Hybrid materials derived from polydopamine-transition metal complexes : formation mechanism and electrocatalytic functions

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NANYANG
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UNIVERSITY

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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

A thesis submitted to the Nanyang Technological
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for the degree of Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

15/12/2017

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Date

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Ang Jia Ming

Abstract

In this PhD study, polydopamine (PDA)-transition metal hybrids synthesized via in situ polymerization of dopamine (DOPA) with the presence of transition metal species are studied. Iron(III) ions and cobalt(II) ions were chosen as the model systems used for this PhD study. Substantial efforts have been devoted to understand the interactions between DOPA/PDA and iron(III)/cobalt(II) ions, and the effects of the transition metal ions on oxidation polymerization and self-assembly behaviours of the hybrids.

For the iron(III) ions system, it was found that the oxidative polymerization of dopamine and Fe(III)-PDA complexation co-contributed to the in situ “polymerization” process. During the polymerization process, the morphology of the complex nanostructure transformed from sheet-like to spherical due to the decrease in hydrophilic groups caused by the covalent polymerization, resulting in re-self-assembly of the PDA oligomers to reduce surface area. For the cobalt(II) ions system, cobalt(II) ions formed complex with hydroxyl ions and not DOPA monomers. With the initiation of oxidation, cyclization and polymerization of DOPA, the hydroxyl ions were then displaced by the oxidized DOPA units or PDA oligomers. When both iron(III) ions and cobalt(II) ions are added into the system, iron(III) ions were observed to play a more dominant role during the in situ polymerization process.

The transition metal/PDA hybrids could be converted into transition metal/carbonized polydopamine (C-PDA) nanocomposites via a facile annealing process. These transition metal/C-PDA nanocomposites, $\text{Fe}_3\text{O}_4/\text{C-PDA}$ and $\text{CoFe}_2\text{O}_4/\text{CoFe/C-PDA}$, were then investigated as oxygen electrocatalyst for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in air cathode of primary and rechargeable zinc-air batteries (ZnABs).

In the last part of this PhD study, the fabrication of a free-standing three dimensional (3D) carbon nanofibrous macrostructure embedded with CoFe/CoFe₂O₄ core/shell nanoparticles was reported. The carbon nanofibrous macrostructure was fabricated by the combination of electrospinning of polyacrylonitrile (PAN) and in situ polymerization of DOPA followed by carbonization. The CoFe₂O₄/CoFe/C-PDA nanofibers showed good ORR and OER electrocatalytic activity and was employed as a binder- and additive-free air cathode in rechargeable ZnAB.

This PhD study has provided insights into the underlying mechanisms for the formation of PDA-transition metal hybrid nanostructures during the in situ polymerization process. With the knowledge obtained from this PhD study, it is possible to better predict and control the morphologies of the transition metal/PDA hybrids and transition metal/C-PDA nanocomposites that can be utilized as efficient oxygen electrocatalysts and also for other electrochemical reactions.

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Abbreviations

1D	One Dimensional
3D	Three Dimensional
Ag	Silver
Au	Gold
B	Boron
BET	Brunauer–Emmett–Teller
CNFs	Carbon Nanofibers
CNTs	Carbon Nanotubes
CoCl ₂ ·6H ₂ O	Cobalt(II) Chloride Hexahydrate
C-PDA	Carbonized-Polydopamine
CV	Cyclic Voltammetry
DMF	Dimethylformamide
DOPA	Dopamine
ESCA	Electron Spectroscopy for Chemical Analysis
EVs	Electric Vehicles
EXAFS	Extended X-ray Absorption Fine Structure
FeCl ₃	Iron(III) Chloride
FTIR	Fourier Transform Infrared Spectroscopy
GDE	Gas Diffusion Electrode
IrO ₂	Iridium(IV) Oxide
IrO ₃	Iridium Trioxide
KOH	Potassium Hydroxide
LIBs	Lithium Ion Batteries
LSV	Linear Sweep Voltammetry
MWCNTs	Multi-Walled Carbon Nanotubes
N	Nitrogen
NaOH	Sodium Hydroxide
NEXAFS	Near Edge X-ray Absorption Fine Structure

O	Oxygen
OER	Oxygen Evolution Reaction
OH ⁻	Hydroxyl Ions
ORR	Oxygen Reduction Reaction
P	Phosphorous
PAN	Polyacrylonitrile
Pd	Palladium
PDA	Polydopamine
PNFs	Porous Nanofibers
PS	Polystyrene
Pt	Platinum
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RDE	Rotating Disk Electrode
RHE	Reversible Hydrogen Electrode
RuO ₂	Ruthenium(IV) Oxide
RuO ₄	Ruthenium Tetroxide
S	Sulfur
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SiO ₂	Silicon Dioxide
SSLS	Singapore Synchrotron Light Source
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TMOs	Transition Metal Oxides
Tris	Trisaminomethane
UV-vis	Ultraviolet-visible
VSM	Vibrating Sample Magnetometer
XAFS	X-ray Absorption Fine Structure
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy

XRD	X-Ray Diffraction
Zn(OH)_4^{2-}	Zincate Ions
ZnABs	Zinc-Air Batteries
ZnO	Zinc Oxide

Chapter 1

Introduction

In this chapter, the motivations and objectives of this PhD study are presented. Firstly, the background of polydopamine (PDA), its self-assembly mechanism and interactions with transition metals are briefly introduced. A short introduction is also presented on potential applications of the nanocomposite materials derived from PDA-transition metal complexes as the electrocatalysts for zinc-air batteries (ZnABs). The motivations behind this PhD study as well as the significance of the studies are then laid out. Based on the motivations, detailed objectives of this PhD study are then stated. Finally, the significant findings derived from this work are highlighted.

1.1 Introduction

1.1.1 Transition Metal-Polydopamine Hybrids

Polydopamine (PDA) is a mussel-inspired material that was brought into the spotlight by Haeshin Lee in 2007. Lee et al. first reported PDA as a material that has similar molecular structure to mussel adhesive's plaques that were responsible for the superior adhesive properties of mussels.¹ Since then PDA has garnered huge amount of interest primarily due to its ability to facilely deposit on almost all kinds of surfaces in slightly basic aqueous solutions. PDA also has good intrinsic adhesion properties, allowing it to interact with both organic and inorganic materials. Additionally, the thickness of the PDA coating can be easily controlled by varying various parameters such as time and concentration. The deposited PDA layer also has good chemical stability and versatility for secondary reactions. Apart from the facile deposition ability with easily controlled thickness, PDA can also form colloidal spheres with easily controllable size.²⁻⁴ Although the mechanism for the formation of PDA is still under debate, it is widely accepted that the process involves both covalent polymerization and non-covalent self-assembly.⁵⁻⁷ PDA has been used in a wide range of applications such as biomedical science, sensors, water treatment, polymer nanocomposites, catalysis and also energy.⁸⁻¹⁴ The application of PDA in energy storage and conversion mainly lies upon the ability of PDA to be converted into nitrogen-doped graphitic-like carbon, which has properties similar to those of nitrogen-doped multi-layered graphene. It has been widely reported that the use of nitrogen-doped carbon as conductive electrodes can bring about improvements in performances of electrochemical devices such as lithium-ion batteries (LIBs), ZnABs and supercapacitors. Similarly, the carbonized PDA (C-PDA) was also reported to have good electrical conductivity which is beneficial to charge transport properties that are important for many electrochemical reactions. The self-assembly and facile surface deposition abilities of PDA together with its ability to produce nitrogen-doped carbon brings about the possibility of facilely tailoring the morphologies of the nitrogen-doped carbon to suit the needs of specific applications.

The ability of dopamine (DOPA) and PDA to bind to various transition metal species through coordination chemistry is another striking feature that has drew considerable amount of attention. The coordination bonds formed between catechol groups and iron(III) ions have been widely studied and reported. On this basis, many iron/PDA hybrids have been formed by incorporating iron species onto PDA or vice versa. Other transition metal species that have been identified to form coordination bonds with PDA includes silver oxide, manganese(II) ions and titanium(IV) oxide.¹⁵⁻¹⁷ The reaction of PDA with the various transition metal species will lead to the formation of transition metal/PDA hybrid materials that can be used in many applications. Formation of transition metal/C-PDA and transition metal oxide/C-PDA nanocomposites from transition metal/PDA hybrids have also been achieved through annealing and used for various electrochemical applications such as electrodes in lithium-ion batteries and electrocatalysts in zinc-air batteries (ZnABs).^{18, 19}

Despite the large amount of works that have been carried out on transition metal/PDA hybrids and also transition metal/C-PDA nanocomposites, most of these works have focused solely on the applications of the hybrids and nanocomposites. There has been no report on the effects of the addition of different transition metal species on the in situ polymerization process of DOPA, where transition metal species are added prior to the polymerization of PDA and the formation of complex and polymerization occur simultaneously. Instead of merely exploring the applications of the hybrid materials, studies should be conducted to investigate how the addition of transition metal species will affect the in situ polymerization process, and the structures and morphologies of the PDA hybrids formed. By establishing an in depth understanding of the formation mechanisms of the PDA hybrids, it is then possible to optimize and manipulate the structures and morphology of the PDA hybrids. With the ability to predict and control the self-assembly process, PDA hybrids with preferred chemical compositions, structures and morphologies can then be facilely fabricated for specific applications.

1.1.2 Electrocatalysts and Zinc-Air Batteries

In this PhD work, in addition to studying the formation mechanisms of the transition metal/PDA hybrids, the applications of the resultant transition metal/C-PDA nanocomposites as electrocatalysts for zinc-air batteries have also been explored.

ZnABs have attracted significant attention over the past few years as an alternatives for LIBs due to its myriad of advantages, such as high theoretical energy density, low cost and environmental benignity.²⁰ Due to the sluggish reaction kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in rechargeable ZnABs, oxygen electrocatalysts are therefore required. Noble metal-based electrocatalysts have been identified to have high electrocatalytic activity. The high costs of these noble metal-based oxygen electrocatalysts have, however, prevented their widespread commercial use. In this respect, many works have been conducted to study alternate materials for ORR, OER and bifunctional electrocatalysts, leading to the reports and discovery of many carbon-based, transition metal oxides-based and transition metal oxides/carbon-based electrocatalysts. The transition metal oxides/carbon-based electrocatalysts are favored as they eliminate the disadvantages of carbon-based and transition metal oxides-based electrocatalysts, such as low active sites density of carbon and leaching and agglomeration of transition metal oxide nanoparticles. The combination of carbon and transition metal oxide nanoparticles may also provide a synergistic effect. In this PhD work, the transition metal/C-PDA nanocomposites are investigated as candidates for bifunctional oxygen electrocatalyst to demonstrate that the in situ polymerization of DOPA is a facile and versatile process to tailor the structure and morphology of the hybrids and corresponding nanocomposites to achieve desired properties.

1.2 Objectives

Based on the above discussion, two major objectives are set out for this PhD study:

1. The first objective is to clarify the effect of different transition metal species on the in situ polymerization process of DOPA and the possible impact of the complexation on structures and morphologies of the hybrids, and demonstrate potential applications of the transition metal/C-PDA nanocomposites. Two transition metals (Fe(III) and Co(II)) are selected as model systems. Through varying synthesis parameters used in the in situ polymerization, probing the formation of coordination bonds, and monitoring the morphological evolution of the PDA hybrids, greater understanding of the in situ polymerization process can be achieved. The understandings derived from this PhD study will allow for the optimization and possible design of morphologies and structures of the transition metal/ PDA hybrids and corresponding nanocomposites for specific applications.
2. The second objective of this PhD study is to utilize the knowledge gained from the aforementioned mechanism studies to fabricate transition metal/C-PDA nanocomposites with desired structures and morphologies, and demonstrate the usefulness of such nanocomposites for practical applications. Specifically, using electrospun porous and solid nanofibers as templates for deposition of PDA hybrids, carbon porous nanofibers and carbon nanofibrous macrostructures with high specific surface area and decorated with transition metal oxide nanoparticles are fabricated and studied as bifunctional oxygen electrocatalyst in order to demonstrate the versatility of this approach in manipulating morphology.

1.3 Dissertation Overview

In *Chapter 1*, the background on PDA, its self-assembly and coordination chemistry with transition metal are briefly discussed. The potential applications of C-PDA nanocomposites derived from transition metal/PDA hybrids as the electrocatalysts for ZnABs are also discussed. Motivations leading to the study as well as the

significance of the studies are addressed. Detailed objectives of this PhD study are then listed. Finally, the significant findings derived from this PhD work are highlighted.

In *Chapter 2*, PDA is introduced with emphasis on its facile surface deposition capability and ‘polymerization’ mechanism. The unique ability of PDA to form complexes with transition metal species is then elaborated, followed by a discussion on the advantages of PDA as a carbon precursor. Studies on transition metal/PDA hybrids and transition metal/C-PDA nanocomposites are also reviewed. To highlight the potential of the C-PDA-based nanocomposites for energy storage and conversion applications, the theory and working principles behind ZnABs are discussed followed by a brief review of recent research on ORR, OER and bifunctional electrocatalysts. The electrospinning technique for producing nanofibers is also introduced with supplementary discussions on the preparation of carbon nanofibers as templates for PDA deposition. Based on the literatures being reviewed, it is identified that a better understanding of the underlying mechanism for the formation of transition metal/PDA hybrids needs to be established. With the combination of hybridization and coating process of PDA with electrospinning, a new facile route for the preparation of high-performance bifunctional oxygen electrocatalysts may be realized.

In *Chapter 3*, experimental methods used to prepare samples for the works carried out in this PhD study are presented. Reasons behind the selection of these methods are also provided. Basic theories and working principles behind the chosen characterization techniques and equipment are discussed, justifying the data collection and analysis methods used.

In *Chapter 4*, the one-pot synthesis of Fe(III)-PDA complex nanospheres is reported, and their structure, morphology evolution and possible formation mechanism are revealed. It is verified with XAFS that both the oxidative polymerization and Fe(III)-PDA complexation contributed to the ‘polymerization’ process. Morphology of the

Fe(III)-PDA complex nanostructures transformed from sheet-like to spherical during the polymerization process. The results suggest that the formation of the spherical morphology is likely driven by covalent polymerization-induced decrease of hydrophilic functional groups, which leads to re-self-assembly of the PDA oligomers to reduce surface area. By simple annealing, the Fe(III)-PDA complex nanospheres are converted to Fe₃O₄/C-PDA nanospheres and used as an electrocatalyst for ORR in primary ZnABs.

In *Chapter 5*, the one-pot synthesis of Co(II)-PDA and Co(II)-Fe(III)-PDA complexes are reported. Cobalt(II) ions do not form coordination bonds with DOPA monomers; instead, they form complex with hydroxyl ions. With the oxidation, cyclization and polymerization of DOPA, the hydroxyl ions are then displaced by the oxidized DOPA units or PDA oligomers. In the Co(II)-Fe(III)-PDA system, iron(III) ions, which form coordination bonds with DOPA are found to have a dominating effect over the morphology of the hybrid nanostructures. With the use of porous nanofibers as template for deposition of PDA hybrids and subsequent annealing, CoFe₂O₄/CoFe/C-PDA porous nanofibers (PNFs) are facilely obtained. Electrochemical studies suggest that the CoFe₂O₄/CoFe/C-PDA PNFs can effectively catalyzes ORR via an ideal 4-electron pathway and outperform commercial Pt/C in catalyzing OER. ZnABs based on CoFe₂O₄/CoFe/C-PDA PNFs also showed longer cycling life and higher cycling stability than their counterparts that are based on commercial Pt/C and CoFe₂O₄/CoFe/C-PDA nanospheres.

In *Chapter 6*, fabrication of a three dimensional (3D) carbon nanofibrous macrostructure decorated with CoFe/CoFe₂O₄ core/shell nanoparticles is achieved via the combination of electrospinning of polyacrylonitrile (PAN) and the facile surface deposition of Co(II)-Fe(III)-PDA hybrids. CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures with good electrocatalytic activities and stabilities for ORR and OER are successfully obtained after the annealing process. The morphology and structure of the nanofibers are studied and discussed.

In *Chapter 7*, the threads of this thesis are being drawn together. The conclusions from the various chapters are summarized and reconciled with the objectives stated in Chapter 1. Significant findings and outcomes derived from the works, including their possible implications on future work, are discussed. Lastly, some recommendations for future works are also proposed.

1.4 Findings and Outcomes

Briefly, this PhD study led to several significant findings and novel outcomes:

1. In this PhD study, for the first time, it is verified that coordination bonds between transition metal and PDA are present in the transition metal/PDA hybrids synthesized via the in situ polymerization process. A mechanism for the in situ polymerization process is also proposed, i.e., both oxidative polymerization of DOPA and Fe(III)-PDA complexation contribute to the formation of the PDA hybrid.
2. From this PhD study, it is proven that the addition of different transition metal as well as the feed ratio of the transition metal to DOPA will affect the final morphology of the transition metal/PDA hybrids. With the addition of two transition metal species, the in situ polymerization and eventual morphology will be dominantly affected by the transition metal that forms coordination bonds with DOPA before the polymerization process is initiated.

The understanding derived from the findings stated above will allow for the design and optimization of the structures and morphologies of the transition metal/PDA hybrids for specific applications. As demonstrated in Chapter 5 and 6 of this thesis, CoFe₂O₄/CoFe/C-PDA PNFs with high specific surface area and 3D CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures can be facilely

fabricated using the in situ polymerization approach and used as effective bifunctional oxygen electrocatalysts.

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Chapter 2

Literature Review

In this chapter, polydopamine (PDA), a mussel inspired material, is firstly introduced with the emphasis on its facile surface deposition capability and “polymerization” mechanism. The unique ability of PDA to form complexes with transition metal species is then elaborated, and the advantages of PDA as a carbon precursor are also discussed. The studies on PDA/metal hybrids and carbonized PDA (C-PDA)/metal/metal oxide nanocomposites are also reviewed. To highlight the potential of the C-PDA-based nanocomposites for energy storage and conversion applications, the theory and working principles behind Zn-Air batteries (ZnABs) are subsequently discussed followed by a brief review of recent research on oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and bifunctional electrocatalysts. The electrospinning technique for producing nanofibers is also introduced with additional discussions on preparing carbon nanofibers as templates for PDA deposition. Based on the literatures being reviewed, it is identified that a better understanding of the underlying mechanism for the formation of PDA/transition metal hybrid materials needs to be established, which can guide us to explore the applications of the hybrids. More specifically, by combining the simultaneous hybridization and coating process of PDA with electrospinning techniques, a facile new route for preparation of high-performance ORR and OER electrocatalysts may be realized.

2.1 Polydopamine

2.1.1 Introduction

Polydopamine (PDA) is a biomimetic material inspired by the excellent adhesion ability of mussels. In 2007, Lee et al. discovered that PDA had similar molecular structure to that of 3,4-dihydroxy-L-phenylalanine present in plaque of mussels and showed that PDA could be facily deposited on almost all kinds of surfaces.¹ The deposition of PDA was achieved by the self-polymerization of dopamine hydrochloride (DOPA) under aerobic, basic aqueous environment and has been demonstrated on various substrates such as metals, oxides, polymers, ceramics, carbon, etc.¹⁻⁴ The main advantage of PDA is that it can be deposited on almost all types of inorganic and organic substrates with controllable film thickness, good stability and chemical versatility. PDA coating of both bulk substrates and nanostructures have gathered interests in a wide variety of fields such as biomedical science, sensors, water treatment, polymer nanocomposites, energy storage/conversion and catalysis.⁵⁻⁹ The study of PDA-based materials has rapidly increased in recent years, as shown by the large increase in number of publications over the years (Figure 2.1).

Figure 2.1 Number of publications of polydopamine sorted by year. Data were collected from “Web of Science”. “Polydopamine” was keyed into the “topic” search box (Date of search: 28 September 2017).

2.1.2 Preparation Methods and Formation Mechanisms of Polydopamine

The polymerization of PDA in aerobic, alkaline aqueous environment is by far the most common method used. The monomer, DOPA, can be oxidized and spontaneously self-polymerize under slightly alkaline conditions ($\text{pH} = 8$) and in the presence of oxygen as the oxidant. The polymerization of DOPA is accompanied with a change in the color of the solution from colorless to pale brown and finally dark brown. The thickness of the PDA film can be facilely controlled by adjusting the concentration of DOPA monomer and the polymerization time. However, the maximum thickness of the PDA film in a single reaction was found to be 50 nm and the further increase of monomer concentration or reaction time will not increase the thickness of the PDA film.¹⁰ Electropolymerization of DOPA in an anaerobic environment has also been studied. The polymerization process proceeds using cyclic voltammetry within a given potential range.¹¹ The electropolymerization method is however limited by the requirement of the use of electrically conductive materials.

Apart from forming PDA films on substrates, PDA was also found to be able to form colloidal spheres with easily controllable dimensions. Ju et al. reported the successful synthesis of PDA nanoparticles through the neutralization of DOPA with NaOH.¹² Several other works have also showed the successful synthesis of PDA nanospheres with well-controlled size by polymerizing PDA in a mixture of water, ethanol and ammonia. The size of the nanospheres was varied by adjusting the ratio of aqueous ammonia and DOPA in the solution.¹³⁻¹⁵ Monodispersed PDA nanospheres with tunable diameter have also been synthesized with mixed solvents of Tris buffer solution and alcohol.¹⁶ Such PDA nanoparticles and nanospheres are useful for producing core/shell nanostructures because of the presence of abundant amine and catechol groups on their surface. These functional groups can serve as both the starting point for covalent modification with desired molecules and also anchors for the loading of other material such as transition metal ions.¹⁷ Core/shell

nanostructures such as PDA/Fe₃O₄ and PDA/Ag have been successfully synthesized.¹⁶

Figure 2.2 Proposed covalent polymerization mechanism of DOPA.¹⁸

Despite the facile polymerization process and vast potential applications of PDA across various fields, the molecular mechanism behind the formation of PDA has not been elucidated due to the complex redox process as well as the production of a series of intermediates during the polymerization process. In the early days, the formation of PDA was believed to proceed to a process similar to the synthetic pathway of melanin.¹⁹⁻²¹ As shown in Figure 2.2, DOPA will first oxidize to dopamine-quinone followed by the intramolecular cyclization via 1,4 Michael-type addition to obtain leucodopaminechrome. The leucodopaminechrome suffers from further oxidation into dopaminechrome and undergoes rearrangement to form 5,6-dihydroxyindole, which is then oxidized to 5,6-indolequinone.²² The two reaction products are capable of forming covalent bonds leading to the formation of dimers and oligomers, and eventually leading to the cross-linked polymer.

Another alternate mechanism for the formation of PDA was also proposed and was in stark contrast to that of the melanin model. Dreyer et al. proposed a

supramolecular aggregate of oxidized DOPA monomers, in the form of 5,6-dihydroxyindole and 5,6-indolequinone, cross-linked together via strong, non-covalent forces such as hydrogen bonding, charge transfer and π -stacking (Figure 2.3).²³

In parallel to the above two models, Hong et al. proposed that the formation of PDA was a result of the combination of both covalent polymerization and non-covalent self-assembly (Figure 2.4).²⁴

Figure 2.3 Proposed non-covalent interactions of DOPA.²³

Figure 2.4 PDA synthesis via two routes: a) covalent bond-forming oxidative polymerization and b) physical self-assembly of DOPA and 5,6-dihydroxyindole.²⁴

2.1.3 Interactions of Polydopamine with Transition Metals

Another attractive feature of PDA is its ability to bind to several transition metal species by the formation of coordination bonds. The transition metal ion binding

capability is attributed to the presence of large amount of functional groups such as catechol and amine groups present on the surface of PDA. Early studies by Wilker et al. and Sever et al. showed that the adhesive plaques in marine mussels, responsible for the superior adhesive property, were formed by the cross-linking of catechol-containing proteins with iron(III) ions.^{25, 26} Mimicking the characteristic of these mussel adhesive proteins, iron(III) ions have since been used to cross-link catechol-containing synthetic polymers to produce self-healing networks or hydrogel. The degree of cross-linking between the catechol groups and iron(III) ions were later found to be highly pH dependent, with one iron(III) ion chelating with one, two or three catechol groups at pH range of <5.6, 5.6-9.1 and >9.1, respectively.²⁷⁻²⁹ Huang et al. also reported that with the addition of a tiny amount of iron(III) salt into an aqueous suspension of PDA-coated clay, they were able to form supramolecular hydrogels at low clay content. This was achieved through the formation of coordination bonds between iron(III) ions and PDA coated clay resulting in the self-assembly into three-dimensional networks.³⁰ The strong coordination bond between catechol groups on PDA and iron(III) ions was also employed to produce PEI/PDA coated CNTs multilayer film. The crosslink between the films were enhanced by the coordination bonds during the layer by layer spraying process.³¹ More recently, Qi and team observed that the addition of iron(III) ions to PDA dots will trigger the transformation of morphology from that of aggregated plate-like to uniform willow leaf-like. The change in morphology was a result of the oxidative nature and coordination ability of iron(III) ions. As such, they also proposed a simple fluorescent detection method for iron(III) ions.³²

Apart from iron(III) ions, there have been a handful of other transition metal species that have been found to be able to form coordination bonds with PDA. Zhang et al. reported the formation of titanium(IV)-catechol coordination complex in protamine/titania/polydopamine hybrid microcapsules. The hybrid microcapsules were shown to display better superior mechanical stability due to the formation of the Ti(IV)-catechol coordination complex between the layers.³³ Hollow, mesoporous three dimensional nanoarchitectures containing ultrafine Mo₂C nanoparticles on

nitrogen-doped carbon nanosheets was fabricated based on the formation of complex between MoO_4^{2-} and dopamine. The synthesized sample was shown to be an effective and cheap electrocatalyst for ORR due to the abundant exposed active sites and good electron transfer.³⁴ Coordination interactions between PDA and silver oxide nanoparticles have also been reported in the production of a tri-layer film of silicon, PDA and silver oxide.³⁵ Miao et al. have also reported the use of manganese(II) chelated PDA nanoparticles as a novel theranostic agent. There was no need for extrinsic chelators due to the intrinsic chelating properties of PDA.³⁶ Nickel(II) ions were reported to be able to accelerate the assembly of DOPA oligomers during the polymerization process by forming coordination bonds with the oligomers.³⁷

Aside from its metal ion chelation ability, PDA is also found to be able to reduce some noble metals under basic environment. Wu et al. reported a facile and green method to synthesize PDA/Ag nanocomposite particles. Silver ions were introduced, absorbed on the surface of PDA nanoparticles and in-situ reduced to metallic Ag nanoparticles with the aid of the active catechol and amine groups.³⁸ Luo et al. also reported the in situ reduction of Au ions on PDA when HAuCl_4 was added to a solution of graphene/PDA.³⁹ The catechol group present in PDA was able to release electrons when oxidizing into quinone leading to the reduction of the metallic cations.

The ability of PDA to interact with the various transition metal species as well as its reduction ability has created substantial interest in the production of a wide range of organic-inorganic hybrid materials that can be converted into transition-metal/carbon hybrid materials which will be discussed below.

2.1.4 Polydopamine as a Carbon Source

PDA has been identified as an excellent carbon precursor as it produces N-doped graphitic-like carbon with high yield. The chemical structure and properties of C-PDA have also been found to differ from those of other carbon source attributed to

the unique structure of PDA. First report for the carbonization of PDA was reported by Dai et al. in 2011.⁴⁰ Liu et al. employed PDA as a carbon source with silica nanospheres as a sacrificial template, producing uniform hollow carbon spheres. PDA was successfully converted into C-PDA at 800 °C in nitrogen and the carbon yield was nearly 60 %. The structure of C-PDA in the form of thin film on oxidized silicon wafer was investigated by Kong and co-workers. They found that C-PDA has a layered structure with an interlayer spacing of 0.37 nm, slightly smaller than that of the PDA film. From XRD, they also verified that C-PDA resembles that of a graphite-like layered structure. XPS analysis showed that nitrogen and oxygen are only partially removed when PDA is annealed at 700 °C.⁴¹ The doped nitrogen in C-PDA was found to consist of graphitic, pyridinic and pyrrolic N.⁴² The carbonization of PDA is usually performed at temperatures of above 700 °C in an inert environment such as flowing nitrogen or argon gas.^{15, 40, 43, 44} The slight difference in chemical structures across the various reports may be due to the different conditions used during the polymerization and annealing process.

Apart from the high temperature annealing to obtain C-PDA, the hydrothermal treatment of DOPA at 180 °C was also found to be able to produce C-PDA.⁴⁵ The as-prepared carbon nanoparticles have an average size of approximately 3.8 nm and have a sp^2 graphitic structure. The surface of the carbon nanoparticles had abundance of functional groups, rendering it good hydrophilicity thus can be suspended in aqueous medium over long period of time.

High electrical conductivity is one of the most attractive properties of C-PDA. The in-plane and through-plane electrical conductivity of C-PDA have been found to be comparable to that of multilayer graphene. The high electrical conductivities could be due to the nitrogen-doping and effective π - π stacking that resulted in a change in molecular charge transfer behavior.⁴¹ Li et al. reported that the electrical conductivity of the C-PDA film is dependent on the carbonization temperature while independent of the film thickness, within a certain thickness range.⁴⁶ The good electrical conductivity of C-PDA is beneficial to charge transport properties, which is

important for electrochemical reactions and various other applications which requires good electrical conductivity.

There has been many works that have been carried out on C-PDA and a variety of morphologies have been explored. Thin films of C-PDA have been the most commonly explored morphology.⁴¹ Typically, thin film of C-PDA is derived from annealing of PDA thin film that is obtained from the facile deposition of PDA on a substrate. The thickness of the C-PDA film can be easily adjusted by varying the DOPA concentration, polymerization time and the number of times the polymerization process was repeated. Dimensions of the C-PDA film can also be varied by simply changing the size of the substrate. C-PDA nanoparticles can also be obtained via the annealing of PDA nanoparticles that are synthesized in the absence of a bulk substrate.¹⁵ Ai et al. successfully carbonized PDA nanospheres at 800 °C in argon to obtain C-PDA sub-micrometer spheres. Hollow C-PDA spheres have also been synthesized through the deposition of PDA on a spherical silica template followed by annealing and etching to remove the silica substrate.⁴⁰ Yan et al. obtained nitrogen-doped porous C-PDA by using nano-CaCO₃ as the substrate for PDA coating followed by annealing to convert C-PDA and removal of CaCO₃ using HCl.⁴⁷ One dimensional C-PDA nanostructures such as mesoporous nanofibers, hollow nanofibers and nanocups-on-microtubes have also been studied. These one dimensional nanostructures were synthesized via PDA coating on various one dimensional substrates that can be subsequently removed.^{48, 49}

2.1.5 PDA/Transition Metal Complex-Derived Carbon Nanocomposites

The ability of PDA to bind to transition metal species through the formation of coordination bonds provides a facile method to produce metal/C-PDA nanocomposites via the annealing of the metal/PDA complex.

The ability of iron(III) ions and DOPA to form complexes offers a simple route to introduce iron species into C-PDA. FeCl₃ was added into DOPA solution with silica

nanospheres template to obtain a hybrid coating containing PDA and iron species. The as-coated nanospheres were annealed at 750 °C followed by the etching of silica with KOH to obtain composite hollow nanospheres. The hollow nanospheres were found to contain highly graphitized C-PDA embedded with homogenously dispersed Fe_3O_4 nanoparticles. The hollow nanospheres were also shown to be an efficient ORR electrocatalyst.⁵⁰

Yang et al. demonstrated that transition metal species such as nickel(II), cobalt(II) and manganese(II) could also be incorporated into PDA and converted to metal-C/PDA or metal oxide/C-PDA after annealing at 800 °C. The metal or metal oxides were uniformly embedded in the highly graphitized C-PDA. Ni, Co and MnO were obtained by using nickel(II), cobalt(II) and manganese(II), respectively. Such metal/C-PDA nanocomposites could be useful in various applications such as energy storage/conversion and electrocatalysis. It should, however, be noted that nickel(II) species does not form a complex with DOPA. Instead, nickel(II) was found to interact with DOPA oligomers, forming Ni(II)-PDA complex. There has been no in depth study of how the cobalt(II) and manganese(II) species are incorporated into PDA during the polymerization process.³⁷

Binary metal oxides/C-PDA nanocomposites have also been synthesized leveraging on the ability of PDA to form complex with transition metal species. C-PDA nanospheres embedded with zinc ferrite (ZnFe_2O_4) nanoparticles have been synthesized by the introduction of zinc chloride (ZnCl_2) and iron chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) into DOPA solution. It was reported that Zn(II), different from iron(III) ions, does not immediately form complex with DOPA. Instead, it forms zinc hydroxide ($\text{Zn}(\text{OH})_2$), which may then form coordination bonds with DOPA. Both zinc and iron species were successfully incorporated into the PDA matrix during the polymerization and resulted in ZnFe_2O_4 after annealing at 600 °C in argon. The nanospheres were utilized as anodes for lithium ion batteries (LIBs).⁵¹

More efforts should be placed on the study of such carbon nanocomposites derived from metal/PDA complex as they offers a green and facile synthesis route as well as the presence of highly graphitized C-PDA that may find useful in many applications.

2.2 Zinc Air Batteries (ZnABs)

2.2.1 Introduction to ZnABs

The synthesis and production of new and advanced materials for the efficient harvesting, storage and usage of renewable energy are at the centre of today's energy research landscape.⁵²⁻⁵⁶ The strong domination of LIBs as an energy storage solution in portable electronics and electric vehicles (EVs) is attributed to its relatively high specific energy, power density and good cycling life.^{57, 58} However, the 'high' specific energy still falls short of the requirements of larger scale applications such as electricity grids and extended range EVs. The high cost of lithium and safety concerns have also prevented their use in these applications. To counter these problems, technologies such as lithium-sulfur, sodium-ion and metal-air batteries have been studied intensely in recent times.⁵⁹⁻⁶² Metal-air batteries have appeared to be a promising alternative because of their high theoretical energy density and the presence of free-oxygen fuel from the atmosphere.⁶¹ Among the various metal-air batteries systems, zinc-air batteries (ZnABs) have attracted significant amount of attention in the past few years due to its high theoretical energy density, safety, low cost, relative stability in alkaline solution and environmental benignity.⁶³ The theoretical energy density of ZnABs is 1086 W h kg^{-1} , approximately five times that of LIBs, while its operating cost is estimated to be only a small percentage of that of LIBs.⁶⁴

Figure 2.5 Schematic of a typical ZnAB consisting of a zinc anode, alkaline electrolyte and air cathode.⁶⁵

The construction of a typical ZnAB is as shown in Figure 2.5. Typically, a ZnAB consists of a zinc anode, an electrolyte and an air cathode containing oxygen electrocatalysts. The electrolyte used is usually an alkaline solution, such as concentrated potassium hydroxide (KOH) or sodium hydroxide (NaOH). During the battery discharge process, at the anode, metallic zinc is oxidized and react with hydroxyl ions (OH^-) to produce soluble zincate ions ($\text{Zn}(\text{OH})_4^{2-}$) which decompose to form an insoluble zinc oxide (ZnO) upon saturation.⁶³ At the air cathode, external oxygen diffuses into the porous electrode driven by the concentration gradient and oxygen reduction reaction (ORR) then take place at the triple phase boundary among the solid electrode, liquid electrolyte and gas phase, producing OH^- .⁶⁶ These OH^- then migrate from the air cathode to the anode through the electrolyte, completing the battery reaction. The discharge reactions are summarized in Eq 2.1. During the recharge process, $\text{Zn}(\text{OH})_4^{2-}$ are reduced back to zinc and plated back on the anode and oxygen released at the air electrode, i.e. oxygen evolution reaction (OER).

The theoretical working voltage of ZnABs is 1.65 V but their practical working voltages during discharge are much lower, typically below 1.2 V, in order to sustain a decent amount of discharge current density. A recharge voltage of approximately 2.0 V or higher is required to reverse the reactions. The noticeable deviation from the theoretical voltage resulted mainly from the sluggish reaction kinetics at the air cathode, possibly mitigated by developing high efficiency bifunctional electrocatalysts, and preventing dendritic growth at the zinc anode.⁶⁵⁻⁶⁷

In a ZnAB, ORR and OER could occur on the same air cathode or two discrete air cathodes. Figure 2.6 shows the possible configurations of a ZnAB with either one or two air cathodes: a single cathode layer with bifunctional electrocatalyst, discrete cathodes for ORR and OER electrocatalysts respectively, and a layered cathode with separate layers for ORR and OER electrocatalysts.⁶⁸ The first configuration is easy to manufacture and incorporate into ZnABs, but will require the use of very stable electrocatalyst that can withstand the continuous oxidizing and reducing environment during charging and discharging. The second configuration separates the ORR and OER electrocatalysts into two different layers and allows the optimization of ORR and OER independent of each other. However, it will inevitably increase the complexity of the system and also add to the weight of the battery. The last configuration could possibly provide improved performance at the expense of increased complexity during the manufacturing process and also possibly increase mass transfer losses.⁶⁸

Figure 2.6 Various construction methods for the air electrode of ZnABs.⁶⁸

The development of rechargeable ZnABs is a complex problem that is associated with factors such as the design of anode, electrolytes and also development of electrocatalysts with bifunctionality, high activity and good stability for both ORR and OER.

2.2.2 Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) in ZnABs

Rechargeable ZnABs require air cathode with bifunctional electrocatalysts to accelerate the sluggish reaction kinetics of both ORR and OER. The ORR process usually contains a few sequential steps: oxygen diffusion from air to the air cathode, oxygen adsorption to the surface of the electrocatalyst, movement of electron from anode to the oxygen molecule, breaking of the oxygen-oxygen bond, chemical reactions, desorption of OH^- and the transfer of OH^- through the electrolyte to the zinc anode.⁶⁴ Even though ORR involves a series of complicated reactions, it is believed that it may proceed in either of two pathways: direct four-electron pathway or a peroxide two-electron pathway.⁶⁹ In the four-electron pathway (Eq 2.2), the oxygen molecules are directly reduced to OH^- under bidentate O_2 adsorption, where two O atoms coordinate with the electrocatalyst.^{64, 67} In the peroxide two-electron pathway (Eq 2.3), the oxygen molecule is indirectly reduced to OH^- via HO_2^- under end-on O_2 adsorption where one O atom coordinates perpendicularly to the electrocatalyst. The two-electron pathway may be followed by either a two-electron reduction of peroxide or the chemical disproportionation of peroxide.^{64, 67} The four-electron pathway is preferred as the two-electron pathway produces corrosive peroxide species and has low energy efficiency. It has been widely reported that the four-electron pathway usually occurs for noble metal catalysts while the two-electron pathway occurs mostly on carbonaceous materials. For other materials such as transition metal oxides or hybrid materials, a mixture of both pathways may occur depending on their specific crystal structure and molecular composition.⁶³

Four-electron pathway:

Two-electron pathway:

OER is another important aspect in electrically rechargeable ZnABs. OER during charging will reverse the actions of ORR, with the aid of a suitable electrocatalyst. Similar to ORR, the OER is also a complex process involving several reactions. The large amount of $\text{Zn}(\text{OH})_4^{2-}$ should be confined close to the zinc anode for oxygen evolution in an ideal scenario. However, the $\text{Zn}(\text{OH})_4^{2-}$ in the electrolyte decomposes to ZnO spontaneously upon saturation. These ZnO powders have low solubility, low conductivity and poor electrochemical reversibility, significantly reducing the ZnABs cycling life.

Apart from noble metal-based electrocatalysts, such as Pt, Ir and Ru, which are considered benchmarks for ORR and OER electrocatalysis, there are few electrocatalysts that can withstand electrocatalysis in an acidic environment due to the extremely harsh conditions. The metal anode may also have undesired reactions with the acidic electrolyte. ZnABs are usually operated in an alkaline environment where the zinc anode is more stable and more non-noble metal-based electrocatalysts are available for the electrocatalysis of oxygen with acceptable level of activity. On top of that, oxygen electrochemistry is more kinetically favorable in alkaline electrolyte than acidic electrolyte with lower overpotential.⁷⁰ However, alkaline medium also have its own disadvantage: sensitivity to carbon dioxide (CO_2) in air. CO_2 present in air will lead to carbonate formation and precipitation over time in the electrolyte. The poor solubility of the carbonate may lead to the blockage of electrolyte channel in the air cathode affecting the performance of the ZnAB. This drawback may be addressed by using air filtered through a selective membrane that is only permeable to oxygen or by using purified air.⁶³

It is of paramount importance to develop new bifunctional electrocatalysts that are able to deliver high ORR and OER performance in alkaline environment at low cost and essentially being environmentally friendly for use in ZnABs.

2.3 ORR and OER Electrocatalysts

2.3.1 Noble Metal-Based Electrocatalysts

In the early days, noble metal such as platinum (Pt) was widely used as electrocatalyst for ORR owing to their excellent electrocatalytic activity and high stability.^{71, 72} Pt is considered the ‘gold’ standard for ORR electrocatalyst and used to benchmark performance of new electrocatalysts being developed.⁷³ Pt nanoparticles evenly dispersed on high surface area carbon are the state-of-the-art ORR electrocatalysts. Studies have shown that the four-electron pathway for ORR will dominate when Pt is utilized as the electrocatalyst in an alkaline environment. Despite its excellent activity and stability, the high cost of Pt and its scarcity has prevented its wide spread use thus there is a huge effort to try and reduce the Pt loading in electrocatalyst and develop new low-cost replacements for Pt-based electrocatalyst. Aside from Pt, other less expensive noble metals such as palladium (Pd), gold (Au) and silver (Ag) and their alloys have been used for ORR electrocatalysis.⁷⁴⁻⁷⁷ Pd can be considered second in line after Pt in terms of ORR activity and has many properties similar to Pt, such as same face-centered cubic crystal structure, similar atomic size and electronic configuration.⁷⁷ In addition, Pd is less expensive and more abundant than Pt. It is believed that ORR catalyzed by Pd will also proceed by the four-electron pathway, similar to that of Pt.^{77, 78} Ag-based electrocatalysts have been reported to have reasonable electrocatalytic activity and stability but are less widely investigated despite their low cost, nearly two orders of magnitude lower than Pt.^{79, 80} Au-based electrocatalysts have also been studied for ORR electrocatalysis and reported that the activity varied with the size and loading amount of the nanoparticles.⁸¹

Although Pt-based electrocatalysts have been widely reported to be the most ORR active, they are not very good electrocatalysts for OER. Rutile-type ruthenium oxide (RuO_2) and iridium oxide (IrO_2) were reported to show excellent OER electrocatalytic activity in both acidic and alkaline environment.^{82, 83} However, at high anodic potential, RuO_2 and IrO_2 will be oxidized to form ruthenium tetroxide (RuO_4) and iridium trioxide (IrO_3), respectively and be dissolved in the solution during OER.⁸⁴ IrO_2 is able to sustain a higher anodic potential than RuO_2 thus slightly more stable for OER. However, both of them like Pt are noble metal-based and have high cost and are scarce in nature, rendering them impractical for large scale industrial applications.

For rechargeable ZnABS, bifunctional oxygen electrocatalysts are highly desired as they are able to catalyze both ORR and OER. Such bifunctional electrocatalysts are essentially also more complex than their counterparts which can only catalyze ORR or OER. Since noble metal-based electrocatalysts have been reported to have good electrocatalytic activity for either ORR or OER, the combinations of such metals are essentially seen as potential candidates for the development of bifunctional electrocatalysts. The physical and chemical combinations of Pt with RuO_2 or IrO_2 have been explored as bifunctional electrocatalysts owing to Pt being a good ORR electrocatalyst and RuO_2 and IrO_2 being good OER electrocatalysts. Zhang and team reported bifunctional RuO_2 - IrO_2 /Pt electrocatalyst for use in regenerative fuel cell. The RuO_2 and IrO_2 were well-dispersed and deposited on the Pt surface.^{85, 86} Kong et al. synthesized IrO_2 via hydrothermal and Pt/ IrO_2 by a microwave assisted polyol process. Electrochemical tests showed that the Pt/ IrO_2 bifunctional electrocatalyst possesses higher activity and durability towards ORR and OER than pure Pt or pure IrO_2 .⁸⁷

No matter how high the electrocatalytic activity and stability of such noble metal-based bifunctional electrocatalysts, the high cost and scarcity of such materials are huge disincentives for the large scale industrial application of the electrocatalysts. Such noble metal-based electrocatalysts, however, are useful for the benchmarking

of newly developed bifunctional electrocatalysts. The efficacy of a bifunctional electrocatalyst can be quantified by the difference between the ORR and OER potentials measured at a fixed current density. A smaller number will indicate a better bifunctional electrocatalyst.

2.3.2 Carbon-Based Electrocatalysts

The use of Pt and other noble metal-based electrocatalysts is not feasible for widespread application, despite their outstanding activity due to the high cost and scarcity. The development of alternative noble metal-free electrocatalysts seems like a more sensible solution to this problem.⁸⁸ One of the most cost-effective alternatives is that of carbonaceous materials, which have attracted significant attention as oxygen electrocatalysts in the recent decade. Carbon materials have several advantages including its low cost, abundance in nature, wettability, large surface areas, high electrical conductivity and good stability in harsh environment.⁸⁹ Carbon materials derived from biomass waste such as leaves, crab shells, fruit peels and corn silks could also significantly bring down the cost of the electrocatalysts.⁹⁰⁻⁹² Some of the developed electrocatalysts are more often than not supported on various carbon substrates.⁹³⁻⁹⁵ Pristine nanocarbons can be modified by surface modifications or doping to elevate the amount of surface defects in an effort to try and increase their electrocatalytic activity.

The doping of carbon with heteroatom such as nitrogen (N), boron (B), phosphorous (P) and sulphur (S) was found to be an effective method for increasing the ORR electrocatalytic activity of nanocarbons, leading to the development of cheap alternatives to noble metal-based electrocatalysts that are essentially metal-free.⁹⁶ Nitrogen is the most commonly used dopant and also the most efficient due to the relatively similar size of N and C atoms. Li et al. reported nitrogen-doped mesoporous carbon nanosheet/carbon nanotube (CNT) hybrids for efficient ORR electrocatalysis. The hybrid displayed comparable performance to commercial Pt/C and better durability.⁹⁷ N-doped porous graphene with high specific surface area and

hierarchical porous structure displaying superior activity and stability towards ORR was prepared via a one-step synthesis method without the additional use of template.⁹⁸

N-doped carbon derived from nature has also been studied for ORR electrocatalysis. Liu et al. reported nitrogen self-doped porous nanoparticles derived from spiral seaweed with high surface area and micro/mesoporous structures. The electrocatalyst showed improved electrocatalytic activity and long term stability for ORR in alkaline environment.⁹² Carbon with hierarchical micro/mesoporous structure was fabricated from waste cotton through a facile sulphuric acidification process followed by melamine activation and showed reasonable electrocatalytic activity in alkaline electrolyte.⁹⁹ N-doping will lead to change in electronic or chemical environment of the adjacent carbon atoms, promoting the adsorption of oxygen, leading to improvement in electrocatalytic activities.⁹⁷ Doped nitrogen atoms can be substituted into carbon in three configurations namely, graphitic N, pyridinic N and pyrrolic N. Graphitic N are N atoms that substitute carbon atoms within the graphene plane, bonded to three other C atoms, and incorporated into the graphene layer. Pyridinic N refers to N atoms at the edges of graphene planes and bonds to two C atoms with one p-electron localized to the aromatic π system of the graphene plane. Pyrrolic N are N atoms that are bonded with two C atoms with two p-electrons localized in the aromatic π system in a five member heterocyclic ring (Figure 2.7).¹⁰⁰ Graphitic N and pyridinic N are generally recognized as the most efficient active sites for ORR.^{92, 97, 101} Ruoff et al. proposed that the presence of graphitic N could increase the limiting current density while the presence of pyridinic N could improve the onset potential for ORR and might help convert the mechanism of ORR from that of two-electron pathway to four-electron pathway.¹⁰²

Figure 2.7 Bonding configurations of different nitrogen atoms in N-doped carbon materials.¹⁰⁰

Apart from nitrogen, studies have also been conducted on doping of carbon with smaller electronegative atoms such as B and P and also atoms with similar electronegativity with carbon such as S. Yang et al. reported sulfur-doped graphene as an efficient metal free electrocatalyst for ORR.¹⁰³ Park et al. also reported the synthesis of sulfur-doped graphene by thermal treatment of exfoliated graphene under carbon disulfide (CS₂) gas flow. The resultant S-doped graphene proved to be a viable electrocatalyst for ORR with improvement in limiting current density and durability.¹⁰⁴ Reports of doping carbon with B and P have also been reported in aiding to improve ORR activity.¹⁰⁵⁻¹⁰⁸ Carbon doped with two or even three heteroatoms have also been reported for use in ORR electrocatalysis. For example, Jiang et al. prepared N and P co-doped three-dimensional porous carbon networks that showed comparable ORR onset potential in both alkaline and acidic medium.¹⁰⁹ Triple-doped carbon nanotubes with N, S and B have also been successfully prepared and exhibited high electrocatalytic activity and good stability for ORR.¹¹⁰

In comparison with ORR, fewer studies have been carried out to investigate the use of carbon-based electrocatalysts for OER. Like the preparation of electrocatalysts for ORR, the design of the electrocatalysts including its structure and surface functional group are common means to improve the OER electrocatalytic property of carbon-based electrocatalysts. Chen et al. reported the synthesis of N and O co-doped

graphene-CNT hydrogel film which showed high current density and low overpotential. The electrocatalyst also showed good electrochemical durability in both alkaline and acidic environment.¹¹¹ Cheng et al. reported a metal-free OER electrocatalyst with high activity and stability by a facile acidic oxidation of commercially available carbon cloth.¹¹² Zhu et al. have also reported hierarchically porous P and N co-doped carbon nanofibers grown on conductive carbon paper prepared from an electrochemically induced polymerization process in the presence of phosphoric acid and aniline monomer. The synthesized electrocatalyst showed robust stability and high activity with low overpotential for OER, comparable to IrO₂ electrocatalyst.¹¹³

Despite the many reports of carbon-based ORR electrocatalysts, there are comparatively fewer reports of carbon-based bifunctional electrocatalysts due to the relatively fewer reports on carbon-based metal-free OER electrocatalysts. Yang et al. reported metal-free three dimensional (3D) graphene nanoribbon networks doped with nitrogen that showed good bifunctional electrocatalytic activity for both ORR and OER with excellent stability in alkaline environment. They also showed that graphitic N was responsible for ORR while pyridinic N helped to promote OER.¹¹⁴ Qu et al. demonstrated the use of N and S co-doped mesoporous carbon nanosheets for use as bifunctional ORR and OER electrocatalyst with excellent durability and favorable kinetics, better than most reported metal-free, heteroatom doped carbon, transition metal and even noble metal-based electrocatalysts.¹¹⁵ Hadidi et al. also reported synthesis of hollow N-doped mesoporous carbon spheres from polymerization and carbonization on a sacrificial spherical silicon dioxide (SiO₂) template followed by template removal by etching using hydrofluoric acid. The electrocatalyst delivered a high ORR onset potential of -0.55 V (vs. Hg/HgO), good stability and also a small charge-discharge voltage polarization of 0.89 V in ZnABs.¹¹⁶ Several other studies have also been conducted to synthesize nanocarbon in various forms such as CNTs, carbon networks, carbon microtube sponge and carbon foam for use as bifunctional ORR and OER electrocatalysts in alkaline electrolyte.^{89, 117-119}

Even though the metal-free heteroatom doped carbon materials discussed above have respectable ORR activity in alkaline electrolyte, most of the works are still a far cry away from the Pt benchmark. Overall electrocatalytic activities are also poorer than noble metal-based electrocatalysts, especially for the OER activity.

2.3.3 Non-Noble Transition Metal Oxides-Based Electrocatalysts

Compared with noble metals, non-noble transition metal oxides (TMOs) are a group of materials that offer a more sensible and sustainable solution to bifunctional oxygen electrocatalyst owing to their lower cost and greater availability.⁶⁶ TMOs in the form of spinel, perovskite and several other structures have been extensively studied for oxygen electrocatalyst.^{88, 120, 121} In some other studies, transition metal carbides, nitrides, oxynitrides, carbonitrides and chalcogenides have surfaced as other possible alternative for oxygen electrocatalysis to noble metals.¹²²

Among the TMOs investigated, manganese oxides are one of the earliest studied for ORR electrocatalyst due to the rich oxidation states, crystal structures, low toxicity, low cost and environmental benignness.¹²³ Early reports have shown that the ORR electrocatalytic performance of manganese oxides follows the sequence of $\text{Mn}_5\text{O}_8 < \text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_3 < \text{MnOOH}$.¹²⁴⁻¹²⁶ Cheng et al. reported that the ORR electrocatalytic activities of MnO_2 have a strong dependence on the crystal structures in the following order: $\alpha > \beta > \gamma$ - MnO_2 . The variation in electrocatalytic activity was due to the tunnel size and electronic conductivity of the various crystal structures. α - MnO_2 possess the largest tunnel size thus favoring the insertion and transfer of ions leading to the more positive onset potential. Despite having a narrower tunnel, β - MnO_2 shows higher activity than γ - MnO_2 due to its higher electrical conductivity.¹²⁷ Nano-sized MnO_2 was also found to display better ORR activity than its micro-sized counterparts due to the increase in surface area. The ORR mechanism for manganese oxides electrocatalysts are still in debate. Both the direct four electron and series four electron pathway have been proposed. Factors such as chemical composition, crystal

structures, phases, valency, morphology, size, surface area and electrical conductivity have been found to have influence of the electrocatalytic performance.⁶²

Besides manganese oxides, many other binary and ternary TMOs have also been studied for ORR electrocatalysis in alkaline electrolyte. Zhu et al. synthesized $M_xFe_{3-x}O_4$ ($M = Mn, Fe, Co, Cu$) and studied the Mn(II) dependence on the ORR electrocatalytic activities. $MnFe_2O_4$ nanoparticles were found to be the most ORR active with activity near to that of commercial Pt/C.¹²⁸ Hollow $ZnCo_2O_4$ microspheres prepared by solution-based assembly followed by calcination in air were tested as ORR electrocatalyst and showed enhanced ORR over bulk $ZnCo_2O_4$. The electrocatalyst also showed good methanol tolerance as well as better stability than commercial Pt/C in alkaline electrolyte.¹²¹

For OER, cobalt oxides are the most frequently studied TMOs electrocatalysts. Co_3O_4 has been identified as a promising noble-metal free electrocatalyst with performance close to that of RuO_2 . Blakemore et al. reported the synthesis of surfactant-free, unsupported quantum-confined Co_3O_4 nanoparticles that showed high OER electrocatalytic activity.¹²⁹ Grzelczak and team have also shown how the OER activity can be controlled by the precise control of the Co_3O_4 nanoparticles size, colloidal stability and the available ligand-free surface.¹³⁰ Similar to manganese oxides for ORR, the electrocatalytic of cobalt oxides is affected by many parameters such as crystal structure, phases, oxidation state, morphology, size, available surface area and electronic conductivity. Menezes et al. reported the preparation of Co_3O_4 nanochains from low temperature degradation of cobalt oxalate dehydrate precursor. The Co_3O_4 nanochains displayed excellent OER electrocatalytic activity at low overpotential in alkaline medium.¹³¹ Rosen and team also reported the synthesis of Co_3O_4 with hierarchical porosity via the leaching of magnesium from Mg-substituted mesoporous Co_3O_4 . The mesoporous Co_3O_4 showed high OER activity and turnover frequency double that of mesoporous Co_3O_4 prepared by conventional hard-template synthesis.¹³²

Many binary and ternary TMOs have also been studied as OER electrocatalysts. Kim et al. studied a series of transition metal doped Co_3O_4 for OER electrocatalysts. The addition of transition metal dopants showed enhanced OER activity with tin doped Co_3O_4 giving the best OER electrocatalytic activity followed by nickel- and iron-doped. The addition of transition metal dopants causes change in the crystallite size of Co_3O_4 leading to the change in OER activity.¹³³ $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_x$ was reported to be the most OER active electrocatalyst in alkaline medium, out of several other thin films of TMOs. The high activity is attributed to the in-situ formation of layered $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{OOH}$ oxyhydroxide species with almost every nickel atom that is electrochemically active.¹³⁴ Mixed Ni-Fe oxides have also been studied as OER electrocatalysts because of its lower overpotential and relative stability.^{135, 136} Li et al. synthesized electrospun MFe_2O_4 ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Mn}$) spinel nanofibers via electrospinning and subsequent thermal treatment processes. The nanofibers have lengths of up to a few dozens of micrometers, average diameter of 150 nm and are porous both on the surface and within. CoFe_2O_4 was reported to have the highest ORR electrocatalytic activity.¹³⁷

Only a handful of TMOs have displayed the ability to catalyze both ORR and OER and most of them are either manganese- or cobalt-based oxides. Ultrathin Co_3O_4 nanofilm with thickness of about 1.8 nm synthesized via template-free hydrothermal displayed ORR and OER bifunctional electrocatalytic activity superior to Co_3O_4 nanoparticles. The ORR on the nanofilm proceeded via a four electron pathway and the overpotential required to achieve an OER current density of 40 mA cm^{-2} was lower than that of RuO_2 .¹³⁸ Sa et al. also reported noble metal-free ordered mesoporous spinel Co_3O_4 as bifunctional electrocatalyst with high activity and stability for ORR and OER. The electrocatalyst showed high activity for OER in alkaline medium, comparable to Ir/C and better than Co_3O_4 nanoparticles and commercial Pt/C. The total overpotential for ORR and OER was 1.034 V, comparable to noble metal-based electrocatalysts.¹³⁹ Thin films of nanostructure manganese oxide were also found to be electrocatalytic active for both ORR and

OER. The overall activity for ORR and OER was found to be similar to noble metal nanoparticle electrocatalysts such as platinum, ruthenium and iridium.¹⁴⁰

Mixed TMOs have also been widely studied for ORR and OER bifunctional electrocatalysts. Si et al. synthesize mesoporous nanostructured spinel-type MFe_2O_4 ($\text{M} = \text{Co}, \text{Mn}, \text{Ni}$) and studied their electrochemical performance for ORR and OER. CoFe_2O_4 was found to be the most active for ORR while NiFe_2O_4 and CoFe_2O_4 have similar OER activity. CoFe_2O_4 electrocatalyst showed the smallest overpotential between ORR and OER and exhibited better methanol tolerance than commercial Pt/C .¹⁴¹ Mn-Co oxides with fibrous structure synthesized by anodic electrodeposition was also found to exhibit high electrocatalytic activity towards ORR and OER.¹⁴² Li et al. reported outstanding ORR and OER activities in alkaline medium of Co_3O_4 modified Mn_3O_4 composites prepared by citrate method.¹⁴³

The low electronic conductivity of most TMOs is a limiting factor for the practical performance of TMOs-based bifunctional electrocatalysts. Hence, TMOs are usually mixed with a large amount of conductive carbon and used as a mixture. The electrically conductive carbon is essentially a non-active material, adding to the weight of the electrocatalyst and will also affect the interfacial contact of the electrocatalyst with the electrolyte. Therefore researchers have started working on growing the TMOs on conductive substrates such as CNTs and graphenes to improve the dispersion of electrocatalyst as well as the electronic conductivity. More about such TMOs/carbon hybrid system will be discussed in the following section.

2.3.4 Transition Metal Oxides/Carbon Hybrid Electrocatalysts

Apart from the low conductivity of TMOs, the aggregation of these TMOs nanoparticles is also another factor that contributes to limiting the electrocatalytic activity and stability for ORR and OER. In order to overcome this problem, scientists have begun to disperse TMOs electrocatalysts on various conductive carbonaceous substrates. An inorganic-carbon hybrid electrocatalyst is able to simultaneously

improve the electrical conductivity of the electrocatalysts and also improves the dispersion of the nano-sized TMOs. Lastly, there could also be synergistic interaction between the electrocatalyst and the carbon substrate leading to improvement in electrocatalytic performance.

Wang et al. reported the hybridization of Fe_3O_4 and N-doped carbon by the annealing of FeOOH nanorods and urea at 500°C . The $\text{Fe}_3\text{O}_4\text{-NC/C}$ showed attractive ORR activity, with ORR half-wave potential only 40 mV less positive than commercial Pt/C. The improvement in ORR activity was attributed to the interaction between Fe_3O_4 and NC and also the improved electronic conductivity brought about by carbon.¹⁴⁴ Li and team synthesized highly dispersed CoO nanoparticles on mesoporous carbon via hydrothermal method and showed that CoO/MC followed the four-electron pathway and has good durability for ORR.¹⁴⁵ Co/ Co_3O_4 core/shell nanoparticles embedded in carbonized polydopamine was synthesized and showed onset potential 60 mV more negative than commercial Pt/C. The improved ORR activity was attributed to the synergistic interaction between Co/ Co_3O_4 and the carbonized polydopamine.⁹ Wang et al. reported a one-pot solvothermal synthesis of Ag-Co Fe_2O_4 /C for electrocatalysis of ORR. The Ag-Co Fe_2O_4 displayed better ORR activity than Ag/C and Co Fe_2O_4 /C, shows only a negative shift of 77 mV when compared to commercial Pt/C and has good durability in alkaline electrolyte.¹⁴⁶ Mesoporous NiCo $_2\text{O}_4$ nanoplates have also been supported on 3D hierarchical porous graphene foam and used for ORR electrocatalysis. The electrocatalyst exhibited enhances electrocatalytic activity with half-wave potential of 0.86 V vs. reversible hydrogen electrode (RHE) and better stability than commercial Pt/C.¹⁴⁷ There have also been a couple of works that studied TMOs/carbon hybrids for OER. Tavakkoli et al. demonstrated the use of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles decorated on carbon nanotubes as a low cost, active and durable OER electrocatalyst.¹⁴⁸ Mixed metal oxide of nickel and iron were deposited on CNTs and used as electrocatalyst for OER. The resultant electrocatalyst showed excellent OER performance with onset potential of 1.43 V vs. reversible hydrogen electrode (RHE) in 1 M NaOH electrolyte as well as good durability. The good performance was attributed to the

increased in interfacial area and strong interactions between the TMOs and CNTs leading to good charge transfer at the interface.¹⁴⁹ CoFe₂O₄ nanoparticles were loaded on polyaniline-multiwalled carbon nanotube via an in-situ process. The introduction of polyaniline was found to improve the synergistic effect between CNTs and the CoFe₂O₄ nanoparticles, promoting good electrical conductivity and stability of the electrocatalyst. The electrocatalyst exhibited good OER activity with current density of 10 mA cm⁻² achieved at overpotential of 314 mV in 1M KOH electrolyte.⁹⁵

Most of the works for TMOs/carbon hybrids have been focused on the ORR and OER bifunctionality instead of only ORR or OER. Co₃O₄ is one of the most commonly studied TMOs deposited on carbon substrate for ORR and OER bifunctional electrocatalyst.^{65, 150, 151} Jiang et al. presented a facile method to synthesize Co₃O₄-coated N- and B-doped graphene hollow spheres as ORR and OER bifunctional electrocatalyst. The electrocatalyst exhibited high electrocatalytic activity for both ORR and OER and also better durability than commercial Pt/C and RuO₂/C. The high electrocatalytic is attributed to the coupling between Co₃O₄ and the graphene hollow spheres, high electrical conductivity and also the large available surface area.¹⁵¹ Zhang and team immobilize Co/CoO nanoparticles on Co- and N-doped carbon for ORR and OER. The electrocatalyst also showed good performance and stability when utilized as air cathode material for rechargeable ZnABs.¹⁵²

Binary and even ternary TMOs/carbon hybrid systems have also been widely studied for ORR and OER bifunctional electrocatalyst. NiCo₂O₄ nanoparticles supported on hollow structured carbon, NiCo₂O₄ nanospheres on CNTs and CoMn₂O₄ nanoparticles anchored on N-doped graphene nanosheets have all also been studied as ORR and OER bifunctional electrocatalyst.^{94, 153, 154} CoFe₂O₄ have also been supported on many different carbon substrates such as CNTs, N-doped graphene and mesoporous carbon for ORR and OER bifunctional electrocatalyst.^{93, 155-158} Bian et al. synthesized a CoFe₂O₄/graphene nanohybrid and apply it as an ORR and OER bifunctional electrocatalyst. The electrocatalyst favored a four-electron pathway for

ORR and demonstrates high electrocatalytic activity for OER. The activity and durability of the catalyst are attributed to the strong coupling between CoFe_2O_4 nanoparticles and graphene.¹⁵⁶ Yan et al. prepared monodispersed porous CoFe_2O_4 nanospheres on reduce graphene oxide sheets via a one-pot solvothermal method. The electrocatalyst shows high activity for both ORR and OER, having an onset potential of -0.11 V (vs. Ag/AgCl) for ORR and onset potential of 0.56 V for OER. The high electrocatalytic activity was also attributed to the coupling between the CoFe_2O_4 nanospheres and graphene sheet preventing the agglomeration of the CoFe_2O_4 nanospheres.¹⁵⁸

2.4 Electrospinning

2.4.1 Introduction

Significant amount of attention have been directed to 1-dimensional (1D) material for use in high technology applications since the start of this millennium. Out of the many 1D nanomaterials, such as nanowires, nanorods and nanotubes, nanofibers have demonstrated great promise as electrode materials for advanced batteries. Nanofibers can be prepared from many methods such as template-directed, vapor-phase approach, solution-liquid-solid technique, solvothermal synthesis, solution phase growth with capping agents, self-assembly and electrospinning. Electrospinning has emerged as a fore runner due to its ease of processing, the low cost involved, versatility and high efficiency.¹⁵⁹ Electrospinning is able to produce continuous fibers with micro- to nano-scale diameter, having solid or hollow centre and having uniform diameter.¹⁶⁰ By coupling electrospinning with thermal treatment, nanofibers with controllable phase, morphologies and compositions can be easily obtained. Electrospun nanofibers from electrospinning have large surface area and high surface to volume ratio providing a huge number of available sites for electrocatalytic reactions in ZnABs.

2.4.2 Principle of Electrospinning

Electrospinning is a method of producing nanofibers by using electric force to draw charged polymer solutions out of a spinneret with fiber diameters in the order of a few hundred nanometers.¹⁶⁰ A typical electrospinning setup is shown in Figure 2.8, and consists of three major components namely a high voltage power source, a spinneret attached to a syringe pump and a grounded collector. Electrospinning inherits characteristics from both electrospraying¹⁶¹ and conventional solution spinning of fibers, using electrostatic force instead of mechanical or shear force to draw fibers from solution. During electrospinning, a viscoelastic polymer solution of a critical viscosity is fed continuously to a conducting spinneret that is attached to a syringe fixed on a syringe pump, responsible for feeding the polymer solution at a constant rate. When a sufficiently high voltage is applied, the drop of polymer solution at the spinneret becomes charged. On the surface of the polymer droplet, the electrostatic repulsion works against the surface tension causing the stretching and elongation of the droplet to a conical shape, commonly known as the Taylor cone.¹⁶² With the increase in voltage, a critical point will be achieved whereby the electrostatic repulsion overcomes the surface tension causing a charged jet to erupt from the tip of the Taylor cone. The charged jet dries in flight due to the evaporation of the solvent. The jet is then elongated by a whipping process caused by the electrostatic repulsion until it is eventually deposited on a grounded collector as a randomly oriented, non-woven mat.¹⁶² The elongation and thinning of the nanofibers resulting from this bending instability leads to the formation of uniform fibers with diameters in the nanometer scale (nanofibers).

Figure 2.8 Schematic of a typical electrospinning setup.¹⁶³

Various modifications can be carried out on the spinneret and collector to tailor the structures and morphologies of the resulting nanofibers. Core/shell or hollow nanofibers can be produced by co-electrospinning two different polymer solutions through a spinneret comprising two coaxial capillaries (Figure 2.9).¹⁶⁴ Selective removal of the core material will result in hollow nanofibers as demonstrated by many groups working on electrospinning.¹⁶⁰ Highly porous nanofibers can also be produced by careful selection of polymers, solvents and electrospinning parameters.¹⁶⁵ It is also possible to achieve porous nanofibers by the selective removal of a component from nanofibers constructed of blend material or making use of phase separation of different polymers during electrospinning.¹⁶⁶ Collection of aligned electrospun nanofibers can be achieved by using rotating drums or tapered wheel-like disk.¹⁶⁷ By using carefully configured conductive collector, uni-axially aligned nanofibers could be collected over long length scales.¹⁶⁸ Free standing random, non-woven mat can be peeled off from the collector for further processing. Loose nanofibers can also be collected by using aqueous collector such as water or ethanol instead of the conventional aluminum foil.⁴² The various morphologies described above are shown in Figure 2.10.

Figure 2.9 Schematic of electrospinning setup with coaxial spinneret.¹⁶⁴

Using electrospinning to produce nanofibers has many advantages such as its simplicity, the low cost involved, high yield and the high degree of reproducibility.¹⁶⁹ By using suitable precursors and also with the addition of additives into the polymer solution, nanofibers have been successfully incorporated with the likes of magnetic nanoparticles, biomolecules and TMOs. Nanofibers produced from electrospinning have extremely long length due to electrospinning being a continuous process, resulting in high aspect ratio. As the nanofibers produced from electrospinning are usually thinner in diameter, therefore have higher surface area and also higher surface area to volume ratio.¹⁶⁹ As electrospinning involves the rapid stretching of a charged jet of polymer solution and swift evaporation of solvent, polymer chains within the solution will experience strong shear force during the process. This strong shear force coupled with the quick solidification will prevent the polymer chain from relaxing back to their equilibrium state resulting in highly aligned polymer chains at the molecular level.¹⁶²

Figure 2.10 SEM and TEM micrographs of electrospun nanofibers with different morphologies.^{160, 170-172}

Characteristics such as the large surface area, high aspect ratio and ability to incorporate other nanoparticles to produce hybrid nanofibers are extremely useful when considering for use as an air cathode material in ZnABs as they enable the simplification of the preparation process and also provides for a large amount of available sites for ORR and OER to occur.

2.4.3 Carbon Nanofibers Derived from Electrospun Polymer Nanofibers

When choosing materials for the cathode of ZnABs, electrical conductivity is one of the crucial parameter that has to be considered. In order for the electrospun nanofibers to be conductive, they will have to be converted to carbon nanofibers (CNFs) via a high temperature annealing process, commonly termed as carbonization.

Carbonization may be a single- or multi-step process depending on the polymer precursor in discussion. In principle, any polymer with a carbon backbone can potentially be used as a precursor. For majority of polymers used, electrospun

nanofibers are converted to CNFs by annealing at around 1000 °C in inert atmosphere such as flowing nitrogen or argon. For precursor such as polyacrylonitrile (PAN), a widely used carbon precursor owing to its high carbon yield and facile spinnability, an additional stabilization process before the high temperature carbonization is vital for the nanofibers to retain their fibrous morphology (Figure 2.11).¹⁷³ PAN is first cross-linked by the transformation of $C\equiv N$ to $C=N$ bonds. Hydrogen atoms are then eliminated during an aromatization process, resulting in an aromatic ladder structure. The stabilization step increases the thermal stability of PAN for the subsequent carbonization process and usually takes place between 180 – 280 °C under atmospheric conditions.^{173, 174} During carbonization, the aromatic growth continues. With the elevation in temperature during the carbonization process, hydrogen atoms will be removed first followed by nitrogen atoms at higher temperatures. As a result, conductive carbon with honeycomb-like structure is produced.¹⁷⁵ During the stabilization and carbonization of polymer nanofibers, significant weight loss and shrinkage will occur leading to the decrease in fiber diameter.

Figure 2.11 Reactions during PAN stabilization and carbonization.¹⁷⁶

2.4.4 Carbon Nanofibers Prepared via PDA Deposition on Electrospun Nanofibers

1D C-PDA nanostructures such as porous nanofibers and hollow nanofibers have been successfully prepared by the deposition of PDA on various 1D templates followed by annealing and subsequent removal of the templates. For the fabrication of C-PDA hollow nanofibers, PDA was first deposited onto a loose lump of electrospun PAN nanofibers suspended in aqueous medium. After successful PDA deposition, the PAN core was removed by immersing in DMF, leaving only the PDA shells without altering the nanostructure. C-PDA hollow nanofibers were then obtained via annealing at 700 °C in argon. The resultant C-PDA hollow nanofibers were reported to have diameter of approximately 560 nm and wall thickness of about 40 nm.⁴² C-PDA hollow nanofibers have also been successfully fabricated by coating PDA on solid PS nanofibers followed by annealing to concurrently remove PS and carbonize PDA.¹⁷⁷ For the preparation of C-PDA porous nanofibers, electrospun PS nanofibers with interpenetrating nanochannels, obtained via electrospinning at relative humidity of approximately 60 %, was used as the template. The deposition of PDA on the PS nanofibers followed by annealing will lead to C-PDA porous nanofibers with interpenetrating pores.^{44, 48, 177}

2.5 Concluding Remarks

Previous researches have shown that the in situ polymerization of DOPA is a useful synthesis route for metal/PDA hybrid materials due to its simplicity and versatility. At the beginning of this PhD study, there has been no published work revealing the mechanism for the formation of the metal/PDA complex; most studies were focused only on the applications of the synthesized end products. There is, therefore, a need to better understand the underlying mechanisms for the formation of various types of metal/PDA complexes, especially the interactions between DOPA and the transition metal species in the in situ polymerization process, so as to be able to better control or even predict the structures and morphologies of the metal/PDA hybrids

and the loading of the metals in the hybrids. Literatures have also stated that morphology is one of the important factors that affect the performance of an oxygen electrocatalyst. By being able to effectively predict and control the morphologies of the in situ synthesized metal/PDA hybrid materials, oxygen electrocatalysts with enhanced performance can be fabricated and used as air cathode in ZnABs.

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Chapter 3

Experimental Methodology

In this chapter, all the experimental methods used to prepare samples for the works carried out in this PhD study are presented, and why these particular methods are appropriate for the various studies are explained. Basic theories and working principles behind the chosen characterization techniques and equipment are also discussed, justifying the data collection and data analysis methods used. Detailed synthesis procedures for the various samples are not included in the chapter; they are presented in Chapter 4, 5 and 6, respectively.

3.1 Rationale for Materials Selection

The discovery of polydopamine (PDA) has led to a large volume of work revolving around the use of its facile surface deposition ability, as discussed in the previous chapter. More recently, the ability of PDA to form coordination bonds with transition metal species has been utilized to synthesize transition metal/PDA hybrids and subsequently transition metal/C-PDA nanocomposite materials. Majority of these studies focused on the use of the synthesized hybrids and nanocomposites for applications and neglect the intricate interactions between the transition metal species and PDA that lead to the formation of the unique hybrid materials. In this PhD study, substantial efforts were devoted to understand how dopamine (DOPA) or PDA oligomers interact with the transition metal species, leading to the eventual formation of various hybrid nanostructures with different shapes and sizes. Two types of transition metal ions, Fe^{3+} and Co^{2+} , were chosen as model systems for the studies, and the reasons are elaborated below.

3.1.1 FeCl_3

When discussing about coordination bonding between catechol groups and transition metal species, iron(III) ions are undoubtedly the most common transition metal ions being studied. The complexation of catechol groups with iron(III) ions, which leads to the formation of mono-, bi- and tris-complexes, has been well studied and understood. The same cannot be said for the in situ polymerization of DOPA in the presence of iron(III) ions as the covalent polymerization of DOPA and self-assembly of PDA may be affected by the presence of catechol-Fe coordination bonds, making the process more complicated. Despite being used in many different applications, the studies on PDA hybrid systems were also mainly focused on the end products and their applications instead of the mechanism studies. The reason why FeCl_3 (or Fe^{3+}) was chosen as the first model transition metal species to study is thus obvious - the current understanding of the interactions of iron(III) ions and DOPA would allow us to understand the formation mechanism for the Fe(III)-PDA complex more easily

than other systems, which will provide a basis for investigating the formation mechanisms for other relevant hybrid systems. Iron oxides also have good ferromagnetism as well as electrocatalytic activity, and hence the Fe(III)-PDA hybrids synthesized via in situ polymerization have the potential to be used in applications such as recyclable catalyst support or electrocatalysts.

3.1.2 CoCl₂

As discussed in the previous chapter, there has been a handful of works that have added cobalt(II) ions into DOPA solution for in situ polymerization to obtain cobalt(II)/PDA complex hybrid materials. However, similar to works for iron(III) ions, none of these works have studied the interactions between cobalt(II) ions and DOPA during the in situ polymerization process and also whether cobalt(II) ions could form coordination bonds with DOPA or PDA. It has been reported that nickel(II) ions do not form coordination bonds with DOPA monomers, instead it forms coordination bonds with PDA oligomers. Cobalt is positioned in between iron and nickel in the periodic table, it will thus be interesting to determine if cobalt(II) ions can form coordination bonds with DOPA monomers similar to that of iron(III) ions or only form complex with PDA oligomers like that of nickel(II) ions. Another motivation behind the selection of cobalt(II) ions as a model system is the good electrocatalytic activity of binary cobalt ferrite (CoFe₂O₄) nanoparticles for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The facile in situ polymerization of DOPA with mixed transition metal species may be a facile route to obtain CoFe₂O₄-containing C-PDA nanocomposites that can be utilized as effective bifunctional oxygen electrocatalyst.

3.2 Rationales for the Selected Material Synthesis Methods

3.2.1 In Situ Polymerization of DOPA

As discussed in the previous chapter, there are a few methods to obtain PDA such as aqueous oxidative polymerization, hydrothermal treatment and also via electrodeposition. Compared to other methods, the oxidative polymerization of DOPA in aqueous solutions is advantageous as it is performed in mild alkaline conditions at room temperature and does not require the use of complicated instruments. It also allows for the facile retrieval of samples at fixed time points for mechanism studies. This method can be further categorized into two branches; surface deposition on an immersed substrate and the formation of PDA nanoparticles in the absence of a substrate. The addition of transition metal species during the polymerization of DOPA has also been widely reported to be a facile method to incorporate transition metal species into PDA nanostructures forming transition metal/PDA hybrid materials. Both in situ polymerization strategies, i.e., with and without substrates, were employed in this PhD study. The in situ polymerization of DOPA without an immersed substrate was employed to study the self-assembly mechanism of transition metal/PDA hybrids while the surface deposition with electrospun nanofibers as the substrates was employed to fabricate transition metal/PDA hybrid with high specific surface area.

3.2.2 Electrospinning

There are several methods to produce nanofibers, such as melt spinning, template-assisted synthesis, chemical vapor deposition, wet chemical synthesis, phase separation and electrospinning. As discussed in the previous chapter, electrospinning stands out amongst the rest due to the ease of processing, high efficiency and versatility. More importantly, electrospinning is able to produce continuous fibers with uniform diameter in the nanometer range. These nanofibers have high aspect ratio resulting from the long continuous fibers and small cross sectional diameter leading to high specific surface area. Furthermore, by modifying the electrospinning setup and parameters to produce hollow nanofibers or porous nanofibers, the specific surface area of the electrospun nanofibers can be further increased. The ease of

producing nanofibers with high specific surface area from electrospinning makes it the ideal synthesis method to be used in this PhD study.

3.3 Characterization Techniques

3.3.1 Scanning Electron Microscope

In this PhD study, the surface morphologies of the synthesized nanospheres and nanofibers were characterized using SEM in order to establish morphology-property relationships.

SEM is a type of electron microscope that can produce images by scanning the surface of a sample with a focused beam of electrons across a rectangular shaped area, also known as a raster scan. The electrons in the electron beam will interact with atoms in the sample, producing various signals that can provide information on the sample's surface morphology and composition. The various signals produced from the electron beam interaction with the samples are shown in Figure 3.1. Of these signals, secondary electrons, backscattered electrons and characteristic X-rays are the most commonly collected signals.¹

Figure 3.1 Signals generated from interaction between specimen and incident electron beam in SEM.²

Secondary electrons are produced from the inelastic scattering interactions of specimen atoms with the electron beam, and usually originate within a few nanometers from the sample surface, due to its low energy. Secondary electron imaging is used to provide topographical information of the sample and can reveal details less than 1 nm in size.

Backscattered electrons are produced by the elastic scattering interactions of the electron beam with specimen atoms that results in the primary electrons being reflected or backscattered out of the specimen. As heavy elements backscatter electrons more strongly than lighter elements, heavy elements will appear brighter in backscattered electron imaging. Backscatter electron imaging is commonly used to observe contrast between areas with different chemical composition in a specimen.

Characteristic X-rays are emitted when outer-shell electrons make discrete transitions to fill a vacancy in the inner-shell of an atom, releasing X-rays that is specific to each element. When an incident electron beam interacts with atom in the specimen, an electron is excited and ejected from the inner-shell of the atom. After the electron is ejected, the atom is left with a 'hole'. Outer-shell electrons will then fall into the inner-shell to fill the 'hole', losing energy in the form of X-rays. Characteristic X-rays are commonly used to identify the element present in a sample. All SEM micrographs were taken using a field-emission scanning electron microscope (FESEM, JEOL 7600) at an accelerating voltage of 5 kV.

3.3.2 Transmission Electron Microscope

As the transition metal nanoparticles are embedded within the C-PDA matrix, transmission electron microscopy (TEM) is used as it is able to probe nanostructures within the C-PDA matrix. TEM is also able to show phase contrast between the transition metal nanoparticles and carbon matrix allowing for the two to be distinguished. In the scanning transmission electron microscopy (STEM), energy

dispersive X-ray spectroscopy (EDX) can also be conducted to provide data on the elemental distribution of the samples.

TEM uses a focused beam of electrons to produce images of specimen. Images produced by TEM are based on the elastic scattering of the electrons during the interaction with the specimen as the beam is transmitted through. The image is then magnified and focused on a florescent screen. The specimens are usually ultrathin, less than 100 nm in thickness. TEM is also able to provide for a higher resolution, owing to the higher accelerating voltage employed, 40 – 300 kV.¹

Figure 3.2 Schematic of components in a traditional TEM.³

TEM operates based on the same basic principles as the light microscope, but instead uses electrons instead of light. A typical TEM consists of four major components namely, the electron source, the electromagnetic lens system, the sample holder and the imaging system (Figure 3.2). The electron source consists of an anode and a cathode and is responsible for accelerating the electron beam towards the specimen. The electromagnetic lens system will then focus the electron beam with a set of electromagnetic lens and metal apertures. Only electrons within a small energy range will be allowed to pass, so that electrons in the electron beam will have a well-defined energy. Sample holder is simply a stage for holding the specimen with the ability to control its position. The imaging system consists of another electromagnetic lens system and a florescent screen. The electromagnetic lens in the imaging system consist of two lens system, one for refocusing the electron beam after they pass through the specimen and the other for magnifying the image and projecting it onto the florescent screen.

Figure 3.3 Difference in beam path in TEM for imaging mode and diffraction mode.⁴

TEM can operate in two different modes namely, imaging mode and diffraction mode, depending on the strength of the intermediate lens (Figure 3.3). In the imaging mode, an image is observed on the florescent viewing screen. The contrast observed in TEM is attributed to the scattering contrast and also mass-thickness contrast. Heavier elements and thicker samples will lead to darker contrast in the observed image when using bright field imaging. Bright field imaging mode is the most common mode of operation for a TEM and occurs when only the direct beam is selected by the objective aperture. Another imaging mode of TEM is known as dark field imaging. In dark field imaging, the objective aperture is shifted such that only one of the diffracted beams contributes to the image formation.

In the diffraction mode, also known as selected area electron diffraction (SAED), a diffraction pattern is projected onto the florescent viewing screen. For single crystalline samples, diffraction pattern will consist of a pattern of dots whereas a series of rings will be formed for polycrystalline or amorphous samples.

All TEM micrographs were taken using a TEM (JEOL 2010) with an accelerating voltage of 200 kV.

3.3.3 X-ray Diffraction

Figure 3.4 Electromagnetic Spectrum.⁵

X-ray diffraction (XRD) was used to provide information about the phases of the transition metals and transition metal oxides present in the samples. The electron diffraction mode from TEM is also able to provide the same phase structure information, but XRD was chosen as it is a relatively easier technique, in terms of operations and data analysis, than electron diffraction.

X-ray is a kind of electromagnetic waves with wavelength ranging from $10^{-8} - 10^{-11}$ m, corresponding to energy range from 100 eV to 100 keV. The relative position of X-ray in the electromagnetic spectrum is shown in Figure 3.4. XRD is one of the commonly used characterization techniques used to provide information on the atomic and molecular arrangement within a material, translating to information of its' crystal structure. During operation, X-ray passing through the material will interact and be scattered by the atoms within the material. When the atoms within the material are regularly arranged (crystalline), constructive interference of the scattered X-rays will occur in certain directions, following the Bragg's law (Eq 3.1) of diffraction. In Bragg's law, d represents the spacing between the lattice planes also known as interplanar spacing, θ represents the incident angle, n can be any positive integer and λ represents the wavelength of the incident wave.⁶

$$2d \sin\theta = \lambda \quad (\text{Eq 3.1})$$

When an incident X-ray hits a lattice plane at an angle, θ , they are elastically scattered by the atoms and are scattered off also at an angle of θ , with respect to the lattice plane (Figure 3.5). When two X-ray with identical wavelength approach a crystalline material and scatter off two different atoms within the material, the lower ray will travel an additional length equivalent to $2d \sin \theta$. Constructive interference will occur when this additional length travelled, $2d \sin \theta$, is equal to an integer multiple of the wavelength of the incident wave. Since the wavelength of the incident wave is a constant, the position of the diffraction peak will be determined by the interplanar spacing, d . For a crystalline structure, a series of diffraction peaks corresponding to the various lattice planes with different interplanar spacing will be

observed. The XRD pattern can be described as the fingerprint of a crystal structure and a powerful tool for identifying the different phase present in the material.

All X-ray diffraction patterns are collected using a Bruker diffractometer (D8 Discover) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation generated at 40 mA and 40 kV. Scan rate used was 1° min^{-1} with a step size of 0.02° from $5 - 90^\circ$.

Figure 3.5 Bragg's Diffraction of X-rays.⁷

3.3.4 Ultraviolet-visible Spectroscopy

UV-vis spectroscopy (UV-vis) was employed to study the coordination behavior of transition metal ions in this PhD study. As the color and absorption characteristic of the transition metal ion solution will change when bonded with different ligands, UV-vis is a straightforward method to detect the formation of transition metal ion complexes.

UV-vis is also known as the absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. It measures the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. UV-vis absorption spectra arise from the transition of electrons from a lower to higher energy. As electronic transition within a system occurs at specific energy, fraction of the light energy will be absorbed if the particular light energy matches the energy

difference of a possible electronic transition, with the electrons promoted to a higher energy state.

When ligands bond to transition metal ions to form a complex, there will be interactions between the electron cloud of the ligands and the d-orbitals of the transition metal, leading to non-degenerate d-orbitals. When light passes through a transition metal ion solution with non-degenerate d-orbitals, energy can be absorbed to promote an electron from a lower energy d-orbital to a higher energy d-orbital (Figure 3.6).⁸

Figure 3.6 Splitting of 5 degenerate d-orbitals.⁹

All UV-vis analysis of solutions was conducted on a Shimadzu UV-vis spectrometer (UV-2700) at wavelength ranging from 190 to 900 nm.

3.3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron (XPS) was used to analyze the surface chemistry of the specimen and confirms the chemical structures of the transition metal species. XPS being surface sensitive can detect the transition metal species near the surface of the specimen and reaffirm the phase information obtained from XRD. It is capable of differentiating chemical states between samples and able to perform quantitative analysis.

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a surface sensitive quantitative spectroscopic technique that can be used to probe the surface chemistry of specimen. XPS is capable of probing the empirical formula, chemical state and electronic state of the elements present within the top layer of a material, usually up to 10 nm in depth.¹⁰

An XPS spectrum is obtained by exposing the specimen of interest with a beam of X-rays while measuring the kinetic energy and number of electrons that escape. When a X-ray photon strikes and transfers its energy to a core-level electron, the electron will be emitted with a certain kinetic energy dependent on the incident X-ray and the binding energy of the atomic orbital from which the electron originated. The binding energy can be calculated by using an equation based on Ernest Rutherford's work (Eq 3.2), where E_{Binding} is the binding energy of the electron, E_{photon} is the energy of the X-ray photon being used, E_{kinetic} is the kinetic energy of the electron and ϕ being the instrument dependent work function.

$$E_{\text{Binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \text{ (Eq 3.2)}$$

The peak intensity of a XPS spectrum is directly proportional to the concentration of a species and the peak positions are characteristic of a species' electronic structure. Each element on the periodic table has its unique 'fingerprint' spectrum.

XPS measurements were collected on a Kratos Analytical AXIS His spectrometer with a monochromatized Al K α X-ray source (1486.6 eV photons).

3.3.6 X-ray Absorption Fine Structure Spectroscopy

X-ray absorption fine structure spectroscopy (XAFS) was employed to study the bonding characteristic of the transition metal species. As XAFS is able to probe structures of bulk samples and detect elements with very low contents, it is used to complement the data that is obtained from XPS. Furthermore, XAFS is able to

provide information such as coordination numbers and bond lengths that cannot be obtained from XPS.

XAFS refers to the study of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of the atom. The extent of X-ray absorption by individual element is largely dependent on parameters such as formal oxidation state, coordination chemistry, bond length, coordination number and species of neighbouring atoms. XAFS is capable of analyzing both amorphous and crystalline materials as it does not require long range order.¹¹

XAFS is commonly divided into two parts, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). XANES, also known as near edge X-ray absorption fine structure (NEXAFS), occurs in the region from the absorption edge to about 50 eV and is sensitive to the formal oxidation state and coordination chemistry of the probed atom. EXAFS occurs in the regions extending from 50 eV above the absorption edge and can be used to determine the bond length, coordination number and neighbouring species. XAFS is a facile and practical method for determining the chemical state and local atomic structure of a selected atomic species. A typical XAFS spectrum is shown in Figure 3.7.

Figure 3.7 Typical XAFS spectra.¹²

When the energy of the incident X-ray beam coincides or is higher than that of the binding energy of the core-level electrons, a photoelectron will be produced together with a core vacancy (Figure 3.8). A sharp rise, known as the absorption edge, in the XANES region of the XAFS spectra can be observed. The photoelectron will have a very short life time and the core vacancy will be filled by either an Auger process or by capturing an electron from another shell followed by the emission of a fluorescent photon. According to the energy values, the absorption coefficient could be determined.

Figure 3.8 Schematic of photoelectric effect.¹³

EXAFS mode looks at the oscillatory features at energy level above the absorption edge. The spectrum is generated by interference created by the outgoing photoelectron wave and the scattered parts of the photoelectron wave function. Due to constructive and destructive interference of the waves, information on the bond length, coordination number and neighbouring species can be determined.

All XAFS experiments were conducted at the XAFCA beam line at Singapore Synchrotron Light Source (SSLS), with photon energy ranging from 1.2 keV to 12.8

keV. All experiments were conducted at room temperature and atmospheric conditions. Data were processed using the Demeter and Athena software.

3.3.7 Fourier Transform Infrared Spectroscopy

In this PhD study, fourier transform infrared spectroscopy (FTIR) is used to obtain the infrared spectra of the samples. FTIR is useful for the analysis of specimens with asymmetrical stretchings and bendings that result in a change in dipole moments. FTIR is considered relatively inexpensive and the drawback of having to prepare the sample by mixing with potassium bromide can be eliminated by the use of a attenuated total reflectance (ATR) accessory.

FTIR is a commonly used technique to obtain an infrared spectrum for the absorption or emission of a sample. Infrared radiation is usually passed through the sample, and some radiation will be absorbed by the sample while some are transmitted through the sample. The resulting spectrum will represent the molecular absorption and transmission, giving a molecular ‘fingerprint’ of the sample. Different chemical structures produces different spectral fingerprints thus making FTIR useful in helping to identify unknown materials.¹⁰

Infrared spectroscopy is also commonly known as vibrational spectroscopy. When the sample is exposed to infrared radiation, molecules will selectively adsorb radiation of explicit wavelength which will cause a change in dipole moment of the sample molecules. The vibrational energy level of the samples molecules will then be promoted to the excited state. Frequency of the absorption peak is determined by the change in vibrational energy of the molecule. The number of vibrational freedom of the molecules will determine the number of adsorption peaks.

A FTIR usually consist of the infrared source, interferometer, sample compartment, detector and a computer. The infrared source will generate the radiation which will pass through the interferometer and reaches the detector before being amplified and

sent to a computer where Fourier transform is carried out. FTIR has several advantages such as being non-destructive, fast signal collection and has good signal to noise ratio.

All FTIR spectra were collected using a PerkinElmer spectrometer (Spectrum GX FTIR) at room temperature from 500 to 4000 cm^{-1} .

3.3.8 Raman Spectroscopy

In this PhD study, Raman spectroscopy was used to confirm the successful conversion of transition metal/PDA hybrids to transition metal/C-PDA nanocomposites. The carbon diffraction peak was not visible in the XRD analysis as it was shadowed by the intense peaks of the transition metal species. Raman spectroscopy also works in complementary to FTIR spectroscopy. In general strong bands in the Raman spectrum corresponds to weak bands in the IR spectrum and vice versa. Symmetrical stretching and bending resulting to a change in polarizability tend to be more Raman sensitive.

Raman spectroscopy is a non-destructive spectroscopic technique based on the inelastic scattering of monochromatic light, usually a laser source. The laser source will be absorbed by the sample and re-emitted with a change in frequency of the re-emitted photons, either up or down in comparison with the original frequency. The shift in frequency can give crucial information about the rotational, vibration and other low frequency transitions in molecules. Raman spectroscopy can be used to analyze solid, liquid or gaseous samples.

Raman shifts are reported in wavenumbers and have units of inverse length as it is directly related to energy. Raman shift can be derived using Eq 3.3, where $\Delta\omega$ is the Raman shift expressed in wavenumber, λ_0 is the excitation wavelength and λ_1 is the Raman spectrum wavelength.

$$\Delta\omega = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) \text{ (Eq 3.3)}$$

Raman spectra were collected using a Renishaw InVia Raman Microscope in backscattering configuration (Leica N Plain EP1 100x objective lens, NA 0.85) equipped with a charge coupling device (CCD).

3.3.9 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to study the content of transition metal species present in the transition metal/PDA hybrids and corresponding C-PDA nanocomposites.

TGA is a thermal analysis method in which changes in mass of the material is measured as a function of increasing temperature in a controlled atmosphere such as air, nitrogen or vacuum. TGA is commonly used to determine selected characteristics of materials by studying the mass loss or gain due to loss of volatile species, oxidation or decomposition and is especially useful for the study of polymeric materials.

TGA analysis was conducted on a TA Instruments thermogravimetric analyzer (TGA Q500) and samples were heated from room temperature to 900 °C in air with a heating rate of 10 °C min⁻¹.

3.3.10 Vibrating Sample Magnetometer

Vibrating sample magnetometer (VSM) is an instrument that measures the magnetic property of a material with high precision, based on Faraday's Law. Faraday's Law states that an electromagnetic force is generated in a coil when there is a change in flux through the coil. Schematic of a VSM is shown in Figure 3.9. A sample is first placed in a constant magnetic field which will magnetize the sample by aligning the magnetic domains with the field. A magnetic field will be created around the sample

and changes as the sample is vibrated sinusoidally. The change in magnetic field will be detected and induce an electric field in the pickup coils. The current in the pickup coil will be proportional to the magnetization of the sample. The greater the magnetization, the greater the induced current in the pickup coil.

All magnetization curves were recorded at room temperature with a VSM (Lakeshore, VSM-7404).

Figure 3.9 Schematic representation of a vibrating sample magnetometer.¹⁴

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Chapter 4

One-Pot Synthesis of Fe(III)-Polydopamine Complex: Morphological Evolution, Mechanism and Application of the Carbonized Nanocomposites for Electrocatalysis

In this chapter, the one-pot synthesis of Fe(III)-PDA complex nanospheres is reported and their structure, morphology evolution and possible underlying mechanism are revealed. It is verified with XAFS that both the oxidative polymerization of DOPA and Fe(III)-PDA complexation contributed to the 'polymerization' process. In the polymerization process, morphology of the complex nanostructures gradually transformed from sheet-like to spherical with Fe(III)/DOPA feed ratio of 1/3. The results suggest that the formation of the spherical morphology is likely driven by covalent polymerization-induced decrease of hydrophilic functional groups, which leads to re-self-assembly of the PDA oligomers to reduce surface area. The Fe(III)-PDA complex nanospheres are converted to C-PDA/Fe₃O₄ nanospheres via a high temperature annealing process and used as an electrocatalyst for ORR in ZnABs. It is believed that the findings from this work would facilitate the future development of new hybrid materials with interesting morphologies for use in various applications.

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4.1 Introduction

As introduced in Chapter 2, mussel adhesive plaques, which are responsible for the excellent adhesion properties of mussels, are formed by the cross-linking of catechol containing proteins with iron(III) ions.¹⁻³ The degree of cross-linking between catechol groups and iron(III) ions was found to be dependent on pH, with one iron(III) ion chelating with one, two or three catechol groups at increasing pH.^{4, 5} Mimicking mussel adhesive proteins, iron(III) ions have been used to crosslink catechol-containing synthetic polymers to produce self-healing hydrogels/networks.⁴ Since then iron(III) ions have been the most widely reported transition metal species when discussing about coordination bonds with catechol groups or DOPA.^{6, 7} Many iron/PDA hybrids have been formed through the incorporation of iron species onto PDA.⁸ For example, Zhou et al. have showed the fabrication of N- and Fe-doped hollow carbon nanospheres by Fe³⁺-mediated polymerization of DOPA on SiO₂ nanospheres, followed by carbonization and subsequent KOH etching of the SiO₂ template.⁹ Despite of the large number of works that have been carried out on fabricating transition metal/PDA hybrids through the addition of transition metal species in the in situ polymerization of DOPA, especially for iron, most of these works have placed their focus on the applications of the derived hybrids and nanocomposites. No attempts have been made to study the possible effects that these transition metal species have on the self-assembly mechanism of PDA.

In this work, Fe(III)-PDA complex nanospheres were synthesized via one-pot iron(III) ion-mediated polymerization of DOPA. Noting that most methods used to produce hybrid nanospheres involve multiple steps or require the use of templates, this method is advantageous being single-step, template-free and performed under mild conditions. To probe how the iron(III) ions affect the polymerization of DOPA and self-assembly of PDA, morphological evolution of the Fe(III)-PDA complex and neat PDA nanospheres was monitored. The effect of varying iron(III) ion/DOPA ratio on the morphology of the Fe(III)-PDA complex nanostructures was also studied. The chemical structures of the Fe(III)-PDA complex nanospheres, in particular the

interactions between iron(III) ion and PDA, were analyzed using various spectroscopic methods, including X-ray absorption fine-structure spectroscopy (XAFS) and X-ray photoelectron spectroscopy (XPS). This study shed some light on the mechanism of the complex process of iron(III) ion-mediated polymerization of DOPA, in which covalent bonding, coordination bonding and physical interaction-induced self-assembly take place simultaneously. Furthermore, using this simple one-pot synthesis method, the complex nanospheres are embedded with homogeneously distributed iron(III) ions and the hybrid nanospheres size is much smaller than those of neat PDA nanospheres reported in literatures. Upon heat treatment, the Fe(III)-PDA complex nanospheres can be easily converted to C-PDA nanospheres with evenly distributed Fe_3O_4 nanoparticles of only 3-5 nm in size, which are potentially good non-noble metal electrocatalyst. Herein it is also demonstrated that such $\text{Fe}_3\text{O}_4/\text{C-PDA}$ nanospheres exhibits ORR electrocatalytic properties and delivers a stable discharge voltage when utilized for the air cathode in primary ZnABs, and are also useful recyclable catalyst support.

4.2 Experimental

4.2.1 Materials

3,4-Dihydroxyphenethylamine hydrochloride (DOPA), tris(hydroxymethyl) aminomethane (Tris) and iron(III) chloride (FeCl_3) were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared using deionized (DI) water.

4.2.2 Preparation of Fe(III)-PDA Complex and $\text{Fe}_3\text{O}_4/\text{C-PDA}$ Composite Nanospheres

3,4-Dihydroxyphenethylamine hydrochloride (DOPA) (1 g L^{-1}) was dissolved in 1000 mL of deionized water (DI water). Iron(III) chloride (FeCl_3) was then added to

the DOPA solution at various concentrations (5.27, 2.64, 1.76, 1.32, 1.05 and 0.88 mM) to achieve iron(III) ions/DOPA molar ratio of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6, respectively. The solution was left to stir on a magnetic stirrer at room temperature for approximately 30 min for the solution to be thoroughly homogenized. The pH of the solutions were adjusted by adding in 1.2114 g (10 mmol) of tris(hydroxymethyl)aminomethane (Tris), and the solution left to stir for approximately 72 h. The solutions were then centrifuged for 30 min at 10000 rpm to separate the solid product (Fe(III)-PDA complex). The isolated solid product were then washed with DI water to remove un-polymerized DOPA and centrifuged again. This process was repeated twice. The final solid product was then immersed in liquid nitrogen followed by freeze-drying. The obtained Fe(III)-PDA complex powder was then annealed in a tube furnace at 650 °C for 3 h under constant argon flow to yield the final product, Fe₃O₄/C-PDA composite nanospheres.

4.2.3 Characterization

UV-vis analysis of the solutions was conducted on a Shimadzu UV-vis spectrometer (UV-2700). The morphologies of the samples were examined using FESEM (JEOL 7600F) at an accelerating voltage of 5 kV and TEM (JEOL 2010) with accelerating voltage of 200 kV. A XRD (Bruker D8 Discover) with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation generated at 40 mA and 40 kV was used to investigate the structure of the nanospheres in 2θ range of 5 to 90 °. Scan rate used was 1 ° min⁻¹ with a step of 0.02 °. Raman spectra were collected using a confocal Raman microscope (Renishaw InVia Raman Microscope) in back scattering configuration (Leica N Plain EP1 100X objective lens, NA 0.85) equipped with a charge coupling device (CCD). The laser source used was Argon ion laser with a wavelength of 785 nm. FTIR measurements were collected using a Perkin-Elmer (Spectrum GX FTIR) spectrometer at room temperature from 500 to 4000 cm⁻¹. XAFS spectroscopy was recorded at the XAFCA beamline¹⁰ at the Singapore Synchrotron Light Source (SSLS). XPS measurements were collected on a Kratos Analytical AXIS His spectrometer with a monochromatized Al K α X-ray source (1486.6 eV photons). Room temperature

magnetization curves of the product were measured using a vibrating sample magnetometer (Lakeshore, VSM-7404).

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were conducted on an Autolab potentiostat/galvanostat (PGSTAT302N) station attached to a rotating disk electrode (RDE) using 0.1 M KOH electrolyte saturated with O₂ or N₂. Ag/AgCl electrode (saturated with 3 M KCl) and a Pt foil were used as the reference and counter electrodes, respectively. The working electrode was prepared by dispersing 20 mg of Fe₃O₄/C-PDA in 1 mL aqueous solution of Nafion (1 wt%, diluted from 5 wt%, Aldrich) by sonicating for 15 min to obtain a consistent catalyst ink. The catalyst ink was pipetted onto a glassy carbon electrode (GCE, 5 mm in diameter) and allowed to dry in air overnight. The loading of catalyst was fixed at 0.5 mg cm⁻².

The number of transferred electrons (η) per O₂ molecule in ORR was calculated by Koutecky-Levich (K-L) equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.2nFC_O(D_O)^{2/3}\nu^{-1/6} \quad (2)$$

$$j_K = nFKC_O \quad (3)$$

where J is the measured current density, J_K and J_L are the kinetic-limiting and diffusion-limiting current density, respectively; ω is the disks' angular velocity, n is the number of electrons transferred per O₂ molecule in ORR, F is Faraday constant, C_O is the bulk concentration of O₂, D_O is the diffusion coefficient of oxygen (O₂), ν is the electrolytes' kinematic viscosity and k is the electron transfer rate constant.

The performance of the primary ZnAB was tested using a self-assembled cell. A two-electrode configuration was used by pairing Fe₃O₄/C-PDA loaded carbon paper electrode (loading of 1 mg cm⁻²) with a polished zinc plate in 6 M KOH. Surface

area of the polished zinc plate exposed to the KOH electrolyte is 4 cm^2 . The discharge tests were performed at room temperature under atmospheric condition.

4.3 Results and Discussion

4.3.1 Chemical Structure of the Fe(III)-PDA Complexes

In this work, the Fe(III)-PDA complex were synthesized by firstly dissolving FeCl_3 into an aqueous solution of DOPA to form Fe(III)-DOPA complex and then adding in Tris buffer to trigger the polymerization of DOPA. Although previous studies have showed that iron(III) ions could effectively cross-link mussel adhesive proteins and catechol-grafted synthetic polymers via Fe(III)-catechol coordination bonds,¹⁻⁴ so far how iron(III) ions would be incorporated into PDA in this one-pot polymerization process has not been clarified. In particular, the self-polymerization of DOPA occurs under basic conditions, and both DOPA and PDA are redox active, which may convert iron(III) ions to species such as iron hydroxides or oxides. UV-vis, FTIR, XAFS and XPS studies were thus conducted to probe the chemical structures of the hybrid obtained. For chemical analysis, the feed molar ratio of iron(III) ions to DOPA was fixed at 1 to 3.

Figure 4.1 UV-vis spectra of the solutions before and immediately after addition of Tris, and the suspension after the addition of Tris for 72 h (inset: picture of the solution at various stage of reaction).

Upon the addition of FeCl_3 , a Lewis acid, into the DOPA solution, the pH of the solution dropped from 5.7 to 2.8 and the color of the solution changed to green, suggesting the formation of Fe(III)-catechol mono-complex.¹¹ Absorption maxima at about 400 and 740 nm were observed in the UV-vis spectrum of the solution, which are consistent with reported values in literatures for the formation of mono-complex.^{4,5,11} With the addition of Tris buffer, instantly the solution turned to purple (inset of Figure 4.1) and the pH was increased to 7.7. From the corresponding UV-vis spectrum (Figure 4.1), it can be observed that the absorption maximum undergoes a blue shift to 558 nm.⁵ The UV-vis spectra and the corresponding pH values indicate that with the addition of Tris buffer, the solution may consist of a mixture of bis- and tris-complex of Fe(III)-catechol, while the tris-complex is formed predominately.^{4,5} In the initial stage of the polymerization process, no solid products could be obtained by subjecting the solution to centrifuge. By freeze-drying the reaction solution, some sheet-like solid products were obtained (Figure 4.2) but they could be completely dissolved in DI water, showing that there was no sufficient covalent polymerization of DOPA and π - π stacking of oligomers, i.e., the product was mainly composed of uncrosslinked complex moieties. After polymerizing for 72 h, a dark colored suspension was formed and the pH was reduced to 6.5. The UV-vis spectrum of the suspension, with an absorption band at 350 nm, suggests the formation of PDA oligomers and other small oxidation products.¹² The solid products obtained by centrifuge are insoluble in water presumably owing to the cross-linking by both covalent and coordination bonds as well as π - π stacking of the oligomers.

Figure 4.2 TEM micrograph of sheet-like solid product obtained at initial stage of polymerization. It can be dissolved in DI water.

In the FTIR spectrum of PDA (Figure 4.3a), the bands at 1508 and 1620 cm^{-1} can be attributed to the stretching vibration of indoline and indole structure of PDA. For the hybrid nanospheres, the band at 1508 cm^{-1} is split into two bands at 1483 and 1546 cm^{-1} , and the intensity of the band at 1620 cm^{-1} is lowered. The decrease in intensity and splitting of band suggests the formation of a Fe(III)-PDA complex in a manner similar to previously reported work.^{2, 13}

Figure 4.3 a) FTIR spectrum of PDA and Fe(III)-PDA, b) XANES spectra of Fe(III)-PDA, Fe_2O_3 and $\text{Fe}(\text{OH})_3$, c) Fourier transformed EXAFS spectra of Fe(III)-PDA, d) XPS spectra of PDA and Fe(III)-PDA, e) O 1s XPS spectra of PDA and Fe(III)-PDA and f) N 1s XPS spectra of PDA and Fe(III)-PDA.

Fe K-edge XAFS was employed to confirm the chemical state and coordination environment of the Fe(III)-PDA complex nanospheres. By comparing the results with known standards (Figure 4.3b), it can be determined that Fe in the sample exists in the trivalent state and not in the form of iron oxide or iron hydroxide. In Figure 4.3c, the Fourier transform of the EXAFS oscillations $\chi(k)*k^3$ of Fe K-edge into R space in the k range of 2 to 12 Å⁻¹ are shown. Curve fitting was performed and the corresponding data are shown in Table 4.1. A strong peak in the R range between 0.9 and 1.9 Å can be attributed to photoelectron backscattering on the nearest neighbor around Fe. The fitting results suggest that the iron(III) ions in the complex nanospheres form coordination bonds with both oxygen and nitrogen with bond length of 2.01 and 1.65 Å, respectively. The ratio of Fe-O and Fe-N coordination numbers is roughly 4.3 to 1.0, indicating that similar to the complexes in the solution, the iron(III) ions in the nanospheres predominately form coordination bonds with catechol groups of PDA, while some Fe-N coordination bonds may form in the polymerization process.

Table 4.1 EXAFS fitting result for Fe K-edge of Fe(III)-PDA. d is bond distances; CN is coordination number; and σ^2 is Debye-Waller factor.

Path	d (Å)	CN	σ^2 (Å ²)
Fe – O	2.01 ± 0.02	4.3 ± 0.4	0.007 ± 0.001
Fe – N	1.65 ± 0.02	1.0 ± 0.1	0.005 ± 0.001

XPS analysis was employed to quantitatively determine the chemical compositions of the Fe(III)-PDA complex. As shown in Figure 4.3d, the peak related to Fe 2p appears in the spectra of Fe(III)-PDA and accounts for 1.90 at% of the Fe(III)-PDA complex. This translates to approximately 8 wt% of Fe in the Fe(III)-PDA complex, which is close to the value estimated using TGA (10 wt%, Figure 4.4). The measured Fe contents are slightly lower than the Fe content calculated based on the feed molar ratio of Fe(III)/DOPA (Fe(III)/DOPA molar ratio of 1:3 is equivalent to about 10.9 wt% Fe), implying that polymerization may occur between the complex *moieties* and some free DOPA monomers that are not bonded to iron(III) ions. In Figures 4.3e and

4.3f, the binding energies of O 1s and N 1s bands of neat PDA are around 533.5 and 402.2 eV, respectively, whereas for Fe(III)-PDA complex, the O 1s band shifts to about 531.6 eV and the N 1s bands to about 400.2 eV, also indicating that the iron(III) ions are bonded to both O and N atoms of PDA, corroborating the data obtained from XAFS.

Figure 4.4 TGA curve of Fe(III)-PDA at different molar ratios.

4.3.2 Morphological Evolution of Fe(III)-PDA Complex Nanostructures

After polymerization for 72 h, both the neat PDA and Fe(III)-PDA complex exhibited spherical morphology as disclosed by FESEM. The size of the complex nanospheres is only about 80 nm, much smaller than that of its neat PDA counterpart of about 180 nm (Figure 4.5a and 4.5b). In an attempt to understand the formation process of the complex nanospheres and account for the aforementioned size difference, a TEM study was conducted to monitor the growth processes of both PDA and Fe(III)-PDA complex nanostructures and the evolution of the nanostructure's morphology over time. 10 mL of the respective reaction solutions were extracted at various time interval during the polymerization process and frozen with liquid nitrogen to immediately stop the polymerization process. The frozen

sample was freeze-dried before TEM observation. Figures 4.5c and 4.5d show the morphology evolution of the PDA and Fe(III)-PDA complex nanostructures, respectively. For both systems, the morphology of the nanostructures is transformed from the initial stacked nanosheets to inter-connected nanospheres on sheets and finally individual nanospheres. The observation of an intermediate state (nanospheres connected on sheets) between the sheet-like morphology and nanospheres suggests that the formation of spherical morphology is likely to be driven by the covalent bonding-induced decrease of hydrophilic functional groups, which causes re-self-assembly of the stacked oligomers to reduce specific surface area. The inter-connected nanospheres observed at the intermediate stage could be at a stage where the rearrangement of the oligomers is still ongoing, where some stacked sheets have rearranged into small spheres while some are still stacked together in the sheet form. The complex nanospheres are much smaller probably because they have less covalent bonds and more functional groups on their surfaces, and hence more hydrophilic and tend to achieve larger specific surface area to interact with the aqueous medium. By contrast, in the absence of iron(III) ions in the system, the functional groups are not consumed by complexation with iron(III) ions and hence there are larger amounts of free DOPA monomers and oligomers, which may increase the extent of covalent polymerization. This may make the neat PDA nanospheres more hydrophobic and hence smaller specific surface area in the aqueous medium.

Figure 4.5 FESEM micrographs of a) PDA and b) Fe(III)-PDA complex nanospheres (scale bar is 100 nm). TEM micrographs showing morphologies of c) PDA and d) Fe(III)-PDA complex nanostructures at different reaction time: (c1 & d1) 3 h, (c2 & d2) 12 h and (c3 & d3) 24 h.

4.3.3 Morphologies of Fe(III)-PDA Complex Nanostructures at Different Fe(III)/DOPA Feed Ratios

To further investigate the formation mechanism of the Fe(III)-PDA complex nanospheres, complex nanostructures were also synthesized by adding different amounts of FeCl₃ to the aqueous solution of DOPA to achieve Fe(III)/DOPA molar ratio of 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6, respectively. A fixed amount of Tris buffer was then added to the solutions and the reaction left to stir for 72 h. Upon the addition of FeCl₃ into the DOPA solution, the color of all the solutions changed to green and the pH values of all the solutions were found to be in the range of 2 to 3 (Table 4.2), suggesting the formation of mono-complex. An absorption maximum at about 740 nm corresponding to mono-complex was also observed in the UV-vis spectra of all the solutions (Figure 4.6).^{4, 5} With the addition of the Tris buffer, the pH was increased to 4.7, 7.2, 7.7 and 8.0 for the Fe(III)/DOPA molar ratio of 1:1, 1:2, 1:3 and 1:4 respectively (Table 4.2), and the solutions turned to colors ranging from blue to wine red for the Fe(III)/DOPA molar ratio of 1:1, 1:2, 1:3 and 1:4 respectively (inset of Figure 4.6). From the corresponding UV-vis spectra (Figure 4.6), it was observed that the absorption maximum undergoes a blue shift to 620, 579, 558 and 513 nm for Fe(III)/DOPA ratio of 1:1, 1:2, 1:3 and 1:4 respectively.⁵ The UV-vis spectra and the corresponding pH value indicate that with the addition of Tris buffer, a mixture of bis- and tris-complex is formed in the various solutions and the content of the tris-complex increases with pH.

Table 4.2 pH values of the various solutions before and after addition of Tris.

Fe ³⁺ -DOPA molar ratio	pH value prior to the addition of Tris	pH value immediately after the addition of Tris	pH value after 72 hours of polymerization
Pure Dopamine	5.7	8.5	7.6
1 – 1	2.4	4.7	3.9
1 – 2	2.6	7.2	5.2
1 – 3	2.8	7.7	6.5
1 – 4	2.9	8.0	7.4

Figure 4.6 UV-vis spectra of the various samples (inset: picture of the solution with different ratio of Fe(III)/DOPA taken immediately after the addition of Tris).

To ascertain that the formation of the various complexes is dominated by the pH of the solution rather than the Fe(III)/DOPA ratio, pH of the solutions with the Fe(III)/DOPA molar ratios of 1:1 and 1:2 was adjusted to approximately 8.5 by the addition of extra Tris and UV-vis spectra of the solutions were observed (Figure 4.7a and b). The UV-vis spectra of both solutions show a blue shift of the absorption maximum when the pH is adjusted to 8.5, confirming that the formation of the various complexes is dominated by the pH of the solution, rather than the Fe(III)/DOPA ratio.

The polymerization of DOPA with different amounts of iron(III) ions (and the fixed amount of Tris buffer) resulted in Fe(III)-PDA complex nanostructures of different morphologies, as shown in the TEM images in Figure 4.8. In all cases, no aggregated Fe species could be observed in the nanostructures, implying that the iron(III) ions are uniformly distributed in PDA owing to the formation of complexes. However, figures 4.8a and 4.8b show that when the feed molar ratio of iron(III) ions to DOPA is kept at 1:1 and 1:2, the Fe(III)-PDA complex has sheet-like morphology. As the

feed molar ratio of iron(III) ions to DOPA decreases to 1:3, TEM micrograph (Figure 4.8c) shows that the morphology evolves into that of a sphere with an average diameter of about 80 nm. Figures 4.8d, e and f show that as the feed ratio of iron(III) ions to DOPA is further decreased to 1:4, 1:5 and 1:6, the size of the Fe(III)-PDA complex nanospheres formed increases significantly to an average diameter of about 200, 250 and 300 nm, respectively, and the nanospheres become more and more inter-connected. The formation of sheet-like morphology at the Fe(III)/DOPA molar ratio of 1:1 and 1:2 is not related to the presence of bis-complex in the initial solutions because even though tris-complex is predominately formed at pH = 8.5, the final morphology obtained from the solution with Fe(III)/DOPA ratio of 1:1 and pH of 8.5 is still sheet-like, as observed from the TEM micrograph (Figure 4.9). A plausible explanation is that the formation of the sheet-like morphology is mainly due to the stacking of planar oligomers formed by complexation and slight covalent bonding, whereas the spherical morphology observed when the molar ratio of iron(III) ion to DOPA is increased to 1:3 and above may be attributed to a higher extent of covalent polymerization due to the presence of free DOPA (not bonded to Fe) in the reaction solution. The molar ratio of 1:3 could be the critical ratio whereby there is a sufficient amount of free DOPA monomers in the solution after all of the iron(III) ions have formed bis- and tris- complexes. These free DOPA monomers may form covalent bonds with the oligomers, consuming hydrophilic functional groups and making the nanostructures more hydrophobic. Thus the self-assembled nanostructures tend to rearrange themselves in a manner to reduce their specific surface area, eventually leading to spherical morphology. The increase in size of the nanospheres with increasing Fe/DOPA ratio could be due to the presence of higher amounts of free DOPA monomers, which increases the degree of covalent polymerization and hence makes the resultant spheres more hydrophobic, leading to larger, inter-connected spheres (insets of Figures 4.8e and 4.8f) with even smaller specific surface area. TGA data (Figure 4.4) show that the samples with feed Fe(III):DOPA molar ratios of 1:1, 1:2 and 1:3 have similar Fe content (approximately 10 wt%), whereas the samples with feed Fe(III):DOPA molar ratios of 1:4, 1:5 and 1:6 have lower Fe contents, indicating that free iron(III) ions, which

have no coordination bonds with DOPA, could not be incorporated into the complex nanostructures, whereas free DOPA monomers do take part in the polymerisation process.

Figure 4.7 a) UV-vis spectra of Fe(III)/DOPA (1:1) solution at various pH and b) UV-vis spectra of Fe(III)/DOPA (1:2) solution at various pH.

Figure 4.8 TEM micrographs of Fe(III)-PDA complex nanostructures with Fe(III)/DOPA feed molar ratios of a) 1:1, b) 1:2, c) 1:3, d) 1:4, e) 1:5 and f) 1:6.

Figure 4.9 TEM micrograph of Fe(III)-PDA complex at Fe(III)/DOPA feed molar ratio of 1:1 with pH adjusted to 8.5. The polymerization time was 72 hrs.

4.3.4 Structure, Morphology and Magnetic Properties of Fe₃O₄/C-PDA Nanospheres

To demonstrate the usefulness of this simple one-pot synthesis method, Fe₃O₄/C-PDA composite nanospheres were prepared by annealing the Fe(III)-PDA complex nanospheres with Fe(III)/DOPA feed ratio of 1:3. Figure 4.10a shows the TEM micrograph of the composite nanospheres obtained by annealing at 650 °C for 2 h. There is no significant change in the size of the nanospheres after the annealing process, while homogeneously distributed nanoparticles with size of only about 3-5 nm are observed. These nanoparticles show characteristic X-ray diffraction peaks at $2\theta = 18.3^\circ$, 30.1° , 35.5° , 37.1° , 43.3° , 53.5° , 57.3° and 62.7° (Figure 4.10c), corresponding to the (111), (220), (311), (222), (400), (422), (511) and (440) planes of Fe₃O₄, respectively.¹⁴ The magnetization curve of the Fe₃O₄/C-PDA nanospheres is shown in Figure 4.10b. The saturation magnetization value (M_s) of the composite nanospheres is about 15 emu g⁻¹, and there is almost no hysteresis loop found in the magnetization curve, suggesting the superparamagnetic property of the Fe₃O₄/C-PDA nanospheres. The magnetic property makes the Fe₃O₄/C-PDA nanospheres an ideal candidate for use as a recyclable catalyst support.

The conversion of neat PDA nanospheres to C-PDA nanospheres by annealing was investigated through X-ray diffraction and Raman spectroscopy studies. Neat PDA,

after annealing, exhibits diffraction peaks at $2\theta = 23.4^\circ$, 43.7° (Figure 4.10c), corresponding to (002) and (100) plane of carbon.¹⁵ However, such diffraction peaks are not visible in the XRD pattern of $\text{Fe}_3\text{O}_4/\text{C-PDA}$ due to the presence of intense peaks of Fe_3O_4 . However, different from that of the Fe(III)-PDA complex nanospheres, the Raman spectrum of the $\text{Fe}_3\text{O}_4/\text{C-PDA}$ composite nanospheres show well defined D and G band of carbon at 1325 and 1581 cm^{-1} , respectively (Figure 4.10d), confirming the formation of C-PDA in $\text{Fe}_3\text{O}_4/\text{C-PDA}$.¹⁶ It is worth noting that several previous studies have shown that the aggregation of metal species and evaporation of organic volatiles during the carbonization process could create mesopores in the C-PDA matrix,^{9, 13} allowing the embedded inorganic nanoparticles be exposed to the surrounding media. Nitrogen adsorption-desorption isotherms of $\text{Fe}_3\text{O}_4/\text{C-PDA}$ shows a relatively high BET specific surface area of $475\text{ m}^2\text{ g}^{-1}$ (Figure 4.11). The pore size distribution curve (inset in Figure 4.11) shows the presence of pores with sizes of about 2 and 9 nm, which are created during the carbonization process. The pore size distribution peak at about 44 nm could be attributed to the inter-sphere spacing among the stacked nanospheres.⁹ In addition, it is also widely reported that C-PDA is highly graphitized and doped with a substantial amount of pyridinic and graphitic N.^{9, 17, 18} These features of C-PDA, together with the abundant extremely small Fe_3O_4 nanoparticles embedded in C-PDA, make the $\text{Fe}_3\text{O}_4/\text{C-PDA}$ nanospheres a good candidate for use as ORR electrocatalysts.

Figure 4.10 a) TEM micrograph, b) VSM curve of $\text{Fe}_3\text{O}_4/\text{C-PDA}$ composite nanospheres, c) XRD patterns of C-PDA and $\text{Fe}_3\text{O}_4/\text{C-PDA}$ composite nanospheres, and d) Raman spectra of Fe(III)-PDA complex and $\text{Fe}_3\text{O}_4/\text{C-PDA}$ composite nanospheres.

Figure 4.11 Nitrogen adsorption-desorption isotherm of $\text{Fe}_3\text{O}_4/\text{C-PDA}$ (inset: BJH pore size distribution curve of $\text{Fe}_3\text{O}_4/\text{C-PDA}$).

4.3.5 ORR Catalytic Activity and ZnAB Performance of Fe₃O₄/C-PDA Nanospheres

The electrochemical performance of the composite nanospheres was evaluated by LSV, CV and RDE measurements in 0.1 M KOH electrolyte purged with O₂ or N₂. In CV measurements, no obvious reduction peak is observed for the N₂-saturated aqueous KOH electrolyte. A change to the O₂-saturated electrolyte leads to the appearance of a cathodic reduction peak at -0.27 V (vs. Ag/AgCl), representing an ORR activity (Figure 4.12a). To have a deeper understanding of the electrocatalytic behaviors of Fe₃O₄/C-PDA, RDE voltammograms were recorded alongside with readings from C-PDA and commercial Pt/C catalyst (20 wt% Pt on carbon black) at a rotation speed of 1600 rpm (Figure 4.12b). Fe₃O₄/C-PDA composite nanospheres exhibit enhanced electrocatalytic activity to ORR when compared with pristine C-PDA nanospheres. This improvement could be brought about by the electrocatalytic activity of Fe₃O₄ towards ORR,¹⁹ large surface area of the Fe₃O₄ particles brought by their very small size and uniform dispersion in C-PDA, and the synergistic effect of Fe₃O₄ and C-PDA, such as the close contact of Fe₃O₄ with electrically conductive C-PDA and the presence of pyridinic and graphitic N surrounding Fe₃O₄.^{9, 17, 18, 20, 21} The onset potentials for C-PDA, Fe₃O₄/C-PDA and commercial Pt/C are -0.27, -0.14 and 0.03 V, respectively. It is clear that in contrast to C-PDA, marked improvement in onset potential is seen for Fe₃O₄/C-PDA. However, when compared to commercial Pt/C, Fe₃O₄/C-PDA shows a slightly negative ORR onset potential. The ORR electrocatalytic activity of Fe₃O₄/C-PDA was also examined with Koutecky-Levich plots (inset of Figure 4.12c) derived from the RDE curves at electrode potential range of -0.4 to -0.7 V (Figure 4.12c). The good linearity and almost constant gradient can be distinctly observed from the plots, suggesting typical first-order kinetics with respect to the concentration of dissolved O₂. The number of electrons transferred (n) per oxygen molecule was calculated to be between 3.30 – 3.58, suggesting that to a large extent, Fe₃O₄/C-PDA promoted ORR in the desirable 4-electron pathway. With the aforementioned synergistic effect of Fe₃O₄ and C-PDA,

the $\text{Fe}_3\text{O}_4/\text{C}$ -PDA nanospheres could be a good candidate for use in electrocatalysis of oxygen reduction reaction.

$\text{Fe}_3\text{O}_4/\text{C}$ -PDA was also tested as an ORR electrocatalyst for a primary ZnAB, using $\text{Fe}_3\text{O}_4/\text{C}$ -PDA loaded carbon paper as an air cathode, zinc plate as the anode and 6 M aqueous KOH as electrolyte. The $\text{Fe}_3\text{O}_4/\text{C}$ -PDA based battery was discharged at a constant current density of 5 mA cm^{-2} and was able to continuously discharge over a period of 250 h, with voltage value above 1.10 V for the first 200 h (Figure 4.12d). The stable discharge voltage could be attributed to the stability of $\text{Fe}_3\text{O}_4/\text{C}$ -PDA when used as an ORR electrocatalyst as the Fe_3O_4 nanoparticles are well protected and separated by C-PDA. As the discharge current was raised to 20 mA cm^{-2} , the discharge voltage of the $\text{Fe}_3\text{O}_4/\text{C}$ -PDA based battery dropped to about 0.90 V.

Figure 4.12 a) CV curve of $\text{Fe}_3\text{O}_4/\text{C}$ -PDA in O_2 - and N_2 -purged 0.1 M KOH, b) LSV curves of C-PDA, $\text{Fe}_3\text{O}_4/\text{C}$ -PDA and commercial Pt/C for ORR at a rotation speed of 1600 rpm, c) RDE data of $\text{Fe}_3\text{O}_4/\text{C}$ -PDA (inset: K-L plots and fitting curves for $\text{Fe}_3\text{O}_4/\text{C}$ -PDA) and d) voltage profile of a $\text{Fe}_3\text{O}_4/\text{C}$ -PDA based ZnAB when fully discharged at a current density of 5 mA cm^{-2} (inset: voltage profile showing voltage difference when fully discharged at current density of 5 mA cm^{-2} and 20 mA cm^{-2} , respectively).

4.3.6 Fe₃O₄/C-PDA Nanospheres as Recyclable Catalyst Support

To showcase its versatility, the Fe₃O₄/C-PDA nanospheres were also evaluated as a recyclable support for catalyst. Pt nanoparticles were deposited on the surface of the composite nanospheres. TEM micrograph (Figure 4.13a) shows the successful attachment of Pt nanoparticles with average size of about 3 nm on the surface of the composite nanospheres. XRD analysis (Figure 4.13b) confirms the presence of Pt nanoparticles, with characteristic peaks of Pt observed. Saturation magnetization value (M_s) of Fe₃O₄/C-PDA/Pt was measured to be 7 emu g⁻¹ (Figure 4.13c). The reduction of p-nitrophenol by NaBH₄ is used as a model reaction to demonstrate the catalytic function of Fe₃O₄/C-PDA/Pt.¹³ The reduction process was monitored by measuring the UV-vis absorption spectra of the solution at various time interval, as shown in Figure 4.13d. In the absence of any catalyst, the characteristic absorption band at 400 nm indicative of p-nitrophenol remains even with the addition of high content of NaBH₄. With the addition of Fe₃O₄/C-PDA/Pt, the intensity of the band at 400 nm progressively decreases and a new band at 295 nm emerges, indicating the formation of p-aminophenol. The bright yellow solution becomes colorless within a short time span of 20 min, which is accompanied by the complete disappearance of the band at 400 nm, indicating the complete reduction of p-nitrophenol to p-aminophenol. Fe₃O₄/C-PDA/Pt could be easily recycled using a magnet owing to its paramagnetic property. The stability and activity of the catalyst was studied by repeating the reduction process using the same batch of catalyst for eight cycles (inset of Figure 4.13d). It is found that Fe₃O₄/C-PDA/Pt is still highly active at the eighth cycle with no significant change in morphology (inset in Figure 4.13d). The facile attachment of Pt nanoparticles on the surface of the composite nanospheres can be attributed to the abundant functional groups of PDA retained on the surface of the nanospheres after the annealing process.²¹ These functional groups are also responsible for the stability of the catalyst, preventing the agglomeration and leaching of the Pt nanoparticles.

Figure 4.13 a) TEM micrograph, b) XRD pattern and c) VSM curve of $\text{Fe}_3\text{O}_4/\text{C-PDA/Pt}$. d) UV-vis absorption spectra of the reduction of p-nitrophenol by NaBH_4 in the presence of $\text{Fe}_3\text{O}_4/\text{C-PDA/Pt}$ (inset: Activity of catalyst after 8 cycles and TEM micrograph of $\text{Fe}_3\text{O}_4/\text{C-PDA/Pt}$ after the catalytic reaction).

4.4 Conclusion

In this chapter, a facile one-pot method for synthesis of Fe(III)-PDA complex nanospheres is demonstrated. The results show that Fe(III)-catechol complexation, covalent bonding and self-assembly take place simultaneously in the “polymerization” process, and the Fe(III)-PDA complex formed gradually transforms from sheet-like to spherical morphology. As the feed ratio of iron(III) ion to DOPA increases, the final morphology of the Fe(III)-PDA complex also changes from sheet-like to spherical morphology. The formation of nanospheres is likely to be driven by the covalent polymerization-induced decrease of hydrophilic functional

groups, which causes re-self-assembly of the stacked oligomers to reduce specific surface area. The complex nanospheres can be easily converted to C-PDA nanospheres with embedded Fe₃O₄ nanoparticles with size of only about 3-5 nm via controlled annealing. Electrochemical studies showed the improved ORR activity of Fe₃O₄/C-PDA compared to the neat C-PDA. More importantly, a stable discharge voltage can be delivered for over 200 h when Fe₃O₄/C-PDA is used as the cathode for a primary ZnAB.

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Chapter 5

One-Pot Synthesis of Co(II)-Fe(III)-Polydopamine Complex: Mechanism and Morphological Design Towards Efficient Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries

In this chapter, the one-pot synthesis of Co(II)-PDA and Co(II)-Fe(III)-PDA complexes are reported. In the Co(II)-PDA system, cobalt(II) ions do not form coordination bonds with DOPA monomers; instead, they form complex with hydroxyl ions. With the oxidation, cyclization and polymerization of DOPA, the hydroxyl ions are then displaced by the oxidized DOPA units or PDA oligomers. In the Co(II)-Fe(III)-PDA system, iron(III) ions, which form coordination bonds with DOPA, are found to have a dominating effect on morphology of the nanostructures formed during the in situ polymerization process. Through the use of porous nanofibers as the template for deposition and subsequent annealing, CoFe₂O₄/CoFe/C-PDA porous nanofibers (PNFs) are facilely obtained. Electrochemical studies suggest that the CoFe₂O₄/CoFe/C-PDA PNFs can effectively catalyzes ORR via an ideal 4-electron pathway and outperform commercial Pt/C in catalyzing OER. ZnABs based on CoFe₂O₄/CoFe/C-PDA PNFs also showed longer cycling life and higher cycling stability than their counterparts that are based on commercial Pt/C and CoFe₂O₄/CoFe/C-PDA nanospheres. This work provides a general strategy to prepare highly active electrocatalysts with high surface area for air cathode of ZnABs.

5.1 Introduction

The work presented in Chapter 4 has clarified the mechanism of the in situ polymerization of DOPA in the presence of iron(III) ions. A facile one-pot method for the synthesis of Fe(III)-PDA complex nanospheres, the conversion of the nanospheres into C-PDA nanospheres with embedded Fe₃O₄ nanoparticles and the use of the C-PDA nanospheres as cathode material in primary ZnABs were demonstrated. However, the electrochemical performance of the Fe₃O₄/C-PDA nanospheres falls significantly short of those of commercial Pt/C catalyst and other state of the art ORR electrocatalysts.¹ Possible alternative to improve the electrocatalytic activity is to select a more electrocatalytic active TMOs such as CoFe₂O₄ and to design the morphology of the nanocomposites to increase the specific surface area for electrocatalytic reactions.²

Noble metal-based electrocatalysts such as Pt on carbon have been proven to have high activity for both ORR and OER.^{2,3} However, the high cost and scarcity of such materials have prevented their use for large-scale applications such as grid energy storage and electric vehicles.² Enormous efforts have been invested into developing non-noble metal-based and metal-free electrocatalysts, leading to the synthesis and discovery of a wide range of good ORR and OER electrocatalyst candidates, such as transition metal oxides,⁴⁻⁷ carbides^{8,9}, nitrides,^{10,11} and nitrogen-doped carbon¹²⁻¹⁴. More recently, binary and ternary TMOs, such as MnCo₂O₄, ZnCo₂O₄, CoFe₂O₄ and NiCoMnO₄, have also been investigated.^{5,15-18} Li et al. reported that CoFe₂O₄ has the highest electrocatalytic activities for OER among other MFe₂O₄ (M = Co, Ni, Cu, Mn, etc.).¹⁹ The superior electrocatalytic activities of CoFe₂O₄ have also been demonstrated by Liu et al. and Bian et al.^{15,20} Table 5.1 features a handful of recently investigated CoFe₂O₄ systems, their oxygen electrocatalyst performance and battery characteristics.

Table 5.1 Summary of bifunctional electrocatalyst and battery characteristics for recently studied CoFe_2O_4 systems^a

Catalyst Material	ORR and OER catalyst and battery characteristics – Primary(P)/Secondary(S)	Ref.
CoFe_2O_4 Nanofibers	OER_{Op} : 1.60 V vs. RHE; E_{js} : 1.64 V vs. RHE	19
CoFe_2O_4 Nanoparticles	OER_{Op} : 1.67 V vs. RHE; E_{js} : 1.75 V vs. RHE	19
CoFe_2O_4	ORR_{Op} : 0.85 V vs. RHE; ORR_{Lcd} : -5.00 mA cm^{-2} E_{j3} : 0.73 vs. RHE $n = 3.93$ OER_{Op} : 1.57 V vs. RHE	21
Ag- $\text{CoFe}_2\text{O}_4/\text{C}$	ORR_{Op} : -0.190 V vs. Hg/HgO; $\text{E}_{1/2}$: -0.130 V vs. Hg/HgO $n = 3.80 - 3.98$ E_{j10} : 0.79 V vs. Hg/HgO	22
CFO/RC-400	ORR_{Op} : -0.10 V vs. Ag/AgCl $n = 3.9 - 4.0$ OER_{Op} : 0.41 V vs. Ag/AgCl; OER_{Lcd} : 25.1 mA cm^{-2}	23
CF/N-rGO-150	ORR_{Op} : -0.020 V vs. Hg/HgO $n = 3.7$ (P) $\text{E}_{\text{discharge}}$: 1.0 V at current density of 20 mA cm^{-2}	24
$\text{CoFe}_2\text{O}_4/\text{graphene}$	ORR_{Op} : -0.136 V vs. Ag/AgCl $n = 3.85 - 3.94$ OER_{Op} : 0.54 V vs. Ag/AgCl; OER_{Lcd} : 29.5 mA cm^{-2}	15
$\text{CoFe}_2\text{O}_4/\text{CNTs}$	ORR_{Op} : -0.124 V vs. Ag/AgCl $n = 3.82 - 3.84$ OER_{Op} : 0.60 V vs. Ag/AgCl	25
CFO-ns/rGO	ORR_{Op} : -0.11 V vs. Ag/AgCl; ORR_{Lcd} : -5.51 mA cm^{-2} $n = 4.0$ OER_{Op} : 0.56 V vs. Ag/AgCl; OER_{Lcd} : 23.9 mA cm^{-2}	26

^aOp: onset potential; E_{j5} : potential at 5 mA cm⁻²; n: electron transfer number; I_{cd} : limiting current density. CFO/CF: cobalt ferrite; RC: rod-like ordered mesoporous carbon; rGO: reduced graphene oxide; CNTs: carbon nanotubes; ns: spinel type.

The performance of a ZnAB cathode is also highly dependent on its morphology, specific surface area and the distribution of the electrocatalytic active nanoparticles on the electrode.²⁷ A system with homogeneously distributed nanoparticles with large specific surface area is preferred. Free metal oxide nanoparticles are, however, prone to problems such as agglomeration and leaching, which may result in the failure of the ZnABs over time.²⁸ Several approaches have been developed to overcome these issues, such as immobilizing the nanoparticles on carbonaceous substrates such as carbon black, carbon nanofibers and nanosheets, or encapsulating the nanoparticles inside carbon nanoshells.^{25, 29-32} In particular, transition metal oxides and nitrogen co-doped carbon nanocomposites have emerged as a breed of electrocatalysts with much promise. Both N-doped carbon and TMOs nanostructures, individually, are known to be efficient ORR and OER electrocatalysts.^{5, 6, 33-36} Carbon, apart from aiding to hold the nanoparticles in place, can also improve the electrical conductivity as most of the TMOs are known to be poor electrical conductor.²⁹ The co-doped carbon showed ORR and OER electrocatalytic activity and/or durability that are comparable or even superior to that of noble metal-based electrocatalysts, possibly benefiting from the synergistic effect brought about by the interactions between the carbon and TMOs.³⁷⁻⁴⁰ The preparation of these electrocatalysts, however, typically involve multi-step processes and the use of an autoclave, which inevitably increases the time and cost of production.

In this chapter, building on from the work reported in the previous chapter, a facile one-pot synthesis method to produce CoFe/CoFe₂O₄ core/shell nanoparticles homogeneously encapsulated in PDA-derived mesoporous carbon nanofibers for use as bifunctional electrocatalysts in rechargeable ZnABs is reported. The mesoporous nanofibers were obtained by simply mixing DOPA with cobalt(II) ions and iron(III) ions in a basic aqueous solution to form a thin coating on porous polystyrene (PS)

nanofibers, followed by controlled annealing (Figure 5.1). Electrochemical studies reveal that the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ porous nanofibers (PNFs) exhibit good electrocatalytic activity towards ORR via an ideal 4-electron pathway and also activity towards OER. The ZnABs based on $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs electrocatalyst showed lower overpotential, high discharge voltage, and excellent cycling stability.

Figure 5.1 Schematics for synthesis of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs.

5.2 Experimental

5.2.1 Materials

3,4-Dihydroxyphenethylamine hydrochloride (DOPA), tris(hydroxymethyl) aminomethane (Tris), iron(III) chloride (FeCl_3), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Polystyrene (PS, $M_w = 350,000$) and Nafion (5 wt% aqueous solution) were purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF) was purchased from Fisher Chemical. All chemicals were used without further purification and all solutions were prepared using deionized (DI) water.

5.2.2 Synthesis of CoFe₂O₄/CoFe/C-PDA Nanospheres

0.5 g of DOPA was dissolved in 500 mL of DI water to form DOPA solution (1 mg mL⁻¹). 0.293 mM of cobalt chloride hexahydrate (CoCl₂·6H₂O) and 0.586 mM of iron(III) chloride (FeCl₃) were added into the DOPA solution under constant stirring. Molar ratio of cobalt(II) ions, iron(III) ions and DOPA was fixed at 1:2:9. The pH of the solution was adjusted by adding in 0.6057 g of Tris, and the solution left to stir for approximately 72 h. The solution was then centrifuged for 30 min at 10000 rpm to separate the solid product. The isolated solid product were then washed with DI water to remove unreacted reactants and centrifuged again. This process was repeated twice. The final solid product was then immersed in liquid nitrogen followed by freeze-drying. The freeze-dried powder was then annealed in a tube furnace at 900 °C for 2 h under constant argon flow before allowing it to cool back to room temperature. The powder is then transferred to a box furnace and heat at 300 °C in air for 3 h to obtain the final product, CoFe₂O₄/CoFe/C-PDA nanospheres.

5.2.3 Synthesis of CoFe₂O₄/CoFe/C-PDA Porous Nanofibers

15 wt% polystyrene (PS) was dissolved in N,N-Dimethylformamide (DMF) on a magnetic stirrer at 60 °C for approximately 24 h to obtain a homogenous polymer solution. 2.0 mL of the polymer solution was fed into a syringe connected to a syringe pump and electrospun into porous nanofibers (PNFs) with a feeding rate of 0.5 mL h⁻¹, working distance of 15 cm and working voltage of 15 kV. Relative humidity was controlled at approximately 60 RH. The electrospun nanofibers were collected in a container of ethanol. The collected nanofibers were washed with DI water for three times to remove any trace of ethanol before being broken up into short nanofibers with the aid of a homogenizer at 5000 rpm for 15 min. The homogenized porous PS nanofibers were immersed in 500 mL of DOPA solution (0.3 mg mL⁻¹) with 0.0879 mM of CoCl₂·6H₂O and 0.176 mM of FeCl₃. Molar ratio of cobalt(II) ions, iron(III) ions and DOPA was fixed at 1:2:9. The pH of the solution was adjusted by adding Tris under vigorous stirring. The polymerization of DOPA

was allowed to proceed for 4 h on a laboratory shaker before the short nanofibers were washed with DI water for three times. The polymerization process was repeated with a fresh batch of solution before being freeze-dried. The nanofibers were then annealed in a tube furnace at 900 °C for 2 h under constant argon flow before allowing it to cool back to room temperature. The nanofibers were then transferred to a box furnace and heat at 300 °C in air for 3 h to obtain CoFe₂O₄/CoFe/C-PDA PNFs.

5.2.4 Characterization

Morphology of the samples was investigated using a field-emission scanning electron microscope (FESEM, JEOL 7600) and a transmission electron microscope (TEM, JEOL 2010). Scanning TEM energy dispersive spectroscopy (STEM-EDX) was also performed. The structure of the samples was studied using an X-ray diffractometer (XRD, Bruker D8 Discover), X-ray photoelectron spectroscopy (XPS, ESCALab 250Xi, Thermo Scientific) and Raman spectroscopy (Leica N Plain EP1 100X objective lens, NA 0.85) with a charge coupling device (CCD). X-ray absorption fine-structure (XAFS) spectroscopy was recorded at the XAFCA beamline at the Singapore Synchrotron Light Source (SSLS).⁴¹ The Braunauer-Emmett-Teller (BET) specific surface area and Barrett-Joyner-Halendar (BJH) pore size distribution were measured using Micrometrics Tristar II-3020. Conditions of the tests were similar to those reported in the previous chapter.^{41, 42}

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted on an Autolab potentiostat/galvanostat (PGSTAT302N) station combined with a rotating disk electrode (RDE) using 0.1 M KOH electrolyte saturated with O₂ or N₂. Ag/AgCl electrode (saturated with 3 M KCl) and a Pt foil were used as the counter and reference electrodes, respectively. The working electrode was prepared as reported in previous work.⁴² The catalyst loading was 0.5 mg cm⁻² for CV test and 0.15 mg cm⁻² for LSV. The number of transferred electrons per O₂ molecule in ORR was calculated by Koutecky-Levich equations as reported in the previous chapter.⁴²

ZnABs were assembled using a custom-made Zn-air cell and evaluated on a battery tester (NEWARE CT-3008). All discharge and discharge-charge tests were conducted at room temperature under atmospheric conditions. A polished zinc plate was used as the anode with 6 M KOH aqueous solution used as the electrolyte. Surface area of the polished zinc plate exposed to the KOH electrolyte is 4 cm^2 . The cathodes with a loading of 1.0 mg cm^{-2} were prepared following a previously reported method.²⁹ In short, homogeneous catalyst ink described earlier in the electrochemical experiments was loaded onto a carbon paper with a pre-prepared catalyst ‘reservoir’ to form a well-defined and uniform catalyst layer after drying. Galvanostatic discharge-charge cycling tests were conducted at a current density of 5 mA cm^{-2} , with each cycle consisting of 30 minutes of discharging followed by 30 minutes of charging.

5.3 Results and Discussion

5.3.1 Chemical Structure and Morphology of Co(II)-PDA Complex

In Chapter 4, it has been reported that iron(III) ions could effectively cross-link PDA via Fe(III)-catechol coordination bonds.⁴² Compared with iron(III) ions, how cobalt(II) ions would interact with DOPA and PDA during the in situ polymerization process and how it is incorporated into the PDA hybrid was almost unknown. To provide insights into the reaction of cobalt(II) ions with DOPA, UV-vis analysis was conducted to probe the chemical structure of the Co(II)-PDA complex. TEM was also conducted to observe the morphology of the Co(II)-PDA complex with different Co(II)/DOPA feed ratio.

By adding iron(III) ions into DOPA solution, absorption maxima at about 400 and 740 nm can be observed in the UV-vis spectrum, signalling the formation of a mono-complex. With the addition of Tris, the absorption maxima at 740 nm undergoes a blue-shift to approximately 558 nm, implying a significant amount of tris-complex formed.⁴² By contrast, when cobalt(II) ions are added into DOPA solution, there is

no observable change in both the colour of the solution and the UV-vis spectrum, implying that there is no coordination bonds formed between cobalt(II) ions and DOPA (Figure 5.2a). However, when Tris is added to cobalt(II) ion solution, there was an observable change in the colour of the solution from bright pink to a darker shade alongside a red-shift in the absorption maxima of the UV-vis spectrum from 500 to about 600 nm. This indicates the possible formation of a complex between cobalt(II) ions and hydroxyl ions in the solution. Accompanying the colour change and shift in UV-vis spectrum, precipitates were also observed when the solution was left to stand. With the subsequent addition of DOPA, the UV-vis spectrum undergoes a blue-shift with the absorption maxima shifting to approximately 450 nm, accompanied by an immediate darkening of the solution, implying the occurrence of cyclization, oxidation and polymerization of DOPA and the displacement of the hydroxyl ions in the cobalt complex by the oxidized DOPA units/oligomers.

Morphologies of Co(II)-PDA complex nanostructures obtained with Co(II)/DOPA feed ratio of 1:1, 1:3 and 1:5 are shown in the TEM micrographs in Figure 5.2b, c and d, respectively. It can be observed that for all three ratios, nanoparticles with irregular morphologies are formed and coalesced together. The difference between the nanoparticles obtained in the cobalt(II) and iron(III) systems could be attributed to the presence of both neat PDA oligomers and Co(II)-PDA oligomers in the nanoparticles. As the amount of DOPA used is increased, the morphology is closer to that of Fe(III)-PDA, i.e., the nanoparticles become larger and more spherical.

Figure 5.2 a) UV-vis spectra of cobalt(II) ions solution, TEM micrographs of Co(II)-PDA with feed ratio of b) 1:1, c) 1:3 and d) 1:5.

5.3.2 Fabrication of Co(II)-Fe(III)-PDA Complex and Chemical Characterization

In the early part of this PhD study, the addition of only one type of transition metal ions into DOPA during the in situ polymerization process was explored. There has been no report on the in situ polymerization of DOPA in the presence of two different transition metal ions. To shed light on the effect of mixed ions, Co(II)-Fe(III)-PDA complex were synthesized by dissolving certain amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and FeCl_3 into an aqueous solution of DOPA, followed by the addition of Tris to initiate the polymerization reaction of DOPA. UV-vis and XAFS studies were conducted to probe the chemical structure of the Co(II)-Fe(III)-PDA complex obtained. The feed molar ratio of cobalt(II) ions, iron(III) ions and DOPA was kept at 1:2:9. Note that the metal ion to DOPA molar ratio was 1:3, which is the optimized ratio for Fe(III)-PDA system, while Co(II)/Fe(III) molar ratio is 1:2, which is the desired ratio for formation of CoFe_2O_4 .

For the co-addition of iron(III) ions and cobalt(II) ions into the DOPA polymerization system, it was observed that iron(III) ions played a dominant role in the polymerization process. From the UV-vis spectrum (Figure 5.3a), it is observed that the addition of DOPA to the mixed transition metal ions solution gives rise to two absorption maxima at approximately 400 and 740 nm, similar to the spectrum of the mono-complex formed when DOPA is added to a solution of iron(III) ions.⁴² When Tris was added to the solution containing the mixed transition metal ions and DOPA, the solution turned purple immediately with the absorption maxima undergoing a blue shift to approximately 500 nm, indicating the formation of predominantly tris-complex with iron(III) ions.⁴³

Fe and Co K-edge XAFS was employed to confirm the chemical state of the Co(II)-Fe(III)-PDA complex. By comparing the results with known and commercially available chemicals (Figure 5.3b), it can be determined that the Fe species in the Co(II)-Fe(III)-PDA complex is in the trivalent state and has chemical environment very similar to that of Fe in Fe(III)-PDA complex.⁴² It is also not in the form of iron oxides or iron hydroxides. From the XAFS results shown in Figure 5.3c, it can be concluded that the Co species in the Co(II)-PDA and Co(II)-Fe(III)-PDA complexes are also identical; they exist in the bivalent state and not in the form of cobalt(II) hydroxides. The above results suggest that in the Co(II)-Fe(III)-PDA complex, PDA form coordination bonds with both cobalt(II) ions and iron(III) ions.

Figure 5.3 UV-vis spectra of a) cobalt(II) ions and iron(III) ions solution. XANES spectra of Co(II)-Fe(III)-PDA complex at b) Fe K-edge and c) Co K-edge.

5.3.3 Morphology and Structure of CoFe₂O₄/CoFe/C-PDA Nanospheres and PNFs

CoFe₂O₄/CoFe/C-PDA nanospheres were prepared by the addition of CoCl₂·6H₂O and FeCl₃ into aqueous DOPA solution, followed by the addition of Tris to initiate the polymerization process for 72 h, without any template. The solid products were isolated from the solution by centrifugation, washing with DI water, freeze-drying, annealing and partial oxidizing. The morphologies of the nanospheres at the various stages were observed with FESEM and TEM. The FESEM and TEM micrographs of the as-synthesized nanospheres are shown in Figures 5.4a and 5.4b, respectively, showing that the average diameter of the nanospheres is about 60 nm. Figures 5.4c and 5.4d show the TEM micrographs of the annealed and oxidized samples respectively. From Figure 5.4c, it is clear that after annealing, nanoparticles of about 10 nm in size are formed in the nanospheres. However, the distribution of these nanoparticles is not homogeneous across the nanospheres; the nanoparticles appear to be absent in some nanospheres. From the TEM micrographs of the nanospheres after oxidation (Figure 5.4d), it can be observed that there is severe agglomeration of the nanoparticles, with majority of the nanoparticles having sizes of about 25 nm. The agglomeration could be attributed to the additional thermal energy supplied to the system during the oxidation process. Mesopores can also be observed on the nanospheres. Other than the evaporation of organic volatiles, severe aggregation of metal species during the annealing and oxidation process may also contribute to the formation of the mesopores.

Figure 5.4 FESEM micrograph of a) as synthesized Co(II)-Fe(III)-PDA complex nanospheres, TEM micrographs of b) as synthesized Co(II)-Fe(III)-PDA complex nanospheres, c) annealed CoFe/C-PDA nanospheres and d) partially oxidised CoFe₂O₄/CoFe/C-PDA nanospheres.

CoFe₂O₄/CoFe/C-PDA PNFs were prepared by immersing the homogenized electrospun PS PNFs into aqueous DOPA solution with CoCl₂·6H₂O and FeCl₃ followed by the addition of Tris to initiate the polymerization process. The polymerization was carried out for 4 h and repeated twice. The as-coated PNFs were then freeze-dried, annealed and partially oxidised to obtain the CoFe₂O₄/CoFe/C-PDA PNFs. The morphologies of the PNFs at various stages were characterized by FESEM and TEM (Figure 5.5). Figures 5.5a and 5.5b show the FESEM micrographs of the as-coated PS PNFs. From the FESEM micrographs, it can be observed that the PNFs have diameter of approximately 600 nm and are highly porous with interpenetrating nanochannels within the nanofibers. The porous nature of the PS

nanofibers is attributed to the use of DMF as solvent and electrospinning at an environmental humidity of approximately 60 %.⁴⁴ Figures 5.5c, d and e show the TEM micrographs of the as-coated, annealed and partially oxidized PNFs, respectively. In Figure 5.5c, a featureless nanofiber can be observed because the metal species exist in the form of ions in the transition metal-PDA complex. From Figure 5.5d, it can be observed that after annealing, there are many small nanoparticles with size of approximately 10 nm distributed homogeneously within the PNFs, similar to the case of the nanospheres. Some bigger nanoparticles of about 20 to 30 nm can also be observed, which are caused by the agglomeration of the smaller nanoparticles during the annealing process. After oxidation, it is observed that most of the nanoparticles still have size of about 10 nm and are distributed homogeneously across the PNFs (Figure 5.5e). However, there are also larger nanoparticles of up to 50 nm, which can be attributed to the additional thermal energy causing more agglomeration of the nanoparticles. Even though the annealing and oxidation conditions used are the same, the agglomeration in the PNFs is not as severe as that in the case of the nanospheres, which can be attributed to the numerous nanochannels in the PNFs with confined space in between that hinders the growth of the nanoparticles. Figure 5.5f shows the high-resolution cross sectional TEM micrograph of the oxidized PNFs with nanoparticles of approximately 10 nm. From the TEM micrographs, it is observed that the partially oxidized PNFs have a diameter of approximately 400 nm, and the nanoparticles are distributed evenly across the nanofibers. Some mesopores can also be observed, which probably resulted from the evaporation of organic volatiles from PDA and PS during the annealing and oxidation process. Figures 5.5g, h and i show the STEM-EDX elemental mapping of Co and Fe for the cross-section of the PNFs, verifying the homogeneous distribution of the transition metal nanoparticles across the PNFs.

Figure 5.5 FESEM micrographs of a) as-coated Co(II)-Fe(III)-PDA complex PNFs and b) cross-section of as-coated Co(II)-Fe(III)-PDA complex PNFs, TEM micrographs of c) as coated Co(II)-Fe(III)-PDA complex PNFs, d) annealed FeCo/C-PDA PNFs, e) partially oxidised $\text{CoFe}_2\text{O}_4/\text{CoFe/C-PDA}$ PNFs, f) high resolution cross-section of $\text{CoFe}_2\text{O}_4/\text{CoFe/C-PDA}$ PNFs and g-i) STEM-EDX elemental mapping results of Co and Fe.

To verify the presence of mesopores in $\text{CoFe}_2\text{O}_4/\text{CoFe/C-PDA}$ nanospheres and PNFs, nitrogen adsorption-desorption measurement was conducted. The N_2 adsorption-desorption isotherm and the pore size distributions of $\text{CoFe}_2\text{O}_4/\text{CoFe/C-PDA}$

PDA nanospheres and CoFe₂O₄/CoFe/C-PDA PNFs are shown in Figure 5.6. The N₂ adsorption-desorption isotherm (Figure 5.6a) of CoFe₂O₄/CoFe/C-PDA nanospheres demonstrates a typical type IV isotherm with a hysteresis loop in the P/P₀ range of 0.4 – 1.0, indicating the mesoporous nature of the sample, and the corresponding BET specific surface area is 278 m² g⁻¹. The pore size distribution curve of CoFe₂O₄/CoFe/C-PDA nanospheres calculated using the BJH model is shown in Figure 5.6b. There are two peaks at approximately at 3 and 35 nm, respectively. The peak at 3 nm could be attributed to pores created by removal of volatile species from PDA, while the broad peak at 35 nm could be attributed to the interspheres spacing between the stacked nanospheres.⁴⁵ The CoFe₂O₄/CoFe/C-PDA PNFs also display a typical type IV isotherm (Figure 5.6c), showing the mesoporous nature of the sample, whereas the corresponding BET specific surface area of 604 m² g⁻¹ is significantly larger than that of its nanospheres counterpart. The pore size distribution curve (Figure 5.6d) indicates a peak at 3 nm and another peak at 27 nm. The peak at 3 nm can again be attributed to the removal of volatile species during the annealing process, while the peak at 27 nm could be due to the removal of the sacrificial PS templates.

Figure 5.6 a) Brunauer-Emmett-Tellett (BET) N₂ adsorption and desorption isotherm curve and b) Barrett-Joyner-Halenda (BJH) pore size distribution of CoFe₂O₄/CoFe/C-PDA nanospheres (inset of b: zoom in of BJH pore size distribution). c) Brunauer-Emmett-Tellett (BET) N₂ adsorption and desorption isotherm curve and d) Barrett-Joyner-Halenda (BJH) pore size distribution of CoFe₂O₄/CoFe/C-PDA PNFs (inset of d: zoom in of BJH pore size distribution).

The phase structure of the obtained nanospheres and PNFs was characterized by X-ray diffraction (XRD), and the resulting XRD patterns are presented in Figure 5.7a and 5.7b respectively. After annealing, 3 well defined peaks at $2\theta = 44.9^\circ$, 65.3° and 82.8° can be observed, which coincide with the (110), (200) and (211) planes of CoFe, implying the presence of CoFe in the C-PDA nanocomposites.⁴⁶ After the partial oxidation process, the three peaks corresponding to CoFe show weakened intensity and five new peaks at $2\theta = 30.1^\circ$, 35.5° , 43.1° , 57.0° and 62.6° are observed. These new peaks are characteristic diffraction peaks corresponding to the (220), (311), (400), (511) and (440) planes of CoFe₂O₄.^{15, 47} From the XRD patterns, it can be concluded that both cobalt and iron are successfully incorporated into PDA during the in situ polymerization process and that they are converted to CoFe nanoparticles during the high temperature annealing process. During the oxidation process, it is likely that the outer surface of CoFe nanoparticles are successfully oxidized into CoFe₂O₄, producing CoFe/CoFe₂O₄ core/shell nanoparticles. The partial oxidation of CoFe to CoFe₂O₄ is a result of the short oxidation time of 3 h used. The typical XRD diffraction peaks of C-PDA at $2\theta = 23.4^\circ$ and 43.7° , corresponding to (002) and (100) planes of carbon, are not observed in both cases due to the high intensity of the transition metal and transition metal oxides peaks. To show the successful carbonization of PDA to C-PDA, Raman spectroscopy was conducted for the PNFs sample. In Figure 5.7c, it can be observed that after annealing and oxidation, the PNFs shows well defined D and G band of carbon at 1310 and 1590 cm⁻¹, respectively, different from that of the as-synthesized PNFs that do not show any obvious peaks.^{42, 48} The Raman spectra of the annealed and oxidised sample are identical, implying that the oxidation process, apart from converting part of the CoFe to CoFe₂O₄ has negligible impact on the structure of C-PDA.

Figure 5.7 X-ray diffraction patterns of a) nanospheres and b) PNFs. c) Raman spectra of PNFs.

To confirm the chemical structures of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA nanospheres and PNFs, the chemical states of the samples were investigated by XPS. As the XPS spectra for the nanospheres and PNFs are identical, only that for $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA PNFs is presented. As expected, the XPS survey spectrum (Figure 5.8a) shows the presence of C 1s, N 1s, O 1s, Fe 2p and Co 2p peaks. The strong C 1s peak shows that C-PDA is the major component of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA PNFs. The high resolution N 1s spectra and the fitting curves (Figure 5.8b) confirm that the nitrogen in C-PDA is mainly in the form of graphitic N (at 401.0 eV) and pyridinic N (at 398.5 eV) with a small peak at 403.0 eV corresponding to oxidised N.^{49, 50} Graphitic N is bonded to three carbon atoms in a graphene plane and pyridinic N is bonded to 2 sp² carbon at the edge of the carbon plane. The presence of graphitic N was shown to greatly increase the limiting current density while the presence of pyridinic N might assist in converting the ORR mechanism to a four-electron dominated process from that of two-electron. Both graphitic N and pyridinic N are of great significance in promoting ORR activity.^{45, 51-53} The high resolution Co 2p and Fe 2p spectra with the fitting

curves are shown in Figures 5.8c and 5.8d, respectively. From the Co 2p spectrum (Figure 5.8c), the first two peaks with binding energies of about 781.0 and 786.1 eV correspond to Co 2p_{3/2} and its satellite peak, while the peaks at higher binding energies of around 796.3 and 803.1 eV were correlated to Co 2p_{1/2} and its satellite peak. The intense Co 2p_{3/2} satellite peak indicated the presence of Co²⁺ species in the sample as the presence of low spin Co³⁺ will lead to a much weaker satellite peak.^{54, 55} In addition, two peaks corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} at binding energies of 711.0 and 724.6 eV were observed on the Fe 2p spectrum (Figure 5.8d). The smaller peaks at binding energies of 718.9 and 733.7 eV correspond to the Fe 2p_{3/2} and Fe 2p_{1/2} satellite peaks, respectively. The spectrum clearly indicates the presence of Fe³⁺ species.^{54, 56} The XPS analysis confirms the successful oxidation of CoFe to CoFe₂O₄.

The high specific surface area of the CoFe₂O₄/CoFe/C-PDA PNFs compared to that of the nanospheres, coupled with the abundant smaller CoFe/CoFe₂O₄ core/shell nanoparticles homogeneously distributed throughout the PNFs and presence of graphitic and pyridinic nitrogen make it an ideal candidate for a bifunctional oxygen electrocatalysts.

5.3.4 Electrochemical Properties of CoFe₂O₄/CoFe/C-PDA Nanospheres and PNFs

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating disk electrode (RDE) were used to study the electrochemical performance of CoFe₂O₄/CoFe/C-PDA nanospheres and PNFs in 0.1 M KOH electrolyte at room temperature with a three-electrode system (Figure 5.9). The CV curves of CoFe₂O₄/CoFe/C-PDA nanospheres, PNFs and commercial Pt/C in O₂ saturated electrolyte are presented in Figure 5.9a. The cathodic reduction peak for commercial Pt/C is about -0.10 V (vs. Ag/AgCl), while those of CoFe₂O₄/CoFe/C-PDA nanospheres and PNFs are about -0.17 V (vs. Ag/AgCl). Such peaks are not present under a pure N₂ atmosphere, confirming the ORR catalytic activity of the samples.

Figures 5.9b and 5.9c present the RDE measurements of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA nanospheres and PNFs, respectively, obtained at various rotation speeds from 400 rpm to 2500 rpm. The RDE measurements were conducted to further understand the ORR kinetics of the samples. The corresponding Koutecky–Levich (K–L) plots are presented as insets in the respective RDE curves. Good linearity and almost constant gradient of the fitted lines can be distinctly observed from the K–L plots, suggesting typical first-order reaction kinetics with respect to the concentration of dissolved O_2 . From the K–L equation, the number of electrons transferred (n) per oxygen molecule was calculated to be 3.3 – 3.8 for nanospheres and 3.8 – 4.0 for PNFs, in the potential range of – 0.3 to – 0.6 V (Figure 5.9d), suggesting that the PNFs are a more favorable electrocatalyst for the promotion of the desired 4-electron pathway transfer process, similar to commercial Pt/C. The cathodic reduction peak for the nanospheres and PNFs are similar owing to their similarity in chemical structures as shown earlier by the XPS results. The current density of the PNFs is almost twice that of the nanospheres, attributed to the higher specific surface area of the PNFs, as confirmed by the BET data. It effectively increases the number of active sites in the PNFs for ORR.

Figure 5.8 a) XPS survey spectrum of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs, and the corresponding high-resolution XPS spectrum of b) N 1s, c) Co 2p and d) Fe 2p.

The OER electrocatalytic activities of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ nanospheres and PNFs alongside that of commercial Pt/C are presented in Figure 5.9e. It is evident that the OER electrocatalytic property of the PNFs is better than that of the nanospheres and commercial Pt/C. The PNFs displays a less positive onset potential and much larger current density as compared with both commercial Pt/C and the nanospheres. For comparison purpose, at a current density of 4 mA cm^{-2} , the potential (vs Ag/AgCl) of the PNFs is 0.68 V, about 70 mV and 100 mV less positive as compared with the nanospheres (0.75 V) and Pt/C (0.78 V), respectively. At the potential of 0.70 V, the current density of PNFs is 5.20 mA cm^{-2} , more than twice that of the nanospheres (1.90 mA cm^{-2}) and 4 times that of Pt/C (1.18 mA cm^{-2}) at the same potential.

The outstanding electrocatalytic activities of the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs towards both ORR and OER may be credited to the presence of graphitic and

pyridinic nitrogen, the large amount of active sites, the possible synergistic effect resulting from interactions between CoFe/CoFe₂O₄ and C-PDA, and the presence of CoFe alloy. These make CoFe₂O₄/CoFe/C-PDA PNFs a promising bi-functional oxygen electrocatalyst.

The stabilities of CoFe₂O₄/CoFe/C-PDA PNFs and commercial Pt/C for ORR were examined using the chronoamperometric method in 0.1 M KOH saturated with O₂ at 400 rpm and potential of -0.4 V (Figure 5.9f). The ORR current density of CoFe₂O₄/CoFe/C-PDA PNFs and commercial Pt/C decreases by 8% and 23%, respectively, after 55,000 s of continuous operation. From the curve, commercial Pt/C suffers from a rapid current loss at the initial stage of discharge, possibly due to the detachment of Pt nanoparticles from the carbon support in alkaline medium.^{28,}
⁵⁷ The chronoamperometric test reveals the stability of CoFe₂O₄/CoFe/C-PDA PNFs for ORR, most likely owing to their tube-like geometry and porous nature of the PNFs that allow them to be “glued” on the carbon support by Nafion better, preventing the detachment of the PNFs during cycling.

Figure 5.9 a) CV curve of commercial Pt/C, CoFe₂O₄/CoFe/C-PDA nanospheres and PNFs in O₂-saturated 0.1 M KOH, b) RDE curves of CoFe₂O₄/CoFe/C-PDA nanospheres at rotating rates of 400 to 2500 rpm (inset: corresponding Koutecky-Levich plots), c) RDE curves of CoFe₂O₄/CoFe/C-PDA PNFs at rotating rates of 400 to 2500 rpm (inset: corresponding Koutecky-Levich plots), d) n numbers for CoFe₂O₄/CoFe/C-PDA nanospheres and PNFs, e) LSV curves of commercial Pt/C, CoFe₂O₄/CoFe/C-PDA nanospheres and PNFs for OER catalytic activity at an electrode rotating speed of 1600 rpm and f) i-t plots of CoFe₂O₄/CoFe/C-PDA PNFs and commercial Pt/C in O₂-saturated 0.1 M KOH at an electrode rotating speed of 400 rpm and -0.4 V.

5.3.5 ZnAB Performance of CoFe₂O₄/CoFe/C-PDA PNFs and Nanospheres

As CoFe₂O₄/CoFe/C-PDA PNFs showed better electrochemical performances as earlier discussed, the performance of CoFe₂O₄/CoFe/C-PDA PNFs as electrocatalysts in rechargeable ZnABs was evaluated using custom-made Zn-air cell. CoFe₂O₄/CoFe/C-PDA nanospheres and commercial Pt/C were also evaluated for comparison. The cycling performances of the ZnABs with the various electrocatalysts are shown in Figure 5.10a, which clearly demonstrate the advantages of CoFe₂O₄/CoFe/C-PDA PNFs as electrocatalysts for ZnABs. The ZnAB with CoFe₂O₄/CoFe/C-PDA PNFs requires an initial charge voltage of 2.35 V, similar to that of the ZnABs with CoFe₂O₄/CoFe/C-PDA nanospheres (2.31 V) and commercial Pt/C (2.34 V). The discharge voltage delivered by the ZnAB with CoFe₂O₄/CoFe/C-PDA PNFs is 1.19 V, similar to that of CoFe₂O₄/CoFe/C-PDA nanospheres and slightly lower than that of Pt/C (1.21 V). After the first 20 cycles, the charge voltage of both the CoFe₂O₄/CoFe/C-PDA PNFs and nanospheres stabilize at 2.20 V, while the discharge voltage stabilizes at 1.22 V. Despite its slightly higher discharge voltage delivered in the initial cycle, the ZnAB with commercial Pt/C electrocatalyst exhibits a significant increase in its charge voltage and a decrease in discharge voltage after the 10th cycle, rapidly decreasing the energy efficiency of the ZnAB. For cycling over long period, PNFs based ZnAB can function robustly over 400 cycles with almost no change in the charge and discharge voltage. By contrast, after 400 cycles, the nanospheres based ZnAB shows an increase of 0.30 V in the charge voltage (2.15 V to 2.45 V) and a decrease of 0.10 V in the discharge voltage (1.15 V to 1.05 V), resulting in an increase of 0.40V in the discharge-charge voltage gap. This further proves that CoFe₂O₄/CoFe/C-PDA PNFs are an efficient and highly stable bifunctional oxygen electrocatalyst. The sudden worsening of the performance of the ZnAB using commercial Pt/C-based catalyst could be attributed to the use of carbon support that has low crystallinity and can be more easily etched by the alkaline electrolyte.⁵⁷ The improved cycling stability of the CoFe₂O₄/CoFe/C-PDA PNFs electrocatalyst could be due to the shielding by the

graphitic C-PDA and the homogeneous distribution of the $\text{CoFe}_2\text{O}_4/\text{CoFe}$ nanoparticles in the PNFs.

Galvanostatic discharge test was also performed to determine the performance of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs as an electrocatalyst for primary ZnABs. Figure 5.10b shows the typical galvanostatic discharge profiles measured at constant current density of 5 mA cm^{-2} . The $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs based ZnAB produces an initial potential of 1.27 V and is able to discharge continuously over a long period of more than 480 h (20 days) with discharge voltage value above 1.10 V for the first 460 h. The primary ZnAB exhibits a slow degradation rate of 0.45 mV h^{-1} . The relatively flat discharge plateau and small voltage drop rate over long period of time without changing the zinc anode or electrolyte are evidence for the activity and stability of the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs electrocatalyst for the primary ZnAB. When galvanostatically discharged at a current density of 2 and 10 mA cm^{-2} for 10 h, little activity decay is observed (inset of Figure 5.11b), showing the stability of the primary ZnAB. The discharge voltage became 1.31 V and 1.24 V at current density of 2 and 10 mA cm^{-2} , respectively.

Figure 5.10 a) Discharge-charge cycling of ZnABs using $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs, nanospheres and commercial Pt/C based air cathode at a current density of 5 mA cm^{-2} with cycle periods of 30 min discharge and 30 min charge per cycle and b) voltage profile of a $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ PNFs based ZnAB when fully discharged at a current density of 5 mA cm^{-2} (inset: voltage profile showing voltage difference when discharged at current density of 2, 5 and 10 mA cm^{-2} , respectively).

5.4 Conclusion

The results presented in this chapter show that different from iron(III) ions, cobalt(II) ions form complex with hydroxyl ions but not DOPA monomers. Only after the oxidation, cyclization and polymerization of DOPA, hydroxyl ions can be displaced by the oxidized DOPA units or PDA oligomers. Co(II)-Fe(III)-PDA complexes with different morphologies were also synthesized using the one-pot process with co-addition of iron(III) ions and cobalt(II) ions. Iron(III) ions were observed to play a dominant role in determining the morphology of the final products when both iron(III) ions and cobalt(II) ions were concurrently added. The Co(II)-Fe(III)-PDA complex can be easily converted into CoFe₂O₄/CoFe/C-PDA with controlled annealing. By using PS PNFs as templates, CoFe₂O₄/CoFe/C-PDA PNFs were achieved. Electrochemical studies revealed the enhanced electrocatalytic performance of the PNFs over that of nanospheres and commercial Pt/C towards ORR and OER. The PNFs produced a higher current density than the nanospheres at the same potential and exhibited an electron transfer number close to 4. The outstanding electrochemical properties of the PNFs are further confirmed by their performance as air cathode in ZnABs. The PNFs had discharge voltage of above 1.10 V for the first 460 h and could undergo steady cycling for over 400 cycles with a current density of 5 mA cm⁻², with little increase in the discharge-charge voltage gap. These results demonstrate the mesoporous N-doped CoFe₂O₄/CoFe/C-PDA PNFs as a promising low-cost and efficient bifunctional oxygen electrocatalyst.

The CoFe₂O₄/CoFe/C-PDA nanospheres obtained in this work showed better electrochemical properties than the Fe₃O₄/C-PDA nanospheres studied in Chapter 4, owing to the better electrocatalytic activity of CoFe₂O₄. Electrochemical tests showed the CoFe₂O₄/CoFe/C-PDA nanospheres having a cathodic reduction peak approximately 100 mV more positive than the Fe₃O₄/C-PDA nanospheres, with higher current density. The electron transfer number, *n*, for the CoFe₂O₄/CoFe/C-PDA nanospheres was also closer to 4 than the Fe₃O₄/C-PDA nanospheres. From electrochemical studies, the CoFe₂O₄/CoFe/C-PDA PNFs was shown to have better performance than CoFe₂O₄/CoFe/C-PDA nanospheres; it was thus selected to be

used as the oxygen electrocatalyst in primary ZnABs. When employed in primary ZnABs, CoFe₂O₄/CoFe/C-PDA PNFs also showed better durability than Fe₃O₄/C-PDA nanospheres. With the OER activity reported for CoFe₂O₄/CoFe/C-PDA PNFs in this chapter, it was also able to be used as a bifunctional electrocatalyst in secondary ZnABs, showing stable performance for up to 400 cycles.

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Chapter 6

CoFe₂O₄/CoFe/C-PDA-Decorated Three Dimensional Conductive Nanofibrous Macrostructures as Free-Standing Air Cathode for Rechargeable Zinc-Air Batteries

In this chapter, a different design for utilizing CoFe₂O₄/CoFe/C-PDA as electrocatalysts is described. Firstly, the fabrication of a three dimensional carbon nanofibrous macrostructure embedded with CoFe/CoFe₂O₄ core/shell nanoparticles is achieved via the combination of electrospinning of polyacrylonitrile and the facile surface deposition of Co(II)-Fe(III)-PDA hybrids. CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures are successfully obtained after the annealing process. The morphology and structure of the nanofibers are studied and discussed. Electrochemical studies show that the three dimensional CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures exhibit good electrocatalytic activities and stabilities for both ORR and OER.

6.1 Introduction

As discussed in Chapter 5, Co(II)-Fe(II)-PDA hybrids and CoFe₂O₄/CoFe/C-PDA nanocomposites can be readily prepared via the one-pot in situ polymerization method. By using porous PS nanofibers as templates, CoFe₂O₄/CoFe/C-PDA PNFs were successfully fabricated and used as electrocatalyst for rechargeable ZnABs. Electrochemical studies show that the CoFe₂O₄/CoFe/C-PDA PNFs have a more positive ORR onset potential and electron transfer number closer to 4 when compared to Fe₃O₄/C-PDA nanospheres, indicating the former as a better ORR electrocatalyst. OER activity was also observed from the CoFe₂O₄/CoFe/C-PDA PNFs, allowing it to be used in rechargeable ZnABs. By carefully selecting the electrocatalytic active TMOs species and designing the morphology of the nanocomposites, electrochemical performances of the electrocatalysts, including the performance in ZnABs, were enhanced. However, the improvements were limited and still fall short of current state of the art technology. To further enhance the electrochemical performances of the electrocatalysts in ZnABs, the use of a binder- and additive-free electrode was explored.

In order for a ZnAB to achieve an acceptable level of performance, the architecture of the air cathode and oxygen electrocatalyst should be carefully designed and selected. The air cathode should be a highly porous structure having large surface area that allows for the fast diffusion of oxygen to the surface of the electrode yet prevents the electrolyte from leaking. For the fabrication of a typical ZnAB air cathode, the oxygen electrocatalyst is usually loaded onto a gas diffusion electrode (GDE), such as carbon fiber paper¹, via the casting of a paste-like mixture. The paste-like mixture usually contains the powder electrocatalyst, polymeric binder (e.g. Nafion^{1, 2}, polyvinylidene fluoride (PVDF)³ or polytetrafluoroethylene (PTFE)⁴) to keep all the components together and a conductive matrix (e.g. Ketjen black⁵ or acetylene black⁶) to improve the electrical conductivity of the air cathode. The inclusion of these additives will lead to an increase in the final weight of the air cathode and also complicates the air cathode preparation process. On top of that, the

addition of the polymeric binder which is insulating will lead to an increase in contact resistance at the interface of the electrocatalyst and the current collector, affecting the electron transfer.⁷ The synthesis of a binder- and additive-free air cathode with high surface area, good electrical conductivity and high electrocatalytic activities will be the way forward, in order to resolve the issues revolving around the use of binders and additives. Several reports have demonstrated the enhanced performance on lithium-air batteries brought about by the use of binder-free electrodes.⁸⁻¹² Riaz et al. fabricated non-precious metal oxides on nickel foam as a binder-free air cathode for lithium-oxygen batteries. The battery delivered a high specific capacity of 2372 mAh g⁻¹ and stable performance over 250 cycles.¹¹ Zhu and team successfully synthesized N-doped worm-like carbon with embedded MoFeNi and MoC nanoparticles on nickel foam for use directly as a binder-free cathode for lithium-oxygen, lithium-air and lithium-carbon dioxide batteries, displaying high oxygen and carbon dioxide reduction and evolution activities.¹⁰ Similar studies have been conducted for the use of a binder-free air cathode in ZnABs.¹³⁻¹⁶ Lee et al. fabricated hierarchical mesoporous Co₃O₄ nanowire array on stainless steel mesh as a efficient bifunctional electrocatalyst for ORR and OER and demonstrated superior charge and discharge potentials at high currents when compared to conventional gas diffusion layer electrodes.¹⁶ Meng and co-workers successfully carbonized string of ZIF-67 on polypyrrole nanofibers network rooted on carbon cloth for ORR, OER and use in cable-type ZnABs.¹⁵

Since the CoFe₂O₄/CoFe/C-PDA nanocomposites have reasonably good performance as ORR and OER electrocatalysts, the facile one-pot synthesis method was used to fabricate 3D macrostructures composed of CoFe₂O₄/CoFe/C-PDA carbon nanofibers (CNFs). The 3D CoFe₂O₄/CoFe/C-PDA CNFs were obtained by the surface deposition of Co(II)-Fe(III)-PDA complex on electrospun polyacrylonitrile (PAN) nanofibers, followed by subsequent heat treatment. It is believed that the overall surface area of the 3D CoFe₂O₄/CoFe/C-PDA CNFs is much larger than its powder counterpart pasted on 2D conductive substrate. Electrochemical studies show the CoFe₂O₄/CoFe/C-PDA CNFs having excellent

ORR electrocatalytic activity, with half-wave potential only 9 mV less positive than commercial Pt/C. The CoFe₂O₄/CoFe/C-PDA CNFs also exhibit good OER electrocatalytic activity when compared to commercial Pt/C, even though still falling short of the benchmark, Ir/C. An attempt was also made to use the CoFe₂O₄/CoFe/C-PDA CNFs as a free-standing 3D air cathode for rechargeable ZnABs.

6.2 Experimental

6.2.1 Materials

3,4-Dihydroxyphenethylamine hydrochloride (DOPA), tris(hydroxymethyl) aminomethane (Tris), iron(III) chloride (FeCl₃), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O), polyacrylonitrile (PAN, M_w = 150,000) and Nafion (5 wt% aqueous aqueous solution) were purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF) was purchased from Fisher Chemical. Multi-walled carbon nanotubes (MWCNTs) were purchased from ACME Research Support Pte. Ltd.. All chemicals were used without further purification and all solutions were prepared using deionized (DI) water.

6.2.2 Synthesis of 3D CoFe₂O₄/CoFe/C-PDA Nanofibrous Macrostructure

10 wt% polyacrylonitrile (PAN) was dissolved in N,N-Dimethylformamide (DMF) with magnetic stirring at 60 °C for approximately 24 h to obtain a homogeneous polymer solution. Multiwalled carbon nanotubes (MWCNTs) was then added to the polymer solution and stirred for another 24 h. 2.0 mL of the resulting polymer solution was fed into a syringe connected to a syringe pump and electrospun into nanofibers with a feeding rate of 0.5 mL h⁻¹, working distance of 15 cm and working voltage of 12.5 kV. The electrospun nanofibers were collected in ethanol. The collected nanofibers were washed with DI water for three times to remove any trace of ethanol. The washed nanofibers were then immersed in 500 mL of DOPA solution

(0.3 mg mL⁻¹) with 0.0979 mM of CoCl₂·6H₂O and 0.176 mM of FeCl₃. Molar ratio of cobalt(II) ions, iron(III) ions and DOPA was fixed at 1:2:9. The pH of the solution was adjusted by adding Tris and the solution left on a laboratory shaker. The polymerization of DOPA was allowed to proceed for 4 h before the nanofibers were washed with DI water for three times, removing any unreacted reactants. The polymerization process was repeated with a fresh batch of solution before being freeze-dried. The nanofibers were then stabilized in a tube furnace by annealing at 280 °C for 2 h in air before being carbonized at 900 °C for 2 h under constant argon flow. The nanofibers were then transferred to a box furnace and heated at 300 °C in air for 3 h to finally obtain 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructure.

6.2.3 Characterization

Morphology of the samples was investigated using a field-emission scanning electron microscope (FESEM, JEOL 7600) and a transmission electron microscope (TEM, JEOL 2010). Scanning TEM energy dispersive spectroscopy (STEM-EDX) was performed with a JEOL 2100 TEM. The structure of the samples was studied using an X-ray diffractometer (XRD, Bruker D8 Discover) and X-ray photoelectron spectroscopy (XPS, ESCALab 250Xi, Thermo Scientific). The Braunauer-Emmett-Teller (BET) specific surface area and Barrett-Joyner-Halendar (BJH) pore size distribution were measured using Micrometrics Tristar II-3020. Thermogravimetric analysis was conducted on a TA Instruments thermogravimetric analyzer (TGA Q500) and samples were heated from room temperature to 900 °C in air with a heating rate of 10 °C min⁻¹. Conditions of the tests were similar to those reported in previous work.¹⁷

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted on an Autolab potentiostat/galvanostat (PGSTAT302N) station combined with a rotating disk electrode (RDE) using 0.1 M KOH oxygen- or nitrogen-saturated electrolyte. Ag/AgCl electrode (saturated with 3 M KCl) and a Pt foil were used as the counter and reference electrodes, respectively. The working electrode was

prepared as reported in previous work. The catalyst loading for all tests was 0.5 mg cm^{-2} . The number of transferred electrons per O_2 molecule in ORR was calculated by Koutecky-Levich equations as reported in previous work.¹⁷

ZnABs were assembled using a custom-made Zn-air cell and evaluated on a battery tester (NEWARE CT-3008). All discharge and discharge-charge tests were conducted at room temperature under atmospheric conditions. A polished zinc plate was used as the anode with 6 M KOH aqueous solution used as the electrolyte. Surface area of the polished zinc plate exposed to the KOH electrolyte is 4 cm^2 . The 3D $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs macrostructures were used directly as the air cathode without any additional preparation steps or use of binders and additives. Galvanostatic discharge-charge cycling tests were conducted at a current density of 5 mA cm^{-2} , with each cycle consisting of 30 minutes of discharging followed by 30 minutes of charging.

6.3 Results and Discussion

6.3.1 Fabrication and Morphology of 3D $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs Macrostructure

In this work, the synthesis of $\text{CoFe}/\text{CoFe}_2\text{O}_4$ core/shell nanoparticles decorated 3D CNFs macrostructures for use as a potential free-standing binder- and additive-free bifunctional oxygen electrocatalysts for ZnABs was proposed. This is achieved by the combination of electrospinning of PAN nanofibers and the facile deposition of $\text{Co(II)-Fe(III)-PDA}$ complex as shown in Figure 6.1a. An image of the final 3D $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs macrostructure is shown in Figure 6.1b.

Figure 6.1 a) Schematics for synthesis of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs and b) image of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs macrostructure after heat treatment (thickness of 1 mm).

$\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs were prepared by first immersing the electrospun PAN nanofibers into aqueous DOPA solution with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and FeCl_3 followed by the addition of Tris to initiate the polymerization process. The polymerization process was carried out for 4 h and repeated twice. The as coated nanofibers were then freeze-dried before being annealed and partially oxidized to obtain $\text{CoFe}/\text{C-PDA}$ CNFs and $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs, respectively. Typical FESEM micrographs of the electrospun PAN nanofibers, $\text{Co(II)-Fe(III)-PDA}$ coated PAN nanofibers, $\text{CoFe}/\text{C-PDA}$ CNFs and $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs are shown in Figure 6.2a, b, c and d, respectively. From the FESEM micrograph in Figure 6.2a, it can be observed that the neat electrospun PAN nanofibers have smooth surface and an average diameter of about 800 nm. There are some spindles that are observed on some of the nanofibers, possibly attributed to the aggregation of some of the MWCNTs during the electrospinning process. From the FESEM micrograph (Figure 6.2b), there was no observable change in the approximate diameter of the nanofibers after the PDA coating process. However, some nanofibers were observed to have roughened surface with nanoparticles on the nanofibers surface. These are free PDA nanoparticles that are formed during the polymerization process. It can be observed that there is a significant reduction in the diameter of the nanofibers to approximately 500 nm after the annealing process (Figure 6.2c). Accompanying the reduction in nanofibers diameter was also an obvious change in the surface morphology of the nanofibers. Many nanoparticles were observed to be distributed across the nanofibers surface. The reduction in nanofibers diameter could be attributed to the removal of

organic volatile species and shrinkage during the annealing process. After the oxidation process, there was no significant change in the diameter of the nanofibers, but slight agglomeration of the nanoparticles on the surface was observed possibly due to the extra thermal energy supplied during the oxidation process (Figure 6.2d).

Figure 6.2 FESEM micrographs of a) neat electrospun PAN nanofibers (inset: higher magnification), b) Co(II)-Fe(III)-PDA coated PAN nanofibers (inset: higher magnification), c) CoFe/C-PDA carbon nanofibers and d) CoFe₂O₄/CoFe/C-PDA carbon nanofibers .

Figure 6.3 shows the TEM micrographs of the nanofibers at the various stages. Figures 6.3a and 6.3b show the TEM micrographs of the annealed CoFe/C-PDA CNFs and partially oxidized CoFe₂O₄/CoFe/C-PDA CNFs, respectively. It can be confirmed that the diameter of the CNFs after annealing and partial oxidation is approximately 500 nm, similar to those observed in the FESEM micrographs (Figure 6.2c and 6.2d). From Figure 6.3a and 6.3b, it is also observed that there are numerous tiny nanoparticles distributed homogeneously across the surface of the CNFs, with slight agglomeration of the nanoparticles in the CNFs observed after the oxidation process, reaffirming the information obtained from the FESEM micrographs in Figure 6.2. In Figure 6.3c, high magnification TEM micrograph of the partially oxidized CNFs, it can be observed that the nanoparticles have an average size of about 10 nm and are encapsulated within thin layer of graphitic-like carbon derived

from polydopamine after annealing. The CNFs, after oxidation, were embedded into epoxy, cut into ultrathin slides using a TEM ultramicrotome and deposited onto copper grid for TEM observation. In Figure 6.3d, the cross-sectional TEM micrograph is shown, illustrating the distribution of the nanoparticles around the circumference of the nanofibers. Most of the nanoparticles should be near the surface of the nanofibers as they are embedded within the thin layer of C-PDA. The nanoparticles that appear in the centre of the nanofibers could be attributed to the shear force experienced during the cutting process, resulting in some of the nanoparticles on the surface of the nanofibers being displaced from the surface onto the cross section. The STEM-EDX elemental mappings of Co and Fe for the cross-section of a nanofiber are shown in Figures 6.3e and 6.3f, respectively, confirming the existence of the two elements in the nanofibers. The mapping results also confirm the distribution of the nanoparticles around the circumference of the nanofibers.

Figures 6.4a and 6.4b show the BET adsorption/desorption isotherm and BJH pore size distribution of the nanofibers, respectively. The BET specific surface area of the nanofibers is approximately $51.7 \text{ m}^2 \text{ g}^{-1}$, while BJH pore size distribution shows two peaks centering at approximately 5 and 40 nm. The BET specific surface area is considerably high for a nanofibrous sample and the increase could be ascribed to the roughening of the surface of the nanofibers due to the presence of the many protruding nanoparticles as illustrated in Figure 6.3c. The formation of the mesopores could be attributed to the removal of small, volatile species present in both PAN and PDA during the annealing process and also the migration of nanoparticles as they agglomerate.

Figure 6.3 TEM micrographs of a) CoFe/C-PDA CNFs, b) CoFe₂O₄/CoFe/C-PDA CNFs, c) high magnification of nanoparticles in (b), d) cross-section of CoFe₂O₄/CoFe/C-PDA CNFs, e) STEM elemental mapping for Co and f) STEM elemental mapping for Fe.

Figure 6.4 a) Brunauer-Emmett-Teller (BET) N₂ adsorption and desorption isotherm curve and b) Barrett-Joyner-Halenda (BJH) pore size distribution of CoFe₂O₄/CoFe/C-PDA CNFs.

6.3.2 Structure of CoFe₂O₄/CoFe/C-PDA CNFs

The formation of CoFe after annealing and a mixture of CoFe and CoFe₂O₄ after partial oxidation were confirmed by the XRD patterns shown in Figure 6.5a. The peak at around 26.0 °, present in both XRD pattern, corresponded to the (002) plane of carbon and is a typical diffraction peak of graphite.¹⁸ The appearance of this intense peak in both samples confirmed the presence of MWCNTs in both the annealed and oxidized samples. After annealing, three peaks corresponding to the (110), (200) and (211) planes of CoFe were observed at $2\theta = 44.9^\circ$, 65.3° and 82.8° , respectively.¹⁹ After the oxidation process, the three peaks corresponding to the CoFe were still present but had a weaker intensity, while six new peaks were observed. The peaks at $2\theta = 18.3^\circ$, 30.1° , 35.5° , 43.1° , 57.0° and 62.6° corresponded to the (111), (220), (311), (400), (511) and (440) planes of CoFe₂O₄.^{20, 21} It can be confirmed that both the cobalt and iron species are successfully incorporated into PDA during the in situ polymerization process and are converted to CoFe nanoparticles during the high temperature annealing process. The presence of XRD peaks for both CoFe and CoFe₂O₄ in the sample after oxidation suggests that during the oxidation process, the CoFe nanoparticles embedded in C-PDA will interact with oxygen present in the surrounding atmosphere to form core/shell

CoFe/CoFe₂O₄ nanoparticles. As the duration allowed for the oxidation process is increased, the CoFe core may fully oxidize, leaving a CoFe₂O₄ nanoparticle.

Figure 6.5 a) XRD patterns and b) TGA curve of CoFe/C-PDA CNFs and CoFe₂O₄/CoFe/C-PDA CNFs.

Based on TGA analysis (Figure 6.5b), the content of CoFe in the annealed sample is approximately 12.0 wt%, while the content of CoFe₂O₄/CoFe in the partially oxidized sample is approximately 33.0 wt%. The increase in transition metal content after the oxidation process could be explained by the loss of carbon through formation of carbon dioxide.

To further confirm the presence of CoFe₂O₄, the chemical states of the oxidized nanofibers were investigated by XPS. In the spectrum for the survey scan (Figure 6.6a), peaks for C 1s, N 1s, O 1s, Fe 2p and Co 2p were clearly observed. The intense peak of C 1s shows that carbon, consisting of PAN derived carbon, MWCNTs and C-PDA, accounts for a major part of the CoFe₂O₄/CoFe/C-PDA CNFs. The high resolution N 1s spectrum and the fitting curves shown in Figure 6.6b confirms the presence of both pyridinic N (at 398.7 eV) and graphitic N (at 400.7 eV) in the carbon nanofibers. The presence of both graphitic N and pyridinic N has been reported to enhance the ORR performance of an oxygen electrocatalyst.²²⁻²⁵ High resolution spectra of Co 2p and Fe 2p alongside the fitting curves are shown in Figures 6c and 6d, respectively. The Co 2p spectrum (Figure 6.6c) can be further fitted into 4 peaks.

The peaks at 780.7 eV and 796.6 eV corresponded to Co 2p_{3/2} and Co 2p_{1/2}, respectively, with a spin orbit separation of approximately 15.9 eV. The peaks that appeared on the higher binding energy side at 787.1 eV and 803.0 eV are two shake-up type satellite peaks. The observation of the strong satellite peaks is attributed to the multiplet splitting for Co with an oxidation state of +2.^{26, 27} Presences of the low spin Co³⁺ will lead to a much weaker satellite peak. The Fe 2p spectrum (Figure 6.6d) can also be further fitted into 4 peaks. The main peaks at 710.9 eV and 724.9 eV corresponded to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The smaller peaks at higher binding energies of 719.2 eV and 732.9 eV corresponded to the Fe 2p_{3/2} and Fe 2p_{1/2} shake-up type satellite peaks. The separation of approximately 14.0 eV implies the presence of Fe³⁺.^{26, 28} The XPS spectra in Figure 6 confirm the successful oxidation of CoFe to CoFe₂O₄. As XPS is a surface analysis technique, scanning only up to 10 nm of the sample's surface, peaks relating to Co⁰ and Fe⁰ originating from CoFe could not be observed as they may be buried below the C-PDA and CoFe₂O₄ layers.

Figure 6.6 a) XPS survey spectrum of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs, and the corresponding high-resolution XPS spectra of b) N 1s, c) Co 2p and d) Fe 2p.

6.3.3 Electrochemical Properties of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating disk electrode (RDE) were used to study the electrochemical performance of the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs in 0.1 M KOH electrolyte at room temperature with a three-electrode system (Figure 6.7). The CV curves of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs in nitrogen- and oxygen-saturated electrolyte are presented in Figure 6.7a. For the oxygen-saturated electrolyte, a clear cathodic reduction peak at about -0.11 V (vs. Ag/AgCl) can be observed. The peak was not observed in the nitrogen-saturated electrolyte, confirming the ORR electrocatalytic activity of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs. Figure 6.7b shows the LSV curves of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs and commercial Pt/C obtained using a rotation speed of 1600 rpm in oxygen-saturated

electrolyte. It can be observed that the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs exhibit performance similar to commercial Pt/C in terms of onset potential and current density. The half-wave potential of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs is approximately -0.115 V, merely 9 mV less positive than that of commercial Pt/C electrocatalyst (-0.106 mV). The current densities between 0.6 to 0.8 V were also found to be only slightly smaller than that of commercial Pt/C. The results suggest high ORR electrocatalytic activity of the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs, comparable to commercial Pt/C.

RDE measurements for $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs were performed at seven rotation speeds between 400 to 2500 rpm to further study the ORR kinetics (Figure 6.7c). The corresponding Koutecky-Levich (K-L) plots are presented in Figure 6.7d. The good linearity and almost parallel fitting lines suggest typical first-order reaction kinetics towards the concentration of dissolved oxygen in the electrolyte for $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs. From the K-L equation, the number of transferred electrons (n) for ORR at the potentials between -0.3 to -0.7 V was calculated to be between 3.7 and 3.9, suggesting that the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs helps to promote the favorable direct four-electron pathway.

The OER electrocatalytic activity of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs was also investigated and the results presented in Figure 6.7e. It can be observed that the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs showed higher OER activity with less positive potential as compared to that of commercial Pt/C at any given current density, but still slightly lower than that of the state-of-the-art OER electrocatalyst, Ir/C. For example, at a current density of 6 mA cm^{-2} , the potential of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs is 0.729 V (vs. Ag/AgCl), 70 mV less positive than that of commercial Pt/C and 43 mV more positive than that of Ir/C.

The stabilities of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs and commercial Pt/C for ORR were examined using the chronoamperometric method in oxygen-saturated 0.1 M KOH at rotating speed of 400 rpm and potential of -0.40 V (vs. Ag/AgCl). Figure 6.7f shows

that after 50,000 s of continuous operation, the ORR current density of $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs and commercial Pt/C decreases by approximately 6 % and 23 %, respectively. From the chronoamperometric study, it can be observed that commercial Pt/C suffers from a rapid current loss at the initial stage of discharge, possibly due to the detachment of platinum nanoparticles from the carbon support in the alkaline environment.^{29, 30} The study also reveals that $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs is considerably stable for ORR, largely attributed to the electrocatalytic active nanoparticles embedded in thin layer of mesoporous C-PDA, preventing the detachment or agglomeration of the nanoparticles during the study.

From the electrochemical studies, it can be concluded that the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C-PDA}$ CNFs is an ideal candidate for bifunctional oxygen electrocatalyst owing to its outstanding electrocatalytic activities towards ORR and OER. The bifunctional electrocatalytic activities could be attributed to the presence of graphitic and pyridinic nitrogen, enhanced electrical conductivity due to the presence of MWCNTs and metallic nanoparticles core, large amount of active sites and also the possible synergistic effect resulting from the close interaction between the transition metal nanoparticles and C-PDA. With such good electrocatalytic properties, the use of such 3D nanofibrous macrostructures as free-standing air cathode for rechargeable ZnABs should be further explored.

Figure 6.7 a) CV curve of CoFe₂O₄/CoFe/C-PDA CNFs in nitrogen- and oxygen-saturated 0.1 M KOH, b) LSV of CoFe₂O₄/CoFe/C-PDA CNFs and commercial Pt/C at 1600rpm, c) RDE curves of CoFe₂O₄/CoFe/C-PDA CNFs at rotating speed of 400 to 2500 rpm, d) corresponding Koutecky-Levich plots and fitting curves derived from the RDE curves in (c) (inset: plot of electron transfer number), e) LSV curves of commercial Pt/C and CoFe₂O₄/CoFe/C-PDA CNFs for OER catalytic activity at an electrode rotating speed of 1600 rpm and f) i-t plots of CoFe₂O₄/CoFe/C-PDA CNFs and commercial Pt/C in O₂-saturated 0.1 M KOH at an electrode rotating speed of 400 rpm and -0.4 V.

6.3.4 Zinc-Air Battery Performance of 3D CoFe₂O₄/CoFe/C-PDA CNFs Macrostructures

As a proof of concept, the 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures were employed as a free-standing binder- and additive-free air cathode for rechargeable ZnABs. The study was conducted using custom-made Zn-air cell with each cycle consisting of 30 minutes of discharging followed by 30 minutes of charging. The cycling performance is shown in Figure 6.8a. The data showed that an initial discharge voltage of only 1.15 V was achieved and the initial charge voltage was 2.01 V. As the cycling proceeded on, the discharged voltage increases slightly and stabilized at 1.20 V while little change was observed for the charging voltage. The ZnAB demonstrated good stability for the first 220 h without significant change in the charge and discharge voltage. After the first 220 h, the ZnAB exhibited a significant decrease in the discharge voltage, while the charge voltage remained relatively constant. Despite the excellent electrocatalytic activity and stability displayed during the electrochemical studies, the performance of the rechargeable ZnABs did not perform as well as expected. Upon the end of the cycling test, the ZnAB was disassembled to try to understand the reasons leading to the poor performance. Figure 6.8b shows the 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures after 300 h of cycling. It can be observed that part of the 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures has already delaminated from the titanium mesh current collector, leaving a hole in the 3D macrostructure where it is exposed to the KOH electrolyte. The KOH electrolyte has also changed from that of a colorless solution to a dark orange solution, implying the dissolution of the CNFs into the electrolyte. The delamination or dissolution of the CNFs could be attributed to the poor mechanical properties of the 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures and more efforts could be devoted to try and improve its mechanical properties in order to fully showcase the excellent electrochemical properties of the CoFe₂O₄/CoFe/C-PDA CNFs macrostructures as free standing binder- and additive-free air cathode for rechargeable ZnABs. In this instance, there are several possible factors that contribute to the poor mechanical properties of the CoFe₂O₄/CoFe/C-

PDA CNFs macrostructures such as the annealing conditions, morphology of the as spun PAN nanofibers and MWCNTs content.

Figure 6.8 a) Discharge-charge cycling of ZnAB using 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures as a binder- and additive-free air cathode with a current density of 5 mA cm⁻² and cycle periods of 30 min discharge and 30 min charge and b) image of 3D CoFe₂O₄/CoFe/C-PDA CNFs macrostructures after 300 cycles.

6.4 Conclusion

Utilizing the facile in situ polymerization approach in combination with electrospinning, 3D carbon nanofibrous macrostructures decorated with CoFe₂O₄/CoFe/C-PDA was successfully fabricated and utilized as a free-standing air cathode for rechargeable ZnABs. The 3D carbon nanofibrous macrostructures have high specific surface area of 51.7 m² g⁻¹ with numerous mesopores present on the surface. Transition metal nanoparticles with size of about 10 nm encapsulated within few layers of C-PDA are distributed evenly across the top surface of the carbon nanofibers. Electrochemical studies revealed that the CoFe₂O₄/CoFe/C-PDA CNFs have good electrocatalytic activity towards ORR, comparable to that of commercial Pt/C but with better stability. The CoFe₂O₄/CoFe/C-PDA CNFs also had reasonable activity towards OER, better than commercial Pt/C, with a small gap to

commercial Ir/C. As a proof-of-concept, the 3D CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures were used as free-standing binder- and additive-free air cathodes for rechargeable ZnABs. Owing to the poor mechanical properties of the CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures, the performance of the rechargeable ZnABs was far from ideal, not reflecting the excellent electrocatalytic properties seen in the electrochemical studies.

The CoFe₂O₄/CoFe/C-PDA CNFs obtained by the in situ polymerization of DOPA with cobalt(II) ions and iron(III) ions in the presence of loose PAN nanofibers collected in aqueous collector show enhanced electrocatalytic activity towards both ORR and OER than the CoFe₂O₄/CoFe/C-PDA PNFs discussed in Chapter 5. From the CV studies, the cathodic reduction peak of CoFe₂O₄/CoFe/C-PDA CNFs, when compared to CoFe₂O₄/CoFe/C-PDA PNFs, has an improvement of approximately 60 mV, i.e., shifted from -0.17 V to -0.11 V. OER electrocatalytic properties is also improved with a less positive onset potential and higher current density. Unfortunately, when used as a free-standing binder- and additive-free air cathode for rechargeable zinc-air battery, the excellent stability for ORR was not observed due to the relatively poor mechanical stability of the CoFe₂O₄/CoFe/C-PDA carbon nanofibrous macrostructures. In order to fully exploit the advantages brought about by the 3D carbon nanofibrous macrostructures, more efforts are needed to improve their mechanical properties so that they are able to withstand the harsh conditions during the cycling process.

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Chapter 7

Conclusion and Outlook

In this chapter, the threads of this thesis are being drawn together. The major conclusions from the respective chapters are summarized and reconciled with the objectives stated in Chapter 1. The presence of coordination bonds between transition metal and PDA in the hybrids obtained via the in situ polymerization process is verified and a mechanism for the in situ polymerization is proposed. The addition of different transition metal and the ratio of the transition metal are proven to have an effect on the morphology of the hybrids. The design and optimization of unique structures and morphologies of the transition metal/PDA hybrids for specific applications can be made possible with the understanding derived from this PhD study. Finally, some possibilities of future work are discussed. More specifically, to extend the study of the in situ polymerization to other transition metals within the periodic table and also to improve the mechanical properties of the three dimensional carbon nanofibrous macrostructures.

7.1 Conclusions

In this PhD research, two model systems are selected to clarify the effect of different transition metal species on the in situ polymerization process of DOPA and the possible impact of the complexation on structures and morphologies of the PDA hybrids. The potential applications for the transition metal/C-PDA nanocomposites obtained through this facile one-pot process were also demonstrated. The key findings are summarized below.

Firstly, Fe(III)-PDA complex hybrid nanospheres are readily synthesized via the use of the one-pot in situ polymerization process of DOPA with the addition of iron(III) ions. It is found that both oxidative polymerization of DOPA and Fe(III)-PDA complexation contribute to the “polymerization” of the PDA hybrids. During the polymerization process, morphology of the nanostructures transform from sheet-like to spherical, driven by the covalent polymerization-induced reduction of hydrophilic functional groups, leading to the re-self-assembly of PDA oligomers to reduce surface area. It is also demonstrated that the $\text{Fe}_3\text{O}_4/\text{C}$ -PDA nanospheres derived from the PDA hybrid has desired morphology for use as a recyclable catalyst support for the reduction of p-nitrophenol as well as an ORR electrocatalyst in primary ZnABs.

Secondly, the effects of addition of cobalt(II) ions as well as the effect of the co-addition of two different transition metal species on the in situ polymerization of DOPA are studied. The work is accomplished by using the facile one-pot in situ polymerization of DOPA, with the addition of cobalt(II) ions or two transition metal species. Cobalt(II) ions do not form coordination bonds with DOPA. Instead, cobalt(II) ions form a complex with hydroxyl ions in the solution. With the initiation of polymerization of DOPA, the hydroxyl ions are displaced by oxidized DOPA or PDA oligomers. In the system with two transition metal species (Fe(III) and Co(II)), the iron(III) ions have a dominant effect on the in situ polymerization process, as well as controlling the morphology of the PDA hybrids. Therefore it is proposed that the transition metal species that could form complex with DOPA would have a larger

degree of control over the polymerization process. To show the adaptability of the facile one-pot in situ polymerization process, porous PS nanofibers were selected as templates for the deposition of PDA hybrids with Co(II) and iron(III) ions. By annealing, porous carbon nanofibers with high surface area and decorated by binary transition metal oxides were obtained. Electrochemical studies reveal good ORR and OER electrocatalytic properties of the $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA PNFs nanocomposites when compared with commercial Pt/C. When used as the air cathode for rechargeable zinc-air battery, the porous carbon nanofibers show long cycling life and good cycling stability than its nanospheres and commercial Pt/C counterparts.

The focus of the last part of this PhD work is on demonstrating the versatility of this simple one-pot in situ polymerization process for fabrication of electrocatalysts with tailored morphologies. 3D carbon nanofibrous macrostructure, for use as free-standing air cathode in rechargeable zinc-air batteries, are fabricated by the deposition of the PDA hybrids on loosely packed electrospun PAN nanofibers. Conventional method to prepare air cathodes for zinc air batteries involves the use of binders and additives that will affect the performance of the batteries. On top of that, the electrocatalysts are simply applied on gas diffusion electrode, limiting the effective surface area. With the fabrication of a free standing 3D binder- and additive-free air cathode, the two problems above are addressed. Electrochemical studies with RDE show that $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA CNFs exhibit excellent ORR activity and stability with acceptable level of OER activity. As a proof-of-concept, the 3D carbon nanofibrous macrostructure are used as a free-standing air cathode for rechargeable zinc-air batteries. Unfortunately, due to the poor mechanical properties of the carbon nanofibrous macrostructure, the zinc-air battery did not show good durability. It is expected that with the improvement in mechanical properties of the nanofibrous macrostructure, excellent electrocatalytic activity can be obtained in the rechargeable zinc-air batteries.

7.2 Novelty and Significant Contributions

The works done in this PhD study period have led to several novel and significant outcomes.

For the first time, Fe(III)-PDA complex nanospheres are synthesized without the need for template. It is also verified that the polymerization of DOPA in the presence of iron(III) ions is due to the combined actions of the oxidative polymerization of PDA and the Fe(III)-PDA complexation. The presence of coordination bonds in the hybrid and the chemical structure of the hybrid are confirmed, for the first time, by XAFS studies.

It is observed for the first time that with the co-addition of two different transition metal species, the in situ polymerization process and also the final morphology of the hybrid are dominantly affected by the transition metal species that is able to form coordination bonds with DOPA before the initiation of the polymerization process.

The understandings derived from this PhD study can guide future studies to better design, control and optimize the structures and morphologies of transition metal/PDA hybrids for specific applications.

7.3 Future Work

7.3.1 Investigation of In Situ Polymerization of DOPA with Other Transition Metals

As mentioned in Chapter 2, there are numerous works that have added different transition metal species to DOPA during the in situ polymerization process, synthesizing transition metal/PDA hybrid materials with different morphologies.¹⁻⁶ However, all of these works have focused solely on the applications of the synthesized transition metal/PDA hybrid materials and devoted no efforts to

understanding the underlying mechanism that leads to the formation of the various morphologies. More recently, Wang et al. reported the synthesise of Mn(III)-, Fe(III)-, Co(II)-, Ni(II)-, Zn(II)- and Ga(III)-loaded PDA nanoparticles via the addition of the respective transition metal ions during the in situ polymerization process, with no mention of the formation mechanism (Figure 7.1). They also studied the doping range and parameters that influenced the final morphology of the nanoparticles.¹

Figure 7.1 TEM images of metal-loaded PDA-NPs: a) Mn(III), b) Co(II), c) Ni(II), d) Cu(II), e) Zn(II), f) Ga(III).¹

In this PhD study, two transition metal species (Fe(III) and Co(II)) were added to the in situ polymerization process of DOPA and studied as model systems. There are a total of 38 transition metals present in the periodic table and this PhD study has only provided insight into less than 10 % of the total elements in the transition metal group. Apart from the sheet-like and spherical morphologies that have been reported in literature^{3, 4, 6}, preliminary investigations show that other interesting morphologies can also be obtained. For example, with the addition of chromium(III) ions during the in situ polymerization process of DOPA, core/shell morphologies were obtained for the Cr(III)/PDA hybrid materials. From TEM micrographs (Figure 7.2), the

particles look like rectangular blocks with lengths ranging from 150 to 300 nm and have a hexagonal cross section. The different morphologies of the hybrid materials could be a result of the different complexation behaviors during the in situ polymerization process; therefore more efforts should be invested into studying the rest of the transition metals to uncover the relationship between the coordination bonding characteristic, polymerization mechanism and final morphology of the PDA hybrids, with hope of identifying a pattern across the periodic table.

Figure 7.2 TEM micrographs of Cr(III)-PDA complex hybrid material.

By shedding light on the mechanism of the in situ polymerization of DOPA with the addition of transition metal species and its effect on the morphology of the synthesized transition metal/PDA hybrid materials, it is possible to control and manipulate the morphology of the transition metal/PDA hybrid material to suit specific applications.

7.3.2 Improving the Mechanical Properties of 3D Carbon Nanofibrous Macrostructures

As mentioned in Chapter 6, the excellent electrocatalytic properties of the 3D $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA carbon nanofibrous macrostructures observed from the electrochemical studies could not be translated into highly active and stable rechargeable ZnABs. The poor performance of the 3D $\text{CoFe}_2\text{O}_4/\text{CoFe}/\text{C}$ -PDA carbon nanofibrous macrostructures based rechargeable ZnABs, was a result of the poor mechanical properties of the carbon nanofibrous macrostructures and it not

being able to withstand the harsh conditions during the discharge-charge cycling process.

To overcome the poor stability issue of the rechargeable ZnABs, efforts should be invested to improve the mechanical properties of the PAN-based carbon nanofibers. Several strategies have been reported to be effective in helping to improve the mechanical properties of electrospun PAN-based carbon nanofibers. Firstly, by varying and controlling the conditions used for electrospinning, stabilization and subsequent carbonization, PAN-based carbon nanofibers with varying mechanical properties can be obtained. Arshad et al. have reported the improvement in mechanical properties of the PAN-based carbon nanofibers with a reduction in the nanofibers diameter of the neat electrospun PAN nanofibers.⁷ Zhou et al. have reported an improvement in both tensile strength and Young's modulus of PAN-based carbon nanofibers with an increase in the final carbonization temperature.⁸ The addition of different amount of MWCNTs has also been reported to be able to improve the mechanical strength of PAN-based carbon nanofibers. Hou et al. reported the improvement in tensile modulus and tensile strength by increasing the concentration of MWCNTs in the PAN nanofibers. The presence of MWCNTs in the PAN nanofibers also helped in effectively reducing the heat shrinkage of the nanofiber sheets during carbonization.⁹ Ge et al. have also reported the improvement in tensile modulus of the PAN-based carbon nanofibers with an increase in the amount of MWCNTs in the electrospun PAN nanofibers.¹⁰

As seen from the above discussion, there are several strategies that can be used to improve the mechanical properties of PAN-based carbon nanofibers. By applying one or a combination of the discussed strategies, PAN-based carbon nanofibers, with improved mechanical properties, that are able to withstand the harsh conditions during the discharge-charge cycling of rechargeable ZnABs can potentially be fabricated.

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