of the CVs was normalized in terms of the electrochemically active surface area (ECSA), obtained from the area of the hydrogen desorption peak after correcting for the double layer charging current.[91]. The values of the reduction peak potential of Pt-OH_{ad} are summarized in Table 5.2. We found that Pt/PAA-CNT and Pt/PSS-CNT showed the more positive reduction peak potential of Pt-OH_{ad} than Pt/PDDA-CNT and Pt/PAH-CNT, indicating reduced oxophilicity of Pt NPs supported on polyanions functionalized CNTs relative to those on polycations functionalized CNTs. This result shows that Pt/PSS-CNT and Pt/PAA-CNT would have weaker chemical adsorption energy with oxygen-containing species (e.g. OH_{ad}, CO_{ad}) than Pt/PDDA-CNT and Pt/PAH-CNT in line with the XPS observation and DFT calculation.

Table 5. 2 Pt-OH_{ad} Reduction Peak Potential, Mass Activity Transfer Coefficient for MOR

Sample	Pt-OH _{ad} reduction-peak potential / V	Current density for MOR / mA mg _{Pt} ⁻¹	Transfer coefficient:α
Pt/PDDA-CNT	0.333	192.24	0.812
Pt/PAH-CNT	0.405	303.48	0.794
Pt/PSS-CNT	0.418	401.77	0.783
Pt/PAA-CNT	0.455	798.57	0.593

Figure 5. 7 The relationships between peak potential (denoted as E_p) and $\log(v)$ in 0.5 M H_2SO_4 + 0.5 M MeOH solution on the four catalysts: Pt/PDDA-CNT (A), Pt/PAH-CNT (B), Pt/PSS-CNT (C), and Pt/PAA-CNT (D).

Finally, we investigated the catalytic activities of the four catalysts for methanol electrooxidation. CV results were collected in 0.5 M H_2SO_4 + 0.5 M MeOH at a scan rate of 50 mV/s, as shown in Figure 5.6B. The peak current densities of the forward scan on the four catalysts were summarized in Table 5.2. As shown in Figure 5.6B and Table 5.2, the peak current of methanol electrooxidation on Pt/PDDA-CNT and Pt/PAH-CNT is $192.24 \text{ mA mg}_{\text{Pt}}^{-1}$ and $303.48 \text{ mA mg}_{\text{Pt}}^{-1}$, respectively. However, that on Pt/PSS-CNT and Pt/PAA-CNT, is $401.77 \text{ mA mg}_{\text{Pt}}^{-1}$ and $798.57 \text{ mA mg}_{\text{Pt}}^{-1}$,

respectively, which are much higher than that of Pt/PDDA-CNT and Pt/PAH-CNT.

Meanwhile, to investigate the methanol oxidation kinetics on Pt/CNTs, the relationship of forward peak potential (E_p) for methanol electrooxidation with the CV scan rates (ν) was plotted in Figure 5.7. Figure 5.7 shows the linear relationships between E_p and $\log(\nu)$ on the four catalysts. As the scan rate increases, E_p on all the four catalysts is shifted positively. The linear slope for the four catalysts have the following sequence, Pt/PDDA-CNT > Pt/PAH-CNT > Pt/PSS-CNT > Pt/PAA-CNT. In general, E_p and $\log(\nu)$ have the following relationship: [106]

$$E_p = A + \frac{2.3RT}{(1-\alpha)nF} \log \nu \quad (5.1)$$

Where A is a constant and α is transfer coefficient which reflects the activation energy of the electrochemical reaction. The α value can be obtained from the slope of the relationship curve of $E_p \sim \log(\nu)$. The as-calculated α values ($n = 6$, [107]) were summarized in Table 5.2, with the following order, Pt/PDDA-CNT > Pt/PAH-CNT > Pt/PSS-CNT > Pt/PAA-CNT. This sequence indicates that the activation energy of methanol electrooxidation on Pt/PAA-CNT and Pt/PSS-CNT is smaller than that on Pt/PDDA-CNT and Pt/PAH-CNT, which further confirms the beneficial effect of polyanions functionalized CNTs as Pt supports. Therefore, Pt NPs supported on polyanions functionalized CNTs could be expected to be effective electrocatalysts.

The enhanced electrocatalytic activity of Pt NPs on polyanions functionalized CNTs could be attributed to the weakened chemisorption of CO intermediate generated in

methanol electrooxidation. Savinova et al.[108] found that the surface mobility of CO significantly influences the electrochemical removal from Pt surface. In the present study, polyanions around CNTs alter the electronic structure of subsequently deposited Pt NP; and the *d*-band center was downshifted resulting in the weakened chemisorption with CO, which significantly releases the surface mobility of CO on Pt NPs.[94, 108] Therefore, it's relatively easier to remove poisonous CO intermediate on Pt NPs supported on polyanions functionalized CNTs. Our results provide a new direction for the design of novel electrocatalysts.

5.3.6. Durability Evaluation

Figure 5. 8 The long-term stability of Pt/PDDA-CNT (A), Pt/PAH-CNT (B), Pt/PSS-CNT (C), and Pt/PAA-CNT (D) in 0.5 M H₂SO₄ + 0.5 M MeOH solution. The potential scan was performed from -0.2 V to 1.0 V vs. SCE and the scan rate was 50 mV/s.

Finally, the long-term stability testing of the four electrocatalysts for MOR was carried out. The long-term stability (durability) is very important for the development of commercially viable catalysts.[23, 56, 57, 94, 105] The forward peak currents on the four catalysts were measured as a function of the number of cycles performed from -0.2 to 1.0 V in 0.5 M H₂SO₄ + 0.5 M MeOH. The current of the 50th cycle of CVs was considered as the initial current which was recorded after the stabilization of catalysts in electrolytes, with which the other subsequently recorded values were normalized, as shown in Figure 5.8. It was found that the decays of peak currents on Pt/PSS-CNT and Pt/PAA-CNT are much faster than those on Pt/PDDA-CNT and Pt/PAH-CNT, which are quite stable during the whole durability testing process. It appears that polycations functionalized CNTs as Pt supports would show enhanced long-term stability compared to polyanions functionalized CNTs. The reasons for this conclusion could be discussed as follows. The positively charged polycations-functionalized CNTs have stronger interaction with Pt NPs *via* electrostatic attraction forces, while for negatively charged polyanions-functionalized CNTs, they only function as active sites for the deposition of Pt NPs *via* physical adsorption instead of stronger electrostatic attraction forces. In contrast, the negative charge nature of polyanions would repulse negative Pt NPs to some content. On the other hand, our XPS results also show that higher BE of Pt 4f were obtained for Pt/PDDA-CNT and Pt/PAH-CNT than Pt/PSS-CNT and Pt/PAA-CNT, confirming the stronger interaction between Pt NPs with CNT supports on the former.

5.4. Conclusion

In conclusion, we for the first time investigate the modification of the electronic structure of Pt NPs *via* electron donation effect induced by the specified functional groups on CNTs. These specified functional groups could be introduced on CNT surface by the simple polymer wrapping technique as described in Chapter 4. Our spectroscopic and electrochemical characterization, and DFT calculation revealed that polyanions having electron-rich functional groups would donate electrons to Pt atoms causing an increase in the electron density around Pt atoms and downshift of d-band center of Pt resulting in a weaker chemisorption of oxygen-containing species (e.g., CO) and, on the other hand, polycations having electron-poor functional groups would have opposite effect. The electrocatalytic activity of methanol oxidation could be tuned by modifying the electronic structures of Pt NPs *via* the designed surface functionalization of CNTs. The present work provides a novel design principle of advanced electrocatalysts.

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Chapter 6 “Correlation between Electrocatalytic Activity and Interconnectivity of Pt Nanoparticles on Multi-walled Carbon Nanotubes”

6.1. Introduction

“In this chapter as a continuation of Chapter 4, we will investigate the Pt loading effect on the electrocatalytic activity of Pt nanoparticles (NPs). Pt/MWCNTs with a variety of Pt loadings (10 wt% ~ 93 wt%) are synthesized *via* the polyol reduction method described in Chapter 4 and the novel seed-mediated growth method for low and high Pt loadings, respectively. Based on the experimental results, we propose the correlation between the electrocatalytic activity and interconnectivity of Pt NPs on MWCNTs.

Due to their high power density, rapid start-up, and low operating temperatures, proton exchange membrane and direct methanol fuel cells (PEMFCs and DMFCs) are promising power sources for vehicles and portable electronic devices.^[2, 4, 109-111] Platinum-based NPs supported on high surface area carbon (e.g., Pt/C) have been extensively investigated and been commonly employed as the electrocatalysts in low temperature fuel cells.^[31, 43, 112-114] However, some serious challenges in electrocatalysis still need to be met before the development and commercialization of PEMFCs and DMFCs technologies. These challenges include the poisoning of Pt-based electrocatalysts at the anode side by carbon monoxide from impurities in reformat or generated as intermediate species during the methanol electrooxidation and at the cathode side by the low electrocatalytic activity of Pt for the oxygen

reduction reaction (ORR).[\[111, 115, 116\]](#) The electrocatalytic activity of Pt-based catalysts can be substantially enhanced by incorporation of other metal or oxide to form binary alloy catalysts such as PtRu, PtSn, PtFe, and PtCo,[\[41, 116-119\]](#) or by forming multidimensional nanostructured catalysts, such as tubes, Y-junctions, wire network, and wire arrays.[\[30, 32, 120, 121\]](#) For example, Kim et al.[\[15\]](#) synthesized Pt nanowires via a polymer template method. A much higher mass activity for methanol oxidation was observed, which was attributed to the high aspect ratio of the Pt nanowires, the reduced interface impedance for electron transfer, and enhanced durability. Chen et al.[\[122\]](#) synthesized a nanoporous PtRu nanowire network with improved CO-tolerance and electrocatalytic activity for the methanol oxidation. Pillai et al.[\[19\]](#) prepared the Pt Y-junction nanostructured electrocatalysts with enhanced specific activity for formic acid and ethanol oxidation. This appears to indicate that the increase in the dimensions of the Pt nanomaterials would increase their electrocatalytic activities.

On the other hand, in the case of Pt-based NPs supported on CNTs, numerous studies report that the Pt/CNT catalysts show a much higher electrocatalytic activity for the methanol oxidation and oxygen reduction reaction of low temperature fuel cells as compared to that on the conventional Pt NPs supported on high surface area carbon.[\[8, 79, 123-125\]](#) Xing et al.[\[79\]](#) synthesized Pt/CNT catalysts by a sonochemical process in nitric and sulfuric acids to create surface functional groups for Pt NP deposition. Cyclic voltammetry measurements in 1.0 M H₂SO₄ showed that the Pt/CNTs are 100% more active for the electrochemical adsorption and desorption of hydrogen than the Pt/C. This enhancement of electrochemical activity was

attributed to the unique structure of CNTs and the interactions between the Pt NPs and the CNT supports. Mu et al.[125] considered that high dispersion of Pt NPs on CNTs is the main factor for the observed higher activity and better tolerance to impurities for the methanol oxidation as compared to the commercial E-TEK Pt/C catalysts. Chen and Kawazoe et al.[126] used density functional theory with the generalized gradient approximation to study the interaction between a single Pt atom and a carbon nanotube. The Pt adsorption on CNTs depends on the sites and the curvature of the tube. For example, for a zigzag nanotube, the most stable site on the outer wall is the bridge site with the underlying C–C bond being parallel to the axis of the nanotube, and bonding strength decreases significantly for the larger nanotube. The studied charge density suggested the weak covalent like bonding between Pt and C atoms of the outer wall of CNTs. This indicates that interaction between Pt NPs and CNTs alone cannot explain the observed high electrocatalytic activity of Pt/CNT catalysts. The fundamental reasons for the enhanced activities of the Pt-based catalysts supported on CNTs remain unclear.

In Chapter 4, we developed a facile and efficient route to deposit Pt NPs on the multiwalled carbon nanotubes (MWCNTs) functionalized by a noncovalent method using poly(diallyldimethylammonium chloride) (PDDA).[13] The noncovalent functionalization by PDDA not only leads to a high density and homogeneous distribution of surface functional groups but also preserves the intrinsic properties of the CNTs without any chemical oxidation treatment. In this chapter, we utilize PDDA–MWCNTs as the template to assemble Pt NPs on MWCNTs with a wide range of Pt NP loadings *via* the polyol reduction method and seed-mediated growth

method. The assembly principle is shown in Scheme 6.1. The Pt NPs with Pt loadings of 10–50 wt % are synthesized on PDDA–MWCNTs by the polyol reduction method. Subsequently, the as-deposited Pt NPs on MWCNT with 50 wt % Pt loading serve as nucleation seeds for the further deposition of Pt NPs using ascorbic acid (AA) as the reducing agent. The results show that Pt/MWCNT catalysts have significantly enhanced electrocatalytic activities for the electrooxidation of CO and methanol and the ORR for low temperature fuel cells. It is further demonstrated that the catalytic activity of Pt/MWCNT catalysts is fundamentally related to the interconnectivity of Pt NPs on MWCNTs

Scheme 6. 1 Illustration of the synthesis of Pt/MWCNT composites.

6.2. Experimental and Characterization Methods

6.2.1 Materials

The reagents and materials used were deionized (DI) water (resistivity > 18.0 M Ω cm), methanol (Fluka), MWCNT (diameter: 20–30 nm, SYST Integration PTE LTD), hexachloroplatinic(IV) acid (Sigma-aldrich), sodium chloride, ethylene glycol (Fluka), Nafion solution (5 wt% in isopropanol and water), 50 wt % Pt/C (E-TEK), PDDA (20 wt % in water, MW = 5000–40 000, Aldrich). These were used without further purification.

6.2.2 Assembly of Pt NPs on PDDA-Functionalized MWCNTs

The noncovalent functionalization of MWCNTs using PDDA is realized according to the same procedure as described in Chapter 4. The synthesis and deposition of Pt NPs on PDDA-functionalized MWCNTs with Pt loading range of 10–50 wt % was performed as described in Chapter 4. Briefly, the PDDA-functionalized MWCNTs (30 mg) were mixed ultrasonically with H₂PtCl₆ in ethylene glycol (EG), and then the pH was adjusted to 12.5 by adding NaOH (2.5 M). By varying the amount of H₂PtCl₆, the Pt loadings were controlled from 10 to 50 wt %. Reduction of platinum was driven to completion by treatment in a microwave oven for 120 s (or by refluxing the solution at 130 °C for 3 h).

To further increase the Pt NP loading, Pt/MWCNTs with 50 wt % Pt loading were used as the seeds. The experimental procedure was as follows: (i) Pt/MWCNT with 50 wt %Pt (10 mg) was dispersed in DI water (50 mL) in an ultrasonic bath at 60 °C for 30 min; (ii) ascorbic acid (AA) was introduced as the reducing agent; (iii) H₂PtCl₆ (11

mM) precursor was added slowly and the AA:H₂PtCl₆ molar ratio was at least 5:1, to ensure that there is excess AA for the complete reduction of Pt precursors; and (iv) the solution was heated continuously for 30 min to complete the reduction of Pt precursor before cooling to ambient temperature. The product was collected by nylon membrane filtration, washed, and dried in vacuum at 70 °C for 24 h. The addition of 3, 8, 12, and 31 mL of H₂PtCl₆ yielded Pt/MWCNTs with Pt loadings of 69, 81.6, 86, and 93 wt % on the MWCNTs, respectively. It should be pointed out here that wt % Pt represents Pt loading on the CNT support, rather than the Pt loading on the carbon electrode.

6.2.3 Characterization

Transmission electron microscopy (TEM, JEOL 2010) was performed at 200 kV in an instrument filled with an ultrahigh resolution objective lens pole piece. X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer with a continuous scanning at a scan rate of 0.025°/s. X-ray photoelectron spectroscopy (XPS) analyzed the surface chemical composition and valence of Pt in the Pt/MWCNTs.

Electrochemical measurements were performed in a conventional three-electrode cell, using a glassy carbon electrode (GCE, 4 mm in diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and Pt foil as the counter electrode at room temperature. All potentials were reported against the SCE reference electrode. To load the Pt/MWCNT electrocatalyst onto the GCE, the electrocatalyst powder was mixed in water to form a homogeneous ink (2 mg/mL), and 20 µL of the ink was deposited on the GCE. Subsequently, 1 µL of the Nafion

solution (0.5 wt% in isopropanol) was added to fix the electrocatalysts on the GCE surface. Due to the differences in the Pt loading on MWCNTs, the actual Pt weight on the GCE is also different. Table 6.1 summarizes the Pt weight on the GCE surface for all the Pt samples studied. The electrochemical active surface areas (ECSAs) of the Pt in Pt/MWCNTs and E-TEK Pt/C were measured by cyclic voltammetry (CV) in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 10 mV s⁻¹. ECSA was obtained by integrating the baseline-corrected hydrogen desorption peak area between -0.2 and +0.1 V, using 210 μC cm⁻² for the oxidation of a monolayer of hydrogen on bright Pt. Thus, the utilization efficiency of Pt catalyst can be estimated by dividing the ECSA with the calculated specific surface area of Pt NPs. Assuming a monodispersed distribution of the Pt spherical particles, the specific surface area of Pt NPs could be obtained from the following equation

$$S = \frac{6 \times 10^3}{d \times \rho} \quad (6.1)$$

where d is the diameter in nm and ρ is the density of Pt (21.45 g cm⁻³). The utilization efficiency of Pt/MWCNTs and E-TEK Pt/C catalysts is given in Table 6.1.

CO stripping was carried out in a N₂-saturated 0.5 M H₂SO₄ solution. The electrolyte solution was first purged with high-purity nitrogen gas. The adsorption of CO on the electrode catalyst was conducted by bubbling CO gas (UHP grade) through the electrolyte solution for 15 min, while the electrode potential was maintained at -0.15 V versus SCE. Then the electrolyte was purged with nitrogen for 20 min to remove residual CO from the electrolyte. The CO stripping CV curves and blank CV

curves were obtained from two consecutive scan cycles. The electrocatalytic activity for the methanol oxidation was characterized by CV in a 0.5 M H₂SO₄ + 0.5 M MeOH solution at a scan rate of 10 mV s⁻¹. The activity for the oxygen reduction reaction was measured by a linear sweep voltammetry in an O₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 5 mV s⁻¹.

Table 6. 1 The final Pt loadings on glassy carbon electrode (GCE) and Pt utilization efficiency for all samples.

Samples	Pt loading on	Pt Utilization
	GCE/ $\mu\text{g cm}^{-2}$	Efficiency/ % ^a
Pt/MWCNT-10wt%	31.8	13.6
Pt/MWCNT-20wt%	63.6	18.9
Pt/MWCNT-30wt%	95.4	27
Pt/MWCNT-40wt%	127.2	25
Pt/MWCNT-50wt%	159	29.4
Pt/MWCNT-69wt%	219.4	39.4
Pt/MWCNT-81.6wt%	259.5	/
Pt/MWCNT-86wt%	273.48	/
Pt/MWCNT-93wt%	295.74	/
E-TEK Pt/C-50wt%	159	30.8

For the purpose of comparison, the electrocatalytic activities of E-TEK Pt/C (Pt loading: 50 wt %) catalysts were also measured under identical experimental conditions as those for the Pt/MWCNT catalysts. Figure 6.1 shows the TEM

micrographs of the E-TEK Pt/C catalysts. The average particle size of Pt NPs in E-TEK Pt/C is ~3 nm.

Figure 6. 1 TEM image of E-TEK Pt/C electrocatalyst.

6.3 Results and Discussion

6.3.1 TEM, XRD, and XPS Characterizations

Figure 6.2 shows the TEM micrographs of the assembled Pt NPs on PDDA-functionalized MWCNTs (Pt/MWCNTs) with Pt loadings varying from 10 to 93 wt % synthesized by the polyol reduction and seed-mediated growth methods. The distribution histograms of the particle size of Pt NPs in Pt/MWCNTs with Pt loadings of 10–69 wt % are shown in Figure 6.3. For the Pt/MWCNT electrocatalysts with a low loading of 10–20 wt %, the Pt NPs are uniformly distributed on CNTs with no

agglomeration and are generally isolated with little interconnection (Figure 6.2a,b). The average particle size is ~1.5 nm. As the Pt loading increases to 30–40 wt %, the density of Pt NPs on the MWCNT support increases, and isolated particles start to coalesce together and interconnect, forming island-like cluster structures (Figure 6.2c, d). The average particle size is ~1.8 nm. Further increases in the Pt loading to 50–69 wt % led to the formation of continuous Pt NP sheaths, in which the Pt NPs are almost completely interconnected, forming a 2D nanostructure (Figure 6.2 e, f). On the other hand, the increase in the size of Pt NPs is relatively small. In the case of Pt/MWCNTs with 50 and 69 wt %, the Pt NP size is ~2.2 and 2.6 nm (Figure 6.3e, f), respectively. The formation of well-dispersed Pt NPs on CNTs without agglomeration and with accurate control of Pt loading demonstrates the advantages of the deposition of Pt NPs on PDDA-functionalized CNTs by the microwave-assisted polyol reduction and seed-mediated growth methods. Once the continuous and interconnected Pt NP sheath is formed on MWCNTs, a further increase in the Pt loading would simply result in the increase in the thickness of Pt NPs, as shown in the case of Pt/PDDA–MWCNTs with Pt loading of 81.6 wt %. Nevertheless, the MWCNTs supports are still clearly visible (Figure 6.2g). With the Pt loading increased to 86 and 93 wt %, the thick Pt NPs completely obscured the MWCNT template (Figure 6.2h, i). In this case, a continuous Pt nanosheath structure was formed.

Figure 6.4 shows the HRTEM micrographs of Pt NPs on MWCNTs with Pt loadings of 50 and 86 wt %. In the case of Pt/MWCNTs with Pt loading of 50 wt %, Pt NPs are uniformly distributed and form monolayer coverage on the outer walls of CNTs (Figure 6.4e). The crystalline plane (111) of Pt nanocrystals was clearly

identifiable; however, the lattice fringes corresponding to the interconnected crystalline domains exhibit random orientation, indicating the formation of grain boundaries (Figure 6.4a). Such random orientations at the grain boundaries could serve as active sites for the electrode reactions in fuel cells. As the Pt loading increased to 86 wt %, a continuous Pt nanosheath structure was formed. As shown in Figure 6.4b, the Pt nanosheath consists of NPs that are compact, highly interconnected with each other, and still polycrystalline in nature. Similar to the Pt NPs in the case of Pt/MWCNTs with a low Pt loading of 50 wt %, the grain boundaries exist between the interconnected Pt NPs with random orientation. Pt NPs appear to be nonspherical, consistent with heterogeneous nucleation of subsequently added metal precursor on the Pt seeds, with subsequent growth forming the sheath structure.[127]

Figure 6. 2 TEM micrographs of Pt/MWCNT catalysts with Pt loadings of (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %, (f) 69 wt %, (g) 81.6 wt %, (h) 86 wt %, and (i) 93 wt %.

Figure 6.3 Particle size distribution histograms of Pt/MWCNTs with Pt loadings of (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %, and (f) 69 wt %.

The crystalline nature of the Pt/MWCNTs with high Pt loading of 86 wt% is confirmed by XRD analysis, as shown in Figure 6.5. For pure MWCNTs, a strong diffraction peak at 2θ value of $\sim 26^\circ$ can be attributed to the graphite-like structure

(curve a in Figure 6.5). Upon the formation of Pt/MWCNTs, the peak at 26° splits into two reflections and moves to smaller diffraction angles, showing that the graphitic layers of the MWCNT template are pushed closer. For the high Pt NP loading, X-ray diffraction from the nanotube templates is blocked. On the basis of Scherrer's equation [12] and line broadening of the Pt (220) peak, the average crystalline size of Pt NPs in the Pt/MWCNTs with Pt loading of 86 wt % was calculated as ~ 3 nm. This is slightly larger than 2.2 nm of the Pt NPs in Pt/MWCNTs with Pt loading of 50 wt % used for the seeds. Nevertheless, this indicates that the seed-mediation growth method does not lead to the significant grain growth during the formation of Pt/MWCNTs with high Pt NP loading.

Figure 6. 4 HRTEM micrographs of (a) Pt/MWCNTs with Pt loading of 50 wt % and (b) Pt/MWCNTs with Pt loading of 86 wt %.

Figure 6. 5 XRD patterns of (a) MWCNTs and (b) Pt/MWCNTs (Pt loading 86 wt %).

Figure 6.6 displays the XPS spectra of the Pt 4f region of E-TEK Pt/C with 50 wt % Pt loading and Pt/MWCNTs with 86 wt % Pt loading. The Pt 4f spectra show a doublet containing a low energy band (Pt 4f_{7/2}) and a high energy band (Pt 4f_{5/2}) at 71.52 and 74.92 eV for the Pt/MWCNTs and 71.9 and 75.1 eV for the Pt/C, respectively. It was also found that the negative shift of Pt binding energies for Pt/MWCNTs relative to that of E-TEK Pt/C occurs. To identify different chemical states of Pt, the spectrum can be fitted by three overlapping curves, labeled Pt (0), Pt (II), and Pt (IV). This indicates that Pt is present in three different oxidation states. The relative amount of Pt species was calculated from the relative intensities of these three peaks, and the results are summarized in Table 6.2. E-TEK Pt/C possesses 58.6% Pt (II) and Pt (IV) oxides, higher than 39.8% platinum oxides for the

Pt/MWCNTs. This result shows that E-TEK Pt/C has a higher oxophilicity than Pt/MWCNTs with a Pt loading of 86 wt %.

Figure 6. 6 XPS spectra of the Pt 4f photoemission from (a) E-TEK Pt/C (Pt loading 50 wt %) and (b) Pt/MWCNTs (Pt loading 86 wt %).

Table 6. 2 Distribution of Pt Species and Relative Intensities in E-TEK Pt/C (Pt loading 50

wt %) and Pt/MWCNTs (Pt loading 86 wt %)

Sample	Pt surface species	Binding Energy/eV	Relative intensities
E-TEK Pt/C	Pt(0)	71.68	41.4%
	Pt(II)	72.65	33.5%
	Pt(IV)	73.62	25.1%
Pt/MWCNTs	Pt(0)	71.48	60.2%
	Pt(II)	72.19	23.3%
	Pt(IV)	72.91	16.5%

6.3.2 Reduction Potential of Pt–OH_{ad} and CO Stripping Voltammetry

Figure 6.7a shows the CV curves for the Pt/MWCNTs (Pt loading 50 wt %) and E-TEK Pt/C (Pt loading 50 wt %) measured in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 10 mV s⁻¹. The current of the CVs was normalized in terms of the ECSA. The CV curves show three characteristic potential regions: the hydrogen adsorption and desorption region (–0.2 to 0.1 V), double layer plateau region (0.1–0.5 V), and the formation and reduction of surface Pt oxide (0.5–1.0 V). Of particular interest are the onset potential of OH_{ad} formation and the peak potential for the reduction of Pt–OH_{ad}. Both are shifted positively for the Pt/MWCNTs, relative to Pt/C, indicating that the Pt/MWCNTs with Pt loading of 50 wt % show reduced oxophilicity, a weakened chemical adsorption energy with oxygen-containing species.

Figure 6. 7 (a) Cyclic voltammograms of Pt/MWCNTs (Pt loading 50 wt %, solid line) and E-TEK Pt/C (Pt loading 50 wt %, dotted line) in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 10 mV s⁻¹. The current was ECSA-normalized. (b) Dependence of the peak potential of Pt-OH_{ad} reduction of Pt/MWCNTs on the Pt loading on MWCNTs. The dotted line in panel b is the peak potential of Pt-OH_{ad} reduction of E-TEK Pt/C catalysts.

The dependence of the peak potential of Pt oxide reduction on the Pt loading on MWCNTs was investigated, and the results are shown in Figure 6.7b. It can be seen that the peak potential of the Pt–OH_{ad} reduction shifts significantly toward more positive values as the Pt loading increases, forming an S-shaped profile. With the increase of Pt loading above 69 wt %, the positive shift of Pt oxide reduction potential becomes much slower and reaches a plateau, indicating that further increase in the Pt loading has little effect on the reduction potential of Pt–OH_{ad} species of the Pt/MWCNTs electrocatalysts. It is evident that the loading or density of Pt NPs on MWCNT significantly affects their chemical adsorption energy with oxygen-containing species, such as CO_{ad} and OH_{ad}.

Figure 6. 8 CO stripping curves on Pt/MWCNTs (Pt loading: 50 wt %; solid line) and E-TEK Pt/C (Pt loading: 50 wt %; dotted line) catalysts in a 0.5 M H₂SO₄ solution.

The CO-tolerance of Pt/MWCNTs (50 wt % Pt loading) and E-TEK Pt/C (50 wt % Pt loading) was investigated by the CO-stripping voltammograms, and the results are shown in Figure 6.8. The characteristic CO stripping curves were observed for both Pt/MWCNTs and E-TEK Pt/C. Hydrogen adsorption/desorption is completely suppressed until the removal of adsorbed CO. The peak potential for the oxidation of adsorbed CO on the Pt/MWCNTs is 0.534 V, lower than 0.540 V for the CO oxidation on E-TEK Pt/C. The onset potential for the CO oxidation reaction on Pt/MWCNTs also shifted negatively, compared with that on the E-TEK Pt/C. This indicates that the adsorbed CO is more readily oxidized on the Pt/MWCNTs catalysts.

Figure 6. 9 Dependence of the peak potential (E_p) of CO electrooxidation on the Pt NP loadings on MWCNTs. Insets are the TEM images of Pt/MWCNTs with various Pt loadings.

Figure 6.9 is the plot of the peak potentials of CO stripping curves on Pt/MWCNTs as a function of Pt loadings on MWCNT. For the purpose of illustration, representative TEM images for the Pt/MWCNTs with different Pt loadings are also included in the figure. The dependence of the peak potential on the Pt loading does not form a linear relationship; rather, it follows an S-shaped profile, similar to that of the reduction potential of Pt-OH_{ad} species (Figure 6.7b). At low Pt loadings on CNTs (10 and 20 wt %), there is little change in the peak potential of the electrooxidation of adsorbed CO. This corresponds to a situation where Pt NPs or clusters are isolated on the surface of MWCNTs. The peak potential shifts significantly to the negative direction for Pt loading >30 wt %, as there is significant interconnection between Pt NPs on the MWCNTs. The changes in the peak potential for the CO oxidation become very small again once the Pt loading is higher than 69 wt %. At a Pt loading of 69 wt %, completely interconnected Pt NPs on CNTs were formed, and a further increase in the Pt loading would simply increase the thickness of the Pt NPs with no effect on the interconnectivity of the Pt NPs/clusters. The results indicate that the high electrocatalytic activity for CO electrooxidation may be related to the magnitude of the interconnectivity of Pt NPs/clusters on CNTs.

The S-shaped dependence of the electrocatalytic activity of Pt/MWCNTs on Pt loading could be explained by the reaction scheme for the electrochemical CO oxidation, as shown below:[108]

In step 6.2, formation of OH_{ad} on the free Pt surface site occurs via adsorption and oxidation. Step 6.3 is the oxidation reaction of absorbed CO on Pt surface, Pt-CO_{ad} . In order for step 6.3 to occur, CO_{ad} and OH_{ad} must be adsorbed at adjacent sites, i.e., sites of Pt-CO_{ad} and Pt-OH_{ad} should be as close as possible. The high Pt loading on MWCNTs increases the density of Pt NPs, leading to the increase in the magnitude of the interconnection of adjacent Pt NPs and, thus, providing more adjacent sites for the intermixing and reaction of CO_{ad} and OH_{ad} on the surface of Pt NPs. On the other hand, Maillard et al.[108] found that the surface mobility of CO_{ad} and OH_{ad} significantly influences the electrochemical CO oxidation on the Pt surface. Here, it is shown by the CV results that Pt/MWCNTs show a reduced oxophilicity with the increased Pt NP loading (Figure 6.7b). Thus, the higher loading of Pt NPs on MWCNTs would lead to the lower oxophilicity and thus higher mobility of oxygen-containing species such as CO_{ad} and OH_{ad} on the surface of Pt NPs. Consequently, step 6.3 would proceed faster with the increase of the Pt loading on MWCNTs. However, the reaction rate for step 6.3 would reach a constant value once the Pt NPs are fully connected with no further increase in the oxophilicity of Pt/MWCNTs catalysts, as shown in Figure 6.8.

6.3.3 Electrocatalytic Activity for Methanol Oxidation and Oxygen Reduction Reactions

The electrocatalytic performance of Pt/MWCNTs (Pt loading 50 wt %) and E-TEK

Pt/C (Pt loading 50 wt %) for the methanol oxidation was investigated in a 0.5 M H_2SO_4 + 0.5 M MeOH solution. In Figure 6.10a, the current density was normalized by ECSA of Pt electrocatalysts. The magnitude of the peak current in the forward scan corresponds to the catalytic activity of the Pt-based catalysts for the methanol oxidation reaction. The peak current densities in the forward scan were 0.65 mA cm^{-2} for Pt/MWCNTs and 0.31 mA cm^{-2} for E-TEK Pt/C. Clearly, Pt/MWCNTs show a much higher area specific activity for the methanol electrooxidation. The onset potential of methanol oxidation is also an important parameter for the methanol oxidation reaction, which can be obtained by overlapping the CV curve obtained in 0.5 M H_2SO_4 and the forward CV for methanol oxidation obtained in a 0.5 M H_2SO_4 + 0.5 M MeOH solution. The onset potential of the methanol oxidation on the Pt/MWCNTs is 0.096 V and it is 0.152 V on the E-TEK Pt/C. This indicates that oxidation of methanol starts at a much lower potential on Pt/MWCNTs catalysts. On the basis of the proposed mechanism of methanol oxidation on Pt electrocatalysts,^[91] the onset potential is related to the breaking of C–H bonds and the subsequent removal of intermediates such as CO_{ad} by the oxidation with OH_{ad} supplied by Pt–OH sites or other sources. The lower onset potential of the methanol oxidation on Pt/MWCNTs indicates that the oxidative removal of the intermediates generated from the methanol oxidation can occur easily as compared to that on the conventional Pt/C catalysts.

Figure 6. 10 (a) Cyclic voltammograms of Pt/MWCNTs (Pt loading 50 wt %; solid line) and E-TEK Pt/C (Pt loading 50 wt %; dotted line) in a N_2 -saturated $0.5\text{ M H}_2\text{SO}_4 + 0.5\text{ M CH}_3\text{OH}$ solution at a scan rate of 10 mV s^{-1} . (b) Plots of the area specific activity of methanol oxidation of Pt/MWCNTs against the Pt NP loadings and (c) plots of the mass activity of methanol oxidation of Pt/MWCNTs against the Pt loadings. The dotted line in panel c is the mass specific activity for the reaction on E-TEK Pt/C catalysts.

Figure 6. 11 (a) Linear sweep curves for O₂ reduction on Pt/MWCNTs (Pt loading 50 wt %; solid line) and E-TEK Pt/C (Pt loading 50 wt %; dotted line) catalysts in O₂-saturated 0.5 M H₂SO₄ at a rotation speed of 1600 rpm and scan rate of 5 mV s⁻¹. (b) Plots of the half-wave potential of oxygen reduction reaction against Pt NP loadings on MWCNTs. The dotted line in panel b is the half-wave potential of oxygen reduction on E-TEK Pt/C catalysts.

Figure 6.10b is the plot of the ECSA specific activity for the methanol electrooxidation on Pt/MWCNTs as a function of Pt loading. The area specific activity of the methanol oxidation on Pt/MWCNT electrocatalysts increases with the increase

of Pt NP loadings on MWCNT and reaches a plateau at Pt loading ≥ 69 wt %, similar to the S-shaped profile observed for the peak potential of Pt-OH_{ad} reduction (Figure 6.8b) and CO oxidation on Pt/MWCNTs (Figure 6.9). On the other hand, the mass activity of Pt electrocatalysts for the methanol oxidation is a critical parameter regarding the practical application in fuel cells. Figure 6.10c shows the dependence of the mass activity (normalized with Pt weight on GCE) of Pt/MWCNTs catalysts on the Pt NP loadings of Pt/MWCNTs. The mass activity of Pt/MWCNTs does not change much in the low Pt loading range of 10–20 wt %. As the Pt loading increases to 30–40 wt %, the mass activity of Pt/MWCNTs increases significantly and reaches a maximum for the Pt/MWCNTs catalysts with Pt loadings of 50–69 wt %. With the further increase of Pt loading on MWCNTs, the mass activity of Pt/MWCNTs decreases significantly, probably due to the overlapping of Pt NPs on MWCNTs for the Pt/MWCNTs with high Pt loading (Figure 6.2h,i). It is interesting to note that in the case of Pt/MWCNTs with Pt loading 50–69 wt %, MWCNT supports are almost completely covered by Pt NPs, forming an interconnected two-dimensional nanostructure on MWCNTs (see Figure 6.2f).

The electrochemical reduction of oxygen on Pt/MWCNTs (Pt loading 50 wt %) and E-TEK Pt/C (Pt loading 50 wt %) was also studied in a O₂-saturated 0.5 M H₂SO₄ solution. The current–potential curves of the oxygen reduction reaction on Pt/MWCNTs and E-TEK Pt/C are shown in Figure 6.11a. The half-wave potential value can be used as an important parameter to evaluate the electrocatalytic activity of the catalysts for ORR, and the more positive half-wave potential indicates the enhanced electrocatalytic activity of the catalysts for ORR. As shown in Figure 6.11a,

the half-wave potential for the ORR on 50 wt % Pt/MWCNT catalyst is 0.510 V, slightly positive as compared to 0.506 V observed on conventional E-TEK Pt/C catalyst.

Figure 6.11b shows the plot of half-wave potentials of oxygen reduction on Pt/MWCNT electrocatalysts as a function of the Pt loadings on MWCNTs. Similar to the observed dependence of the peak potentials of Pt–OH_{ad} reduction, CO stripping, and specific activity for methanol oxidation reaction, the half-wave potentials of oxygen reduction shift toward more positive values with the increase of Pt loading, following a characteristic S-shaped profile of the Pt/MWCNT catalysts. This indicates that the electrocatalytic activity of Pt/MWCNTs for ORR is also closely related to the loading or density of the Pt NPs/clusters on MWCNTs.

6.3.4 Interconnectivity and Electrocatalytic Activity of Pt NPs on MWCNTs

If the electrocatalytic activity of Pt NPs is only related to the unique structures of CNTs and the interactions between the Pt NPs and the CNTs[79] or the better dispersion of Pt NPs on CNTs,[125] it would be expected that the catalytic activities such as the Pt mass specific activity of Pt/MWCNT catalysts would decrease or at least would not increase with the increase in the loading of Pt NPs on CNTs. However, this is clearly not the case, as shown in the present studies. In contrast, the mass specific activity of Pt/MWCNTs for the methanol oxidation reaction increases with the Pt NPs loading (Figure 6.10c). Similarly, the electrocatalytic activity of Pt/MWCNTs for the CO oxidation and oxygen reduction reactions also increases with

the increase in the Pt loading on MWCNTs. This clearly demonstrates that the interaction between the Pt NPs and CNTs or the high dispersion of Pt NPs is not the primary reason for the high electrocatalytic activity of Pt NPs on CNTs.

Figure 6. 12 (a) A calculation example of the interconnectivity for 14 spherical particles. The number on the spherical particle represents the number of interconnected particles with the

particle concerned. (b) Dependence of interconnectivity and size of Pt NPs of Pt/MWCNTs catalysts on Pt loadings.

The effect of Pt particle size on the catalytic activity in particular on the CO oxidation has been extensively investigated.[128-130] The smaller particle size has been correlated with more positive values of CO stripping potential.[130] It is generally considered that larger particles have more defects that can act as active sites for OH adsorption, lower number of low coordination sites, and faster CO surface diffusion, thus resulting in a faster CO electrooxidation reaction. Gu et al.[129] studied the effect of the Pt particle size on CO electrooxidation reaction in a well-designed and controlled experiment. Well-isolated Pt NPs with size ranging from 2.5 to 9.7 nm were deposited on polished glass carbon surfaces. The CO stripping peak potential shifts to more negative values as the Pt NP size increases. CO stripping peak potential is 0.96 V (vs RHE) for 2.5 nm Pt NPs and decreased to 0.91 V (vs. RHE) for 9.7 nm Pt NPs, indicating that preadsorbed CO is easier to oxidize on the surface of larger Pt particles. The change in the CO stripping peak potential is 50 mV for the Pt particle range of 2.5–9.7 nm. In the present study, the CO stripping peak potential decreases from 0.61 V (vs SCE) for Pt/MWCNTs with Pt particle size of 1.47 nm (10 wt % Pt) to 0.44 V for Pt/MWCNTs with Pt particle size of 3 nm (81.6 wt % Pt). The change in the CO stripping potential is 170 mV, substantially larger than 50 mV reported by Gu et al.,[129] even though the particle size range in our study is from 1.47 to 3.0 nm, significantly smaller than that in the Gu's study. This indicates that the effect of particle size on the electrocatalytic activity of Pt/MWCNTs catalysts for the electrooxidation of CO only plays a small part under the conditions of

the present study. On the other hand, Gu et al.[129] showed that the Pt catalysts with the smallest particles (2.5 nm) had the highest specific peak current density normalized by active surface area for methanol oxidation, and the area specific current density decreased with the increase in Pt particle size. In the case of the methanol oxidation reaction, the effect of particle size on the activity of methanol oxidation electrocatalysts remains controversial.

Figure 6. 13 (a) Plots of the mass specific activity for the methanol oxidation reaction (data

from Figure 6.8c) and the peak CO stripping potential (data from Figure 6.8) as a function of the interconnectivity of Pt NPs on MWCNTs. (b) Plots of the half-wave potential for ORR (data from Figure 6.11) as a function of the interconnectivity of Pt NPs on MWCNTs.

As shown in Figure 6.2, the increase in the loading of Pt NPs on MWCNTs supports results in the significant change in the environment of Pt NPs. In the case of low loading of Pt NPs on the support (10–20 wt %, Figure 6.2a and b), Pt NPs are more or less individually distributed. As the Pt loading on the support increases, there is significant increase in the interconnections between Pt NPs, forming Pt NP clusters (Figure 6.2c,d). In the case of Pt/MWCNTs with Pt loading of 69 wt %, the CNTs are covered by a monolayer of Pt NP (Figure 6.2f). The TEM results clearly indicate that the increase in the loading of Pt NPs on CNTs increases the interconnection between Pt NPs. In order to quantitatively correlate the interconnectivity of Pt NPs with their electrocatalytic activity, we introduce the concept of interconnectivity. Interconnectivity is defined as the ratio of the total number of particle interconnections divided by the total number of particles involved.

$$\text{Interconnectivity} = \frac{\sum \text{number of particle interconnections}}{\sum \text{number of particles}} \quad (6.4)$$

Assuming spherical particles with equal diameter, the interconnectivity ratio would vary between 0 and 6 for 2D planar assembled NPs. Figure 6.12a shows an example of the calculation of interconnectivity for 14 particles, and the interconnectivity was 1.7 in this case. The interconnectivity of Pt NPs of Pt/MWCNTs with different Pt loadings was measured on the basis of the measurement of a total of 100 Pt NPs. Figure 6.12b

is plots of the interconnectivity and size of Pt NPs of Pt/MWCNTs catalysts as a function of Pt loading. The particle size increases with the Pt loading, and the relationship between the particle size and Pt loading is almost linear. The interconnectivity value of Pt particles also increases with the increase of Pt loading; it starts with 0.6 for 10 wt % Pt and reaches the maximum value of 6 for the Pt/MWCNTs with Pt loading above 69 wt %. Most interesting, the relationship between the interconnectivity and Pt loading also follows an S-shaped profile, just like the S-shaped profiles observed for the reduction potential of Pt–OH_{ad}, CO stripping peak potentials, and area specific activity of the methanol oxidation on the Pt/MWCNTs as the function of Pt loadings. The observation of the same and distinctive S-shaped profile of the interconnectivity of Pt NPs and the electrocatalytic activity of Pt/MWCNTs catalysts indicates the close correlation between the interconnectivity of Pt NPs and their electrocatalytic activity for fuel cell reactions.

Shown in Figure 6.13a are the plots of the mass specific activity for the methanol oxidation reaction (data from Figure 6.10c) and the CO stripping peak potential (data from Figure 6.9) as a function of the interconnectivity of Pt NPs on MWCNTs. The CO stripping peak potential decreases linearly with the interconnectivity of Pt NPs on CNTs, indicating that the kinetics of the CO oxidation increases with the increase in the interconnectivity of Pt NPs. The mass specific activity of Pt/MWCNTs for methanol oxidation also increases linearly with the interconnectivity of Pt NPs, and the increase of the activity is much slower once the interconnectivity is above 3, corresponding to the Pt/MWCNTs with the Pt loading of 50 wt %. This indicates that the optimum interconnectivity for Pt NPs for the electrocatalytic activity for methanol

oxidation reaction would be around 3. A similar linear relationship between the catalytic activity and the interconnectivity of Pt NPs is also observed for ORR (Figure 6.13b). The half-wave potential values increase linearly with the increase of the interconnectivity of Pt NPs on MWCNTs, and when the interconnectivity is higher than ~3, the half-wave potentials deviate from linear relationship and the increase in half-wave potentials becomes very slow, indicating the strong dependence of ORR electrocatalytic activity of Pt NPs on their interconnectivity.

With the increase of the Pt loading, the interconnectivity of Pt NPs on MWCNTs increases. The linear relationship between the performance and interconnectivity of Pt NPs indicates that the electrocatalytic activity of Pt/MWCNTs depends strongly on the interconnectivity. The reasons for the enhanced catalysis with the increased interconnectivity of Pt NPs could be considered as follows: (1) the multidimensional nanostructure provides more facile pathway for the electrons transfer by reducing the interface resistance between the NPs. For Pt/MWCNTs electrocatalysts with low Pt NPs interconnectivity (low Pt loading), the Pt NPs exist as isolated particles, which are likely to impose a high impedance for electron transfer from particle to particle. (2) The increased interconnectivity of Pt NPs leads to the significant increase in the grain boundaries between the NPs (as shown in Figure 6.4). These grain boundaries provide a large number of defect sites, generating discontinuities in the crystal planes of interconnected Pt NPs in Pt/MWCNTs, providing active sites for CO removal and methanol oxidation reactions. (3) The high interconnection of Pt NPs increases the number of adjacent Pt NPs for subsequent adsorption of Pt-CO_{ad} and Pt-OH_{ad} and thus promotes the oxidation rate of absorbed CO on Pt surface. Thus, the increased

interconnectivity of Pt NPs weakens their chemical adsorption with oxygen-containing species (i.e., CO_{ad} and OH_{ad}), resulting in the promoted electrocatalytic activity for the CO oxidation. The increases of the electrocatalytic activity of Pt NPs with the increase in the interconnectivity is also consistent with the enhanced electrocatalytic activity for the methanol oxidation observed on multidimensional Pt nanostructures, relative to Pt NPs.[15, 19] However, as shown in Figure 6.13, the activity increases linearly with the interconnectivity, and the optimum interconnectivity for the mass specific activity of Pt NPs on CNTs is ~ 3 . This can be understood by considering that the increase in the interconnectivity would increase the activity, as discussed above, but at the same time, the increased interconnectivity also reduces the accessible interconnected sites and therefore reduces the effective surface area for catalyzing a reaction. Thus, when on average every Pt NP is in contact with three NPs, the electrocatalytic activity of Pt catalysts is maximized by the optimum balance of the increased interconnectivity and reduced effective surface area of the interconnected Pt NPs. The present study also shows that the electrocatalytic activity of Pt catalysts supported on high surface area carbon, e.g., E-TEK Pt/C, is not necessarily poorer than that of Pt catalysts supported on CNTs. However, it appears that it may be much easier to form interconnected Pt NPs on the outer wall surface of CNTs as compared to high surface area carbon.

6.4 Conclusions

In summary, the platinum NPs are successfully assembled on MWCNTs using a novel noncovalent PDDA-functionalized MWCNTs and seed-mediated growth technique. The loading of Pt NPs on MWCNTs supports was controlled in the range

from 10 to 93 wt %. The electrochemical characterizations show that the catalytic activity of Pt/MWCNTs depends strongly on the loading of Pt NPs on MWCNTs and the catalytic activity of Pt/MWCNTs for methanol electrooxidation, CO electrooxidation, and oxygen electroreduction increases with the Pt loading, following a characteristic S-shaped profile. It is demonstrated that for the first time that the electrocatalytic activities of Pt/MWCNTs catalysts are fundamentally correlated to the interconnectivity of Pt NPs on CNTs. The magnitude of the interconnectivity of Pt NPs is a critical factor influencing their electrocatalytic activity, and the interconnected Pt NPs are more active than the isolated Pt NPs. The high electrocatalytic activity of highly interconnected Pt NPs is considered to be related to the increased active intergrain boundaries, which promote significantly the electrocatalytic activity of Pt NPs. On the other hand, the interconnected Pt NPs would significantly weaken their chemical adsorption with oxygen-containing species (i.e., CO_{ad} and OH_{ad}), resulting in the promoted electrocatalytic activity for CO and methanol oxidation and oxygen reduction. The increase of interconnectivity of Pt NPs also reduces the interface resistance among particles for electron transfer.”

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Chapter 7 Pt Nanowire Network vs. Pt Nanoparticles as Electrocatalysts for Oxygen Reduction and Methanol Oxidation

7.1. Introduction

The conclusion in Chapter 6 that interconnected Pt nanoparticles (NPs) are more electrochemically active than the isolated ones motivates us to synthesize highly interconnected metal nanostructures such as nanowire and nanowire networks and to characterize their electrocatalytic activity for fuel cell reactions. Therefore, in the coming two chapters (Chapter 7 and 8), we aim at synthesizing Pt and Pd nanowire networks and studying their activities.

Methanol electrooxidation (MOR) and oxygen electroreduction (ORR) are key anodic and cathodic reactions in DMFCs, respectively. However, even with the state of the art electrocatalysts, which are usually nanostructured platinum or platinum-based alloy materials supported on high surface area carbon supports,[30, 55] sluggish MOR and ORR still cause a large overpotential.[1] In the recent years, various strategies have been developed to improve the electrocatalytic activity for both MOR and ORR, including the addition or incorporation of a second element in Pt electrocatalysts and the proper morphological (shape and size) control.[32, 37, 113, 120, 121, 131-134]

“Due to the strong dependence of their physical and chemical properties on the size, shape, and dimensions, the morphology controlled synthesis of Pt nanostructures have attracted extensive attentions. Traditionally, particle-shaped Pt in the nanometer scale

is used as electrocatalysts from the perspective of maximizing Pt utilization.[12, 13] However, the problem of the dispersed Pt NPs on carbon supports is that it would lead to serious interface impedance from particle to support and from particle to particle, because of the presence of huge amount of interfaces. As an alternative approach, multi-dimensional nanostructures, such as nanowire, nanotube, Y-junction nanostructure, nanowire network (NWN), and nanowire array, have been developed as the promising electrocatalysts in the recent years.[15, 19, 122, 135, 136] For examples, Sung et al.[137] synthesized 3 nm Pt nanowires in MCM-41 hard template, which shows improved specific and mass activity. Chien et al.[136] reported the synthesis of Pt and Pt-Ru nano-networks in a void space of a self-assembled, layered template of polystyrene nanosphere by chemical reduction deposition, using which as electrocatalysts in fuel cell testing, the performance is 3~4 times that of conventional DMFCs on particle-shaped electrocatalysts. Kim et al.[15] reported synthesis of Pt nanowire via polymer template method. The as-prepared Pt nanowire shows higher mass activity for methanol electrooxidation. Chen et al.[122] synthesized nanoporous PtRu NWN with improved CO-tolerance and electrocatalytic activity for methanol oxidation. However, most of the above works use hard template method which generally produces low metallic interconnectivity due to the poor continuity of precursors in the hard template. Also the removal of the hard template normally requires the use of hydrofluoric acid, which causes serious concerns for the environment and safety. Besides, the as-synthesized nanomaterials are usually of large size (diameter), which is undesirable for fuel cell application. It is believed that a soft template synthesis method is more suitable to synthesize ideal multi-dimensional Pt

nanostructures for fuel cell application.”

In this chapter, we aim to synthesizing Pt NWN by a phase-transfer method, in which a soft surfactant template, cetyltrimethylammonium bromide (CTAB) is used.[138] It would be of great interest to investigate and compare the intrinsic advantages of multi-dimensional Pt nanostructures with Pt NPs for various characteristic electrochemical reactions in fuel cells. Various electrochemical investigation tools were utilized to study their electrocatalytic activity for methanol oxidation. Compared to Pt NP electrocatalysts, it is found that Pt NWN show significantly enhanced electrocatalytic performance for MOR (higher specific activity). Finally, the origin of the enhanced electrocatalytic activity is also discussed.

7.2. Experimental Section

7.2.1. Materials.

“Materials used in the present work include deionized water (resistivity > 18.0 M Ω cm), methanol (Fluka), Potassium tetrachloroplatinate (II) (Sigma-Aldrich, K₂PtCl₄, 99.99%), cetyltrimethylammonium bromide (CTAB, Acros), Chloroform (Fluka), Sodium borohydride (Sigma-Aldrich), Carbon black (Vulcan XC-72), Nafion solution (5 wt% in isopropanol and water), E-TEK Pt/C, sulfuric acid (99.5%, Fluka). All the chemicals were used as received without further purifications.”

7.2.2. Synthesis of Pt NWN.

Pt NWN was synthesized by a soft template based phase-transfer method, as

reported by Shelnutt et al.[138] Briefly, in a typical synthesis process, 10 mL of a 20 mM K_2PtCl_4 aqueous solution was mixed with 10 mL of chloroform containing 40 mM CTAB under stirring. To ensure the complete transfer of Pt complex into the chloroform phase, the stirring was kept for 1 h, followed by the addition of 80 mL of pure water under stirring. After 15 min, 10 mL of fresh ice-cold sodium borohydride (300 mM) in aqueous solution was added while keeping the stirring at a speed of 1000 rpm. The reduction of Pt complex to metallic Pt was indicated by the color change from yellow to dark brown.

7.2.3. Deposition of Pt NWNs on Carbon Support.

Before the deposition of as-prepared Pt NWNs on carbon black (XC-72), CTAB-stabilized Pt NWNs were separated from excess CTAB by centrifugation twice (at 15000 rpm). The solid Pt NWN residue was re-dispersed with distilled water (50 ml), followed by the TEM (Transmission electron microscopy, JEOL 2010, at an acceleration voltage of 200 keV) characterization. Meanwhile, 159 mg of carbon black was dispersed in 50 ml of pure water by ultrasonication for 30 min. The as-formed well-dispersed carbon black suspension was mixed with the centrifuged Pt NWN dispersion under vigorous stirring for 30 min, followed by the addition of 200 ml of ethanol to thoroughly remove CTAB stabilizing Pt NWN and release Pt NWN to deposit on carbon black. After 24 h, Pt NWN supported on carbon black was collected by repeated filtration and dried in vacuum oven at 70 °C for 12 h. The Pt loading of Pt NWN on XC-72 was designed to be 20 wt% based on the feeding amount.

7.2.4. Physical and Electrochemical Characterization.

“Subsequently, Pt NWN supported on XC-72 were characterized by XRD (X-ray diffraction, with a continuous scanning at a scan rate of $0.025^{\circ}/\text{s}$.), XPS (X-ray photoelectron spectroscopy), and electrochemical characterization. The XPS characterization was carried out on using Kratos, AXIS Ultra system with a 150 W, 15 kV Monochromatic Alumina $K\alpha$ source. The powder samples are made into pellets. For spectra analysis, the background correction was made using Shirley’s method. All the binding energies were corrected for the signal for C1s at 284.6 eV as an internal standard. Deconvolutions of the XPS spectra were carried out using the software XPSPeak 4.1. The relative concentrations of the surface species are equal to the corresponding deconvoluted peak areas divided by the total XPS signal area extracted from the experimental XPS core level regions of Pt 4f.

The electrochemical measurements were performed in a conventional three electrode cell, using glassy carbon electrode (GCE, 4 mm in diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and Pt foil as the counter electrode at room temperature. To load electrocatalyst suspension onto GCE, the electrocatalyst powder was ultrasonically mixed in water to form a homogeneous ink with the catalyst concentration of 2 mg/mL, followed by dropping 20 μL of the electrocatalyst ink onto the surface of GCE. Then, 1 μL of Nafion solution of 0.5% in isopropanol was added to fix the electrocatalysts on GCE surface. All potentials reported in the present study were given versus SCE reference electrode. The electrocatalytic activity for methanol oxidation was characterized by collecting

CVs in nitrogen-purged 0.5 M H₂SO₄ + 0.5 M MeOH solution at a scan rate of 10 mV s⁻¹. CO stripping was carried out in 0.5 M H₂SO₄ solution. The electrolyte solution was first purged with high purity nitrogen gas. The adsorption of CO on the electrode catalyst was conducted by bubbling CO gas (UHP grade) through the electrolyte solution for 15 min, while maintaining the electrode potential at -0.1 V versus SCE. Then the electrolyte was purged with nitrogen for 20 min to remove residual CO from the electrolyte. The CO stripping CV curves and blank CV curves can be obtained from two consecutive scan cycles in the potential range between -0.2 to 1.0 V at a sweep rate of 10 mV s⁻¹.”

7.3. Results and Discussion

7.3.1. TEM Characterization

The synthesis of Pt NWN was performed in a two-phase water-chloroform system using CTAB as a soft template. As proposed by Shelnutt et al.,[138] CTAB existing at the interface of the two-phase aqueous and chloroform mixture forms interconnected micelle networks. With the addition of Pt precursor (K₂PtCl₄), Pt complex is formed within the CTAB micelles via the electrostatic interaction. The confined Pt complex was then reduced under the reduction reaction conditions to produce Pt NWN. As shown in Figure 7.1, the TEM images confirm the successful synthesis of Pt NWN in the presence of CTAB as stabilizers. It could be seen that the Pt nanowires were interconnected to form two-dimensional (2D) NWN with multi-grained boundaries. The high magnification TEM image (Figure 7.1B) reveals that the average

cross-sectional diameter is 2.5 nm with uniform diameter distribution. The electron diffraction pattern (Figure 7.1 inset) of Pt NWN indicates that they are polycrystalline.

The polycrystallinity of the NWN can be clearly seen from the HRTEM (high-resolution TEM) image. As shown in Figure 7.2, the Pt NWN consists of randomly oriented grains and shows the alternation of small domains with varied orientations of the atomic lattice fringes along the nanowire. Furthermore, grain boundaries were observed along the nanowire. The presence of grain boundaries are normally observed in the nanowire or nanowire network structures. For examples, Ramanath et al.[139] have successfully assembled gold nanowire network by agitating Au NPs in a toluene-aqueous mixture. The Au nanowire network synthesized in their work also has grain boundaries along nanowires. More recently, Remita et al.[16] utilized hexagonal mesophases as the template to fabricate palladium nanowires used for ethanol electrooxidation. In the as-fabricated Pd nanowire, twinning grain boundaries and stacking defaults were observed along the nanowires. It has been proposed that the emergence of grain boundaries to the surface would enhance the electrocatalytic activity.[120]

Figure 7. 1 TEM images of Pt NWN at low (A) and high (B) magnification. Inset: the electronic diffraction pattern of Pt NWN; (C). TEM image E-TEK Pt/C

Figure 7. 2 HRTEM image of Pt NWN; the grain boundaries were indicated by the arrows.

7.3.2. XRD Characterization

The XRD patterns in Figure 7.3 also confirmed the polycrystalline nature of Pt NWN, where the diffraction peaks at 39.7° , 46.7° , 67° can be ascribed to Pt (111), Pt (200), and Pt (220), consistent with the face-centered cubic (fcc) structure of Pt. For comparison purpose, the TEM picture and XRD pattern of E-TEK Pt/C were also presented. As shown in Figure 7.1C, the average Pt size is about 2.7 nm. Similarly, the diffraction peaks at the corresponding positions were also observed for E-TEK Pt/C in Figure 7.3. The inset of Figure 7.3 is the selected region for Pt (220) diffraction peak, from which it is found that the Pt NWN diffraction peaks are slightly shifted to higher

value relative to the E-TEK Pt/C, which is probably caused by the anisotropic structure of the NWN.[15]

Figure 7. 3 XRD patterns of E-TEK Pt/C (a) and Pt NWN (b). Inset: the selected region of XRD patterns around Pt (220) diffraction peak.

Figure 7. 4 ECSA-normalized cyclic voltammograms of E-TEK Pt/C and Pt NWN in

nitrogen-saturated 0.5 M H₂SO₄ at a scan rate of 10 mV s⁻¹.

7.3.3. CV Curves in 0.5 M H₂SO₄ Electrolyte

Surface oxophilicity of the catalysts is a very important indicator of their electrocatalytic activity. To investigate the surface oxophilicity of the Pt NWN, CV test in the supporting 0.5 M H₂SO₄ electrolyte on Pt NWN was performed and compared with commercial E-TEK Pt/C electrocatalysts (Figure 7.4). As the comparison of the original voltammograms is not as straight-forward as for single crystals[140] due to the different surface areas of the two catalysts, the current of the CVs was normalized in terms of the electrochemically active surface area (ECSA), which can be obtained from the area of the hydrogen desorption peak after correcting for the double layer charging current from the CVs. As shown in Figure 7.4, both curves show three characteristic potential regions: the hydrogen adsorption and desorption region (-0.2 to 0.1 V), double layer plateau region (0.1 to 0.5 V), and the formation and reduction of surface Pt oxide (0.5 to 1.0 V). It's interesting to notice the potential region of the reduction of Pt oxide (Pt-OH_{ad}) in the CV curves. The peak potential in the reduction of Pt-OH_{ad} positively shifted for Pt NWN, relative to E-TEK Pt/C, which indicates that Pt NWN shows reduced oxophilicity, that is, weakened chemical adsorption with oxygen-containing species (e.g. CO_{ad} and OH_{ad}). Similar observations have been made by other groups[91, 108, 141, 142] when investigating the particle size effect, that is, small NPs have relatively negative peak potential for Pt-OH_{ad} reduction than large NPs or bulk polycrystalline Pt, which is attributed to the stronger bonding of OH_{ad} to the smaller NPs. Although the average cross-sectional

diameter of Pt NWN is close to the average diameter of Pt NPs in E-TEK Pt/C, the nanowire nature definitely provides larger size, which can contribute to the reduced oxophilicity, that is, weaker bonding of CO_{ad} and OH_{ad} . It has been well known that the proportion of low coordinated atoms (edges and corners) increases with the decrease of the cluster size, while the low coordinated atoms have the stronger adsorption with the oxygen-containing species.[143] On the other hand, it's also likely that size confinement in small particles induces changes in the electronic structure of metal particles, which results in an increase of oxygen binding energies.

Figure 7. 5 XPS spectra of the Pt 4f photoemission from E-TEK Pt/C (A) and Pt NWN (B).

7.3.4. XPS Characterization

“The above results could be confirmed by the XPS characterization. Figure 7.5 presents the XPS spectra of the Pt 4f region of E-TEK Pt/C (Figure 7.5A) and Pt NWN (Figure 7.5B). The Pt 4f spectra show a doublet containing a low energy band

(Pt 4f7/2) and a high energy band (Pt 4f5/2) at 71.55 and 74.76 eV for Pt NWN and 71.90 and 75.10 eV for E-TEK Pt/C, respectively. It is found that a negative shift of Pt binding energies for Pt NWN relative to that of E-TEK Pt/C occurs, which could be ascribed to the particle size effect.[141, 144] Although the cross-sectional diameter of Pt NWN is close to that of Pt NPs in E-TEK Pt/C, the longitude size of Pt NWN is much bigger. To identify different chemical states of Pt, the spectrum was deconvoluted into three components, as labeled by Pt (0), Pt (II), and Pt (IV). The relative ratio of various Pt species was calculated from the relative intensities of these three peaks, and the results are summarized in Table 7.1. It was found that Pt NWN possesses relatively less amount of oxide state (Pt (II) and Pt (IV)) than E-TEK Pt/C. This result confirmed that Pt NWN has a weaker oxophilicity than E-TEK Pt/C, in agreement with the above electrochemical analysis. The different oxophilicity of Pt NWN and E-TEK Pt/C could be used to partially explain their different electrocatalytic behavior for CO electrooxidation and MOR, as discussed below.”

Figure 7. 6 CO stripping curves over Pt NWN and E-TEK Pt/C electrocatalysts. The solid line is the CO stripping (1st scan); the dotted line is the 2nd scan.

7.3.5. CO Stripping Results

Since CO is the main intermediate from the methanol electrooxidation, the investigation of CO tolerance of Pt NWN was performed, prior to the detailed study of methanol electrooxidation on Pt NWN. Figure 7.6 shows the CO stripping voltammograms for both Pt NWN and E-TEK Pt/C, which were normalized by their ECSA values. It could be observed that both show the characteristic CO stripping curves. Prior to the oxidation of adsorbed CO, the hydrogen adsorption/desorption is completely suppressed; but the peak associated with hydrogen adsorption appears after the removal of adsorbed CO. It was found that the peak potential and onset potential for the adlayer CO oxidation on Pt NWN negatively shifted relative to E-TEK Pt/C electrocatalysts, indicating that the pre-adsorbed CO is easier to be

oxidized on Pt NWN than on E-TEK Pt/C. The investigation of CO tolerance of Pt electrocatalysts is of typical interest. The reaction scheme for the electrochemical CO oxidation can be given by the following equations:[108]

In step (1), formation of OH_{ad} on the free Pt surface site occurs via adsorption. In order that step (2) can occur, CO_{ad} and OH_{ad} must be adsorbed at adjacent sites, which implies a higher mobility of either of these adsorbates will facilitate the reaction. Savinova et al.[108] have shown that the surface mobility of CO_{ad} and OH_{ad} significantly influenced the electrochemical CO oxidation on Pt surface. As discussed above, the Pt NP electrocatalysts have stronger bonding with oxygen-containing species than Pt NWN due to the relatively small particle size, which would restrict the mobility of CO_{ad} and OH_{ad} . Therefore, the diffusion or intermixing of CO_{ad} and OH_{ad} would be easier on Pt NWN than Pt NPs, resulting in easier CO electrooxidation. Furthermore, Savinova et al.[128] found that the grained boundaries of Pt aggregates with interconnected NPs are particularly active for CO adlayer oxidation. On the basis of this observation, Pt NWN consisting of large amounts of multi-grained boundaries would show improved catalytic activity for CO electrooxidation, in line with the experimental result in Figure 7.6.

7.3.6. Methanol Oxidation Reaction (MOR)

Figure 7. 7 CVs of Pt NWN (dotted line) and E-TEK Pt/C (solid line) in nitrogen-saturated 0.5 M H₂SO₄ + 0.5 M MeOH solution at a scan rate of 10mV s⁻¹.

To investigate their electrocatalytic performance for methanol oxidation reaction (MOR), the cyclic voltammogram (CV) curves of methanol oxidation on Pt NWN and E-TEK Pt/C were also collected in 0.5 M H₂SO₄ + 0.5 M MeOH and presented in Figure 7.7, where the current density is normalized by ECSA. The voltammetric features are consistent with literature reports and are typical of the oxidation of methanol. The peak current densities of methanol electrooxidation in the forward CV scan were 0.96 mA cm⁻² for Pt NWN and 0.31 mA cm⁻² for E-TEK Pt/C. Clearly, Pt NWN shows much higher (3 times) specific activity for methanol electrooxidation than commercial Pt/C. On the other hand, the current peak ratio of I_f (the forward peak current density)/ I_b (the backward peak current density) could be used to indicate the

CO tolerance on Pt surface. The higher I_f/I_b ratio indicates better CO tolerance. The I_f/I_b ratios are 0.961 for the Pt NWN and 0.871 for E-TEK Pt/C, which further demonstrates the enhanced CO tolerance on Pt NWN, in line with the above discussion based on CO stripping analysis (Figure 7.6). The origin of the enhanced activity for MOR of Pt NWN could be attributed to the similar reasons based on the interpretation for enhanced CO electrooxidation. Furthermore, to investigate the intrinsic methanol electrooxidation kinetics on Pt NWN and E-TEK Pt/C, the activation energies for methanol electrooxidation on both catalysts were extracted using an Arrhenius plot and the data are presented in Figure 7.8. The activation energy value was 32.2 kJ mol⁻¹ and 49.4 kJ mol⁻¹ for MOR on E-TEK Pt/C and Pt NWN, respectively. This result shows methanol oxidation reaction occurs at lower activation energy on Pt NWN than that on Pt NPs.

Figure 7. 7 Arrhenius plots for methanol reaction on Pt NWN (sphere dot) and E-TEK Pt/C (square dot) electrodes in 0.5 M H₂SO₄ + 0.5 M MeOH solution at 0.6 V vs. SCE.

Although Pt alone is not a practical catalyst for CO or methanol oxidation, the activity difference between NWN and NP morphology observed in this work may provide new idea for the design of more efficient electrocatalyst. For example, based on same argument, Pt alloy NWN, such as PtRu or PtMo, may achieve better performance than Pt alloy NPs for methanol oxidation. Alternatively, we can also synthesize PtFe or PtCo NWN targeting at ORR. The synthesis of various Pt based alloy NWNs is currently undergoing in our lab.

7.4. Conclusions

Pt NWN was synthesized with a phase-transfer method templated against CTAB. The potential application Pt NWN was utilized as electrocatalyst for methanol oxidation reaction. Pt NWN shows significantly enhanced electrocatalytic performance compared to the particle-shaped E-TEK Pt/C electrocatalyst. The improved catalytic performance may be caused by the intrinsic physicochemical properties of the two-dimensional (2D) Pt nanowire network structure. (i) The Pt NWN electrocatalysts have reduced oxophilicity, that is, weaker adsorption with oxygen-containing species (CO_{ad} and OH_{ad}) than E-TEK Pt/C due to the decrease of low co-ordinated Pt atoms in Pt NWN relative to NP, leading to more available active sites for ORR on Pt NWN and enhanced surface mobility of CO_{ad} and OH_{ad} for CO and methanol oxidation. (ii) The 2D structure of Pt NWN facilitates the mass transport and electron transfer during the reaction. The multi-dimensional structure significantly reduced the interface impedance for mass transport and electron transfer. (iii) Pt NWN consists of large amounts of grained boundaries, which have particularly high activity

for CO electrooxidation and MOR. In all, the present work demonstrates the benefits of nanowire network structure over NP structure for fuel cell reactions.

Chapter 8 “Controllable Self-assembly of Pd Nanowire Networks as Highly Active Electrocatalysts for Direct Formic Acid Fuel Cells”

8.1. Introduction

In this chapter as a continuation of Chapter 6 and 7, we focus on the controllable synthesis of Pd nanowire networks and their use as electrocatalysts for formic acid oxidation in acid medium.

“Direct formic acid fuel cells (DFAFCs) have attracted considerable interests recently as portable power applications. Formic acid is a liquid-like methanol but it has a lower crossover through the Nafion-based membrane and a higher kinetic activity than methanol. Thus DFAFCs can be operated at a higher voltage than direct methanol fuel cells.[145, 146] Pd-based catalysts were found to possess superior performance in formic acid oxidation in DFAFCs compared with Pt-based electrocatalysts.[35, 147] However, the Pd particle size in the conventional Pd/C electrocatalysts prepared with the general reduction method is difficult to control.[148] As shown by Ge et al, the electrocatalytic activity of Pd-based nanocatalysts is sensitive to both the shape and size of Pd NPs.[149] Therefore, tunable or controllable synthesis of the supported Pd electrocatalysts with tailored size and nanostructures is highly desirable.

In this chapter, we present a novel, templateless and polysodium-p-styrenesulfonate (PSS) polyelectrolyte-mediated self-assembly process to synthesize highly dispersed and uniform porous Pd nanowire networks (NWNs). The benefit of the templateless

and PSS-mediated self-assembly is that i) no chemical treatment and harsh chemicals are needed as in the case of template method; ii) the shape and size of the Pd nanostructures can be tailored via the pH of the reaction solution and the reducing agents used; iii) the synthesis process is simple and does not require the sophisticated equipment and set-ups. The results show that highly dispersed and uniform Pd nanowire networks (NWNs) synthesized by the templateless and PSS-mediated self-assembly have a very high aspect ratio and are highly active for the formic acid electrooxidation in acid media for DFAFCs.

8.2. Experimental Section

8.2.1. Materials

PdCl₂ (99.9%, Sigma-Aldrich), PSS (MW = 70,000, Sigma-Aldrich), DI water, Ethanol, NaOH, NaBH₄, PDDA (MW = 20,000, Sigma-Aldrich), Nafion (5 wt% solution, DuPont) and PAA (MW = 450,000, Sigma-Aldrich), Formic acid, H₂SO₄

8.2.2. Synthesis of Pd Nanostructures

Pd nanostructures from cubic NPs to NWNs were prepared as follows: 4 ml of PdCl₂ solution (20 mM, 99.9%, Sigma-Aldrich) was mixed with appropriate PSS (MW = 70,000, Sigma-Aldrich) based on the molar ratio between monomer units of PSS to PdCl₂. Then ~55 ml of DI water was added into the mixture followed by the continuously stirring for 30 min. Ethanol was added to the solution and the volume ratio of ethanol and water was 4:6. The pH of the solution was controlled by NaOH

(1.0 M) aqueous solution. The color of the solution changed from light yellow to dark brown, indicating the reduction of Pd (II) to Pd (0). In the case of synthesis of Pd NWNs using NaBH₄ as a reducing agent, PSS and PdCl₂ (molar ratio = 1:1) were mixed in DI water, Then a fresh and ice-cold NaBH₄ aqueous solution was added into the solution. The reduction of Pd (II) was indicated by the instantaneous color change. The synthesis of Pd NPs and Pd NWNs in the presence of PDDA, Nafion and PAA was carried out under conditions of polyelectrolyte: Pd = 1:1 and pH = 12 using ethanol as the reducing agent.

8.2.3. Physical and Electrochemical Characterization Method

The microstructure of Pd nanostructures was examined by TEM using JEOL 2010. An X-ray diffractometer (XRD) using Cu K α 1 (λ = 1.54056 Å) as the radiation source was used for the identification of the crystalline structure.

To perform the electrochemical test, the synthesized Pd NWNs were deposited on XC-72 carbon to form Pd NWN/C electrocatalysts. Pd NPs supported on XC-72 carbon (Pd NP/C) were also synthesized using NaBH₄ as the reducing agent. Cyclic voltammtry (CV) curves were measured with a three-electrode electrochemical cell at room temperature. Pd NWN/C and Pd NP/C electrocatalysts were deposited to a glassy carbon electrode (GCE). The Pd loading was 0.01 mg cm⁻². A Pt wire and a saturated calomel electrode (SCE, 0.224 V vs SHE) were used as the counter and reference electrodes, respectively. The electrolyte, consisting of a solution of 0.5 M H₂SO₄ + 0.5 M HCOOH, was saturated with nitrogen for 30 min before CV

measurements. The CVs were collected between -0.2 and 1.0 V with a scan rate of 50 mV s⁻¹. Chronoamperometric experiments were performed at 0.1V *versus* SCE in 0.5 M H₂SO₄ + 0.5 M HCOOH solution at room temperature.

8.3. Results and Discussion

Scheme 8. 1 A schematic illustration of the controllable and PSS-mediated self-assembly of Pd NWNs and NPs

The principle of the templateless and tunable synthesis of Pd nanostructures *via* the polysodium-*p*-styrenesulfonate (PSS) polyelectrolyte-mediated self-assembly process is shown in Scheme 8.1. In solution, self-assembly occurs between positively charged Pd²⁺ ions and negatively charged SO₃⁻ function groups attached to the pendent aromatic ring of PSS, forming anisotropic Pd²⁺-PSS networks in solution. If the nucleation rate of Pd NPs along the PSS molecular chains is fast, the crystallization

and growth of Pd atoms would adopt the anisotropic Pd²⁺-PSS network, forming Pd NWNs. The assembly and formation of Pd NPs and NWNs occurs simultaneously. This is very different from other low-temperature wet-chemical processes such as polymer-mediated NP assembly[76] and NP assembly at water/toluene liquid interface[139, 150] where NPs are formed before the assembly. On the other hand, if the nucleation rate of Pd NPs along the PSS polymeric chain is slow, the grain growth of Pd NPs would be dominant. The random nucleation and grain growth would disturb the anisotropic Pd²⁺-PSS network in solution and form isolated Pd NPs instead.

Figure 8. 1 TEM micrographs of Pd nanostructures synthesized in the presence of PSS polyelectrolyte. (a) Pd nanocubes synthesized at pH=2, (b) Pd cuboctahedrons at pH=6, (c) Pd nanorods at pH=8, and (d) Pd nanowire networks at pH=12. PSS/Pd ratio was 1:1 and ethanol was used as reducing agent. Inset is the high magnification TEM image.

8.3.1 TEM and XRD Characterization

Figure 8.1 shows transmission electron microscopy (TEM) micrographs of Pd nanostructures synthesized at different pH using ethanol as a reducing agent. PSS/Pd ratio was 1:1. The pH value of the solution has drastic effect on the Pd nanostructure formed in the presence of PSS polyelectrolyte. When pH = 2, Pd nanocubes with average diameters as large as 200 ± 10 nm were formed (Figure 8.1a). As the pH increased to 6, Pd NPs crystallized in cuboctahedron and the average diameter of the cuboctahedrons is 25 ± 3 nm (Figure 8.1b), significantly smaller than that of the Pd nanocubes formed at pH 2. The different microstructure and morphologies of Pd nanocrystals formed at pH = 2 and 6 may be due to the difference in ratios, R , between the growth rates along the Pd $\langle 100 \rangle$ and Pd $\langle 111 \rangle$. As reported by Xiong and Xia,[151] a lower R favors the formation of cubic nanocrystals, while a high R promotes the growth of cuboctahedron. Increase in the pH of the solution increases the reduction rate of Pd(II) to Pd (0).[152] Thus, the relatively fast polyol reduction at pH = 6 increases the crystallization rate along the Pd $\langle 100 \rangle$ and Pd $\langle 111 \rangle$ facets and thus the R value, leading to the growth of cuboctahedrons with smaller diameter. Pd nanorods start to form when the pH value is increased to 8. Nevertheless, the connectivity between nanorods is low (Figure 8.1c). With the pH 12 solution, Pd nanowires (NWs), networked together, are formed (Figure 8.1d). The diameter of the Pd NWs is 3 nm. The formation of NWNs indicates the fast reduction rate of Pd (II) to Pd (0) at high pH value of 12.[152] The above results indicate that the synthesis solution pH is a key factor that influences both the morphology and size of Pd

nanostructures. The transition from nanocubes, nanorods to nanowire networks with the increase in the solution pH clearly indicates that Pd nanostructure is controllable in the presence of PSS polyelectrolyte.

The XRD pattern was obtained on the Pd NWNs supported on high surface area carbon black (Figure 8.2). The diffraction peaks at the 2 theta of 40.25°, 46.53°, 68.08° and 83.02° were indexed as the (111), (200), (220) and (311) facets of the palladium face-centered cubic (fcc) phase, indicating the formation of metallic Pd nanocrystals by the templateless and PSS-mediated self-assembly process.

Figure 8. 2 XRD pattern of the Pd NWNs supported on high surface area carbon black.

8.3.2. Formation Mechanism of Pd Nanowire Network

The salient features of the tunable PSS-mediated assembly of Pd NWNs can be qualitatively understood as follows. In solution, there exist Pd^{2+} ions and PSS polymer chains with SO_3^- attached to the pendent aromatic ring. One divalent Pd^{2+} ion would be attracted to two single charged SO_3^- groups of PSS *via* ionic interactions. Due to

the bulky size of the aromatic rings in PSS, it would be difficult for Pd^{2+} ions to be assembled with two neighboring SO_3^- groups. Most likely, Pd^{2+} ions would be attached to SO_3^- groups of different PSS, forming a sandwich-like orientation network matrix, PSS- Pd^{2+} -PSS (Scheme 8.1). The addition of the reducing agent, ethanol causes the reduction of Pd (II) ions assembled along the PSS molecular chains, forming Pd (0) nuclei. At low pH (e.g., below 7), the reduction reaction rate of Pd (II) to Pd (0) is slow, resulting in low yield of Pd nuclei. Only part of the Pd (II) species assembled along the PSS chains are reduced and thus further crystallization and grain growth would be random, disturbing the ordered anisotropic orientation network of Pd^{2+} -PSS matrix and forming isolated and large Pd NPs (Figure 8.1a and b). On the other hand, under high pH conditions (e.g., at pH = 12), the reduction of Pd (II) to Pd (0) is fast. Thus the formation of Pd (0) nuclei along the PSS chain is simultaneous and instantaneous, preserving the anisotropic PSS- Pd^{2+} -PSS network matrix. The subsequent crystallization and grain growth of Pd (0) would adopt their ordered and anisotropic network configuration along the PSS molecular chains, forming highly distributed Pd NWNs (Fig.8.1d).

Figure 8. 3 TEM micrograph of Pd NWNs obtained using NaBH_4 as a reducing agent under conditions of $\text{pH} = 2$ and PSS: Pd ratio = 1:1. The inset is the high magnification TEM image.

To confirm the proposed mechanism of the PSS-mediated assembly of Pd NWNs, we replaced the reducing agent ethanol with NaBH_4 . Because NaBH_4 is a much stronger reducing agent as compared to ethanol, the fast reduction of Pd (II) to Pd (0) would occur at a much lower pH. Thus, the formation of Pd NWNs should occur at a much lower pH with NaBH_4 as compared to that with ethanol. This is just the case, as shown in Figure 8.3 of the TEM image of Pd NWNs obtained at a $\text{pH} = 2$ in the presence of PSS using NaBH_4 as the reducing agent. The PSS/Pd ratio was 1:1. The microstructure of the Pd NWNs synthesized in the presence of NaBH_4 as the reducing agent is very similar to that formed using ethanol as the reducing agent but at $\text{pH} 12$ (Fig. 8.1d). The diameter of the Pd NWNs is ~ 2.5 nm, also close to ~ 3 nm of Pd NWNs obtained using ethanol as the reducing agent (Fig. 8.1d). This indicates that formation of Pd NWNs can also be controlled by reducing agents.

8.3.3. Effect of the PSS/Pd Molar Ratio on the Morphology of Pd NWN

The interconnection and microstructure of Pd NWNs depend strongly on the molar ratio between the molecular units of PSS polyelectrolyte and Pd^{2+} precursors. Figure 8.4 shows TEM micrographs of Pd NWNs synthesized at different PSS to Pd ratios at pH 12 in the presence of ethanol as the reducing agent. When the PSS/Pd molar ratio is 1:4, the interconnectivity of Pd NWNs is low and agglomeration of Pd NWNs is observed (Figure 8.4 a). This may be caused by the excess of Pd^{2+} ions in the solution. With excess Pd^{2+} ions in solution, there would be insufficient PSS molecular chains to form complete anisotropic PSS- Pd^{2+} -PSS networks in solution. This may lead to the formation of isolated Pd NWNs patches (Figure 8.4 a). The reduction in Pd^{2+} concentration or the increase in PSS would increase the interconnection of the PSS- Pd^{2+} -PSS network in solution, thus improving the dispersion and connectivity of the Pd NWNs. The interconnectivity of Pd NWNs improves significantly with the increase of the PSS/Pd ratio (Figure 8.4 b and c). When the PSS: Pd molar ratio increases to 1:1, well interconnected 2D networks are formed (Figure 8.4 d). The network appears to be well dispersed and no agglomerates can be found (Figure 8.4 e). The diameter of the nanowires also slightly decreased. However, with a further increase of PSS concentration, the connectivity of NWNs decreases again, forming isolated Pd NWN segments with less agglomeration (Figure 8.4f-h). This could be explained by the fact that excess PSS would encase portion of the ordered and anisotropic orientated Pd-PSS matrix, which would stabilize and also at the same time inhibit the complete interconnecting of Pd NWNs, forming isolated small NWN segments. Pd NWNs with best interconnectivity and dispersion can be obtained at the

PSS/Pd ratio of 1:1.

Figure 8. 4 TEM micrographs of Pd NWNs synthesized at different PSS: Pd ratios of (a) 1:4,

(b) 1:3, (c) 1:2, (d) 1:1, (e) 1:1, (f) 2:1, (g) 3:1, and (h) 4:1 at pH = 12. Ethanol was used as the reducing agent.

8.3.4. Effect of Types of Polyelectrolytes

We also investigated the effect of polyelectrolytes on the formation of Pd nanostructures using the templateless and polyelectrolyte-mediated self-assembly method. Figure 8.5 is the TEM micrographs of Pd nanostructures synthesized with different polyelectrolytes under pH=12 and polyelectrolyte/Pd ratio=1:1. As shown, the microstructure of Pd nanostructures depends strongly on the nature of polyelectrolytes. When polydiallyldimethylammonium chloride (PDDA) polyelectrolyte is used, Pd NPs, not Pd NWNs, are obtained (Figure 8.5 a). PDDA is a positively charged polyelectrolyte. Thus there is no ionic interaction force to form an ordered and anisotropic orientation of Pd^{2+} -PDDA networks in solution as in the case of PSS. Here, PDDA primarily functions as stabilizers for the formation of Pd NPs. In contrast, when negatively charged Nafion and polyacrylate acid (PAA) are used in the reaction systems, Pd NWNs are obtained as expected (Figure 8.5 b, c). However, the dispersion and quality of Pd NWNs prepared in the presence of Nafion and PAA are not as good as that in the presence of PSS. Pd NWNs formed are not uniform and significant agglomeration of Pd NWNs is clearly visible. Agglomeration in Pd NWNs would be detrimental to the electrochemical surface areas and electrocatalytic activities of the Pd NWNs. Such significant differences in the quality of Pd NWNs are likely attributed to the significant differences in the polymeric molecular structure among PAA, Nafion and PSS. Thus, based on the results in the present study, PSS is a

suitable directing agent to synthesize uniformly distributed and highly dispersed 2-D Pd NWNs. The presence of bulky aromatic ring in the pendent group of PSS appears to be critical in the separation of PSS molecular chains during the self-assembly process, forming ordered and anisotropic networks in solution (Scheme 8.1).

Figure 8. 5 TEM micrographs of Pd nanostructures synthesized in the presence of (a) PDDA, (b) Nafion, and (c) PAA under conditions of pH = 12 and polyelectrolyte: Pd ratio of 1:1. Ethanol

was used as the reducing agent.

8.3.5. Electrochemical Characterization

The electrocatalytic activity of Pd NWNs for the electrooxidation of formic acid in acid medium was studied at room temperature. For the purpose of comparison conventional Pd nanocatalysts supported on high surface area carbon (Pd NP/C) was prepared by alcohol reduction method. Figure 8.6 shows the TEM micrograph of the Pd NP/C electrocatalysts. Particle size of Pd NPs deposited on high surface area carbon (XC-72) is in the range of 2.6-4.7 nm and the average diameter is ~3.5 nm. This is in the similar range of the diameter of nanowires (i.e., ~3 nm) of the Pd NWNs synthesized at pH 12 and PSS/Pd ratio 1:1.

Figure 8. 6 TEM micrograph of Pd NP/C electrocatalyst prepared by alcohol reduction method.

Figure 8.7(a) shows cyclic voltammograms (CVs) of formic acid oxidation in a 0.5 M H_2SO_4 + 0.5 M HCOOH solution on a Pd NWNs deposited on XC-72 carbon black (Pd NWN/C) and Pd NPs deposited on XC-72 carbon black (Pd NP/C). Pd NWNs were synthesized at pH 12 with PSS/Pd=1:1 using ethanol as the reducing agent. In both cases, Pd loadings on the glassy carbon electrode (GCE) were 0.01 mg cm^{-2} . Pd NWN/C and Pd NP/C show typical separated anodic peaks in the forward and reverse scans, similar to that of the ethanol oxidation reaction on Pd-based electrocatalysts in alkaline media.[135] Thus, the magnitude of the anodic peak current in the forward scan is also directly proportional to the amount of formic acid oxidized at the Pd electrocatalysts. The peak current for the formic acid electrooxidation is 2.82 mA on the Pd NWN/C electrode, significantly higher than 1.50 mA on the conventional Pd NP/C electrode. The forward peak potential for the electrooxidation of formic acid on the Pd NWN/C electrocatalysts is 0.145 V (*vs* SCE); lower than 0.192 V (*vs* SCE) for the reaction on the Pd NP/C electrocatalysts. The high peak oxidation current and low anodic peak potential show that Pd NWN/C electrocatalysts have higher electrocatalytic activity and faster kinetics than conventional Pd NP/C electrocatalysts, most likely due to the high density of active sites and large surface area of nanowire nanostructures with high-aspect-ratio, as shown in Figure 8.1. This indicates that the shape of nanostructures is important for the electrochemical activity of electrocatalysts, as reviewed recently by Welch and Compton.[153]

The electrochemical stability of Pd NWN/C and Pd NP/C electrodes for formic acid electrooxidation was also investigated by the chronoamperometric experiments at 0.1 V versus SCE in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at room temperature (Figure

8.7b). The polarization current for the formic acid oxidation shows a rapid decay, similar to that on the Pt-based electrocatalysts.[154] The electrooxidation reaction of HCOOH to CO₂ on Pd electrocatalysts could proceed via a dual path mechanism, a direct pathway in which HCOOH is oxidized directly to CO₂ and an indirect pathway with the formation of CO_{ads} intermediates.[155, 156] The decay in the anodic current could be related to the intermediate species poisoning of the HCOOH electrooxidation via the CO pathway or to the deactivation of the Pd electrocatalysts by an organic poisoning species.[29, 146] The decay for the reaction on the conventional Pd NP/C electrocatalysts is very sharp and fast, and at the end of the test the anodic current is 8×10^{-4} mA, close to zero. However, the current decay for the formic acid electrooxidation reaction on the Pd NWN/C electrocatalysts is significantly slower. With the increase of time, the difference between the current output for the reactions on Pd NWN/C and Pd NP/C electrocatalysts increases, indicating the high tolerance of Pd NWN/C electrocatalysts towards poisoning of the intermediates of the reaction in comparison with the conventional Pd NP/C electrocatalysts. This indicates that Pd NWN structure enhances the electrochemical stability of Pd electrocatalysts for the formic acid oxidation in acid solution. PSS electrolytes with SO₃⁻ function groups attached to Pd NWNs could also promote the electrocatalytic activity and stability of the Pd electrocatalysts for the formic acid electrooxidation reaction.[54]

Figure 8. 7 (a) CVs measured on Pd NWN/C and Pd NP/C electrodes in a 0.5 M H_2SO_4 + 0.5 M HCOOH solution at a scan rate of 50 mV s^{-1} , and (b) chronoamperometric curves for formic acid electrooxidation at 0.1 V versus SCE on a Pd NWN/C and Pd NP/C electrode in a 0.5 M H_2SO_4 + 0.5 M HCOOH solution. The Pd loading was 0.01 mg cm^{-2} .

8.3.6. Effect of PSS/Pd Molar Ratio on Their Electrocatalytic Activities for Formic Acid Oxidation.

Figure 8. 8 CVs measured on Pd NWN/C synthesized with different PSS/Pd molar ratios electrodes in a 0.5 M H_2SO_4 +0.5 M HCOOH solution at a scan rate of 50 mV s^{-1}

Finally, the electrocatalytic activities for the formic acid electrooxidation on Pd NWNs synthesized with the different molar PSS/Pd ratios were also studied, as shown in Fig. 8.8. Pd NWNs were deposited on high surface area carbon, forming Pd NWNs/C electrocatalyst and Pd loading was 0.01 mg/cm^2 . It was found that Pd nanowire networks synthesized with PSS/Pd ratio 1:1 show highest anodic current density for the formic acid electrooxidation and those synthesized with PSS/Pd ratio

1:4 show the lowest anodic current density. The high electrocatalytic activity of Pd NWNs synthesized with PSS/Pd ratio 1:1 can be attributed to the well-dispersed and well-interconnected network structure, as shown in Figure 8.4 d and e. With the decrease of the PSS/Pd molar ratio, the anodic current decreased significantly, clearly due to the aggregation of Pd NWNs, as shown in Figure 8.4 a-c. On the other hand, with the further increase of the PSS/Pd molar ratio, the anodic peak current also decreased as compared to that for the reaction on Pd NWNs/C synthesized with PSS/Pd ratio 1:1, nevertheless, the reduction in the anodic peak current is more gradual than that of the Pd NWNs/C synthesized with PSS/Pd ratio lower than 1:1. The most likely reason could be related to the observation that, with the increase of the PSS/Pd molar ratio, the nanowire networks became smaller and patched but the agglomeration of Pd NWNs is not as serious as that synthesized with PSS/Pd ratios lower than 1:1. The present results indicate that interconnectivity of Pd NWNs is an important factor for the highly effective electrocatalytic activity for the electrooxidation of formic acid probably due to the effective electronic conduction and passage through the highly interconnected nanowire networks for the electrochemical oxidation reactions.

8.4. Conclusions

This study presents a novel synthesis method of Pd NWNs using ionic polyelectrolytes as directing agents. Pd nanostructures from nanocubes to nanowire network can be synthesized via the control of the reduction rate of Pd (II) to Pd (0) by adjusting pH of the solution or by use of ethanol or NaBH₄ reducing agent. Pd NWNs

with high aspect ratio, uniform dispersion and high interconnectivity were obtained under conditions of PSS/Pd ratio 1:1 and pH 12. Most importantly, the Pd NWN/C electrocatalysts show a much better electrocatalytic activity and better stability than conventional Pd NP/C electrocatalysts. The results indicate that Pd NWNs are promising high performance electrocatalysts in DFAFCs. The templateless and PSS polyelectrolyte-mediated assembly method for the synthesis of nanowire structure is also advantageous as compared to other methods such as template-based method, being simple and avoiding the use of hard templates and environmental unfriendly chemicals.”

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Chapter 9 Conclusions and Recommendations for Future Work

9.1. Conclusions

The present research work focuses on the synthesis of nanostructured electrocatalysts with improved electrocatalytic performance for the reactions in PEMFCs (including DMFCs and DFAFCs). “On one hand, carbon nanotubes as electrocatalyst supports were investigated in details. In this part, we first developed novel non-covalent functionalization methods for CNTs as electrocatalyst supports, resulting in enhanced electrocatalytic activity; meanwhile, the further fundamental study on Pt/CNT electrocatalysts leads to some important and interesting results and conclusions: (1) the electrocatalytic activity of methanol oxidation on Pt NPs could be effectively tuned by introducing specified functional groups during the surface functionalization process of CNTs; (2) the correlation between the electrocatalytic activity and the interconnectivity of Pt nanoparticles on CNTs was proposed. On the other hand, on the basis of the conclusion from the above fundamental study that interconnected Pt NPs are more active than isolated ones, we designed novel Pt and Pd electrocatalysts with nanowire network structures and found that their performances for electrocatalytic reactions (methanol oxidation and oxygen reduction reactions and formic acid oxidation reaction, respectively) were significantly improved, compared to the conventional particle-shaped electrocatalysts. Specifically, the significant findings of this work are shown below in details:

The Pt/MWCNT (or PtRu/MWCNT) electrocatalysts with increased

electrochemical surface area and electrochemical accessibility, improved utilization efficiency, and enhanced electrocatalytic activity for methanol oxidation reaction were obtained. By developing novel non-covalent functionalization methods (including bifunctional molecule stacking and polymer wrapping technique) for CNT modification, we successfully synthesized PtRu/1-AP-MWCNTs and Pt/PDDA-MWCNTs. It was found that the metal NPs on the as-functionalized MWCNTs were well-dispersed and uniformly distributed with fine average particle size. The as-developed electrocatalysts are more active than those supported on acid oxidized MWCNTs. Besides, such functionalization methods also preserve the perfect structure of MWCNTs without introducing any defect sites on them.

On the basis of the as-developed non-covalent functionalization method, we successfully introduced some specified and charged functional groups. Our spectroscopic and electrochemical characterization and DFT calculation for the first time showed that negatively charged functional groups could weaken the chemical adsorption with the poisonous CO intermediate generated in methanol oxidation on Pt NPs and thus enhance their electrocatalytic activity. The enhanced activity is attributed to the electron donation effect from the negatively charged functional groups to Pt surface. This research provides a novel guideline for the design of efficient electrocatalysts, that is, through the modification of the electronic environment of Pt NPs.

The correlation between the electrocatalytic activity and interconnectivity of Pt NPs on MWCNTs was for the first time proposed. Interconnectivity is another factor that

can be used to modify the catalytic activity of Pt NPs. This correlation should be able to be extended to other metal electrocatalysts. It has been illustrated that the emergence of the grain boundaries in the interconnected particles contributes to their enhanced activity related to the isolated particles. According to this conclusion, we designed novel highly interconnected electrocatalyst: Pt (Pd) nanowire networks.

We successfully synthesized Pt (Pd) nanowire network (NWN) using surfactant or polyelectrolyte as soft templates and our experimental results demonstrated that the NWN structured electrocatalysts are more active than the particle-shaped electrocatalysts. This finding also confirms the conclusion in Chapter 6 that interconnected Pt particles have higher electrocatalytic activity than isolated particles.”

9.2. Recommendations for Future Work

While we have obtained efficient nanostructured electrocatalysts for the electrocatalytic reactions in PEMFCs and addressed the origin of the enhanced electrocatalytic activity, the further studies are needed to develop the current work. The following research directions are suggested:

- 1) Using the as-developed functionalization method to modify other types of CNTs, such as single-walled CNTs and double-walled CNTs, and to study their electrocatalytic performances as catalyst supports. It is worthy pointing out that the seed-mediated growth method of Pt NPs on CNTs as described in Chapter 6 could be utilized for the synthesis of Pt/SWCNTs with ultrahigh Pt loading,

which could be potentially used for the electronic nano-devices.

- 2) Investigating the effect of the amount of functionalized groups on the electrocatalytic activity. For example, for the functionalization of CNTs by PDDA, the amount of PDDA may be controlled by modifying the parameters during the functionalization process. Furthermore, their effect on electrocatalytic activity of Pt should be addressed.
- 3) Using some advanced spectroelectrochemical equipments such as in situ infrared spectroscopy (in-situ FTIR) and differential electrochemical mass spectrometry (DEMS) to characterize the as-prepared electrocatalysts for the mechanistic study of the electrochemical reactions. For example, FTIR and DEMS could be used to study the origin of enhanced electrocatalytic activity of interconnected Pt NPs and negatively charged functional groups modified Pt NPs.
- 4) The relationship between the electrocatalytic activity and interconnectivity of bimetallic NPs (i.e., PtRu NPs) could be studied further.
- 5) Using other molecules to non-covalently functionalize CNTs. For example, heteropolyacid could be self-assembled on PDDA wrapped CNTs, which is subsequently used as electrocatalyst supports. It's believed that the existence of metal oxide component in heteropolyacid may enhance the electrocatalytic activity of Pt or Pt-based alloy NPs.
- 6) Fuel cell testing on the synthesized electrocatalysts. For the practical final application of these electrocatalysts, the fuel cell testing should be performed.

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