齊魯工業大學
QILU UNIVERSITY OF TECHNOLOGY

Undergraduate Graduation Thesis

Palladium Nanoparticles Loaded on the Hybrids of TiO_2 and Graphene (Pd/TiO_2-Gr) and the Enhanced Electrocatalytic Activity for Formic Acid Oxidation

College Name **School of Chemical and Pharmaceutical Engineering**

Professional Class **Applied Chemistry (English) Class 15-1**

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May 18, 2019

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ABSTRACT

Fuel cells are widely used and play an important role in today's society and in the future. In recent years, people have paid great attention to the research work of fuel cells. The research and preparation of high performance and low cost anode catalysts have far-reaching significance for promoting the development of fuel cells, but there are still major challenges. The catalyst currently commonly used in acid fuel cell anodes is a Platinum (Pt) based catalyst. It is found that metal Pd and Pt have similar crystal structure and electronic properties. Pd has lower cost and better catalytic activity and anti-toxicity than Pt catalyst. Therefore, Pd-based catalyst becomes the preferred anode catalyst for acid fuel cell. In recent years, many efforts have been made to improve the electrocatalytic performance of palladium-based catalysts in acid fuel cells. The catalytic performance of the metal catalyst is mainly related to the structural characteristics of the catalyst, the compound composition and the carrier structure. The loading of the metal nanoparticle catalyst onto the catalyst carrier not only improves the catalytic efficiency of the catalyst, but also increases the dispersion of the metal nanoparticles by the high specific surface area and the porous structure of the carrier, thereby inhibiting the agglomeration of the nanoparticles. Therefore, our work mainly includes improving the catalyst carrier and preparing a binary palladium-based compound catalyst. This paper focuses on the anode electrocatalysts of acid fuel cells. We prepared different palladium compounds as well as different supports and different extrinsic conditions. Then screen them to find high-performance catalysts. We prepared Pd/C and Pd/TiO_2-graphene catalysts, and studied the catalytic performance of formic acid oxidation. The activity and stability tests were carried out by electrochemical measurements such as cyclic voltammetry (CV), linear scanning (LSV), and so on. The main results are as follows:

1. Hybrids of Titanium dioxide and reduced graphene oxide (TiO_2-rGO) were prepared by solvothermal method using graphene oxide (GO) and tetra butyl titanate as precursors. Pd was supported on the carrier by sodium borohydride reduction method to synthesize Pd/ TiO_2-rGO catalyst. We prepared a total of four different ratios of Pd/TiO_2-rGO catalysts (precursor mass ratio TBT: GO = 0.5, 1.0, 2.0, 4.0), and then studied its electrocatalytic activity under acidic conditions, and then selected the catalyst. The highest activity ratio showed that TiO_2-rGO is a good carrier. In our newly prepared catalyst, the TBT and GO mass ratio of 1 is the most active and the electrocatalytic activity is the best.

2. Illumination was applied to the electrode to study the photo-assisted formic acid oxidation at the Pd/TiO_2-rGO catalyst. The results show that the photo-assisted effects depend on the proportions of Pd/TiO_2-rGO catalysts. The activity of formic acid oxidation (FAO) at the catalyst that TBT : GO = 0.5:1 (mass ratio) was decreased after illumination. So was the catalyst that TBT : GO = 1:1 (mass ratio). The catalysts with mass ratio TBT : GO = 2.:1 (or 4:1) exhibit enhanced activity after illumination.

Keywords: Formic acid oxidation; Fuel cells; Palladium-based catalyst; Illumination

摘 要

燃料电池用途广泛,在当今社会乃至未来生活中都扮演重要的角色。近年来，人们对燃料电池的研究工作给予了高度重视。具有高性能、低成本的阳极催化剂的研究与制备对促进燃料电池的发展具有深远的意义,但目前仍存在着较大的挑战。目前普遍应用于酸性燃料电池阳极的催化剂是钯（Pd）基催化剂。研究发现金属Pd和铂（Pt）具有相似的晶体结构和电子特性，Pd的成本较低且具有比Pt催化剂更好的催化活性和抗毒化能力，因此Pd 基催化剂成为酸性燃料电池首选的阳极催化剂。近年来，在提高酸性燃料电池中钯基催化剂的电催化性能方面做了许多努力。金属催化剂的催化性能主要和催化剂的结构特征、合金组成和载体结构等因素有关。将金属纳米粒子催化剂负载到催化剂载体上，不仅能提高催化剂的催化效率,而且载体的高比表面积和多孔结构还能增大金属纳米粒子的分散度，从而抑制纳米粒子的团聚。所以我们的工作主要是改进催化剂载体和制备二元钯基化合物催化剂。本论文重点对酸性燃料电池的阳极电催化剂进行了探究。我们主要通过制备不同的钯基化合物以及不同载体和不同的外在条件来改变性能以备筛选。我们制备了Pd/C 、Pd/TiO_2-graphene催化剂，研究了在酸性条件下对甲酸、硫酸以及碱性条件下NaOH还有光照条件下的电氧化反应的催化性能。通过循环伏安技术(CV)，线性扫描技术(LSV)等一系列电化学测试进行了活性及稳定性测试，主要研究结果如下：

1. 以氧化石墨烯（GO）和钛酸四丁酯为前驱体通过溶剂热方法制备二氧化钛-还原氧化石墨烯（TiO_2-rGO）作为载体，通过硼氢化钠还原法将Pd 负载到载体上合成Pd/TiO_2-rGO催化剂。我们总共制备了4种不同比例的Pd/TiO_2-rGO 催化剂，(前驱体质量比TBT ： GO = 0.5，1.0，2.0，4.0)，进而研究其在酸性条件下的电催化活性，然后选出催化活性最高的质量比，结果表明TiO_2-rGO是一种很好的载体，在我们新制备的催化剂中，TBT与 GO质量比为1时活性最大，电催化活性最好。

2. 我们又对催化外在环境条件进行了适当的改变,即进行测试的时候加光照来研究Pd/TiO_2-rGO催化剂在甲酸氧化反应表现出的电催化活性。结果表明，不同比例的Pd/TiO_2-rGO催化剂受光照的影响不同，其中质量比TBT ： GO = 0.5，1.0的催化剂加光照后反应活性减弱，质量比TBT ： GO = 2.0，4.0的催化剂光照后反应活性增强。

关键词： 甲酸燃料电池　钯基催化剂　甲酸电氧化　光照

Chapter 1 Introduction

1.1 The Fuel Cell

1.1.1 Overview of Fuel Cells and Research Implications:

With the development of society, people pay more and more attention to the environment. Dasgupta et al. [1] pointed out that a good economic market is more inclined to develop in a clean and friendly environment. Energy-efficient and environment-friendly science and technology are highly respected in today's society. Countries with more developed economic structures are more inclined to improve environmental conditions by exploring and applying environmentally friendly technologies and encouraging energy conservation and emission reduction. People's daily life is inseparable from energy, and the use of energy is closely related to the sustainable development of human beings. Due to the declining fossil fuel reserves and concerns about greenhouse gas emissions, the global energy system is shifting to a new energy model that has slowly shifted the source of energy supply from fossil fuels to renewable energy. In addition, the release process of fossil fuels such as fossils is accompanied by a series of environmentally harmful gases such as carbon dioxide, carbon monoxide, sulfur dioxide, sulfur trioxide, and nitrogen oxides. These substances can react in the atmosphere to form acid rain, photochemical smog. The greenhouse effect causes the global climate to warm, which in turn creates a series of hazards. At the same time, the dust generated by combustion is one of the important reasons for the formation of smog. The main hazard components of smog include PM10 and PM2.5, among which PM2.5 refers to particles that can be inhaled into the lungs, which is very good for human life and health. Great harm. Studies have shown that the energy structure is related to environmental pollution. As long as the coal consumption in energy increases, the concentration of respirable lung particles in the atmosphere will increase accordingly. Therefore, people are eager to change the energy structure and look for a high-quality resource that is safe, non-toxic, and energy-efficient, to meet people's needs for production and life.

Fuel cell, as a device that directly converts chemical energy into electrical energy, greatly satisfies people's environmental emission requirements. Unlike previous heat engines, its energy conversion efficiency is high, and it is not limited by the Carnot cycle principle. No pollution, less disturbance by external factors, and no noise pollution, has gradually become the ideal way of energy transformation in people's minds. The theoretical research of fuel cell originated earlier. William Grove proposed the theory through the reverse reaction of hydrolysis process in 1839. The first single cell was synthesized with hydrogen and oxygen as the research object, which laid the foundation for the future research of fuel cell. Initial fuel cell research was slow to develop, and after a century, Francis T. Bacon broke the limits of its application and made it widely used in life. In the 1960s, due to the special needs of spacecraft and deep-sea submersibles for power supply, fuel cells were widely developed and

successfully applied to the Apollo 11 spacecraft as a power source. In 1973, the oil crisis triggered the development of fuel cell power stations. The craze, phosphoric acid fuel cells (PAFC), molten carbonate batteries and solid oxide fuel cells (SOFC) were developed. Then, due to the easing of the oil crisis, the craze for fuel cell research has receded. However, in 1987, American studies showed that the content of exhaust pollutants in the atmosphere accounted for more than 90% of atmospheric pollutants, and fuel cells have become a hot research topic. In 1993, Ballard Power Company of Canada showed a bus powered by a proton exchange membrane fuel cell. Toyota's fuel cell vehicles have been introduced to the market in 2015. On November 22, 2017, Weichai Power Co., Ltd. announced that it has signed a strategic cooperation framework agreement with Robert Bosch. The two sides will establish a world-class fuel cell vehicle technology innovation chain and industrial chain to jointly develop and produce hydrogen fuel cells and related components. On October 30, 2018, Toyota released a modified modified sedan fuel cell vehicle (FCV) Mirai. This is the first improvement since its launch in December 2014. Under the policy blessing, fuel cell vehicles have been popular in the past two years. According to data released by the China Association of Automobile Manufacturers, sales of new energy vehicles reached 299,000 units in the first quarter of this year, of which 273 vehicles were sold in the first quarter. In the report released by CICC, the fuel cell vehicle's comprehensive performance in energy density, cruising range and fuel refueling time is much higher than that of new energy vehicles equipped with lithium batteries, which is expected to become the driving force of the fuel cell industry chain. It is estimated that the fuel cell industry chain will reach 25.5 billion US dollars in 2024, and the average annual compound growth rate will exceed 20%. From these data, we can see the future development of fuel cells.

1.1.2 Classification of Fuel Cells

There are many types of fuel cells, and the classification methods are also different. The classification methods can be classified according to working temperature, combustion treatment method, and electrolyte.

According to working temperature: low temperature type (less than 120 °C), medium temperature type (120-260 °C), high temperature type (260-750 °C), ultra high temperature type (750-1200 °C).

According to the combustion treatment temperature: connection type, indirect type, renewable type.

According to the electrolyte: Proton Exchange Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Solid Oxide Fuel Cell (Solid) Oxide Fuel Cell (SOFC) and Molten Carbonate Fuel Cell (MCFC) [2, 3].

1.1.3 Characteristics of Fuel Cells

(1) High Power Generation Efficiency

A fuel cell is a device that directly converts chemical energy into electrical energy. Unlike a conventional power plant, it does not need to perform energy conversion such as chemical energy-thermal energy-mechanical energy-electric energy through boilers, steam turbines, generators, and the like. Its efficiency is not limited by the Carnot cycle principle, and the theoretical energy conversion efficiency can reach 85% to 90%. However, due to various factors, the actual conversion efficiency is not so high, but it can reach 40% to 60% in all aspects, so the fuel cell is considered to be a more efficient device.

(2) Less Harmful to The Environment

When the fuel of the fuel cell is pure hydrogen, the product is water, and there are no emissions such as CO, NOx, SOx, dust, etc., so that the environmental damage is greatly reduced. When the fuel is rich in hydrogen, CO_2 emissions are reduced by about 40% compared to other heat engines, reducing greenhouse gas emissions. Moreover, the fuel gas undergoes a strict desulfurization process before the reaction is carried out. When the reaction gas is hydrogen-rich or pure hydrogen, the emissions of sulfur compounds and nitrogen-containing compounds in the product are greatly reduced.

(3) Noise-free Pollution

The fuel cell is an electrochemical device that does not have the collision friction and mechanical loss of the device like other heat engines, so the noise is greatly reduced during operation.

(4) Flexible Device Load Adjustment

The power generation device of the fuel cell is a modular device, which is simple and convenient to install or disassemble, and the power generation capacity is relatively easy to control, and can provide both large electric energy and small electric energy supply. The arrangement of the power generating device can be concentrated or dispersed. use. No matter whether it is at rated power or overload operation or lower than rated power, the efficiency is stable, it can withstand and the efficiency does not change much.

(5) High Reliability

It operates highly reliably and can be used as a power source for emergency and uninterruptible power supplies as well as for distributed power plants.

(6) Wide Range of Fuel Sources

The fuel cell fuel is in line with the requirements of energy diversification. Any substance containing hydrogen atoms can be used as a reactant fuel, such as methanol, ethanol and other alcohols, gas, biogas, natural gas and other hydrogen-containing

gases, light oil and diesel. A variety of substances.

1.1.4 Fuel Cell Applications

(1) Used for Electricity Generation

Fuel cells are widely used in a series of advantages such as high energy efficiency, low pollution, wide fuel source, simple device, high reliability and high stability. It is also considered as the fourth generation power generation device after the emergence of hydraulic, thermal and nuclear energy. It is also a potential power unit to replace the internal combustion engine. Fuel cell power generation is a distributed power generation technology that can be used as a supplement to traditional power generation [4, 5] to help avoid large-scale power outages caused by war or large-scale power grid failures. People with conservative views believe that large-scale power plants have low cost in considering cost issues, so distributed power generation does not have much advantage. However, as market demand changes, distributed power generation has more and more The advantages are revealed and the cost is continuously decreasing. Its specific advantages are as follows: First, it can provide independent power supply for users, and balance fuel and electricity. The second is to share the pressure on the power supply system and ease the tension. Third, flexible power supply can be provided according to specific regions and conditions to promote the improvement of power supply efficiency. Fourth, the equipment is simple, and the maintenance is simple. Fuel cells have long been considered an excellent alternative to conventional power generation, and they can be used in large and decentralized power plants to take full advantage of these advantages. PAFC is a first-generation fuel cell technology. It uses a phosphoric acid aqueous solution as an electrolyte and uses natural gas or methanol with a high hydrogen purity as a fuel. It operates at a high temperature of 200 ° C and has a power generation efficiency of about 40%. Such a battery requires a platinum catalyst, the cost is high, and the platinum catalyst gradually increases in particle size during use, forming agglomerates and shortening the service life of the battery, so a second generation fuel cell MCFC has been developed. The MCFC operates at a high temperature of 600-700 °C, and the chemical reaction is extremely active, and high-priced catalysts such as platinum are not required. In addition to using hydrogen-rich natural gas, it can also use carbon monoxide-containing fuels such as gas. The molten carbonate fuel cell has a power generation efficiency of about 50%, and can also utilize its high-temperature heat rejection to combine with a steam turbine to realize composite power generation and further improve power generation efficiency. SOFC, which develops rapidly and has strong applicability, has become a third-generation fuel cell [6]. Its electrolyte uses ceramic compounds (such as solid zirconia sintered body), so it can be operated at 800-1000 °C, and the power generation efficiency can reach 50-60%. PEMFC has high energy density and energy efficiency and is a fuel cell that is currently developed and operated commercially. PAFC is mainly a power station and a decentralized power station with natural gas and hydrogen-rich substances as fuel, and realizes cogeneration for enterprises and the like. UTC has produced more than 200 200 kW PC-25 fuel cells. A small power station with a capacity of 50 kW can supply power

for weather stations, terrestrial communications, etc. The medium-sized power station with a power generation capacity of 200-500 kW can provide power supply for hospitals, schools, coastal defense, and Hainan Airlines. MCFC power plants with a power generation of more than 1000 kW can be combined with heat engines to implement large-area power supply. In 1996, the US ERC Company built the Santa C lara power plant using molten carbonate fuel cell technology, which took two months and was successfully operated. The plant's fuel is natural gas and petroleum liquefied gas, and the maximum output is The power is 1930 kW and the power generation efficiency is 53.7%. Since 1981, the MCFC research and development technology has been started in Japan. Among them, the 100-1000 kW experimental power station was assembled under the Moonlight Project and the New Sunshine Project, which has improved efficiency and longevity. SOFC is an all-solid-state energy conversion device. It has the same structure as a general fuel cell device. Its electrolyte is a dense solid oxide, and the reaction gas is not in direct contact [7]. SOFC has two types of structures: tubular and flat. Germany has operated a tubular SOFC plant with an annual power generation of 4 MW. Canada Global is committed to decentralized power supply, the development of the home market for the development of medium-temperature flat-panel SOFC.

(2) Used to Study the Preparation of Mobile Power

Fuel cells have a wide range of applications. At present, small portable power supplies and secondary battery chargers have gradually become one of the hot spots of research and development. Although the advantage of fuel cells is that they have a wide range of fuel sources and the generation of electrical energy can be based on many types of chemical reactions, many applications and research are focused on hydrogen and oxygen, which is impractical for many small fuel cells. of. Hydrogen compression, liquefaction, and transportation have many difficulties in the use of hydrogen fuel cells. This has driven people to focus on the research of small batteries to liquid fuels such as methanol and formic acid. In the entire fuel cell system, the function of methanol is to supply hydrogen, and the oxygen required for the reaction has an air supply. Therefore, the battery using methanol as a reaction raw material is also called a direct methanol fuel cell (DMFC). Methanol liquid has many advantages as a fuel. This liquid has higher specific energy, wider fuel source, relatively cheap price, and simple carrying and storage. The battery device has the advantages of simple structure, small occupation volume, simple disassembly and assembly, and convenience and flexibility. The DMFC has an absolute advantage in energy storage, and the specific energy density of a lithium ion battery is only one tenth. At the beginning of the battery exploration, people positioned their markets as mobile phones and notebook computers, in order to satisfy the desire of long-term standby and small space.

In 2003, President Bush used the power system to make a call for the DMFC mobile phone. Countries have introduced electric appliances that use fuel cells as a portable power source. The small DMFC prepared by the German Smart Fuel Cell company can supply more than eight hours of notebook computers with a fuel consumption of only

125 ml of methanol. The Toshiba Corporation's first DMFC power supply notebook prototype in 2003 can be continuous. For five hours of operation, simply use 50 ml of methanol. Many companies are gradually interested in micro-DMFCs. It is undeniable that this will be a revolution in the battery field and will also promote the birth of high-tech. At present, in order to meet the diversification of life, people have extended their research fields to the charger market. Take the Dynario TM charger released by Toshiba as an example [8], which can solve the shortcomings of the power consumption of mobile phones. The phone is quickly charged via the USB interface in just 20 seconds, and consumes very little fuel. The two conventional mobile phones consume only 14 ml of high-concentration methanol. Of course, opportunities and challenges are interdependent. The development of DMFC technology also has challenges. At present, the most important ones are as follows: In the normal temperature environment, the electrooxidation speed of methanol fuels is not fast and the current density is not large. Second, the precious metal catalyst used for its electrooxidation requires a high cost and is easily poisoned by an intermediate product such as CO. Third, the shorter battery life is due to the high fuel permeability during operation.

(3) Application of Underwater Submarines

After a century of development, the conventional submarine has undergone many baptisms of war and has achieved remarkable results. It has gradually become an important equipment for the navy of the world to maintain coastal defense safety. In recent years, the propulsion system used in conventional power submarines is mainly the traditional diesel-electric system. The lead-acid battery is the energy source for the submarine to advance and propel underwater. The capacity of the battery will determine the distance of the submarine. However, the storage capacity of the battery is limited, and the normal diesel-powered submarine has a short duration of normal operation, and the energy storage will be consumed in about two to three days. If the submarine wants to continue moving, it must be floated and charged to sail after it reaches the snorkel. This becomes a fatal flaw in the development of the submarine. After being floated up, it is easily detected by the enemy radar, which exposes it. At the same time, the lead-acid battery generates a large amount of noise generated by the internal combustion engine during charging, which will also attract the attention of the other party. Therefore, in order to develop a submarine that is concealed, it is necessary to solve the problem of reducing the number of floating and extending the sailing time. This improvement will be of great significance to the survival of the maritime battlefield.

In recent years, the development of the Air Independent Propulsion (AIP), which does not rely on external air energy supply, has perfectly met the concealability and long-haul demand of conventional submarines. The power of the AIP system comes from fuel cells, which use its own fuel and oxygen to generate electricity. Oxygen is stored as liquid oxygen. In terms of output energy, the fuel cell does not need to undergo combustion, thermal power conversion (turning thermal energy into mechanical energy), mechanical energy to drive generator power generation, etc., and can directly convert chemical energy into electrical energy output, and the sound during the reaction

process is small. It is easily captured by the other party's sonar. The emission rate of pollutants is basically zero, and the energy conversion rate can reach 50%-80%. On the other hand, fuel cells are higher in specific power and specific energy than other types of batteries such as lead-acid batteries, zinc-manganese, and nickel-hydrogen batteries. They do not require external charging, only fuel and oxidant are needed, and further Said that the fuel cell's power range is much larger than the lithium battery. The submarine powered by the AIP system has been applied in practical applications. The most influential is the U209 series submarines currently used by the German Navy. The fuel cell AIP technology for submarines has developed rapidly in the past decade, and the subscription order and transaction volume of fuel cell AIP submarines are also rising. Proton membrane fuel cells (PEMFC) have higher specific power, safe and reliable process, and suitable operating temperature. Countries have invested more in this technology research. In the current situation, PEMFC has a huge potential in many different types of AIP systems. When the PEMFC-AIP system is applied to the submarine, the energy of the infrared radiation received in the seawater is reduced, and there is no noise release inside the fuel cell during driving, and the characteristics are much smaller than the diesel-electric propulsion device, so the stealth concealment is obtained. The rapid improvement has been greatly enhanced by its invisible combat capability in military warfare. At the same time, the small size of the PEMFC device can increase the space utilization efficiency of the cabin.

(4) Aerospace Applications

The power system is an integral part of the spacecraft and its reliability can be directly linked to the life of the spacecraft. Spacecraft power requirements are more stringent, taking into account a variety of factors such as missions, spacecraft flight life and power requirements. Spacecraft development requires conditions such as greater power, longer life, and relatively stable power systems. In the 1960s, fuel cells have emerged in aerospace technology. This power source is characterized by light weight and high efficiency, and is the primary choice for US space technology.

The power source used in the "Apollo" moon landing spacecraft is an alkaline electrolyte fuel cell. The "Apollo" moon landing spacecraft served from 1966 to 1978, after 18 missions, fuel cell reliability and safety performance. excellent. The weight of the power system must be considered in the development of the spacecraft. The excessive power quality will greatly increase the operating cost. For example, in 2003, the small satellite launched by China, the 16.6% of the satellite quality is the power system. The pursuit of high energy density power supplies is very attractive to people. The energy density of fuel cells used in aerospace is 100-1000 Wh/kg [9]. For some power-based aircraft that operate at high altitudes and require long flight times, the specific energy required to operate above 400 Wh/kg, fuel cells can better meet this requirement.

(5) Automotive Power Energy

Automobiles are becoming more and more popular in people's lives, and problems such

as automobile exhaust emissions are becoming more and more serious. Reducing the emission of polluting exhaust gas is a problem that people need to solve. Fuel cell vehicles have three major advantages, such as low emissions, wide fuel selectivity, and high efficiency, while driving farther than electric vehicles powered by pure batteries.

In the early 1990s, the United States proposed the "New Generation Vehicle Program". In 1993, Ballard Company of Canada introduced the first bus with a fuel cell as the energy supply system, which runs 2000 km. In 1996, the US Energy Corporation introduced the experimental model “Green Car” with 1.5 kW PEMFC power. Germany's Daimler-Benz developed the NECAR III drive train in August 1998. Its energy supply system is a proton exchange membrane (PEM) fuel cell. The fuel consumed in operation is methanol. The raw materials are converted into hydrogen by a reactor in the vehicle, and the generated hydrogen is oxidized in the fuel cell to release energy to ensure the operation of the vehicle. The peak of fuel cell research in China was first developed in the 1970s [10]. During the “Tenth Five-Year Plan” period, the state implemented the “Special Science and Technology Special Project for Electric Vehicles”, which made the application of fuel cells in the automobile manufacturing industry progress in China, and the fuel cell-powered cars and buses were successfully manufactured. In the 2003 Shanghai Industrial Expo, China's research and development beyond the No. 1 prototype successfully appeared, it is the first fuel cell power car developed in China.

1.2 Direct Formic Acid Fuel Cell

1.2.1 Overview of Direct Formic Acid Fuel Cells

At the end of the 20th century, the development of proton exchange membrane fuel cells (PEMFC) has made great breakthroughs [11, 12], but in the process of commercialization, the hydrogen source problem is more prominent, and hydrogen storage and transportation are more difficult. Direct methanol fuel cells (DMFC) are an extension of proton exchange membrane fuel cells [13-15]. However, methanol is toxic and flammable and volatile. The commonly used methanol fuel cell anode catalyst is Pt catalyst, and the toxic intermediate CO formed during methanol electrocatalysis is adsorbed on the surface of Pt catalyst, thereby inhibiting the catalytic activity of the catalyst. In recent years, people are trying to study methanol fuel cells, and are also looking for a suitable methanol alternative fuel. The methanol alternative fuels currently found include ethanol, ethylene glycol, propanol, formaldehyde, dimethoxymethane, dimethyl ether, dimethyl oxalic acid, formic acid, oxalic acid and the like. These methanol alternative fuels have the advantages of low toxicity and low permeability of Nafion membrane. However, some of these fuels are gas at room temperature, and some of the oxidation properties are worse than methanol, and some are easily decomposed into methanol in the aqueous phase, so they have not been thoroughly studied. But liquid fuel formic acid is likely to be a substitute for methanol.

Direct formic acid fuel cells (DFAFC) have the following advantages compared to methanol fuel cells [16-21]:

(1) Formic acid is non-toxic and can be used as a food additive;
(2) Formic acid is not flammable, safe and convenient for storage and transportation;
(3) Although the energy density of formic acid is low, formic acid can work normally at high concentration and has very good oxidation performance, and the most suitable working concentration of methanol is 2 mol L^{-1};
(4) The theoretical open circuit potential of formic acid fuel cell is 1.48 V, which is higher than that of direct methanol fuel cell;
(5) The formate ion $COOH^-$ has a repulsive effect with the sulfonate SO_3^{2-} in the Nafion membrane, so that the permeability of the formic acid to the Nafion membrane is much smaller than that of methanol;
(6) The electrochemical oxidation process of formic acid is mainly carried out through a direct reaction pathway, which avoids catalyst poisoning. Due to the many advantages of formic acid, DFAFC research has been widely favored. As a new type of liquid fuel cell, it is expected to be the first to achieve commercial development.

1.2.2 Basic Structure and Oxidation Mechanism of Direct Formic Acid Fuel Cells

(1) Basic Structure of the Fuel Cells and Its Working Principle

The direct formic acid fuel cell is similar in structure to the direct methanol fuel cell, and mainly includes an anode, a cathode, a proton exchange membrane (Nafion membrane), a bipolar plate, and an auxiliary component. The basic structure is shown in Figure 1.1.

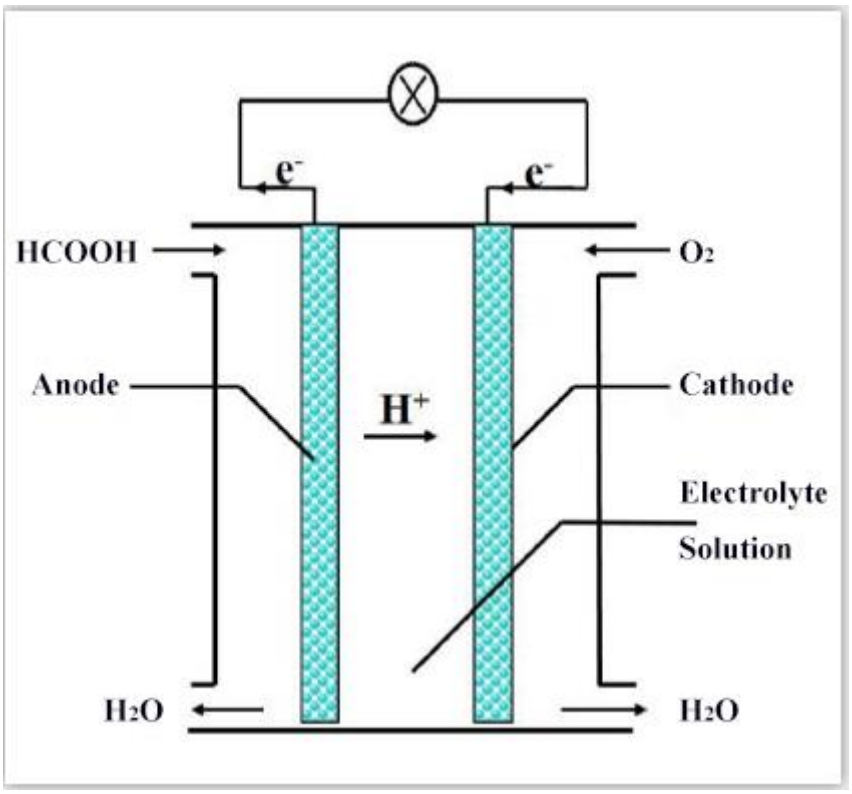

Figure 1.1. DFAFC single fuel cell basic structure diagram

The DFAFC works as follows:

The half reaction of anodic acid oxidation is:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e- \qquad 1\text{-}1$$

The half reaction of cathodic formic acid oxidation is:

$$1/2O_2 + 2H^+ + 2e- \rightarrow H_2O \qquad 1\text{-}2$$

The total battery response is:

$$HCOOH + 1/2O_2 \rightarrow CO_2 + H_2O \qquad 1\text{-}3$$

(2) Study on the Mechanism of Formic Acid Oxidation

After in-depth study of the mechanism of electrocatalytic oxidation of formic acid, what is currently accepted is the “three-way mechanism”, namely the direct oxidation pathway, the indirect oxidation pathway and the formate pathway [22-24], as shown in Figure 1.2.

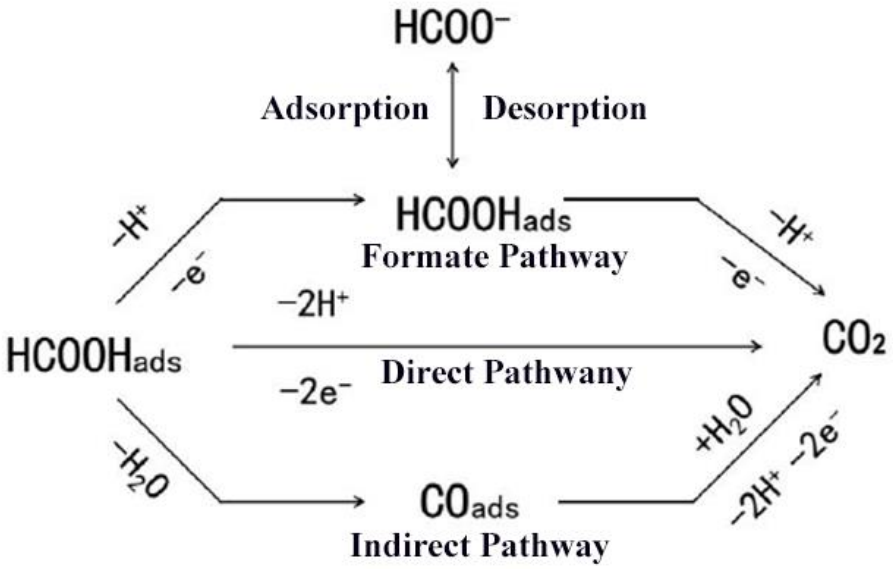

Figure 1.2. Three-way mechanism of electrocatalytic oxidation of formic acid

The direct oxidation pathway is the direct removal of protons by formic acid and the formation of carbon dioxide.

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e- \quad (1\text{-}4)$$

The direct oxidation process has no intermediate product formation, avoids catalyst poisoning, and speeds up the reaction rate. Therefore, the direct oxidation pathway is the ideal path we most expect [21,25]. The indirect oxidation pathway is also called the "CO pathway", which is the COads that HCOOH easily poisons the catalyst through the dehydration process, and then further oxidizes the COads to carbon dioxide at high potential.

$$HCOOH \rightarrow COads + H_2O \quad (1\text{-}5)$$
$$CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e- \quad (1\text{-}6)$$

In the indirect pathway, COads will cover the active site of the catalyst, reducing the activity of the catalyst and causing catalyst poisoning [21-25].

The formate passes through HCOOH to remove H+ to form an intermediate species of formate, which is then oxidized to form CO_2 [31, 32],

$$HCOOH \rightarrow HCOO_{ads} + H^+ + e- \rightarrow CO_2 + 2H^+ + 2e- \quad (1\text{-}7)$$

1.2.3 Research Status of Catalytic Materials for Direct Formic Acid Fuel

Cells

Electrocatalysis was first proposed by Nikolai Kobozev in 1936, but it has not attracted much attention. It was not until the 1960s that electrocatalytic research was widely carried out. The catalyst is generally composed of nanoparticles and a conductive support supported thereon, and is catalytically reacted with the reactant molecules on the surface of the catalyst [33-35]. The composition, particle size and surface structure of the catalyst nanoparticles are critical to the activity of the catalyst. Therefore, the key to improving the performance of the catalyst is to consider the composition, size, electronic structure and carrier of the catalyst.

As a direct catalyst for formic acid fuel cells, generally, it should have the following characteristics: one is that the catalytic oxidation of formic acid is highly active, and the other is that the catalyst is not easily affected by the reaction intermediates to lose or reduce the activity, that is, the anti-toxic ability of the catalyst. Should be stronger. The third is stable phase and durability. At present, there are two main developments for anode catalysts, namely platinum-based and palladium-based catalysts.

(1) Study of Pt-based Catalysts

For the study of DFAFC catalysts, people initially concentrated on Pt catalysts. With the mechanism and study of the electrooxidation process of DFAFC on the surface of Pt catalyst [36 37], it was found that the oxidation of formic acid on the surface of Pt catalyst was two processes:

First, HCOOH was adsorbed on the surface of Pt to form carbon-containing intermediates.

$$HCOOH + Pt \rightarrow Pt\text{-}CO + H_2O \qquad 1\text{-}8$$

Then, H_2O dissociates to produce oxygenated species,

$$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e\text{-} \qquad 1\text{-}9$$

Finally, the oxygenated species Pt-OH reacts with Pt-CO to release CO_2.

$$Pt\text{-}CO + Pt\text{-}OH \rightarrow 2Pt + CO_2 + H^+ + e\text{-} \qquad 1\text{-}10$$

Therefore, Pt catalyzes the electrooxidation of formic acid mainly through the "indirect route" for the electrooxidation of formic acid. The Pt catalyst is susceptible to poisoning by intermediate species such as CO, showing poor catalytic activity. After intensive research, it has been found that the addition of other components to the Pt catalyst accelerates the dissociation of water and affects the formation of carbon-containing intermediates. People have been working to add a second metal to promote the

electrocatalytic formic acid oxidation activity of Pt. The second metals added are Ru, Pd, Au, Pb, Bi, Sb, Tb, Sn and Mn [38 39], and most of these metals have a significant effect on the oxidation of formic acid. The geometric hindrance effect caused by the addition of the second metal inhibits the formation of carbon-containing intermediates, reduces the poisoning effect of CO produced by HCOOH oxidation on Pt, and increases the rate of formic acid oxidation on the surface of Pt catalyst.

Based on the above points, people have been working on various Pt-based catalysts, including Pt-Ru binary composite catalysts. Chen et al. [40] studied the electrocatalytic oxidation of formic acid on Ru modified Pt-based catalysts. It was found that Ru increased the catalytic activity of pure Pt catalyst for formic acid oxidation to some extent. Ru is a more noble precious metal than Pt. The addition of Ru allows the catalyst to undergo a formic acid oxidation reaction at a lower potential. Li et al. [41] performed X-ray photoelectron spectroscopy (XPS) on the prepared Pt-Ru catalyst. It was found that Pt is mainly in a reduced state and contains a part of Pt-O component; Ru is mainly in the form of an oxidation state, and a small amount of metal Ru is present in the bulk phase of the catalyst. However, Ru (RuO_2•xH2O, RuOxHy and amorphous RuOx) in the oxidation state are still controversial. Zhao et al. [42] studied the electrocatalytic oxidation behavior of HCOOH on Pt-Sn/C catalysts. It was found that the catalyst had the best catalytic activity for HCOOH oxidation when the Pt content was 20% and the Sn content was 60%.

In addition to Pt-based binary alloy catalysts, ternary Pt-based composite catalysts and quaternary Pt-based composite catalysts have also been studied. Recent studies have shown that the addition of tungsten oxide-based Pt or Pt-Ru catalysts has a high catalytic activity for the oxidation of methanol, formic acid and ethyl formate [43-45]. The currently successful three-way catalysts include Pt-Ru-Os, Pt-Ru-Mo, Pt-Ru-Ni, Pt-Sn-Ni, Pt-Ru-Sn, etc. [46-49]. The quaternary catalyst is also based on the optimization of the choice of catalyst components to build a high performance, high stability catalyst. The reaction mechanism of the four-way catalyst is more complicated, and the corresponding reports are relatively few. At present, there are mainly Pt-Ru-Fe-W, Pt-Ru-Sn-W, Pt-Ru-Os-Ir, and Pt-Ru-Mo-Sn, Pt-Ru-Ir-Sn, etc. [50-54].

(2) Study of Pd-based Catalysts

The metal Pd catalyst has good catalytic performance for the electrocatalytic oxidation of formic acid [55-57]. Formic acid is directly oxidized on the Pd surface by direct direction to form CO_2 [58]. The precious metal Pd has more content on the earth than the precious metal Pt. The use of the precious metal Pd can make the cost of the catalyst relatively cheaper, and thus has received extensive attention. Although Pd has a similar electronic structure to Pt, it is significantly different from Pt, and Pd exhibits excellent catalytic formic acid oxidation performance and very low CO poisoning phenomenon [59]. Ha et al. [60] studied the electrocatalytic oxidation performance of Pd black catalyst for formic acid in DFAFC. They found that the fuel cell with pure Pd as catalyst has

low temperature (22 ° C) and higher temperature (30-50 ° C). The density is higher than with the Pt catalyst. The catalytic oxidation performance of Pd black and Pt-Ru catalysts on formic acid was compared. It was found that the catalytic activity of Pd began to decrease during the initial period of formic acid oxidation. Ha et al. used AC impedance techniques to investigate the cause of the decrease in Pd catalyst activity, probably due to the formation of unknown non-CO intermediates.

Although Pd has a higher electrooxidation activity for formic acid, the stability of Pd needs to be improved. In order to improve the catalytic activity and stability of the Pd catalyst, a second metal or non-metal, metal oxide is added to the Pd catalyst to improve its catalytic performance. Binary metal catalysts play an important role in the field of catalysis. Similarly, the oxidation activity of Pd alloy catalysts for formic acid has been extensively studied, including: Pd-Sn [61], Pd-Co [62], Pd-P [63] and Pd-Ir [64]. In general, the physical and chemical properties of binary metal nanocatalysts can be altered by adjusting their surface structure, composition, and elemental polymerization state, which in turn affects the catalytic performance of the final catalyst [65]. Xing [66] et al. studied the catalytic performance of Pd-Sn/C catalyst for electrocatalytic oxidation of formic acid. They found that Pd-Sn alloys can enhance the electrocatalytic activity and stability of Pd formic acid. The electronic effect of the metal Sn changes the electronic structure of Pd, which reduces the adsorption of CO, thereby promoting the oxidation of formic acid by direct route. Lu et al. [67] prepared a Pd-P binary catalyst. It is found that the addition of non-metallic element P reduces the average particle size of Pd nanoparticles, and the electronic effect of P and metal Pd reduces the 3d electron cloud density of Pd and the adsorption strength of CO on Pd surface, thus making Pd-P catalyst. The electrocatalytic performance of formic acid is higher than that of conventional Pd/C catalysts. The catalytic activity is also enhanced by adding a series of rare earth oxides, heteropolyacids, WO3 and other species rich in active oxygen and metal carrier interactions into the Pd/C system to form a composite catalyst. For example, WO_3 can assist in the dispersion of Pd nanoparticles while promoting the dehydrogenation pathway of formic acid oxidation, promoting the direct pathway of formic acid oxidation and inhibiting the poisoning of CO [68,69].

(3) Study of Other Catalysts

The price of precious metal catalysts used in fuel cells is relatively high, and the development and use of non-precious metal electrocatalysts have gradually attracted people's attention. Capon et al. [70] studied the catalytic performance of Pt, Rh, Ir, Au catalysts for the oxidation of formic acid. However, so far no non-precious metal catalyst can be compared with the performance of precious metal catalysts, and research in this field has a long way to go. However, the doping effect of non-precious metals has not only promoted the catalytic effect on the precious metal catalyst, but also reduces the cost of the catalyst and improves the utilization rate of the precious metal, which has greater research value.

1.2.4 Factors affecting the performance of fuel cell catalysts

There are many factors affecting the catalytic performance of fuel cell catalysts, including catalyst composition, surface structure, dissolution of nanoparticles, and carrier effect.

(1) Effect of Catalyst Composition and Surface Structure on Its Catalytic Performance

The catalytic reaction of the fuel cell is mainly carried out on the surface, and the composition of the catalyst, the particle size and the surface structure directly affect the catalytic performance. For the same composition of the catalyst, when the particle size is reduced from 10 micrometers to 10 nanometers, the surface area is increased by 106 times. It can be seen that the size of the catalyst can increase the surface area, thereby significantly increasing the utilization of the catalyst. However, the current reduction in catalyst particle size has approached the limit. The performance of an electrocatalyst depends not only on the particle size, but also on the particle composition and its surface structure.

In recent years, nano-catalysts with different electronic structures and morphologies such as alloys, core shells, nano-branches, and surface modifications have been rapidly developed. Dong et al. [71] synthesized Pd Pt, Pd Au nanowires and used them for electrochemical detection of glucose. Zhang et al. [72] developed an electrochemical method and successfully synthesized Pd Pt alloy, which has significantly better electrocatalytic activity for formic acid than commercial palladium black catalyst. In addition, the doping of non-noble metals, such as Bi and Pb, can effectively increase the poisoning ability of intermediates such as CO in Pt catalyzed formic acid [73, 74], and achieve direct oxidation of formic acid to form CO_2.

For the same composition of the catalyst, the difference in surface structure also affects its catalytic activity. Face-centered cubic nanocrystals (such as Pt, Pd, Au, etc.) surrounded by high-index crystal faces, have high-density low-coordination surface steps and kinked atoms, have an open surface structure, and have higher catalytic performance than (100), (111) and other low-index crystal faces. Therefore, the preparation of metal nanoparticles with an open surface structure is an effective way to improve their catalytic performance.

(2) Dissolution of Nanoparticles

The particle size and dispersibility of the nanoparticles also directly affect the electrocatalytic performance of the catalyst. Therefore, we need to adopt appropriate methods to inhibit the dissolution of the nanoparticles and improve the dispersion of the nanoparticles. The dissolution of the nanoparticles can be suppressed by adding a complexing agent, a stabilizer, or the like to the solvent in which the catalyst is prepared. In addition, the catalyst carrier can also improve the dispersion of nanoparticles.
Studies have shown that under the working potential of fuel cells and acidic electrolytes, the dissolution of catalyst nanoparticles is easy to occur, and the increase in humidity

and the presence of oxygen accelerate the dissolution of nanoparticles. Catalyst dissolution increases the particle size of the metal particles and reduces the active area of the catalyst, which severely inhibits the catalytic activity and stability of the catalyst. Lu et al. [75] soaked the catalyst nanoparticles in an acidic electrolyte and confirmed the dissolution of the nanoparticles. Liao et al. [76] also confirmed the dissolution of the catalyst in a strong acid electrolyte. They found that the dissolution phenomenon was alleviated when a weakly acidic electrolyte solution was used.

(3) Support Material Effect

The electrocatalytic systems actually used in fuel cells are all supported catalysts. The support material can improve the catalytic efficiency, and the high specific surface area and the porous structure of the carrier can also promote the uniform dispersion of the catalyst, can inhibit the aggregation of the catalyst nanoparticles without the stabilizer, and improve the utilization and stability of the catalyst. The specific functional groups and spatial structures on the surface of the support can also act as anchoring catalysts to provide the catalyst with suitable shape, size and mechanical strength to meet practical application requirements. The selection and modification of the support is critical. For example, when palladium is supported on a carbon support, the carrier molecules and functional groups on the surface thereof can be adsorbed on the surface of the catalyst to reduce the surface energy of the catalyst and maintain a small scale of the particles. Carbon black is the most widely used catalyst carrier [79-81]. Other carbon materials, such as mesoporous carbon, carbon nanotubes, carbon fiber, and graphene [78] can significantly improve the performance of the catalyst and reduce the catalyst loading compared with conventional carbon black materials. Carbon carriers also corrode. Although people are working tirelessly to improve the stability of carbon materials, their stability problems have not been completely solved. At present, metal oxide carriers have also attracted widespread attention. For example, loading Pt on metal oxides such as TiO_2 and SnO_2 increases the interaction between the metal and the catalyst and improves the stability of the carrier. However, the electrical conductivity and specific surface area of metal oxides are far less than that of carbon carriers.

1.3 The main research direction and content of this paper

Two methods were used in this paper to try to improve the catalytic performance of Pd-based electrocatalysts for FAO. First, changing the catalyst support material. Second, changing the external conditions of electrocatalysts.

The main content of this article:

1. Different ratios of TiO_2-graphene carrier were prepared by ethanol thermal method, then palladium was supported on the support material by sodium borohydride reduction method, and the prepared catalyst was used for electrooxidation of formic

acid to screen the best carrier component.

2. The prepared catalyst was used for the electrooxidation study of formic acid by changing the external conditions, that is, adding light, thereby screening out the best carrier component.

Chapter 2 Experiment

2.1 Experimental Instrument Device

Electrochemical workstation (CHI832B, Shanghai Chenhua Instrument Co., Ltd.); three-electrode system: modified glassy carbon (GC) electrode as working electrode, high-purity carbon rod as counter electrode, Hg/Hg_2SO_4 electrode (saturated K_2SO_4) used as reference electrode in acid media, Hg/HgO electrode used as the reference in alkaline solutions. The glassy carbon electrode used in the experiment is 3 mm in diameter and must be cleaned and polished before use. Electronic balance (FA1004N type, Shanghai Precision Scientific Instrument Co., Ltd., Shanghai); KQ-50B type ultrasonic cleaning machine (Kunshan) Ultrasonic Instrument Co., Ltd., Kunshan City, Jiangsu Province; DZF-6020 Vacuum Drying Box (Gongyi City, China Instrument Co., Ltd., Gongyi City); 2XZ-1 Rotary Vane Vacuum Pump (Zhejiang Huangyan Ningxi Medical Instrument Co., Ltd., Zhejiang), PTFE high pressure reactor (Beijing TB-20 hydrothermal synthesis reactor)

2.2 Preparation of Materials, Reagents and Solutions

Table 2-1 Experiment reagents

Name	Chemical Formula	Manufacturer	Purity
Activated Carbon	Vulcan XC-72R	American Cabot Corporation	
Natural Graphite Flakes		Alfa Aesar (Tianjin) Chemical Co., Ltd.	99.8%
Palladium Chloride	$PdCl_2$	Sinopharm Chemical Reagent	AR
Potassium Persulfate	$K_2S_2O_8$	Sinopharm Chemical Reagent	AR
Phosphorus Pentoxide	P_2O_5	Sinopharm Chemical Reagent	AR
Potassium Permanganate	$KMnO_4$	Laiyang Economic and Technological Development Zone Fine Chemical Plant	AR
Chromium Nitrate	$Cr(NO_3)_3 9H_2O$	Tianjin Damao Chemical Reagent Factory	AR
Sodium Borohydride	$NaBH_4$	Shanghai Diyun Chemical Co., Ltd.	AR
Absolute Ethanol	C_2H_5OH	Sinopharm Chemical Reagent	AR
Sodium Hydroxide	NaOH	Sinopharm Chemical Reagent	AR

Nafion Solution	5% Nafion	DuPont	AR
Sulfuric Acid	H_2SO_4	Laiyang Economic and Technological Development Zone Fine Chemical Plant	AR
Phosphate	H_3PO_4	Tianjin Guangcheng Chemical Reagent Co., Ltd.	AR
Hydrochloric Acid	36% HCl	Tianjin Guangcheng Chemical Reagent Co., Ltd.	AR
Formic Acid	HCOOH	Sinopharm Chemical Reagent	AR

Preparation of 0.2 mol/L $PdCl_2$ solution: Pipette accurately 0.1 mL 36% concentrated hydrochloric acid was diluted with water to 5.8 mL to obtain 0.2 mol/L hydrochloric acid solution. Accurately weigh 0.141 g $PdCl_2$ powder and add 3.975 mL 0.2 mol/L. The HCl solution was allowed to stand at the bottom without powder, and $PdCl_2$ was completely dissolved, and the 0.2 mol/L $PdCl_2$ solution was prepared.

Preparation of 1.0 mol/L H_2SO_4 solution: Take 54.4 mL of 98% sulfuric acid, dilute with water, and calibrate with a 1000 mL volumetric flask to obtain 1.0 mol/L H_2SO_4 solution.

Preparation of 1.0 mol/L HCOOH solution: 98% formic acid 38.5 m L diluted with water and calibrated with a 1000 mL volumetric flask to obtain a 1.0 mol/L HCOOH solution.

Preparation of 1.0 mol/L NaOH solution: Weigh 40 g of NaOH solid dissolved in 1000 mL of water to obtain 1.0 mol/L NaOH solution.

Preparation of 5% $NaBH_4$ solution: Analytical balance Weigh 0.5 g of $NaBH_4$ solid and dissolve it in 10 mL of water. This solution should be used now, and the weighing time should be fast.

2.3 Catalyst Preparation

2.3.1 Preparation of Graphene Oxide

Graphene oxide (GO) is obtained from natural graphite flakes by the modified Hummer method [77]. The specific operation method is as follows:

(1) Weigh 3 g of natural graphite and concentrate with concentrated sulfuric acid, add 5 g of $K_2S_2O_8$ and 5 g of P_2O_5, stir and incubate at 80 ° C for 5-6 h. Then cool to room temperature, rinse off the residual acid with deionized water, and dry naturally;

(2) The pre-oxidized graphite was added to a mixture of H_2SO_4 (180 mL) and H_3PO_4 (20 mL), and the mixture was cooled in an ice bath, stirred, and then slowly added

$KMnO_4$ (15 g) to keep the temperature below 20 °C. Otherwise it is easy to cause an explosion;

(3) The mixture was heated to 35 ° C and incubated for 8 h, then slowly poured into deionized water (250 mL) under ice bath, at which time the mixture turned brown and accompanied by bubble generation, stirring for 2 h;

(4) The solution was diluted with deionized water (700 mL) and stirred for 2 h until no more bubbles were formed. Then H_2O_2 was added to react with excess $KMnO_4$, and the color of the solution immediately turned bright yellow.

(5) The obtained bright yellow solution was washed with 5% diluted hydrochloric acid to remove metal ions, and then washed with deionized water to remove hydrochloric acid. The product was dried in a vacuum oven at 60 ° C to obtain graphite oxide.

(6) A certain amount of graphite oxide was weighed and dissolved in a certain amount of deionized water, and various concentrations of graphene oxide solution were obtained by ultrasonic stripping.

2.3.2 Preparation of Pd/C catalyst:

Weigh 50.8 mg of activated carbon, add 31.75 mL of double distilled water (the ratio of activated carbon to distilled water is prepared according to the ratio of 160 mg: 100 mL), add a few drops of absolute ethanol to reduce the surface tension, avoid toner floating, and sonic for 20 minutes. Add 0.6 mL of 0.2 mol/L $PdCl_2$ solution according to 20% metal loading, sonicate for 30 minutes, then add a few drops of 1 mol/L NaOH solution to adjust the pH to about 10, then add 5% $NaBH_4$ solution. 0.5 g of $NaBH_4$ powder was added to 10 mL of double distilled water and stirred well, and stirred while stirring, and stirred for 15 minutes. Allow to stand overnight. Filter and wash. It was washed with 300 mL of deionized water and then placed in a vacuum oven at 130 ° C for 6 hours to obtain a Pd/C catalyst.

2.3.3 Preparation of graphene-titanium dioxide supported palladium (Pd/TiO_2-rGO) catalyst

(1) 40.3 mg, 40.5 mg, 41.7 mg, and 40.1 mg of GO were weighed and dispersed in 50.24 mL, 50.625 mL, 52.125 mL, and 50.125 mL of absolute ethanol, and ultrasonically dispersed for 8 hours to completely disperse GO in ethanol.

(2) Then, 85.8 μL, 172.5 μL, 355.21 μL, and 683.16 μL of TBT were slowly added in proportion to the stirring (precursor TBT and GO mass ratio were TBT: GO = 0.5, 1.0, 2.0, 4.0, respectively), stirring half. hour.;

(3) The mixed solution was transferred to a Teflon liner, placed in a stainless steel reaction vessel, and incubated at 180 ° C for 12 h.;

(4) The solvothermally reacted product was taken out, washed first with ethanol, washed with water, and the final product was dried in a vacuum oven at 60 °C.

(5) Ultrasonic dispersion of 40 mg TiO_2/graphene in 25 mL water, adding a certain amount of $PdCl_2$ solution (metal loading rate is 20%), adjusting pH to about 10 with 1 mol/L NaOH solution, adding excess 5 % $NaBH_4$ and stirring for 6 h. A certain amount of graphite oxide was weighed and dissolved in a certain amount of deionized water, and various concentrations of graphene oxide solution were obtained by ultrasonic stripping.

(6) The resulting product was filtered and washed and dried at 60 °C.

According to this method, we prepared the target product of different mass ratio of titanium dioxide to graphene. The mass ratio of precursor TBT to GO was TBT : GO = 0.5, 1.0, 2.0, 4.0 respectively. For convenience, the prepared TiO_2-rGO carrier was named as TG1, TG2, TG3, TG4. The preparation process of different components of Pd/TiO_2-rGO catalyst is shown in Figure 2.1. The process in Figure 1 is a solvothermal process in which different components of TiO_2-rGO composite carrier are synthesized, and 2 is a loading process of palladium nanoparticles. In this step, we prepared palladium on TG1, TG2, TG3, TG4. The metal loading rate is 20% Pd/TG1, Pd/TG2, Pd/TG3, Pd/TG4 catalyst.

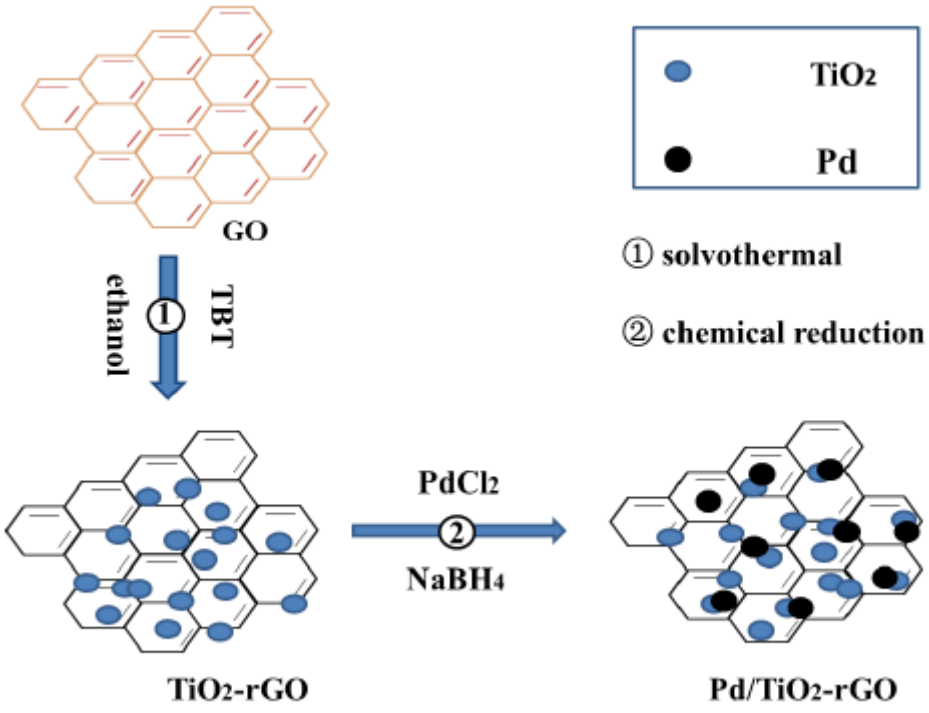

Figure 2.1 Schematic diagram of Pd/TiO_2-rGO formation process

2.4 Preparation of Working Electrode

2.4.1 Preparation of Pd/C Working Electrode:

Weigh 5.9 mg of Pd/C catalyst, add 0.295 mL of double distilled water and 0.295 mL of absolute ethanol (the ratio of Pd/C catalyst to double distilled water and absolute ethanol is 10 mg : 0.5 mL : 0.5 mL) Formulated). Ultrasonic to Pd/C catalyst to complete dispersion (about 60 min). Pipette 20 μL (4 μL × 5) of the dispersed droplets onto the pre-cleaned glassy carbon electrode (glass-carbon electrode is first polished with Al2O3 powder for 3-5 min, then rinsed with deionized water), and dried naturally. 4 μL of 5 % Nafion solution was dropped and allowed to dry naturally to obtain a working electrode.

2.4.2 Preparation of Pd/TiO_2-rGO Working Electrode:

Weigh 10 mg of catalyst powder, dissolve it in a mixture of 0.5 m L of water and 0.5 mL of ethanol, shake it for half an hour, and pipette 4 μL of suspended droplets onto the surface of the glassy carbon electrode. Allow to stand at room temperature and dry. After that, add it again, for a total of 5 times. After the catalyst suspension was completely dried, 3 μL of Nafion solution was added dropwise, and dried for use.

2.5 Electrochemical Test

2.5.1 Cyclic Voltammetry Test:

High concentration of pure N_2 was deaerated in the electrolytic cell for 20 minutes before each measurement. The measurement was carried out under nitrogen atmosphere. The cyclic voltammogram of the working electrode in a 0.5 mol/L H_2SO_4 solution (25 mL of double distilled water and 25 mL of 1.0 mol/L H_2SO_4 solution) was first tested (three sets of each solution). Then test the cyclic voltammogram of 0.5 mol/L H_2SO_4 solution and 0.5 mol/L HCOOH solution (25 mL of 1.0 mol/L H_2SO_4 solution and 25 mL of 1.0 mol/L HCOOH solution)
Contrast Electrode: Carbon Rod
Reference Electrode: Hg-Hg_2SO_4 Electrode (Acidic Condition)
Sweep Speed: 10 mV/s

2.5.2 Linear Scan Voltammetry Test:

A high concentration of pure O_2 is passed through the cell to saturation (about 20 min) before each measurement. Oxygen remains on during measurement. A linear scan of the working electrode on a 0.1 mol/L NaOH solution (loaded into a 220 mL pre-configured NaOH solution in a 250 mL beaker) was first tested. 8 sets of graphs were measured for each solution, in which the rotation speed was 1000 r/min, 2000 r/min, 3000 r/min voltage was 10 mV, and the two groups were rotated at 2000 r/min and the voltage was 1 mV.
Contrast Electrode: Carbon Rod
Reference Electrode: Hg-HgO Electrode (Alkaline Condition)
Sweep Speed: 10 mV/s and 1 mV/s

Electrolyte: 0.1 mol/L NaOH Solution

2.5.3 Lighting Test：

For the graphene-titanium dioxide supported palladium (Pd/TiO_2-rGO) catalyst, we studied the effect of light on it by adding light. Linear scanning test, high concentration of pure N_2 deoxidation was introduced into the electrolytic cell before each measurement. minute. The measurement was carried out under nitrogen atmosphere. Test the linear scan of the working electrode on a 0.5 mol/L H_2SO_4 solution (25 mL of double distilled water and 25 mL of 1.0 mol/L H_2SO_4 solution) (three sets of each solution), and measure the light for 200 s. One group was measured, and after cooling for 10 minutes, the light was measured for 200 s, and each sample was irradiated 4 times in total, and 5 sets of data were measured each time.
Contrast Electrode: Carbon Rod
Reference Electrode: Hg-Hg_2SO_4 Electrode (Acidic Condition)
Sweep Speed: 10 mV/s

Chapter 3 Results and Discussion

2.1 Pd/C Catalyst

2.1.1 Electrochemical Surface Area of the Catalyst

In order to identify the electrochemically active area of the Pd/C catalyst, the cyclic voltammogram (CV) of the Pd/C catalyst in 1 mol/L H_2SO_4 solution was determined. The scanning potential ranged from -0.6 to 0.5 V and the scanning speed was 10 mV /s. Figure 3-1 shows the cyclic voltammetry of a Pd/C catalyst in a 1 mol/L H_2SO_4 solution. The peak appearing in the range of -0.6 ~ -0.4 V is the absorption and desorption peak of hydrogen on the catalyst electrode. In addition, the peak appearing in the potential range higher than 0.6 V is considered to be the oxidation peak and oxidation of palladium. Reduction peak of palladium. From the figure, we can see that the peak of the peak of the adsorption and desorption of hydrogen on the Pd/C catalyst electrode is large. It is indicated that the Pd/C catalyst has an electrochemically active area and can provide an active site, which is effective for electrocatalytic oxidation of formic acid.

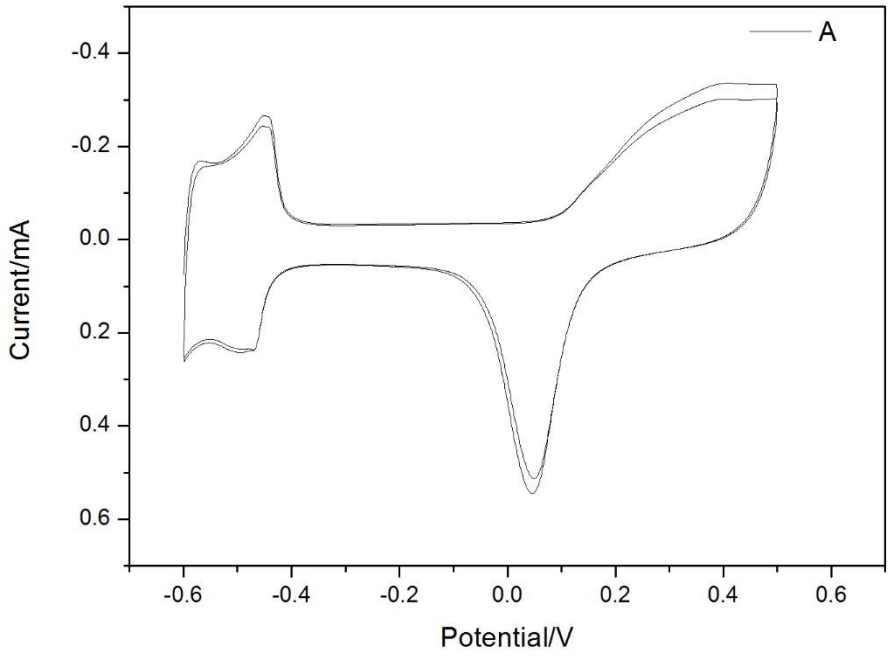

Figure 3-1 Cyclic voltammetry of catalyst Pd/C in 0.5 mol/L H_2SO_4 solution at a scan rate of 10 mV/s.

2.1.2 Effect of Pd/C Catalyst on Electrocatalytic Activity of Formic Acid Oxidation

Figure 3-2 shows the linear sweep voltammetry of Pd/C catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution at a scan rate of 10 mV/s. It can be seen from the figure that there is a large oxidation peak in the range of -0.4 to -0.2 V and a small oxidation peak in the range of 0.1 to 0.3 V. The large oxidation peak indicates that formic acid is mainly oxidized on the surface of the catalyst by direct route, that is, formic acid is directly oxidized to CO_2; and the small oxidation peak indicates that formic acid is oxidized by an indirect route, that is, formic acid is first oxidized to form an adsorbed CO, and then adsorbed on the surface of the electrode. The oxide species react to form CO_2. It can be seen from the figure that formic acid is mainly oxidized on a Pd-based catalyst by a direct route, thereby reducing the poisoning of the catalyst by CO.

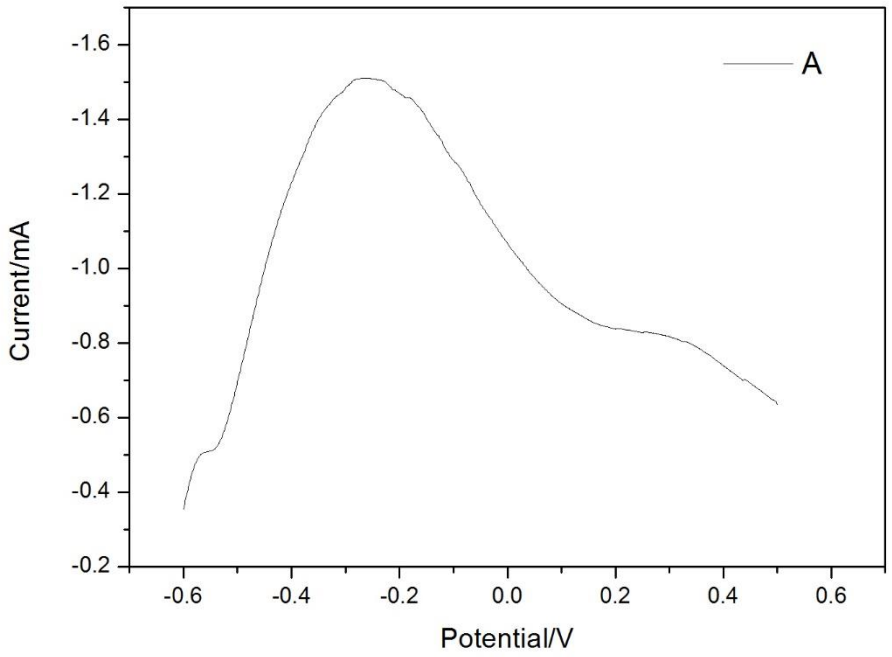

Figure 3-2 Linear sweep voltammetry of catalyst Pd/C in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution at a scan rate of 10 mV/s.

2.2 Pd/TiO_2-rGO Catalyst

2.2.1 Electrochemical Surface Area of the Catalyst

In order to identify the electrochemically active area of Pd/TiO_2-rGO catalyst, the cyclic voltammogram (CV) of Pd/TG1, Pd/TG2, Pd/TG3, Pd/TG4 catalyst in 1 mol/L H_2SO_4 solution was determined. The potential range is -0.6 ~ 0.5 V and the scanning speed is

10 mV/s. Figure 3-3 shows the cyclic voltammetry curves of Pd/TG1, Pd/TG2, Pd/TG3, and Pd/TG4 catalysts in 1 mol/L H_2SO_4 solution. The peak appearing in the range of -0.6 ~ -0.4 V is the absorption and desorption peak of hydrogen on the catalyst electrode. In addition, the peak appearing in the potential range above -0.1 V is considered to be the oxidation peak of palladium and Reduction peak of palladium oxide. The Pd/TG2 catalyst electrode has the highest hydrogen absorption and desorption peak and the largest peak area. It is indicated that the Pd/TG2 catalyst has a larger active area and can provide more active sites, which makes the Pd/TG2 catalyst have better electrochemical activity, which is beneficial to the electrocatalytic oxidation of formic acid.

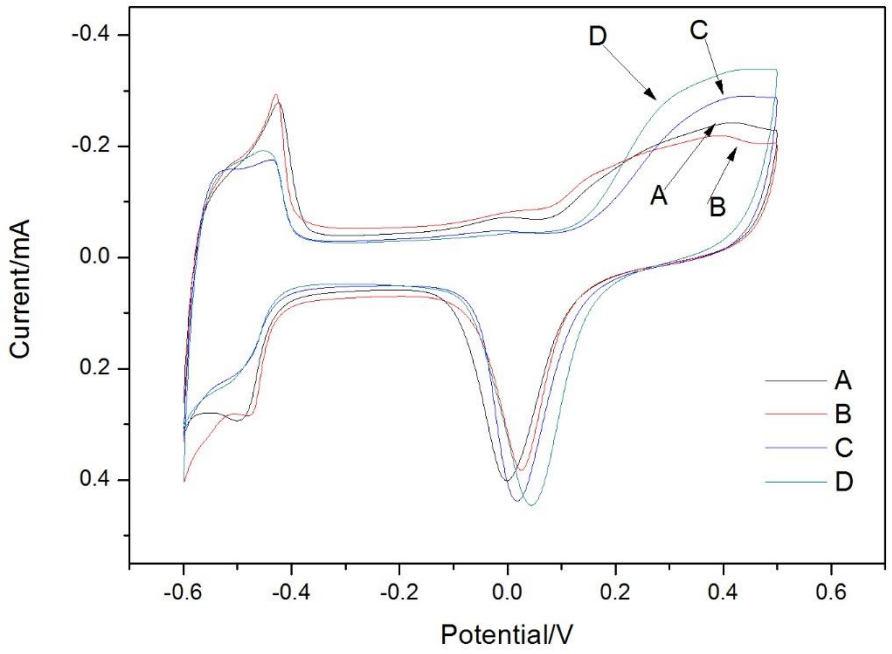

Figure 3-3: Cyclic voltammetry curves of catalyst Pd/TG1 (A), Pd/TG2 (B), Pd/TG3 (C), Pd/TG4 (D) in 1 mol/L H_2SO_4 solution, Scanning speed 10 mV/s.

2.2.2 Comparison of Electrocatalytic Activity of Different Ratios of Pd/TiO_2-rGO Catalysts for Oxidation of Formic Acid

Figure 3-4 shows the linear sweep voltammetry curves of Pd/TG1, Pd/TG2, Pd/TG3, Pd/TG4 catalysts in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution at a scanning speed of 10 mV/s. It can be seen from the figure that there is a large oxidation peak in the range of -0.5 ~ -0.3 V, and a small oxidation peak in the interval of 0 to 0.2V. The large oxidation peak indicates that formic acid is mainly oxidized on the surface of the catalyst by direct route, that is, formic acid is directly oxidized to CO_2; and the small oxidation peak indicates that formic acid is oxidized by an indirect route, that is, formic acid is first oxidized to form an adsorbed CO, and then adsorbed on the surface of the electrode. The oxide species react to form CO_2. It can be seen from the figure that

formic acid is mainly oxidized on a Pd-based catalyst by a direct route, thereby reducing the poisoning of the catalyst by CO.

catalyst by direct route, that is, formic acid is directly oxidized to CO_2; and the small oxidation peak indicates that formic acid is oxidized by an indirect route, that is, formic acid is first oxidized to form an adsorbed CO, and then adsorbed on the surface of the electrode. The oxide species react to form CO_2. It can be seen from the figure that formic acid is mainly oxidized on a Pd-based catalyst by a direct route, thereby reducing the poisoning of the catalyst by CO.

It can be seen from Fig. 3-4 that the peak potential of the Pd/TiO_2-rGO catalyst is negatively shifted relative to the Pd/C catalyst, indicating that the electrocatalytic performance of the formic acid on the Pd nanoparticles is improved. The peak potentials of Pd/TG1, Pd/TG2, Pd/TG3, and Pd/TG4 were 120 mV, 100 mV, 90 mV, and 90 mV, respectively, lower than Pd/C. Among them, the oxidation current density of the Pd/TG2 catalyst is large. It indicated that formic acid had the fastest oxidation rate, the highest electrocatalytic activity and the strongest electrocatalytic oxidation ability on Pd/TG2 catalyst. Compared with Pd/C, the activity of Pd/TG series catalysts has been greatly improved, and the effect of Pd/TG2 is most obvious.

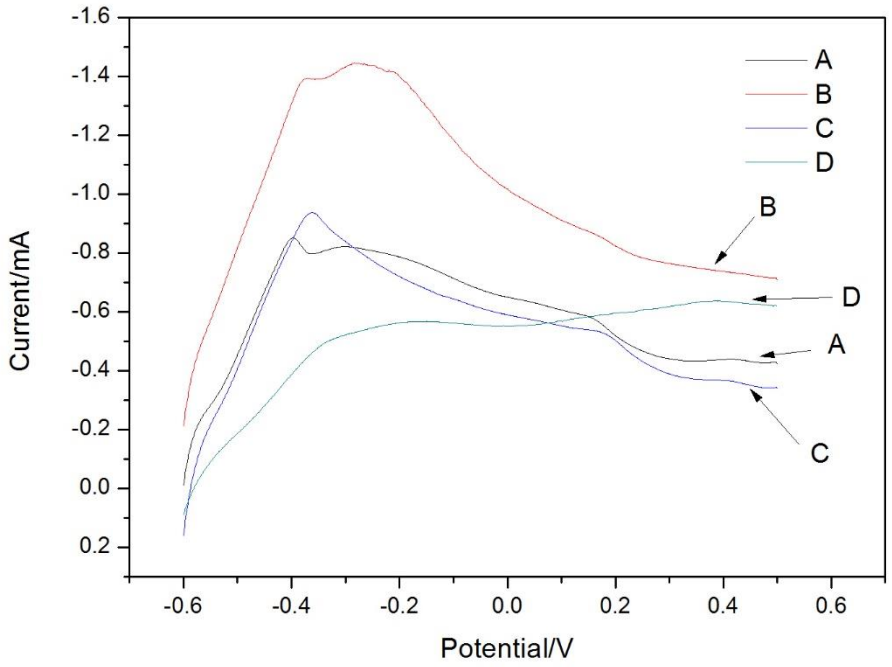

Figure 3-4: Linear scanning of Pd/TG1 (A), Pd/TG2 (B), Pd/TG3 (C), Pd/TG4 (D) catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H2SO4 solution Voltammetry curve, scanning speed 10 mV / s.

2.2.3 Comparison of Electrocatalytic Activity of Different Ratios of Pd/TiO_2-rGO Catalysts for Oxidation of Formic Acid after Light Irradiation

In order to identify the effect of different ratios of Pd/TiO_2-rGO catalyst on the electrocatalytic activity of formic acid oxidation, we determined Pd/TG1, Pd/TG2, Pd/TG3, Pd/TG4 catalyst at 0.5 mol/L HCOOH + The linear sweep voltammetry curve after adding light in 0.5 mol/L H_2SO_4 solution, the scanning speed was 10 mV/s. And compared with no light.

Figure 3-5, 3-6 are linear sweep voltammetry curves of Pd/TG1, Pd/TG2 catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution, and the scanning speed is 10 mV/s. It can be seen from the figure that after the illumination, the peak potentials of the catalysts Pd/TG1 and Pd/TG2 did not change significantly, and the peak potential did not change significantly, but the peak current density became relatively small, indicating that the addition of light reduced the catalyst. The active surface area effect inhibits the electrocatalytic performance of formic acid on Pd nanoparticles to some extent.

Figures 3-7 and 3-8 show the linear sweep voltammetry curves of Pd/TG3 and Pd/TG4 catalysts in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution at a scanning speed of 10 mV/s. It can be seen from the figure that the peak current density of Pd/TG3 and Pd/TG4 is relatively large after illumination, indicating that the addition of light increases the active surface area effect of the catalyst and promotes the formic acid on Pd nanoparticles to some extent. Electrocatalytic performance.

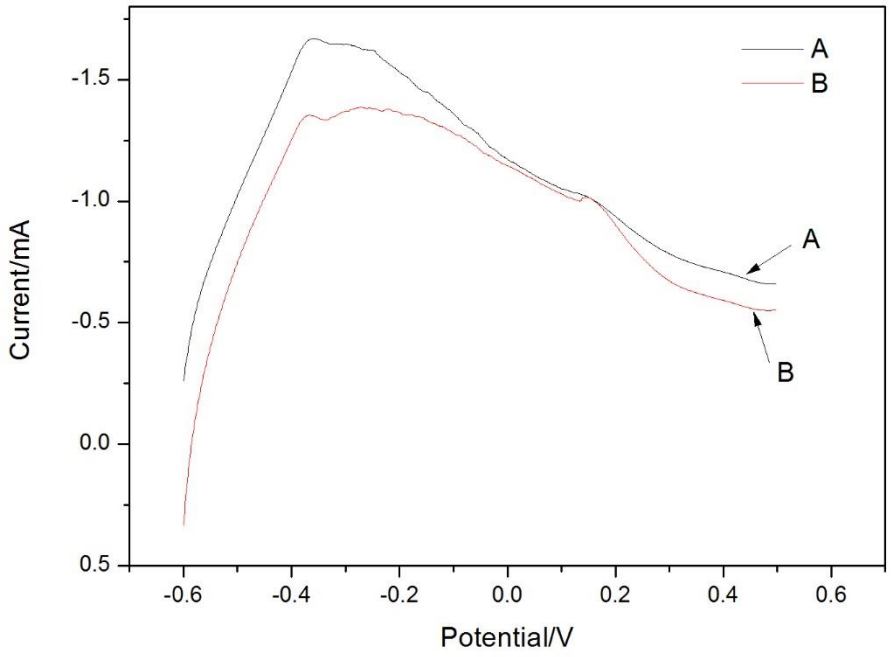

Figure 3-5: Linear sweep voltammetry of Pd/TG1 catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution, scanning speed 10 mV/s, A: before illumination, B: after illumination.

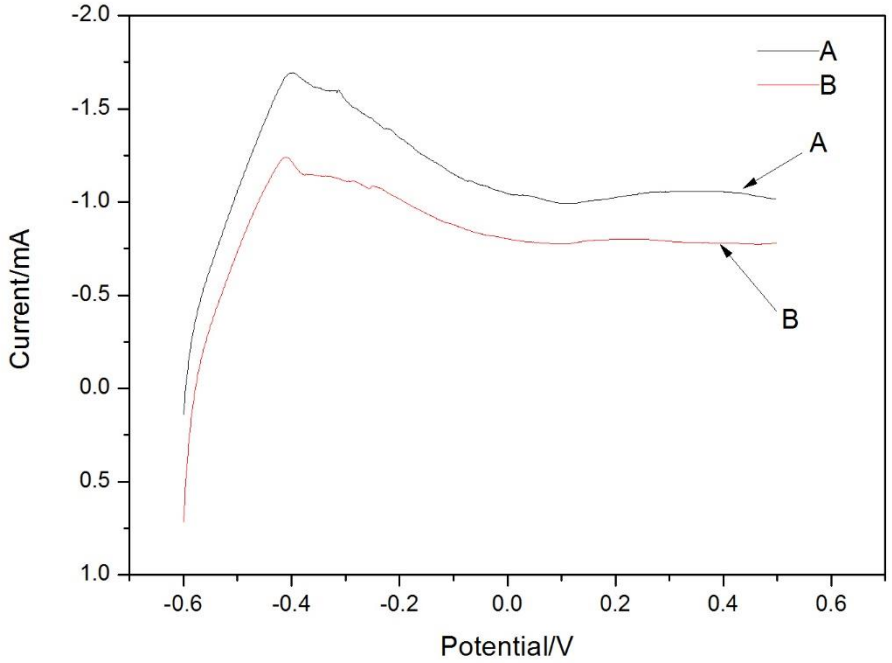

Figure 3-6: Linear sweep voltammetry of Pd/TG2 catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution, scanning speed 10 mV/s, A: before illumination, B: after illumination

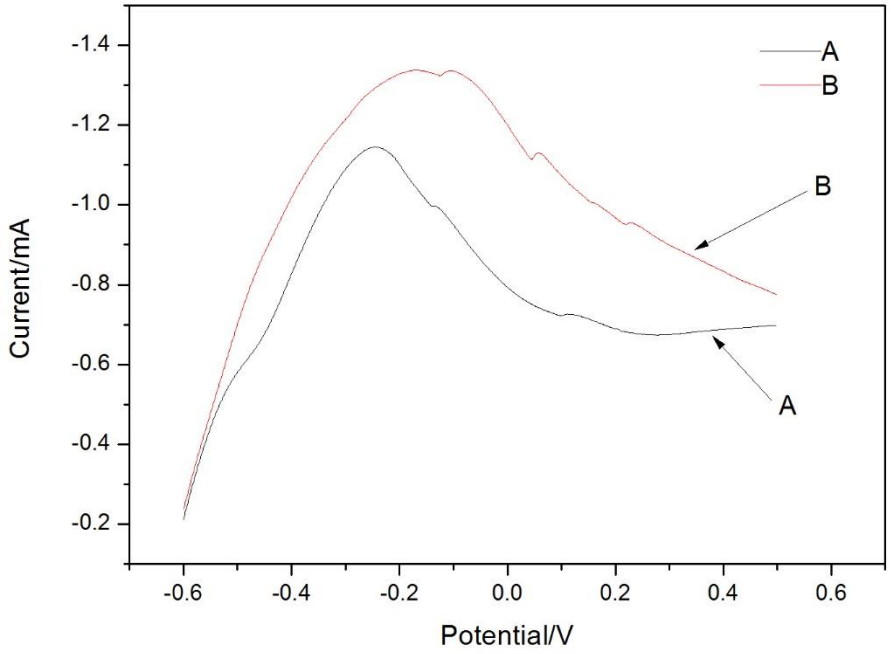

Figure 3-7: Linear sweep voltammetry of Pd/TG3 catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution, scanning speed 10 mV/s, A: before illumination, B: after illumination.

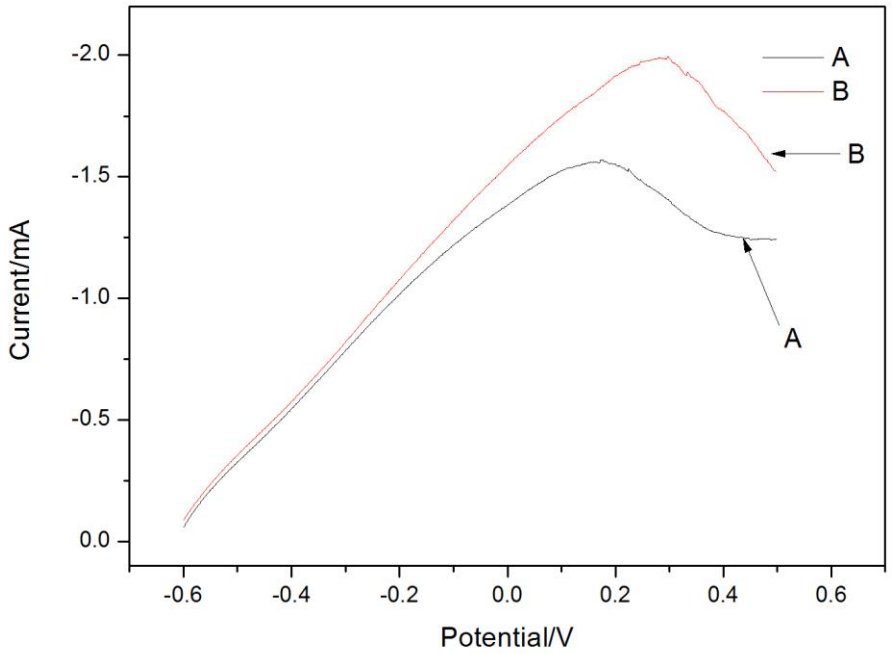

Figure 3-8: Linear sweep voltammetry of Pd/TG4 catalyst in 0.5 mol/L HCOOH + 0.5 mol/L H_2SO_4 solution, scanning speed 10 mV/s, A: before illumination, blue: after illumination.

Conclusion

In summary, the TiO_2-rGO support was successfully synthesized by a simple ethanol solvothermal method, and the Pd nanoparticles were further reduced by sodium borohydride to the prepared support. The catalyst Pd/TG2 with the highest peak current density was selected by electrochemical test. The peak current density of Pd/TG2 is 1.42 mA, which indicates that Pd/TG2 is expected to be used in direct formic acid fuel cells. It is a promising catalyst with outstanding catalytic effect; Moreover, proper reduction of light for the formic acid fuel cell using the Pd/TG2 catalyst can make the catalytic effect better. At the same time, it also discloses that the TiO_2-rGO mixture is also an excellent electrocatalyst support material.

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Acknowledgements

This paper was completed under the careful guidance of Associate Professor Li Wenpeng. In the course of the experiment, Dr. Li gave me great help, and I sincerely thank Dr. Li for his teaching and care. From the selection of the subject, the implementation of the project, to the final completion of the thesis, Mr. Li always gave me patient guidance and support. The instructor's broad vision, rigorous academic attitude, and work style of excellence have deeply infected and inspired me. During my four years of undergraduate study, his rigorous academic attitude and meticulous professionalism have benefited me a lot. I was constantly inspired to overcome the difficulties in the progress of the project.

Thanks to the lab members, Dong Guang, Zhao Shihao, Liu Jinghua, Lu Xiaohui, Guo Tingbao and Zhang Haoquan's. They gave a lot of help, and I would like to express my heartfelt thanks.

Finally, I want to thank my family and friends for their support and care. I am greatly appreciate their meticulous care in my thoughts and life.

Academic paper results and awards published during the reading period

[1] Fuping Li, Wenpeng Li*, Huiling Liu, Changshuo Liu, Guang Dong, Jinghua Liu, Kaichen Peng, Palladium nanoparticles loaded on the hybrids of TiO_2 and graphene (Pd/Ti O_2-Gr) and the enhanced electrocatalytic activity for formic acid oxidation, *Russian Journal of Physical Chemistry A . 2018*, Vol.92 (8), pp.1550-1557. published (SCI).

[2] Meiying Lv, Wenpeng Li*, Huiling Liu, Wenjuan Wen, Guang Dong, Jinghua Liu, Kaichen Peng Enhancement of the formic acid electrooxidation activity of palladium using graphene/carbon black binary carbon supports, *Chinese Journal of Catalysis2017(5)* page 939-947. published (SCI).