Metal nanoparticles on graphene based materials used as catalysts for alcohol electro-oxidation

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**NANYANG
TECHNOLOGICAL
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**Metal Nanoparticles on Graphene Based Materials Used as
Catalysts for Alcohol Electro-Oxidation**

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Abstract

The research work presented in this thesis is mainly to develop metal nanoparticles (NPs) on graphene based support and apply these composites as catalysts for the methanol and glycerol electro-oxidation. The purpose is to promote the activity and selectivity of catalysts in alcohol electro-oxidation by tuning properties of graphene based supports.

Firstly, we obtained various water-soluble polymer functionalized graphene in dimethyl sulfoxide under ultrasonication. The atomic force microscope analysis and control experiment showed that polymer possessing the stronger interaction with graphene surface produced graphene with a thinner layer. Such polymer/graphene exhibited high conductivity and tunable surface property. As a result, a catalyst based on polyvinyl pyrrolidone (PVP)/graphene showed better methanol oxidation performance than that based on PVP/ reduced graphene oxide. By changing to another polymer, poly (4-vinylpyridine)/graphene showed stable and reversible response to pH, demonstrating its potential for sensor application.

Secondly, Au NPs supported on various supports with different metal support interaction were synthesized and tested for glycerol electro-oxidation. Through off-line HPLC analysis, it was found that Au NPs supported on extended poly(4-vinylpyridine) functionalized graphene (Au-P4P/G) showed a much higher activity and better selectivity for three carbon products than those on carbon black, P4P functionalized reduced graphene oxide (Au-P4P/rGO) and poly(m-aminophenol) (PmAP) wrapped graphene (Au-PmAP/G). Based on XPS results, we proposed that lower d-band center in Au nanoparticles could change their adsorption ability for oxygen-containing groups, which might induce higher three carbon selectivity in glycerol electro-oxidation.

Thirdly, a hybrid support consisting of nitrogen doped graphitic carbon and graphene (CN_x/G) was prepared by annealing polypyrrole/GO at 800 °C. Pd NPs were then loaded onto the support by a microwave-polyol method. Pd- CN_x/G was used as a catalyst for glycerol electro-oxidation. Through the comparison with Pd NPs on carbon black (CB), it was revealed that Pd NPs on support which containing nitrogen atoms could promote selectivity towards three carbon products as well as increase activity. Moreover, CN_x/G showed higher surface area than CN_x annealed from wire structured polypyrrole. It

caused smaller size of Pd NPs on CN_x/G and further increased its selectivity towards three carbon products.

Keywords: nanoparticles, graphene, polymer, methanol electro-oxidation, glycerol electro-oxidation

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List of Publications

1. Wang, H.; Maiyalagan, T.; Wang, X. *ACS Catal.* **2012**, 2, 781-794.
2. Wang, H.; Xia, B.; Yan, Y.; Li, N.; Wang, J.; Wang, X. *J. Phys. Chem. B* **2013**, 117, 5606-5613.
3. Wang, H.; Xie, M.; Thia, L.; Fisher, A.; Wang, X. *J. Phys. Chem. Lett.* **2014**, 5, 119-125.
4. Wang, H.; Thia, L.; Li, N.; Ge, X.; Liu, Z.; Wang, X. *Appl. Catal. B* **2015**, 166-167, 25-31.
5. Wang, H.; Thia, L.; Li, N.; Ge, X.; Liu, Z.; Wang, X. *ACS Catal.* **2015**, 5, 3174-3180.
6. Tao, L.*; Wang, H.*, Xie, M.; Thia, L.; Chen, W. N.; Wang, X. *Chem. Commun.* Under revision (* co-first author)
8. Li, N.; Wang, H.; Thia, L.; Wang, J.; Wang, X. *Analyst* **2015**, 140, 449-455
9. Xiao, P.; Ge, X.; Wang, H.; Liu, Z.; Fisher, A.; Wang, X. *Adv. Funct. Mater.* **2015**, 25, 1520-1526.
10. Wang, Y.; Liu, H.; Wang, Li.; Wang, H.; Du, X.; Wang, F.; Qi, T.; Lee, J. M.; Wang, X. *J. Mater. Chem. A* **2013**, 1, 6839-6848.
11. Zhang, W.; Zhu, J.; Ang, H. X.; Wang, H.; Tan, H.; Yang, D.; Xu, C.; Xiao, N.; Li, B.; Liu, W. L.; Wang, X.; Hng, H. H.; Yan, Q. *ACS Appl. Mater. Interfaces* **2014**, 6, 7164-7170.
12. Xia, B.; Wu, H. B.; Yan, Y.; Wang, H.; Wang, X. *Small* **2014**, 10, 2336-2339.

Chapter 1

Introduction and Scope of the Thesis

1.1. Introduction

Energy, the driving force of life, has kept the ecosystem running for billions of years. It creates the geography and climate of the world, it makes fire and electricity possible, but it also devastates living animals and plants without any mercy. To against the energy from nature, human beings master the energy from the combustion of fuels. It propels the progress of society to an extraordinary level. Power stations are built to generate electricity from energy; vehicles are manufactured to use power from energy. The entire society benefits from the harness of energy. However, combustion of fuels release gases such as carbon dioxide, carbon monoxide, sulfur dioxide and nitric oxide, they are responsible for environmental problems like global warming and acid rain. To reduce air pollutants, fuel cell technology is highly valued as one of the possible ways. It offers following benefits to us: ¹

i) Fuel cells can convert fuels directly into electricity without combustion, thus theoretically zero greenhouse gas emission can be achieved. This also prevents the release of air pollutants (i.e., carbon monoxide, sulfur dioxide and nitric oxide)

ii) Fuel cells offer the petroleum-free way to generate power. Actually, diverse fuels, such as hydrogen, biomass-based fuels and natural gas can be used in fuel cells. It effectively reduces the consumption of oil.

iii) Fuel cells are friendly to end users. It provides quiet operation environment and requires less maintenance than traditional technologies.

Therefore, several kinds of fuel cells, such as proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC), have been developed for the potential application in consumer electronics (up to 100W), backup power generators (1-5 kW), vehicles (50-125 kW) and centralized power generation (1-200 MW or more). Among these fuel cells, PEMFC has attracted more intense attention. The low operating temperature and exceptional power scalability (5W-100kW) make it extremely versatile. It is now the dominant technology in transportation and small stationary power applications.²

To push PEMFC technology to a commercial success, the cost of system should reach to \$30/kW (500,000 units/year).³ However, an investigation projected that the cost of PEMFC was still around \$55/kW when the production was 500,000 units per year at 2013. The cost of catalyst took around 49% in the entire system (Fig.1.1).³ Thus it is especially important to reduce the price of catalyst by improving its catalytic activity and efficiency.

Fig.1.1. Breakdown of the 2013 projected PEMFC stack cost at 1,000 and 500,000 units per year.

PEMFC can be divided into several types according to the fuels used. Among these types, direct methanol fuel cell (DMFC) is aimed to replace the batteries for portable devices. Researches of catalysts in DMFC are mainly focused on their activity. As for direct glycerol fuel cell, theoretically it has a higher energy density (6300 Wh L^{-1}). The electro-oxidation of glycerol gives rise to various products, such as glyceric acid, hydroxypyruvic acid, mesoxalic acid and tartronic acid. To achieve its maximum value, the selectivity towards specific valuable chemical during the electro-oxidation of glycerol is also required. In other words, both the selectivity and activity are required for catalysts used in direct glycerol fuel cell.

1.2. Scope of the thesis

Study in this thesis is mainly to develop metal nanoparticles (NPs) on graphene based support and apply these composites as catalysts in the direct methanol fuel cell and direct glycerol fuel cell. In the study of direct methanol fuel cell, our major purpose is to promote the activity of catalysts. In the study of direct glycerol fuel cell, the aim is to promote the selectivity of catalysts towards specific chemicals while keeping or promoting the activity. These purposes are achieved by tuning properties of graphene based supports.

Specifically, in the work of methanol electro-oxidation, we loaded Pt NPs on graphene surface which the latter was obtained through ultrasonication-assisted exfoliation strategy. The electrocatalytic activity of catalyst was studied. In the work of glycerol electro-oxidation, Au NPs and Pd NPs are supported on graphene based materials through their interactions with extended polymer chains and nitrogen atoms, respectively. Their selectivity in glycerol electro-oxidation was investigated.

The detailed scope of thesis is shown as the following:

Chapter 1 gives a short introduction about the background of fuels, the importance of fuel cell, the role of PEMFC in fuel cells, the reason why study catalysts and the objective of our research work. Moreover, the scope of this thesis is also introduced.

Chapter 2 gives an introduction of fuel cell, different types of PEMFC including direct methanol fuel cell, direct formic acid fuel cell and direct glycerol fuel cell and also oxygen reduction reaction. Then we give a literature review of various carbon supports used in PEMFC, like carbon black, carbon nanofiber, mesoporous carbon, carbon nanotubes and graphene. Among these materials, a systematic review of graphene from synthesis methods to different types of graphene based materials is presented.

In chapter 3, we first obtain the aqueous dispersions of graphene through the exfoliation of graphite by a series of water-soluble polymers under ultrasonication. Then Pt nanoparticles are loaded on polyvinyl pyrrolidone (PVP)/graphene surface and used as catalysts in methanol electro-oxidation.

In this work, we present that the interaction between polymer and graphene surface determines the layer distribution of graphene. Compared to polymers such as poly(4-vinylpyridine), polyvinyl pyrrolidone and polyvinyl alcohol, poly(3-aminobenzoic acid) is more favoured to exfoliate graphite into thin layer graphene. The strongest interaction between poly(3-aminobenzoic acid) and graphene is the crucial factor. Moreover, Pt NPs on PVP/graphene show a better electrocatalytic performance than Pt NPs on PVP/rGO in methanol oxidation. The better conductivity of PVP/graphene is believed to play an important role. Furthermore, it is revealed that poly(4-vinylpyridine)/graphene shows stable and reversible response to pH. This demonstrates that the as-synthesized polymer/graphene has the potential to be used in various fields, for example, biosensor as demonstrated in this work.

In chapter 4, Au nanoparticles (NPs) supported on various supports with different metal support interaction are synthesized and tested for glycerol electro-oxidation. Through off-line HPLC analysis, it is found that Au NPs supported on extended poly(4-vinylpyridine) functionalized graphene (Au-P4P/G) shows a higher mass current density and better selectivity for three carbon products than those on carbon black, P4P functionalized reduced graphene oxide (Au-P4P/rGO) and poly(m-aminophenol) (PmAP) wrapped graphene (Au-PmAP/G), e.g., the glyceric acid production reaches 68.6% at 0.2 V (vs. HgO/Hg), and the ratio between three carbon products and other products is 4.92 for Au-P4P/G compared with 0.96 of Au-CB. XPS results indicate that lower d-band center in Au nanoparticles induces higher three carbon selectivity and the changed adsorption ability for oxygen-containing groups might be the main reason.

In chapter 5, a hybrid support consisting of nitrogen doped graphitic carbon and graphene (CN_x/G) is prepared by annealing polypyrrole/GO at 800 °C. Pd nanoparticles (NPs) are then loaded onto the support by the microwave-polyol method. Pd- CN_x/G is used as a catalyst for glycerol electro-oxidation. Through the comparison with Pd NPs on carbon black (CB), it is revealed that Pd NPs on support which containing nitrogen atoms can promote selectivity towards three carbon products as well as increase activity for glycerol electro-oxidation. Moreover, CN_x/G shows higher surface area than CN_x annealed from wire structured polypyrrole. It causes smaller size of Pd NPs on CN_x/G . This further increases its selectivity towards three carbon products.

In chapter 6, we anneal Co-PPy/GO at high temperature and studied the ORR activity of Co- CN_x/rGO with different weight ratio between PPy and GO. The doping of cobalt into CN_x/rGO shows an obvious promotion of electron transfer number compared with CN_x/rGO , especially for Co- CN_x/rGO (1:1). The electron transfer number reaches to 3.2 even in the kinetic/diffusion mixed region. The existence of GO greatly contributes to the good ORR activity. We also reveal that wire structure PPy provides cobalt a unique environment to form compounds with sulphur during annealing process. The existence of GO and the cobalt sulphur compounds all increase the ORR activity of catalysts.

Chapter 7 summarizes the results and provides the recommendations for future work.

Chapter 2

Literature Review

2.1. Fuel cell

Fuel cell is the device directly converting diverse fuels into electricity. It is more efficient than conventional combustion engine and power plant because it's not limited by Carnot Cycle and the electricity is directly produced through chemical energy. Therefore, fuel cell has got the continuous interest and investment in recent 20 years. Till now, fuel cell has shown the potential usage in various fields, such as distributed energy and combined heat and power system, potable power and backup power system.¹

Depending on different electrolytes, fuel cell can be divided into five types (Table 2.1). Different electrolytes mean different reactions occur in fuel cells and they require different operating temperature, which further determines the catalyst chosen. The catalysts and operating temperature, in turn, effect the possible application of different fuel cells.

Table 2.1. Summary of fuel cell type

Type	Electrolyte	Operating Temperature/ °C	Electrochemical Reactions
Proton Exchange Membrane Fuel Cell (PEMFC)	Solid organic polymer poly-perfluorosulfonic acid	50-100	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Alkaline Fuel Cell (AFC)	Aqueous solution of potassium hydroxide (soaked in matrix)	90-100	Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Phosphoric Acid Fuel Cell (PAFC)	Liquid phosphoric acid (soaked in matrix)	150-200	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
Molten Carbonate Fuel Cell (MCFC)	Liquid solution of lithium, sodium or potassium carbonates (soaked in matrix)	650-700	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

			Cell: $\text{H}_2 + \frac{1}{2}\text{O}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2$
Solid Oxide Fuel Cell (SOFC)	Solid zirconium oxide stabilized by small amount of yttria	700-1000	Anode: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ Cathode: $\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ Cell: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

Among these fuel cells, fuel cell systems with AFC and PAFC stacks have shown the good reliability and high efficiency. Because both hydrogen and carbon monoxide are electrochemically oxidized, the induced thermal integration/management design produces high system efficiency (~50%).⁴ This makes these fuel cells the best candidate for stationary power generation. However, further decrement of the capital cost has met severe problems, which causes the limited application of AFC and PAFC in the future.⁴ In PEMFC, because Pt is used as the catalyst, it possess the short start-up time, high efficiency (twice than combustion engine) and good power density at low temperature, which make it the competitive candidate for vehicles and power generation.⁵

2.2. Proton exchange membrane fuel cell (PEMFC)

Report shows that PEMFC has dominated the fuel cell market with higher unit shipment because of its versatility.² The typical structure of PEMFC is shown in Fig.2.1. The proton exchange membrane (PEM) acts the role to transport protons from anode to cathode and separate the gas. Catalyst layer (CL) consists of binder and carbon supported Pt or Pt alloys. The electrochemical reaction mainly occurs inside this layer. The diffusion layer (DL) is mainly the PTFE-hydrophobized carbon paper or cloth. It's used to transport the reactant gas and flow water out. Moreover, the bipolar plate (BPP) containing metal plate or carbon plate is used as the current collector, commonly it can't be permeated by gas. When hydrogen flows through the flow field which is between BPP and DL at anode, it's oxidized, then the produced H^+ transports across PEM to anticipate the reduction of oxygen at cathode. The electron produced in the process is collected through BPP and then the power is generated.⁶

Fig.2.1. The structure of PEMFC and the way it works. Reprinted with permission from ref 6. Copyright Elsevier.

2.2.1. Direct methanol fuel cell (DMFC)

PEMFCs are also aimed to replace the batteries for portable devices. However, hydrogen is difficult to transport, thus DMFC which using methanol to replace hydrogen is proposed. In the acid environment of DMFC, the complete electro-oxidation of methanol to carbon dioxide involves the transfer of six electrons (Eq. 1), so the oxidation reaction rate in DMFC is far slower than PEMFC.⁷

From a general perspective, Pt-based catalyst is usually used in the electro-oxidation of low weight organic molecules (including methanol). The entire process usually involves two steps, one is hydrogenation step and another is chemisorption of CO. Take methanol as example, firstly a sequence of dehydrogenation steps occurs as the following:⁷

During this process, several intermediates (H_2CO , HCOOH , et al.) are produced.⁸

Without the promoting element, the discharge of H_2O also occurs at high anodic overpotential on the Pt surface. It gives rise to the formation of Pt-OH.

Finally the absorbed Pt-CO will react with the neighboring Pt-OH and give CO_2 .

Studies have shown that the discharge of H_2O on Pt surface (potential is about 0.7 V) is involved into the rate determining step.^{7, 9} Therefore, catalyst which can low the water discharging potential would has better methanol oxidation performance.

2.2.2. Direct formic acid fuel cell (DFAFC)

Similar with DMFC, DFAFC is proposed to be used for portable devices. Because methanol in DMFC is easy to crossover the Nafion[®] membrane, the concentration of methanol is usually limited at about 1-2 M. This limits the efficiency of DMFC.¹⁰ On the contrary, formic acid shows lower crossover through Nafion[®] membrane, the performance of DFAFC can surpass DMFC at high formic acid concentration although theoretically the volumetric energy density of formic acid is only 2104 Wh L⁻¹ (for methanol, it is 4900 Wh L⁻¹).

The electro-oxidation of formic acid has two pathways. One is dehydrogenation path (or direct oxidation path) and another one is dehydration path. The dehydrogenation path is the way completely oxidizing the formic acid to CO_2 without forming the intermediate CO (Eq.8).^{10, 11}

In the dehydration path, formic acid firstly absorbs on the surface of Pt to produce the intermediate absorbed CO. Then it's oxidized to CO_2 end product (Eq.9).^{10, 11}

Because the dehydration path requires higher potential to oxidize absorbed CO to form CO_2 , the catalyst will be poisoned and the overall cell efficiency is

low. Catalyst which has better selectivity for dehydrogenation path is more favored in formic acid oxidation.

2.2.3. Direct glycerol fuel cell

To overcome the drawbacks of methanol in DMFC, several higher molecular weight alcohols and polyalcohols have been proposed as the fuel in fuel cell. Due to their low toxicity and high specific energy, ethanol, ethylene glycol, glycerol and 1, 2-propanediol is commonly used. Among these fuels, glycerol has the very high theoretical volumetric energy density of 6300 Wh L^{-1} .^{12, 13} Moreover, as the by-product of biodiesel production, the large quantity and cheap price of glycerol bring it great advantage in industry used as the crude material.¹⁴⁻¹⁸ Therefore, studies in glycerol electro-oxidation have been increased in recent years.

Since glycerol contains three hydroxyl groups, its electro-oxidation gives various products, such as glyceric acid, hydroxypyruvic acid, mesoxalic acid, tartronic acid, and other one or two carbon products *via* C-C bond breaking.¹⁹⁻²¹ The electro-oxidation process of glycerol is more complex than other alcohols containing one or two hydroxyl groups, it can be influenced by pH, temperature, catalyst loading and even system flow.²²⁻²⁷ The research group of Koper et al. combined online high-performance liquid chromatography (HPLC) with online electrochemical mass spectrometry (OLEMS) technique and studied the glycerol oxidation mechanism on Au and Pt surface in the half cell.²⁰

Fig.2.2. The glycerol oxidation mechanism on Au and Pt electrode in alkaline solution. Reprinted with permission from ref 20. Copyright John Wiley and Sons.

It's revealed that glycerol has different oxidation route on Au and Pt electrode in alkaline solution (Fig.2.2). On Pt surface, glycerol is firstly oxidized into glyceraldehyde then glyceric acid through the two-electron transfer step. On Au surface, glyceraldehyde is unstable due to the high overpotential; glycerol is directly oxidized into glyceric acid. In the next two-electron transfer step on both electrodes, glyceric acid is oxidized into glycolic acid and formic acid in despite that this process will be deactivated on Pt surface when potential close to 0.9 V. Glycolic acid and glyceric acid are further oxidized on Pt surface into oxalic acid and tartronic acid. On Au electrode, it's reported that oxalic acid and tartronic acid can hardly be obtained. However, from the study of our and other groups, increasing the Au loading and changing work conditions can also promote the production of oxalic acid and tartronic acid on Au surface.^{23, 26} On Pt electrode, glycerol can be also oxidized into dihydroxyacetone and then hydroxypyruvic acid and finally ketomalonic acid. Moreover, carbonate can be oxidized from formic acid on Pt surface.²⁸ We also have revealed that carbonate may be produced on Au when it has lower d-band center.²⁶

Besides Au and Pt, Pd and its alloy is often used in the glycerol electro-oxidation. The electro-oxidation mechanism of glycerol over Pd is much similar to that on Au,²⁹ except that glycolic acid may be oxidized into formic acid on Pd surface.

2.2.4. Oxygen reduction reaction (ORR)

Apart from the reaction on the anode in low temperature fuel cell, oxygen reduction reaction on cathode is also widely studied. The performance of catalyst on cathode is the key factor which influences the performance of the entire fuel cell because of its sluggish kinetics.¹¹

The entire ORR process includes two overall pathways (Table 2.2).³⁰

Table 2.2. Thermodynamic electrode potentials of ORR in acidic and alkaline medium.^{31, 32}

Acidic aqueous solution	Alkaline aqueous solution
Path 1: Direct 4-electron pathway $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0 = 1.229V$	Path 1: Direct 4-electron pathway $O_2 + H_2O + 4e^- \rightarrow 4OH^-$ $E^0 = 0.401V$
Path 2: Peroxide pathway $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	Path 2: Peroxide pathway $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$

$E^{\circ} = 0.70V$ $H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$ $E^{\circ} = 1.76V$ or $2H_2O_2 \rightarrow 2H_2O + O_2$	$E^{\circ} = -0.065V$ $HO_2^{-} + H_2O + 2e^{-} \rightarrow 3OH^{-}$ $E^{\circ} = 0.867V$
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Depending on the electrode, catalyst and electrolytes, the intermediates in ORR is very different. The most extensively studied catalyst in ORR is Pt. Although both the 4-electron pathway and 2-electron pathway (peroxide pathway) occur on the surface of Pt, the 4-electron pathway takes the predominant role. Pt and Pt-based catalyst in ORR help to inhibit the formation of adsorbed oxygenated species at potential over 0.8 V, which makes the ORR more favourable of the 4-electron pathway.³³ However, catalyst with higher electrocatalytic activity is still required in ORR. For ORR in the cathode of DMFC, another problem should be considered is the crossover of methanol from the anode. Novel metal or non-metal catalysts with high methanol tolerance in cathode are highly required.

2.3. Support in the fuel cell

Reported from U.S. department of energy (DOE), improving the durability and performance, reducing the cost are still the primary objectives of fuel cell research.¹ The final target of the cost-reduction is \$30/kW at 2017. In order to reduce the cost and improve the durability, developing catalyst with higher performance is highly required. It's well known that the support can greatly promote the stability and activity of catalyst compared with catalyst without support, thus a great number of works are focusing on developing novel support with high conductivity and porosity. Till now, various support, such as conventional carbon black, carbon nanotubes, carbon nanofibers, and non-carbonaceous materials, have been developed. Here we mainly focus our scope on the carbon materials.

2.3.1. Carbon black

Carbon black usually is produced by heating petroleum products under the inert, oxygen-free environment. It's a form of amorphous carbon with the near-spherical structure. The size of carbon black is usually below 250 nm, and it contains several graphite-like layers which is stacking in parallel.³⁴ The interlayer spacing is around 0.35-0.38 nm.³⁵ The specific particle size and

distribution is different with the source and treating process. Commonly, carbon black contains both the high surface area and good conductivity. For example, the surface area and conductivity (packing fraction 0.3) of commonly used Vulcan XC-72R (Cabot Corp) is 245 m²/g and 4.5 S/cm, respectively.³⁶ The surface area and conductivity of Black Pearl 2000 (BP2000, Cabot Corp) is 1635 m²/g and 2.2 S/cm, respectively.³⁶ Moreover, carbon black is easily available and can be mass produced. These advantages make it the most commonly used catalyst support.

However, carbon black still suffers several problems: (1) The organically bound unfavourable in carbon black.³⁷ (2) The inaccessible pores are staying in carbon black, which reduced the catalytic activity. Because the size of Nafion[®] micelles is larger than 40 nm, metal nanoparticles (NPs) anchored inside the pore which is below 40 nm will not access to Nafion[®] and the activity will decrease.³⁷ (3) Carbon black is thermochemically instable.³⁷ Catalyzed by the Pt, carbon is very easy to be oxidized (Eq.10).³⁸ When the potential is greater than 1.4 V, the reaction rate is very appreciable.

Fig.2.3. The schematic drawings of the degradation of PtRu catalyst on carbon support. Reprinted with permission from ref 38. Copyright Elsevier.

As shown in Fig.2.3, carbon can be oxidized into CO₂. It will cause the losing of metal nanoparticle on surface because of the decrement of support, further decreasing the catalyst performance. Therefore, other more robust carbon supports or functionalized carbon support are proposed.³⁹

2.3.2. Carbon nanofiber

CNFs are materials produced by decomposing selected hydrocarbons over metal particles.⁴⁰ The first application of carbon nanofiber as support is proposed by Rodriguez et al.⁴¹ Compared with active carbon and γ -alumina used as support, the carbon nanofiber growing on Fe-Cu (7:3) particles showed better catalytic activity towards the hydrogenation of ethylene. The methanol oxidation of platinum on different types of GNF was studied by Steigerwalt et al.⁴² Depending on different metal catalyst and precursors, three common types of GNFs (Fig.2.4), “platelet”, “ribbon” and “herring-bone”(or “stacked-cup”), were obtained and studied. Pt supported on “platelet” and “ribbon” CNFs showed the much higher methanol oxidation current than that on carbon black. Another similar study showed Pt-Ru supported on “herring-bone” GNF showed ~50% enhanced performance compared with Pt-Ru without support.⁴³ These studies showed that the crystallographic orientation in GNF played the very important role to prevent the CO poisoning. In the ORR study, the “platelet” GNFs exhibited the best ORR activity compared with activated carbon and “herring” bone GNFs because the higher ratio of edge atoms to basal atoms.⁴⁴

Fig.2.4. The schematic drawings of a) “platelet”, b) “ribbon”, c) “herring-bone” structured CNFs. Reprinted with permission from ref 43. Copyright American Chemical Society.

Apart from conventional acid treated CNFs, small molecule (1-Aminopyrene, 1-AP) functionalized CNFs also shows the good property as support.⁴⁵ It was revealed that PtRu NPs could be better dispersed onto the surface of 1-AP functionalized CNFs, which causing the better catalytic activity in methanol

oxidation. Recently, the novel hybrid structure of Pt/CNFs with Nafion® was prepared by filtration.⁴⁵ Due to the high aspect ratio which allowing the formation of continuous conducting network, it showed the improved performance in the test.

2.3.3. Mesoporous carbon (MC)

The mesoporous carbon is referred to as carbon materials with pores size distribution among 2-50 nm.⁴⁶ As we have mentioned above, carbon materials with micropores (< 2nm) is not preferred in PEMFC because of the size of Nafion® micelles. For macroporous carbon material, although the mass transport efficiency is improved compared with microporous carbon material, the surface area is much lower if considering the low area-to-volume ratio.⁴⁷ Therefore, mesoporous carbon materials are preferred in PEMFC because it can provide both good mass transport efficiency and high surface area. Moreover, mesoporous carbon materials are also promising for the application in electrochemical double-layer capacitor, lithium batteries, et al. According to the structure and morphology, mesoporous carbon (MC) can be divided into two types, one is ordered mesoporous carbon (OMC) and another is disordered mesoporous carbon (DOMC). Because DOMC usually contains a great number of isolated or irregularly interconnected pores, therefore, OMC is more preferred.^{47, 48}

Joo et al. firstly reported the application of OMC as the support for ORR (Fig.2.5a, b).⁴⁹ OMC was obtained by using ordered mesoporous silica as the templates. The OMC supported Pt catalyst showed increased catalytic activity compared with Pt on carbon black (Fig.2.5c, d). Studies have showed that the activity of MC supported catalyst was influenced by many factors. For example, the pore morphology can affect the catalytic activity.⁵⁰ Song et al. have compared the effect of using OMC and wormhole-like mesoporous carbon (WMC) as support. Although these two MCs showed the similar pore characteristics, Pt/OMC exhibited the superior catalytic activity than Pt/WMC. Moreover, the pore size,⁵¹ porosity⁵² and even the catalyst size⁵³ could greatly influence the activity. Evidently, OMCs have attracted enormous attention because they can provide improved mass transport efficiency.

Fig.2.5. a) TEM image of OCM and corresponding Fourier diffraction pattern. b) TEM image of Pt on OCM. c) The catalytic activity in amperes per gram of Pt at 0.9V (vs. NHE) and the rotating speed is 10,000 r.p.m. d) The activity-potential relation for Pt/OCM and Pt/carbon black at 10,000 r.p.m. with the scan rate of 50 mV S⁻¹. Reprinted with permission from ref 49. Copyright Nature Publishing Group.

2.3.4. Carbon nanotubes (CNTs)

The structure of CNTs synthesized through arc-discharge evaporation was firstly confirmed by Ijima.⁵⁴ It provided a breakthrough in the carbon nanomaterial. CNTs are formed by rolling up several sheets of sp² carbon atoms which are arranged in hexagonal structure. Usually CNTs are classified into single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).⁵⁵ SWCNTs are formed by a single sheet of graphene while MWCNTs are formed by several layers of graphene. The interlayer distance among graphene layers in MWCNTs is about 0.34 nm. Both SWCNTs and MWCNTs have been used as the support in PEMFC.^{56, 57} Che et al. obtained PtRu NPs anchored on MWCNTs membrane through high temperature annealing (Fig.2.6a), the membrane showed the strong methanol oxidation peaks in CV test (Fig.2.6b).⁵⁶ To date, because the lower cost, better availability

and easier dispersibility, MWCNTs have been predominantly used as support in PEMFC.

Fig.2.6. a) The transmission electron micrograph (TEM) of PtRu nanoparticles supported on CNTs, b) cyclic voltammograms of PtRu/CNTs for methanol oxidation (2 M methanol in 1M H₂SO₄). Reprinted with permission from ref 56. Copyright Nature Publishing Group.

Till now, various methods, such as impregnation,⁵⁸ polyol or microwave assisted polyol,^{59, 60} and electrochemical deposition,^{61, 62} have been applied to obtain CNTs supported NPs. The major problem for metal NPs/CNTs catalyst is the functionalization of CNTs. Because the surface of CNT is hydrophobic and chemical inert, it's difficult to distribute metal NPs homogeneously. Therefore, functionalization the surface of CNTs is indispensable. The very widely used way is introducing the oxygen group to the CNTs surface. Oxidants, such as HNO₃,⁶³ KMNO₄,⁶⁴ OsO₄,⁶⁵ and RuO₄,⁶⁶ all can be used. Among these, H₂SO₄-HNO₃ mixture is the most effective oxidants.⁶⁷ Pt and Pt alloys homogeneously deposited on the oxidized CNTs surface have been reported.⁶⁷⁻⁶⁹ Park et al. showed that Pt NPs on COOH-functionalized CNTs (1.8% COOH group) had slower degradation and higher corrosion resistance compared with XC-72.⁷⁰

Apart from covalent functionalization, noncovalent methods are also reported. Small molecules and polyelectrolyte have been used to functionalize CNTs.⁷¹ Different with covalent functionalization, noncovalent methods can avoid the structure damage of CNTs, thus keeping the conductivity better. This further promotes the catalytic activity of metal NPs on CNTs.

2.3.5. Graphene

Graphene is a kind of nanomaterial with the single sheet of carbon atoms packed in a hexagonal lattice. Former researches have shown graphene possessed many fascinating properties, such as a high surface area,⁷² fast charged carrier mobility,⁷³ high thermal conductivity,⁷³ and strong Young's modulus.⁷⁴ Therefore, graphene has become the very promising material in various fields since it's firstly reported in 2004.⁷⁵ Tremendous studies have focused on different ways to synthesize graphene. To further broaden the application of graphene, metal nanoparticles are used and loaded on its surface. Several different kinds of graphene based materials have been developed. In this part of thesis, we mainly introduce ways synthesizing graphene and types of graphene based materials used as supports.

2.3.5.1. Synthesis methods of graphene

Various preparation methods, such as chemical vapour deposition (CVD),^{76, 77} micro mechanical exfoliation from graphite,^{75, 78} epitaxial growth on insulating surface⁷⁹ and reduction from graphene oxide (GO) suspensions⁸⁰, have been proposed to synthesize graphene.

2.3.5.1.1. Exfoliation and cleavage

The starting materials used in exfoliation and cleavage method can be graphite or graphite intercalation compounds. These materials are stacked by layers of graphene sheets, bonded together with van der Waals force. Exfoliation and cleavage is the way using mechanical or chemical energy to break van der Waals force and separate graphene sheets from these starting materials. The earliest try was conducted by Viculis et al..⁸¹ They used potassium metal to intercalate graphite and then sonicated the intercalated graphite in ethanol solution. This produced the graphitic sheets which further scrolled into carbon nanoscrolls in the solution (Fig.2.7a). The nanoscrolls had the thickness of around 40 nm (Fig.2.7b, c, d). In the following work, Novoselov et al. used mechanical exfoliation to get few-layer graphene.⁷⁵ Specifically, scotch tape was applied to repeatedly peel flakes of graphite off the mesas and got few-layer graphene in the photoresist. After washed with acetone, few-layer graphene were transfer onto a silicon wafer to form films. They exhibited a strong ambipolar electric field effect.

Fig.2.7. a) Schematic of the intercalation/exfoliation process, b) graphitic sheets in the process of scrolling, c) isolated carbon nanoscroll with open ends, d) mass of scrolled materials, representative of the bulk of the sample. Reprinted with permission from ref 81. Copyright the American Association for the Advancement of Science.

Theoretically, high quality graphene can be obtained using this method because few functional groups are introduced into the carbon lattice. Most of works now are focusing on increasing the production and controlling the layer distribution. The exfoliation process always occurs in the solvent system. Hernandez et al. exfoliated graphene from graphite in the solvent of N-methylpyrrolidone (NMP).⁸² The yield of monolayer graphene was around 1wt.%, which could increase to 7-12 wt.% with further processing. Another work from the same group revealed that few-layer graphene could also be obtained in the sodium dodecylbenzene sulfonate (SDBS)/water solution after ultrasonication.⁸³ In other works, Li et al. reported a new route (exfoliation–reintercalation–expansion) to obtain the high quality single-layer graphene (Fig.2.8).⁸⁴ Specifically, expandable graphite was firstly exfoliated by heating to 1000 °C for 60 s (Fig.2.8a). Then the exfoliated graphite was grounded in order to intercalate it with oleum. After inserting tetrabutylammonium hydroxide (TBA) into the oleum-intercalated graphite (Fig.2.8b), the material was sonicated in the DSPE-mPEG contained DMF solution for 60 min and single-layer graphene was produced (Fig.2.8c).

Fig.2.8. Schematic of the exfoliation–reintercalation–expansion process. Reprinted with permission from ref 84. Copyright Nature Publishing Group.

Apart from the exfoliation in solvent system, solid phase exfoliation can also produce graphene. The commonly used way is ball milling. Lin et al. produced the graphene-sulfur composite by ball milling expandable graphite with sulphur.⁸⁵ It exhibited an excellent electrochemical behaviour for lithium-sulfur batteries.

2.3.5.1.2. Chemical vapor deposition (CVD)

Apart from exfoliation and cleavage, CVD can also produce high quality graphene. It has been the most promising way for large-scale production of single and few layer graphene.

The first work using CVD to synthesis graphene was reported by Somani et al..⁸⁶ In their work, camphor was evaporated and used as the precursor. After pyrolyzed at 700-850 °C, graphene with thickness of about 20 layers was obtained on Ni sheet. In the work of Obraztsov et al., a mixture of H₂ and CH₄ was first activated by a DC discharge.⁸⁷ Then the mixture was deposited on the surface of Ni at low pressure and high temperature. Graphene with a thickness of 1.5 ± 0.5 nm could be obtained. The following work of Yu et al. exhibited that the thickness of graphene synthesized from CVD could be controlled.⁸⁸ A segregation process was reported (Fig.2.9). Hydrocarbon molecules first

decomposed at the Ni surface and diffused into the metal, the concentration of carbon decreased exponentially from the surface into the bulk. Then during the cooling process, different cooling rates led to different segregation behaviour. A medium cooling rate produced high quality graphene. Obraztsov also reported the large scale production of graphene based on similar way.⁸⁹ Kong et al. developed the substrate and found that polycrystalline Ni films could also grow large scale graphene ($\sim 20 \mu\text{m}$).⁹⁰

Fig.2.9. Illustration of carbon segregation at metal surface. Reprinted with permission from ref 88. Copyright Applied Physics Letters.

Apart from Ni substrate, Cu also has been used in the CVD method to fabricate graphene. Li et al. grew graphene on Cu foils at temperature up to 1000°C with the mixture of methane and hydrogen.⁹¹ Due to the low C solubility in Cu and poor C saturation, the source for graphene was mainly from the decomposed CH_4 on Cu surface with minimal diffused carbon inside Cu.⁹¹ When the surface was fully covered with graphene, growth will be terminated. Thus large-area graphene film with predominant single layer was obtained (less than 5%).

2.3.5.1.3. Thermal decomposition on SiC and other substrate

Graphene produced through ultrahigh vacuum (UHV) annealing of SiC surface at high temperature has attracted attention since no transfer is required before processing devices.⁹² The carbide is decomposed at high temperature

under UHV. After silicon atoms sublime from the surface of substrate, carbon atoms left rearrange into the graphene layers.⁹³ By using this method, Berger et al. found ultrathin graphite with several monolayers was formed.^{79, 94} After using the nanolithography method, the fabricated graphene layer showed the promising transport properties.

The following works in this field focused on improving the synthesis conditions and finding other substrates. To improve severe conditions, Juang et al. coated thin Ni films on the silicon carbide substrate and used it to extract carbon atoms from substrate under rapid heating.⁹⁵ Large-area graphene film was obtained at a temperature of 750°C. Emtsev et al. successfully controlled the growth of graphene at atmospheric pressure in an argon atmosphere.⁹⁶ To find out new substrates, lots of metal materials including Ru(0001) and Co(0001) have been used to grow graphene.^{97, 98}

2.3.5.1.4. Reduced from graphene oxide (GO)

Reducing GO to synthesize graphene is one common used way because of its good reproducibility and scalability. Specifically, graphite is first oxidized into graphene oxide in the presence of strong acid and oxidants. The most classic way preparing GO is developed by Hummers et al, who using KMnO_4 as the oxidants in H_2SO_4 solution.⁸⁰ Hydroxyl group, epoxide groups and minor component of carboxylic or carbonyl groups are produced during the oxidation process.⁹⁹ The oxidation level of GO is controlled by adjusting the reaction conditions. Then graphene is obtained from GO through methods such as chemical reduction,¹⁰⁰ solvothermal reduction¹⁰¹ and thermal annealing reduction.¹⁰² In a typical example, Li et al. reduced GO sheets under basic condition (pH=10) by hydrazine (Fig.2.10). The negatively charged carboxylate groups on graphene surface kept the dispersion stable.¹⁰³

Fig.2.10. Schematic of the chemical route to synthesize the aqueous graphene dispersion. Reprinted with permission from ref 103. Copyright Nature Publishing Group.

2.3.5.2. Surface functionalized graphene as support

For pristine graphene used in PEMFC, similar with CNT, the inert and hydrophobic surface is very unfavourable to support NPs. To overcome this problem, GO oxidized from graphite is preferred to be used as the starting material because of the functional groups (hydroxyl group, carboxylic group, epoxide group) on surface. However, since GO itself is electrical insulating and conductivity is very poor, further reducing it into reduced graphene oxide (rGO) is usually required in order to improve the conductivity of support. By mixing Pt salt with rGO powder in ethanol and annealing powder at 400 °C, Yoo et al. loaded Pt clusters onto rGO surface.¹⁰⁴ The synthesized catalyst showed a characteristic CO oxidation peak. However, due to the lack of functional groups, it was revealed that the size distribution of Pt NPs was larger than Pt on carbon black. Therefore, several functionalization methods have been developed to load nanoparticles onto the surface.

(1) Because rGO lacks necessary amount of functional groups to keep it stable during the reduction process, aggregation often happens after high extent of reduction. It drastically decreases the surface area of support. One common used way is adding stabilizer during the reduction process. This also provides necessary anchor points for nanoparticles. Stankovich et al. firstly used poly(sodium 4-styrenesulfonate) (PSS) to functionalize rGO when N_2H_4 was used as reductant.¹⁰⁵ In the work of Guo et al., they functionalized rGO with polyvinylpyrrolidone (PVP) during the reduction process. Then Pt-on-Pd bimetallic nanodendrites were well-dispersed on the surface of PVP/rGO (Fig.2.11a). The catalyst showed much better performance than commercial Pt on carbon black (Fig.2.11b).¹⁰⁶

Fig.2.11. a) The TEM image of Pt/Pd on PVP/graphene, b) the CVs of platinum black (trace a), E-TEK (trace b) and Pt/Pd on PVP/graphene (trace c) on glassy carbon electrode in

aqueous solution containing 0.5 M H_2SO_4 and 1 M methanol. Reprinted with permission from ref 106. Copyright American Chemical Society.

In some cases, GO can also be functionalized by solvent or its decomposition products at high temperature. Ai et al. revealed that GO was reduced by DMF at 153 °C due to the strong reducibility of released CO (Fig.2.12).¹⁰⁷ DMF acted as the stabilizer to prevent the agglomeration of rGO. In the following work, Guo et al. synthesized FePt NPs and loaded NPs on this kind of support.¹⁰⁸ FePt/rGO exhibited a much better ORR behaviour than FePt NPs on carbon black.

Fig.2.12. Schematic illustration of the preparation of rGO sheets. Reprinted with permission from ref 107. Copyright Royal Society of Chemistry.

(2) Functionalization of rGO can be achieved by mixing medium-extent reduced rGO with small molecules or polyelectrolytes. This will introduce functional groups onto rGO and make rGO stable. After that, metal NPs can be deposited on the surface of rGO. For example, Li et al. firstly reduced GO with hydrazine hydrate (N_2H_4) at 100 °C, then rGO was functionalized with Keggin-type heteropolyanions of molybdenum (Pmo_{12}) and PtRu NPs were deposited.¹⁰⁹ It showed the better methanol oxidation performance than PtRu on graphene. Choi et al. prepared rGO through annealing GO at 830 °C, then Pt NPs were anchored on the surface through the interaction with residual functional groups¹⁰². Better performance was obtained compared with Pt/C.

(3) In the third way, GO is first mixed with metal salt in solvent (typically ethylene glycol). After heating, metal nanoparticles form on the surface of GO. This prevents the restacking of rGO in solvent. What's more, formed metal NPs play a pivotal role in catalytic reduction of graphene oxide with ethylene glycol.

Xu et al. synthesized Pt/rGO composite in water-ethylene glycol system.¹¹⁰ The as synthesized catalyst showed the potential application in DMFC. Guo et al. synthesized Pt/rGO with the similar method and found Pt/rGO improved the detection limit for H₂O₂ and trinitrotoluene (TNT).¹¹¹

2.3.5.3. Heteroatoms doped graphene as support

Apart from functionalization, doping graphene with heteroatoms has also been used to tailor the graphene property.¹¹² Due to the introduction of anchor points, metal NPs can be loaded on the surface. Among various heteroatoms, nitrogen is most often used. Methods such as CVD, solvothermal and plasma treatment have been applied. Qu et al.¹¹³ synthesized N-graphene (NG) by CVD method and used it as the metal-free catalyst for ORR. Compared with 20% Pt/C, the N-graphene exhibited 3 times higher current density (Fig.2.13a). They also observed the one-step four-electron reduction pathway on cathode. Moreover, NG showed an excellent stability and the good tolerance toward methanol and CO (Fig.2.13b, c, d). These properties indicated the as-synthesized NG could be a promising material used for ORR. In another work, it's observed that the dual doping (N and S) could be used to improve the ORR activity compared with graphene only doped with N.¹¹⁴

Fig.2.13. a) Oxygen reduction voltammogram of graphene, 20% Pt/C and NG. Electrode rotating rate: 1000 rpm. Scan rate: 0.01 V/s. b) Current density-time chronoamperometric

responses of Pt/C and NG obtained at -0.4 V in air saturated solution, the array indicated the addition of 2% (w/w) methanol. c) Current-time chronoamperometric response of Pt/C and NG to CO. d) Cyclic voltammograms of NG before and after a continuous potentiodynamic swept for 200000 cycles. Scan rate: 0.1 V/s. Reprinted with permission from ref 113. Copyright American Chemical Society.

The role of nitrogen atoms in catalytic application has been studied for several years. Former studies reported that carbon atoms adjacent to the nitrogen atoms become the catalytic active sites because of the positive charge density,^{115,116} another recent study showed the pyridinic N located at the edge of graphene could bond with oxygen directly through the lone pair electrons.¹¹⁷ These studies indicate that nitrogen atoms can directly participate into the reaction or by altering the property of adjacent carbon atoms. However, the relationship between the catalytic activity and the nitrogen content and nitrogen species is still unclear. Taking ORR as an example, former study of N-CNTs showed both graphitic^{118,119} and pyridinic^{120,121} nitrogen had the dominant effect for the ORR activity. Moreover, Luo et al¹²² obtained NG with only the pyridinic nitrogen. It was showed the NG possessing higher nitrogen content (16 at.%) exhibited poorer ORR activity than which possessing lower nitrogen content (2.2 at.%). Optimal nitrogen content might be required for the highest ORR activity.

N-graphene has been used as the support to anchor nanoparticles or nanoplatelets for various applications. For example, Pt/N-graphene composites were used as catalysts in the fuel cell.^{123,115} It was claimed that Pt nanoparticles dispersed better on the surface of N-graphene with the existence of N atoms in carbon lattice.¹¹⁵ Besides, the conductivity of N-graphene was improved at high temperature (800°C). These two factors made Pt/N-graphene exhibit high electrocatalytic activity towards methanol oxidation. Meng et al. incorporated p-type MoS₂ nanoplatelets into n-type N-graphene. It revealed that the composite greatly increased the solar hydrogen production compared with MoS₂ and MoS₂ on rGO.¹²⁴ Nanoscale p-n junction induced from the hybrid structure was believed to be the critical factor as it facilitated charge generation and migration while suppressed charge recombination.

2.3.5.3. Three-dimensional (3D) graphene as support

Compared to 2D graphene, 3D structure provides much more pores and thus increases the mass transfer efficiency in reactions. A large number of works have been dedicated into this field. One commonly used way to synthesize 3D

graphene is by template-directed CVD. Typically, graphene is first precipitated on the surface of 3D Ni foam through CVD, then 3D graphene is obtained by Ni etching.¹²⁵ Another way is hydrothermal method.¹²⁶ GO is self-assembled into 3D structure in the hydrothermal condition with or without additives. The fabricated 3D graphene can be used to deposit metal NPs for various applications. For instance, Sattayasamitsathit et al. electrodeposited various metal NPs on 3D graphene, it showed the enhanced electrocatalytic activity.¹²⁷

Metal NPs/3D-graphene hybrid composites can also be synthesized in one step. Cong et al. obtained Fe_xO_y /3D-graphene through the reduction of GO sheets by ferrous ion under the synergistic effects (Fig.2.14).¹²⁸ The type of iron oxide could be controlled by adjusting pH value. Controlling pH at low value produced α - FeOOH nanorods while at high value generated magnetic Fe_3O_4 NPs into the 3D graphene. These composites proved their efficiency as adsorbents for the removal of pollutants from waste waters.

Fig.2.14. Schematic illustration of the formation of iron oxide/graphene hydrogels. Reprinted with permission from ref 128. Copyright American Chemical Society.

Wu et al. hydrothermally treated aqueous GO solution with iron acetate at the presence of polypyrrole.¹²⁹ Fe_3O_4 NPs were grown inside the 3D graphene during hydrothermal treatment. After freeze-dried and high temperature annealed (600°C), Fe_3O_4 NPs on nitrogen doped 3D graphene ($\text{Fe}_3\text{O}_4/\text{N-3D-G}$) were obtained (Fig.2.15a). The combination of Fe_3O_4 NPs with 3D NG exhibited higher current density than Fe_3O_4 NPs anchored on 2D NG ($\text{Fe}_3\text{O}_4/\text{N-GS}$) (Fig.2.15b). It showed the potential application in PEMFC for non-precious metal catalyst.

Fig.2.15. a) The SEM image of Fe₃O₄/N-Gas, b) Oxygen reduction voltammogram of Fe₃O₄/N-Gas, Fe₃O₄/ N-GSs and Fe₃O₄/ N-CB at 1600rpm in O₂ saturated 0.1M KOH electrolyte. Reprinted with permission from ref 129. Copyright American Chemical Society.

Chapter 3

Water-Soluble Polymer Exfoliated Graphene: as Catalyst

Support and Sensor*

3.1. Introduction

Liquid phase exfoliation from graphene oxide followed by reduction to reduced graphene oxide (rGO) has been one of the most commonly used approaches for large scale production of graphene.¹³⁰ Unfortunately, the conductivity of the rGO is significantly compromised because of the defects or even sp^3 characteristics remaining in rGO after the reduction.⁸² Thus, with the ability to preserve the pristine graphene structure and introduce surface functionalization, direct exfoliation from graphite facilitated by certain auxiliary agents is of practical importance for the above mentioned applications.¹³¹⁻¹³⁴

Till now, graphene exfoliated by small molecules (N-methylpyrrodine (NMP),⁸² pyrene derivatives,¹³⁵ et al.) or surfactants¹³⁶ has been well studied. For polymer exfoliated graphene, although several works about exfoliation from expanded graphite were reported,^{134,137} researches about polymer/graphene exfoliated directly from graphite have not gone very deep. The earliest work is graphite exfoliated by polyvinylpyrrodine (PVP) in the aqueous solution, where the pyrrodine group is believed to play a key role, similar to the case of NMP.¹³⁸ Recently a detailed study about graphene exfoliated by a series of water-insoluble polymer in non-polar solvent was reported.¹³⁹ A model is also proposed to predict the exfoliation efficiency of various combination of polymer/solvent in nonpolar system. Compared to nonpolar or other organic solvent, an aqueous solution of exfoliated graphene is always preferred from practical application point of view.

In this chapter, we obtained the aqueous dispersions of graphene which was exfoliated from graphite by a series of water-soluble polymers under ultrasonication. It showed that the water-soluble polymer was the crucial part to help solvent molecules separate interlayer. The stronger interaction between polymer and graphene surface was, the thinner layer distribution could produce. The as-synthesized polymer/graphene exhibited high conductivity and tunable

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surface property. As the result, Pt on polyvinyl pyrrolidone (PVP)/graphene showed the better performance because of the higher conductivity than PVP/reduced graphene oxide (PVP/rGO). By changing to another polymer, poly (4-vinylpyridine)/graphene showed stable and reversible response to pH, and demonstrates its potential for sensor application.

3.2. Materials and methods

3.2.1. Material preparation

All solvents (GC grade) were purchased from Sigma. Graphite (size below 20 μm) and poly (4-vinylpyridine) (P4P, MW=160,000) were purchased from Sigma-Aldrich. polyvinyl pyrrolidone (PVP, MW=8000) is from Acros, polyvinyl alcohol (PVA, MW=11000~31000) was purchased from Alfa Aesar, poly(3-aminobenzoic acid) (PABA) was synthesized according to previous literature procedure.¹⁴⁰

To prepare PVP or PVA functionalized graphene, 0.02 g of polymer was dissolved into 0.8 ml DMSO, followed by the addition of 0.1 g of graphite. After 10 h of ultrasonication, the black residual solution was mixed with 4 ml of DI water and ultrasonicated for 10 min. After overnight, the sediment in the solution was discarded. Then it was further mixed with 20 ml of ethanol and centrifuged at 15000 rpm for 40 min, where the upper solution was discarded. This step was repeated 3 times. Then 20 ml of DI water was added and the mixture was centrifuged at 10000 rpm for 40 min to remove the upper solution and 3000 rpm for 5 min to discard the sediment. This process was repeated 3-4 times. The final black residue was dissolved with appropriate amount of DI water. If graphite was ultrasonicated at the same condition without the presence of polymer, no black solution can be obtained. To prepare P4P and PABA functionalized graphene solution, washing solvent was changed to the diluted HCl solution (pH=2.0) and NaOH aqueous solution (pH=10) respectively, while other parameters were unchanged.

PVP wrapped rGO was synthesized according to the previous literature.¹¹¹ Briefly, 2 g of 2.25 wt.% GO water solution was diluted with DI water into 150 ml, followed by the addition of 0.7 g PVP (MW=8000) and being stirred for over 12 h at room temperature. After that, 60 μl of N_2H_4 (64%-65%) and 0.7 ml of NH_4OH were added and vigorously stirred for 3 min. The mixture then was transferred to the oil bath and stirred at 95 $^\circ\text{C}$ for 2 h. The black colour

dispersion was centrifuged at 12000 rpm for 40 min three times and dissolved into DI water; the final concentration is about 6.22 mg/ml.

To synthesize Pt-PVP/rGO and Pt-PVP/graphene, 0.5 ml of PVP/graphene or PVP/RGO solution was added into 20 ml of EG solution. After $\text{H}_2\text{PtCl}_6/\text{EG}$ solution was added according to the specified loading, the pH was adjusted to 11.5 by NaOH/EG solution. The mixture was placed in a microwave oven for 1 min on medium power. After cooled down to room temperature, the pH of the dispersion was adjusted to 1.5 and then stirred for 12 h. The mixture was centrifuged in water for one time and ethanol for three times, then the product was dissolved in ethanol and stored.

3.2.2. Physicochemical characterization

The morphology was observed by using scanning electron microscopy (SEM) at JEOL JSM6701F and the compositional analysis using Energy-dispersive X-ray spectroscopy (EDX) was performed at JEOL JSM-6700F. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern were obtained by JEOL-2012 with accelerating voltage of 200 KeV. The X-ray diffraction patterns are collected by Bruker D2 Phaser. Thermo gravimetric analysis (TGA) was carried out at SDT Q600 with a temperature ramp rate of 10 °C from 80 to 800 °C under air atmosphere. The Raman spectra were measured by Raman spectroscopy (Renishaw), using He/Ne laser with a wavelength of 514 nm. The atomic force microscope (AFM) images of various samples on mica were collected from MFP-3D-SA (Asylum Research) in AC mode.

3.2.3. Electrochemical characterization

All electrochemical tests were carried out at room temperature in conventional three-electrode cell using Autolab PGSTAT302 potentiostat.

To test the activity of Pt supported on polymer/graphene catalyst, Pt foil and saturated calomel electrode were used as counter and reference electrode, glassy carbon electrode with 5 mm diameter was used as the working electrode. The sample was prepared by mixing catalyst dispersion with 0.05 wt% Nafion solution, and dropping the mixture to the glassy carbon electrode. The final loading on the glassy carbon electrode was 0.02 mg of catalysts (Pt-PVP/rGO or Pt-PVP/graphene) and 5 μl of 0.05% Nafion solution. Before the electrochemical test, 0.5 M H_2SO_4 was purged with nitrogen for 20 min to

remove oxygen. To determine the electrochemical surface area (ECSA) of Pt, the 30th scan in 0.5 M H₂SO₄ was collected. Then ECSA was determined by integrating the hydrogen desorption region after correcting the double-layer charging current, the conversion factor used was 0.21 mC cm⁻²_{Pt}. In the methanol oxidation test, the data were collected after 20 cycles at 50 mV s⁻¹ between 0 to 1 V versus SCE. In the electrochemical impedance spectroscopy (EIS) test, Ag/AgCl (saturated KCl) was used as reference electrode. The supporting solution was prepared by using 5 mM K₃[FeCN₆]/K₄[FeCN₆] (1:1) as redox probe and 0.1 M KCl as supporting electrolyte.

To test the pH responsibility of P4P/graphene, Pt foil and Ag/AgCl (saturated KCl) were used as counter and reference electrode, glassy carbon electrode with 5 mm diameter was used as the working electrode. The as-synthesized P4P/graphene ethanol solution (1.2 mg/ml) was dropped directly to the polished glassy carbon electrode. The final Pt-P4P/graphene loading on the glassy carbon electrode is 0.02 mg. The supporting solution was prepared as follows: Firstly Britton-Robinson buffer solution (10 mM acetic acid, 10 mM boric acid, 10 mM phosphoric acid and appropriate amount of NaOH) was prepared. Then 5 mM K₃[FeCN₆]/K₄[FeCN₆] (1:1) and 0.1 M KCl was dissolved in the buffer solution as redox probe and supporting electrolyte, respectively. Before the test, sample on carbon electrode were immersed in DI water overnight to fully impregnate P4P/graphene.

3.3. Results and discussion

3.3.1. Formation mechanism of polymer/graphene

AFM is used to obtain the height information of synthesized polymer/graphene sheet. The large scale AFM images (Fig.3.1, Fig.3.2a) show that P4P/graphene flakes tend to fold on the surface, indicating the relatively thin thickness of P4P/graphene. This is also confirmed by the TEM image (Fig.3.2c). If lowering the height scale to 4nm (Fig.3.1a), layers with about 0.5nm height can be clearly observed around P4P/graphene sheets. Because P4P/graphene sheets are deposited on mica surface from its aqueous HCl solution and P4P polymer chain would extend in acid environment,¹⁴¹ the layer surrounding P4P/graphene is very likely to be the extended P4P polymer. The free polymer chain of P4P on graphene indicates that it is partially absorbed onto the graphene surface, which agrees with previous research.¹³⁹ Because the thickness of polymer layer adsorbed on the graphene surface is similar with that

of the surrounding polymer layer, we assume that the thickness of absorbed polymer layer is also about 0.5 nm.

Fig.3.1. a) AFM height image of P4P/graphene with the low height scale, the inset shows the height profile along the red line, the layer height is ~ 0.5 nm. b) AFM amplitude image of P4P/graphene deposited on mica surface, scan size 2×2 μm . c) The typical AFM height image used for height statistics.

We then obtained the histogram of the height of P4P/graphene by measuring over 100 graphene sheets (Fig.3.1c). It is found that the lowest height of graphene is about 0.8 nm (Fig.3.2b). Because P4P chains form a polymer layer surrounding graphene, the cross-sectional line we drew in AFM image is over P4P/graphene and the extended polymer layer. The real height of P4P/graphene should include the height of extended polymer layer. Therefore, the real height of P4P/graphene is 1.3 nm which containing two adsorbed polymer layer (~ 0.5 nm) and one graphene layer. The graphene thickness is calculated to be 0.3 nm, corresponding to the single layer graphene. Moreover, the obvious high peak in the height profile (Fig.3.2b) could be ascribed to the condensed polymer or polymer wrapped small carbon dots produced along polymer/graphene, causing the rough surface of P4P/graphene. Furthermore, the crystalline structure of P4P/graphene is revealed by the well-defined diffraction spots in the inner and outer ring in selected area electron diffraction (SAED) pattern (Fig.3.2d). The inner ring comes from the (1100) plane and the outer ring comes from the (1120) plane. The intensity of spots in the inner ring is obviously weaker than that in

the outer ring, which demonstrates that P4P/graphene sheets here are mainly multilayer.⁸² Generally speaking, AFM, TEM and SAED images show that high quality P4P/graphene consisting of both single- and multi- layers can be obtained after graphite is exfoliated by P4P.

Fig.3.2. a) AFM height image of P4P/graphene deposited on mica surface, scan size $2 \times 2 \mu\text{m}$ b) AFM height image of single sheet P4P/graphene, the inset shows the height profile along the red line. c) The TEM image and d) corresponding SAED pattern of P4P/graphene.

Fig.3.3. Typical AFM height images of a) PVA/graphene, c) PVP/graphene and e) PABA/graphene, SEM images of b) PVA/graphene, d) PVP/graphene and f) PABA/graphene.

Apart from P4P, a series of water soluble polymer including PVA, PVP and PABA are also used to exfoliate graphene (Fig.3.3, Fig.3.4a). In the AFM height images of PVP/graphene and PABA/graphene, the thinnest thickness we can obtain is around 1.3 nm (Fig.3.4c, d). Because this height contains two absorbed polymer layer and one graphene layer, the thickness of graphene is around 0.3 nm if assuming the polymer layer is 0.5 nm. Therefore, it is concluded that PVP and PABA can also exfoliate the single layer graphene from graphite. From the larger scale SEM and AFM images (Fig.3.3), thin layer polymer/graphene with several hundred nm size can be obtained.

Fig.3.4. a) The dispersion of polymer/graphene. Among this, PVA/graphene and PVP/graphene are dispersed in DI water, P4P/graphene is dispersed in HCl solution and PABA/graphene is dispersed in NaOH solution. AFM height image of b) PVA/graphene (scan size $\sim 0.5 \times 0.5 \mu\text{m}$) c) PVP/graphene (scan size $\sim 0.65 \times 0.65 \mu\text{m}$) d) PABA/graphene (scan size $\sim 0.6 \times 0.6 \mu\text{m}$), the inset shows the height profile along the red line.

As indicated in previous research,¹³⁹ the concentration of polymer plays a very important role to exfoliate graphite in DMSO. For example, if the concentration of PVP is lowered from 50 mg/mL to 4 mg/mL in DMSO, only small amount of graphene can be dispersed in the solution. When there is no

polymer in DMSO, no apparent black dispersion can be observed after adding water (Fig.3.5).

Fig.3.5. After 0.1 g graphite was ultrasonicated in a) 0.04 g PVA+0.8 ml DMSO b) 0.04 g PVA+0.8 ml DMF c) 0.8 ml DMSO for 4 h, DI water was added and placed for 7 days, then these pictures were taken.

Recently, the group of Coleman et al. developed a model to predict the exfoliation efficiency for polymer/solvent/graphite system.¹³⁹ It's reported that similar Hildebrand solubility parameters (δ) among solvent, polymer and graphite produce the largest concentration of graphene in nonpolar solvent system ($\delta_s \approx \delta_p$ and $\delta_G \approx \delta_p$). However, polar system used in current work seems do not match with this model after considering the large difference between DMSO ($\delta_s = 29.7 \text{ MPa}^{1/2}$)¹⁴² and polymer (PVP, $\delta_p = 25.6 \text{ MPa}^{1/2}$; P4P, $\delta_p = 24.5 \text{ MPa}^{1/2}$).^{142, 143} In the experiment, it's observed that graphite ($\delta_G = 21.25 \text{ MPa}^{1/2}$) can't be efficiently exfoliated by PVA ($\delta_p = 27$)¹⁴⁴ in DMF ($\delta_s = 24.8$)¹⁴² compared with that in DMSO ($\delta_s = 29.7 \text{ MPa}^{1/2}$, Fig.3.5) although DMF and DMSO show the similar ability for interlayer separation.^{145, 146} The reason may be ascribed to the fact that PVA is more favorable to be adsorbed to the surface in DMSO than in DMF if considering the adsorption energy difference;¹³⁹ thus it can provide larger energy barrier which is helpful for small solvent molecules to separate the interlayer. Furthermore, from the height histogram of different graphene/polymers (Fig.3.6), thin layer (<3) graphene sheets take a larger proportion (~35%) in PABA/graphene. On the contrary, PVA/graphene shows a very wide height distribution, where the thin layer graphene only accounts for about 2.5% in the total amount. In PVP/graphene and P4P/graphene, the thin

layer graphene takes about 25% and 18%, respectively. This may be ascribed to the difference in adsorption ability of different polymers. Among the four polymers, PABA shows the strongest interaction with the graphene lattice because of its rigid structure and benzene group, inducing more amount of thin layer polymer/graphene can be exfoliated. For PVP/graphene and P4P/graphene, because the pyrrolidone group shows stronger interaction with graphene surface than pyridine group,⁸² PVP/graphene possesses more thin layer than P4P/graphene.

Fig.3.6. Histogram of the height of a) P4P/graphene, b) PVA/graphene, c) PVP/graphene and d) PABA/graphene.

To sum up, the adsorption of polymer plays a very important role to exfoliate graphene. The polymer chain will firstly adsorb to the edge of interlayer and provide the energy barrier which is helpful for solvent molecules to penetrate and separate the interlayer. Gradually, the polymer will move into the deeper position along with the penetration of solvent molecules. Finally water soluble polymer/graphene is obtained. The interaction between polymer and graphene surface is critical to determine the graphene layer thickness. The polymer interacting more strongly with carbon lattice will provide larger energy barrier,

it can separate the interlayer of graphite more efficiently, which leads to thinner layer graphene.

In Raman spectra of polymer/graphene (Fig.3.7), the significant intensity increment of the D band is observed compared with graphite. The reason should be ascribed to the large amount of edges around small size graphene.^{82, 147} Because the size of laser spot is larger than 1 μm , large quantity of edges around the small size graphene would contribute a lot to the D (1354cm^{-1}), D' (1625cm^{-1}) and (D+D') (2953cm^{-1}) band in the Raman spectrum. For the 2D band of polymer/graphene, it doesn't broaden apparently. This suggests the structure of the basal plane in graphene is similar to that in graphite, which agrees with the SAED result. Compared with PVP/rGO (Fig.3.8), the intensity of D band in polymer/graphene is much lower. It indicates that the exfoliated graphene possesses fewer defects on the basal plane. Compared with polymer/rGO, the better crystalline structure implies better conductivity in polymer/graphene. Moreover, in the Raman spectra of PABA/graphene, peaks appearing at 1410 , 1453 and 1245 cm^{-1} are ascribed to the characteristic peaks of PABA polymer on graphene surface (Fig.3.8).

Fig.3.7. The Raman spectra of PVP/graphene, P4P/graphene, PVA/graphene, PABA/graphene and graphite.

Fig.3.8. The Raman spectra of PABA and PVP/rGO.

3.3.2. PVP/graphene used as support for methanol oxidation

Fig.3.9. The synthesis process of Pt-PVP/graphene.

Pt-PVP/graphene was synthesized according to the process shown in Fig.3.9. The TEM image of Pt-PVP/graphene clearly shows that Pt nanoparticles (NPs) are anchored on the surface of support uniformly (Fig.3.10a). In the XRD patterns (Fig.3.10b), Pt-PVP/graphene shows the obvious diffraction peaks at about 26.6° and 54.7° , corresponding to the $3.4 \text{ \AA}$ basal plane spacing of graphite. It's suggested large amount of multi-layer graphene in Pt-PVP/graphene, which is agree with the AFM results. In Pt-PVP/rGO, the diffraction peak appearing at 21.53° shows that the interlayer distance (d_{002}) of rGO is about $4.1 \text{ \AA}$. Because d_{002} in GO is usually around $9 \text{ \AA}$, the different interlayer distance indicates PVP wrapped rGO is obtained. Moreover, diffraction peaks appearing at 39.6° , 46.2° , 67.6° , 81.1° are assigned to Pt (111), (200), (220) and (311), respectively. According to the Scherrer's equation,¹⁴⁸ the mean sizes of Pt NPs are about 1.5 nm for Pt-PVP/graphene and 1.6 nm for Pt-

PVP/rGO. This means that Pt NPs possess similar size distribution on PVP/graphene and Pt-PVP/rGO.

Fig.3.10. a) TEM image of Pt-PVP/graphene. b) X-ray diffraction (XRD) patterns of Pt-PVP/graphene and Pt-PVP/rGO.

The quantitative analysis from EDX (Fig.3.11) shows that the mass percentage of oxygen (2.89%) in Pt-PVP/rGO is about 4 times higher than that in Pt-PVP/graphene (0.78%), which indicates that PVP wrapped rGO still contains non-negligible amount of oxygen group on surface after reduction. The unreduced functional group may influence both the loading of Pt NPs and the conductivity of rGO.

Fig.3.11. The Energy-dispersive X-ray (EDX) spectra of a) Pt-PVP/graphene and b) Pt-PVP/rGO.

Furthermore, the weight percentage of Pt on PVP/graphene and PVP/rGO is determined by the TGA (Fig.3.12). The weight loss is in the range from 130 °C to about 650 °C. TGA curve of Pt-PVP/graphene shows the obvious weight loss from 130 °C to 230 °C, it is ascribed to the decomposition of PVP. The much larger weight loss occurring at about 450 °C can be attributed to the carbon oxidation. For Pt-PVP/rGO, the weight loss from 130 °C to about 350 °C is caused by both the decomposition of PVP (~130-230 °C) and residual oxygen contained group (~200-350 °C)¹³⁶ on the surface of rGO. The oxidation of carbon in rGO is at about 400 °C, indicating the lower thermal stability of carbon structure in rGO than PVP/graphene. The Pt loading in Pt-PVP/graphene and Pt-PVP/rGO are 36.7 wt% and 34.1 wt%, respectively. Moreover, it's noteworthy that the weight percentage of PVP in Pt-PVP/graphene is about 16 wt%, it's much higher than that in Pt-PVP/rGO (~8 wt%) even if regardless of the decomposition of oxygen-containing groups from 200 to 230 °C.

Fig.3.12. Thermal gravimetric analysis (TGA) of Pt-PVP/graphene and Pt-PVP/rGO in air atmosphere (heating rate: 10°C/min, flow rate: 100 ml/min).

From above characterization, it is clear that Pt NPs on PVP/graphene and PVP/rGO have the similar loading and size distribution. However, support PVP/graphene shows very different properties against PVP/rGO. The EDX spectra and TGA curves show PVP/graphene has much less oxygen containing groups in spite of more amount of PVP on its surface. These differences indicate that the following different electrochemical activity between Pt-

PVP/graphene and Pt-PVP/rGO would mainly arise from the support rather than Pt NPs.

The electrochemical impedance spectroscopy is conducted to study the conductivity difference between Pt-PVP/rGO and Pt-PVP/graphene. A semicircle corresponding to the charge transfer process in high-frequency region and the linear part ascribed to the diffusion process in lower frequency region are observed. A simple equivalent circuit $R_s(C_{dl}(R_{ct}Z_w))$ (inset in Fig.3.13) is employed to fit the high and medium frequency data,¹⁴⁹ in which R_s is the solution resistance, C_{dl} is the double-layer capacitance, R_{ct} is the electron transfer resistance and Z_w is the finite length Warburg impedance element. R_{ct} in bare CE, Pt-PVP/graphene and Pt-PVP/RGO are about 113, 107 and 762.9 Ω , respectively. It demonstrates a more rapid charge transfer at the interface between Pt-PVP/graphene and electrolyte, which is caused by the much better conductivity in Pt-PVP/graphene.¹⁵⁰ The result is in agreement with Raman and EDX (Fig.3.8, Fig.3.11) test, where PVP/rGO shows more defects and functional groups, leading to the reduction in the conductivity.

Fig.3.13. Nyquist impedance plots of bare carbon electrode, Pt-PVP/graphene, and Pt-PVP/rGO. Frequency range: 0.1 Hz-100 kHz. Inset is the equivalent circuit.

Fig.3.14a shows very typical voltammetric response of Pt NPs in acid solution, including the hydrogen desorption and adsorption peaks at low

potential, Pt oxidation and reduction peaks at higher potential. The Pt oxidation peak of Pt-PVP/rGO exhibits a more negative reduction potential (~ 0.35 V) compared with that of Pt-PVP/graphene (~ 0.50 V), indicating that the Pt NPs are more oxophilic on PVP/rGO than PVP/graphene. Moreover, the ECSA in Pt-PVP/rGO is much larger than that in Pt-PVP/graphene (~ 72.3 m²/g vs ~ 40.1 m²/g). The low oxophilicity and ECSA of Pt NPs on PVP/graphene can be ascribed to the higher loading of PVP as determined by TGA (Fig.3.12). Because the size of the as-synthesized Pt is small, PVP is very easy to wrap most of the catalytic site of Pt if there is excess amount of PVP on the surface, which will decrease the electrocatalytic performance of Pt.¹⁵¹ However, the intrinsic electrocatalytic activity (normalized by ECSA, Fig.3.14b) of Pt-PVP/graphene towards methanol oxidation is still much higher than that of Pt-PVP/rGO (0.32 mA/cm²_{Pt} vs 0.20 mA/cm²_{Pt}). It demonstrates that the conductivity of the graphene plays a very important role to improve the catalytic activity of Pt.

Fig.3.14. Cyclic voltammograms (CV) of Pt-PVP/rGO and Pt-PVP/graphene in a) nitrogen saturated 0.5 M H₂SO₄ b) 0.5 M methanol/0.5 M H₂SO₄ with the scan rate of 50 mV/s.

The durability of Pt-PVP/graphene and Pt-PVP/rGO was also tested (Fig.3.15). The current density of Pt-PVP/graphene shows a much slower decrement compared with Pt-PVP/rGO. This may also be ascribed to the excess amounts PVP around Pt NPs, which may hinder the agglomeration of Pt NPs and prolong the stability of catalyst.

Fig.3.15. The long-term stability of Pt-PVP/graphene and Pt-PVP/rGO in 0.5 M methanol/0.5 M H₂SO₄. The potential scan is performed from 0 V to 1 V, the scan rate is 50 mV/S.

3.3.3. P4P/graphene used as pH sensor

It has been observed that the dispersion of P4P/graphene solution can be controlled by adjusting the pH value (Fig.3.16). By changing the pH of P4P/graphene solution to 12.0, obvious aggregation occurred. If the solution pH was adjusted back to 2.0, the sediment was re-dispersed into the solution again. This phenomenon indicates that the polymer chain of P4P would shrink because of the deprotonation of pyridyl ring at high pH value, which has been verified by previous research.¹⁴¹ Such kind of reversible shrink might influence the surface environment of graphene, which may make P4P/graphene a potential pH sensor. Thus we fabricate P4P/graphene based sensor to study its pH response.

Fig.3.16. The reversible aggregation and dissolve process of P4P/graphene solution by tuning pH value.

The impedance response of P4P/graphene at various pHs was investigated (Fig.3.17a). After fitting these plots with the same equivalent circuit $R_s(C_{dl}(R_{ct}Z_w))$ (Fig.3.17b), it can be observed that the R_{ct} increases linearly with pH from 6 to 8. When pH is higher than 8.5, the resistance ($\sim 450 \Omega$) increase over 20 times compared with that at low pH ($\sim 20 \Omega$). Such a change in R_{ct} is also in agreement with the different redox peaks obtained in CV measurement at different pH (Fig.3.18a).

Fig.3.17. a) Nyquist impedance plots of P4P/graphene in solution with different pH. The frequency range is 0.02 Hz-100 kHz. Inset is the enlargement of the spectra at high frequency region in the solution of pH 3.68 and 4.43. b) The corresponding electron transfer resistance (R_{ct}) at different pH.

The drastic change of R_{ct} in P4P/graphene could be ascribed to following two reasons: (1) Positive charge on the polymer chain introduced by the protonation of pyridine at low pH. The positive charge will enhance the interaction between P4P chain and the redox probe $\text{FeCN}_6^{3-}/\text{FeCN}_6^{4-}$ and therefore increase the electron transfer rate. (2) The different conformation of polymer chain at different pH environment. In previous research,¹⁴¹ it has been observed that the polymer would repulse each other and form an extended chain conformation at low pH because of the electrostatic interaction, the extended polymer chain on the graphene surface would facilitate the electron transfer rate; on the contrary, the polymer chain would shrink and form a coil chain on graphene surface at high pH, which could insulate the electron transfer and increase R_{ct} .¹⁵²

The durability is also studied through CV at different pH (Fig.3.18a). After 1000 cycles, the redox peak in CV remains unchanged. This indicates that the conformation of the chain could keep stable for long time at specific pH environment. Moreover, R_{ct} can be reversibly switched through pH control (Fig.3.18b). The stable and tunable properties make it a potential device for sensor.

Fig.3.18. a) CV of P4P/graphene in solution of pH 4.43, 6.82 and 9.33 at 1st and 1000th cycles with the scan rate of 100 mV/s. b) R_{ct} change upon switching pH at 9.33 and 4.43.

3.4. Conclusions

Graphene is successfully exfoliated in water-soluble polymer/DMSO system. Apart from surface functionalization, water-soluble polymer also provides a large energy barrier which is indispensable and crucial for solvent molecules to separate the interlayer of graphite. Although the exfoliated graphene still contains single layer and multi-layers, it's revealed that the layer distribution of

polymer/graphene varies from different polymer. This provides a possible way to control graphene with different layers. In this article, the polymer/graphene exfoliated directly from graphite shows two advantages. Firstly, the planar structure of graphite is well kept after exfoliation, leading to the good crystalline structure and high conductivity of polymer/graphene, as confirmed by Raman and other characterization methods. Therefore, the PVP/graphene based catalyst shows much better electrochemical activity than PVP/rGO. Secondly, various kinds of water-soluble polymer can be used for exfoliation. Thus the resulting polymer/graphene can have different surface properties and be used in aqueous and polar system for further applications, depending on the choice of polymer. For example, we demonstrated that P4P/graphene based material shows reversible and stable response to the change of pH.

Chapter 4

Selective Electro-Oxidation of Glycerol over Au Supported on Extended Poly(4-vinylpyridine) Functionalized Graphene*

4.1. Introduction

Recently growth of the biodiesel industry has greatly increased the production of glycerol.^{153, 154} To utilize excess glycerol, applying glycerol as fuel for the co-generation of valuable chemicals and electricity has attracted more attention. Although the mechanistic study of glycerol electro-oxidation in alkaline solution began twenty years ago, only a few investigations were devoted to this subject due to its complexity.^{27, 155-157} As a three carbon alcohol containing three hydroxyl groups, the electro-oxidation of glycerol gives rise to various products, such as glyceric acid, hydroxypyruvic acid, mesoxalic acid, tartronic acid, and other two or one carbon products *via* C-C bond breaking.¹⁹⁻²¹ The diverse range of products renders a great challenge in controlling both activity and selectivity during the glycerol electro-oxidation process.

Several ways have been developed to improve the electro-oxidation selectivity of glycerol. One way is to control the selectivity by the mediation of other molecules and adatoms. With the presence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) in buffer solution (pH=9.1), 1,3-dihydroxyacetone (DHA) can be selectively oxidized from glycerol.¹⁵⁸ Kwon et al. applied several kinds of adatoms (Bi, Sb, Pb, In and Sn) on the surface of Pt and found that glycerol was fully converted to DHA when Bi was present in the solution.^{159, 160} Selectivity can also be controlled by tuning the operating conditions. Kim et al. achieved the glyceric acid selectivity of 87% in the continuous-flow electrocatalytic reactor at 60 °C after 10 h.²² The group of Li obtained high selectivity toward tartronic acid, glycolic acid, mesoxalic acid in fuel cell at the optimized temperature, potential and flow rate.²³⁻²⁵ In other studies, Pd alloyed with other metals was used to investigate the electro-oxidation of glycerol. Simões et al. showed different Pd alloys produced different products.¹³⁵ Zalineeva et al. studied the electrocatalytic behaviour of PdBi alloys in glycerol oxidation.^{161, 162} Moreover, Marchionni et al. loaded Pd nanoparticles (NPs) on (Ni-Zn)/C supports, it showed the limited improvement

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of selectivity in the glycerol oxidation.²⁹

On the other hand, Au NPs have been widely studied because of its enhanced selectivity in the liquid phase oxidation.¹⁶³⁻¹⁶⁵ Selectivity of glyceric acid can reach 100% under optimized conditions.¹⁶³ However, in the electro-oxidation, the glyceric acid production only dominated at potential lower than the onset potential (0.8 V vs. RHE) in the three electrode cell. At potential higher than the onset potential, two-carbon (glycolic acid) and one-carbon (formic acid) products are predominant in the largest proportions (~ 90%).¹⁶⁶ This is also confirmed in this paper by using Au NPs on carbon black.

In this chapter, we chose Au supported on extended poly(4-vinylpyridine) wrapped graphene (Au-P4P/G) as the catalyst to selectively oxidize glycerol into glyceric acid during electro-oxidation of glycerol. Although several ways including introducing foreign substances and controlling working potential have been developed to selectively electro-oxidize glycerol, there have been few studies conducted to determine the impact of the intrinsic electronic properties of catalyst via metal-support interaction during the electro-oxidation process. Most studies focus on the influence of electronic structure of metal catalysts for their oxidation activity.¹⁶⁷⁻¹⁶⁹ Through carefully controlling the interaction between Au NPs and polymer on graphene surface, we obtained Au based catalysts with varying extents of electron enrichment. Different with conventional designed polymer wrapped carbon material, the highly extended polymer wrapped graphene in this paper shows a more powerful ability to alter the intrinsic electronic property of Au NPs. Through off-line HPLC analysis, it demonstrated that Au-P4P/G showed a higher activity and much better selectivity for three carbon products than Au NPs on carbon black, P4P functionalized reduced graphene oxide (Au-P4P/rGO) and poly(m-aminophenol) (PmAP) wrapped graphene (Au-PmAP/G), e.g., the glyceric acid production reaches 68.6% at 0.2 V (vs. HgO/Hg), and the ratio between three carbon products and other products is 4.92 for Au-P4P/G compared with 0.96 of Au-CB. XPS results indicated that lower d-band center in Au nanoparticles was responsible for the higher three carbon selectivity due to the changed adsorption ability for oxygen-containing groups on Au.

4.2. Materials and methods

4.2.1. Materials

Poly (4-vinylpyridine) (P4P, MW = 160,000) were purchased from Sigma-Aldrich. Poly(m-aminophenol) (PmAP) was prepared according to previous literature procedure.¹⁷⁰

4.2.2. Preparation of catalysts

Polymer functionalized graphene (polymer/G):¹⁷¹ 0.04 g of polymer was dissolved into 0.8 ml of DMSO, followed by the addition of 0.1 g graphite. After ultrasonication for 20 h, the black solution was placed overnight and the sediment was discarded. Then polymer wrapped graphene in the upper solution was washed by centrifuging at 10000 rpm for several times. Specifically, PmAP wrapped graphene was washed with 0.01 M NaOH, P4P/graphene was washed with 0.02 M HCl. Finally the synthesized polymer/graphene was dispersed in DI water.

P4P functionalized reduced graphene oxide (P4P/rGO): rGO was synthesized according to the literature.¹⁰³ Specifically, 12.5 mg of GO was dissolved into 50 ml of DI water, then 13.5 μ l of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (64%-65%) solution was added, followed by 0.175 ml of 25% NH_4OH . The product was collected and centrifuged after slowly stirred at 90 °C for 90 min. After that, the synthesized rGO was dissolved into 40 ml of 1:1 (v/v) ethanol/water mixed solvent. Meanwhile, 0.125 g of P4P was dissolved into 60 ml of 1:1 (v/v) ethanol/water mixed solvent. After mixing and stirring these two solutions overnight, polymer wrapped rGO was purified by centrifuged three times with ethanol. Finally it was stored in ethanol solution.

4 nm Au sol-gel solution: 1 ml of 1% $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ was added into 100 of ml DI water. The solution was stirred for 1 min. Then 1 ml of 1% aqueous sodium citrate solution was added. 1 min later, 1 ml fresh prepared 0.075% NaBH_4 in 1% sodium citrate was quickly added. The solution was continuously stirred for 5 min and then stored at 4 °C.

Au NPs loaded on carbon black (Au-CB), P4P/graphene (Au-P4P/G), PmAP/graphene (Au-PmAP/G) and P4P/rGO (Au-P4P/rGO): Appropriate amount of support dispersion and Au nanoparticle solution were mixed under ultrasonication for 1h. The mixture was stirred overnight. Then the pH was adjusted below 2 by using 0.2 M HCl, the solution was continuously stirred for 1 h. The product was centrifuged at 10000 rpm and washed with DI water three times. Then the product was dried below 80 °C.

4.2.3. Physicochemical characterization

The morphology was observed by using transmission electron microscopy (TEM) at JEOL JEM-3010. The X-ray diffraction patterns are collected by Bruker D2 Phaser. Thermo gravimetric analysis (TGA) was carried out at SDT Q600 with a temperature ramp rate of 10 °C under air atmosphere. The atomic force microscope (AFM) images of various samples on mica were collected at MFP-3D-SA (Asylum Research) in AC mode. In order to study the electronic property of Au NPs, X-ray photoelectron spectroscopy (XPS) spectra were carried out. In the common XPS spectra studying carbon materials, the binding energy of C1s is used for calibration. However, here four support CB, P4P/G, PmAP/G and P4P/rGO contain amorphous carbon, benzene rings and C-C chains, these types of carbon functional groups render different binding energy.¹⁷² Therefore, samples were collected at VG ESCALAB 200i-XL after coated with Pt. Pt(0) 4f_{7/2} and 4f_{5/2} at 71.1 and 74.4 eV were used as the reference for charge correction (Fig.4.1).¹⁷³

Fig.4.1. The XPS spectra of Pt 4f in Au-CB, Au-PmAP/G, Au-P4P/G and Au-P4P/rGO as the calibration peak.

4.2.4. Electrochemical characterization

All electrochemical tests were carried out at room temperature in conventional three-electrode cell using Autolab PGSTAT302 potentiostat. Pt foil and Hg/HgO (6 M KOH) were used as the counter and reference electrode, glassy carbon electrode with 5 mm diameter and carbon cloth ($1.4 \times 1.4\text{cm}^2$, Gashub) were used as the working electrode. The sample was prepared following the below procedure: firstly 2 mg of catalyst was dispersed in 2.5 ml of ethanol solution by ultrasonication for 5 min; then 0.5 ml of 0.05 wt% Nafion solution was added and ultrasonicated for 10 min to obtain the black dispersion. In the cyclic voltammograms (CV) test, 30 μl of catalyst dispersion was dropped on the glassy carbon electrode. After drying, the test was conducted in the 0.5 M NaOH + 0.5 M glycerol solution. The electrochemical impedance spectroscopy (EIS) test was operated at open-circuit potential, Ag/AgCl (saturated KCl) was used as reference electrode. The supporting solution was prepared by using 5 mM $\text{K}_3[\text{FeCN}_6]/\text{K}_4[\text{FeCN}_6]$ (1:1) as redox probe and 0.1 M KCl as supporting electrolyte. In the chronoamperometric experiments, 0.02 mg of catalyst was dropped onto glassy carbon (GC) and 1 mg and 2 mg of catalyst was dropped onto carbon cloth (CC) to prepare samples with different loading. The working electrode was firstly immersed in 0.5 M NaOH + 0.5 M glycerol while the solution was stirred for 10 h to fully saturate the electrode, then it was washed carefully with DI water. After that, it was immersed inside 20 ml of 0.5 M NaOH + 0.5 M glycerol solution during the test. After setting and applying the specific potential on the working electrode for 2 h, 1 ml of solution was collected for the high performance liquid chromatography (HPLC) analysis.

4.2.5. Chromatographic determination of products

The obtained products were analyzed by high performance liquid chromatography (HPLC, Agilent 1260 Infinity). The determination of oxalic acid was conducted by Alltech OA-1000 Organic Acid column. In other cases, column Aminex HPX 87-H (Bio-Rad) was used. The eluent was sulfuric acid (4 mM). During the test, 20 μl of sample was injected into the column and the temperature of the column was kept at 65 $^\circ\text{C}$. The flow rate was 0.2 ml/min. The separated compounds were detected with both the refractive index (RID) detector and UV-Vis detector. The expected glycerol oxidation products were analyzed at the same condition to produce the calibration curves (glyceric acid, glycolic acid, formic acid, oxalic acid, and tartronic acid).

4.3. Results and discussion

4.3.1. TEM, XRD and TGA characterization of catalysts

Four different materials, including carbon black (CB), Poly(*m*-aminophenol) and Poly(4-vinylpyridine) wrapped graphene (PmAP/G and P4P/G), Poly(4-vinylpyridine) functionalized reduced graphene oxide (P4P/rGO), were carefully chosen as support in this work. CB has weak interaction with Au NPs because few functional groups on the surface. PmAP and P4P functionalized graphene can donate a pair of electrons generated from -N= groups although in PmAP most -N= groups form the hydrogen bond with -OH groups,¹⁷⁰ inducing a different extent of electron donation from support to Au NPs. The use of P4P/rGO is to examine the effect of support conductivity. PmAP/G and P4P/G were synthesized through ultrasonication and P4P/rGO was obtained by chemical reduction. Then as-synthesized Au nanoparticles were loaded onto these supports and also CB. The morphology of Au nanoparticles was investigated by TEM and XRD. TEM images show that Au NPs are homogeneously deposited onto different support surface (Fig.4.2a, b, c, d). As catalysts are prepared from the same sol-gel solution, Au NPs exhibit similar particle size distribution in all these catalysts (Fig.4.2e). The calculated average diameter of Au NPs in Au/CB, Au-P4P/G, Au-PmAP/G and Au-P4P/rGO is 4.1, 4.3, 4.3 and 4.0 nm, respectively. XRD was also conducted to characterize catalysts (Fig.4.2f). Peaks in the range from 22 ° to 26 ° are ascribed to the inter-spacing of (002) graphite planes. Peaks appearing at 38.2 °, 44.5 °, 64.7 ° and 77.8 ° are assigned to the (111), (200), (220) and (311) planes of face-centered-cubic (FCC) Au. Based on the Debye-Scherrer equation, the calculated average size of Au NPs on P4P/G, PmAP/G and P4P/rGO is 4.8, 4.9 and 4.6 nm while on CB is 7.9 nm. The particle size of Au NPs on CB calculated via XRD is much larger than that from TEM. This may be caused by the aggregation of Au nanoparticles on carbon black due to the relatively weak interaction between CB and Au. The weight percentage of different components in catalysts was analyzed by TGA (Fig.4.2g). For Au-CB, weight loss at low temperature (< 400 °C) may be induced from the decomposition of amorphous carbon.¹⁷⁴ While for other samples, the weight loss from 220 to 400 °C is largely caused by the decomposition of polymer and below 220 °C is ascribed to absorbed water or residual functional groups on rGO.^{136, 175} Oxidation of carbon occurs at higher temperatures (400 - 600 °C). Final Au loading on P4P/G, PmAP/G, CB and P4P/rGO is 28%, 39%, 34% and 36%, respectively.

Fig.4.2. TEM images of a) Au-CB, b) Au-P4P/G, c) Au-PmAP/G, and d) Au-P4P/rGO. e) The particle size histogram of Au-CB, Au-P4P/G, Au-PmAP/G, and Au-P4P/rGO. f) X-ray diffraction (XRD) patterns of Au-P4P/G, Au-PmAP/G, Au-P4P/rGO and Au-CB. g) Thermal gravimetric analysis (TGA) of Au-P4P/G, Au-PmAP/G, Au-CB and Au-P4P/rGO in air atmosphere.

4.3.2. HPLC analysis of products

The products of glycerol electro-oxidation were determined by HPLC (Fig.4.3). Most of products can be detected by using RID detector. The retention time of oxalic acid, tartronic acid, glyceric acid and glycolic acid is 19.9, 23.3, 32.3, 36.5 min, respectively. Although signals of products can also be observed by using UV detector, the relative low intensity of peak would cause greater error after peak integration. Therefore, we mainly used RID detector to analyse products. Moreover, due to the overlap of signal peaks between glycerol and formic acid when using RID detector, UV detector was only used to analyse the formation of formic acid. The retention time of formic acid is around 40.3 min.

Fig.4.3. The HPLC analysis of the glycerol oxidation products with a) RID detector and b) UV-Vis detector. Catalyst: Au/CB, 2 mg on carbon cloth, column: Aminex HPX 87-H.

Production of mesoxalic acid has been reported when glycerol oxidation was carried out on Pt and Au based catalysts.^{23, 176} After comparing the retention time of product to mesoxalic acid (MA) and oxalic acid (OA) standards, it's clearly shown that the retention time of product is located in the range of 1-10 mM OA rather than MA (Fig.4.4). Therefore, here we are sure that only oxalic acid can be produced in the reaction system.

Fig.4.4. The HPLC analysis of the glycerol oxidation products of Au/CB (2 mg on carbon cloth at 0.4 V for 2 h, Au/CB CC 0.4 V), oxalic acid (OA) and mesoxalic acid (MA). Column: Alltech OA-1000 Organic Acid.

4.3.3. Electrocatalytic activity of catalysts

We then compared the electrocatalytic activity of Au NPs loaded on different supports. In the CV test, with the increase of potential, the glycerol oxidation peak appears at around 0.5 V (vs. HgO/Hg) for Au-CB, Au-P4P/G and Au-PmAP/G. During the reverse scan, another oxidation peak appears at around 0.2 V (vs. HgO/Hg) for Au-CB, Au-P4P/G and Au-PmAP/G, which is mainly ascribed to the oxidation of absorbed intermediates after the reactivation of catalyst surface. Among these three catalysts, Au-CB and Au-PmAP/G exhibit similar oxidation current density which are much lower than that of Au-P4P/G (Fig.4.5a). It indicates that Au-P4P/G possesses higher electrocatalytic activity. Moreover, Au-P4P/rGO shows no obvious glycerol oxidation peak. This means the oxidation of glycerol is very sluggish over Au-P4P/rGO. EIS test was conducted to extract the equivalent series resistance (ESR) and charge transfer resistance R_{ct} (Fig.4.5b).¹⁷⁷ ESR which includes resistances from electrolytes, electrodes and electrical contacts is used to compare the conductivity of catalysts, as the remaining parts in the three electrode cell are the same. ESR of Au-CB, Au-PmAP/G, Au-P4P/G and Au-P4P/rGO is around 68, 73, 72 and 76 Ω and R_{ct} is 22.2, 83.1, 245.7, 613.9 Ω , respectively. The lowest conductivity and highest R_{ct} of Au-P4P/rGO induces its low activity. For the case of Au-P4P/G, although its conductivity is lower and charge transfer resistance is higher than Au-CB, higher activity was still observed, indicating some other

factors also play important role in the electrocatalytic activity, other than the conductivity. A possible reason might be the appropriate adsorption strength of the species on the catalysts surface via the tuning of the d-band center.¹⁶⁷⁻¹⁶⁹ Details will be discussed in the part of 4.3.4.

Fig.4.5. Cyclic voltammograms (CV) of Au-CB, Au-P4P/G, Au-PmAP/G and Au-P4P/rGO in 0.5 M glycerol + 0.5 M NaOH with a scan rate of 50 mV/s. b) Nyquist impedance plots of Au-CB, Au-P4P/G, Au-PmAP/G and Au-P4P/rGO. Frequency range: 0.01 Hz-10000 Hz. Inset are the equivalent circuit and the enlarged spectra of catalysts at high frequency region.

We also compared the electrocatalytic activity of catalysts based on the electrochemical active surface area (EASA) of Au NPs. EASA was estimated by quantitatively considering the reduction peak of Au oxide in H₂SO₄ aqueous solution (Fig.4.6a).^{178, 179} The equation for calculation was described as:

$EASA = \int IdU / (a * v)$, Where I and U are the current and potential in the CV curve, v is the scanning rate, a is $400 \mu Q.cm^{-2}$ for Au.

Corresponding to the CV curves of catalysts in 0.5 M NaOH/Glycerol (Fig.4.5a), Au-P4P/rGO doesn't show the obvious reduction peak. This may be mainly ascribed to more amount of polymer on rGO surface. Au NPs on surface will tend to be embedded. This makes Au NPs hard to form oxide and be reduced. After calculation, the EASA of Au-CB, Au-PmAP/G and Au-P4P/G are $27.46 m^2g^{-1}$, $27.83 m^2g^{-1}$ and $40.14 m^2g^{-1}$, respectively. Then the electrocatalytic activity of catalysts was estimated after normalized by the EASA (Fig.4.6b). It demonstrates that Au-P4P/G still shows higher activity than other catalysts, which is corresponding to the mass current density of catalysts.

Fig.4.6. Cyclic voltammograms (CV) of Au-CB, Au-P4P/G, Au-PmAP/G and Au-P4P/rGO in a) 0.5 M H₂SO₄, b) 0.5 M NaOH + 0.5 M Glycerol, normalized by electrochemical active surface area. The scan rate is 50 mV/s.

4.3.4. Electro-oxidation mechanism of catalysts

The activity of different catalysts was also investigated by HPLC after holding at a series of potentials in 0.5 M NaOH + 0.5 M glycerol solution for 2 h, these potentials are much higher than the onset potential of catalysts (around -0.2 V vs. HgO/Hg). Firstly, in order to clarify that glycerol oxidation only occurs over Au NPs rather than the support, we applied same potential on the support without Au NPs and after then analysed products in the solution. At the typical potential of 0.2 and 0.6 V (Fig.4.7, others not shown), supports without Au NPs barely show any products produced. This demonstrates that supports do not participate in the electro-oxidation of glycerol.

Fig.4.7. The HPLC analysis of glycerol oxidation products of CB, P4P/rGO, PmAP/G and P4P/G at 0.2 V with a) RID detector, b) UV-Vis detector, at 0.6 V with c) RID detector and d) UV-Vis detector, with the contrast of Au NPs on these supports at same condition. Catalysts amount: 2mg, electrode substrate: carbon cloth.

Then we analysed the oxidation products of catalysts at different potential. During the test, it was observed that higher potential commonly leads to higher

glycerol conversion (Fig.4.8a). Among these catalysts, Au-P4P/G shows higher activity than Au-CB and Au-P4P/rGO as observed from their similar glycerol conversion despite its lower Au loading (Fig.4.2g). This agrees with the results from CV test (Fig.4.5a). Apart from the activity, Au NPs on different supports also show very diverse selectivity for glycerol oxidation. Au NPs on either CB or PmAP/G have very similar selectivity. After changing polymer from PmAP to P4P on exfoliated graphene surface, the production of glyceric acid is largely enhanced, e.g., when the potential is 0.2 V, the glyceric acid production in Au-CB, Au-PmAP, Au-P4P/rGO and Au-P4P/G are 34.5%, 42.2%, 57.4% and 68.6%, while the glycolic acid production are 12.7%, 17.8%, 11.3% and 7.0% respectively (Fig.4.8a). The selectivity of 3-carbon products especially glyceric acid is much higher for Au-P4P/rGO and Au-P4P/G than Au-CB and Au-PmAP/G throughout the low to medium potential range (0.2-1 V, Fig.4.8b). Since glyceric acid is easily to be oxidized into glycolic acid and formic acid on Au at high potential,¹⁶⁶ the enhanced production of glyceric acid means that further oxidation on Au-P4P/rGO and Au-P4P/G is effectively hindered (Fig.4.8c). Interestingly, the production of formic acid is roughly equal to the production of glycolic acid and oxalic acid for Au-CB and Au-PmAP/G between 0.2 V to 1 V, while for Au-P4P/rGO and Au-P4P/G, the production of formic acid is less than the production of two carbon products. This indicates that the formic acid in Au-P4P/rGO and Au-P4P/G is more easily oxidized into carbonate (Fig.4.8c).¹⁶⁶

Fig.4.8. a) The product selectivity and glycerol conversion b) The three-carbon products selectivity over Au on different supports (CB, P4P/G, PmAP/G and P4P/rGO) at various potentials. The catalyst loading is 1 mg cm^{-2} and the working electrode is carbon cloth. Reproducibility test shows the deviation is within 10%. c) The scheme of glycerol oxidation over Au/C, Au-PmAP/G, Au-P4P/rGO and Au-P4P/G. Red colour arrow means the reaction yield is increased while the blue arrow means the yield is decreased.

Because carbonate may be produced during the glycerol electro-oxidation process,²⁸ we also estimated the amount of carbonate through following equation, Carbonate Amount (%) = Glycolic acid Amount (%) + Oxalic acid Amount (%) - Formic acid Amount (%). This equation is based on the glycerol electro-oxidation mechanism in Fig.4.8c. It's shown that even after taking the possible production of carbonate into account (Fig.4.9), we can still reach the same conclusion that P4P/G shows improved selectivity towards three carbon products.

Fig.4.9. The product selectivity of Au on different support (CB, P4P/G, PmAP/G and P4P/rGO) at various potential (V vs. Hg/HgO) after calculating the amount of carbonate. The catalysts amount is 2 mg and the working electrode is carbon cloth.

To understand the different activity and selectivity of Au NPs, we studied the electronic structure of Au NPs on different supports by XPS spectra after the samples are coated and calibrated by Pt (Fig.4.1). Peaks corresponding to the Au $4f_{7/2}$ core level of Au-CB, Au-PmAP/G, Au-P4P/rGO and Au-P4P/G are at 82.65, 82.55, 82.41 and 82.19 eV (Fig.4.10d), respectively. Since Au NPs on different supports possess almost the same particle size, the influence of the particle size for XPS can be excluded.¹⁸⁰ So the shift of Au $4f_{7/2}$ peak to a lower binding energy on graphene and rGO supported samples could be explained by the negatively charged Au NPs,^{167, 169} which means a lower d-band center. Among these catalysts, -N= group in the PmAP chain shows much weaker electron-donating ability compared with pyridine group in P4P chain due to its hydrogen bonding with the *m*- position -OH group.¹⁷⁰ This leads to a slightly decrement of Au $4f_{7/2}$ peak in the Au-PmAP/G while resulting in a significant shift of Au $4f_{7/2}$ peak in P4P functionalized support. For the different electronic property between Au-P4P/rGO and Au-P4P/G, it can be ascribed to the different orientation of P4P chain on the support surface. In the AFM image of P4P/G, the thickness of polymer layer surrounding graphene is about 0.5 nm (Fig.4.10a). However, the polymer thickness surrounding rGO is only about 0.1 nm when the noise of the substrate is neglected (Fig.4.10b). Besides, TGA of P4P/rGO

and P4P/G shows that the polymer weight percentage in P4P/G (7.8 %) is much lower than that in P4P/rGO (15.1%) (Fig.4.10c). Therefore, it is reasonable to conclude that above the exfoliated graphene surface most P4P chains are extended while on rGO they tend to lie on surface. This forms a much thicker polymer layer despite of the lower polymer percentage on exfoliated graphene surface, which agrees with our previous research.¹⁷¹ When Au NPs are loaded, more sites of the NPs surface are wrapped by P4P, which thus induces the lowest d-band center among these four catalysts (Fig.4.11). The different extent of electron enrichment in turn induces the varied adsorption ability of oxygen containing groups for these catalysts.¹⁸¹ Therefore, for Au-P4P/G, Au NPs may have the weakest adsorption ability with glyceric acid, which enhances the production of glyceric acid and hinders the further decomposition to glycolic acid and formic acid.

Fig.4.10. AFM height images of a) P4P/G and b) P4P/rGO deposited on mica surface. c) TGA curves of P4P/G, P4P/rGO and rGO in air atmosphere. d) The XPS spectra of Au 4f in Au-CB, Au-PmAP/G, Au-P4P/G and Au-P4P/rGO.

Fig.4.11. The schematic drawing of the loading of Au NPs on P4P/rGO and P4P/G.

We also studied the effect of catalytic loading on the reaction selectivity since previous report has indicated the loading of catalysts could influence the selectivity in glycerol oxidation.²² At the catalyst loading of 0.1 mg cm^{-2} , we observed that Au-P4P/G has better selectivity towards three-carbon products than Au-CB and Au-PmAP/G (over 2 times) (Fig.4.12a). When the loading of catalyst increases, the selectivity difference is enlarged between Au-P4P/G and Au-CB (by comparing Fig.4.8b and 4.12a). This means the increment of catalyst loading is more effective for Au-P4P/G than other catalysts in promoting the selectivity. The reason may be ascribed to the competitive adsorption between glyceric acid and other oxidized species. Since the concentration of oxidized species increases along with the catalytic loading (Fig.4.12b), the adsorption competition between glyceric acid and other oxidized species would become more intense. Part of the adsorbed glyceric acid may be replaced by other oxidized species, this causes the slightly increment of the selectivity towards three carbon products in Au-CB at low potential when loading is increased. For the case of Au-P4P/G, due to its lowest d-band center, glyceric acid on the surface may be more easily replaced by other species. This caused its significant promotion in selectivity towards three carbon products when the loading is increased.

Fig.4.12. a) The product selectivity of different catalysts (Au-CB, Au-P4P/G, Au-PmAP/G) at 0.2 and 0.4 V (vs. Hg/HgO), the catalyst loading is 0.1 mg cm^{-2} and the working electrode substrate is glassy carbon. b) The product selectivity of different loading of Au/CB at different potential (V vs. Hg/HgO) on carbon cloth electrode. The black line represents the glycerol conversion of Au/CB with varied loading at potential of 0.4 V, the red line represents the glycerol conversion of Au/CB with varied loading at potential of 1 V.

4.4. Conclusions

In this paper, we developed a new catalyst by loading Au NPs on extended Poly(4-vinylpyridine) (P4P) functionalized graphene for glycerol oxidation in alkaline solution. The as-synthesized Au-P4P/G shows the highest activity and selectivity towards three carbon product compared with other catalysts (Au-CB, Au-PmAP/G and Au-P4P/rGO). Due to the extended P4P chain on graphene surface in P4P/G, Au-P4P/G possesses the lowest d-band center which is confirmed by XPS analysis. On the contrary, Au NPs on carbon black and

PmAP/G retain their pristine property. The lowest d-band center in Au-P4P/G causes the weakest interaction between Au NPs and glyceric acid, which makes glyceric acid easier to desorb from Au surface and hinders the further decomposition of glyceric acid into two and one carbon products. Moreover, compared to Au-P4P/rGO, Au-P4P/G has far less polymer on surface. This makes Au NPs less tending to be embedded. The higher conductivity of support, less polymer on surface and also lower D-band center, these all contribute its much higher activity. This indicates that Au-P4P/G can serve as a potential catalyst with better control of products in the fuel cell system while producing higher current density.

Chapter 5

Pd Nanoparticles on CN_x/graphene Used as Catalyst for the Selective Electro-Oxidation of Glycerol

5.1. Introduction

As introduced in Chapter 4, we have demonstrated that extended polymer chains can largely tailor the electronic property of Au NPs and greatly enhance the selectivity towards glyceric acid. However, the activity difference between Au-P4P/G and Au-CB is not obvious (Fig.4.8a). The reason lies in the stability of these two catalysts. Comparing the chronoamperometry curves of these two catalysts at the loading of 0.1 mg cm^{-2} , Au-P4P/G shows lower stability than Au-CB (Fig.5.1). At higher loading of 1 mg cm^{-2} , the Coulomb amount of Au-CB calculated from chronoamperometry curves is 444 C. However, Coulomb amount of Au-P4P/G is 348 C, which is lower than Au-CB. This means that more amount of glycerol can be electro-oxidized on the surface of Au-CB. Although Au NPs on P4P/G exhibit better mass activity than Au NPs on CB in the CV test (Fig.4.5b, Fig.4.6a), the long-term performance of P4P/G in fuel cell is not promising.

Fig.5.1. Chronoamperometry curves of Au-CB and Au-P4P/G at 0.4 V on the electrode of glassy carbon electrode.

Moreover, there have been still few works investigating selectivity improvement by tuning metal-support interaction. Only in our previous work, it is reported that extended polymer chains on support can largely change the electronic property of Au NPs and thus greatly enhance its selectivity to glyceric acid.²⁶ On the other hand, it has been reported that the existence of nitrogen in carbon materials could enhance the interaction between metal NPs and support, and thus increase its activity in reactions such as the electro-oxidation of methanol, the liquid phase oxidation of alcohols, and oxygen reduction.¹⁸²⁻¹⁸⁵ However, there has been no report on the effect of metal-nitrogen interaction in the glycerol electro-oxidation.

Therefore, in this chapter, we developed a catalyst containing Pd NPs which are supported on the surface of nitrogen doped graphitic carbon/graphene (Pd-CN_x/G). Of which the latter was annealed from polypyrrole/GO (PPy/G) at 800 °C. We determined that the interaction between Pd NPs and nitrogen containing carbon materials not only increased activity but also selectivity of three carbon products during glycerol electro-oxidation. Furthermore, due to the high surface area of graphene,⁷² the synthesized CN_x/G results in Pd NPs of smaller sizes. This also benefits the enhancement of the production of three carbon products.

5.2. Materials and methods

5.2.1. Materials

Chemicals used in this work were purchased from Sigma-Aldrich.

5.2.2. Preparation of catalysts

Preparation of graphene oxide (GO): GO was synthesized from graphite flakes by using the modified Hummers method.¹⁸⁶ It includes two steps, the pre-oxidation step and oxidation step. In the pre-oxidation step, 2 g of K₂S₂O₈ and 2 g of P₂O₅ were first dissolved into 8 ml of 98% H₂SO₄ at 80 °C after being stirred for 10 min. 2 g of graphite flakes was then added and the suspension was kept stirring for 4.5 h at 80 °C. After being cooled down to room temperature, the ingredients were diluted with 300 ml of DI water and filtered with 0.2 μm Nylon membrane. The black powder was washed with DI water three times and dried in air overnight. In the oxidation step, the pre-oxidized graphite flakes was added into 80 ml of 98% H₂SO₄. While keeping the temperature at 5 °C by ice bath, KMnO₄ was gradually added under vigorous stirring. After KMnO₄ was fully dissolved, the suspension was stirred at 35 °C for 2 h. 160 ml of DI water

was then added under stirring while the temperature was maintained at 35 °C for 2 h. After that, 460 ml of DI water and 13 ml of 30% H₂O₂ was added in sequence under vigorous stirring. The suspension was placed overnight, then centrifuged and washed with 300 ml of 10% HCl and 300 ml of DI water in sequence. After the pH of suspension was almost neutral, 150 ml of DI water was added. The solution was sonicated for 30 min. Upper solution was collected and diluted into 200 ml to obtain GO suspension. The final concentration was estimated at about 2 wt.%.

Preparation of polypyrrole/GO (PPy/GO): it was synthesized according to the literature procedure with modification.¹⁸⁷ Firstly, 7.2 g of CTAB was dissolved into 80 ml of 1 M HNO₃ solution, then 0.8 g GO dispersion (10 mg ml⁻¹) was added under stirring. After the temperature reached to 10 °C, 0.8 g of pyrrole was added and stirred for 60 min. 20 ml of ammonium persulfate (APS, 2.7g, molar ratio of APS to pyrrole was 1:1) was added to initiate the polymerization. After 180 min, the solid product was filtered and washed with DI water and methanol in sequence, then was vacuum dried at 40 °C for one day. Wire structured PPy was synthesized at the same condition without the addition of GO.

Preparation of Pd-CN_x/G, Pd-CN_x and Pd-CB: firstly PPy/GO and PPy were annealed under Ar atmosphere at 800 °C for 2 h to obtain CN_x/G and CN_x, then 4 mg of annealed support and 1.6 ml of K₂PdCl₄/EG (3 mg ml⁻¹) was added into 10 ml of EG. The solution was ultrasonicated for 0.5 h. After adding 8.4 ml of EG and 0.2 ml of 2 M NaOH/EG, the suspension was microwaved at medium power (300 W) for 110 s using a household microwave oven. The solution was filtered and washed with ethanol several times after it was cooled down. The final product was dried at 60 °C for one day.

5.2.3. Physicochemical characterization

The morphology was observed by using scanning electron microscopy (SEM) at JEOL JSM6701F and transmission electron microscopy (TEM) at JEOL JEM-3010. The X-ray diffraction patterns were collected by Bruker D2 Phaser. The Pd loading in different sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer ICP Optima 2000DV instrument after samples were dissolved by 36% HCl/ 69% HNO₃ (v/v=3/1), Pd loading in Pd-CB, Pd-CN_x and Pd-CN_x/G is 24.55%, 26.35% and 23.93%, respectively. The X-ray photoelectron spectroscopy (XPS) spectra were collected at VG ESCALAB 200i-XL and calibrated by the C1s peak

(284.6 eV). The BET surface area of catalyst was performed by nitrogen adsorption/desorption at 77 K on the Quantachrome Autosorb-6B.

5.2.4. Electrochemical characterization

Electrochemical tests of glycerol oxidation were carried out at room temperature in conventional three-electrode cell using Princeton Applied Research VMP2 multichannel potentiostat. Pt coil and Hg/HgO (6 M KOH) were used as the counter and reference electrode, glassy carbon electrode with 5 mm diameter and carbon paper (CP, $1 \times 1 \text{ cm}^2$, Gashub) were used as the working electrode. The sample was prepared as the following procedure: firstly 1 mg of catalyst was dispersed in 1.45 ml of ethanol solution by ultrasonication for 5 min; then 0.05 ml of 0.5 wt.% Nafion solution was added and ultrasonicated for 10 min to obtain the black dispersion. After that, 30 μl of dispersion was dropped on the glassy carbon electrode and dried to prepare sample with the loading of 0.01 mg cm^{-2} . Moreover, 1 mg of catalyst was dispersed in 0.3 ml of ethanol and 0.05 ml of 0.5 wt.% Nafion solution, then the dispersion was dropped onto CP to prepare sample with the loading of 1 mg cm^{-2} . After being dried, the working electrode was firstly immersed in 0.5 M NaOH + 0.5 M glycerol under stirring for 10 h to fully saturate the electrode, then washed carefully with DI water. It was immersed inside 20 ml of 0.5 M NaOH + 0.5 M glycerol solution during the test. Then 1 ml of solution was collected for the high performance liquid chromatography (HPLC) analysis after setting and applying the specific potential on the working electrode for 2 h.

CO stripping measurement was carried out in 0.5 M HClO_4 by using Ag/AgCl as the reference electrode. After holding potential at 0 V for 40 min while purging CO into the solution, the electrode was removed out of the solution and immersed into fresh 0.5 M HClO_4 which was pretreated by purging N_2 for 30 min. CV then was collected by scanning from -0.166 V to 1.2 V at a scan rate of 50 mV S^{-1} . The oxidation charge of CO monolayer on Pd surface is assumed as $420 \mu\text{C cm}^{-2}$.

5.2.5. Chromatographic determination of products

The obtained products were determined by using Alltech OA-1000 Organic Acid column for high performance liquid chromatography (HPLC, Agilent 1260 Infinity). The eluent was sulfuric acid (4 mM). During the test, 10 μl of sample was injected into the column and the temperature of the column was kept at 80°C . The flow rate was 0.2 ml min^{-1} . The separated compounds were detected

with both the refractive index (RID) detector and UV-Vis detector. The expected glycerol oxidation products were analysed at the same condition to produce the calibration curves.

5.3. Results and discussion

5.3.1. SEM, TEM, XPS, XRD characterization of catalysts

CN_x/G and CN_x were synthesized from PPy/GO and wire structured PPy respectively by annealing them at high temperature (Fig.5.2). In SEM image of CN_x, it's observed that wire structured CN_x forms aggregation to some extent. While in CN_x/G, CN_x is loaded on the surface of graphene, which possesses a larger surface area. This is confirmed by the calculated BET surface area (Fig.5.5). In XPS spectra, the N1s peak of CN_x/G can be deconvoluted into four peaks (Fig.5.3), with pyridinic N, pyrrolic N, quaternary N and pyridine oxide at 398.2, 399.7, 400.8 and 402.1 eV, respectively.²³ Compared to the N1s peak of PPy/GO, CN_x/G shows the obvious increment in the pyridinic N and quaternary N peaks while simultaneously showing a sharp decrement in the pyrrolic N. This demonstrates that most of pyrrolic N in polypyrrole is converted into pyridinic N and quaternary N after high temperature annealing, resulting in the formation of nitrogen doped graphitic carbon materials (CN_x).

Fig.5.2. SEM images of a) CN_x and b) CN_x/G .

Fig.5.3. $\text{N}1s$ XPS spectra of PPy/GO and CN_x/G which is obtained by annealing PPy/GO at 800°C .

Pd NPs were then loaded onto the respective supports via the microwave-polyol method. XRD patterns of Pd-CB, Pd-CN_x and Pd-CN_x/G show the typical face-centered cubic (fcc) structure of Pd (Fig.5.4d). Peaks present at 40.2°, 46.8°, 68.2°, 82.1° can be assigned to the (111), (200), (220) and (311) facets, respectively. Pd NPs on the CN_x/G support show lower peak intensity compared with Pd NPs on CN_x and CB. This indicates smaller particle sizes of Pd NPs on CN_x/G. The mean particle size of Pd is calculated from the Scherrer formula, $d=0.9\lambda/(B*\cos\theta)$, where λ is the wavelength of X-ray, 1.54056 Å, B is the full-width half-maximum of respective diffraction peak and θ is the peak position. After calculation, the mean particle size of Pd-CB, Pd-CN_x and Pd-CN_x/G obtained from XRD patterns is 7.5 nm, 7.6 nm and 6.9 nm respectively.

TEM images were carried out to further confirm the different size distributions (Fig.5.4a, b, c). It is observed that the size of Pd NPs on CN_x/G support is smaller than those present on the CB and CN_x support. The mean diameter of Pd NPs on CN_x/G is 4.40 nm while it is 5.79 nm on CB and 6.30 nm on CN_x, which is smaller than that derived from the XRD patterns. Both TEM and XRD show that Pd NPs on CN_x/G possess the smallest size while Pd NPs present on CN_x support has the largest size distribution. This is caused by the difference of supports. From nitrogen adsorption-desorption isotherms (Fig.5.5), the BET surface area of CN_x, CN_x/G and CB is calculated as 151, 168, 194 m²/g, respectively. Since CN_x has the smallest surface area although it contains the nitrogen atoms on surface, Pd NPs forming on its surface is larger. Compared to CN_x, CN_x/G shows larger surface area. Although its surface area is still lower than CB, the existence of nitrogen atoms makes Pd NPs on CN_x/G exhibit the smallest size distribution.

Fig.5.4. TEM images of a) Pd-CB, b) Pd-CN_x, c) Pd-CN_x/G, insets are the corresponding particle size histograms. d) X-ray diffraction (XRD) patterns of Pd-CB, Pd-CN_x and Pd-CN_x/G.

Fig.5.5. Nitrogen adsorption-desorption isotherms of CB, CN_x and CN_x/G.

5.3.2. Pd utilization of catalysts

In the TEM images (Fig.5.4), the aggregation of Pd NPs is observed in all these samples due to the high loading. In order to examine the extent of aggregation, we studied the Pd utilization of these catalysts. Firstly, CO stripping was carried out to obtain the electrochemical active surface area (EASA) (Fig.5.6a, b, c, d). CO stripping is a common way to calculate the EASA of Pd NPs through the oxidation of absorbed CO. As shown in Fig.5.6a, b and c, an obvious CO stripping peak at around 0.75 V is observed. The calculated EASA of Pd-CB, Pd-CN_x and Pd-CN_x/G is 274, 258, 318 cm² mg⁻¹, respectively. Unsurprisingly, Pd NPs on CN_x/G support show the largest ECSA amongst these three catalysts. Secondly, the chemical surface area (CSA) is derived from equation $CSA = 6/(\rho_{Pd} \cdot \bar{D})$ (where ρ_{Pd} is 12 g/cm³ and $\bar{D}$ is the mean diameter) (Table 5.1). Then Pd utilization is derived from the equation $Pd\ utilization = EASA/CSA$. Pd-CN_x/G shows the smallest Pd utilization while Pd-CN_x and Pd-CB show similar higher Pd utilization. This means that Pd NPs on CN_x/G have the most serious degree of aggregation, although the difference among these catalysts is small.

Fig.5.6. CO stripping voltammetry of a) Pd-CB, b) Pd-CN_x and c) Pd-CN_x/G in 0.5 M HClO₄ solution at a scan rate of 50 mV s⁻¹. d) CO stripping peaks plotted for different samples, the current has been derived by subtracting the first cycle from the second one.

Table 5.1. The particle size, EASA, CSA and Pd utilization of catalysts.

Sample	Particle size / nm	EASA / cm² mg⁻¹_{Pd}	CSA / cm² mg⁻¹_{Pd}	η_{Pd} / %
Pd-CB	5.79	274	863	31.7
Pd-CN_x	6.3	258	793	32.5
Pd-CN_x/G	4.4	318	1136	28.0

5.3.3. Electrocatalytic activity of catalysts

Electrocatalytic activity of the catalysts was studied by using CV in the glycerol alkaline solution. It is observed that Pd-CN_x and Pd-CN_x/G show higher mass-specific peak current density than Pd-CB (Fig.5.7a). They also exhibit higher peak current densities normalized by ECSA (Fig.5.8). If considering the largest mean diameter of Pd NPs on CN_x while the smallest on CN_x/G, the high current density of both these catalysts indicates that the interaction between Pd NPs and nitrogen atoms plays the major factor rather than particle size. We then investigated the stability of these catalysts. Pd-CN_x/G and Pd/CB exhibit better stability than Pd-CN_x (Fig.5.7b). Although Pd NPs on CN_x show slightly better dispersion compared with Pd-CB and Pd-CN_x/G, this is not a major factor in improving catalytic stability. Larger mean size distribution may be the major contributing reason for the instability of Pd-CN_x. Improved activity and stability of Pd-CN_x/G makes it a potential catalyst for glycerol oxidation.

Fig.5.7. a) Cyclic voltammograms (CV) and b) long-term stability of Pd-CB, Pd-CN_x, Pd-CN_x/G in 0.5 M glycerol + 0.5 M NaOH with a scan rate of 50 mV/s. In stability test, the potential scan was performed from -0.8 V to 0.5 V and data was collected after 20 cycles.

Fig.5.8. Cyclic voltammograms (CV) of Pd-CB, Pd-CN_x, Pd-CN_x/G normalized by EASA in 0.5 M glycerol + 0.5 M NaOH with a scan rate of 50 mV/s.

Catalytic activity was also examined at the loading of 1 mg cm^{-2} on carbon paper. It is observed that the current density of Pd-CN_x/G is much higher than that of Pd-CB (~ 1.5 times) at the potential of 0 V (Fig.5.9a). The Coulomb of Pd-CB is 88606 mC/cm^2 , while that of Pd-CN_x/G is 122747 mC/cm^2 . From this we can conclude that Pd-CN_x/G demonstrates higher activity than Pd-CB. Tests at other potentials also support this point (Fig.5.9c, d). However, when the potential increases to 0.6 V, current density of catalysts drops sharply (Fig.5.9b). This was also observed in a previous study where Pd was used as a catalyst in a direct formate fuel cell.¹⁸⁸ The reason is due to the formation of Pd oxide on surface,¹⁸⁹ which drastically decreases the activity of catalysts. Interestingly, the concentration of formic acid reaches the highest value while other components decrease drastically when the deactivation occurs (Fig.5.10). This means that most of glycerol in the oxidation process is converted to formic acid ($\sim 70\%$) on the surface of Pd oxide at high potential.

Fig.5.9. Chronoamperometry curves of Pd-CB, Pd-CN_x and Pd-CN_x/G at a) 0 V, b) 0.6 V, c) 0.2 V and d) 0.4 V with the loading of 1 mg cm^{-2} at 1 cm^2 carbon paper. Inset is the enlarged curves of Pd-CN_x and Pd-CN_x/G at 0.6 V.

Fig.5.10. The concentration of products of a) Pd-CB, b) Pd-CN_x, c) Pd-CN_x/G produced at different potential. The loading is 1 mg cm⁻² and the working electrode is 1 cm² carbon paper.

5.3.4. Electro-oxidation selectivity of catalysts

The selectivity of different catalysts was firstly studied at the low loading (0.1 mg cm⁻², Fig.5.11a). When using Pd-CB as catalyst, the concentration of formic acid is much higher than the total concentration of glycolic acid and oxalic acid (~10%-20% higher). However, the amount of formic acid produced is far more than the total amount of glycolic acid and oxalic acid, especially considering that some of the formic acid produced can be converted to carbonate.^{29, 190, 191} A carbon balance analysis on the glycerol electro-oxidation process and the results shows that there is around 20% carbon deficiency. Since HPLC was used for the determination of various products and the relevant errors introduced during the sampling and measurement are within 3%, the observed carbon deficiency is mainly due to the formation of carbonate ion. In the oxidation process, it is likely that some glycolic acid was oxidized into formic acid through path a (Fig. 5.11b) on Pd-CB. While in the case of Pd-CN_x/G, the amount of formic acid is slightly lower than the total amount of glycolic acid and oxalic acid. This means that path a is suppressed with Pd-CN_x/G. Moreover, the concentration of oxalic acid is slightly higher than that on

Pd-CB, suggesting that the oxidation of glycolic acid on the Pd-CN_x/G favors the path of oxalic acid.

Fig.5.11. a) The product selectivity of Pd NPs on different supports (CB, CN_x, CN_x/G) at various potential. The catalyst loading is 0.1 mg cm⁻² and working electrode is glassy carbon. b) The scheme of glycerol oxidation over Pd-CB, Pd-CN_x and Pd-CN_x/G.

From the product analysis, it can be revealed that Pd-CN_x/G shows enhanced selectivity towards glyceric acid (~10-15% higher) and reduced selectivity towards formic acid (~15% lower) as compared to Pd-CB. Although the concentration of oxalic acid also increases, the ratio between three carbon products and other products in Pd-CN_x/G is still much higher than that in Pd-CB. It is 1.8 times at 0 and 0.2 V and 3.4 times at 0.4 V compared to Pd-CB. We then compared these three catalysts to clarify factors that influencing the selectivity. It is shown that the ratio of three carbon products in Pd-CN_x/G is higher than Pd-CN_x (Fig.5.11a). This is very likely due to the smaller size of Pd NPs in CN_x/G. Moreover, we also observed higher selectivity towards three

carbon products in Pd-CN_x than Pd-CB despite of its larger particle size. This indicates that the interaction between Pd NPs and nitrogen atoms also contributes towards the improvement in selectivity. Because the interaction between metal NPs and adatom-doped carbon support as well as the metal particle size can tailor the electronic property of metal nanoparticles. This may weak the adsorption ability of metal NPs towards three carbon products, especially glyceric acid. Considering the competitive adsorption among three carbon products and other species, weaker adsorption means the oxidation of three carbon products are not preferred compared with other species and more three carbon products are obtained. These two factors enable Pd-CN_x/G to be more selective towards three carbon products compared to the other two catalysts.

Table 5.2. The product selectivity of Pd-CB, Pd-CN_x and Pd-CN_x/G at various potential when the loading is 1 mg cm⁻² and working electrode is carbon paper.

	Pd-CB			Pd-CN _x			Pd-CN _x /G		
	0 V	0.2 V	0.4 V	0 V	0.2 V	0.4 V	0 V	0.2 V	0.4 V
Formic acid	14.0	14.8	16.2	15.4	13.6	26.1	12.2	12.2	15.6
Glycolic acid	6.4	8.9	13.0	7.2	7.1	13.8	5.2	6.7	12.6
Oxalic acid	4.6	4.5	4.9	4.6	5.2	4.0	5.4	5.8	5.7
Glyceric acid	66.0	64.8	59.9	63.6	65.4	51.0	66.3	66.0	59.4
Tartronic acid	9.0	7.0	6.0	9.2	8.7	5.1	10.8	9.3	6.6

When loading is increased to 1 mg cm⁻² and potential is 0 or 0.2 V, selectivity of glyceric acid in all three catalysts exceeds 60% (Table 5.2). At 0.4 V, deactivation occurs in Pd-CN_x (Fig.5.9d) and selectivity of formic acid is obviously higher compared to the other two catalysts. For the selectivity of tartronic acid, it shows a steady increment from Pd-CB to Pd-CN_x and Pd-CN_x/G. Comparing to the selectivity of these catalysts at loading of 0.1 mg cm⁻², these catalysts do not demonstrate a significant difference at 1 mg cm⁻² loading. In our previous work, it is revealed that increasing the loading of Au based

catalysts could effectively enlarge their selectivity difference.²⁶ However, here we can observe that the selectivity towards glyceric acid is almost same in spite that it reaches to around 60%. The disagreement with our previous work might due to the high ratio of glyceric acid produced. As demonstrated in our previous work,²⁶ increasing the loading of catalysts could make the competitive adsorption among different products more intense. Then glyceric acid is more likely to desorb from the surface of Au NPs due to the adsorption of other products, causing the increment of glyceric acid. However, when the selectivity of glyceric acid is over 60%, large amount of glyceric acid in solution will hinder the further desorption of glyceric acid. This means that excess amount of glyceric acid will be further oxidized into other products. It leads to the fact that we can only obtain almost the same selectivity of glyceric acid (~60%) of these catalysts. Moreover, because the smaller particle size and nitrogen interaction in Pd-CN_x/G, more amount of glyceric acid is slowly oxidized into tartronic acid,^{23, 192} causing the slight increment of tartronic acid in Pd-CN_x/G.

5.4. Conclusions

We developed Pd NPs on CN_x/G as a catalyst for application in glycerol oxidation. The larger surface area of CN_x/G compared to CN_x results in smaller sized Pd nanoparticles being loaded on its surface. Due to the smaller particle size and nitrogen interaction with Pd NPs, Pd-CN_x/G shows better activity and also improved stability. Moreover, for the selectivity, we determine that differences in selectivity are suppressed at high loadings (1 mg cm⁻²) owing to the high ratio of glyceric acid (> 60%) present in the solution. However, at lower loadings (0.1 mg cm⁻²), differences are still observed. Part of glycolic acid is oxidized into formic acid when Pd-CB is used as catalyst, while this path is likely to be suppressed when using Pd-CN_x/G as the catalyst. This causes a decrement in the formation of formic acid in Pd-CN_x/G. So comparing to Pd-CB, the nitrogen interaction with Pd NPs in Pd-CN_x/G induces better selectivity to three carbon products, which amounts to more than three times what Pd-CB produces. Besides, compared to Pd-CN_x which having larger particles size, smaller size of Pd NPs on CN_x/G shows improved selectivity towards three carbon products. Therefore, we have found two possible ways, including interacting with nitrogen atoms and decreasing particle size, are effective to enhance the selectivity in the glycerol electro-oxidation.

Chapter 6

The Effect of Cobalt and Sulphur in Nitrogen Doped Carbon/Graphene Material for Oxygen Reduction Reaction

6.1. Introduction

In alcohol fuel cell, the electricity is produced through the oxidation of alcohol at anode and reduction of oxygen at cathode. The oxygen reduction activity of catalyst at cathode is an important factor determining the performance of fuel cell. Usually Pt or Pt based catalysts are used in cathode due to their good oxygen reduction ability.^{193,194} However, due to the scarcity of Pt, other catalysts, such as nitrogen doped carbon materials,^{113,117} have been proposed to replace Pt based catalysts for oxygen reduction reaction (ORR) in alkaline solution at cathode.

Due to the introduction of nitrogen atoms, the spin density and charge distribution of neighboring carbons are largely changed. This causes the activation of carbon region on the surface of nitrogen doped carbon materials.¹⁹⁵ As a result, oxygen adsorption is enhanced and a better ORR activity is favoured. Generally speaking, there are several ways to synthesize nitrogen doped carbon materials. Chemical vapour deposition,¹⁹⁶ solvothermal approach¹⁹⁷ and thermal annealing of nitrogen contained materials¹⁹⁸ all can produce nitrogen contained materials. Among various nitrogen doped carbon materials, nitrogen contained polymer/graphene hybrid material has attracted our interest because of their easy availability.

In previous study, Lai et al. annealed polypyrrole (PPy)/GO and polyaniline (PANI)/GO at high temperature.¹⁹⁹ An improved ORR activity can be achieved after annealing PPy/GO or PANI/GO at 850 °C. The electron transfer number is around 3.3 at -0.4 V vs. Ag/AgCl. Lin et al. annealed PANI/GO at 1000 °C and the as-synthesized catalyst exhibited a typical 4-electron ORR pathway.²⁰⁰ Furthermore, Jiang et al. loaded Co nanoparticles on PPy/GO surface.²⁰¹ After annealing at 800 °C, the catalyst showed a comparative performance of Pt/C. However, the effect of the ratio between polymer and GO in these works is not investigated. Here in this thesis, we carefully studied the effect of the ratio between PPy and GO for ORR activity. Moreover, we doped cobalt ions into PPy/GO hybrid material. After annealing, it showed an improved ORR activity compared with annealed PPy/GO, depending on the ratio between PPy and GO.

We also annealed Co-PPy/GO with sulphur powder and the improvement of ORR activity was observed.

6.2. Materials and methods

6.2.1. Materials

Chemicals used in this work were purchased from Sigma-Aldrich.

6.2.2. Preparation of catalysts

Preparation of graphene oxide (GO): GO was synthesized from graphite flakes by using the modified Hummers method.¹⁸⁶ Firstly, 2 g of $K_2S_2O_8$ and 2 g of P_2O_5 were first dissolved into 8 ml of 98% H_2SO_4 at 80 °C after being stirred for 10 min. 2 g of graphite flakes was then added and the suspension was kept stirring for 4.5 h at 80 °C. After being cooled down to room temperature, the ingredients were diluted with 300 ml of DI water and filtered with 0.2 μm Nylon membrane. The black powder was washed with DI water three times and dried in air overnight. In the oxidation step, the pre-oxidized graphite flakes was added into 80 ml of 98% H_2SO_4 . While keeping the temperature at 5 °C by ice bath, $KMnO_4$ was gradually added under vigorous stirring. After $KMnO_4$ was fully dissolved, the suspension was stirred at 35 °C for 2 h. 160 ml of DI water was then added under stirring while the temperature was maintained at 35 °C for 2 h. After that, 460 ml of DI water and 13 ml of 30% H_2O_2 was added in sequence under vigorous stirring. The suspension was placed overnight, then centrifuged and washed with 300 ml of 10% HCl and 300 ml of DI water in sequence. After the pH of suspension was almost neutral, 150 ml of DI water was added. The solution was sonicated for 30 min. Upper solution was collected and diluted into 200 ml to obtain GO suspension. The final concentration was estimated at about 2 wt.%.

Preparation of polypyrrole/GO (PPy/GO):

Flake form PPy on GO (F-PPy/GO) was synthesized according to the literature procedure. To prepare F-PPy/GO with weight ratio of 1:1 (pyrrole: GO), 90 mg GO was added (10 mg ml^{-1}) into CTAB contained water solution (0.2 g/ 800 ml). The solution was stirred for 24 h and filtered. Then CTAB/GO was dissolved into 100 ml DI water, 80 μl phosphoric acid (H_3PO_4) and 0.09 g pyrrole monomer was added dropwise. The solution was continuously stirred at 15 °C for 2 h. Then APS (Pyrrole: APS=1:1 mol ratio) in 2 ml DI water was slowly added. The polymerization was carried out at 15 °C for 4 h with stirring.

The black sample was filtered and washed with capricious distilled water and methanol, and then dried in vacuum oven.

Wire form PPy on GO (PPy/GO) was synthesized according to the literature procedure.¹⁸⁷ To prepare PPy/GO with weight ratio of 8:1 (pyrrole: GO), 7.2 g of CTAB was dissolved into 80 ml of 1 M HNO₃ solution, then 0.1 g GO dispersion (10 mg ml⁻¹) was added under stirring. After the temperature reached to 10 °C, 0.8 g of pyrrole was added and stirred for 60 min. 20 ml of ammonium persulfate (APS, 2.7g, molar ratio of APS to pyrrole was 1:1) was added to initiate the polymerization. After 180 min, the solid product was filtered and washed with DI water and methanol in sequence, then was vacuum dried at 40 °C for one day. Wire structured PPy was synthesized at the same condition without the addition of GO. PPy/GO with other ratio was synthesized by varying the amount of GO.

Preparation of cobalt in nitrogen doped carbon/graphene material (Co-CN_x/rGO). Firstly 30 mg PPy/GO was dispersed into 30 ml methanol/water (1:1, v:v) solution. Then excess amount of Co(CH₃COO)₂ (23 wt% Co, Co: PPy=0.23) was added. The solution was kept at 60 °C and stirred overnight. After that, product was filtered and washed repeatedly with DI water three times. The product was dried at 80 °C overnight. To obtain the final product, sample was placed in the furnace at Ar atmosphere for 1 h at 700 °C.

Preparation of sulphur doped Co-CN_x/rGO material (Co-S-CN_x/rGO). Same amount of sulphur powder and Co-CN_x/rGO was mixed and grounded for 10 min. Then the mixture was annealed at 700 °C for 1 h to obtain Co-S-CN_x/rGO.

6.2.3. Physicochemical characterization

The morphology was observed by using scanning electron microscopy (SEM) at JEOL JSM6701F. The FTIR spectrum was collected at FTIR-ATR (Bruker). The Raman spectra were measured by Raman spectroscopy (Renishaw), using He/Ne laser with a wavelength of 514 nm. The atomic force microscope (AFM) images of various samples on mica were collected from MFP-3D-SA (Asylum Research) in AC mode. The X-ray photoelectron spectroscopy (XPS) spectra were collected at VG ESCALAB 200i-XL and calibrated by the C1s peak (284.6 eV).

6.2.4. Electrochemical characterization

All electrochemical tests were carried out at room temperature in conventional three-electrode cell using Princeton Applied Research VMP2 multichannel potentiostat. To test the ORR activity of catalyst, Pt foil and Hg/HgO electrode (6 M KOH) were used as counter and reference electrode, glassy carbon electrode with 5 mm diameter was used as the working electrode. The sample was prepared by mixing catalyst dispersion with 0.05 wt% Nafion solution, and dropping the mixture to the glassy carbon electrode. The final loading on the glassy carbon electrode was 0.02 mg of catalysts and 5 μ l of 0.05% Nafion solution.

6.3. Results and discussion

6.3.1 Material characterization

Fig.6.1. AFM height image of GO. The inset shows the height profile along the red line, the layer height is $\sim$ 0.5 nm.

Fig.6.2. SEM images a) wire structured PPy, b) PPy/GO (8:1), c) PPy/GO (4:1), d) PPy/GO (1:1).

We first used AFM to characterize GO in solution. As shown in Fig.6.1, the thickness of GO is around 0.7 nm. Because both sides of GO have the functional groups ($-\text{COOH}$ and $-\text{OH}$) on surface, the thickness of carbon lattice then should be around 0.3 nm. This shows that the synthesized GO was single layer.

Then pyrrole was polymerized onto the surface of GO with different weight ratio (Fig.6.2). When the ratio of PPy to GO is 8:1, large amount of wire structured PPy can be observed and GO is embedded inside. When the ratio is decreased to 1:1, PPy/GO hybrid material can be observed. However, when the ratio reaches to 1:2, even from the sample we can observe an obvious shrink. This shows that the optimised ratio between PPy and GO is around 1:1. When PPy amount is higher than this value, we can obtain excess amount of wire structured PPy. While decreasing this value would lower the amount of PPy and not keep GO stable, this causes the serious aggregation of GO.

Fig.6.3. The FT-IR spectra of GO, wire PPy and PPy/GO (weight ratio 1:1).

FT-IR test was carried out to study the molecular structure change of PPy/GO (Fig.6.3). For GO, peak at 1729 cm^{-1} is assigned to C=O stretching vibration. Peaks at 1220 and 1050 cm^{-1} are C-O (epoxy) and C-O (alkoxy) stretching peaks, respectively.²⁰² For PPy, peaks at 1547 and 1038 cm^{-1} are associated with C-N asymmetric ring-stretching and C-H/N-H vibration, respectively. Peaks at 1176 and 907 cm^{-1} are related to the doping state of PPy.²⁰³ As for the strong and sharp peak at 1384 cm^{-1} , this is assigned to the NO_3^- which is introduced by HNO_3 in solution.²⁰⁴ After pyrrole is polymerized on the surface of GO (PPy/GO), it is observed that peaks associated with the PPy doping state and C-H/N-H vibration shift to a higher position. This shows that part of PPy interacts with the surface of GO and the vibration energy of the bond is changed.

Fig.6.4. The Raman spectra of a) wire structured PPy and CN_x (PPy annealed at 700 °C), b) PPy/GO and CN_x/rGO .

Then Raman spectrum was applied to study the structure change of sample before and after annealing at 700 °C. Through the intensity ratio of D band and G band, we can monitor the defects change on carbon surface. Smaller value means more defects on surface. It is shown that for only PPy annealed after 700 °C, I_D/I_G increases from 0.82 to 0.88; while in PPy/GO this value increases from 0.92 to 0.98. This indicates the graphitic structure of PPy and GO in PPy/GO is both enhanced after annealing due to the formation of nitrogen doped carbon material (CN_x) and reduced GO (rGO).

6.3.2 Effect of the ratio between PPy and GO for the ORR activity of CN_x/rGO

Fig.6.5. Oxygen reduction polarization curves of a) CN_x, b) CN_x/rGO (1:2), c) CN_x/rGO (1:1), d) CN_x/rGO (8:1) in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at different rotation rates and their corresponding Koutechy-Levich plots at different potential.

The ORR activity of CN_x and CN_x/rGO with different ratio is first evaluated by calculating the electron transfer number from Koutechy-Levich (K-L) equation. Specifically, in K-L plot, the linear and the parallel form of these plots indicate the first-order kinetics with respect to molecular oxygen. From following K-L equation, 1/B can be determined.

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{B\omega^{1/2}}$$

Where i is the measured current, i_k is the kinetic current, B is the constant, and ω is the rotation rate (rad/s).

Then from equation $B = 0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}$, where the values of the diffusion coefficient of O₂ (D_{O_2}) is 1.93×10^{-5} cm² s⁻¹, the kinetic viscosity of the solution ν is 1.009×10^{-2} cm² s⁻¹, the concentration of dissolved O₂ in solution (C_{O_2}) is 1.26×10^{-3} mol L⁻¹, F is the Faraday, we can get the electron transfer number at different potential.

Here in thesis, we evaluated the electron transfer number of materials at kinetic/diffusion mixed region and diffusion controlled region. It is shown that the CN_x/rGO with weight ratio no less than 1 has the similar electron transfer

number compared with CN_x . When the ratio is less than 1, the electron transfer number even decreases to around 1.5. The decrement of electron transfer number at lower ratio may be ascribe to the aggregation of GO. This decreases the surface area of CN_x . Unlike other studies,^{199,200} here the introduction of PPy on GO does not enhance the ORR activity of the hybrid material. This may ascribes to the still thick PPy layer on GO.²⁰⁰ In Lin et al.'s work, the amount of PANI is half of GO. In our work, although we tried to lower the amount of GO. The aggregation of GO occurs if lowering the amount of PPy, this causes the decrement of ORR activity.

6.3.3 Effect of cobalt in CN_x/rGO ($\text{Co-CN}_x/\text{rGO}$)

Fig.6.6. Oxygen reduction polarization curves of a) Co-CN_x, b) Co-CN_x/rGO (1:2), c) Co-CN_x/rGO (1:1), d) Co-CN_x/rGO (4:1), e) Co-CN_x/rGO (8:1) in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at different rotation rates and their corresponding Koutechy-Levich plots at different potential.

We then doped cobalt ion into CN_x/rGO by annealing Co-PPy/GO at $700\text{ }^\circ\text{C}$. Different from CN_x and CN_x/rGO , cobalt doping causes an obvious enhancement in $\text{Co-CN}_x/\text{rGO}$ (1:1) compared with Co-CN_x without GO. The electron transfer number increases to around 3.2 even in the kinetic/diffusion mixed region. By contrast, $\text{Co-CN}_x/\text{rGO}$ (8:1) shows the similar electron transfer number than Co-CN_x ; $\text{Co-CN}_x/\text{rGO}$ (1:2) shows smaller electron transfer number. This demonstrates that the existence of GO will be helpful to form the active ORR sites. However, excess amount of PPy causes large part of CN_x can not interact with GO, this decreases the ORR activity of $\text{Co-CN}_x/\text{rGO}$ possessing higher CN_x ratio. On the other hand, small amount of PPy causes serious aggregation and also decreases the ORR activity of $\text{Co-CN}_x/\text{rGO}$ with lower CN_x ratio. The better ORR activity of $\text{Co-CN}_x/\text{rGO}$ (1:1) also is confirmed by its lower Tafel slope (Fig.6.7, Table 6.1).^{205,206}

Fig.6.7. Tafel plots for various catalysts in O_2 -saturated 0.1 M KOH with a sweep rate of 5 mV s^{-1} at 1600 rpm.

Table 6.1. Tafel slope of catalysts

Sample	Co-CN_x	$\text{Co-CN}_x/\text{rGO}$ (1:2)	$\text{Co-CN}_x/\text{rGO}$ (1:1)	$\text{Co-CN}_x/\text{rGO}$ (4:1)	$\text{Co-CN}_x/\text{rGO}$ (8:1)
Tafel slope/ mV dec^{-1}	41	54	40	40	44

6.3.4 Effect of sulphur in Co-CN_x/rGO (1:1)

Fig.6.8. Oxygen reduction polarization curves of Co-S-CN_x/rGO (1:1) in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at different rotation rates and their corresponding Koutechy-Levich plots at different potential.

Fig.6.9. Oxygen reduction polarization curves of a) Co-F-CN_x/rGO (1:1) and b) Co-S-F-CN_x/rGO (1:1) in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at different rotation rates and their corresponding Koutechy-Levich plots at different potential.

We also annealed sulphur with Co-PPy/GO (1:1) at 700 °C to obtain Co-S-CN_x/rGO (1:1). Surprisingly, Co-S-CN_x/rGO (1:1) shows the typical four electron transfer pathway in oxygen reduction (Fig.6.8). By contrast, the electron transfer number of Co-CN_x/rGO (1:1) without sulphur is around 3.5. To understand the enhancement, we also annealed sulphur with Co-F-CN_x/rGO (1:1). In F-CN_x/rGO (1:1), there is no wire structured PPy on GO surface due to the very small amount of CTAB.²⁰⁷ Co-F-CN_x/rGO (1:1) and Co-S-F-CN_x/rGO (1:1) show the similar ORR electron transfer number (Fig.6.9). Therefore, the reason for the improvement of electron transfer number in Co-CN_x/rGO (1:1) by sulphur should be ascribed to the wire structure of PPy. We also annealed sulphur with Co-PPy/GO (8:1) and Co-PPy/GO (1:2), similar enhancement of the electron transfer number is also observed (not shown here).

Fig.6.10. The XPS spectra of Co 2p in a) Co-S-CN_x/rGO and c) Co-S-F-CN_x/rGO, S 2p in b) Co-S-CN_x/rGO and d) Co-S-F-CN_x/rGO.

XPS spectra were carried out to study the difference among these materials. The Co 2p peak in both Co-S-CN_x/rGO (1:1) and Co-S-F-CN_x/rGO (1:1) can be deconvoluted into similar six peaks.²⁰⁸ However, the S 2p peak in Co-S-

CN_x/rGO (1:1) is clearly deconvoluted into three peaks,²⁰⁹ in which contains the S⁴⁺ and S⁶⁺ mixed peak. This peak may be assigned to the compounds formed by Co and S after annealing. Because active ORR sites contained cobalt in wire structured PPy is much easier to be exposed, part of cobalt will be transformed into cobalt sulphur compounds. By contrast, in F-CN_x/rGO, most active sites is embedded by PPy. They are hard to interact with sulphur powder, and thus difficult to form cobalt sulphur compounds. This causes the major difference among these two catalysts in oxygen reduction.

6.4. Conclusions

We annealed PPy/GO at high temperature and studied the ORR activity of CN_x/rGO with different weight ratio between PPy and GO. CN_x/rGO with smaller ratio PPy (GO:PPy = 2:1) shows worse ORR activity due to the aggregation. Moreover, the doping of cobalt into CN_x/rGO shows an obvious promotion of electron transfer number, especially for Co-CN_x/rGO (1:1). The electron transfer number reaches to 3.2 even in the kinetic/diffusion mixed region. The existence of GO largely contributes to the good ORR activity. We also studied the doping effect of sulphur by annealing sulphur with Co-PPy/GO. The electron transfer number of Co-S-PPy/GO (1:1) reaches to 4. The improvement of ORR activity is ascribed to the formation of cobalt sulphur compounds. The wire structure PPy provides cobalt a unique environment to form compounds with sulphur during annealing process. Generally speaking, we studied the doping effect of cobalt and sulphur in PPy/GO. It is revealed that the existence of GO and the cobalt sulphur compounds all increase the ORR activity of catalysts.

Chapter 7

Conclusions and Recommendations for Future Work

7.1. Conclusions

In this thesis, we developed metal nanoparticles (NPs) on graphene based support and applied these composites as catalysts in the methanol and glycerol electro-oxidation. During the process using graphene based materials as supports, we revealed that i) improvement in the conductivity of graphene could greatly enhance the electrocatalytic activity in methanol oxidation; ii) the introduction of pyridine groups through extended polymer chain could effectively tailor the electronic structure of Au NPs, which changed the adsorption ability of Au NPs for oxygen-containing groups and further promoted the selectivity towards glyceric acid in glycerol electro-oxidation; iii) the interaction between Pd NPs and nitrogen containing carbon materials and the size of NPs could both increase the selectivity of three carbon products in glycerol electro-oxidation. Specifically, major findings are shown as the following:

(1) Graphene was successfully exfoliated in water-soluble polymer/DMSO system. It was found that stronger interaction between polymer and graphene produced thinner layer of graphene. This provided a possible way to control graphene with different layers. Because the planar structure of graphite was well kept after exfoliation, it led to the high conductivity of polymer/graphene. Although excess amount of polymer on the surface was disadvantageous for activity enhancement, improved conductivity overcame this drawback and largely increased the electrocatalytic activity of methanol. Moreover, we demonstrated that P4P/graphene based material showed reversible and stable response to the change of pH. It indicated that the as-synthesized polymer/graphene could have different surface properties and be used for various applications, depending on the choice of polymer.

(2) Au NPs on extended P4P chain functionalized graphene was developed as catalyst for glycerol oxidation in alkaline solution. The as-synthesized Au-P4P/G showed the highest activity and selectivity towards three carbon product compared with other catalysts (Au-CB, Au-PmAP/G and Au-P4P/rGO). Due to the extended P4P chain on graphene surface in P4P/G, Au-P4P/G possessed the lowest d-band center which was confirmed by XPS analysis. The lowest d-band center in Au-P4P/G caused the weakest interaction between Au NPs and

glyceric acid, which made glyceric acid easier to desorb from Au surface and hindered the further decomposition of glyceric acid into two and one carbon products.

(3) In order to investigate other factors which may influence the selectivity in glycerol electro-oxidation, Pd NPs on hybrid CN_x/G was synthesized. Due to the interaction between nitrogen atoms and Pd NPs, Pd- CN_x/G showed better activity than Pd-CB and also selectivity. Moreover, its larger surface area compared to CN_x resulted in smaller sized Pd NPs being loaded on the surface of support. This further increased the selectivity of three carbon products. As a result, Pd- CN_x/G produced more than three times of three carbon products compared to what Pd-CB produced. Thus, we have provided two possible ways to enhance the selectivity in the glycerol electro-oxidation.

7.2. Recommendations for future work

The future work is shown as the following:

(1) As shown in chapter 3, polymer exfoliated graphene contains excess amount of polymer on surface due to the adsorption. In most cases, this will bring disadvantages to application. Besides, improving the exfoliation production is still a big problem as far as the sonication assisted liquid-phase exfoliation is concerned. Although small molecules such as pyrene containing derivatives have been used to exfoliate graphene,²¹⁰ studies about the structure effect is very limited. Our future work in this field is to synthesize benzene containing molecules and study their structure effect on the graphene exfoliation.

(2) To achieve the selective electro-oxidation of glycerol, our work is to tailor the interaction between support and metal NPs. The future work in this area will include two parts, i) modifying metal surface with pore containing materials such as metal-organic frameworks, this might confine glycerol or other intermediates inside the pore and promote selectivity; ii) decorating the surface of inert metal NPs with Au or Pd atoms. The density control of Au or Pd atoms on surface might be helpful to achieve the selective electro-oxidation of glycerol.

References

- 1 *The US DOE Hydrogen and Fuel Cell Plan*. Washington, DC **2011**.
- 2 *The Fuel Cell Industry Review UK: FuelCellToday*: **2012**
- 3 Ciesielski, A.; Samori, P. *Chem. Soc. Rev.* **2014**, *43*, 381-398.
- 4 Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345-352.
- 5 *IEA Energy Technology Essentials: Fuel Cells*. France: International Energy Agency: **2007**.
- 6 Shao, Y.; Yin, G.; Wang, Z.; Gao, Y. *J. Power Sources* **2007**, *167*, 235-242.
- 7 Arico, A. S.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, *1*, 133-161.
- 8 Parsons, R.; VanderNoot, T. *J. Electroanal. Chem.* **1988**, *257*, 9-45.
- 9 Chandrasekaran, K. *J. Electrochem. Soc.* **1990**, *137*, 518-524.
- 10 Yu, X.; Pickup, P. G. *J. Power Sources* **2008**, *182*, 124-132.
- 11 Chen, A.; Holt-Hindle, P. *Chem. Rev.* **2010**, *110*, 3767-3804.
- 12 Palma, L. M.; Almeida, T. S.; De Andrade, A. R. *ECS Trans.* **2013**, *58*, 651-661.
- 13 Bellini, M.; Bevilacqua, M.; Innocenti, M.; Lavacchi, A.; Miller, H. A.; Filippi, J.; Marchionni, A.; Oberhauser, W.; Wang, L.; Vizza, F. *J. Electrochem. Soc.* **2014**, *161*, D3032-D3043.
- 14 McCoy, M. *Chem. Eng. News* **2006**, *84*, 7.
- 15 Wilson, E. K. *Chem. Eng. News* **2002**, *80*, 46-49.
- 16 Ma, F.; Hanna, M. A. *Bioresource Technol.* **1999**, *70*, 1-15.
- 17 Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044-4098.
- 18 Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, *10*, 13-30.
- 19 Bambagioni, V.; Bianchini, C.; Marchionni, A.; Filippi, J.; Vizza, F.; Teddy, J.; Serp, P.; Zhiani, M. *J. Power Sources* **2009**, *190*, 241-251.
- 20 Kwon, Y.; Schouten, K. J. P.; Koper, M. T. M. *ChemCatChem* **2011**, *3*, 1176-1185.
- 21 Qi, J.; Xin, L.; Chadderdon, D. J.; Qiu, Y.; Jiang, Y.; Benipal, N.; Liang, C.; Li, W. *Appl. Catal. B: Environ.* **2014**, *154-155*, 360-368.
- 22 Kim, H. J.; Lee, J.; Green, S. K.; Huber, G. W.; Kim, W. B. *ChemSusChem* **2014**, *7*, 1051-1054.
- 23 Xin, L.; Zhang, Z.; Wang, Z.; Li, W. *ChemCatChem* **2012**, *4*, 1105-1114.
- 24 Zhang, Z.; Xin, L.; Li, W. *Appl. Catal. B: Environ.* **2012**, *119-120*, 40-48.
- 25 Zhang, Z.; Xin, L.; Qi, J.; Chadderdon, D. J.; Sun, K.; Warsko, K. M.; Li, W. *Appl. Catal. B: Environ.* **2014**, *147*, 871-878.
- 26 Wang, H.; Thia, L.; Li, N.; Ge, X.; Wang, J.; Liu, Z.; Wang, X. *Appl. Catal. B: Environ.*, doi:10.1016/j.apcatb.2014.11.009.
- 27 Roquet, L.; Belgsir, E. M.; Lbger, J. M.; Lamy, C. *Electrochim. Acta* **1994**, *39*, 2387-2394.
- 28 Falase, A.; Garcia, K.; Lau, C.; Atanassov, P. *Electrochem. Commun.* **2011**, *13*, 1488-1491.
- 29 Marchionni, A.; Bevilacqua, M.; Bianchini, C.; Chen, Y. X.; Filippi, J.; Fornasiero, P.; Lavacchi, A.; Miller, H.; Wang, L.; Vizza, F. *ChemSusChem* **2013**, *6*, 518-528.
- 30 Song, C.; Zhang, J. *PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and applicatios*. Springer London: **2008**.
- 31 Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*. New York: Wiley: **1980**.
- 32 Yeager, E. *J. Mol. Catal* **1986**, *38*, 5-25.
- 33 Murthi, V. S.; Urian, R. C.; Mukerjee, S. J. *J. Phys. Chem. B* **2004**, *108*, 11011-11023.
- 34 Bayer, J.; Ergun, S. *Carbon* **1967**, *5*, 107-111.

- 35 Dicks, A. L. *J. Power Sources* **2006**, *156*, 128-141.
- 36 Pantea, D.; Darmstadt, H.; Kaliaguine, S.; Roy, C. *Appl. Surf. Sci.* **2003**, *217*, 181-193.
- 37 Sharma, S.; Pollet, B. G. *J. Power Sources* **2012**, *208*, 96-119.
- 38 Knights, S. D.; Colbow, K. M.; St-Pierre, J.; Wilkinson, D. P. *J. Power Source* **2004**, *127*, 127-134.
- 39 Yu, X.; Ye, S. *J. Power Sources* **2007**, *172*, 145-154.
- 40 Baker, R. T. K. *Carbon* **1989**, *27*, 315-323.
- 41 Rodriguez, N. M.; Kim, M.; Baker, R. T. K. *J. Phys. Chem.* **1994**, *98*, 13108-13111.
- 42 Steigerwalt, E. S.; Deluga, G. A.; Cliffel, D. E.; Lukehart, C. M. *J. Phys. Chem. B* **2001**, *105*, 8097-8101.
- 43 Bessel, C. A.; Laubernds, K.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem. B* **2001**, *105*, 1115-1118.
- 44 Zheng, J.; Zhang, X.; Li, P.; Zhu, J.; Zhou, X.; Yuan, W. *Electrochem. Commun.* **2007**, *9*, 895-900.
- 45 Lin, Z.; Ji, L.; Krause, W. E.; Zhang, X. *J. Power Sources* **2010**, *195*, 5520-5526.
- 46 Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. *Adv. Mater.* **2001**, *13*, 677-681.
- 47 Xu, J. B.; Zhao, T. S. *RSC Adv.* **2013**, *3*, 16-24.
- 48 Chang, H.; Joo, S. H.; Pak, C. *J. Mater. Chem.* **2007**, *17*, 3078-3088.
- 49 Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169-172.
- 50 Song, S.; Liang, Y.; Li, Z.; Wang, Y.; Fu, R.; Wu, D.; Tsiakaras, P. *Appl. Catal. B Environ.* **2010**, *98*, 132-137.
- 51 Chai, G. S.; Yoon, S. B.; Yu, J. S.; Choi, J. H.; Sung, Y. E. *J. Phys. Chem. B* **2004**, *108*, 7074-7079.
- 52 Sun, Z. P.; Zhang, X. G.; Liang, Y. Y.; Tong, H.; Xue, R. L.; Yang, S. D.; Li, H. L. *J. Electroanal. Chem.* **2009**, *633*, 1-6.
- 53 Joo, S. H.; Lee, H. I.; You, D. J.; Kwon, K.; Kim, J. H.; Choi, Y. S.; Kang, M.; Kim, J. M.; Pak, C.; Chang, H.; Seung, D. *Carbon* **2008**, *46*, 2034-2045.
- 54 Lijima, S. *Nature* **1991**, *354*, 56-58.
- 55 Tan, C. W.; Tan, K. H.; Ong, Y. T.; Mohamed, A. R.; Zein, S. H. S.; Tan, S. H. *Environ. Chem. Lett.* **2012**, *10*, 265-273.
- 56 Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346-349.
- 57 Girishkumar, G.; Vinodgopal, K.; Kamat, P. V. *J. Phys. Chem. B* **2004**, *108*, 19960-19966.
- 58 Matsumoto, T.; Komatsu, T.; Arai, K.; Yamazaki, T.; Kijima, M.; Shimizu, H. *Chem. Commun* **2004**, 840-841.
- 59 Liu, Z.; Lee, J. Y.; Chen, W.; Han, M.; Gan, L. M. *Langmuir* **2004**, *20*, 181-187.
- 60 Jeng, K. T.; Chien, C. C.; Hsu, N. Y.; Yen, S. C.; Chiou, S. D.; Lin, S. H. *J. Power Source* **2006**, *160*, 97-104.
- 61 Day, T. M.; Unwin, P. R.; Macpherson, J. V. *Nano. Lett.* **2007**, *7*, 51-57.
- 62 Day, T. M.; Unwin, P. R.; Wilson, J. V.; Macpherson, J. V. *J. Am. Chem. Soc.* **2005**, *127*, 10639-10647.
- 63 Lago, R. M.; Tsang, S. C.; Lu, K. L.; Chen, Y. K.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1355-1356.
- 64 Tsang, S. C.; Chen, Y. K.; Harris, J. P. F.; Green, M. L. H. *Nature* **1994**, *372*, 159-162.
- 65 Hwang, K. C. *J. Chem. Soc., Chem. Commun.* **1995**, 173-174.
- 66 Hiura, H.; Ebbesen, T. W.; Tanigaki, K. *Adv. Mater.* **1995**, *7*, 275-276.
- 67 Yu, R.; Chen, L.; Liu, Q.; Lin, J.; Tan, K.; Ng, S. C.; Chan, H. S. O.; Xu, G.; Andy Hor, T. S. *Chem. Mater* **1998**, *10*, 718-722.

- 68 Li, W.; Liang, C.; Zhou, W.; Qiu, J.; Li, H.; Sun, G.; Xin, Q. *Carbon* **2004**, 42, 436-439.
- 69 Zhao, X.; Li, W.; Jiang, L.; Zhou, W.; Xin, Q.; Yi, B.; Sun, G. *Carbon* **2004**, 42, 3263-3265.
- 70 Park, S.; Shao, Y.; Kou, R.; Viswanathan, V. V.; Towne, S. A.; Rieke, P. C.; Liu, J.; Lin, Y.; Wang, Y. *J. Electrochem. Soc.* **2011**, 158, B297-B302.
- 71 Wang, S.; Jiang, S. P.; Wang, X. *Nanotechnology* **2008**, 19, 265601.
- 72 Stoller, M. D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R. S. *Nano Lett.* **2008**, 8, 3498-3502.
- 73 Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. *Nano Lett.* **2008**, 8, 902-907.
- 74 Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008**, 321, 385-388.
- 75 Novoselov, K. S.; Geim, A. K.; Morozow, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, 306, 666-669.
- 76 Eizenberg, M.; Blakely, J. M. *Surf. Sci.* **1970**, 82, 228-236.
- 77 Aizawa, T.; Souda, R.; Otani, S.; Ishizawa, Y.; Oshima, C. *Phys. Rev. Lett.* **1990**, 64, 768-771.
- 78 Lu, X.; Yu, M.; Huang, H.; Ruoff, R. S. *Nanotechnology* **1999**, 10, 269-272.
- 79 Berger, C.; Song, Z.; Li, X.; Wu, X.; Brown, N.; Naud, C.; Mayou, D.; Li, T.; Hass, J.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. *Science* **2006**, 312, 1191-1196.
- 80 Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, 80, 1339-1339.
- 81 Viculis, L. M.; Mack, J. J.; Kaner, R. B. *Science* **2003**, 299, 1361-1361.
- 82 Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Ko, Y. K. G. U. N.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. *Nat. Nanotechnol.* **2008**, 3, 563-568.
- 83 Lotya, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De, S.; Wang, Z.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N. *J. Am. Chem. Soc.* **2009**, 131, 3611-3620.
- 84 Li, X.; Zhang, G.; Bai, X.; Sun, X.; Wang, X.; Wang, E.; Dai, H. *Nat. Nanotechnol.* **2008**, 3, 538-542.
- 85 Lin, T.; Tang, Y.; Wang, Y.; Bi, H.; Liu, Z.; Huang, F.; Xie, X.; Jiang, M. *Energy Environ. Sci.* **2013**, 6, 1283-1290.
- 86 Somani, P. R.; Somani, S. P.; Umeno, M. *Chem. Phys. Lett.* **2006**, 430, 56-59.
- 87 Obraztsov, A. N.; Obraztsova, E. A.; Tyurnina, A. V.; Zolotukhin, A. A. *Carbon* **2007**, 45, 2017-2021.
- 88 Yu, Q.; Lian, J.; Siriponglert, S.; Li, H.; Chen, Y. P.; Pei, S. S. *Appl. Phys. Lett.* **2008**, 93, 113103.
- 89 Obraztsov, A. N. *Nat. Nanotechnol.* **2009**, 4, 212-213.
- 90 Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. *Nano Lett.* **2009**, 9, 30-35.
- 91 Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, 324, 1312-1314.
- 92 Charrier, A.; Coati, A.; Argunova, T.; Thibaudau, F.; Garreau, Y.; Pinchaux, R.; Forbeaux, I.; Debever, J. M.; Sauvage-Simkin, M.; Themlin, J. M. *J. Appl. Phys.* **2002**, 92, 2479-2484.
- 93 Forbeaux, I.; Themlin, J. M.; Debever, J. M. *Phys. Rev. B* **1998**, 58, 16396-16406.
- 94 Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. *J. Phys. Chem. B* **2004**, 108, 19912-19916.

- 95 Juang, Z.; Wu, C.; Lo, C.; Chen, W.; Huang, C.; Hwang, J.; Chen, F.; Leou, K.; Tsai, C. *Carbon* **2009**, *47*, 2026-2031.
- 96 Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Rohrl, J.; Rotenberg, E.; Schmid, A. K.; Waldmann, D.; Weber, H. B.; Seyller, T. *Nature materials* **2009**, *8*, 203-207.
- 97 Sutter, P. W.; Flege, J. I.; Sutter, E. A. *Nature materials* **2008**, *7*, 406-411.
- 98 Winterlin, J.; Bocquet, M. L. *Surf. Sci.* **2009**, *603*, 1841-1852.
- 99 Park, S.; Ruoff, R. S. *Nat. Nanotechnol.* **2009**, *4*, 217-224.
- 100 Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558-1565.
- 101 Nethravathi, C.; Rajamathi, M. *Carbon* **2008**, *46*, 1994-1998.
- 102 Choi, S. M.; Seo, M. H.; Kim, H. J.; Kim, W. B. *Carbon* **2011**, *49*, 904-909.
- 103 Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nat. Nanotechnol.* **2008**, *3*, 101-105.
- 104 Yoo, E.; Okata, T.; Akita, T.; Kohyama, M.; Nakamura, J.; Honma, I. *Nano Lett.* **2009**, *9*, 2255-2259.
- 105 Stankovich, S.; Piner, R. D.; Chen, X.; Wu, N.; Nguyen, S. T.; Ruoff, R. S. *J. Mater. Chem.* **2006**, *16*, 155-158.
- 106 Guo, S.; Dong, S.; Wang, E. *ACS Nano* **2010**, *4*, 547-555.
- 107 Ai, K.; Liu, Y.; Lu, L.; Cheng, X.; Huo, L. *J. Mater. Chem.* **2011**, *21*, 3365-3370.
- 108 Guo, S.; Sun, S. *J. Am. Chem. Soc.* **2012**, *134*, 2492-2495.
- 109 Li, H.; Zhang, X.; Pang, H.; Huang, C.; Chen, J. *J. Solid State Electrochem.* **2010**, *14*, 2267-2274.
- 110 Xu, C.; Wang, X.; Zhu, J. *J. Phys. Chem. C* **2008**, *112*, 19841-19845.
- 111 Guo, S.; Wen, D.; Zhai, Y.; Dong, S.; Wang, E. *ACS Nano* **2010**, *4*, 3959-3968.
- 112 Wang, H.; Maiyalagan, T.; Wang, X. *ACS Catal.* **2012**, *2*, 781-794.
- 113 Qu, L.; Liu, Y.; Baek, J.; Dai, L. *ACS Nano* **2010**, *4*, 1321-1326.
- 114 Liang, J.; Jiao, Y.; Jaroniec, M.; Qiao, S. Z. *Angewandte Chemie* **2012**, *51*, 11496-11500.
- 115 Shao, Y.; Zhang, S.; Engelhard, M. H.; Li, G.; Shao, G.; Wang, Y.; Liu, J.; Aksay, I. a.; Lin, Y. *J. Mater. Chem.* **2010**, *20*, 7491-7496.
- 116 Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, *323*, 760-764.
- 117 Deng, D.; Pan, X.; Yu, L.; Cui, Y.; Jiang, Y.; Qi, J.; Li, W.-x.; Fu, Q.; Ma, X.; Xue, Q.; Sun, G.; Bao, X. *Chem. Mater.* **2011**, 1188-1193.
- 118 Nagaiah, T. C.; Kundu, S.; Bron, M.; Muhler, M.; Schuhmann, W. *Electrochemistry Communications* **2010**, *12*, 338-341.
- 119 Niwa, H.; Horiba, K.; Harada, Y.; Oshima, M.; Ikeda, T.; Terakura, K.; Ozaki, J.-i.; Miyata, S. *J. Power Sources* **2009**, *187*, 93-97.
- 120 Kundu, S.; Nagaiah, T. C.; Xia, W.; Wang, Y.; Dommele, S. V.; Bitter, J. H.; Santa, M.; Grundmeier, G.; Bron, M.; Schuhmann, W.; Muhler, M. *J. Phys. Chem. C* **2009**, *113*, 14302-14310.
- 121 Biddinger, E. J.; Deak, D.; Ozkan, U. S. *Top. Catal.* **2009**, *52*, 1566-1574.
- 122 Luo, Z.; Lim, S.; Tian, Z.; Shang, J.; Lai, L.; MacDonald, B.; Fu, C.; Shen, Z.; Yu, T.; Lin, J. *J. Mater. Chem.* **2011**, *21*, 8038-8044.
- 123 Imran Jafri, R.; Rajalakshmi, N.; Ramaprabhu, S. *J. Mater. Chem.* **2010**, *20*, 7114-7117.
- 124 Meng, F.; Li, J.; Cushing, S. K.; Zhi, M.; Wu, N. *J. Am. Chem. Soc.* **2013**, *135*, 10286-10289.
- 125 Cao, X.; Shi, Y.; Shi, W.; Lu, G.; Huang, X.; Yan, Q.; Zhang, Q.; Zhang, H. *Small* **2011**, *7*, 3163-3168.

- 126 Tang, Z.; Shen, S.; Zhuang, J.; Wang, X. *Angewandte Chemie* **2010**, *122*, 4707-4711.
- 127 Sattayasamitsathit, S.; Gu, Y.; Kaufmann, K.; Jia, W.; Xiao, X.; Rodriguez, M.; Minter, S.; Cha, J.; Burckel, D. B.; Wang, C.; Polsky, R.; Wang, J. *J. Mater. Chem. A* **2013**, *1*, 1639-1645.
- 128 Cong, H.; Ren, X.; Wang, P.; Yu, S. *ACS Nano* **2012**, *6*, 2693-2703.
- 129 Wu, Z. S.; Yang, S.; Sun, Y.; Parvez, K.; Feng, X.; Mullen, K. *J. Am. Chem. Soc.* **2012**, *134*, 9082-9085.
- 130 Park, S.; Ruoff, R. S. *Nature nanotechnology* **2009**, *4*, 217-224.
- 131 Khan, U.; May, P.; Neill, A. O.; Coleman, J. N. *Carbon* **2010**, *48*, 4035-4041.
- 132 Liang, Y. T.; Hersam, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 17661-17663.
- 133 May, P.; Khan, U.; Neill, A. O.; Coleman, J. N. *J. Mater. Chem.* **2012**, *22*, 1278-1282.
- 134 Salavagione, H. J.; Ellis, G.; Segura, J. L.; Gomez, R.; Morales, G. M.; Gerardo, M. *J. Mater. Chem.* **2011**, *21*, 16129-16135.
- 135 Simões, M.; Baranton, S.; Coutanceau, C. *Appl. Catal. B: Environ.* **2010**, *93*, 354-362.
- 136 Wang, G.; Yang, J.; Park, J.; Gou, X.; Wang, B.; Liu, H.; Yao, J. *J. Phys. Chem. C* **2008**, *112*, 8192-8195.
- 137 Wajid, A. S.; Das, S.; Irin, F.; Ahmed, H. S. T.; Shelburne, J. L.; Parviz, D.; Fullerton, R. J.; Jankowski, A. F.; Hedden, R. C.; Green, M. J. *Carbon* **2012**, *50*, 526-534.
- 138 Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. A.; Stubos, A. K.; Trapalis, C. *Solid State Commun.* **2009**, *149*, 2172-2176.
- 139 May, P.; Khan, U.; Hughes, J. M.; Coleman, J. N. *J. Phys. Chem. C* **2012**, *116*, 11393-11400.
- 140 Rivas, B. L.; Sanchez, C. O. *J. Appl. Polym. Sci.* **2003**, *89*, 2641-2648.
- 141 Li, D.; He, Q.; Cui, Y.; Li, J. *Chem. Mater.* **2007**, *19*, 412-417.
- 142 Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed. John Wiley & Sons: New York: **1999**.
- 143 Sauer, B. B.; Dee, G. T. *Macromolecules* **2002**, *35*, 7024-7030.
- 144 Spyriouni, T.; Vergelati, C. *Macromolecules* **2001**, *34*, 5306-5316.
- 145 Hernandez, Y.; Lotya, M.; Rickard, D.; Bergin, S. D.; Coleman, J. N. *Langmuir* **2010**, *26*, 3208-3213.
- 146 Shih, C.; Lin, S.; Strano, M. S.; Blankschtein, D. *J. Am. Chem. Soc.* **2010**, *132*, 14638-14648.
- 147 Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozow, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Boukhvalov, D. W.; Katsnelson, M. I.; Geim, A. K.; Novoselov, K. S. *Science* **2009**, *323*, 610-613.
- 148 Radmilovic, V.; Gasteiger, H. A.; Ross, P. N. *J. Catal.* **1995**, *154*, 98-106.
- 149 Sugimoto, W.; Iwata, H.; Yokoshima, K.; Murakami, Y. *J. Phys. Chem. B* **2005**, *109*, 7330-7338.
- 150 Guo, H.; Wang, X.; Qian, Q.; Wang, F.; Xia, X. *ACS Nano* **2009**, *3*, 2653-2659.
- 151 Long, N. V.; Ohtaki, M.; Nogami, M.; Hien, T. D. *Colloid Polym. Sci.* **2011**, *289*, 1373-1386.
- 152 Zhou, J.; Wang, G.; Hu, J.; Lu, X.; Li, J. *Chem. Commun.* **2006**, 4820-4822.
- 153 Bianchini, C.; Shen, P. K. *Chem. Rev.* **2009**, *109*, 4183-4206.
- 154 Yu, E. H.; Krewer, U.; Scott, K. *Energies* **2010**, *3*, 1499-1528.
- 155 Avramov-Ivić, M. L.; Leger, J. M.; Lamy, C.; Jović, V. D.; Petrović, S. D. *J. Electroanal. Chem.* **1991**, *308*, 309-317.
- 156 Avramov-Ivic, M.; Léger, J. M.; Beden, B.; Hahn, F.; Lamy, C. *J. Electroanal. Chem.* **1993**, *351*, 285-297.
- 157 Schell, M.; Xu, Y.; Zdraveski, Z. *J. Phys. Chem.* **1996**, *100*, 18962-18969.

- 158 Ciriminna, R.; Palmisano, G.; Pina, C. D.; Rossi, M.; Pagliaro, M. *Tetrahedron Lett.* **2006**, 47, 6993-6995.
- 159 Kwon, Y.; Birdja, Y.; Spanos, I.; Rodriguez, P.; Koper, M. T. M. *ACS Catal.* **2012**, 2, 759-764.
- 160 Kwon, Y.; Hersbach, T. J. P.; Koper, M. T. M. *Top. Catal.* **2014**, 57, 1272-1276.
- 161 Coutanceau, C.; Zalineeva, A.; Baranton, S.; Simoes, M. *Int. J. Hydrogen Energy* **2014**, 39, 15877-15886.
- 162 Zalineeva, A.; Serov, A.; Padilla, M.; Martinez, U.; Artyushkova, K.; Baranton, S.; Coutanceau, C.; Atanassov, P. B. *J. Am. Chem. Soc.* **2014**, 136, 3937-3945.
- 163 Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Hutchings, G. J. *Chem. Commun.* **2002**, 696-697.
- 164 Zope, B. N.; Hibbitts, D. D.; Neurock, M.; Davis, R. J. *Science* **2010**, 330, 74-78.
- 165 Rodrigues, E. G.; Carabineiro, S. A. C.; Delgado, J. J.; Chen, X.; Pereira, M. F. R.; Órfão, J. J. M. *J. Catal.* **2012**, 285, 83-91.
- 166 Kwon, Y.; Schouten, K. J. P.; Koper, M. T. M. *ChemCatChem* **2011**, 3, 1176-1185.
- 167 Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. *J. Am. Chem. Soc.* **2009**, 131, 7086-7093.
- 168 Kim, H. J.; Choi, S. M.; Green, S.; Tompsett, G. A.; Lee, S. H.; Huber, G. W.; Kim, W. B. *Appl. Catal. B: Environ.* **2011**, 101, 366-375.
- 169 Wang, S.; Yang, F.; Jiang, S. P.; Chen, S.; Wang, X. *Electrochem. Commun.* **2010**, 12, 1646-1649.
- 170 Kar, P.; Pradhan, N. C.; Adhikari, B. *Mater. Chem. Phys.* **2008**, 111, 59-64.
- 171 Wang, H.; Xia, B.; Yan, Y.; Li, N.; Wang, J. Y.; Wang, X. *J. Phys. Chem. B* **2013**, 117, 5606-5613.
- 172 Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray photoelectron spectroscopy*. Perkin-Elmer Corporation: Minnesota, **1979**.
- 173 Ono, L. K.; Croy, J. R.; Heinrich, H.; Roldan Cuenya, B. *J. Phys. Chem. C* **2011**, 115, 16856-16866.
- 174 Osswald, S.; Yushin, G.; Mochalin, V.; Kucheyev, S. O.; Gogotsi, Y. *J. Am. Chem. Soc.* **2006**, 128, 11635-11642.
- 175 Vijaya Kumar, R.; Koltypin, Y.; Cohen, Y. S.; Cohen, Y.; Auibach, D.; Palchik, O.; Felner, I.; Gedanken, A. *J. Mater. Chem.* **2000**, 10, 1125-1129.
- 176 Zhang, Z.; Xin, L.; Li, W. *Appl. Catal. B* **2012**, 119-120, 40-48.
- 177 Sugimoto, W.; Iwata, H.; Yokoshima, K.; Murakami, Y. *J. Phys. Chem. B* **2005**, 109, 7330-7338.
- 178 Park, I.; Lee, K.; Jung, D.; Park, H.; Sung, Y. *Electrochim. Acta* **2007**, 52, 5599-5605.
- 179 S., T.; Petrii, O. A. *Pure & Appl. Chem.* **1991**, 63, 711-734.
- 180 Zhang, P.; Sham, T. *Phys. Rev. Lett.* **2003**, 90, 245502.
- 181 Lima, F. H. B.; Zhang, J.; Shao, M. H.; Sasaki, K.; Vukmirovic, M. B.; Ticianelli, E. A.; Adzic, R. R. *J. Phys. Chem. C* **2007**, 111, 404-410.
- 182 Ma, Y.; Jiang, S.; Jian, G.; Tao, H.; Yu, L.; Wang, X.; Wang, X.; Zhu, J.; Hu, Z.; Chen, Y. *Energy Environ. Sci.* **2009**, 2, 224-229.
- 183 Imran Jafri, R.; Rajalakshmi, N.; Ramaprabhu, S. *J. Mater. Chem.* **2010**, 20, 7114-7117.
- 184 Zhang, L. S.; Liang, X. Q.; Song, W. G.; Wu, Z. Y. *Phys. Chem. Chem. Phys.* **2010**, 12, 12055-12059.
- 185 Chan-Thaw, C. E.; Villa, A.; Veith, G. M.; Kailasam, K.; Adamczyk, L. A.; Unocic, R. R.; Prati, L.; Thomas, A. *Chemistry, an Asian journal* **2012**, 7, 387-393.
- 186 Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chem. Mater.* **1999**, 11, 771-778.

- 187 Zhang, L. L.; Zhao, S.; Tian, X. N.; Zhao, X. S. *Langmuir* **2010**, *26*, 17624-17628.
- 188 Bartrom, A. M.; Haan, J. L. *J. Power Sources* **2012**, *214*, 68-74.
- 189 Bolzán, A. E. *J. Electroanal. Chem.* **1995**, *380*, 127-138.
- 190 Bambagioni, V.; Bevilacqua, M.; Bianchini, C.; Filippi, J.; Marchionni, A.; Vizza, F.; Wang, L. Q.; Shen, P. K. *Fuel Cells* **2010**, *10*, 582-590.
- 191 Lin, J.; Ren, J.; Tian, N.; Zhou, Z.; Sun, S. *J. Electroanal. Chem.* **2013**, *688*, 165-171.
- 192 Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Kiely, C. J.; Hutchings, G. J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1329-1336.
- 193 Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. *Appl. Catal. B: Environ.* **2005**, *56*, 9-35.
- 194 Lim, B.; Jiang, M.; Camargo, P. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. *Science* **2009**, *324*, 1302-1305.
- 195 Zhang, L.; Xia, Z. *J. Phys. Chem. C* **2011**, *115*, 11170-11176.
- 196 Reddy, A. L. M.; Srivastava, A.; Gowda, S. R.; Gullapalli, H.; Dubey, M.; Ajayan, P. M. *ACS Nano* **2010**, *4*, 6337-6342.
- 197 Zhang, C.; Fu, L.; Liu, N.; Liu, M.; Wang, Y.; Liu, Z. *Adv. Mater.* **2011**, *23*, 1020-1024.
- 198 Wen, Z.; Wang, X.; Mao, S.; Bo, Z.; Kim, H.; Cui, S.; Lu, G.; Feng, X.; Chen, J. *Adv. Mater.* **2012**, *24*, 5610-5616.
- 199 Lai, L.; Potts, J. R.; Zhan, D.; Wang, L.; Poh, C. K.; Tang, C.; Gong, H.; Shen, Z.; Lin, J.; Ruoff, R. S. *Energy Environ. Sci.* **2012**, *5*, 7936-7942.
- 200 Lin, Z.; Waller, G.; H.; Liu, Y.; Liu, M.; Wong, C. *Carbon* **2013**, *53*, 130-136.
- 201 Jiang, S.; Zhu, C.; Dong, S. *J. Mater. Chem. A* **2013**, *1*, 3593-3599.
- 202 Zhang, J.; Yang, H.; Shen, G.; Cheng, P.; Zhang, J.; Guo, S. *Chem. Commun.* **2010**, *46*, 1112-1114.
- 203 Yang, S.; Shen, C.; Liang, Y.; Tong, H.; He, W.; Shi, X.; Zhang, X.; Gao, H. *Nanoscale* **2011**, *3*, 3277-3284.
- 204 Qian, R.; Qiu, J.; Shen, D. *Synth. Met.* **1987**, *18*, 13-18.
- 205 Coutanceau, C.; Croissant, M. J.; Napporn, T.; Lamy, C. *Electrochim. Acta* **2000**, *46*, 579-588.
- 206 Grolleau, C.; Coutanceau, C.; Pierre, F.; Leger, J. M. *Electrochim. Acta* **2008**, *53*, 7157-7165.
- 207 Yang, S.; Shen, C.; Liang, Y.; Tong, H.; He, W.; Shi, X.; Zhang, X.; Gao, H. *Nanoscale* **2011**, *3*, 3277-3284.
- 208 Olson, T. S.; Pylypenko, S.; Atanasov, P. *J. Phys. Chem. C* **2010**, *114*, 5049-5059.
- 209 Periyat, P.; Pillai, S. C.; McCormack, D. E.; Colreavy, J.; Hinder, S. J. *J. Phys. Chem. C* **2008**, *112*, 7644-7652.
- 210 Ciesielski, A.; Samori, P. *Chem. Soc. Rev.* **2014**, *43*, 381-398.