Synthesis of platinum-based nanostructures and metal-organic framework-derived carbon for electrocatalytic applications

Zhou, Huiming

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS OF PLATINUM-BASED
NANOSTRUCTURES AND METAL-ORGANIC
FRAMEWORK-DERIVED CARBON FOR
ELECTROCATALYTIC APPLICATIONS**

ZHOU HUIMING

**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING**

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ELECTROCATALYTIC APPLICATIONS**

ZHOU HUIMING

School of Chemical and Biomedical Engineering

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Abstract

Fuel cell is one of the most promising candidates of renewable energy that have been highlighted in many researches these days. The main reason for this is the depleting non-renewable energy resources and the skyrocketing demand for energy in various applications to support current situation of technology development in a variety of fields. However, the main challenge of commercializing usage of fuel cells is the electrodes used in fuel cells. This major challenge revolves around the materials used as electrodes and their corresponding catalytic activities. It was discovered that nanoparticles can be used in construction of these electrodes. Thereby, large number of researches is going on investigating on various morphologies and crystal structures of nanoparticles. Among the so many kinds of nanostructured materials, platinum nanostructures have been broadly used for catalysis and fuel cells, owing to that Pt could catalyze both the oxidation and reduction reactions. Many researches have seen different synthetic routes proposed and carried out by researchers from around the world attempting to synthesize Pt nanoparticles since Pt could function as electrocatalyst for not only the oxygen reduction reaction (ORR) but also the fuel oxidation reactions, for example, formic acid oxidation reaction (FAOR), with the highest efficiency. As the demand for Pt grows while the Pt resource is scarce, the price of Pt has increased, and it could be predicted that the price will keep climbing later on. Finding new ways to lessen Pt utilized in a specific application by improving its catalytic activity is in need so as to overcome the prohibitive cost barrier.

In this project, we focus on the rational design and synthesis of Pt-based nanostructures and MOF-derived carbon for electrocatalytic performance.

In the first part of the research work, 3D Pt nanodendrites with clean surface and good catalytic performance were synthesized by a facile inorganic species assisted strategies. The possible specific adsorption of iron and nitrate ions would assist the growth of this 3D Pt nanostructure. Thanks to their unique 3D morphology composed of interconnected 1D Pt nanorods/wires, the clean unsupported 3D Pt NDs exhibit higher stability and enhanced activity than commercial carbon black supported Pt nanoparticles and Pt black electrocatalyst for the oxygen reduction reaction and oxidation of small fuel molecules.

Incorporation of the transition metals with Pt during the preparation of Pt-based catalysts could significantly improve the activity and the poisoning tolerance while reducing the cost of catalysts. Of all the bimetallic Pt-based catalysts examined hitherto including PtRu, PtSn, PtPb, PtCo etc., PtBi exhibits the powerful activity for formic acid oxidation. Inspired by this, PtBi nanosheets with tunable composition and 2D structure is prepared with an effective thermal decomposition method and investigate the composition effect on the catalytic activity for formic acid oxidation reaction (FAOR). The addition of NH_4Cl plays an important role on the formation of well-defined nanosheet structures. Due to the unique nanosheet structures and optimized composition, the as-prepared PtBi catalyst demonstrates the excellent electrocatalytic performance of FAOR.

In addition to synthesizing bimetallic/trimetallic electrocatalysts by introducing transition metal, various support materials for Pt and Pt contained nanocatalysts have also been investigated in depth and employed widely with the mutual purpose of significantly reducing of Pt cost while gaining fantabulous electrochemical performance. Nitrogen-doped CNT@Co-Pt composite using zeolitic imidazole framework-67 (ZIF-67) derived hierarchical nitrogen-doped CNT@Co frameworks as the carbon matrix was prepared with a facile method in our research work. The unique structure of the framework enables the catalyst with excellent structural merits including high accessibility, strong structural stability and sufficient loading site for the Pt nanoparticles. Meanwhile, the small amounts of carbon-nitrogen species would generate some extrinsic defects and active sites. In addition, the inner wrapped cobalt nanocrystals might provide extra conductivity. When applied as an advanced catalyst of ORR, the hybrid displays superior performance compare with commercial Pt/CB catalyst.

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List of Abbreviations

0D: zero-dimensional

1D: one-dimensional

2D: two-dimensional

3D: three-dimensional

AFC: alkaline fuel cell

Ar: argon

CB: carbon black

CNTs: carbon nanotubes

CO: carbon monoxide

CV: cyclic voltammetry

DFT: density functional theory

ECSA: electrochemical active surface area

DI: deionized

DMFC: direct methanol fuel cell

EDX: energy-dispersive X-ray spectroscopy

EG: ethylene glycol

EtOH: ethanol

eV: electro voltage

FC: fuel cell

FeCl₃: iron chloride

Fe³⁺: iron ion

FESEM: field-emission scanning electron microscope

FTIR: fourier transform infrared spectroscopy

GC RDE: glassy carbon rotating disk electrode

GO: graphene oxide

HRTEM: high-resolution transmission electron microscope

HTFC: high-temperature fuel cell

JCPDS: international centre for diffraction data

LTFC: low-temperature fuel cell

MCFC: molten carbonate fuel cell

MFC: microbial fuel cell

MOF: metal-organic framework

MOR: methanol electro-oxidation reaction

MWCNT: multi-walled carbon nanotube

N₂: nitrogen

ND: nanodendrite

NH₄Cl: ammonium chloride

NP: nanoparticles

NS: nanosheet

NTA: nanotube array

NW: nanowire

ORR: oxygen reduction reaction

PAFC: phosphoric acid fuel cell

Pd: palladium

PEMFC: proton exchange membrane fuel cell

Pt: platinum

PVP: polyvinylpyrrolidone

RHE: reversible hydrogen electrode

SAED: selected-area electron diffraction

SCE: saturated calomel electrode

SOFC: solid oxide fuel cell

SWNT: single walled carbon nanotube

TEM: transmission electron microscope

TGA: thermogravimetric analysis

TPB: triple-phase boundary

V/V: volume to volume

XRD: X-ray diffraction

XPS: X-ray photoelectron spectroscopy

ZIF 67: zeolitic imidazolate framework-67

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Chapter 1. Introduction

1.1. Background

Over the past several decades, there has been an increasing request for clean and sustainable energy sources to replace fossil fuels, such as petroleum, coal and natural gases, due to extending pollution issue and depletion of nonrenewable.^[1-3] This requirement is quite related to both the economic development of society as well as better quality of human life. As a result, novel kinds of energy resources have drawn more and more concentration from researchers. Actually, this work calls for the improvement of greatly effective, cost-efficient and environmentally friendly choices for both electrochemical energy transformations along with storage devices for various customer devices.^[1, 4]

Fuel cells, with different kinds and diverse applications, are thought as one of the best promising candidates. Fuel cells are more advantageous than the conventional power generating devices like combustion engines, as fuel cells operate without combustion of fuels and involves fewer parts.^[3, 5, 6] This is deemed to be more environmentally friendly and energy favorable than fuel combustion devices. In addition to low emission of pollutants, fuel cell is also capable in providing high energy conversion efficiency and simplifying energy conversion process from chemical to electrical energy. In a fuel cell, the electricity is principally produced by an electrochemical reaction between various kinds of fuels and oxygen to form water.

There are many kinds of fuel cells, consisting of alkaline fuel cells, direct methanol fuel cells, molten carbonate fuel cells, phosphoric acid fuel cells, proton exchange membrane fuel cells, and solid oxide fuel cells and so on. Besides, fuel cells can operate at both high and low operating temperature, thus they are also being categorized as high-temperature fuel cells (HTFCs) and low-temperature fuel cells (LTFCs). These low-temperature fuel cells have drawn significant attention owing to their high power density, low operating temperature ($<120^{\circ}\text{C}$), rapid start up process which is a result of the low operating temperature, and low pollution as a novel power source for automobiles and portable electronic devices.^[3, 7]

Many researchers have made great efforts and progresses in exploration and development of fuel cells. However, some factors, for instance, power density, durability as well as the cost still pose a big challenge for them at a standstill before commercializing any type of fuel cells. Fuel cell materials, namely the electrocatalysts, electrolyte membranes and catalyst supports and so on, all of them play significant roles during the operation of fuel cells. Besides that, they are directly associated to the major limitations and challenges in fuel cells, such as methanol crossover for direct methanol fuel cell and sluggish anode kinetics and so on. To conquer these challenges, it is of great importance to develop or search for novel fuel cell materials, particularly the novel electrocatalysts.

As has been reported many times before, among the so many noble metal based catalysts, electrocatalysts based on platinum have shown great potential in fuel cell applications and have get widely utilized nowadays due to the excellent catalytic

activity for electrochemical reactions at room temperature. The development about nanostructured Pt-based catalysts became a hot topic ever since the notice of the excellent catalytic performance of Pt.^[8-11]

1.2. Overall Objective

There has been greatly increasing interest revolving about FCs, especially the alkaline fuel cells nowadays, attributable to their promising beneficial function in broad applications as an alternative for energy resources in the future. Therefore, the main objective of this project is to design and synthesize the novel morphological Pt-based nanostructures and novel Pt contained nanostructures, which could function as electrodes in fuel cells. The nanostructured noble metals are expected to accomplish aspiration of increasing catalytic activity as well as decreasing the overall cost of construction, which apparently are the two major barriers in commercialization of fuel cells. Novel morphological Pt-based nanostructures and novel Pt contained nanostructures with exceptional electrochemical properties would be identified and further used to promote the performance of fuel cells. Specifically, the objective of this project can be categorized into the following three aspects.

1.2.1. To Develop 3D Pt Nanodendrites with Clean Surface and Good Catalytic Performance

Although many successes have been made in preparation of 3D Pt dendrites for

electrocatalysts, most of them are involved with the use of surfactants/organics and assisted by templates and substrates, which make the preparation process complicated. It is therefore significantly challenging to develop a direct synthesis approach for 3D Pt nanodendrites (NDs) with clean surface for fuel cells application. To achieve this target, 3D Pt NDs have been prepared with clean surface by a facile inorganic species assisted strategy. Consisting of multiarmed and interconnected 1D Pt nanowires, the as-synthesized 3D Pt NDs exhibit higher stability and activity than commercial carbon black supported Pt nanoparticles and Pt black electrocatalyst.

1.2.2. To Develop 2D PtBi Nanosheets with Tunable Composition and Outstanding Catalytic Activity for FAOR

The catalytic performance depends a lot on the shape, structure and compositions of the Pt-based electrocatalyst. By selectively incorporating the transition metals with Pt, the bimetallic Pt-based catalysts would have the potential to display enhanced activity for formic acid oxidation reaction. Inspired by these, we would like to develop a direct synthesis approach for PtBi nanosheets with 2D structure. To achieve this target, PtBi nanosheets have been prepared with the optimized initial addition ratio. Moreover, the catalytic activity for FAOR of the as-prepared PtBi nanosheets would also be investigated. Because of the unique nanosheet structures and optimized composition, the as-prepared PtBi catalyst demonstrates the excellent electrocatalytic performance towards FAOR.

1.2.3. To Develop Carbon Nanotube Frameworks as the Robust Support for Electrocatalyst with Enhanced Electrochemical Activity and Stability

To produce cost-effective catalysts, carbon-based materials are usually employed as support for the precious Pt. A typical example is carbon black, which is utilized in commercial Pt/CB catalyst as the support matrix. However, carbon black is with poor graphitic degree thus possesses poor anti-corrosion and oxidation in the harsh environments. Recently, metal-organic frameworks (MOFs) have emerged as a novel platform to produce new nanocarbon composites. Synthesis of CNT structures with well-defined morphologies using only MOF precursor is very attractive and of great challenge. Inspired by these, we would like to prepare CNTs from zeolitic imidazolate framework-67 (ZIF-67) and use it as support for Pt. Because of the unique robust framework structure of support material and the instinct superior property of Pt, nitrogen-doped CNT@Co-Pt composite possesses both high electrocatalytic activity and stability.

1.3. Organization

The thesis is composed of 6 parts, including introduction (Chapter 1), literature review (Chapter 2), general synthetic method and measurements (Chapter 3), research findings (Chapter 4 to 6), and conclusions and future perspectives (Chapter 7). The detail is listed as below:

Chapter 1 is a brief introduction of the background, objectives and research scope

of this research project. In Chapter 2, a literature review about recent research progress in the rational design and preparation of Pt nanoparticles and carbon supports is elucidated as a foundation of the research. The general synthetic methodology, materials characterization techniques, and electrochemical measurement procedures applied in this project are summarized in Chapter 3. Chapter 4 to 6 present the experiments and research findings from each part. Each chapter contains introduction of project, experimental section, results and discussions, and conclusions. Chapter 4 discusses about the synthesis of 3D Pt nanodendrites (NDs) surface by a facile inorganic species assisted strategy, and their electrocatalytic performance. Chapter 5 reports on the preparation of intermetallic PtBi nanosheets with controlled size and composition by a one-pot method for fuel cells application and their electrocatalytic performance. In chapter 6, metal-organic framework-derived carbon nanotube were used to be the support for Pt nanoparticles. The as-prepared CNT@Co-Pt showed good intrinsic ORR activity as well as stability. Lastly, the general conclusions drawn from the discussed studies are reviewed. Based on that, perspectives extended from this thesis and possible directions for future study are proposed as a continuation of this work.

Chapter 2. Literature Review

2.1. Overview of Fuel Cells and Pt Based Electrocatalysts

As human's awareness about the environmental consequences of fossil fuel use in producing electricity and for propulsion of automobiles has been increasing, the conversion of chemical energy into electrical energy which is clean and sustainable is considered to be arguably one of the most significant concerns in the 21st century, which is ultimately related to our daily lives, global environment/economy, and human health.^[1, 3] Even though combustion-based energy technologies will keep on playing a dominant role in meeting our energy requests in the short term, they come with a tremendous cost, including the speedy growth of greenhouse gas emissions as well as long-lasting environmental contamination. In this respect, fuel cells (FCs), as a typical electrochemical energy conversion system, are becoming more and more appealing than ever, as FCs have witnessed significant progresses as well as promising potential in various applications, including portable electronics, hybrid/pure electric vehicles, smart grids, and other rechargeable environmentally friendly electronic devices. More importantly, FCs could efficiently convert chemical energy straight into electrical energy with little or even no pollution.^[3, 9, 12, 13]

A fuel cell is a device converts the chemical energy from a fuel into electricity through a chemical reaction of positively charged hydrogen ions with oxygen or another oxidizing agent.^[9, 13, 14] As an electrochemical conversion device, fuel cells

have a continuous supply of fuel such as hydrogen, natural gas, or methanol and an oxidant such as oxygen, air or hydrogen peroxide. Besides, fuel cells may also have some auxiliary parts to supply the device with reactants along with a battery to provide energy for start-up.^[15] There are various kinds of fuel cells, all of which consist of an anode, a cathode and an electrolyte that allows positively charged hydrogen ions or protons to move between the two sides of fuel cell. The anode and cathode contain catalysts causing the fuel to undergo oxidation reactions that generate positively charged hydrogen ions and electrons. The hydrogen ions are drawn through the electrolyte after the reaction. At the same time, electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. At the cathode, hydrogen ions, electrons, and oxygen react to form water. A representative sketch of fuel cell is shown in Figure 2.1.^[5]

Figure 2.1. A simplified representation of a H₂-fed PEMFC. Reproduced with permission from ref. 5. Copyright 2014 Wiley.

Till now, lots of research have been devoted to the study of fuel cells, and there

have been six main types of fuel cells, including (1) proton exchange membrane fuel cell (PEMFC) including direct methanol fuel cell (DMFC), (2) alkaline fuel cell (AFC), (3) phosphoric acid fuel cell (PAFC), (4) molten carbonate fuel cell (MCFC), (5) solid oxide fuel cell (SOFC) and (6) microbial fuel cell (MFC). Also, fuel cells can operate at both high and low operating temperature, thus they are also being categorized as high-temperature fuel cells (HTFCs) and low-temperature fuel cells (LTFCs).^[15] These low-temperature fuel cells have drawn significant attention owing to their high power density, low operating temperature ($<120^{\circ}\text{C}$), rapid start up process which is a result of the low operating temperature, and low pollution as a novel power source for automobiles and portable electronic devices.^[16]

Many researchers have made great efforts and progresses in exploration and development of fuel cells. However, some factors, for instance, power density, durability as well as the cost still pose a big challenge for them at a standstill before commercializing any type of fuel cells. Fuel cell materials, as follows, the electrocatalysts, electrolyte membranes and catalyst supports and so on, all of them play significant roles during the operation of fuel cells.^[6, 11, 17-22] Besides that, they are directly associated to the major limitations and challenges in fuel cells, such as methanol crossover for direct methanol fuel cell and sluggish anode kinetics and so on.^[9, 13, 18, 23, 24] To conquer these challenges, it is of primary importance to develop or search for novel fuel cell materials, particularly the novel electrocatalysts. Currently, the most effective electrocatalyst for fuel cells is well known to be Pt, which has near zero overpotential.^[17, 19, 20, 25, 26] So far, Pt nanostructures, Pt/C and Pt-modified or

alloyed catalysts are the most popular used catalysts because of their low overpotential and high catalytic activity.^[17, 18, 26-29] However, the high cost and short storage are still the barriers of the application of Pt. There is thereby an urgent but it is still a significant challenge to synthesize Pt contained nanocatalysts with outstanding catalytic performance and less amount of Pt dosage.

It is well established that many characteristics of functional materials, such as composition, crystalline phase, structural and morphological features, and also the synthesis methodology would greatly influence the performance of these Pt nanocatalysts.^[1, 11, 30-32] Besides, for Pt/C, the carbon support can also influence the catalytic performance effectively.^[22, 33-35] In the following sections, we will review the fundamental understanding of relationship between structure and activity, recent progress of synthesis methods, and some commonly used carbon support of the Pt based nanostructures for electrocatalytic applications.

2.2. Fundamental Understanding of Relationship between Structure and Activity

On the basis of the researchers' many years research about Pt-based nanostructured catalysts, size, dimension, shape and composition, are considered to be the significant and distinctive parameters for tailoring catalytic performance.^[5, 36]

2.2.1. Particle Size Effect

The size of nanocatalyst not only controls the specific surface area of the nanocatalyst, but also determines the ratio between surface and bulk atoms.

Nanostructured catalysts made from noble metal with large electroactive surface area should be controllable so as to make the best use of their activity. For example, in the methanol electro-oxidation reaction (MOR), studies about the size effect on the efficiency have shown that the platinum nanocatalysts with the size in the vibration among 3–10 nm have highest mass specific activity, whereas particles with sizes below or above have exhibited the loss of activity.^[22, 37] For nanoparticles with smaller size, the activity loss may be attributed to morphologies, while for the bigger ones, it can be contributed to the desorption kinetics which is caused by the fuel. The as obtained indefinite results caused by the wide variation of size distribution of the electrocatalyst materials raise a demand for the utilization of particles with narrow variation of size distribution for high efficient catalytic properties.

A phenomenon has been observed recently that the crystal structure of Pt nanoparticles with the sizes within 1 nm has a spontaneous collapse, resulting in lowering the catalytic activity to hydrogen oxidation reaction owing to the induced quantum size effects.^[26] Pt nanoparticles translate from crystal structure to amorphous structure, supposing important estimation about the lower Pt use size barrier boundary of 1 nm for catalytic property. This phenomenon has been suggested by both the density functional calculations as well as the molecular dynamics simulations. Significant result into the relationship between structure-property and the size has

been obtained from the computational research about size-dependent catalytic properties of platinum nanocatalysts by using molecular dynamics. Using efficient medium theory to the four virtual Pt cubic particles with various sizes (1 nm, 1.5 nm, 2 nm, and 2.5 nm), the molecular dynamics simulations put forward different types of atom-packing structures as shown in Figure 2.2(a).^[38] Ordered structures with the well-defined (100) facet and (111) facet, were reserved in succeeding heating and annealing processes so as to get bigger nanoparticles.

Figure 2.2. Molecular dynamic simulations using the effective medium theory. (a) Four Pt cubic particles with different diameters, defined in this work as the diameter of a sphere with a volume equal to the cubic, were heated in vacuum to 2000 K and then slowly cooled down to 300 K, resulting in different atom-packing structures as a function of the particle size. (b) A virtual Pt cubic particle of 1 nm diameter was thermostatically kept at 300 K in vacuum for a period of time, a spontaneous collapse in the crystalline structure occurring quickly. Reproduced with permission from ref. 38. Copyright 2007 ACS.

On the other hand, kink structure started to appear at the surface when the

diameter of the nanoparticles is lessened, which is closely related to the decrease in the size of (100) facet and (111) facet as shown in Figure 2.2(b). All these studies provide evidence that, if the size of the nanoparticles is reduced to less than 1 nm, the crystalline structure becomes amorphous. In addition, as suggested by density functional theory (DFT) calculations, the upward shift in the d band center appears in regard to E_F and there is also an enhancement at the Fermi level in density of states, since the d band get narrowed which is caused by the reduction of size. As a result of such a modification of electronic structure, a better interaction between the surface and the adsorbed catalyst molecules is achieved; and in this manner, the catalytic efficiency gets decreased when particle size is reduced.

According to the discussion above, it could be summarized that, the dimension of Pt nanoparticles, especially an extraordinary size range is one of the chief factors in carrying out higher catalytic performance when being the electrocatalyst, while nanoparticles with sizes either below or above would be less effective.

2.2.2. Dimension Effect

According to the study in recent years, dimensionality has been suggested to play an extremely significant role in deciding the properties of nanomaterials because of some reasons, for example, one of them is that in various structures, the diverse ways electrons interact with each other.^[39-43] In most cases, 0 Dimensional (0D) ultrasmall structures have a quick reduction of the activity because they can simplify the dissolution and ripening procedures during the fuel cell performance. While in

contrast to 0D ultrasmall structures, the 1 Dimensional (1D) structure motifs, 2 Dimensional (2D) nanosheets, and 3 Dimensional (3D) array networks usually have a much better stability because of their structures. The 3D structures could not only help overcome the weaknesses, but also benefit the activity for long term.^[44] The intrinsic anisotropy of the 1D and 2D systems, for instance, the nanotubes, nanowires, nanosheets and so on, is rather essential to the distinctive properties they possess, making them extremely attractive in fuel cells accordingly. In contradiction of their corresponding 0D nanomaterials, these materials own numerous exclusive properties, for example, higher aspect ratios, smaller amount of defect sites, superior exposure of greatly active facets, low-energy facets, the longer segment of smooth crystal planes, and improved electron transport, due to their highly anisotropic growth.^[45-51]

The physical ripening process is restrained because of the asymmetry of these structure; accordingly, such nanomaterials are intrinsically stabilized from both Ostwald ripening and dissolution. With the defect sites that are vulnerable to decomposition and oxidation get removed, such structural anisotropy greatly improves the stability, in particular. Consequently, for the reason that they would not suffer from the alike propensity to ripen, as well as aggregate, these low-dimensional nanostructures are theoretically less prone to call for a carbon support.^[52]

Due to the various advantages that 1D and 2D nanomaterials hold, both single-component 1D Pt nanomaterials and multicomponent Pt-based 1D materials, have attracted a wealth of attention and interest from many researchers. Self-supported 1D Pt nanorods synthesized by Yamauchi and co-workers were with

various lengths varied from 0.6–3.2 mm and the size and wall-thickness ranges from approximately 6–8 nm and 2–3 nm respectively, showing a high density of mesopores.^[48] Moreover, the as prepared Pt nanorods also displayed outstanding stability as it lost only 31% of the initial ECSA after 2000 cycles. Some other examples, like FePt and CoPt nanowires (NWs) with different tunable compositions prepared by Sun and co-workers^[53] and porous PtNiP composite nanotube arrays (NTAs) synthesized by Ding and co-workers,^[54] have also exhibited both enhanced activity and good long-term stability.

In recent times, 2D nanostructure systems have been recognized as promising and talented long-term lasting electrocatalysts for fuel cells.^[55, 56] 2D Pt nanosheets prepared through an in situ chemical- vapor reaction in molten salt by Yang and co-workers were highly active for ORR since they were carbon-free and surfactant. The unique advantage of 2D materials makes them greatly promising fuel cell catalysts to realize the practical applications.^[57]

The sizes of some 3D nanostructures, for example, the greatly branched structures, hollow nanocages, and porous networks, generally are within the range of about 50-200 nm, which are obviously much larger than those of the conventional catalysts nanoparticles.^[34, 58-60] However, these structures have shown excellent resistance to aggregation, since the Pt consumption they possess are very low and the distributions of the Pt sites of them are extensive spatial. For example, PtNi bimetallic nanobundles (NBs) prepared by Li's group, with a highly branched starlike structure which is aggregation-resistant and stepped surfaces, lost only 45% of initial current density

peak after 4000 cycles for MOR, while the conventional Pt nanoparticles (NPs) lost 90%.^[34] Xia *et al.* synthesized the nanowire assemblies made up of ultrathin and ultralong Pt nanowires.^[61] Nanowire assemblies with 3D interconnected networks displayed large surface areas as well as great porosities, exhibiting remarkably high stability which benefited from improved electron transport and catalyst utilization on account of the anisotropic structure.

2.2.3. Crystal Facet Effect

The shape of the nanocatalyst controls the facets, surface structure, and fractions of atoms at both corners and edges of a nanocrystal. As has been demonstrated by recent research and investigations, catalytic activity of nanoparticles depends more on shape rather than on size.^[62] It is well known that MOR on bulk platinum with small surface area is structurally sensitive.^[63] Pt (111) surface was proved to own the lowermost activity and have the onset potential for MOR. Nevertheless when compared with (100) and (110) miller index planes, it could take the maximum CO tolerance. Owing to the difference in adsorptivities of sulfate ions of the facets, Pt (100) has the higher ORR activity than Pt (111).^[64] The catalytic activity of polyhedral structured Pt nanocrystals and platinum nanocubes exhibits larger current density for Pt nanocubes with size of 7 nm, which was three times higher than those of 3 nm polyhedral and 5 nm truncated cubic Pt nanoparticles during ORR.

During exploration for new types of Pt nanoparticles, tetrahexahedral structured Pt nanocrystals have been well produced with high-index facets, for instance (730) facet,

(210) facet, and (520) facet and so on.^[65]

During electro-oxidation reaction of small organic molecules, such as methanol, ethanol and formic acid, these Pt nanocatalysts have displayed good catalytic activity, which may benefit from the high density of atomic kinks and steps that function as active sites during chemical bonds breaking process.^[65]

According to the above, the performance of nanocatalysts depends much more on the shape than on the size. Therefore, preparing catalyst structures that are with high-index surface facets is a promising way to further improve the catalytic activity of nanocatalyst. These above results are especially beneficial to design and develop new kinds of catalyst nanostructures with plentiful corner and edge sites as well as the most high-index planes in growth process.^[66, 67]

Recognition of the basics of growth of crystal will help design and synthesize nanocatalysts with multifaceted structures. Accordingly, understanding the progression of crystallization, which mainly relies on basic steps of nucleation and growth is the marrow of shape control. Uniform and monodispersed nanomaterials with anticipated shapes could be generated if the factors which affect both the nucleation and growth kinetics can get controlled over simultaneously. Nevertheless, managing the crystallization process to gain an ideal crystal is not easy. The aggregation of atoms and molecules which forms the nuclei causes the nucleation which will further develop to form preferred nanostructures. During the growth, nuclei normally perform as seeds. Under kinetic and thermodynamic considerations, the seeds can grow into various shapes including 1D anisotropic nanoparticles for

example rods and wires, 2D nanoparticles for example nanodiscs and nanoplates, furthermore 3D nanoparticles for example multipods and nanostars. Based on thermodynamic considerations, surface energies of various crystal surfaces could decide the shapes of fcc metals. Facets with high surface energies grow much quicker than others during the crystal growth, thus they are mostly removed from surface of the synthesized crystal. Therefore, as shown in Figure 2.3, low-index facets get enlarged and crystals take the shapes.^[68]

According to the discussion above, a conclusion can be drawn that shape control of Pt nanoparticles is very significant in deciding catalytic performance. And it is certainly of great importance during developing new synthetic approaches to design perfect electrocatalysts.

Figure 2.3. Unconventional shapes of fcc metals whose surface is enclosed by high-index facets. The Miller indices $\{hkl\}$ obey the order $h > k > l$. Reproduced with permission from ref. 68. Copyright 2007 Wiley.

2.2.4. Composition Effect

Composition, which includes the sorts of component elements along with their proportions, directly relating with shape and size of a material, is the fundamental essence of a catalyst. To decrease Pt utilization in view of the fact that Pt is a kind of expensive metal, and further develop catalytic performance of Pt, including both its activity and stability, some efforts have been made to introduce a foreign metal into the Pt catalyst, which is now considered as the most promising approach.

The enhanced bimetallic/trimetallic electrocatalytic performances are typically proposed to be explained by two effects, bifunctional effect and electronic effect, also called ligand effect.^[69] The accurate mechanism for a bimetallic system is usually not easy to be defined. During majority cases, an electrochemical procedure benefits from both bifunctional effect and electronic effect simultaneously. For instance, the hollow mesoporous PtRu alloy particles synthesized by Ataee-Esfahani *et al.* as greatly CO-tolerable catalysts for the MOR, and they designated that the preeminent performance derived from two parts, one is the downshifted d-band which comes from the electronic effect, and the other one is the adsorbed oxygen-containing materials on ruthenium atoms which is originated from the bifunctional effect.^[40]

Summarizing the approaches to get some foreign metal into Pt so as to get a novel kind of electrocatalyst, as shown in Figure 2.4, there have been three probable categories of mixing modes for two or three kinds of metals generally:^[38, 70, 71]

1) Homogeneously mixed alloys. In the homogeneously mixed alloys, the two different kinds of metals are blended in either a statistically random mode or an

atomically mode. The ordered intermetallic alloys, which have been less-frequently reported than the alloys with random mode, are featured with long-range atomic sequence.^[72, 73]

2) Heterogeneous structured alloys (sub-cluster-segregated nanoalloys). In the heterogeneous structured alloys, two kinds of metal constituents share one interface. Pt-based heterogeneous structures are usually equipped by covering the substrate which is a less-cost metal-NPs with a small quantity of Pt NPs on the surface, so that the Pt utilization can be greatly lower and the spatially distribution of Pt sites can be broadly developed. Consequently, thanks to the third-body effect, electronic effect, as well as the increased interface area and so on, heterogeneous bimetallic nanomaterials usually exhibit superior resistance against aggregation and are extremely active and stable during fuel cells reactions.^[57-60, 74, 75]

Figure 2.4. Bimetallic/trimetallic nanocrystals with different mixing patterns: (a) Alloy structures: ordered intermetallic alloy (top) and random alloy (bottom); (b) heterostructures; (c) core-shell structures: single-shell structure (top) and multi-shell structure (bottom). Reproduced with permission from ref. 71. Copyright 2008 ACS.

3) Core-shell structures. Core-shell structures comprise of a core of one kind of atom surrounded with a shell (single shell) of another kind of atoms. Besides, there exists not only the monolayer-encapsulated structure, multiple-shell structures have also been successfully synthesized, which are with layered structured or onion-like shells. With the exploitation of a variety of theoretical and synthetic methodologies, abundant composite structures have been successfully obtained. Core-shell structures stand for an efficient structural model, with either a single layer or some layers of Pt atoms covered on the less-cost core materials, the Pt spending get greatly decreased since plurality of platinum atoms could get scattered at the interface of the electrochemical reaction. More than that, the core material can effectively tailor the structure and properties of a Pt shell because of the structure-induced strain or geometry effect, as well as the electronic effects or alloying effect.^[34, 62-67, 76, 77]

2.3. Recent Progress about Pt-Carbon Composites

Since platinum has displayed the best catalytic activity performance in fuel cells, Pt nanoparticles are commonly utilized to be the catalysts for fuel cells, however, the high cost is always a barrier hard to get over. Hence, lots of efforts have been put to reduce the price and make the utilization ratio as high as possible meanwhile. Several approaches have been developed using various support materials for Pt and Pt contained nanocatalysts. The support materials need to meet some requirements which could be summarized as follows: high specific surface area to increase the

dispersion of nanocatalysts; low flammability at low temperature in both humid and dry air conditions; extraordinary chemical and electrochemical stability; high conductivity and so on.^[21, 27, 78-85] Interaction between support and nanocatalysts also plays an essential role in enhancing both activity and durability of the catalysts. Among the so many techniques to realize such a goal, utilizing carbon material as the supports for Pt or Pt contained alloys clusters has attracted a lot of attention from researchers.^[34, 70, 79, 86, 87] Vulcan XC-72 carbon black has become the most commonly used support carbon material. Besides, some other novel catalyst supports, for instance, carbon nanotubes, carbon nanofibers, mesoporous carbon, graphene and so on, have also been developed during recent years.^[13, 21, 24, 88-95]

Herein, we make a simple summarization about the latest progress in some significant support carbon materials and discuss about the problems related as well as upcoming challenges.

2.3.1. Carbon Black

Among the so many kinds of carbons that can be used as supports for both Pt and Pt contained alloy nanocatalysts for fuel cells, carbon blacks, for instance, have become the most popular used ones in many studies and commercial applications. Carbon black plays an important part when being a catalyst support.^[78, 96-99] It doesn't only function to penetrate and wet precursors, but also limit the growth of nanoparticles.

Carbon blacks, consisting of near-spherical shaped particles of graphite, of which

diameter is smaller than 50 nm, are regularly synthesized by pyrolysing hydrocarbons like natural oil or gas fractions taken from petroleum processing. These near-spherical particles of graphite combine into particle agglomerates or aggregates with diameter of about 250 nm. These graphite particles are with polycrystallite structures, gathering to constitute non-discrete 3D groupings. Every micro crystal is made of some “turbostratic” layers which usually have an interplanar crystal spacing of around 0.35 nm to 0.38 nm. Both particle size distribution and morphology of CB depends largely on the provenience material as well as the thermal decomposition process. CBs have many relative advantages, such as the high surface area ($\sim 250\text{m}^2\text{ g}^{-1}$ for Vulcan XC-72), easy availability and low cost, which could decrease the total cost of fuel cells.^[98, 100]

Though commonly utilized as catalyst–support, there still occurs some problems, for instance, the existence of foreign matters, recesses or deep micropores trapping the catalyst nanoparticles, leading them to be unreachable to reagents therefore reducing the catalytic activity.^[101, 102] The contact between the catalyst nanoparticles and Nafion ionomer is also affected by the size and distribution of the pores. The recesses in the carbon black is smaller than size of Nafion micelles, which is $>40\text{ nm}$, as a result, any metal nanocatalysts existing within the pores and with diameter smaller than size of the micelle would be not available to Nafion, thus contributing hardly to electrochemical activity. Additionally, carbon black does not have a good thermochemical stability, which plays a significant role in the acidic environments of typical PEMFC/ DMFC. Lack of thermochemical stability will bring about the

corrosion of the carbon support.^[103-105] As a result, the catalyst layer would get disintegrated.

Accordingly, much effort has been made to get some improvement of enhanced catalyst efficiency and greater ECSAs, so as to make the catalyst more efficient. These properties are exceedingly needed for decreasing catalyst loadings and in this manner making the total cost of fuel cells lower. Therefore, lots of studies on nanostructured carbons, for instance, carbon nanotubes, mesoporous carbon along with carbon nanofibers and so on have brought.

2.3.2. Carbon Nanotubes

Carbon materials with nanostructures have been explored as good options of catalyst supports because of their unique structures and properties over the recent years. And the most famous nanostructured carbon is carbon nanotubes (CNTs). Carbon nanotubes have been developed significantly since 1991 to the present-day.^[105] A great deal of successes has been achieved by numerous scientists in the fields of both science and technology, especially in the area of nanotechnology, in order to synthesize carbon nanotubes. Among the so many methods of synthesis of carbon nanotubes, the most up-and-coming one is the catalytic decomposition from gas or solid that contains carbons.^[106-108]

CNTs have shown quite a few awesome advantages over the conventional carbon black when acting as the fuel cell electrocatalyst supports, for instance:^[25] 1) exclusive structure and electrical properties would help afford an extraordinary

conductivity and a particular contact between the CNT supports and catalytic metals because of the π electrons from CNTs and d electrons from the platinum, both of which are delocalized, issuing in higher catalytic activity consequently; 2) CNTs are with fewer foreign matters, whereas CB, for example, Vulcan carbon XC-72, comprises quite a lot of organo-sulfur impurities, tending to poison the platinum; 3) CNTs do not suffer deep cracks which exist inside CB where the deposited Pt nanoparticles will be unable to show catalytic activity as a result of the absence of the electrochemical triple-phase boundary (TPB). The ordered catalyst layer constructed by CNTs would provide supports for mass/electron transport, and produce greater cell performance. CNTs are with the 2D nanostructures and can be generally categorized into three kinds, namely single walled (SWNT),^[33, 106] double walled (DWNT)^[109] and multi-walled (MWNT) CNTs.^[88, 90, 110] The carbon atoms arranged hexagonally, are formed into the walls by rolling up in the shape of single sheets. SWNTs could be active of conducting, namely metallic along with semi-conducting in nature, owing to the structure. CNTs are the one of the best known carbon nanostructures that have been most widely explored to function as fuel cell catalyst support by now. SWNTs as well as DWNTs and MWNTs have been broadly explored for fuel cell catalyst support. According to the research result that has been reported, MWNTs have exhibited better conductivity while SWNTs afford larger surface areas.^[111] For example, Wang's group developed a facile procedure to synthesize CNTs/IS-ILs/Pt hybrids via directly mixing IS-IL-functionalized CNTs, Pt precursor, AA, and water in an ambient environment. As shown in Figure 2.5, the result displayed that ultrahigh small Pt NPs with uniform

Figure 2.5. (A, B) TEM images of IS-IL-functionalized CNTs; (C) SEM and (D, E) TEM images of CNTs/IS-ILs/Pt hybrid nanostructures. (F) The corresponding size distribution of Pt NPs in (E). Reproduced with permission from ref. 112. Copyright 2010 Wiley.

dispersion and good size distribution (~ 3 nm) could adhere to the surface of IS-IL-functionalized CNTs, which could be easily tuned by simply changing reaction parameters. Most importantly, the as-prepared hybrids exhibit higher electrocatalytic activity towards MORs than those of E-TEK and CNTs/PDDA/Pt hybrid catalysts.^[112]

Although CNT could offer many advantages, some disadvantages still exist that will limit the application of CNT for fuel cells. The challenges faced now contain the synthesis technique because current techniques have not been able to product the CNT

in large scale. Besides, the cost limitation is still a problem, though the cost have been reduced greatly over the past several years. Development of methods with low cost and large scale production is still in need.

2.3.3. Graphene

Since graphene is discovered by Geim *et al.* in 2004, it has attracted tremendous interest from researchers.^[113] Graphene is an atomically thin monolayer sheet made up of carbon atoms that are arranged hexagonally, with a dense honeycomb crystal structure.

Owing to its exclusive nanostructure and outstanding properties, such as large surface area, high electron transfer capacity and high conductivity, graphene sheets become eye-catching as prospective nanoscale structured blocks for novel nanocatalysts.^[93, 114-116] Both the edge planes and basal planes of carbon sheet could attach catalyst nanoparticles well because of the 2D planar structure of graphene; moreover, structure of graphene, which is rippled but then planar sheet shape, as well helps to offer high surface area, which assist a lot when interact with the catalyst nanoparticles. As a result, graphene has been broadly investigated for different applications containing being catalyst support for fuel cells, for example, Soin *et al.* has studied about using the vertically aligned graphene nanoflakes (FLGs) in MOR.^[115] With sputtering technique Pt nanoparticles were deposited on the FLGs. The as synthesized Pt/FLG electrodes revealed fast electron transfer kinetics according to the

CV curves tested. Besides, it also displayed higher resistance against CO poisoning compared with Pt/CB as well during the MOR studies. Liu *et al.* demonstrated the production of Pt nanoparticles deposited expandable graphene sheet which was fabricated on conductive indium tin oxide (ITO) glass electrodes through electrochemical synthetic method.^[114] Figure 2.6 shows the representative FESEM figures of the as-prepared expandable graphene oxide, the derived expandable graphene sheet and Pt loaded expandable graphene sheet. As graphene could afford fast electron transport mechanism, graphene could make great contributions to ORR performance in fuel cells as it is able to predominantly expedite the ORR more speedily and efficiently.^[116, 117]

Figure 2.6. FESEM figures of the as-prepared expandable graphene oxide (a), the derived expandable graphene sheet (b) and Pt loaded expandable graphene sheet (c and c1). Reproduced with permission from ref. 114. Copyright 2010 Elsevier.

In addition to graphene itself, its oxidized counterparts, for instance, graphene oxides (GOs), have also been very interesting and attractive. Though compared to graphene, GOs usually display lower conductivity, it could provide some different properties, like better hydrophilicity, higher mechanical strength, and better chemical durability and so on, making it possible to realize various uses. The defect sites which are generated on both edge and surface planes of GO by the introduced oxygen groups during synthesis of GO, could function as anchoring positions as well as nucleation centers to grow metal nanoparticles.^[118-120] One of the most recent applications of GO is being the catalyst support material in fuel cells, which have displayed encouraging results.^[121, 122] In addition, doping nitrogen into graphene is also a promising way to get better usage of graphene. Research result about nitrogen doped graphene has been presented to achieve attractive results for ORR particularly. Similar to GO, due to the nitrogen atoms incorporated, the disorders and defects in nitrogen doped graphene are known to be anchoring sites and nucleation centers for growth of metal nanoparticles.^[116, 123]

2.4. Categories of Synthetic Methods

To overcome high cost barrier of Pt for commercialization of fuel cells, recent research into electrocatalysts has been centered on finding new ways to synthesize Pt based catalysts with less cost and enhanced catalytic performance. And according to the summarization above, the catalytic performance depends quite a lot on the

structure of catalyst in all respects, while it is still very challenging and demanding to accomplish the regulation and control about morphology of electrocatalysts at the nanoscale with only traditional synthetic methods. Consequently, novel synthetic methods which can control the Pt based electrocatalysts on both size and shape become hotspots during recent years.

It could be achievable to meet the above talked requirements by using different methods of introducing diverse morphologies of Pt with the features like larger surface area, high utilization rate of Pt as well as some attractive chemical properties and promising catalytic performance at nanoscale.^[17, 32, 64, 124, 125] Besides, using monocrystal Pt layer, hollow Pt nanostructures, as well as Pt contained core shell assemblies with Pt layer as the shell to cover non-noble metal as the core is also a promising cost-efficient approach which can significantly reduce Pt loading and do not need to sacrifice the catalytic activity.^[126-130] And simultaneously, utilization of Pt can be further enhanced with the employment of nanotube structures, porous framework or innovative nanostructured backing materials which have nanochannels.^[82, 83, 111] Moreover, with a simple technique of modification in the morphology of conventional catalysts, novel multiple junction nanostructures can be generated. Innovative approaches by using plentiful non precious metals and small amount of Pt with no need of compromising its catalytic activities could be exploited.^[17, 40, 71] Another method to reduce the spending for Pt and get a stable distribution of electrode material with enhanced performance is to use supporting materials during the synthesis of Pt based electrocatalyst.^[21, 33, 34, 79, 103]

Latest progresses about Pt based electrocatalysts is discussed in the following sections.

2.4.1. Template-based Synthesis

Template-based synthesis method is very popular for the generation of inorganic nanocrystals. During this method, a template with desired size and shape is employed to function as the scaffold to generate the desired nanostructures. The fundamental idea of template-based synthesis is that the desired material is fabricated into the pores, tubes or channels provided by template with porous structures.^[30, 91, 131, 132]

In general, templates can be categorized into two main styles, i.e., hard templates and soft templates. Hard templates, which are usually involved physically would get detached separately after synthesis.^[133] Examples of Pt nanostructures with hard templates for synthesis include Pt-Ru alloy nanoparticles and sandwiched Ru/C nanocomposites.^[83, 134] Soft templates that are usually involved with chemical synthesis processes and it is feasible in a pure form with soft templates to gain nanostructures.^[135] Some typical instances of hard templates for synthesis of Pt nanostructures are liposomes for the preparation of 2D and 3D Pt nanostructures and wormlike micelles for the growth of Pt nanowires.^[136, 137]

Because of its advantages, such as simplicity, cost-effectiveness, and high efficiency and so on, the template-based method is of great popularity. Template-based synthesis is believed to be quite practical, in view of the fact that it could realize the design and generation of an extensive variety of nanostructures with

particular surface characteristics as well as the specified geometry.

2.4.2. Galvanic Replacement Reaction

Hollow nanostructured catalyst, which could successfully reduce the cost because of the less need for noble metal content compared with other kinds of nanostructures, is a valuable and promising option for application. In order to synthesize hollow nanostructured catalyst, one of the foremost methods is galvanic replacement reaction, in which metal ions in solutions get reduced, while the substrate material get oxidized afterwards, resulting in the decomposition of atoms on surface.^[138-141] This simple and easy method can selectively precipitate metals upon the oxidizable metal supports while it requires neither a reducing agent nor an exterior voltage source in the solution.

Noble metals, like Pt, which have been very attractive in catalysis, can be settled onto a less cost metal substrate for example, Ag. One of the benefits of this routine is that it can operate with a lower temperature while other advanced methods usually need a higher reaction temperature in comparison. After galvanic displacement reaction, the support material could be dissolved with chemical etching subsequently, with the hollow metal nanostructures as the product. Some interesting and exciting results for their outstanding catalytic activities can be got since the hollow nanostructures are with distinct structural properties. And typical examples of hollow Pt based electrocatalysts synthesized with galvanic replace reaction include Pt hollow nanospheres prepared by the reaction between Co particles and Pt solutions, Pt and

PtPd nanotubes/nanofibers generated from the displacement of Ag from silver nanowires, porous hollow Pt nanospheres with Ag cores and hollow Ag-Pt nanospheres, and bimetallic clusters like Au/Pt/C.^[127, 142-145]

2.4.3. Electrochemical Synthesis

Preparation of inorganic nanocrystals with electrochemical methodology has got full exploration by the researchers. The electrochemical route has been proved to be an easy, speedy and efficient technique. Both surface morphologies of the deposits along with the sizes of the nanoparticles could be controlled very well by altering the synthetic parametric quantities, for example, the amount of precursors, current densities, reaction time and so on. Numerous reports have demonstrated the synthesis of Pt with faceted nanostructures, such as spherical Pt clusters, nanoporous Pt, and tetrahedral Pt nanostructures and so on that have been attained by using electrochemical synthesis.^[45, 146, 147] This method permits nanostructures to grow under control, resulting in patterned and faceted crystal nanostructures, which is the main advantage of it. Some other advantages of the electrochemical approach are simplicity, reproducibility, and monodispersity of the synthesized nanoparticles.

2.4.4. Impregnation Method

As a highly efficient routine to prepare electrocatalysts with large surface area because of the easiness in synthesizing carbon supported electrocatalysts for instance, Pt/C and PtRu/C, the conventional impregnation method has been broadly used.

Founded on wet impregnation, fundamental procedure of conventional preparation techniques is usually impregnating support with the desired noble metal element contained precursor salts and then reducing the salts within gaseous reducing atmosphere or by some reductants.^[86, 148, 149]

Carbon black with high surface area is commonly employed to function as the catalyst support, and metal precursors are blended in water solution in the support in order to obtain homogenous mixtures. Various reducing agents can be used to reduce the metal precursors. Concentration of reductant could impact the distribution and surface composition of the prepared nanoparticles. Different metal loading ratios of the catalyst could get realized by the way of changing precursor concentrations till great scattering is achieved.

Increasing metal loading issued in metal nanoparticles aggregation, thus decrease the methanol oxidation activities. So far, using the conventional impregnation method to obtain Pt catalysts with high loadings which would be higher than 60 wt%, together with small particles, sizes of which vary ranging from about 1nm to 2 nm is still challenging. Particle size is significantly enlarged if the loading content of metal is enriched from 10 wt% to 60 wt%.

Both structural and electrocatalytic properties of Pt/C and PtRu/C have get changed when different types of precursors are employed. Besides, selecting precursor species has an extremely important structural impact on the aggregation phenomenon of Pt contained nanoparticles. Nanoparticles with both various metal loadings along with homogeneous dispersion on carbon supports are obtained by

employing various precursors. Generally speaking, nanocatalysts synthesized by conventional impregnation method are featured with large average size, as well as wide-ranging size distribution which influence the catalytic performance quite a lot.

Another main problem associated is that catalyst could hardly gain high catalytic activity even after enhanced with higher loading amount, for the reason that it is hard for the reactant to get contact with the nanoparticles trapped inside the micropores, which show sensibly low electrochemical activity. An optimized impregnation technique containing an added precipitation procedure by varying pH of the solution before reduction step, so as to prevent nanoparticles from aggregating, can be used to avoid some of these problems above. Nevertheless, it is still hard to achieve the control of monodispersity and size by means of impregnation method.

2.4.5. Colloidal Method

Colloidal method is another extensively explored preparation route for Pt contained nanocatalyst. One typical example is the PtRu/C nanoparticle catalyst with accurate size control. The following common steps are: (1) Preparing colloids containing PtRu; (2) depositing the prepared colloids onto carbon support; (3) reducing the mixture.^[14, 20, 23, 150]

Stabilization of colloids which requires the use of a protective agent or stabilizer to avoid the colloids from aggregating is a crucial part. There are a variety of instances of stabilizers, including long-chain alcohols, polymers, solvents, block copolymers, organometallics, and surfactants and so on. The natural instincts of

protective agents, like hydrophilic or hydrophobic, are featured with the properties of hydrophilicity or hydrophobicity, which could significantly stabilize the metal colloid. The size of resulting metal colloids is usually decided by the relative velocities of nucleation and growth of the particles. With the influences of electrostatic stabilization among particles as well as steric effect of organic molecules absorbed on the surface of metallic nanoparticles, a narrow size distribution can generally be achieved. Even though PtRu catalysts with high dispersion rate are attained, colloidal method is too complex, comparatively expensive with inefficiency, and it suffers loss of precious metals during the repeated filtration and washing procedure. Besides, after reduction reaction finished, the difficulty in the stabilizer removal step, greatly affecting the electrochemical activity of the prepared nanocatalyst, is considered to be the key disadvantage of the method.

For this reason, a requirement is put forward, as a modified method to generate colloidal nanoparticles, which could avoid the employment of protecting agents, is desired. This aim could be realized by appropriately adjust the combination among the precursors, reductants, and solvents. The so called glycol colloidal process, during which colloidal Pt nanoparticles were generated with ethylene glycol, which functions as both the solvent for reaction as well as the protecting agent, is thought to be a very promising way to synthesize large scale of metal nanoparticles.

2.4.6. Microemulsion Method

One of the most suitable definitions of microemulsion is by Danielsson and

Lindman “a microemulsion is a system of water, oil and an amphiphile which is a single optically isotropic and thermodynamically stable liquid solution”. Since firstly employed into synthesize monodispersed nanoparticles, various microemulsion systems have been used to prepare desired nanoparticles.^[27, 29, 80, 151-153] The overturn microemulsion system, in which oil phase functions as the continuous medium, while water as dispersed liquid phase, is called as water-in-oil system. Each tiny drop of water which contains precursor within a restricted space surrounded by surfactant performs as a nanoscale reactor, in which the reduction of precursor occurs. The dispersal of reductant, like sodium borohydride, hydrazine and soon, in the water core brings about the nucleation, and the growth is carried out by the swap amongst different cores, and simultaneously the surrounding surfactant materials restrict the further growth of the nanoparticles. The function of the surrounding surfactant which may be anionic, cationic or nonionic, is to prevent agglomeration of the synthesized nanoparticles. The range of size variation in the system can be controlled by varying the molar ratio between water and surfactant.

Microemulsion method has many advantages over the conventional impregnation and colloidal methods, for example, it could control size range better within restricted size distribution as well as the composition. Moreover, it is promising to control the size of particles by varying the molar proportion between water and surfactant with the usage of water-in-oil microemulsion system method. Besides, microemulsion method could be utilized to synthesize carbon supported bimetallic electrocatalyst. The bimetallic nanoparticles with a high alloying degree can be obtained at room

temperature whereas conventional preparation methods are generally carried out under high temperatures.

PtRu/C, which is a bimetallic catalyst, can be prepared with both one-step microemulsion method and two-step microemulsion method, in which individual microemulsion containing Pt and Ru were mixed later. Distribution of the particle size depends on neither the overall quantity of precursor nor the generation means.^[27] For the two-step microemulsion method, the degree of alloying was higher than that of the one-step microemulsion method. Besides, pH of the environment is another important factor for that it affects the electrostatic environment of surfactant intensely. In spite of control over size distribution, microemulsion method can hardly be used to vary the shape of nanoparticles. It is appropriate to synthesis nanocatalysts in large scale owing to the use of costly surfactant molecules with superfluous washing steps.

2.5. Summary

A detailed literature review reveals that advanced Pt based nanostructures can be very promising as the electrocatalyst for fuel cells. Controlling the structure and composition of the Pt based electrocatalysts has been demonstrated as an effective and practically feasible approach to realize the excellent electrochemical properties of such fascinating materials. Specially, the utilization of novel nanostructures, complex alloy or hollow structures, and support materials shows many attractive structural merits as smart materials for fuel cell applications. Although some encouraging advances have already achieved, the research related to Pt based nanostructured

electrocatalysts is still at the early stage and there remains large room for improvement. More advanced design is required to meet the ever-growing demand of future fuel cells. Optimization of various methodologies such as different novel synthetic methods, supporting approaches, alloying strategies, are greatly essential for reduction of cost and improvement of the fuel cell performance in the case of the commercialization of fuel cells.

Chapter 3. Experimental Section

3.1. Materials Characterizations

3.1.1. Morphology and Microstructure Analysis

The morphologies and microstructures of the samples were taken on field-emission scanning electron microscope (FESEM; JEOL, JSM-7600F/JSM-6700F, 5 kV), transmission electron microscope (TEM; JEOL, JEM-2010/JEM-2100F, 200 kV), and high resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, 200 kV). The nitrogen adsorption-desorption isotherm was measured using Autosorb 6B at liquid-nitrogen temperature.

3.1.2. Crystallography and Composition Analysis

Selected-area electron diffraction (SAED) was performed to study the crystallinity and structure of the samples. The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded from KBr disks using a Perkinelmer GX in the wavenumber range of 4000-400 cm^{-1} . The crystal structures of the samples were examined by X-ray powder diffraction (XRD) with a Bruker D2 phaser at a voltage of 30 kV and a current of 10 mA. Elemental composition was analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM. X-ray photoelectron spectroscopy (XPS) spectra were taken on a VG ESCALAB MKII spectrometer that uses an Mg $\text{K}\alpha$ X-ray

source. The survey scans were collected by using a pass energy of 160 eV. Thermogravimetric analysis (TGA) was performed with Pyris Diamond TGA at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air.

3.2. Electrochemical Measurements

3.2.1. Reaction Apparatus

Our electrochemical reaction system is a three-electrode cell conducting at room temperature and connected to an on-line Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands). The sketch is shown in Figure 3.1.

Figure 3.1. Scheme of the three-electrode configuration cell for the electrochemical measurements.

3.2.2. Test Conditions

The electrochemical activities measurements were evaluated on an Autolab potentiostat/galvanostat (Model PGSTAT-302, Eco Chemie, Netherlands) with rotation control (Model 636) using a three-electrode system consisting of a glassy carbon (GC) rotating disk electrode (RDE), a Pt plate counter electrode, and a saturated calomel electrode (SCE).

The working electrode was prepared with a procedure similar to that in previous reports. Typically, the catalyst ink was prepared by mixing 5 mg of catalyst, 2.4 mL of ethanol and 0.1 mL of Nafion solution (5 wt%) followed by 30 min of ultrasonication. A GC disk electrode (5 mm in diameter) served as the substrate to support the catalyst. The GC electrode was polished with aqueous alumina suspension on felt polishing pads before use. The working electrode was dried under N₂ flow at room temperature.

The ORR measurements were performed in an oxygen-saturated H₂SO₄ solution (0.5 M) at room temperature at the sweep rate of 10 mV s⁻¹. For convenience, all potentials in ORR tests are referenced to the reversible hydrogen electrode (RHE). Current densities were normalized in reference to the geometric area of the GC RDE. Before the ORR test, the working electrode was first cycled for 20 cycles at 50 mV s⁻¹ in a N₂ saturated H₂SO₄ (0.5 M) solution to generate clean electrode surface. The stability tests were recorded at a scan rate of 50 mV s⁻¹ in a 0.5 M H₂SO₄ solution. Before the cycling tests, the electrolyte was purged by N₂. The electrochemical active surface area (ECSA) of Pt catalysts can be estimated by integrating the charge passed during the hydrogen adsorption/desorption from the electrode surface after the double

layer correction.

Before the FAOR test, the working electrode was first cycled for 20 cycles at 50 mV s^{-1} in a N_2 saturated HClO_4 (0.5 M) solution to generate clean electrode surface. The FAOR measurements were performed in a nitrogen-saturated 0.5 M HClO_4 containing 0.5 M HCOOH solutions at room temperature at the sweep rate of 50 mV s^{-1} .

Chapter 4. Facile Synthesis of 3D Platinum Dendrites with a Clean Surface as Highly Stable Electrocatalysts[†]

4.1. Introduction

As introduced in Chapter 2, platinum is one of the most important components for many environmental and energy applications, especially as electrocatalysts for low-temperature fuel cells.^[3, 8, 154-156] However, the longterm stability of Pt catalysts with high activity at the cathode for fuel cells is still a key challenge that must be addressed before their practical application.^[157] State-of-the-art electrocatalysts primarily consist of Pt nanoparticles supported on carbon black (Pt/CB). Corrosion of the carbon support and Pt dissolution/aggregation result in the loss of Pt electrochemical surface area (ECSA) over time, which is considered to be one of the major contributors to the degradation of fuel cells performance.^[144, 158] Recent studies have shown that the design and synthesis of unsupported Pt nanostructures is the promising way to resolve the problems of carbon corrosion and the dissolution/aggregation of Pt nanocrystals.^[159, 160]

Supported Pt catalyst requires a high surface-area support (e.g. carbon black), while the unsupported do not. The unsupported Pt catalysts contain ultrasmall isotropic 0D Pt nanoparticles (e.g. platinum black) and self-supported (1D-3D) Pt

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[†] Reproduced and modified from [T. Wu, H. M. Zhou, B. Y. Xia, P. Xiao, Y. Yan, M. S. Xie, X. Wang, *ChemCatChem*, 6, 1538-1542 (2014)] by permission from *John Wiley and Sons*. Copyright 2014.

nanostructures (e.g. nanowires, nanosheets, nanodendrites) which can provide high platinum surface area by their nanometer-sized structures without the need for a high-surface-area support (e.g. carbon black). Because of the unique morphology and structure of self-supported interconnected Pt catalyst, mass transport to Pt catalytic sites get improved and catalyst utilization could be enhanced. Compared to carbon-supported Pt nanoparticles, self-supported interconnected Pt catalyst can facilitate electron transport by eliminating the interfacial contact between Pt and carbon. The self-supported Pt catalysts also reduces the thickness of catalyst layer on the electrode, which is beneficial for shortening the electron transport path and thus improves the catalytic activity. The poor durability of the supported Pt catalyst, such as Pt/C, can be summarized as follows 1) loss of platinum nanoparticles from the electrical contact because of corrosion of the carbon support, 2) platinum dissolution and redeposition or Ostwald ripening of the platinum nanoparticles, 3) platinum-nanoparticle aggregation driven by surface-energy minimization, and 4) platinum-nanoparticle dissolution and subsequent migration of the soluble Pt^{2+} species within the polymer electrolyte and the eventual chemical reduction by hydrogen crossed-over from the anode through the proton-exchange membrane.^[144] While for self-supported Pt catalysts, they have the potential to eliminate or significantly reduce all of the four degradation pathways discussed above as a result of their unique morphology and structure: First, they do not require a support, and thus the support-corrosion problem is eliminated. Second, their structures make them less vulnerable to dissolution, Ostwald ripening, and aggregation during fuel cell

operation than the platinum nanoparticles (0D nanostructure). Thus, self-supported Pt catalysts could possess higher stability and better durability.

1D Pt nanostructures including Pt nanorods, nanotubes, and nanowires have been demonstrated as effective electrocatalysts to overcome the drawbacks of nanoparticle-based electrocatalysts in fuel cells.^[161, 162] For example, Yan and co-workers reported that unsupported Pt nanotubes exhibited an enhanced catalytic activity and durability as the catalysts for oxygen reduction reaction (ORR).^[144] Sun's and Yu's groups also synthesized Pt nanorods and Pt nanowires for the improved electrocatalytic activities and stability for cathode ORR reactions.^[163, 164] Moreover, the assembly of 1D Pt nanocrystals into 2D and even 3D architectures also further improves the electrochemical performance.^[61, 165, 166] These nanostructures have a unique combination of dimension and their 1D properties.^[167] Furthermore, the emergence of high porosity, large surface area, and interconnected open-pore structure arisen from the assembly process also play important roles in the potential environmental and energy areas, especially as the electrocatalysts in fuel cells.^[168] For example, Xia's recent work reported the synthesis of 3D interconnected Pt nanowires and their application as electrocatalysts for the ORR. Although much success has been made in preparation of 3D Pt dendrites for electrocatalysts, most of them involve the use of surfactants/organics or assistance by templates and substrates,^[169-171] which make the preparation process complicated.^[172, 173] It still remains challenging to develop a direct synthesis approach without involving surfactant or ligand for 3D Pt nanodendrites (NDs) with clean surface for fuel cells application.^[174]

We report herein the preparation of 3D Pt NDs with a clean surface free from surfactant or ligand by a facile inorganic-species-assisted strategy. We found that the possible specific adsorption of iron and nitrate ions would assist the growth of this 3D Pt nanostructure. Thanks to their unique 3D morphology composed of 1D Pt nanorods/wires, the clean unsupported 3D Pt dendrites, consisting of multiarmed and interconnected 1D Pt nanowires, exhibit higher stability and activity than commercial CB-supported Pt nanoparticles and Pt black electrocatalyst.

4.2. Experiment Section

4.2.1. Synthesis of Pt Nanodendrites

In a typical synthesis, 4.2 mg H_2PtCl_6 , 18 mg NaNO_3 , 0.054 mg FeCl_3 , were dissolved in 15 mL ethylene glycol (EG). After ultrasonication for 30 min, the resultant homogeneous and transparent solution was transferred into a 25 mL Teflon-lined autoclave. The autoclave was maintained at 160 °C for 10 h, and then cooled down to room temperature. The gray solution was mixed with ethanol and then centrifuged to get black precipitate. The precipitate was collected and washed by ethanol and DI water for several times, and dried at 80 °C overnight for the further using.

4.2.2. Electrochemical Measurements

The prepared catalyst ink was pipette onto the GC surface, leading to a Pt loading

of about 0.1 mg cm^{-2} . The ORR measurements were performed in an oxygen-saturated H_2SO_4 solution (0.5 M) at room temperature at the sweep rate of 10 mV s^{-1} . The stability tests were recorded at a scan rate of 50 mV s^{-1} within the potential range from $-0.241 - 1 \text{ V vs. SCE}$ in a 0.5 M H_2SO_4 solution for 1000 cycles. Before the cycling tests, the electrolyte was purged by N_2 . Additionally, formic acid and methanol oxidation experiments were carried out with a scan rate of 50 mV s^{-1} in a solution containing 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ and 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$, respectively. For the long term stability test, accelerated cycling tests were also conducted up to 1000 cycles.

4.3. Results and Discussion

4.3.1. Formation of Pt NDs and Material Characterizations

Figure 4.1. FESEM (a) and TEM (b-d) images of Pt dendrites. Inset of (a) shows the single Pt dendrites. TEM image (c) of an individual Pt dendrites and enlarged HRTEM image (d).

In Figure 4.1a a representative field-emission scanning electron microscopy (FESEM) image of the Pt NDs is shown. The as-prepared Pt NDs are highly uniform with an average size of approximately 200 nm. Interestingly, the subunits of the Pt

Figure 4.2. (a) XRD patterns of Pt NDs, Pt black and Pt/CB catalysts. (b) Wide scan XPS spectra of Pt NDs. No typical peaks at about 712 eV for iron and 400 eV for nitrate species are observed.

nanorods point out in various directions to form the 3D dendritic structure. The higher magnification FESEM image (inset of Figure 4.1a) clearly shows that the individual Pt ND has multiarmed nanorods. Energy-dispersive X-ray (EDX) analyses and X-ray diffraction (XRD) patterns confirmed that the as-prepared samples consisted exclusively of Pt (Figure 4.2) with a face-centered cubic (fcc) structure (JCPDS card No. 04-0802).

The morphology and structure of the NDs were further characterized by TEM. An overview TEM image of the product shows that each Pt ND has a size of about 200

nm (Figure 4.1b), consistent with the observation of the FESEM image (Figure 4.1a). The selected-area electron-diffraction (SAED) pattern (inset of Figure 4.1b) of the Pt NDs shows concentric rings, composed of bright discrete diffraction spots, which are indexed to (111), (200), (220), (311), and (222) crystal planes of fcc Pt, indicating the high degree of crystallinity of the individual Pt nanorods; this observation agrees with the XRD results (Figure 4.2a). Each 3D dendrite consists of dozens of Pt nanorods with 50–200 nm in length and 10–20 nm in diameter (Figure 4.1c). Note that these nanorods are interconnected at the center, suggesting that the formation of Pt ND might involve growth from a common point rather than the simple aggregation of preformed nanorods. The detailed structural features of the nanorods were characterized by high-resolution (HR) TEM, revealing clear lattice fringes with an interplanar distance of approximately 0.22 nm, corresponding well to the interplane spacing of Pt (111) planes (Figure 4.1d).

Figure 4.3. Representative EDX spectrum of Pt NDs. In the EDX spectrum, the additional signals correspond to Si arise from the substrate.

The HRTEM image also reveals the single crystal nature of the nanorods, with a growth direction along the $\langle 111 \rangle$ direction. The open-pore structure formed by the

interconnect Pt NDs with good crystallinity would be beneficial for the consequent electrochemical measurements. HRTEM observation also reveals fewer surface defects on the clean surface of Pt nanorods, which has a closer resemblance to the surface of large single Pt crystals and would be helpful for longterm electrochemical operation. In the formation of the 3D Pt nanostructure, only inorganic materials are involved in the process. Moreover, the introduced iron and nitrate species could be removed easily by a simple washing process. Therefore, the obtained surface was free from any surfactant/ligand, as also confirmed by EDX, FTIR and XPS analyses, which is similar to other commercial catalysts (Figure 4.2, 4.3, and 4.4).

Figure 4.4. FT-IR spectra of Pt NDs, Pt black and Pt/CB catalysts.

The presence of nitrate plays an important role in the formation of this nanostructure. In the absence of nitrate, only Pt particles with large sizes are obtained (Figure 4.5a). With the introduction of nitrate, the dendritic structure is formed (Figure 4.1). With the further introduction of more nitrate ions, few dendritic Pt nanocrystals along with many Pt nanoparticles are formed as shown in Figure 4.5b. It

is proposed that the corrosive reaction of nitrate would occur on the surface of the Pt nanocrystals and thus lead to the formation of dendrites structure, even small Pt nanoparticles.^[175] Therefore, the presence of the nitrate would alter the reaction kinetics and, thus, result in the formation of rod like dendritic Pt. As the sample

Figure 4.5. FESEM images of Pt dendrites obtained with a) 0, b) 144 mg NaNO_3 and c) 0, d) 0.9 mg FeCl_3 .

morphology evolves, Fe^{III} ion also takes part in the formation of this dendritic structure. Only irregular nanodendrites with rough surfaces are obtained without the addition of Fe^{3+} (Figure 4.5c). If an excess of FeCl_3 (0.9 mg) is used, there are fewer rods found in the products (Figure 4.5d) than with as-prepared Pt NDs (Figure 4.1). Besides, these structures are irregular with less sharp rods, and the length of most rods

ranges from 10 nm to 30 nm, which is much smaller than that of the Pt dendrites in Figure 4.1. This result suggests that the amount of Fe^{3+} affects the shape and size of Pt formed dendritic structures.^[46] It is proposed that the possible selective adsorption of appropriate Fe^{3+} on the specific facets of Pt dendritic would assist the growth of the Pt dendritic structure composed of multiarmed Pt nanorods. It has been reported that the trace amount of Fe^{3+} species can reduce the level of supersaturation of Pt atoms and, thus, lower the growth rate by slowing down the reduction reaction: $2 \text{Fe}^{3+} + \text{Pt} \rightarrow 2\text{Fe}^{2+} + \text{Pt}^{2+}$.^[125, 161, 176]

4.3.2. Electrochemical Measurements

The electrocatalytic activity of the Pt NDs was next evaluated. For comparison, commercial electrocatalysts of carbon-supported Pt nanoparticles (Johnson Matthey, 50% Pt/CB) and unsupported Pt black (Sigma Aldrich) were also tested under identical conditions. As shown in Figure 4.6a, the cyclic voltammetry (CV) profiles of the as-prepared Pt NDs, commercial Pt/CB, and Pt black are recorded at room temperature in a N_2 -purged H_2SO_4 solution (0.5 M) with a sweep rate of 20 mV s^{-1} . CV curves exhibit strong peaks associated with hydrogen adsorption/desorption (HAD) and Pt oxide formation/reduction. Well-defined hydrogen adsorption and desorption peaks on low-index Pt surface can be observed for the Pt NDs and the carbon-supported Pt nanoparticles (Figure 4.6a), confirming the resultant clean

Figure 4.6. (a) Cyclic voltammetric curves of Pt/CB, Pt black, and Pt NDs electrocatalysts recorded in 0.5 M H₂SO₄ solution with the scan rate of 20 mV s⁻¹. (b) Rotation-dependent polarization curves of Pt NDs for ORR in an O₂ saturated 0.5 M H₂SO₄ solution; (c) Koutecky-Levich plots and (d) polarization curves of Pt/CB, Pt black, and Pt NDs for ORR (1600 rpm; sweep rate: 10 mV s⁻¹). (e) The mass activities and (f) specific activities.

surface of Pt NDs. Moreover, a larger current density associated with the adsorption/desorption of oxygen containing species can be observed on the Pt NDs in the potential range of 0.4–0.8 V, which reveals a higher density of Pt atomic steps on the surface of the Pt NDs over the Pt black and commercial Pt/C catalysts. The electrochemical surface areas (ECSA) were calculated by measuring the charge associated with the HAD between -0.24 and 0.2 V, after correction for double layer

capacitance. The specific ECSA of the 3D Pt NDs is $42.3 \text{ m}^2\text{g}^{-1} \text{ Pt}$, which is approximately 87% of that of commercial Pt/CB catalysts ($48.8 \text{ m}^2\text{g}^{-1}$) and much higher than that of Pt black catalysts (about $9 \text{ m}^2\text{g}^{-1}$). The catalytic activities of different Pt catalysts were first evaluated in terms of ORR by using a glassy carbon rotating disk electrode (RDE) at various rotating rates (Figure 4.6b). The number of electrons calculated from Koutecky–Leveche plots is 3.93 for the Pt NDs (Figure 4.6c), which indicates that the ORR on the Pt NDs favors more on four-electron path. In Figure 4.6d, typical ORR polarization curves of the Pt NDs, Pt/CB, and Pt black catalysts are shown obtained at room temperature in O_2 -saturated $0.5\text{M H}_2\text{SO}_4$ at 1600 rpm with a sweep rate of 10 mVs^{-1} . The halfwave potentials for the Pt NDs and Pt/CB catalysts are 0.8 and 0.78 V, respectively, indicating that the catalytic activity of Pt NDs is higher than that of the commercial Pt/CB catalyst composed of Pt nanoparticles and carbon black. Mass (Figure 4.6e) and specific activities (Figure 4.6f) for Pt NDs are $14 \text{ Ag}^{-1} \text{ Pt}$ and 0.34 Am^{-2} at 0.8 V, which is approximately 1.9 and 2.2 times of that of the commercial Pt/CB (7.5 Ag^{-1} and 0.15 Am^{-2}), respectively.

Pt black exhibits the smaller mass activity, but the highest specific activity, which can be explained by its extremely low ECSA. This improvement agrees well with those reported 1D Pt nanostructures as electrocatalysts. The Pt NDs are also evaluated as an electrocatalyst for the oxidation of small fuel molecules such as methanol and formic acid. Excellent activity and stability was observed, as shown in Figure 4.7 and 4.8. The improved activity of the Pt NDs compared with that of Pt/CB and Pt black

Figure 4.7. CV profiles for Pt NDs, Pt black and Pt/CB toward to the electro-oxidation of formic acid (a), stability test for Pt NDs (b), Pt/CB (c) and Pt black (d) in 0.5 M formic acid + 0.5 M H₂SO₄ solution at sweeping rate of 50 mV s⁻¹ for 1000 cycles.

could be a result of the unique morphology and structure, which is composed of interconnected Pt nanorods. The 3D interconnected open-pore structure can improve mass transport to Pt catalytic sites and enhance catalyst utilization. Compared to carbon-supported Pt nanoparticles, such interconnected nanorods can facilitate electron transport by eliminating the interfacial contact between Pt and carbon. Moreover, the self-supported 3D Pt NDs also reduces the thickness of catalyst layer on the electrode, which is beneficial for shortening the electron transport path and thus improves the catalytic activity.

Figure 4.8. CV profiles for Pt NDs, Pt black and Pt/CB toward to the electro-oxidation of methanol (a), stability test for Pt NDs (b), Pt/CB (c) and Pt black (d) in 0.5 M CH₃OH + 0.5 M H₂SO₄ solution at sweeping rate of 50 mV s⁻¹ for 1000 cycles.

The accelerated durability tests of the catalysts are conducted by potential cycling between -0.24 and 1.0 V versus saturated calomel electrode (SCE) in 0.5M H₂SO₄ at room temperature with a sweeping rate of 50 mVs⁻¹. After 1000 cycles, CV profiles show that the featured HAD characteristics of the Pt NDs remains and the current density exhibits a very small drop (Figure 4.9 a). However, the commercial Pt/CB and Pt black catalysts exhibit significant current density loss (Figure 4.9b and 4.9c). Typically, the double layer for Pt/CB also displays a decrease, which is related to the corrosion of carbon supports (Figure 4.9b).^[21] The loss of ECSA with cycling numbers is plotted in Figure 4.9d. After 1000 cycles, the Pt NDs catalyst lost only 17.5% of the initial Pt ECSA, which might be a result of possible mild dissolution of Pt, whereas the commercial Pt/CB and Pt black lost 68% and 58%, respectively. The

Figure 4.9. Electrochemical durability of (a) Pt NDs, (b) 50% Pt/CB, and (c) Pt black recorded at room temperature with a sweep rate of 50 mV s⁻¹ in 0.5M H₂SO₄. (d) Normalized ECSA loss of Pt NDs, 50% Pt/CB, and Pt black catalysts with the number of CV cycles.

excellent electrochemical stability for Pt NDs is mainly ascribed to the unique structure composed of 1D Pt nanorods with good crystallinity (Figure 4.1). The larger ECSA loss for the Pt black and Pt/CB catalysts indicates that Pt nanoparticles are more prone to dissolution/aggregation owing to the presence of more surface defects (Figure 4.9b and 4.9c). Furthermore, the very low stability of the Pt/CB is mainly attributed to the more severe support corrosion of carbon black, as can be seen from the significant loss of double layer capacitance (Figure 4.9b and 4.9d). The corrosion of carbon support would result in the migration and aggregation of Pt nanoparticles owing to the small size and high surface energy of zero-dimensional (0D) structure. On the contrary, the unsupported 3D Pt NDs catalysts do not suffer from the carbon corrosion problem and, thus, enhance the stability. Similar excellent electrochemical

stability for the Pt NDs towards the oxidation of small fuel molecules is also observed compared to that of the Pt black and Pt/CB catalysts. In order to display the electrochemical measurement result more clearly, the result is summarized in table 4.1.

Table 4.1. Electrochemical performance of Pt/CB, Pt NDs and Pt black catalysts.

Material	ECSA (m^2g^{-1})	Mass Activity (A g^{-1})	Specific Activity (A m^{-2})	Durability * (%)
3D Pt NDs	42.3	14	0.34	82.5
Pt/CB	48.8	7.5	0.15	32
Pt Black	9	5	0.52	42

*Evaluated by current density loss after 1000 cycles.

Figure 4.10. TEM images of Pt dendrites after the durability measurement.

As the durability test was conducted by potential cycling for 1000 cycles, the TEM characterization on the Pt NDs was done after the durability test. As it can be seen from the TEM figures in Figure 4.10, the morphology of Pt NDs has been

generally retained after the durability measurement with some degradation. The length of the rods was shortened and the surface of the rods became rough compared with the structure of the original catalyst. These changes might be due to the partial dissolution and redeposition of Pt on the surface of the rods during the durability measurement, leading to the loss of ECSA, which is used to evaluate the durability performance of the catalyst.

As listed in the table 4.2 and 4.3, the mass and specific activities for the oxygen reduction reaction of our 3D Pt NDs are comparable or superior to many other Pt based alloy and composites as electrocatalysts, but are still inferior to the benchmark ones.

According to the table 4.3, in which listed the ORR activities (mass activity and specific activity), it could be seen that the activity measured in HClO_4 is generally higher than measured in H_2SO_4 .^[177] As is well known, the ORR activity measured in the non-adsorbing electrolyte (e.g. HClO_4 solution) is much higher than that in the adsorbing electrolyte (e.g. H_2SO_4 solution). The adsorption of SO_4^{2-} ions on the surface of the catalyst would lead to partial blockage of the active catalytic sites on the surface of the catalyst, resulting in a lower activity.^[178] Moreover, the performance of our catalyst is comparable to that of other Pt based catalysts measured in the same condition.^[165, 179]

Table 4.2. Electrochemical performance of Pt NDs and some other Pt nanostructures.

Material	Size (nm)	ECSA (m ² g ⁻¹)	Mass Activity (Ag ⁻¹)	Specific Activity (Am ⁻²)	Durability* (%)	Reference
3D Pt NDs ^{a)}	50-200	42.3	14	0.34	82.5	This thesis
Pt nanocubes/rGO ^{a)}	5	51.0	13.9	0.28	n.a.	[179]
Pt nanoassemblies ^{b)}	200	40.8	12.4	0.26	72.5	[165]
Pdtrun.octa.@30 wt% Pt ^{c)}	30.1	130.26	11.2	n.a.	88	
Pdtetrapod@30 wt% Pt ^{c)}	39.5	212.94	5.8	n.a.	90	[180]
Pdtetrapod@50 wt% Pt ^{c)}	53.0	43.44	0.6	n.a.	92.5	
Pt _{0.5} Pd _{0.5} /C ^{d)}	2.52±0.45	25.59	8.5	0.22	n.a.	[181]
C _{Orich} core-Pt _{rich} shell/C ^{e)}	1-6	66.39	15.544	0.23413	n.a.	[182]
1-PtNP/MWCNT ^{f)}	16	n.a.	5.0	0.42	n.a.	
2-PtNP/MWCNT ^{f)}	16	n.a.	4.7	0.37	n.a.	[183]
3-PtNP/MWCNT ^{f)}	16	n.a.	3.3	0.42	n.a.	
(100)Pt-Vulcan ^{g)}	200	n.a.	6.14	n.a.	n.a.	[184]

a) For ORR at 0.80 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1600rpm from 0.3 to 1.2 V (RHE) in 0.5M H₂SO₄.

b) For ORR at 0.85 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1600rpm from 0.4 to 1.1 V (RHE) in 0.5M H₂SO₄.

c) For ORR at 0.90 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1600rpm from 0.2 to 1.1 V (RHE) in 0.5M H₂SO₄.

d) For ORR at 0.85 V determined from positive-going sweeps at 5 mV/s and a rotation rate of 1600rpm from 0.3 to 1.0 V (RHE) in 0.5M H₂SO₄.

e) For ORR at 1.0155 V determined from positive-going sweeps at 5 mV/s and a rotation rate of 1600rpm from 0.2 to 1.2 V (RHE) in 20% H₂SO₄.

f) For ORR at 0.90 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1900rpm from 0.1 to 1.1 V (RHE) in 0.5M H₂SO₄.

g) For ORR at 0.90 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 3000rpm from 0.1 to 1.0 V (SHE) in 0.5M H₂SO₄.

Table 4.3. Mass and specific activities of ORR of Pt NDs and benchmark ones.^[177]

Material	Mass Activity (A mg ⁻¹ _{Pt})		Specific Activity (μA cm ⁻² _{Pt})	
	<i>0.1M HClO₄</i>	<i>0.5M H₂SO₄</i>	<i>0.1M HClO₄^{a)}</i>	<i>0.5M H₂SO₄</i>
Pt NDs ^{a)}		0.014		34
Pt nanocubes/rGO ^{a)}		0.0139		28
Pt nanoassemblies ^{b)}		0.0124		26
Pt-black (HiSpec1000, JM) ^{c)}	0.042		720	
Pt-black (HiSpec1000, JM) ^{c)}	0.030		620	
40% Pt/Vu (ETEK) ^{c)}	0.069		190	
40% Pt/Vu (ETEK) ^{c)}	0.062		200	
20% Pt/Vu (ETEK) ^{c)}	0.16		230	
20% Pt/Vu (ETEK) ^{c)}	0.13		200	
45.9% Pt/HSC-E (TKK) ^{c)}	0.16		190	
45.9% Pt/HSC-E (TKK) ^{c)}	0.16		210	
46.5% Pt/HSC-E (TKK) ^{c)}	0.17		220	
27% Pt/Ketjen (in-house) ^{c)}	0.18		150	
20% Pt/Vu (ETEK) ^{c)}	0.16		210	

a) Specific activities and mass activities, for the ORR at 0.80 V determined from positive-going sweeps at 10 mV/s from 0.3 to 1.2 V (RHE).

b) Specific activities and mass activities, for the ORR at 0.85 V determined from positive-going sweeps at 10 mV/s from 0.4 to 1.1 V (RHE).

c) Specific activities and mass activities, for the ORR at 0.90 V determined from

positive-going sweeps at 5 mV/s from 0 to 1.0 V (RHE).

4.4. Summary

In summary, we have demonstrated a facile solvothermal method to prepare clean 3D Pt NDs composed of interconnected 1D Pt nanorods. The presence of iron and nitrate ions would play an important role on the formation of this 3D Pt nanostructure. Compared with Pt black and commercial carbon-supported Pt nanoparticle catalysts, the electrocatalysts based on Pt NDs exhibit both better catalytic activity and remarkable durability, which are believed to be a promising candidate for fuel cells applications. The novel 3D Pt NDs structure may also be used in other industrial applications.

Chapter 5. Synthesis of Intermetallic PtBi Nanosheet with Enhanced Electrocatalytic Activity toward Formic Acid Oxidation

5.1. Introduction

Direct formic acid fuel cells (DFAFCs) have attracted growing attention particularly for the powering of portable devices due to a few advantages of high energy density, convenient storage and transport of liquid formic acid.^[12] Platinum (Pt) is the promising electrocatalyst for the oxidation of formic acid to CO₂ *via* a dual path mechanism, involving a reactive intermediate (dehydrogenation pathway) and adsorbed CO as a poison species (dehydration pathway).^[6] However, the scarcity and high cost of Pt severely limit the wider application.^[124] Moreover, pure Pt is inefficient to provide surface oxygenate species at low potential and thus promote the full oxidation of CO-like intermediates.^[185] Therefore, incorporation of the transition metals with Pt, tremendous efforts toward the preparation of Pt-based catalysts have been made to increase the activity as well as the poisoning tolerance while reducing the cost of catalysts.^[186-188] Of all the bimetallic Pt-based catalysts examined hitherto including PtRu, PtSn, PtPb, PtCo etc.,^[189-192] PtBi exhibits the powerful activity for formic acid oxidation.^[193] The enhanced activity would be related to the electronic and geometric effects which provide the enhanced adsorption of formic acid and the reduced affinity for CO-like poisoning species.^[194-196]

Another direction to improve the activity is controlled synthesis of Pt-based nanostructures, which could maximize the utilization of active surface through the surface atomic arrangement and coordination.^[124, 197] Inspired by this intention, a variety of chemical protocols have been developed for achieving partial control of the morphology of Pt-based nanocrystals with various shapes.^[13, 92, 198] Recently, two-dimensional nanosheets have attracted enormous research interest due to its unique architectures containing abundant unsaturated atomic edges and steps, which typically function as active sites for breaking chemical bonds and lead to much higher electrocatalytic activity than the regular facets.^[124] Nevertheless, it is particularly challenging to generate energetically unfavorable 2D Pt NSs due to the intrinsic isotropic crystal growth behavior and inner stress of Pt.^[199, 200] Besides, the previously synthesized PtBi intermetallics are mostly in nanoparticle form,^[201] which cannot get the clear information on the oxidation of formic acid. Therefore, the reasonable design and controllable synthesis of 2D PtBi nanosheet is important to investigate and improve the electrochemical activity of formic acid oxidation.^[92, 202-204]

Herein, we report an effective thermal decomposition method to prepare PtBi nanosheets with tunable composition. The addition of NH_4Cl is quite essential for the generation of well-defined nanosheet structures. Furthermore, we also investigate the composition effect of PtBi nanosheet on the catalytic activity for formic acid oxidation reaction (FAOR). Because of the unique nanosheet structures and optimized composition, the as-prepared PtBi catalyst demonstrates the excellent electrocatalytic performance of FAOR.

5.2. Experiment Section

5.2.1. *Synthesis of Intermetallic PtBi Nanosheets*

In a typical synthesis, 50 mg Pt(acac)₂, 38.8 mg BiCl₃, 273mg NH₄Cl were dissolved into 20 mL Oleylamine (OAm) in a three-neck flask. After ultrasonication for 30 min, the resultant homogeneous and transparent solution was heated to 90 °C with vigorous magnetically stirring under an argon stream and kept for 30 min, and then the solution turned from primrose yellow to lemonchiffon. The solution was then heated to 200 °C under the argon stream and kept for 5 min, and the heating rate was about 2.5 °C /min. The heat source was removed afterwards, and the reaction was cooled to room temperature. The black product was collected by centrifugation and washed with hexane and ethanol for several times, and dried at 80 °C overnight for the further using.

5.2.2. *Electrochemical Measurements*

Before the FAOR test, the working electrode was first cycled for 20 cycles at 50 mV s⁻¹ in a N₂ saturated HClO₄ (0.5 M) solution to generate clean electrode surface. The FAOR measurements were performed in an N₂-saturated 0.5 M HClO₄ containing 0.5 M HCOOH solutions at room temperature at the sweep rate of 50 mV s⁻¹.

5.3. Results and Discussion

5.3.1. Formation of PtBi Nanosheet and Material Characterizations

Figure 5.1. (a) FESEM image of tiled PtBi nanosheets; Insert of (a) shows the FESEM image of side-by-side assembled PtBi nanosheets; (c) TEM image of tiled PtBi nanosheets; Insert of (b) shows the SAED pattern; (c) TEM image of side-by-side assembled PtBi nanosheets; (d) HRTEM image of PtBi nanosheets; Insert of (d) shows the HRTEM image of flank side of PtBi nanosheets.

In a typical synthesis, PtBi nanosheets are prepared by reducing $\text{Pt}(\text{acac})_2$ and BiCl_3 in the oleyamine in the presence of NH_4Cl at 200 °C. The morphologies of products are firstly examined by field-emission scanning electron microscopy (FESEM). The FESEM image in Figure 5.1a clearly displays the relatively uniform nanoplates morphology with a size of ~50 nm. Interestingly, the PtBi nanosheets assemble in side-by-side way, which could lower the surface energy of such tiny

nanosheet. The thickness of PtBi nanosheets is estimated by 7~8 nm from the inset of Figure 5.1a. The structure is further examined by transmission electron microscopy (TEM) observation. TEM image with the low magnification of PtBi nanosheets demonstrate the various contours such as hexagon and triangle. The selected -area electron diffraction (SAED) pattern of PtBi nanosheets shows concentric rings, composed of bright discrete diffraction spots, indicative of high crystallinity (inset of Figure 5.1b). The side-by-side assembly of PtBi nanosheets is also observed by TEM technique (Figure 5.1c). The smooth surface can be found in the nanosheet assemblies, and the thickness of nanosheet is about 7 nm, which corresponding to ~ 20 layers of PtBi (102). High resolution (HR) TEM image reveals PtBi nanosheets has a lattice fringe with interplane spacing of 0.37 nm, indexing to the (102) plane of intermetallic PtBi. The basal surface information is provided in Figure 5.1d, and the interplane spacing of PtBi nanosheet is ca. 0.31 nm, corresponding to the (101) crystal plane of intermetallic PtBi. The formation mechanism of these two unique structures could be generally explained as follows: PtBi possesses a chemically ordered intermetallic hexagonal close packed (hcp) structure. Using this uniaxial crystal structural character of PtBi, two-dimensional (2-D) PtBi nanosheets could be successfully synthesized. If PtBi nanosheets are single crystals, it will grow in 6 directions with the similar speed, which couldn't change the contour. However, the as-synthesized PtBi nanosheets are hcp polycrystals, so the growth rates in the six directions will be different, resulting in the nanosheets with different contours.^[205]

Energy dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD) are

then used to investigate the chemical constitution and crystal structure of the as-synthesized products. The XRD pattern of PtBi in Figure 5.2a shows the typical diffraction peaks at 28.9° , 40.8° and 41.9° , corresponding to the (101), (102) and (110) respectively, for a chemically ordered PtBi intermetallic crystal structure. Moreover, no obvious reflection of the impurities of Pt and Bi composites is identified from the patterns. Based on the analysis of structure, it can be concluded that the intermetallic PtBi nanosheet is successfully prepared by this wet-chemistry method. EDX results

Figure 5.2. (a) XRD pattern of PtBi nanosheets; The markers indicates the peaks PtBi (JCPDS: 01-072-5643) phase; (b) XPS survey scan spectrum of the PtBi nanosheets; Representative high-resolution XPS spectra: (c) Pt 4f of PtBi nanosheets; (d) Bi 4f of PtBi nanosheets.

shows that the products are constituted of Pt and Bi elements, and the atomic ratio between Pt and Bi is approximately 52: 48, which is very close to the initial reactant ratio in the synthetic system (Figure 5.3). The structure and composition analysis indicates the formation of intermetallic crystalline. The surface composition and

electronic properties of PtBi products are also investigated by X-ray Photoelectrochemical spectroscopy (XPS). The XPS analysis indicates that the surface atomic composition of PtBi nanosheets is Pt₄₉Bi₅₁ (Figure 5.2b). The Pt 4f spectrum shows a doublet consisting of a low energy band (Pt 4f_{7/2}) and a high energy band (Pt 4f_{5/2}), which indicates the metallic status of Pt (Figure 5.2c). The spectrum is

Figure 5.3. EDX images of nanosheets obtained with the ratio of: Pt / Bi = 1:1.

further deconvoluted into two pairs of peaks, which are at 71.2, 74.5 eV for Pt(0) and 72.3, 75.6 eV for Pt (II), respectively, in the intermetallic PtBi nanosheets. The Bi 4f spectrum is also deconvoluted into two pairs of peaks (Figure 5.2d). The pair of binding energy at 157.3 eV and 162.6 eV is assigned to pure metallic Bi(0), while the peaks at 158.9 eV and 164.2 eV might be attributed to the Bi(III) oxidation state on the surface of the PtBi nanosheets.

Figure 5.4. FESEM images of nanosheets obtained with: (a) Pt / Bi = 1:3; (b) Pt / Bi = 3:1.

The molar ratio of Pt and Bi precursors regulates the morphology and size of the product.^[206] When the molar ratio between Pt and Bi is 1:3, the products demonstrates the curly sheet structures (Figure 5.4a). And when the molar ratio of Pt and Bi is increased to 3:1, the aggregated products compose of irregular plates, while the size and the thickness become larger (Figure 5.4b). The EDX results indicate that the atom

Figure 5.5. EDX images of nanosheets obtained with the ratio of: (a) Pt / Bi = 3:1; (b) Pt / Bi = 1:3.

percentages of Pt and Bi in the as-synthesized products are 26.31 % and 73.69 %, 76.09 % and 23.91 % respectively (Figure 5.5), which is consistent to the initial addition ratios of the input reagents. However, XRD patterns of products obtained

Figure 5.6. XRD patterns of PtBi_3 and Pt_3Bi . The markers indicate the peaks for the Bi (Blue, JCPDS: 26-0214), PtBi (Black, JCPDS: 01-072-5643) and Pt (Green, JCPDS: 00-001-1190) phases.

from two different atomic ratios demonstrate the similar diffraction peaks for PtBi (Figure 5.2a), demonstrating that the main product under the same conditions is the intermetallic PtBi irrespective the initial atomic ratios (Figure 5.6). While Pt and PtBi_2 are found in the products of Pt_3Bi and PtBi_3 due to the delayed reduction of Bi (III) owing to lower reduction potential than that of Pt(II) ($\phi_{\text{Pt(II)}/\text{Pt}} = 1.188 \text{ V}$; $\phi_{\text{Bi(III)}/\text{Bi}} = 0.308 \text{ V}$).^[207-209] Additionally, NH_4Cl has a significant effect on the formation of nanosheets. Without the addition of NH_4Cl , the product turns out to be curving bulky aggregates (Figure 5.7a), while the product becomes the mixture of the nanosheets and some irregular particles with excess amount of NH_4Cl (Figure 5.7b).

Figure 5.7. FESEM images of nanosheets obtained with: (a) 0 NH_4Cl ; (b) 500 mg NH_4Cl .

Previous results show the halide ions can be used as the capping agents to prepare shape controlled nanocrystals.^[205] In the current synthesis system, it is proposed that chloride ions could adsorb preferably on the (101) facets and thus promote the formation of anisotropic PtBi nanosheets (Figure 5.1).

5.3.2. Electrochemical Measurements

Figure 5.8. Cyclic voltammetric curves of Pt black and PtBi (a), PtBi₃ (b), Pt₃Bi (c) nanosheets electrocatalysts recorded in 0.5M HClO₄ solution with the scan rate of 50 mV s⁻¹.

The electrochemical properties of PtBi nanosheets are next evaluated by cyclic voltammogram (CV) technique. The typical curves of PtBi product and commercial Pt black catalyst in N₂-purged 0.5 M HClO₄ at a sweep rate of 50 mV s⁻¹ are shown in Figure 5.8a. Compared with the commercial Pt black catalyst, PtBi exhibit the less obvious characteristics for hydrogen ads-/desorption between -0.2 - 0.2 V (vs. SCE).

However, PtBi exhibits the prominently oxidation and reduction peaks at the range of 0.5-0.8 V (*vs.* SCE). It implies that PtBi has better ability to adsorb oxygenated species and consequent oxidization easily. According to the hydrogen adsorption charge, the electrochemically surface area (ECSA) of PtBi catalyst is determined to be $12.72 \text{ m}^2 \text{ g}^{-1}$, which slightly lower than that of commercial Pt black ($19.1 \text{ m}^2 \text{ g}^{-1}$). This is due to the decrease of Pt active sites with the introduction of Bi atom on the surface. The electrocatalytic activity of PtBi nanosheets and Pt black for the formic acid oxidation is next investigated by CV technique in a saturated $0.5 \text{ M HClO}_4 + 0.5 \text{ M HCOOH}$ solution. Obviously, the highest current density and lower oxidation potential of PtBi (10.9 mA cm^{-2} at 0.6 V) indicate the best activity compared with other PtBi (9.6 mA cm^{-2} Pt₃Bi and 0.4 mA cm^{-2} for PtBi₃) and commercial Pt black (5.0 mA cm^{-2} at 0.73 V) catalysts.

Previous results suggest that the oxidation of formic acid on Pt catalyst follows the dual-pathway. In the direct way, formic acid is oxidized to intermediates and then form the final CO₂ through main dehydrogenation way. While in the indirect way,^[210] formic acid is oxidized to CO like species,^[211] which could adsorb on the catalyst surface.^[212] In Figure 5.9, the peak I at 0.33 V and peak II at 0.73 V for Pt black correspond to the oxidation of formic acid *via* the dehydrogenation pathway and dehydration pathway, respectively, While the peak I and peak II for PtBi catalysts are located at 0.6 V and 0.73 V . The ratio between peak I and peak II is used to determine the pathway of FAOR on electrocatalysts. For the Pt black (Figure 5.9), peak I current is four time slower than peak II current and the ratio of peak I and peak

Figure 5.9. Cyclic voltammetric curves of Pt black and PtBi (a), PtBi₃ (b), Pt₃Bi (c) nanosheets electrocatalysts recorded in 0.5M formic acid + 0.5M HClO₄ solution with the scan rate of 50 mV s⁻¹.

II is 0.25 which indicate dehydration pathway is predominant for Pt black catalyst.

For PtBi nanosheets, the peak I current is close to peak II current. The peak ratio at 0.6 V and 0.73 V is 1.17, indicating that alloying Pt with Bi to get PtBi intermetallic could facilitate the dehydrogenation pathway of the FAOR relative to pure Pt.

The mass activity (the current density are normalized with respect to Pt mass) of PtBi is about 220 A g⁻¹ (Figure 5.10a), which is much higher than that of Pt₃Bi and

Figure 5.10. (a) The mass activities and (b) specific activities of PtBi₃, PtBi, Pt₃Bi and Pt black.

PtBi₃ catalysts (Figure 5.10a), and is about 4.4 times of Pt black (50 A g⁻¹). The specific activity, which is normalized by electrochemical surface area, demonstrate much more active properties for PtBi nanosheet (17.3 A m⁻²) catalyst than Pt black (2.5 A m⁻²) and other PtBi catalysts (Figure 5.10a). The enhanced activity of PtBi nanosheet is mainly attributed to the two-dimensional surface with intermetallic structure. Previous results suggest the surface and the arrangement of Pt atoms may efficiently affect the reaction pathway of the FAOR.^[213, 214] As stated by the ensemble effect, three neighboring Pt atoms are essential for the dehydration pathway, however, only one isolated Pt atom is sufficient for the dehydrogenation pathway of FAOR. In the current case, the ensemble effect raise by the separated Pt with Bi and thus can successfully catalyze the FAOR. Moreover, the abundant low-coordinated atoms (i.e.,

Figure 5.11. Current–time curves measured by chronoamperometry at 0.6 V for PtBi₃, PtBi, Pt₃Bi and Pt black.

isolated atoms) in the (101) facets of PtBi nanosheets would provide more efficiently active sites to make the dehydrogenation pathway dominant on the PtBi intermetallic.^[215] In addition, the chronoamperometry results also demonstrate the superior electrochemical stability of PtBi nanosheets catalyst for its good crystallinity and robust intermetallic structures (Figure 5.11).

5.4. Summary

In summary, PtBi intermetallic nanosheets are successfully prepared through a facile thermal decomposition method. The molar ratio of Pt and Bi precursors determines the morphology and size of the product, while the introduction of halides also plays an important role on the formation of nanosheet structure. The as-prepared PtBi nanosheet show enhanced electrocatalytic activity towards formic acid oxidation due to the unique nanosheet structure and intermetallic structures. The current study

may provide some useful insights to design and synthesis of the further catalysts for the electrochemical reactions.

Chapter 6. Carbon Nanotube Frameworks as the Robust Support for Electrocatalyst with Enhanced Electrochemical Activity and Stability

6.1. Introduction

Low-temperature fuel cells (LTFCs) have aroused lots of interest in virtue of high power density, low carbon footprint, ambient operation and promising aspects in electric vehicle and portable power supply.^[165, 216] The oxygen reduction reaction (ORR) has been measured as one of the critically significant reactions for LTFCs.^[217] Of note, the activity of catalyst in cathodic ORR plays an important role in the performance of LTFCs.^[218, 219]

Amongst available candidates, Pt is considered to be the most operative catalyst to boost the ORR process in both acid and alkaline circumstances.^[220-222] However, its high cost is the major bottleneck for the practical application. To produce cost-effective catalysts, carbon-base materials are usually employed as the support for the precious Pt with significant progress in this field.^[34, 35, 82] As a typical example, carbon black is utilized in the commercial Pt/CB catalyst as the support matrix to load Pt nanocrystals.^[78, 102] Of note, the heterogeneous structure can effectively reduce the surface energy to prevent the Pt nanoparticles from agglomeration during the electrochemical process. However, carbon black has the poor graphitic degree thus possess the poor anti-corrosion and oxidation in the harsh environments.^[223] The

corrosion and oxidation of carbon black would result in the catalytic Pt nanoparticle de-attach from the support and aggregate, and thus lose the activity and stability of Pt catalyst system. To overcome the disadvantages of amorphous carbon support, the development of highly graphitic carbon with high surface area have been extensively explored as the support for Pt electrocatalysts.^[35, 114, 224] Among various new nanocarbons including mesoporous carbons, graphene, carbon nanotube exhibits the promising potential as the support for its unique structure, corrosion resistance together with high conductivity.^[111, 158, 225, 226] Compared with carbon black support, one-dimensional (1D) carbon nanotubes are more attractive as the supporting substance due to their splendid physicochemical features such as high tensile strength along with large surface area, high electrical and thermal conductivity. However, the previous synthesis of carbon nanotube often involves chemical vapor deposition (CVD) method at high temperature.^[108] The complicated process and the complex instruments limit the further application. Therefore, it is highly desirable to prepare the carbon nanotubes (CNT)-Pt hybrid structure as catalyst for ORR. Within this area, a lot of works have been done with inspiring results.

Recently, metal-organic frameworks (MOFs) have emerged as a new platform to produce new nanocarbon composites.^[35, 227, 228] As a subclass of MOFs, zeolitic imidazolate frameworks (ZIFs) are excellent precursors for nanocarbon electrocatalysts due to the abundant carbon, nitrogen species. Moreover, the uniformly distributed metals ligated by N-containing ligands would offer opportunities to form nitrogen bonds and sufficient N dopants in the periodical structures during the in-situ

N doping and carbonization process.^[229, 230] Unfortunately, the main products of MOFs-derived composites are mostly microporous structured and of poor graphitic degree, which are regarded unfavorable to mass transport and electron transfer.^[231] With a much higher graphitization degree, CNTs exhibit higher electrochemical corrosion resistance than carbon black. Besides, the doping of CNTs with other elements (e.g., nitrogen) could be a particularly interesting way to modify their electronic performance and mechanical properties. Dissolution and aggregation also occur to Pt nanoparticles on N doped CNT, but to a lesser extent compared with Pt on carbon black support. In addition, due to the strong electron donor behavior of nitrogen and the enhanced π -bonding, N doped CNT as the catalyst support is expected to considerably improve the durability of the catalyst.^[25, 232, 233] Moreover, it is rarely reported to use solely MOFs as precursor to prepare CNT structures so far. Therefore, the synthesis of CNT structures with well-defined morphologies using only MOF precursor remains a largely unexplored challenge.

Herein, we report a facile method to prepare nitrogen-doped CNT@Co-Pt composite using zeolitic imidazolate framework-67 (ZIF-67) derived hierarchical nitrogen-doped CNT@Co frameworks as the carbon matrix. Besides, we can further tailor the Pt loading on the final catalyst to make sure that the Pt particles are uniform dispersed on the carbon support. Of note, the robust 3D nitrogen-doped CNT@Co framework enables the catalyst with excellent structural merits including high accessibility, strong structural stability and sufficient loading site for the Pt nanoparticles. Meanwhile, the small amounts of carbon-nitrogen species would

generate some extrinsic defects and active sites. In addition, the inner wrapped cobalt nanocrystals might provide extra conductivity. When applied as an advanced catalyst of ORR, the hybrid displays superior performance compare with commercial Pt/CB catalyst.

6.2 Experiment Section

6.2.1. Synthesis of ZIF-67

In a typical synthesis, $C_4H_6N_2$ (1.97 g) is dissolved in the mixed solution of 20 mL methanol and 20 mL ethanol. $Co(NO_3)_2 \cdot 6H_2O$ (1.746 g) is dissolved in another mixed solution of 20 mL methanol and 20 mL ethanol. The above both solutions are then mixed under continuous stirring for 10 s, and the final solution is incubated for 20 h at room temperature. The purple precipitates are collected by centrifugation and rinsed by ethanol several times and dried at 80 °C.

6.2.2. Synthesis of CNT@Co

The ZIF-67 particles are dispersed in a ceramic boat and heated to 350 °C and maintained for 1.5 h in a tube furnace. The temperature in furnace is further raised to 750 °C with a ramp rate of 2 °C min⁻¹ and kept for 2 h, respectively. After then the furnace is cooled down to room temperature naturally. During the pyrolysis process, the furnace is under Ar/H₂ flow (95%/5% in volume ratio). The as-prepared black powder products are treated in 0.5 M H₂SO₄ solution for 6 h. The resulting samples

are collected by centrifugation, repeatedly rinsed with DI water and dried at 80 °C overnight for the further use.

6.2.3. Synthesis of CNT@Co-Pt

In a typical synthesis, 40mg CNT@Co and 10mg H₂PtCl₆·6H₂O were dissolved in the mixture of 40 mL ethylene glycol (EG) and 40mL DI water in a three-neck flask equipped with a reflux condenser and a magnetic stirring bar. After ultrasonication for 30 min, the resultant homogeneous and transparent solution was heated at 130 °C for 4 h. The gray solution was collected by centrifugation, washed with ethanol several times to remove ethylene glycol and dried at 80 °C overnight for the further use.

6.2.4. Electrochemical Measurements

The Pt loading was controlled to be 20 µg cm⁻² for all of the catalysts. The stability tests were recorded at a scan rate of 50 mV s⁻¹.

6.3 Results and Discussion

6.3.1. Formation of ZIF-67, CNT@Co and CNT@Co-Pt with Controlled Morphologies

As seen from the representative field-emission scanning electron microscopy (FESEM) images (Figure 6.1a, b), the as synthesized ZIF-67 particles are highly dispersed with a typical polyhedral shape. These polyhedrons have a narrow size

distribution in the range of 1200 to 1600 nm. An enlarged transmission electron microscopy (TEM) image (Figure 6.2a) of an individual ZIF-67 polyhedron indicates its well-defined configuration with a glazing surface without any secondary subunits.

Figure 6.1. (a, b) FESEM image of ZIF-67; (c, d) FESEM image of CNT-Co; (e, f) FESEM image of MOF derived CNT.

After heat treatment at 750 °C in an Ar/H₂ flow, the large-scaled FESEM image of as-obtained nitrogen-doped (carbon nanotubes) CNT@Co particles (Figure 6.1c)

shows that the overall morphology is well retained with a significant shrinkage in size, demonstrating the potential loss of vast organic substances. Meanwhile, the carbonization process changes the outermost surface of these micro-sized polyhedrons into a rather rough state with clustered nanoparticles (Figure 6.1d and Figure 6.2b). After part of metallic cobalt nanocrystals have been removed *via* acid etching process, some distinguishable CNTs emerge from the surface of the CNT@Co (Figure 6.1e, f).

Figure 6.2. (a) TEM image of ZIF-67; (b) TEM image of Co-CNT; (c, d) TEM images of MOF derived CNT.

Further TEM studies (Figure 6.2c, d) confirm the presence of CNTs with a small diameter. It is difficult to tell the actual length of individual CNT due to their tangled states with each other. X-ray diffraction (XRD) patterns in Figure 6.3 show that the cobalt has been partly removed from the CNT@Co after the treatment of H_2SO_4 , while there still exists some cobalt particles since they are packed inside and acid can't

penetrate through outer carbon to dissolve them. N₂ sorption isotherms of ZIF-67-derived CNT exhibit a type-IV curve with a pronounced hysteresis loop as shown in Figure 6.4, suggesting the formation of mesoporous structure. Moreover, ZIF-67-derived CNT has a relatively broad meso/macropore distribution with an average pore size of ~3.9 nm, which is derived from desorption branch of the N₂ sorption isotherm by the Barrett-Joyer-Halenda (BJH) method. The specific surface area estimated by the Brunauer-Emmett-Teller (BET) method and the total volume of the ZIF-67-derived CNT are 291 m² g⁻¹ and 0.26 cm³ g⁻¹ respectively, indicating that it would be a suitable candidate as the support material.

Figure 6.3. XRD patterns of CNT@Co, acid treated CNT@Co, CNT@Co-Pt (20%) and CNT@Co-Pt (50%).

Figure 6.4. (a) N₂ sorption isotherm; (b) the pore size distribution and average pore size.

Figure 6.5. (a, b) FESEM images; (c) TEM image; (d) partial enlarged TEM image of Pt of CNT@Co-Pt (20%).

The Pt particles are loaded onto the CNT@Co through EG-based reduction reaction. The platinum loading can be easily controlled by adjusting the relative weight ratio of the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and the MOF derived CNT support material. Figure 6.5 shows the morphology details of nitrogen-doped CNT@Co-Pt catalysts with the Pt loading weight percentage of 20%. Due to small size of Pt, the entire configuration is well-kept with slight agglomeration between each other at this concentration of CNT (Figure 6.5a, b). No obvious morphology variation can be observed from TEM image in Figure 6.5c. The successful loading of Pt on CNT can be further confirmed through TEM observation in Figure 6.5d, where Pt nanoparticles are uniformly loaded

on the exterior of MOF derived CNT. EDX result of nitrogen-doped CNT@Co-Pt

Figure 6.6. (a) EDX result, (b) TGA analysis and (c) XRD pattern of CNT@Co-Pt (20%).

(20%) in Figure 6.6a reveals that the weight percentage of Pt is about 20.45%, approaching the ideal value. Meanwhile, the spectrum confirms the existence of a large amount of residual cobalt element within the final product. However, the content of nitrogen is too low to detect through EDX. The amount of metallic nanoparticles loaded was further determined by TGA in air, which shown in Figure 6.6b. Due to the

remaining content of cobalt nanoparticles within the MOF derived CNT support, the residual weight of the sample is higher than 20%, which could be further proved by the XRD (Figure 6.6c) results. Besides, XRD pattern again demonstrates the successful loading of Pt nanoparticles on the surface of CNT@Co. Three well-defined characteristic peak corresponding to the (1 1 1), (2 0 0), and (2 2 0) crystal planes of fcc Pt can be observed, corresponding to the typical Pt phase. The peaks corresponding to cobalt show up further indicates the remains of undissolved cobalt particles. The X-ray photoelectron spectroscopy (XPS) is also carried out to see the surface chemical state of CNT@Co-Pt. As seen in Figure 6.6a, the existence of nitrogen element within the CNT@Co-Pt can be confirmed from the survey scan spectrum of XPS. Meanwhile, the small amounts of carbon-nitrogen species are believed to generate some extrinsic defects and active sites. The Pt 4f XPS spectrum of Pt/N-GT is presented in Figure 6.7b, which can be divided into two doublet pairs. The pair centered at the lower binding energies of 70.8 eV and 74.2 eV can be attributed to photoelectrons emitted from Pt element in the metallic state.^[35] Whereas, the other pair at higher binding energies (71.5 eV and 74.8 eV) could be assigned to the oxidized states in PtO or Pt(OH)₂.^[234] These data again demonstrate that Pt

Figure 6.7. (a) XPS survey spectra; (b) Pt 4f XPS spectra; (c) C 1s XPS spectra for CNT@Co-Pt (20%) and commercial Pt/CB; (d) N 1s XPS spectra of CNT@Co-Pt (20%).

element has been effectively loaded onto the CNT@Co-Pt. Besides, the two main peaks for CNT@Co-Pt are found to be slightly moved to higher binding energies

compared with commercial Pt/CB, which can be ascribed to the potential interaction between Pt and N. In addition, the C 1s XPS spectrum for CNT@Co-Pt displays a more symmetric and narrow peak in contrast to Pt/CB, demonstrating the enhanced graphitized carbon content (Figure 6.7c).^[235] The high-resolution N 1s spectrum reveals the presence of two types of nitrogen species, pyridine N at ~ 398.5 eV and pyrrolic N at ~ 400.8 eV (Figure 6.7d).

Figure 6.8. (a) SEM and (b) TEM images of CNT@Co-Pt (50%).

For the CNT@Co-Pt (50%), the excessive Pt nanoparticles aggregated at the surface to form large larger clusters, resulting in the adhesion of CNT@Co particles (Figure 6.8). It should be mentioned that the aggregation can be detrimental to usage of Pt nanocrystals in the electrochemical reactions due to the large reduced active sites.

6.3.3. Electrochemical Measurements

The electrocatalytic activities of the nitrogen-doped CNT@Co-Pt (20%) catalyst for the ORR are further investigated on a glassy carbon rotating disk electrode (RDE) in 0.5 M H₂SO₄ solution. As references, commercial carbon-supported Pt

nanoparticles (Johnson Matthey, Pt/CB, carbon content: 20%) and CNT@Co-Pt (50%) are also tested under identical conditions. The CV curves of CNT@Co-Pt (20%)

Figure 6.9. (a) CV curves at a sweep speed of 50 mV s⁻¹ in a N₂-saturated 0.5 M H₂SO₄; (b) ORR steady-state RDE polarization plots in an O₂-saturated 0.5 M H₂SO₄ solution with a rotating speed of 1600 rpm and a scanning speed of 10 mV s⁻¹; (c) Koutecky–Levich plots for CNT@Co-Pt (20%); (d) Normalized ECSA loss of CNT@Co-Pt (20%) and commercial Pt/CB.

display pronounced peaks corresponding to hydrogen adsorption/desorption process formation/decomposition reaction of Pt oxide (Figure 6.9a). Similar features can be observed for the CNT@Co-Pt (50%) and Pt/CB samples with largely inferior current densities. Moreover, a broad peak related to the adsorption/desorption for oxygen containing substance could be observed on the CNT@Co-Pt (20%) in the potential window from 0.4 to 0.8 V. Whereas, the commercial Pt/CB catalyst and CNT@Co-Pt (50%) represent rather compromised performance, indicating lower efficiency of Pt species compared with CNT@Co-Pt (20%). The ORR polarization curves for CNT@Co-Pt (20%), commercial Pt/CB and CNT@Co-Pt (50%) samples are

measured and compared in Figure 6.9b. As displayed by the distinction of half-wave voltage ($\Delta E_{1/2}$) in RDE tests, the activity gap between the CNT@Co-Pt (20%) and the Pt/CB is about 33 mV (0.781 vs. 0.748 V). Also, the performance of CNT@Co-Pt (20%) catalyst could be ascribed to two following aspects. Firstly, MOF derived CNT is electroactive in nature for the ORR owing to the formation of highly-graphitized carbon during annealing process. The graphitized content is thought to be highly tolerant to carbon corrosion, which is different from conventional carbon black. Secondly, the synergistic effect between CNT substrate and Pt ensure the improvement within the electronic structure of Pt, thus leading to enhancement of ORR property. Mass-based activity (Figure 6.10a) for CNT@Co-Pt (20%) is 78.37 A g_{Pt}⁻¹ at 0.781 V, corresponding to 1.9 times of those of the Pt/CB (35.96 A g_{Pt}⁻¹).

Figure 6.10. (a) The mass activity of CNT@Co-Pt (20%) and commercial Pt/CB; (b) Rotation-dependent polarization curves of CNT@Co-Pt (20%) for ORR in an O₂-saturated 0.5 M H₂SO₄ solutions.

The rotation-dependent polarization profiles of CNT@Co-Pt (20%) are then evaluated and plotted in Figure 6.10b. The number of electrons calculated from Koutecky–Levich curves is 3.97 (Figure 6.9c), indicating that the ORR in this catalyst is more likely a four-electron path. The direct four-electron pathway is as follows:^[236]

The detailed dissociative mechanism is as follows:

The electrochemical stability is another important parameter to evaluate catalysts. In our work, accelerated durability tests (ADT) for different samples are performed by cycling between -0.2 to 1.0 V.

Figure 6.11. (a, b) Electrochemical stabilities of CNT@Co-Pt (20%) and commercial Pt/CB recorded with at a sweep speed of 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ solution; (c, d) ORR steady-state RDE polarization plots recorded with a rotating speed of 1600 rpm for CNT@Co-Pt (20%) and commercial Pt/CB after 3000 cycles at room temperature with at a scanning speed of 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ solution.

Figure 6.11a and b show the CV plots of the CNT@Co-Pt (20%) and commercial Pt/CB obtained at different cycles, respectively. For the CNT@Co-Pt, there is a slight decrease in the current density for in hydrogen adsorption/desorption. On the contrary, the Pt/CB catalyst undergoes huge current loss about 35% after 3000 cycles, demonstrating the severe carbon corrosion. In contrast, the CNT@Co-Pt (20%) exhibits a relatively slight drop in the current density of the peaks in hydrogen region. After long-term cycling, no obvious half-wave potential loss can be identified for the CNT@Co-Pt (20%) with slightly reduced diffusion-limited current (Figure 6.11c). However, the Pt/CB experience a striking loss in potential ($\sim 60 \text{ mV}$) with a huge decay in the diffusion-limited current (Figure 6.11d). Moreover, the ECSA loss for CNT@Co-Pt (20%) and Pt/CB during cycling process is plotted in Figure 6.9d. The

results show that the CNT@Co-Pt (20%) loses about 30% of the original value. Meanwhile, about 65% of initial ECSA is lost for Pt/CB. The highly-graphitized content in CNT with enhanced tolerance might be the important factor for the splendid electrochemical stability of CNT@Co-Pt catalyst. At the same time, carbon black support for the Pt/CB can suffer great corrosion during long-term cycles, resulting in much inferior stability. For CNT@Co-Pt (50%), the Pt nanoparticles could not disperse uniformly and begins to aggregate on the surface of the CNT because of the overloading quantity. And some Pt nanoparticles get aggregated by themselves because of the limited available surface of the CNT. These lead to a result that the CNT@Co-Pt (50%) cannot get a high ESCA and result in lower activity compared to the rest.

MOF derived CNT@Co supported CNT@Co-Pt (20%) gives higher activity compared to commercial one because of its high ESCA ($58.54 \text{ m}^2\text{g}^{-1}$) compared to that of commercial Pt/C ($28.78 \text{ m}^2\text{g}^{-1}$) since it has a high level of dispersion of Pt nanoparticles on CNTs. In addition, CNT is intrinsically active for the ORR compared with tradition pristine carbon black supports (as shown in Figure 6.12); and in the ORR test of CNT@Co-Pt (20%), with the selected CNT loading amount, CNT act as the support more than as catalyst, a synergistic effect stem from the interaction between CNT supports and Pt can be capable of changing the electronic structure of Pt and in that way successfully increases the ORR activity.

Figure 6.12. ORR steady-state RDE polarization plots in an O_2 -saturated 0.5 M H_2SO_4 solution with a rotating speed of 1600 rpm and a scanning speed of 10 mV s^{-1} , (a) The bare MOF derived CNT@Co loading was in the same with CNT@Co-Pt (20%), Pt loading was $20 \mu\text{g cm}^{-2}$ for all Pt containing catalysts; (b) Improved the bare MOF derived CNT@Co loading.

TEM characterization of the CNT@Co-Pt after the durability test was done and shown in Figure 6.13. As it can be seen from the TEM figures, the morphology of CNT@Co-Pt has been generally retained after the durability, which is ascribed to the robust framework structure composed of the interconnected CNT subunits. The Pt particles on the surface of CNT get aggregated a little bit, which might be owing to platinum-nanoparticle aggregation driven by surface-energy minimization, and platinum-nanoparticle dissolution and subsequent migration of the soluble Pt^{2+} species within the polymer electrolyte. Because of such a robust framework structure of the support material, the as synthesized CNT@Co-Pt displayed good

durability performance during the measurement.

Figure 6.13. (a) TEM image and (b) partial enlarged TEM image of Pt of CNT@Co-Pt (20%) after durability test.

Table 6.1. Electrochemical performance of CNT@Co-Pt and some other Pt carbon composite nanostructures.

Material	Mass Activity (Ag^{-1})	Reference
CNT@Co-Pt ^{a)}	78.37	This thesis
Pt _{0.5} Pd _{0.5} /C ^{b)}	8.5	[181]
Co ^{rich} core-Pt ^{rich} shell/C ^{c)}	15.544	[182]
1-PtNP/MWCNT ^{d)}	5.0	[237]
2-PtNP/MWCNT ^{d)}	4.7	
3-PtNP/MWCNT ^{d)}	3.3	
(100)Pt-Vulcan ^{e)}	6.14	[184]

a) For ORR at 0.85 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1600rpm from 0.2 to 1.2 V (RHE) in 0.5M H₂SO₄.

b) For ORR at 0.85 V determined from positive-going sweeps at 5 mV/s and a rotation rate of 1600rpm from 0.3 to 1.0 V (RHE) in 0.5M H₂SO₄.

c) For ORR at 1.0155 V determined from positive-going sweeps at 5 mV/s and a

rotation rate of 1600rpm from 0.2 to 1.2 V (RHE) in 20% H₂SO₄.

d) For ORR at 0.90 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 1900rpm from 0.1 to 1.1 V (RHE) in 0.5M H₂SO₄.

e) For ORR at 0.90 V determined from positive-going sweeps at 10 mV/s and a rotation rate of 3000rpm from 0.1 to 1.0 V (SHE) in 0.5M H₂SO₄.

As listed in the table 6.1, electrocatalytic performance for the oxygen reduction reaction of our 3D Pt NDs is comparable or superior to many other Pt and carbon composites as electrocatalysts.

6.4 Summary

In this work, nitrogen-doped CNT@Co framework derived from ZIF-67 is employed as an alternative support material for Pt nanoparticles to prepare nitrogen-doped CNT@Co-Pt composite with the optimized Pt loading. With unique robust 3D structure, the nitrogen-doped CNT@Co framework enables the catalyst with excellent structural merits including high accessibility, strong structural stability and sufficient loading site for the Pt nanoparticles. The small amounts of carbon-nitrogen species would generate some extrinsic defects and active sites, while the inner wrapped cobalt nanocrystals might provide extra conductivity simultaneously. And the robust framework also assist in the superior electrochemical durability for its unique heterogeneous structure can successfully diminish the surface energy to prevent the agglomeration of Pt nanoparticles during the electrochemical

process. Based on the advantages stated above, the as-prepared hybrid also presents superior performance towards ORR compared with commercial Pt/CB catalyst. Consequently, the nitrogen-doped CNT@Co framework prepared could be a cost-effective and durable electrocatalyst for oxygen reduction in fuel cell and many other industrial applications.

Chapter 7. Concluding Remarks and Outlook

7.1. Concluding Remarks

Fuel cells, with different kinds and diverse applications, are thought as one of the best promising candidates to substitute the conventional power generating devices due in respect to the consideration about the environmental problems. Electrocatalysts, one of the most important fuel cell materials, plays an extremely essential role during the fuel cell performance. Thus, developing novel kinds of electrocatalysts is of great significance. This research project focuses the rational design and synthesis of Pt-based nanostructures and MOF-derived carbon support, including Pt NDs, PtBi NSs, and ZIF-67 derived carbon nanotubes which could be utilized as the support material, and their electrochemical performance as well. The main results and critical findings are summarized as follows.

In this research project, we report the synthesis and electrochemical performance of the three-dimensional Pt nanodendrites.

Using a facile inorganic species assisted strategy, the as-synthesized clean 3D Pt NDs with surface are composed of interconnected 1D Pt nanorods. The presence and amount of iron and nitrate ions are of great importance during the formation and growth of the 3D Pt NDs. And during the electrochemical measurement, compared with Pt black and commercial carbon-supported Pt nanoparticle catalysts, the electrocatalysts based on Pt NDs show both higher catalytic activity as well as

outstanding durability, which may be a result of the unique 3D interconnected open-pore structure. Based on these above, we can conclude that the 3D Pt NDs could be a promising candidate for fuel cells applications.

In the second study, two dimensional PtBi nanosheets are prepared by a facile thermal decomposition method, and electrocatalytic activity towards formic acid oxidation of PtBi NSs are also measured.

According to the study, the morphology and size of PtBi NSs depend on the initial addition molar ratio between Pt and Bi precursors a lot, while the introduction of halides is also essential during the generation and growth of PtBi NSs. With the optimized technique, the product displays a relatively uniform nanoplates morphology as well as the intermetallic structures, which contribute quite a lot to their electrocatalytic performance. The enhanced electrocatalytic activity towards formic acid of PtBi NSs are because the reaction path of FAOR is dependent on the surface and arrangement of Pt atoms, and the ensemble effect elevated by the separated Pt and Bi atoms can effectively catalyze the FAOR. Additionally, the as-prepared PtBi NSs possess plentiful low-coordinated atoms in the (101) facets, which would also make contributions by providing more efficiently active sites.

In the third study, we report a facile method to prepare nitrogen-doped CNT@Co-Pt composite using zeolitic imidazolate framework-67 (ZIF-67) derived hierarchical nitrogen-doped CNT@Co frameworks as the carbon matrix.

Zeolitic imidazolate framework-67 (ZIF-67) is synthesized first, and used as precursor for further preparation of MOF derived hierarchical nitrogen-doped

CNT@Co frameworks. With the as-synthesized CNT@Co as the carbon support, Pt nanoparticles were further generated, dispersing on the surface on this robust substrate. Pt loading of the final catalyst was tailored to achieve uniform dispersion. Of note, the robust 3D nitrogen-doped CNT@Co framework enables the catalyst with admirable structural merits including high accessibility, strong structural stability and sufficient loading sites for the Pt nanoparticles. Meanwhile, the modicum of carbon-nitrogen species would generate some extrinsic defects and active sites. In addition, the inner wrapped cobalt nanocrystals might provide extra conductivity. The unique robust heterogeneous structure is also beneficial to the electrochemical stability as it could reduce the surface energy to avoid the aggregation of Pt nanoparticles. When applied as an advanced electrocatalyst for ORR, the hybrid displays superior performance compared with commercial Pt/CB catalyst.

While talking about the usage and commercialization of Pt based catalyst, as is known to common, most MEA catalysts used today are based on Pt (in the form of nanoparticles dispersed on carbon black supports), with the high price of this scarce precious metal having a decisive impact on costs. How to reduce costs by reducing cathode loadings to $< 0.1 \text{ mg Pt cm}^{-2}$ without loss of performance or durability is the subject of most electrocatalyst research.

For the self-supported Pt catalyst in the Chapter 4, 3D Pt dendrites with large surface area were directly used, and no carbon based supporting materials are needed to keep the high catalytic performance. Therefore, the first advantage of this novel structure in fuel cell is the improved cycling stability without the carbon corrosion.

Furthermore, the 3D structures are robust enough to withstand the dissolution/aggregation of Pt nanocrystals. However, this strategy must face the high cost of the precious noble metals.

For the PtBi alloys in the Chapter 5, intermetallic PtBi nanosheet can largely reduce the cost of cathode materials as another kind of self-supported catalyst with enhanced stability. However, the uniform and monodisperse nanostructures is hard to be produced for the PtBi sample. As a consequence, it is very difficult to optimize its catalytic performance through the structural control.

For the CNT@Co-Pt sample in Chapter 6, the N-doped CNT framework supports can improve transport or water management. However, concerns about the possible adverse health effects of carbon nanotubes without the counterweight of a significant functional performance or processing advantage may make them unattractive for high-volume electrode manufacturing.

7.2. Outlook

7.2.1. Research Work

Despite the continuous development and great progress in the synthesis of Pt-based nanostructures and various kinds of carbon support for them during the recent years and their applications for fuel cells, the deployment of advanced electrocatalysts based on Pt is still at its early stage. Therefore, researchers still face great challenges towards both the synthesis and practical application of these novel

materials. Along these lines, several possible suggestions provided below for the future research on electrocatalysts for fuel cells applications.

- 1) In-depth investigation into the formation mechanisms of Pt based nanostructures in both solvothermal and hydrothermal systems. Both experimental and theoretical analysis would be necessary to better illustrate the roles of the solvents and additives in various systems, for example, how they interact with the Pt or Pt contained alloys surface, and how the anisotropic growth of these nanocrystals takes place. A better understanding of the fundamental chemistry would possibly provide some guidance for the design and development of novel systems that could produce Pt based nanostructures in a more controllable way.
- 2) Deeper understanding the fundamental correlations between the nanostructures and electrochemical performance. Some brief comparison and discussion have been provided in this thesis to reveal the effects of diverse nanostructures on the electrocatalytic performance. However, more thorough studies would be necessary to discover how the structural features, including geometric shape, exposed facets, porosity and surface area, influence the electrochemical characteristics, such as the electrochemical activity and durability. Moreover, composing element is also a research hotspot during future work since the introduction of other ingredient element to build alloys or composites would make contribution to enhanced electrochemical performance and lower cost so as to obtain more extensive use for fuel cell applications.

- 3) Exploring novel methods to synthesize Pt-based nanostructures with better electrocatalytic performance and lower cost. Development of the preparation of Pt-based electrocatalysts with various morphologies, different alloy compounds, and innovative support materials would lead to a transcendent revolution, which grasps the key points of next generations of green energy devices. Although much effort has been devoted to the exploitation of Pt-based nanostructures, there still exists enormous developing space. Novel techniques which can contribute to the reduction in cost and CO poisoning need to be further investigated and adopted during future work so as to get more extensive fuel cells applications.
- 4) Searching for or synthesizing novel types of support materials. Utilization of support material for the noble catalyst could effectively reduce the dosage and achieve high utilization ratio of the noble metal. Novel kinds of support materials with high specific surface area to increase the dispersion of nanocatalysts, low flammability in both humid and dry air conditions, low solubility, extraordinary chemical and electrochemical stability as well as high electronic conductivity is so in need for future applications. The stability, oxidant resistance and poison-tolerance capability still need to get optimized for carbon support materials so as to improve the durability of fuel cells. Besides, rather than the traditional carbon-based support materials, alternative noncarbon support materials with the properties of strong physicochemical and electronic interaction with catalytic metals to improve catalytic activity and durability

should also be further explored. Some research work has focused on the development of nitrides, carbides, mesoporous silicas, conducting polymers and metal oxides and so on, but there still exists technological gaps need to be closed.

5) Although not as extensively reported as Pt, synthesis of non-Pt based nanostructures such as Pd, Au and so on, which is another promising candidate as electrocatalyst, has been achieved in particular systems. The synthetic difficulties of these non-Pt based nanostructures with controllable nanostructures greatly hinder the investigation of their electrochemical properties. Further exploring synthetic methods of non-Pt based nanostructures, as well as developing novel systems would play an important role to evaluate their potential as anode materials for fuel cells, and provide feasible nanostructuring strategy to optimize the performance. Besides, the noble metal based electrocatalysts, research about non-noble metal electrocatalysts and nonmetallic material is also a promising area to get exploited, which could make cost down at the extreme.

7.2.1. Commercialization of Pt based catalyst

As Pt is a kind of precious and low-abundance noble metal, it is of great significance to enable better efficiency of use of Pt. Reducing the Pt loading (particularly in the cathode catalyst layer) without compromising fuel cell

performance is an effective strategy to meet the cost requirements for fuel cell commercialization. In other words, the design of novel catalysts requires both reducing the amount and cost of Pt used and also enhancing catalytic activity and durability.

In order to address these requirements, several research approaches could be developed to help achieve better commercialization of Pt, including (1) making nanostructures to increase the surface-to-volume ratio; (2) using an alloying technique to incorporate non-precious metals into the nanostructures; (3) the synthesis of catalysts with large, highly coordinated {111} facets; and (4) and the use of de-alloyed or annealed surface structures with increased surface area and a modulated composition that improves the activity of the topmost Pt layer. In each such approach, the effects of shape (zero-, one-, two- or three-dimensional nanostructures), morphology (exposed facets), and catalyst composition on electrocatalytic activity and stability should be considered. In synthesis processes, optimizing catalyst shape, morphology and composition with respect to catalytic activity and stability is critical to achieve successful electrocatalysts.

Apart from these, in the manufacture of catalyst, high manufacturing rates, high quality and low costs are the requirements of producing Pt catalyst. At the required low Pt loadings, trying to produce catalyst which could deliver in a fuel-cell environment the necessary high power, durability and robustness is the approach to achieve better commercialization of Pt. Impressive kinetic activity will not suffice to make a catalyst system attractive for large-scale production. We should aim to achieve

(at the required low Pt loadings) the durability and power targets using something that can be manufactured at high volumes with the requisite quality, throughput and yields.^[238]

References

- [1] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon, W. Van Schalkwijk, *Nat. Mater.* **2005**, 4, 366.
- [2] D. R. Rolison, *Science* **2003**, 299, 1698.
- [3] R. F. Service, *Science* **2002**, 296, 1222.
- [4] J. Maier, *Nat. Mater.* **2005**, 4, 805.
- [5] M. N. Cao, D. S. Wu, R. Cao, *ChemCatChem* **2014**, 6, 26.
- [6] C. Rice, S. Ha, R. I. Masel, A. Wieckowski, *J. Power Sources* **2003**, 115, 229.
- [7] J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, *Science* **2007**, 315, 220.
- [8] V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C. A. Lucas, G. F. Wang, P. N. Ross, N. M. Markovic, *Nat. Mater.* **2007**, 6, 241.
- [9] H. S. Liu, C. J. Song, L. Zhang, J. J. Zhang, H. J. Wang, D. P. Wilkinson, *J. Power Sources* **2006**, 155, 95.
- [10] Y. G. Guo, J. S. Hu, L. J. Wan, *Adv. Mater.* **2008**, 20, 2878.
- [11] K. W. Park, Y. E. Sung, *J. Ind. Eng. Chem.* **2006**, 12, 165.
- [12] X. W. Yu, P. G. Pickup, *J. Power Sources* **2008**, 182, 124.
- [13] X. L. Ji, K. T. Lee, R. Holden, L. Zhang, J. J. Zhang, G. A. Botton, M. Couillard, L. F. Nazar, *Nat. Chem.* **2010**, 2, 286.
- [14] H. Bonnemann, K. S. Nagabhushana, *J. New Mater. Electrochem. Syst.* **2004**, 7, 93.
- [15] P. E. Dodds, L. Staffell, A. D. Hawkes, F. Li, P. Grunewald, W. McDowall, P. Ekins, *Int. J. Hydrogen Energy* **2015**, 40, 2065.
- [16] D. J. Ham, J. S. Lee, *Energies* **2009**, 2, 873.
- [17] Y. H. Bing, H. S. Liu, L. Zhang, D. Ghosh, J. J. Zhang, *Chem. Soc. Rev.* **2010**, 39, 2184.
- [18] N. Fujiwara, Y. Shiozaki, T. Tanimitsu, K. Yasuda, Y. Miyazaki, *Electrochemistry* **2002**, 70, 988.

- [19] Y. G. Chen, J. J. Wang, H. Liu, R. Y. Li, X. L. Sun, S. Y. Ye, S. Knights, *Electrochem. Commun.* **2009**, *11*, 2071.
- [20] H. Bonnemann, R. Brinkmann, S. Kinge, T. Ould-Ely, M. Armand, *Fuel Cells* **2004**, *4*, 289.
- [21] X. Wang, W. Z. Li, Z. W. Chen, M. Waje, Y. S. Yan, *J. Power Sources* **2006**, *158*, 154.
- [22] Z. Z. Jiang, Z. B. Wang, W. L. Qu, H. Rivera, D. M. Gu, G. P. Yin, *Nanoscale* **2012**, *4*, 7411.
- [23] A. M. C. Luna, G. A. Camara, V. A. Paganin, E. A. Ticianelli, E. R. Gonzalez, *Electrochem. Commun.* **2000**, *2*, 222.
- [24] E. S. Steigerwalt, G. A. Deluga, D. E. Cliffl, C. M. Lukehart, *J. Phys. Chem. B* **2001**, *105*, 8097.
- [25] Y. Y. Shao, G. P. Yin, Y. Z. Gao, *J. Power Sources* **2007**, *171*, 558.
- [26] Y. Shimazaki, S. Hayasaka, T. Koyama, D. Nagao, Y. Kobayashi, M. Konno, *J. Colloid Interface Sci.* **2010**, *351*, 580.
- [27] S. Rojas, F. J. Garcia-Garcia, S. Jaras, M. V. Martinez-Huerta, J. L. G. Fierro, M. Boutonnet, *Appl. Catal., A. Gen.* **2005**, *285*, 24.
- [28] H. Abe, F. Matsumoto, L. R. Alden, S. C. Warren, H. D. Abruna, F. J. DiSalvo, *J. Am. Chem. Soc.* **2008**, *130*, 5452.
- [29] L. Xiong, A. Manthiram, *Solid State Ionics* **2005**, *176*, 385.
- [30] E. Ramirez, L. Erades, K. Philippot, P. Lecante, B. Chaudret, *Adv. Funct. Mater.* **2007**, *17*, 2219.
- [31] K. Kinoshita, *J. Electrochem. Soc.* **1990**, *137*, 845.
- [32] Y. J. Song, Y. Yang, C. J. Medforth, E. Pereira, A. K. Singh, H. F. Xu, Y. B. Jiang, C. J. Brinker, F. van Swol, J. A. Shelnutt, *J. Am. Chem. Soc.* **2004**, *126*, 635.
- [33] G. Wu, Y. S. Chen, B. Q. Xu, *Electrochem. Commun.* **2005**, *7*, 1237.
- [34] D. L. Wang, H. L. Xin, H. S. Wang, Y. C. Yu, E. Rus, D. A. Muller, F. J. DiSalvo, H. D. Abruna, *Chem. Mater.* **2012**, *24*, 2274.
- [35] Q. Li, H. Y. Pan, D. Higgins, R. G. Cao, G. Q. Zhang, H. F. Lv, K. B. Wu, J. Cho,

G. Wu, *Small* **2015**, *11*, 1443.

[36] C. H. Cui, S. H. Yu, *Acc. Chem. Res.* **2013**, *46*, 1427.

[37] Y. J. Kang, X. C. Ye, J. Chen, Y. Cai, R. E. Diaz, R. R. Adzic, E. A. Stach, C. B. Murray, *J. Am. Chem. Soc.* **2013**, *135*, 42.

[38] Y. Sun, L. Zhuang, J. Lu, X. Hong, P. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 15465.

[39] J. H. Jiang, A. Kucernak, *J. Electroanal. Chem.* **2009**, *630*, 10.

[40] H. Atae-Esfahani, Y. Nemoto, M. Imura, Y. Yamauchi, *Chem. Asian J.* **2012**, *7*, 876.

[41] H. J. Wang, M. Imura, Y. Nemoto, L. Wang, H. Y. Jeong, T. Yokoshima, O. Terasaki, Y. Yamauchi, *Chem. Eur. J.* **2012**, *18*, 13142.

[42] Y. Yamauchi, A. Tonegawa, M. Komatsu, H. J. Wang, L. Wang, Y. Nemoto, N. Suzuki, K. Kuroda, *J. Am. Chem. Soc.* **2012**, *134*, 5100.

[43] Z. M. Peng, H. J. You, H. Yang, *Adv. Funct. Mater.* **2010**, *20*, 3734.

[44] C. Chen, Y. J. Kang, Z. Y. Huo, Z. W. Zhu, W. Y. Huang, H. L. L. Xin, J. D. Snyder, D. G. Li, J. A. Herron, M. Mavrikakis, M. F. Chi, K. L. More, Y. D. Li, N. M. Markovic, G. A. Somorjai, P. D. Yang, V. R. Stamenkovic, *Science* **2014**, *343*, 1339.

[45] Y. Ding, Y. Gao, Z. L. Wang, N. Tian, Z. Y. Zhou, S. G. Sun, *Appl. Phys. Lett.* **2007**, *91*.

[46] B. W. Lim, X. M. Lu, M. J. Jiang, P. H. C. Camargo, E. C. Cho, E. P. Lee, Y. N. Xia, *Nano Lett.* **2008**, *8*, 4043.

[47] N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, *Science* **2007**, *316*, 732.

[48] C. L. Li, T. Sato, Y. Yamauchi, *Angew. Chem., Int. Ed.* **2013**, *52*, 8050.

[49] S. Kuchibhatla, A. S. Karakoti, D. Bera, S. Seal, *Prog. Mater. Sci.* **2007**, *52*, 699.

[50] M. Watanabe, S. Motoo, *J. Electroanal. Chem.* **1975**, *60*, 267.

[51] H. G. Liao, D. Zhrebetskyy, H. L. Xin, C. Czarnik, P. Ercius, H. Elmlund, M. Pan, L. W. Wang, H. M. Zheng, *Science* **2014**, *345*, 916.

[52] J. K. Nørskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, *Nat. Chem.* **2009**, *1*, 37.

[53] S. J. Guo, D. G. Li, H. Y. Zhu, S. Zhang, N. M. Markovic, V. R. Stamenkovic, S.

- H. Sun, *Angew. Chem., Int. Ed.* **2013**, *52*, 3465.
- [54] L. X. Ding, A. L. Wang, G. R. Li, Z. Q. Liu, W. X. Zhao, C. Y. Su, Y. X. Tong, *J. Am. Chem. Soc.* **2012**, *134*, 5730.
- [55] M. Chhetri, M. Rana, B. Loukya, P. K. Patil, R. Datta, U. K. Gautam, *Adv. Mater.* **2015**, *27*, 4430.
- [56] C. Xu, J. Yang, B. L. Pence, K. Gath, P. Pietrasz, M. Sulek, K. Sun, E. Sohm, G. Meng, *Polym. Electrolyte Fuel Cells* **2014**, *64*, 181.
- [57] Z. M. Peng, H. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 7542.
- [58] Z. L. Zheng, H. F. Li, Y. H. Shen, R. Cao, *Chem. Eur. J.* **2011**, *17*, 8440.
- [59] D. S. Wu, Z. L. Zheng, S. Y. Gao, M. N. Cao, R. Cao, *Phys. Chem. Chem. Phys.* **2012**, *14*, 8051.
- [60] H. B. Liao, Y. L. Hou, *Chem. Mater.* **2013**, *25*, 457.
- [61] B. Y. Xia, H. Bin Wu, Y. Yan, X. W. Lou, X. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 9480.
- [62] C. Koenigsmann, A. C. Santulli, K. P. Gong, M. B. Vukmirovic, W. P. Zhou, E. Sutter, S. S. Wong, R. R. Adzic, *J. Am. Chem. Soc.* **2011**, *133*, 9783.
- [63] K. A. Kuttiyiel, K. Sasaki, Y. M. Choi, D. Su, P. Liu, R. R. Adzic, *Nano Lett.* **2012**, *12*, 6266.
- [64] L. Gan, M. Heggen, S. Rudi, P. Strasser, *Nano Lett.* **2012**, *12*, 5423.
- [65] J. H. Yang, X. J. Chen, X. F. Yang, J. Y. Ying, *Energy Environ. Sci.* **2012**, *5*, 8976.
- [66] S. Tanwar, M. C. Chuang, K. S. Prasad, J. A. A. Ho, *Green Chem.* **2012**, *14*, 799.
- [67] H. Atae-Esfahani, L. Wang, Y. Yamauchi, *Chem. Commun.* **2010**, *46*, 3684.
- [68] Y. J. Xiong, B. J. Wiley, Y. N. Xia, *Angew. Chem., Int. Ed.* **2007**, *46*, 7157.
- [69] X. Y. Lang, G. F. Han, B. B. Xiao, L. Gu, Z. Z. Yang, Z. Wen, Y. F. Zhu, M. Zhao, J. C. Li, Q. Jiang, *Adv. Funct. Mater.* **2015**, *25*, 230.
- [70] S. Mukerjee, J. McBreen, *J. Electroanal. Chem.* **1998**, *448*, 163.
- [71] R. Ferrando, J. Jellinek, R. L. Johnston, *Chem. Rev.* **2008**, *108*, 845.
- [72] C. Koenigsmann, S. S. Wong, *Energy Environ. Sci.* **2011**, *4*, 1161.
- [73] J. T. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.

- [74]H. X. Liu, N. Tian, M. P. Brandon, J. Pei, Z. C. Huangfu, C. Zhan, Z. Y. Zhou, C. Hardacre, W. F. Lin, S. G. Sun, *Phys. Chem. Chem. Phys.* **2012**, *14*, 16415.
- [75]Q. S. Chen, Z. Y. Zhou, F. J. Vidal-Iglesias, J. Solla-Gullon, J. M. Feliu, S. G. Sun, *J. Am. Chem. Soc.* **2011**, *133*, 12930.
- [76]S. Papadimitriou, S. Armyanov, E. Valova, A. Hubin, O. Steenhaut, E. Pavlidou, G. Kokkinidis, S. Sotiropoulos, *J. Phys. Chem. C* **2010**, *114*, 5217.
- [77]M. Mohl, D. Dobo, A. Kukovecz, Z. Konya, K. Kordas, J. Q. Wei, R. Vajtai, P. M. Ajayan, *J. Phys. Chem. C* **2011**, *115*, 9403.
- [78]H. Nakano, W. Z. Li, L. B. Xu, Z. W. Chen, M. Waje, S. Kuwabata, Y. S. Yan, *Electrochemistry* **2007**, *75*, 705.
- [79]G. Wu, R. Swaidan, D. Y. Li, N. Li, *Electrochim. Acta* **2008**, *53*, 7622.
- [80]Y. C. Liu, X. P. Qiu, Z. G. Chen, W. T. Zhu, *Electrochem. Commun.* **2002**, *4*, 550.
- [81]Y. Y. Shao, J. Liu, Y. Wang, Y. H. Lin, *J. Mater. Chem.* **2009**, *19*, 46.
- [82]T. H. Yeh, C. W. Liu, H. S. Chen, K. W. Wang, *Electrochem. Commun.* **2013**, *31*, 125.
- [83]J. H. Zeng, F. B. Su, Y. F. Han, Z. Q. Tian, C. K. Poh, Z. L. Liu, J. Y. Lin, J. Y. Lee, X. S. Zhao, *J. Phys. Chem. C* **2008**, *112*, 15908.
- [84]J. M. Sieben, M. M. E. Duarte, C. E. Mayer, *J. Appl. Electrochem.* **2008**, *38*, 483.
- [85]P. F. B. D. Martins, E. A. Ticianelli, *Chemelectrochem* **2015**, *2*, 1298.
- [86]Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, W. Sugimoto, *J. Electrochem. Soc.* **2000**, *147*, 4421.
- [87]K. Ye, D. M. Zhang, H. Y. Zhang, K. Cheng, G. L. Wang, D. X. Cao, *Electrochim. Acta* **2015**, *178*, 270.
- [88]W. Z. Li, C. H. Liang, W. J. Zhou, J. S. Qiu, Z. H. Zhou, G. Q. Sun, Q. Xin, *J. Phys. Chem. B* **2003**, *107*, 6292.
- [89]C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. S. Yan, *Nano Lett.* **2004**, *4*, 345.
- [90]Y. H. Lin, X. L. Cui, X. R. Ye, *Electrochem. Commun.* **2005**, *7*, 267.
- [91]H. Chang, S. H. Joo, C. Pak, *J. Mater. Chem.* **2007**, *17*, 3078.

- [92] J. Shim, J. Lee, Y. Ye, J. Hwang, S. K. Kim, T. H. Lim, U. Wiesner, J. Lee, *ACS Nano* **2012**, *6*, 6870.
- [93] S. J. Guo, S. J. Dong, E. K. Wang, *ACS Nano* **2010**, *4*, 547.
- [94] C. Z. Zhu, S. J. Dong, *Nanoscale* **2013**, *5*, 1753.
- [95] D. Higgins, M. A. Hoque, M. H. Seo, R. Y. Wang, F. Hassan, J. Y. Choi, M. Pritzker, A. P. Yu, J. J. Zhang, Z. W. Chen, *Adv. Funct. Mater.* **2014**, *24*, 4325.
- [96] M. Uchida, Y. Aoyama, M. Tanabe, N. Yanagihara, N. Eda, A. Ohta, *J. Electrochem. Soc.* **1995**, *142*, 2572.
- [97] E. Antolini, R. R. Passos, E. A. Ticianelli, *J. Power Sources* **2002**, *109*, 477.
- [98] A. L. Dicks, *J. Power Sources* **2006**, *156*, 128.
- [99] C. L. Lin, Y. C. Yeh, *Res. Chem. Intermed.* **2014**, *40*, 2207.
- [100] H. Y. Qian, S. W. Chen, Y. S. Fu, X. Wang, *J. Power Sources* **2015**, *300*, 41.
- [101] H. L. Riley, *Q. Rev., Chem. Soc.* **1947**, *1*, 59.
- [102] Y.-C. Park, K. Kakinuma, M. Uchida, H. Uchida, M. Watanabe, *Electrochim. Acta* **2014**, *123*, 84.
- [103] A. Witkowska, G. Greco, S. Dsoke, R. Marassi, A. Di Cicco, *J. Non-Cryst. Solids* **2014**, *401*, 169.
- [104] B. Avasarala, R. Moore, P. Haldar, *Electrochim. Acta* **2010**, *55*, 4765.
- [105] S. Iijima, *Nature* **1991**, *354*, 56.
- [106] P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. Smith, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *313*, 91.
- [107] M. J. Bronikowski, P. A. Willis, D. T. Colbert, K. Smith, R. E. Smalley, *J. Vac. Sci. Technol., A* **2001**, *19*, 1800.
- [108] A. M. Cassell, J. A. Raymakers, J. Kong, H. Dai, *J. Phys. Chem. B* **1999**, *103*, 6484.
- [109] W. Li, X. Wang, Z. Chen, M. Waje, Y. Yan, *J. Phys. Chem. B* **2006**, *110*, 15353.
- [110] Y. Lin, X. Cui, C. H. Yen, C. M. Wai, *Langmuir* **2005**, *21*, 11474.
- [111] G. Wu, B.-Q. Xu, *J. Power Sources* **2007**, *174*, 148.

- [112] S. J. Guo, S. J. Dong, E. K. Wang, *Adv. Mater.* **2010**, 22, 1269.
- [113] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [114] S. Liu, J. Q. Wang, J. Zeng, J. F. Ou, Z. P. Li, X. H. Liu, S. R. Yang, *J. Power Sources* **2010**, 195, 4628.
- [115] N. Soin, S. S. Roy, T. H. Lim, J. A. D. McLaughlin, *Mater. Chem. Phys.* **2011**, 129, 1051.
- [116] L. T. Qu, Y. Liu, J. B. Baek, L. M. Dai, *ACS Nano* **2010**, 4, 1321.
- [117] S. Scirè, C. Crisafulli, S. Giuffrida, G. Ventimiglia, C. Bongiorno, C. Spinella, *J. Mol. Catal. A: Chem.* **2010**, 333, 100.
- [118] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, R. S. Ruoff, *Nature* **2007**, 448, 457.
- [119] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, 3, 270.
- [120] G. Williams, B. Seger, P. V. Kamat, *ACS Nano* **2008**, 2, 1487.
- [121] J. D. Qiu, G. C. Wang, R. P. Liang, X. H. Xia, H. W. Yu, *J. Phys. Chem. C* **2011**, 115, 15639.
- [122] S. Y. Wang, S. P. Jiang, X. Wang, *Electrochim. Acta* **2011**, 56, 3338.
- [123] Z. J. Lu, S. J. Bao, Y. T. Gou, C. J. Cai, C. C. Ji, M. W. Xu, J. Song, R. Y. Wang, *Rsc Adv* **2013**, 3, 3990.
- [124] A. C. Chen, P. Holt-Hindle, *Chem. Rev.* **2010**, 110, 3767.
- [125] L. Ma, C. M. Wang, M. Gong, L. W. Liao, R. Long, J. G. Wang, D. Wu, W. Zhong, M. J. Kim, Y. X. Chen, Y. Xie, Y. J. Xiong, *ACS Nano* **2012**, 6, 9797.
- [126] H. Atae-Esfahani, J. Liu, M. Hu, N. Miyamoto, S. Tominaka, K. C. W. Wu, Y. Yamauchi, *Small* **2013**, 9, 1047.
- [127] H. M. Chen, R. S. Liu, M. Y. Lo, S. C. Chang, L. D. Tsai, Y. M. Peng, J. F. Lee, *J. Phys. Chem. C* **2008**, 112, 7522.
- [128] J. W. Hong, S. W. Kang, B. S. Choi, D. Kim, S. B. Lee, S. W. Han, *ACS Nano* **2012**, 6, 2410.
- [129] X. Wang, S. I. Choi, L. T. Roling, M. Luo, C. Ma, L. Zhang, M. F. Chi, J. Y.

- Liu, Z. X. Xie, J. A. Herron, M. Mavrikakis, Y. N. Xia, *Nat. Commun.* **2015**, *6*, 7594.
- [130] Z. F. Chen, S. R. Ye, A. R. Wilson, Y. C. Ha, B. J. Wiley, *Energy Environ. Sci.* **2014**, *7*, 1461.
- [131] K. S. Napolskii, P. J. Barczuk, S. Y. Vassiliev, A. G. Veresov, G. A. Tsirlina, P. J. Kulesza, *Electrochim. Acta* **2007**, *52*, 7910.
- [132] Y. Piao, H. Lim, J. Y. Chang, W. Y. Lee, H. Kim, *Electrochim. Acta* **2005**, *50*, 2997.
- [133] G. Surendran, L. Ramos, B. Pansu, E. Prouzet, P. Beaunier, F. Audonnet, H. Remita, *Chem. Mater.* **2007**, *19*, 5045.
- [134] S. H. Liu, W. Y. Yu, C. H. Chen, A. Y. Lo, B. J. Hwang, S. H. Chien, S. B. Liu, *Chem. Mater.* **2008**, *20*, 1622.
- [135] H. R. Wang, Y. J. Song, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2006**, *128*, 9284.
- [136] Y. Song, R. M. Garcia, R. M. Dorin, H. R. Wang, Y. Qiu, E. N. Coker, W. A. Steen, J. E. Miller, J. A. Shelnutt, *Nano Lett.* **2007**, *7*, 3650.
- [137] Y. J. Song, R. M. Dorin, R. M. Garcia, Y. B. Jiang, H. Wang, P. Li, Y. Qiu, F. van Swol, J. E. Miller, J. A. Shelnutt, *J. Am. Chem. Soc.* **2008**, *130*, 12602.
- [138] H. M. Chen, R. S. Liu, K. Asakura, L. Y. Jang, J. F. Lee, *J. Phys. Chem. C* **2007**, *111*, 18550.
- [139] Y. G. Sun, Y. N. Xia, *Nano Lett.* **2003**, *3*, 1569.
- [140] S. J. Kim, C. S. Ah, D. J. Jang, *Adv. Mater.* **2007**, *19*, 1064.
- [141] J. Park, L. Zhang, S. I. Choi, L. T. Roling, N. Lu, J. A. Herron, S. F. Xie, J. G. Wang, M. J. Kim, M. Mavrikakis, Y. N. Xia, *ACS Nano* **2015**, *9*, 2635.
- [142] H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan, C. L. Bai, *Angew. Chem., Int. Ed.* **2004**, *43*, 1540.
- [143] Y. P. Bi, G. X. Lu, *Chem. Mater.* **2008**, *20*, 1224.
- [144] Z. W. Chen, M. Waje, W. Z. Li, Y. S. Yan, *Angew. Chem., Int. Ed.* **2007**, *46*, 4060.
- [145] X. W. Teng, X. Y. Liang, S. Maksimuk, H. Yang, *Small* **2006**, *2*, 249.

- [146] F. Ye, J. J. Li, T. T. Wang, Y. Liu, H. J. Wei, J. L. Li, X. D. Wang, *J. Phys. Chem. C* **2008**, *112*, 12894.
- [147] Y. S. Hu, Y. G. Guo, W. Sigle, S. Hore, P. Balaya, J. Maier, *Nat. Mater.* **2006**, *5*, 713.
- [148] M. S. Nashner, A. I. Frenkel, D. Somerville, C. W. Hills, J. R. Shapley, R. G. Nuzzo, *J. Am. Chem. Soc.* **1998**, *120*, 8093.
- [149] T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, *J. Catal.* **2005**, *229*, 176.
- [150] M. Watanabe, M. Uchida, S. Motoo, *J. Electroanal. Chem.* **1987**, *229*, 395.
- [151] Z. L. Liu, J. Y. Lee, M. Han, W. X. Chen, L. M. Gan, *J. Mater. Chem.* **2002**, *12*, 2453.
- [152] M. Boutonnet, S. Logdberg, E. E. Svensson, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 270.
- [153] J. Wang, L. S. Ee, S. C. Ng, C. H. Chew, L. M. Gan, *Mater. Lett.* **1997**, *30*, 119.
- [154] T. Maiyalagan, X. C. Dong, P. Chen, X. Wang, *J. Mater. Chem.* **2012**, *22*, 5286.
- [155] Y. Liu, D. G. Li, S. S. Sun, *J. Mater. Chem.* **2011**, *21*, 12579.
- [156] Y. Kang, M. Li, Y. Cai, M. Cargnello, R. E. Diaz, T. R. Gordon, N. L. Wieder, R. R. Adzic, R. J. Gorte, E. A. Stach, C. B. Murray, *J. Am. Chem. Soc.* **2013**, *135*, 2741.
- [157] S. J. Guo, E. K. Wang, *Nano Today* **2011**, *6*, 240.
- [158] S. Y. Wang, S. P. Jiang, T. J. White, J. Guo, X. Wang, *J. Phys. Chem. C* **2009**, *113*, 18935.
- [159] Z. M. Peng, H. Yang, *Nano Today* **2009**, *4*, 143.
- [160] T. K. Sau, A. L. Rogach, F. Jackel, T. A. Klar, J. Feldmann, *Adv. Mater.* **2010**, *22*, 1805.
- [161] E. P. Lee, Z. Peng, D. M. Cate, H. Yang, C. T. Campbell, Y. Xia, *J. Am. Chem. Soc.* **2007**, *129*, 10634.

- [162] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, Y. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.
- [163] C. Wang, Y. L. Hou, J. M. Kim, S. H. Sun, *Angew. Chem., Int. Ed.* **2007**, *46*, 6333.
- [164] H. W. Liang, S. Liu, J. Y. Gong, S. B. Wang, L. Wang, S. H. Yu, *Adv. Mater.* **2009**, *21*, 1850.
- [165] B. Y. Xia, W. T. Ng, H. B. Wu, X. Wang, X. W. Lou, *Angew. Chem., Int. Ed.* **2012**, *51*, 7213.
- [166] M. Rauber, I. Alber, S. Muller, R. Neumann, O. Picht, C. Roth, A. Schokel, M. E. Toimil-Molares, W. Ensinger, *Nano Lett.* **2011**, *11*, 2304.
- [167] S. I. Lim, I. Ojea-Jimenez, M. Varon, E. Casals, J. Arbiol, V. Puentes, *Nano Lett.* **2010**, *10*, 1970.
- [168] M. A. Mahmoud, C. E. Tabor, M. A. El-Sayed, Y. Ding, Z. L. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 4590.
- [169] S. H. Sun, D. Q. Yang, D. Villers, G. X. Zhang, E. Sacher, J. P. Dodelet, *Adv. Mater.* **2008**, *20*, 571.
- [170] D. H. Wang, H. M. Luo, R. Kou, M. P. Gil, S. G. Xiao, V. O. Golub, Z. Z. Yang, C. J. Brinker, Y. F. Lu, *Angew. Chem., Int. Ed.* **2004**, *43*, 6169.
- [171] S. H. Sun, G. X. Zhang, D. S. Geng, Y. G. Chen, R. Y. Li, M. Cai, X. L. Sun, *Angew. Chem., Int. Ed.* **2011**, *50*, 422.
- [172] S. Mourdikoudis, L. M. Liz-Marzan, *Chem. Mater.* **2013**, *25*, 1465.
- [173] Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki, C. H. Ko, H. J. Shin, R. Ryoo, *Angew. Chem., Int. Ed.* **2000**, *39*, 3107.
- [174] M. Sanles-Sobrido, M. A. Correa-Duarte, S. Carregal-Romero, B. Rodriguez-Gonzalez, R. A. Alvarez-Puebla, P. Herves, L. M. Liz-Marzan, *Chem. Mater.* **2009**, *21*, 1531.
- [175] T. Herricks, J. Y. Chen, Y. N. Xia, *Nano Lett.* **2004**, *4*, 2367.
- [176] J. Y. Chen, T. Herricks, Y. N. Xia, *Angew. Chem., Int. Ed.* **2005**, *44*, 2589.
- [177] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Appl. Catal., B.*

Environ. **2005**, *56*, 9.

[178] X. W. Zhang, H. J. Yin, J. F. Wang, L. Chang, Y. Gao, W. Liu, Z. Y. Tang, *Nanoscale* **2013**, *5*, 8392.

[179] B. Y. Xia, H. B. Wu, Y. Yan, H. B. Wang, X. Wang, *Small* **2014**, *10*, 2336.

[180] T. T. Nguyen, C. J. Pan, J. Y. Liu, H. L. Chou, J. Rick, W. N. Su, B. J. Hwang, *J. Power Sources* **2014**, *251*, 393.

[181] I. E. Pech-Pech, D. F. Gervasio, A. Godinez-Garcia, O. Solorza-Feria, J. F. Perez-Robles, *J. Power Sources* **2015**, *276*, 365.

[182] M. H. Lee, P. S. Wang, J. S. Do, *J. Solid State Electrochem.* **2008**, *12*, 879.

[183] L. Tamasauskaite-Tamasiunaite, A. Balciunaite, A. Zabielaite, J. Vaiciuniene, A. Selskis, V. Pakstas, E. Norkus, *J. Electroanal. Chem.* **2013**, *707*, 31.

[184] V. Grozovski, H. Kasuk, J. Nerut, E. Hark, R. Jager, I. Tallo, E. Lust, *Chemelectrochem* **2015**, *2*, 847.

[185] M. Fayette, J. Nutariya, N. Vasiljevic, N. Dimitrov, *ACS Catal.* **2013**, *3*, 1709.

[186] E. Casado-Rivera, D. J. Volpe, L. Alden, C. Lind, C. Downie, T. Vazquez-Alvarez, A. C. D. Angelo, F. J. DiSalvo, H. D. Abruna, *J. Am. Chem. Soc.* **2004**, *126*, 4043.

[187] Y. J. Kang, J. B. Pyo, X. C. Ye, T. R. Gordon, C. B. Murray, *ACS Nano* **2012**, *6*, 5642.

[188] Z. M. Cui, H. Chen, M. T. Zhao, D. Marshall, Y. C. Yu, H. Abruna, F. J. DiSalvo, *J. Am. Chem. Soc.* **2014**, *136*, 10206.

[189] L. J. Zhang, D. G. Xia, *Applied Surface Science* **2006**, *252*, 2191.

[190] J. R. Croy, S. Mostafa, L. Hickman, H. Heinrich, B. R. Cuenya, *Appl. Catal., A. Gen.* **2008**, *350*, 207.

[191] F. Matsumoto, C. Roychowdhury, F. J. DiSalvo, H. D. Abruna, *J. Electrochem. Soc.* **2008**, *155*, B148.

[192] Y. J. Kang, L. Qi, M. Li, R. E. Diaz, D. Su, R. R. Adzic, E. Stach, J. Li, C. B. Murray, *ACS Nano* **2012**, *6*, 2818.

- [193] A. V. Tripković, K. D. Popović, R. M. Stevanović, R. Socha, A. Kowal, *Electrochem. Commun.* **2006**, *8*, 1492.
- [194] M. L. Yang, *J. Power Sources* **2013**, *229*, 42.
- [195] D. L. Wang, H. L. L. Xin, R. Hovden, H. S. Wang, Y. C. Yu, D. A. Muller, F. J. DiSalvo, H. D. Abruna, *Nat. Mater.* **2013**, *12*, 81.
- [196] M. X. Gong, F. M. Li, Z. G. Yao, S. Q. Zhang, J. W. Dong, Y. Chen, Y. W. Tang, *Nanoscale* **2015**, *7*, 4894.
- [197] S. H. Li, Y. Zhao, J. Chu, W. W. Li, H. Q. Yu, G. Liu, *Electrochim. Acta* **2013**, *92*, 93.
- [198] B. A. Kakade, T. Tamaki, H. Ohashi, T. Yamaguchi, *J. Phys. Chem. C* **2012**, *116*, 7464.
- [199] J. B. Wu, P. P. Li, Y. T. Pan, S. Warren, X. Yin, H. Yang, *Chem. Soc. Rev.* **2012**, *41*, 8066.
- [200] F. Saleem, Z. C. Zhang, B. Xu, X. B. Xu, P. L. He, X. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 18304.
- [201] S. H. Li, Y. Zhao, J. Chu, W. W. Li, H. Q. Yu, G. Liu, Y. C. Tian, *Front. Environ. Sci. Eng.* **2013**, *7*, 388.
- [202] D. T. Zhang, F. X. Wu, M. H. Peng, X. Y. Wang, D. G. Xia, G. S. Guo, *J. Am. Chem. Soc.* **2015**, *137*, 6263.
- [203] C. Roychowdhury, F. Matsumoto, V. B. Zeldovich, S. C. Warren, P. F. Mutolo, M. Ballesteros, U. Wiesner, H. D. Abruna, F. J. DiSalvo, *Chem. Mater.* **2006**, *18*, 3365.
- [204] J. V. Perales-Rondon, A. Ferre-Vilaplana, J. M. Feliu, E. Herrero, *J. Am. Chem. Soc.* **2014**, *136*, 13110.
- [205] H. B. Liao, J. H. Zhu, Y. L. Hou, *Nanoscale* **2014**, *6*, 1049.
- [206] W. X. Du, D. Su, Q. Wang, A. I. Frenkel, X. W. Teng, *Cryst. Growth Des.* **2011**, *11*, 594.
- [207] D. G. Xia, G. Chen, Z. Y. Wang, J. J. Zhang, S. Q. Hui, D. Ghosh, H. J. Wang, *Chem. Mater.* **2006**, *18*, 5746.

- [208] J. D. Lović, M. D. Obradović, D. V. Tripković, K. D. Popović, V. M. Jovanović, S. L. Gojković, A. V. Tripković, *Electrocatalysis* **2012**, 3, 346.
- [209] B. I. Podlovchenko, Y. M. Maksimov, S. A. Evlashin, T. D. Gladysheva, K. I. Maslakov, V. A. Krivchenko, *J. Electroanal. Chem.* **2015**, 743, 93.
- [210] I. S. Park, K. S. Lee, J. H. Choi, H. Y. Park, Y. E. Sung, *J. Phys. Chem. C* **2007**, 111, 19126.
- [211] A. M. Remona, K. L. N. Phani, *Fuel Cells* **2011**, 11, 385.
- [212] Z. F. Liu, G. S. Jackson, B. W. Eichhorn, *Angew. Chem., Int. Ed.* **2010**, 49, 3173.
- [213] N. Kristian, Y. S. Yan, X. Wang, *Chem. Commun.* **2008**, 353.
- [214] N. Kristian, Y. L. Yu, P. Gunawan, R. Xu, W. Q. Deng, X. W. Liu, X. Wang, *Electrochim. Acta* **2009**, 54, 4916.
- [215] A. Ferre-Vilaplana, J. V. Perales-Rondon, J. M. Feliu, E. Herrero, *Acs Catalysis* **2015**, 5, 645.
- [216] Y. Ma, X. D. Wang, S. H. Li, M. S. Toprak, B. Zhu, M. Muhammed, *Adv. Mater.* **2010**, 22, 1640.
- [217] J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Nørskov, *Nat. Chem.* **2009**, 1, 552.
- [218] G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* **2011**, 332, 443.
- [219] Z. H. Sheng, L. Shao, J. J. Chen, W. J. Bao, F. B. Wang, X. H. Xia, *ACS Nano* **2011**, 5, 4350.
- [220] B. Lim, M. J. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. M. Lu, Y. M. Zhu, Y. N. Xia, *Science* **2009**, 324, 1302.
- [221] J. S. Spendelov, A. Wieckowski, *Phys. Chem. Chem. Phys.* **2007**, 9, 2654.
- [222] W. C. Sheng, H. A. Gasteiger, Y. Shao-Horn, *J. Electrochem. Soc.* **2010**, 157, B1529.
- [223] S. M. Alia, G. Zhang, D. Kisailus, D. S. Li, S. Gu, K. Jensen, Y. S. Yan, *Adv. Funct. Mater.* **2010**, 20, 3742.

- [224] S. Sharma, A. Ganguly, P. Papakonstantinou, X. P. Miao, M. X. Li, J. L. Hutchison, M. Delichatsios, S. Ukleja, *J. Phys. Chem. C* **2010**, *114*, 19459.
- [225] Y. G. Li, W. Zhou, H. L. Wang, L. M. Xie, Y. Y. Liang, F. Wei, J. C. Idrobo, S. J. Pennycook, H. J. Dai, *Nat. Nanotechnol.* **2012**, *7*, 394.
- [226] D. C. Higgins, J. Y. Choi, J. Wu, A. Lopez, Z. W. Chen, *J. Mater. Chem.* **2012**, *22*, 3727.
- [227] A. Morozan, F. Jaouen, *Energy Environ. Sci.* **2012**, *5*, 9269.
- [228] E. Proietti, F. Jaouen, M. Lefevre, N. Larouche, J. Tian, J. Herranz, J. P. Dodelet, *Nat. Commun.* **2011**, *2*.
- [229] P. Horcajada, S. Surble, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki, G. Ferey, *Chem. Commun.* **2007**, 2820.
- [230] A. Dhakshinamoorthy, M. Alvaro, P. Horcajada, E. Gibson, M. Vishnuvarthan, A. Vimont, J. M. Greneche, C. Serre, M. Daturi, H. Garcia, *ACS Catal.* **2012**, *2*, 2060.
- [231] H. X. Zhong, J. Wang, Y. W. Zhang, W. L. Xu, W. Xing, D. Xu, Y. F. Zhang, X. B. Zhang, *Angew. Chem., Int. Ed.* **2014**, *53*, 14235.
- [232] M. Glerup, M. Castignolles, M. Holzinger, G. Hug, A. Loiseau, P. Bernier, *Chem. Commun.* **2003**, 2542.
- [233] S. Maldonado, K. J. Stevenson, *J. Phys. Chem. B* **2005**, *109*, 4707.
- [234] F. Sen, G. Gokagac, *J. Phys. Chem. C* **2007**, *111*, 5715.
- [235] J. S. Lee, G. S. Park, S. T. Kim, M. L. Liu, J. Cho, *Angew. Chem., Int. Ed.* **2013**, *52*, 1026.
- [236] Y. Jiao, Y. Zheng, M. T. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.* **2015**, *44*, 2060.
- [237] K. Jukk, J. Kozlova, P. Ritslaid, V. Sammelselg, N. Alexeyeva, K. Tammeveski, *J. Electroanal. Chem.* **2013**, *708*, 31.
- [238] M. K. Debe, *Nature* **2012**, *486*, 43.