Strained silver nanowires for enhanced oxygen reduction reaction performance

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**STRAINED SILVER NANOWIRES FOR ENHANCED
OXYGEN REDUCTION REACTION PERFORMANCE**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

STRAINED SILVER NANOWIRES FOR ENHANCED OXYGEN REDUCTION REACTION PERFORMANCE

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2021

Statement of Originality

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

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Assoc Prof HUANG YIZHONG

Authorship Attribution Statement

This thesis contains material from 1 paper published in the following peer-reviewed journal(s) in which I am listed as the first author.

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The contributions of the co-authors are as follows:

- A/Prof Huang Yizhong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Cao Xun and Prof Huang Yizhong.
- I co-designed the study with A/Prof Huang Yizhong and Prof Junsheng Wu and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me and Dr Cao Xun Dr Peng Dongdong and Dr Lu Yu in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Peng Dongdong assisted in the conducting of the X-ray diffraction data.
- Dr Zhang Bowei and Dr Huang Kang assisted in the interpretation of the transmission electron microscope data.
- Dr Zhang Tianyuan conducted the density functional theory computational data.

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WANG ZHENG

Abstract

Oxygen reduction reaction (ORR) can be efficiently catalyzed by noble metals. Amongst all these catalysts, Ag has a better performance to cost ratio due to its low price and abundant reserve. Surface energy is known to play an important role in the catalytic reaction and straining of electrocatalysts is an effective method to increase their surface energy that weakens the binding towards adsorbates and inhibits the formation of passivation films.

In this research, sonication becomes an efficient and simple method to induce strain into Ag nanowires (NWs) via plastic deformation. The ORR performance of Ag NWs before and after the straining is evaluated in an alkaline medium using linear sweep voltammetry (LSV) through electrochemical cathodic polarization test. The measured diffusion limiting current density produced from Ag NWs increases by more than 20% (from -4.98 mA/cm^2 to -6.00 mA/cm^2) after sonication straining with the onset potential that remains almost constant (i.e. 0.95 V vs RHE). The enhanced electrocatalytic performance on ORR is a result of strain induction which contribute to more active sites on the surface and higher reaction kinetics.

Besides, high-index facets are generated on Ag NWs through laser irradiation. The original (1 1 1) facets in many surface areas are transformed into (1 1 5) and (1 1 6) high-index facets via the rearrangement of atoms operated by laser irradiation. High-index facets have been proved to possess higher surface free energy than low-index facets which can promote the ORR activity. Moreover, the ORR performance including the onset potential and diffusion limiting current is evaluated to depend on the power of laser irradiation from 2 W to 8 W. Ag NWs subject to 4 W laser irradiation reach the highest onset potential with a decrease of 0.034 V vs RHE of overpotential and most negative diffusion limiting current with a 26% improvement comparing with the original silver nanowires. Hence, it indicates that the generation of high-index facets could be the reason that significantly enhances the ORR activity of Ag NWs

Lay Summary

The reserves of fossil fuels such as petroleum and coal decrease constantly with the pass of days. Therefore, it becomes especially critical to seek methods to create new energy resources that replace these fossil fuels. Fuel cells have been identified to be a kind of promising energy conversion system because of its high conversion efficiency and harmless products. But the sluggish kinetics of the cathodic reaction (ORR) has been a hinder for the commercialization of all kinds of fuel cells in large scale. In this case, searching effective catalysts enabling overcoming this problem to improve the ORR performance becomes a key point. Pt and Pt based metals are commonly accepted to be the most suitable catalysts for the ORR. However, they are not desirable for commercialization due to their high cost and rare abundance.

Among all those noble catalysts, Ag has a 50 times lower price compared with Pt and is far more abundant than other precious metals. In addition, nanostructured Ag has been claimed to be an enhanced ORR catalyst because it owns a larger specific surface area with many active sites and high surface free energy to trigger the catalysis. Thus, Ag NWs are chosen to be the original sample for this work.

The performance of ORR is evaluated by the onset potential and diffusion limiting current density which are characterized by using electrochemical test. A higher onset potential and a bigger absolute value of diffusion limiting current density indicate a better ORR capability which also means a fast kinetics. Theoretically, two main pathways have been widely accepted for ORR process i.e. two-electron pathway and four-electron pathway. Two-electron pathway states that two electrons are transferred when the reaction happens, and oxygen are reduced as hydroperoxyl in alkaline medium because Ag has been studied to perform a better electrocatalytic activity in alkaline than acid medium. For four-electron pathway, the electron transfer number is four and oxygen is reduced into hydroxyl which is preferred for ORR since hydroperoxide is reported to be poisonous for the ORR process.

In this project, there are two distinct treatment methods on Ag NWs in order to boost the ORR performance with one being strain and the other laser irradiating. By means of the

characterization of transmission electron microscope, defects as a result of deformation and energy deposition can be observed within Ag NWs samples. Furthermore, high-index facets transformed from low index (1 1 1) during the laser irradiation further improve the effective catalysis of Ag NWs. Hence, sonication and laser irradiation process are proposed and engaged to realize the goal of this thesis in the promotion of the electrochemical ORR performance of Ag NWs.

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Abbreviations

ORR	Oxygen Reduction Reaction
Ag	Silver
Pt	Platinum
NWs	Nanowires
DFT	Density Function Theory
MW	Mega Watt
CO	Carbon Monoxide
CH ₄	Methane
ICE	Internal Combustion Engine
AFC	Alkaline Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
SOFC	Solid Oxide Fuel Cell
MCFC	Molten Carbonate Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
DMFC	Direct Methanol Fuel Cell
RRDE	Rotating Ring Disk Electrode
RHE	Reversible Hydrogen Electrode
HRTEM	High Resolution Transmission Electron Microscopy
NPs	Nanoparticles
RPM	Revolution Per Minute
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
RDE	Rotating Disk Electrode
GC	Glassy Carbon

CA	Chronoamperometry
FFT	Fast Fourier Transform
iFFT	Inverse Fast Fourier Transform
FCC	Face Centered Cubic
STEM	Scanning Transmission Electron Microscopy
ADF	Annular Dark-field Imaging

Chapter 1 Introduction

With the decrease of natural fossil fuel storage, fuel cells have been testified to be a promising substitute of traditional fossil fuel engines. Among them, alkali fuel cell (AFC) can be operated in alkaline medium and room temperature with hydrogen and oxygen as reactants. The working efficient could reach up 70% with the release of environmental friendly byproducts. The obstacles in the recent development of the alkaline fuel cell are elaborated in this chapter. The merits and drawbacks of commonly used cathodic catalysts are presented. The chapter also reviews that even though many catalysts have been studied by many researchers, they are still not appropriate for commercialization due to various kinds of drawbacks. In addition, strain has been addressed enabling the enhancement of the electrocatalysis.

1.1 Hypothesis

Noble metals have been studied in catalysis for ORR. Platinum (Pt) has been identified as one of the best performed catalysts due to its high performance comparing to other noble metals. But the expensive cost and rare storage of Pt make the commercialization become very challenging. Therefore, silver (Ag) has begun to draw the attention of researchers because of its high performance to cost ratio¹⁻⁵. Even though the Ag catalyst is structured in the form of nanowires presenting large surface area to volume ratio and excellent steady durability, the ORR activity of normal Ag NWs is still not efficient highly enough to replace Pt catalysts⁶⁻⁹. Hence, this project is aimed to explore the research methods capable of further advancement of the catalytic activity of Ag NWs.

To enhance the electrochemical catalysis, increasing the surface energy ought to be a feasible and effective method. But this requires some special techniques that transfer external energy to the surface preserved at active sites. In this thesis, the sonication and laser irradiation will be adopted to process Ag NWs followed by performing systematic experiments to prove the hypothesis.

1.2 Objectives and Scope

The aim of the research is to improve the electrocatalytic performance of Ag NWs in ORR. As mentioned above, it could be achieved by raising the surface energy of the catalyst. Electrochemical experiments are to be operated to assess the catalytic performance of Ag NWs in correlation with their lattice structures.

Sonicated and laser irradiated Ag NWs are both prepared with different sonication duration and various laser power densities. The relationship between the morphology and the electrochemical performance will be studied against original Ag NWs comparatively. It is expected that the sonication energy and laser power are able to transfer the external energy into the Ag NW surface at the active sites resulting in a high surface energy with defects and high-index facets.

1.3 Dissertation Overview

The thesis introduces the methods developed to improve the electrocatalytic performance of Ag NWs in ORR, to solve the bottle neck problem in the fuel cell area and ease the current energy crisis.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the current situation of the energy utilization. Catalysts for the cathodic reaction and the mechanism of ORR are reviewed. Previous methods, which are to improve the catalytic performance of the noble metals with many kinds of nanostructures, are also introduced.

Chapter 3 discusses the principles underlying the sample preparation, characterization and testing techniques employed.

Chapter 4 elaborates the first major set of results. Ag NWs were sonicated in a solvent with two Titanium (Ti) foils for a certain duration. HRTEM characterizations have revealed the formation of defects which were proved to be related to the increasing of the surface free energy based on the density function theory (DFT) calculation. The systematic electrochemical test identified the ORR catalytic performance of the sonicated sample has been improved comparing the original Ag NWs.

Chapter 5 elaborates the second major set of results. The sample was laser irradiated in a solvent with various of power density. Almost all different power level of laser irradiation might contribute to the enhancement of surface free energy and the ORR performance. High-index facets are found on the laser irradiated samples which don't show up on the surface of the original Ag NWs. Hence, the discussion about relation between the ORR performance and the facet transformation is proceeded in this chapter.

Chapter 6 draws together the threads of the thesis. Reconnaissance studies that did not warrant a complete chapter are also included. A framework for further studies is recommended based on the findings of the current research in this project.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating that sonication and laser irradiation could be the most convenient and effective methods to induce strain inside nanostructures and transfer low-index facets into high-index facets. The large-scale preparation might lay a firm foundation for the commercialization of Ag NWs.
2. The increase of the surface free energy could be a significant point for the improvement of the electrocatalytic performance of Ag NWs on ORR.
3. Directly observing the defects (like stacking faults, twinning crystals and dislocations) and high-index facet through advanced materials characterization techniques. Deformed structures lead to the great improvement in the electrocatalytic performance of Ag NWs.
4. Gaining a systematic understanding of Ag-catalyzed ORR under various physical conditions in terms of loading of catalysts, duration of sonication and different laser power intensities.
5. Correlating the key parameters in electrochemistry (such as surface free energy) with the performance of Ag NWs (i.e. onset potential, diffusion limiting current density).

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Chapter 2 Literature Review

The noble metals (i.e. Pt, Pd, Au, Ag) are widely utilized as efficient catalysts for chemical reactions. All of them play a crucial role in the development of the modern society. Therefore in this project, the comparison of the catalytic performance in ORR among these noble metals is discussed. The methods to improve the electrochemical activity are to be analysed in terms of the nanostructures and ORR mechanism.

2.1 Energy Crisis and Current Solutions

Since the decrease of the fossil fuel storage, the whole world is seeking solutions to this due to its key position on many industrial sectors and the development of the modern society. Currently, some replacement of energy sources of fossil fuels has been executed including wind and solar energy which are renewable and clean. The development of energy storage and energy conversion system gain a great advance as well, for example, batteries, supercapacitors, solar cells, fuel cells and gas storage.

2.1.1 Renewable Energies

Renewable energy is a term representing sustainable and clean energy sources (sunlight, wind and tidal energy). These energy sources can somehow replace fossil fuels in lots of industrial sectors. Moreover, some energy conversion systems utilizing renewable energies have been commercialized and used a part of the total energy consumption of the whole world¹.

Sunlight is considered as a type of environmental-friendly, free and infinite energy source. Technologies such as solar cells are used to convert solar energy to electric energy, therefore, solar energy ideally has the potential to completely take the place of the traditional fossil fuels. However, it still has some drawbacks which are the low conversion efficiency from solar energy to electric energy, low performing balance of system, and cost-performance obstacles². Thus, solar energy is still limited by all those disadvantages mentioned above even though it works as an energy source for certain industrial sectors.

In fact, wind energy is caused by the different temperature on various regions of the earth surface. It has been roughly calculated that there are about 10 million MW of sustainable wind energy³. Also, it has been widely used around the world and become a necessary part of energy supply. But there are still many negative environmental impacts existing in the technique of harvesting the wind energy including noise pollution, bird fatality, greenhouse gas emission and land surface usage and demaging⁴.

The formation of tidal energy is mainly due to the gravitational pull and the centrifuge forces of the earth-moon system. The core conversion system of the energy transfer technique is made use of a tidal current turbine which converts tidal energy to electricity. Although the tidal energy is environmentally friendly and sustainable, the current turbine technology could not overcome the large scale installation in terms of its high construction cost and aggressive environmental conditions⁵.

2.1.2 Fuel Cells

Fuel cells are a typical energy conversion system which converts chemical energy to electricity with electrocatalysts inside a cell by the consumption of fuels (such as pure hydrogen, CO and CH₄). Fuel cells are designed to provide electricity both in the large and small-scale applications such as mobile power stations, the portable computers and military communication equipment. Comparing with conventional internal combustion engine (ICE), fuel cells show more outstanding energy conversion efficiency (ranging from 40-85%)⁶. Moreover, the fuels that are utilized by fuel cells are clean and less harmful to the environment.

Figure 2.1: Basic working mechanism of fuel cells⁷.

Fuel cells are comprised of several parts including anode, cathode, electrolyte and the external circuit, to form a closed circuit. Oxidation reaction of fuels is carried out at the anode and the reduction of oxygen is held at the cathode. The common types include Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Proton Exchange Membrane Fuel Cell (PEMFC), Direct Methanol Fuel Cell (DMFC)⁸ with their properties are listed in **Table 2.1** below. Among these fuel cells mentioned above, AFC and PEMFC are much more suitable for commercialization because their installation costs are only about half of the price of the other fuel cells. Besides, the relatively high efficiency and low working temperature make the cost of operating decrease comparing with other fuel cells.

Table 2.1: Comparison of various fuel cells

Parameters	Fuel cell types					
	PEMFC	AFC	PAFC	MCFC	SOFC	DMFC
Electrolyte	Liquid solution of KOH	Phosphoric acid	Lithium and potassium carbonate		Stabilized solid oxide electrolyte	Solid polymer membrane

	50-200	~200	~650	800-1000	60-200
Operating temperature (°C)					
Fuel	Pure H ₂	Pure H ₂	H ₂ , CO, CH ₄ , other	H ₂ , CO, CH ₄ , other	CH ₃ OH
Efficiency	~50%	40%	>50%	>50%	40%
Installation Cost (US\$/kW)	~1800	2100	~2000-3000	3000	-

2.2 Materials for Catalysts

2.2.1 Background

The theoretical output voltage is supposed to be around 1.2 V at room temperature which has not been ever reached so far. The potential loss is mainly because of the ohmic loss⁷ such that a lot of fuel and oxygen cannot be fully reacted at the anode or cathode. In particular, the potential loss at the cathode is especially obvious to be observed. Therefore, noble metals are currently working as the catalyst for both electrodes of fuel cells because oxygen can be strongly absorbed by noble metals like platinum or palladium. As a result, the reactants are more likely able to participate in reactions leading to the reduction of the potential loss. To get a comprehensive understanding of the cathodic process of ORR, the mechanism of it is elaborated in the next section.

2.2.2 ORR mechanism

The process of ORR is quite complex and involves multiple steps producing many intermediates during the entire process. Basically, there are two main reaction pathways for ORR: 2-electron pathway and 4-electron pathway in alkaline media or acidic media which are shown in Equation (1)-(6). ORR has different reaction process in alkaline and acid medium, the details are given in **Figure 2.2** and **Figure 2.3**.

Indirect 2-electron pathway in alkaline electrode:

Direct 4-electron pathway in alkaline electrode:

Indirect 2-electron pathway in acidic electrode:

Direct 4-electron pathway in alkaline electrode:

In conclusion, the mechanism at the cathode is via the adsorption to oxygen on the electrode to ensure as much reactant to participate in the cathodic reaction through a 2-electron or 4-electron pathway to reduce oxygen back to water in the end.

Figure 2.2: the mechanism of ORR in alkaline medium⁹. **Figure 2.3:** the mechanism of ORR in acid medium¹⁰.

2.2.3 Introduction of common-used catalytic materials

Nobles are elements occupying group 8-11 and periods 5-6 in the Periodic Table of the Elements, including platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt), Au and Ag. The noble metals are not only worthwhile in the business area, but also able to be applied in research and industrial fields^{11, 12}. In electrochemical research, noble metals are considered as the widely used catalysts for electrochemical reaction such as ethanol oxidation and ORR¹³.

The unique catalytic performance of noble metals is original from their electronic configurations with hybridized bands in the d-orbital electrons. Currently, Pt performs the best ORR catalytic ability^{14, 15}, however, the expensive price of Pt indeed inhibits the development of fuel cells. Comparing with Pt, Ag displays a better long-term stability and performance to cost ratio with abundant storage (15 times more than Pt) and very low price (about 50 times lower than Pt)^{16, 17}.

Table 2.2: noble metals price data in USD per troy ounce from 2015 to 2019. All prices are average of period. [taken from focus-economics.com]

	2015	2016	2017	2018	2019
Gold	1159.8	1248.54	1258.46	1269.41	1393.23
Silver	15.71	17.15	17.15	15.72	16.22
Palladium	690.55	614.03	869.99	1030.5	1538.2
Platinum	1051.85	987.37	948.13	879.15	863.77

Figure 2.4: the crustal abundance of platinum, silver and gold [taken from silverbullion.com]

2.3 Electrocatalytic Activities of Ag

As silver has been proved to be a promising substance of Pt for ORR catalysis^{18, 19}, a proper operating environment for Ag catalysts including a moderate pH value and suitable structures has been considered and settled.

2.3.1 The pH Effect

The effect of pH value has a huge impact on the performance of ORR activities. Researches of the pH effect on Ag (1 1 1) facet have been performed and analyzed²⁰, and are operated in both acid and alkaline media through a rotating ring disk (RRDE) way. The results demonstrate that the ORR catalysis of Ag catalysts in acid medium is dominated by 2-electron pathway with a high production of hydroperoxide and sluggish ORR performance shown in **Figure 2.5**. In alkaline medium, it was found that the catalytic reaction was processing mainly via a mix of 2-electron and 4-electron pathway with a ultralow production of hydroperoxide and a relatively better ORR performance. In addition, the calculated electron-transfer number is close to 4, resulting in a faster reaction kinetics. Therefore, it can be concluded that ORR performs higher in alkaline medium than acid medium.

Figure 2.5: ORR performance of Ag (1 1 1) single crystal in alkaline medium (a) polarization curves of ORR with various of rotating speed, (b) current-potential curve of ORR on the ring electrode²¹

Figure 2.6: ORR performance of Ag (1 1 1) single crystal in acid medium (a) polarization curves of ORR with various of rotating speed, (b) current-potential curve of ORR on the ring electrode²¹

2.3.2 The Morphology Effect

The performance of ORR can be affected not only by the pH value, but also by the morphologies of the silver catalysts such as lattice facet²² and morphological size.

Previous study indicates that various facets of Ag single crystal have contributed to different ORR performances. The sequence for ORR capability is ordered as $(1\ 1\ 0) > (1\ 1\ 1) > (1\ 0\ 0)$. Among those facets, Ag $(1\ 1\ 1)$ single crystal displays the most positive onset potential locating at about 0.9 V with almost no production of H_2O_2 , which demonstrates that facet $(1\ 1\ 1)$ catalyzes ORR in the fastest kinetics via a 4-electron pathway.

Figure 2.7: LSV curves of $(1\ 1\ 1)$, $(1\ 0\ 0)$ and $(1\ 1\ 0)$ single crystal in 0.1 M KOH with rotation rate of 1600rpm²².

In addition, size variation of different Ag nanostructures also affects the ORR performance shown in **Figure 2.8**. For Ag nanoparticles (NPs), smaller size particles perform more active catalytic characters with a lower overpotential, which is mainly due to the increasing of the specific surface area as the diameter of the Ag NPs decrease. The increasing specific surface areas provide more active sites for ORR. As for Ag nanowires (NWs), longer nanowires possess a better activity on ORR. Comparing those two types of nano structures, 25nm Ag NWs show a 5.3 times improvement on ORR activity than 2.4 nm Ag NPs²³. Thus, Ag NWs is much more suitable as a catalyst for ORR comparing with Ag NPs because a four-electron pathway with less formation of H_2O_2 was preferred to happen in the surface of Ag NWs, on the contrast a two-electron pathway was easier occurred in the surface of Ag NPs. This is because the formation Moreover, the aspect ratio²⁴ of nanowires has influence on the catalytic performance of Ag, which means the length affects the ORR activity when the diameter is constant. According to the previous research (**Figure 2.9**), Ag NWs with higher aspect ratio produce higher peak current density in CV associated with the diffusion limiting current density in LSV curves. So, the aspect ratio of nanowires is also considered as a key contribution for ORR.

Figure 2.8: (a) polarization curves of Ag NWs with various of diameters, (b) polarization curves of Ag NPs with various of sizes²³.

Figure 2.9: Cyclic voltammetry curves of silver nanowires with different aspect ratio²⁴.

2.3.3 Current Challenges

Even though Ag has the abundant storage and relatively low cost comparing with Pt, there are still some challenges facing for now, which include not very satisfactory ORR performance which results in a poor efficiency of fuel cells. The challenges are considered to be attributed from the sluggish kinetics of ORR which might be caused by the adsorption of the intermediates formed in the ORR. Moreover, the basic mechanism of the ORR on materials like Ag remains unsettled and further research of it is required²⁵.

2.4 Enhancing Electrocatalytic Performance

To move forward in terms of enhancing electrocatalytic performance of catalysts, a variety of methods are applied, for example, tuning the morphology of Ag nanostructures as mentioned in the last section, synthesis of Ag based bi-metal alloy and inducing strain inside Ag nanostructure via multiple ways. The effort of all these methods is made to solve the current challenges faced by ORR catalysis process with low overpotential, high diffusion limiting current density and better stability of ORR.

2.4.1 Ag Alloy

Alloying Ag with other non-noble metals such as Cu^{26, 27}, Fe²⁸, Co^{29, 30} and In³¹, has been studied by researchers to further lower the cost as well as raise the ORR activity. The results tested in oxygen-saturated alkaline environment show that Au-Cu alloy performs best improvement in the onset potential on ORR (**Figure 2.10**). In addition, the amount of Cu also has effect on the ORR performance. This is because the electronic structure might be affected through alloying with non-noble metals. Accordingly, an upper shift of d-band center is discovered via high-resolution X-ray photoelectron spectroscopy (XPS) test among the alloys which improves the ORR kinetics. Additionally, Ag-Cu alloy displays the best ORR activity with the stoichiometry of Ag₅₀Cu₅₀ as it has the highest specific activity with upshift d-band center and the best balance of bind energy between oxygen and anions. Moreover, Cu alloyed with Ag could adjust the ORR performance with certain amount of Cu element incorporation. However, excessive amount of Cu might affect the exposure of the catalytic surface active sites³¹.

Figure 2.10: The ORR LSV curves of Ag-based alloy with various of elements, Ag-Cu alloy with different amount of Ag and Cu³¹.

The effect of alloying on the electron structure is given in **Figure 2.11**. In **Figure 2.11a** and **Figure 2.11b**, the density of states (DOS) of silver alloys including (Cobalt, Iron and Copper) show obvious rise demonstrating the upshift of the d-band center comparing with pure silver according to the result of Hofmann et al³². **Figure 2.11c** and **Figure 2.11d** display the relationship between the specific activity and the d-band center. The elements alloyed with Ag contribute to an upshifted d-band center which resulting in an increased ORR performance

Figure 2.11: Valence band spectra (VBS) of the a) $\text{Ag}_{75}\text{M}_{25}$ and b) $\text{Ag}_x\text{Cu}_{100-x}$ alloys as measured by high-resolution XPS. c) Relationships between experimentally measured specific activity (SA) at 0.85 V_{RHE} versus the d-band center position for $\text{Ag}_{75}\text{M}_{25}$ alloys with various kinds of alloy composition. d) Relationships between specific activity (SA) at 0.85 V_{RHE} versus the d-band center position for $\text{Ag}_x\text{Cu}_{100-x}$ alloys with various content of Cu.

2.4.2 Strain Effect

Apart from alloying non-noble metals, strain in nanostructures has also been considered as a valid method to enhance the electrochemical on ORR due to the adjustment of the surface structure of catalysts. Thus, many methods to induce strains have been studied such as compressive strain induction by synthesizing alloy with the core-shell nanostructure³³. The mechanism of the strain induction is due to the different radius of atoms that the incorporation of them will produce either compressive or tensile residual strain in catalyst materials. As an example, the XPS spectra shown in **Figure 2.12** indicates that the peaks

at 71.2 and 74.6 eV (strongest peak intensities) represent the metallic Pt and the weak peaks at 72.3 and 75.9 eV contribute to the formation of Pt oxides and Pt(OH)₂. The shift of peaks is caused by the strain induced through the effect of smaller core lattice parameters on the shell materials. This strain at least partially improves the ORR stability and mass activity of the catalyst.

Figure 2.12: (A) Diffraction patterns of various of nanoparticles, (B) XPS spectra of those catalysts.

Pb nanosheets with different thickness has been studied which has a improved ORR performance including both specific and mass activities shown in **Figure 2.12**. With the decreasing of the thickness of Pb slabs from 8 ML to 3 ML, the onset potential of ORR shift negatively indicating an improved ORR performance.

Figure 2.13: (a) LSV curves of Pb nanostructures with different thickness of 3 ML, 5 ML and 8 ML in 0.1 M alkaline medium (inset: halfwave potential vs RHE), (b) specific and mass activity of ORR at 0.95 V vs RHE, (c) enhancement on ORR comparing with Pb nanoparticles³⁴.

As the thickness of Pb nanosheets drops, the strain has been tested to rise through DFT calculations shown in **Figure 2.13**. The mechanism of strain induction is displayed in **Figure 2.13a** which indicates there is larger amount of strain while the thickness of nanosheets decreases. Therefore, it could be concluded that the strained Pb nanosheets have a higher ORR performance and the strain in thinner slabs is larger leading to a more positive shift of onset potential.

Figure 2.14: The relation between bulk modulus (B), surface stress (τ) and lattice strain (ε) of platinum group and coinage metal slabs. (a) mechanism of strain induction in bulk materials and nanosheets, (b) surface stress of fcc (1 1 1) and hcp (1 1 1) surface compared to the bulk modulus, (c) ratio of the pressure (p) of the close-packed surfaces, induced by surface stress, and the bulk modulus for 11 transition metals, (d) Potential energy profile of strained versus unstrained Pb (1 1 1) slabs with thickness of 8 ML, 4 ML and 2 ML, (E to G) intrinsic in-plane strain of fcc (1 1 1), fcc (1 0 0) and the [1 0 0] direction of unreconstructed fcc (1 1 0) slabs, with thicknesses from 1 ML to 12 ML³⁴.

The mechanism of how strain affect the ORR performance has been reported in several literatures³⁵⁻³⁷. The widely accepted theory is that strain can induce defects like twin crystals, dislocations and stacking faults, which could increase the surface energy of catalysts to increase the reaction kinetics and weaken the adsorption of the intermediates produced during reaction to release more active site for oxygen reduction.

2.4.3 High-Index Facets

High-index facet has been identified to possess an improvement on the performance of catalytic reaction within noble metals such as platinum and palladium according to the recent studies^{38, 39}. For example, Platinum cubes with high-index facets show a larger specific activity and mass activity on ORR⁴⁰. The high-index facets could make the absorption of oxygen molecules on to the catalysts easier⁴¹, which could enhance the catalytic process with a higher electron transfer number. Different structures of platinum also affect the catalytic process, and this is because the change of active sites on those structures shown in **Figure 2.16**. Meanwhile, the ORR tests displayed in **Figure 2.17** demonstrates that catalytic performances of almost all catalysts with high-index facets are enhanced comparing with the low-index planes such as (1 1 1), (1 1 0) and (1 0 0)⁴².

Figure 2.15: Different structures of high-index facets of platinum.

Figure 2.16: ORR polarization curves of high-index planes on platinum in oxygen-saturated environment (a) $n(1\ 1\ 1)-(1\ 1\ 1)=(n-1)(1\ 1\ 1)-(1\ 1\ 0)$, (b) $n(1\ 1\ 1)-(1\ 0\ 0)$, (c) $n(1\ 0\ 0)-(1\ 1\ 1)$, (d) $n(1\ 0\ 0)-(1\ 1\ 0)$.

2.4.4 Laser Irradiation

Laser is a method to deposit huge energy on to the catalysts via emitting coherent light with a narrow size spectrum. It could produce stimulated emission of electromagnetic radiation, thus, the electrons inside the lattice of catalysts could be excited to higher energy level. Therefore, laser irradiation with certain range of wavelength emits energy onto the surface of catalysts. As a consequence, the excited electrons after irradiation might drive the reorganization of the structures due to the thermal emission while the excited electron jump to the ground level. This process might also provide hot electrons for the reduction reaction^{43, 44}. It has been researched that excited catalysts by laser irradiation have an enhanced electrochemical performance with excited hot-electron or strain induction⁴⁵. **Figure 2.16** indicates that extinction and absorption spectra, it could be figured out that the absorption peaks of silver nanowires, nanoparticles and nanotriangles are at around 360, 388 and 579 nm. Accordingly, the wavelength of laser irradiation on silver could be confirmed.

Figure 2.17: (a) TEM images of silver nanowires (i), silver nanoparticles (ii) and silver nanotriangles (iii), (b) extinction spectra of different silver nanostructures, (c) stimulated extinction and absorption spectra of silver nanostructures.

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Chapter 3 Experimental Methodology

This chapter illustrates the sample preparation method, explains the basic theory and work principle of RDE equipment and introduces the facilities employed such as XRD, SEM and TEM. The parameters of the electrochemical tests including scan rates, rotating rates and the electrodes and electrolyte of the half-cell are clarified. Moreover, the parameters of the Koutecky-Levich plot, used for calculating the number of the electrons transferred, are also stated.

3.1 Rationale for Selection

RDE equipment (AFMSRCE 101708, PINE Research, Country) was used to maintain the dynamic stability of the O_2 concentration, which is comprised of GC, insulator (Teflon) and a shaft used to connect the brush contact of rotating system. Catalysts was loaded firmly on GCE and the RDE works as the working electrode. The thickness of the diffusion layer around the electrode is controlled by the rotating speed of RDE¹. A thinner dynamic stability layer requesting a faster rotating speed is in capable of providing adequate reactants because the adsorbed oxygen in electrolyte can diffuse into the electrode surface swiftly leading to a larger current density².

Figure 3.1: a typical schematic diagram of RDE.²

Normally, sonication is used for cleaning or dispersing. The working principle of sonication can be explained by **Figure 3.2**. The sound energy of sonication equipment can form a cavitation in solvent. With the absorption energy of cavitation increasing, the bubble grows until implosion resulting in a fluid flow from the imploded center. The flow is the key factor for inducing strain into nano structures by carrying nanostructures to impact

with thin films to form a plastic deformation and the strain could be observed around the necking area (**Figure 3.3**).

Figure 3.2: Mechanism of sonication.

Figure 3.3: Mechanism of strain induction via sonicating

3.2 Preparation of Samples

The ultralong Ag NWs was purchased from XFNANO Materials Tech Co., Ltd, China sealed in KCl solution. The original nanowires are physical characterized via TEM and SEM and XRD to get the initial information of the silver nanowires about their average length, diameter and XRD patterns before conducting sonication and laser irradiation

3.3 Techniques Used

3.3.1 Physical Characterization

Electromagnetic (EM) waves comprise of a spectrum of waves with different wavelengths. Amongst these, the wavelengths of X-rays are typically in the order of angstroms ($1 \text{ \AA} = 10^{-10} \text{ m}$), which are comparable to the radii of atoms. This allows a wide spectrum of applications of X-rays in modern technology, such as obtaining radiographs in medical science, radiation therapy, airport security checks and detection of counterfeit artworks. In the field of materials science and engineering, it is widely employed for the study of crystallography. Some of the most common applications of XRD include determination of crystallinity of materials, identification of phases and corresponding unit cells, measurement of crystallite size, as well as analysis of textures and strain mapping. Advanced application of XRD may assist in studying potential defects and phase transition of crystals, thereby helping in construction of phase diagrams in alloys and solid solutions.

In crystalline materials, atoms are orderly arranged in arrays with well-defined inter-atomic spacing (the d-spacing, denoted as $d_{(hkl)}$) between lattice planes. Since the wavelengths of X-rays have a comparable size to the d-spacing of crystals, the structures of materials could be revealed by precise matching of experimental results of XRD against a standard database.

In this project, thin film X-ray diffractometer (XRD-6000, Shimadzu, Japan) was employed to get the diffraction pattern of Ag NWs using Cu K α 1 radiation running at 40kV and 30mA with $\lambda \approx 1.5405980 \text{ \AA}$. The Ag NWs were scanned in the range of $30^\circ \leq 2\theta \leq 90^\circ$ with an X-ray grazing angle of 1.0° at the scanning rate of $1.0^\circ/\text{min}$ and a step size of 0.02° .

Figure 3.4: Photo of Shimadzu XRD-6000 thin film XRD used in this project.

Microscopies are the express ways to have an enlarged view of tiny features. Apart from light microscopes which use visible light as the incident beam, electron microscopes utilize a beam of accelerated electrons emitted from the electron gun. An electron gun contains a filament, which emits electrons upon heating or application of strong electric field. It could

be classified into thermionic emission and field-emission guns (FEG), and the FEGs can be further divided into cold and thermal FEGs³.

The most commonly obtained signals include secondary electron imaging (SEI), backscattered electron imaging (BEI), elastically transmitted electrons (bright field TEM imaging), diffracted electrons (dark field TEM imaging) and X-rays (energy-dispersive X-ray (EDX) spectroscopy). These signals correspond to morphological observation, viewing of phase distribution, resolving the internal structures of materials and elemental analyses, respectively.

SEM is an efficient method to perform surface analysis on samples. When the electron beam is emitted from the electron gun and passes through the SEM column, the scanning coil controls the scanning pathway of the electrons. The magnification of an image is defined as the ratio between the area of screen and the area of scanned region. The accelerating voltage of SEM is normally up to 30 kV and the theoretical magnification is usually within the range of 25-1000000X.

In the field of materials science, TEM and STEM are powerful and advanced analytical tools. In a modern TEM/STEM, three fundamental functions are provided – imaging, diffraction and spectroscopy. The modern TEM/STEM is usually operated at the accelerating voltage of 80-300 kV, the wavelength of incident electron beam could reach picometre scale and thus TEM/STEM is capable of presenting more information compared to SEM, for example, resolving much smaller features like crystal lattice and forming diffraction patterns of samples. On the other hand, the major limitation of TEM/STEM arises from the thickness of specimens – they need to be ~ 100 nm or less in order to be electron “transparent”, and that creates challenges in the sample preparation procedures.

The TEM/STEM is a complex instrument with many sub-systems. As shown in **Figure 3.5**, the instrument can be generally divided as the vacuum system, the electron source, the illumination and imaging systems, the sample holder, as well as the recording system.¹⁰ Similar to other electron microscope systems, the TEM/STEM also works in a vacuum environment; the electron beam is produced by the electron gun and first passes through

the condenser lens and aperture in the illumination system, so as to get focused onto the specimen at the suitable stage height. There are many types of specimen holders for various applications. Conventional holders may have single/double-tilt configurations, such that the specimen could be oriented by tilting along either the X-axis or both X- and Y-axes (with Z-axis parallel to the optical axis) for study in crystal structures and diffractions. There are special holders for specific requirements, for example, low-background holders have Be windows for EDX analyses with minimum Bremsstrahlung and characteristic X-rays; multiple-specimen holders realize quick switching of samples without the need to remove the specimen holder; cryo-transfer holder ensures the transfer of cold specimens without the condensation of water vapour; tomography holder allows 360° tilting of specimen for 3D reconstruction purpose; in-situ holders could assist scientists in understanding the responses of specimens to external stimuli, such as heating, cooling, straining, probing, charging, being in liquid/gas environment, and so on⁴.

Figure 3.5: Photo of JEOL JEM-2100F FEG-TEM/STEM used in this project and the inset diagram is the schematic illustration of the instrument structure, where blue marks the electron source part; yellow marks the illumination system and green marks the imaging system

In this project, all images of morphologies were obtained via field-emission gun scanning electron microscope (FEG-SEM 7600F) conducted at the accelerating voltage of 5 kV and high-resolution transmission electron microscope (HRTEM JEM-2100F, JEOL, Japan) operated at the accelerating voltage of 200 kV was mainly utilised to capture atomic-resolution images of the Ag NWs to reveal the lattice structures of original and deformed regions.

3.3.2 Electrochemical Characterization

All electrochemical tests were operated in a cell with three-electrode system linked to an electrochemical workstation (PGSTAT302N, Metrohm Autolab, Netherlands). The sample ink was drop-casted onto GCE (E5 Fixed-Disk, PINE Research, USA) served as the working electrode. The counter and reference electrodes were a thin Pt foil (99.9% purity) and a saturated Ag/AgCl electrode respectively. The ORR polarisation tests were implemented by linear sweep voltammetry (LSV). The LSV curves were obtained by varying the rotation speed (400-2500 rpm) at the scanning rate of 10 mV/s with a step size of 0.00244 V. The cyclic voltammograms were obtained at the scanning rate of 20 mV/s within a suitable potential range for 5 consecutive cycles at a step size of 0.00224 V. The chronoamperometry (CA) profiles were measured at the constant potential of 0.7 V (versus RHE) over a total duration of 15000 s. All measurements were carried out in an O₂-saturated electrolyte of 0.1 M KOH (pH = 13). Koutecky-Levich plots were analyzed in several different potentials to gain the electron transfer number (n) via calculating the slopes of their linear fit lines based the Koutecky-Levich equation.

Figure 3.6: Photo of PINE rotating system

$$j^{-1} = j_k^{-1} + j_d^{-1} = j_k^{-1} + (Bw^{1/2})^{-1} \quad (7)$$

$$j_k = nFkC_0 \quad (8)$$

$$j_d = 0.2nFC_0D_0^{2/3}v^{-1/6}w^{1/2} \quad (9)$$

$$B = 0.2nFD_0^{2/3}v^{-1/6}C_0 \quad (10)$$

The meaning of j , j_k and j_d are the current density collected directly from the workstation in O_2 environment, the kinetic current density gathered in N_2 environment and the diffusion limiting current density calculated via j and j_k respectively. w is the angular velocity of the RDE (rpm), n is the transferred electron number, F is the Faraday constant (96485 C mol^{-1}), C_0 is the saturation concentration of oxygen in the bulk ($1.26 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient in 0.1 M KOH ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v is the kinematic viscosity ($1.09 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

Measured potentials versus saturated Ag/AgCl are converted to potentials versus reversible hydrogen electrode (RHE) via Eq 11⁵.

$$E(RHE) = E\left(\frac{Ag}{AgCl}\right) + 0.197 + 0.0592 \times pH \quad (11)$$

Figure 3.7: Photo of Metrohm Autolab PGSTAT302N electrochemical workstation used in this project.

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Chapter 4 Catalysis of Sonicated Ag NWs on ORR

The main results of physical and electrochemical characterization are displayed in this chapter including the XRD tests identifying the composition of prepared catalysts, the SEM and TEM characterization images with macroscopic plastic deformation and microscopic defects on the surface. In addition, the electrochemical experiments such as cyclic voltammograms, ORR polarization curves and stability test results are presented. In addition, the results of contrast among different extents of deformation and loading are shown in LSV images. The connection between defects and electrocatalytic activity of strain is explained via all those outcomes above.

*This section is published substantially as “Strained Ultralong Silver Nanowires for Enhanced Electrocatalytic Oxygen Reduction Reaction in Alkaline Medium” in *The Journal of Physical Chemistry Letters* (DOI: 10.1021/acs.jpclett.1c00249).¹ Reprinted with permission. Copyright (2021) American Chemical Society.

4.1 Preparation of Sonicated Ag NWs

The original and strained Ag NWs were prepared with several steps. First, 400 μl Ag NWs (3.27 mg), 800 μl absolute ethanol, 200 μl deionized water (DI water) and 15 μl Nafion (5 wt%) were mixed uniformly in a 15 ml centrifuge tube. After that, 400 μl of the homogeneous mixture (0.00234 mg/ μl) was transferred into a 1.5 ml microtube and used as the control sample (the original Ag NWs); the deformed Ag NWs were produced by sonication of another set with the inclusion of 2 pieces of Ti foils (length: 1 cm; width: 0.25 cm; thickness: 1 mm) in a 1000 W ultrasonicator (Elmasonic S180H, Germany) for 1 min. Then, 40 μl of each ink (original and deformed Ag NWs) was separately loaded onto GCE with even distribution over the surface and dried at around 60 $^{\circ}\text{C}$.

4.2 Physical Characterization of Sonicated Ag NWs

Figure 4.1a is the original Ag NWs that are physical characterized to have a length of about 30 μm with a diameter of around 30 nm at a low magnification. **Figure 4.1b** presents the deformed Ag NWs with one minute sonication where the necking regions are clearly found on almost all nanowires. The crystalline phase of the AgNWs was identified by XRD with the pattern demonstrated in **Figure 4.1c**. The X-ray diffraction peaks of the nanowires locating at 38.121 $^{\circ}$, 44.307 $^{\circ}$, 64.456 $^{\circ}$, 77.414 $^{\circ}$ and 81.557 $^{\circ}$ are attributed to (1 1 1), (2 0 0), (2 0 2), (3 1 1) and (2 2 2) lattice planes respectively, and the Ag NWs can be confirmed to have a FCC structure.

Figure 4.1. FESEM images of Ag NWs (a) before sonication and (b) after 1 min sonication, (c) XRD pattern of Ag NWs.

Figure 4.2. TEM images of original Ag NWs. (a) A low magnified image of original samples, (b) A high magnified images of original Ag NWs, (c) a zoom-in TEM image taken from the selected square area in image (b) demonstrating the lattice structure of original Ag NWs (inset: FFT pattern), (d-f) the IFFT images transformed along (d-e) $\langle 1\ 1\ 1 \rangle$ and (f) $\langle 1\ 0\ 0 \rangle$ planes.

Figure 4.2 displays a bright-field TEM image of the sample without sonication taken at low magnification (**Figure 4.2a**). Upon zooming-in, the high magnification image of an Ag NW is shown as **Figure 4.2b**, and the HRTEM image magnified from the dash square area is displayed in **Figure 4.2c**. The FFT pattern (inset of **Figure 4.2c**) indicates that the sample was oriented along $[1\ 0\ 1]$. **Figure 4.2d-f** present the IFFT images retrieved from the correlated FFT pattern. The lattice along the $\langle 1\ 1\ 1 \rangle$ and (f) $\langle 1\ 0\ 0 \rangle$ planes appear perfect structure with no defects in the original Ag NWs.

Figure 4.3a shows a low magnified TEM image of Ag NWs with necking regions. Apparently, plastic deformation could be found at almost every Ag NWs. **Figure 4.3b** presents a single Ag NW with necking area and displays an interface between two regions and a straight line (pointed by a red arrow). **Figure 4.3c** is a magnified image of the square area in **Figure 4.3b** showing the line caused by the distortion of lattice due to the strain induction. The FFT pattern (**Figure 4.3d**) corresponding to the yellow squared region demonstrates that the line is observed along the zone axis of $[-1\ 1\ 1]$. The image at the atomic scale (**Figure 4.3e**) indicates that there are stacking faults positioned at the line with transform the original stacking structure ABCABCABC to ABCABABCA. The existence of the stacking fault could also be identified via the IFFT images (**Figure 4.3f** and **Figure 4.3g**) which are marked by the red wavy lines. Viable dislocations are further proven to be existing except the stacking fault defect. An example is given in **Figure 4.3h** presenting dislocations distributed across lattice plane of $(1\ 1\ -1)$. **Figure 4.3i** shows another single nanowire where the necking phenomenon proves the occurrence of plastic deformation. Many stacking faults (pointed by red arrows) can be apparently observed in the zoom-in image (**Figure 4.3j**) and imaged along the zone axis of $[1\ 1\ -1]$ demonstrated from its corresponding FFT pattern (**Figure 4.3k**). The IFFT pattern imaged from the yellow square area in **Figure 4.3j** indicates a crystal twin with the twinning plane of $(0\ 2\ 0)$ and the twinning boundary of $\langle 1\ 1\ 1 \rangle$.

Figure 4.3. TEM images of Ag NWs with deformation around the necking region. (a) Ag NWs observed at low magnification, (b) A zoom-in image of a single deformed Ag NWs, (c) A magnified image of the squared yellow area in image (b), (d) FFT pattern of the marked square region observed from image (c), (e). A HRTEM image presenting the atomic lattice of the strained sample observed from the marked square area in image (c), (f-h) The IFFT images performed across the (0 -2 0), (-1 1 1) and (1 1 -1) lattice planes, (i) A single strained nanowire image at high magnification, (j) A zoom-in TEM image Ag NW taken from the marked yellow square area in image (i), (k) FFT pattern of yellow square region in image (j), (l) Atom lattice of the yellow square are selected in image (i).

Figure 4.4. (a) Strained Ag NWs at low magnification, (b) A high resolution TEM image of yellow square region in image (a), (c) high magnified HRTEM image of the strained sample of the selected yellow square region in image (b), (d) FFT pattern of image (c).

Figure 4.4a-b indicates the necking region of a single nanowire. The visible deformed crystal lattice plane is formed due to the necking region presented in **Figure 4.4c**. The necking region indicates two sets of diffraction spots (**Figure 4.4d**) because of the mismatch of the lattice plane. This would effectively weaken the adsorption between Ag NWs and formed species such as O and OH². As a consequence, the formation of AgOH will be inhibited and the more active sites on the surface of the catalyst will be free to expose to electrolyte³. The mechanical deformation induced by sonication enables rearranging the crystal structure that increases the surface energy to drive the reduction

reaction². Ag becomes more active on ORR after deformation and creates stronger interaction occurring between Ag and O₂ molecules. In addition, an upshift of the Ag-O d-band centre strengthens the bonding of Ag-O but weakens O-O bond so that the breakage of O-O bond turns out to be much easier after strain induction. Therefore, the formation of HOO⁻ species is hindered and the ORR kinetics is improved.

Figure 4.5: Low magnifying HR-TEM images for quantification (a) Strained Ag NWs around necking area was separated every 100 nm by red lines, (b) Strained Ag NWs away from necking area was separated every 100 nm by red lines.

Figure 4.5a and **b** is the strained Ag NWs near and away from the necking area, among these nanowires, two of them in each image are separated into five parts by red lines, each interval means 100 nm length of Ag NWs. it can be seen there are contrast existing in almost every interval of the strained silver nanowires. However, contrast can hardly be found in the intervals of the original nanowires. This is because the contrast means there are defects generating around the area with contrast, therefore, quantification can be done by calculating the ratio of the area with contrast. For strained Ag NWs, there are 10 selected parts in two different nanowires and 8 intervals have strong contrast, hence, the strained part could be estimated to be 80% around the necking regions. As for the area far away from the necking area, it can be calculated via **Figure 4.5b**. Ten separated parts are selected

from two different Ag NWs, it can be clearly seen that there are only 3 intervals having contrast. Therefore, the strained part could be calculated to be 30% around the place away from the necking regions.

Figure 4.6: (a) A high-resolution TEM image of strained area, (b) FFT pattern of image (a), (c) Strain map of image (a) in X axis direction, (d) Strain map of image (a) in Y axis direction.

In **Figure 4.6a**, a high-resolution TEM image of strained area is given. **Figure 4.6b** is the FFT pattern of **Figure 4.6a**, the red spots in this image are the standard FFT pattern of (1

1 1) lattice plane, strain in each lattice planes could be calculated by $(d_2-d_1)/d_1$, where d_1 and d_2 are the d spacing of the specific lattice plane before and after the deformation. This equation can be transferred in to $(R_1-R_2)/R_2$, where R_1 and R_2 are shown in **Figure 4.6b**. The strain value calculated by this method is displayed in **Table 4.1**. Another way to quantify strain in deformed Ag NWs is shown in **Figure 4.6c** and **Figure 4.6d** which are strain maps in two dimensions. Green color means strain free area which is standard lattice planes of silver. Regions in red and blue colors represent the lattice planes where tensile strain and compression strain exist, in other words, it is the regions where defects are formed. In conclusion, the strain in deformed Ag NWs could be proved existing and quantified.

Table 4.1: Strain calculation of the deformed area in **Figure 4.6**.

Lattice planes	R_1 (nm ⁻¹)	R_2 (nm ⁻¹)	Strain Value
2 0 -2	6.92	4.27	-62.1%
-2 2 0	6.92	4.08	-69.8%
0 2 -2	6.92	4.16	-66.5%

Figure 4.7: (a) High magnification TEM image of sonicated Ag NWs after CV for 1 hour, (b) FFT pattern of red square area in image (a), (c) A HRTEM image presenting the atomic lattice of the strained sample observed from the marked square area in image (a), (d) The IFFT images performed across the $(-2\ 0\ 2)$ lattice planes

A strained Ag NWs sonicated for 1 minute is used to conduct CV test for an hour which could prove if the defects induced by sonication are permanent. In **Figure 4.7a**, it can be seen there is still a necking area existing after electrochemical test in this HRTEM image. **Figure 4.7b** shows the FFT pattern of the square area around the necking region. The lattice structure of the square region in **Figure 4.7a** is given in **Figure 4.7c** and stacking fault is found arranging in the order of ABCABABC. In the IFFT images transformed from $\langle -2\ 0\ 2 \rangle$ planes (**Figure 4.7d**), dislocations are observed which are shown in the form of yellow

T. Therefore, it could be concluded that the defects induced by sonication are a kind of plastic deformation which are permanent and will not vanish even after long duration of electrochemical experiment.

4.3 Electrochemical Characterization

Figure 4.7a presents the CV curve of the original (black) and deformed (red) Ag NWs in 0.1 M KOH. The intermediates formed during ORR process are attributed from the two oxidation peaks located at 1.18 V and 1.29 V. Accordingly, **equation 13** is corresponding to the oxidation peak at 1.18 V because of the dissolution of silver and the formation of the monolayer silver oxide⁴. The peak located at 1.29 V represents the formation of the bulk silver peroxide and silver oxide (**Equation 12-13**)⁵. Reduction peaks positioned at 0.89 V and 1.01 V attribute from the formation of the bulk silver peroxide and silver oxide. Meanwhile, there is only one oxidation peak positioned at around 1.22 V shown in the CV curve of deformed Ag NWs, which represents the formation of a surface monolayer of silver peroxide film. In addition, a negative shift of the peak attributed to the reduction of silver oxide can be apparently observed. Furthermore, the decrease of the peak intensities can be seen in the CV curves of the deformed sample indicating that there are less intermediates formed comparing with the original sample, which means a less formation of the passivation layer and release more surface active sites. The induction of strain could lead to the decrease of the formation of silver intermediates because of the weak adsorption of adsorbates such as O and OH (**Equation 12, 13**). Comparing with the strained samples, the original Ag NWs has been identified to have a stronger adsorption towards adsorbates, which might be easy to form a passivation layer leading to a sluggish ORR kinetics⁶.

Figure 4.8 (a) CV curves of the original and strained Ag NWs in O_2 -saturated electrolyte (inset: an enlarged image ranging from 0.8 V to 1 V), (b) CV curves of the strained samples in N_2 -saturated and O_2 -saturated electrolyte. (c) Polarization curves of the original (dashed curves) and strained (solid curves) samples in O_2 -saturated 0.1 M KOH with rotating speed varying from 400 rpm, 900 rpm to 1600 rpm and 2500 rpm, (d) K-L plots of the original and strained Ag NWs at 0.3 V (dashed lines) and 0.6 V (solid lines).

According to the analysis of the CV curves displayed in **Figure 4.8a**, a higher peak intensity demonstrates a better catalytic performance of deformed Ag NWs on ORR⁷. As shown in **Figure 4.8b**, the peak positioned at 0.9 V, which correlated to the reduction of oxygen, shows up only in oxygen-saturated KOH. **Figure 4.8c** represents the LSV curves of Ag NWs tested in nitrogen-saturated and oxygen-saturated alkaline medium with various of rotating speed ranging from 400 rpm to 2500 rpm. The diffusion limiting current densities of the original and strained Ag NWs, which is a key evaluation on the performance of ORR, are tested to be around -4.98 mA/cm^2 and -6.00 mA/cm^2 respectively at 1600 rpm. A more than 20% enhancement on ORR performance is presented by the

strained sample comparing with the original sample. **Figure 4.8d** displays the K-L plots measured at 0.3 V and 0.6 V, attributed from the strained (pink) and original (blue) samples. According to the K-L plots, the electron transfer numbers can be calculated via K-L equations, 4.27 for the strained sample and 3.49 for the original sample. A higher electron transfer number of deformed Ag NWs could lead to a more negative diffusion limiting current density contributing to a faster ORR kinetics.

The onset potentials of the original samples with loadings of 20 μl , 40 μl and 60 μl are given in **Figure 4.9a**. It could be seen that the onset potential shifts positively when the sample loadings increase. **Figure 4.9** shows the LSV curves of strained samples with different sample loadings. Moreover, enhancement on the onset potentials also can be observed due to the raise on loading of samples. The effect of loading on diffusion limiting current density is also presented in **Figure 4.9a-b**. Accordingly, an 11.8% improvement on the diffusion limiting current density can be observed while the loading increases from 20 μl to 40 μl , likewise, the diffusion limiting current drops by 4.8% with the increasing of loading from 40 μl to 60 μl . By rising the loading from 20 μl to 40 μl , the diffusion limiting current density increases by 10.7%, however, a decrease of 10.2% is experienced while the loading varies from 40 μl to 60 μl . **Table 4.2** lists the details of parameters on ORR.

Table 4.2: Different ORR properties of tested samples influenced by sample loading.

Sample loading	Property	Original NWs	Ag Deformed NWs
0.238 mg/cm ² (20 μl)	Onset potential	0.95 V	0.95 V
	Current density	-5.42 mA/cm ²	-5.97 mA/cm ²
0.477 mg/cm ² (40μl)	Onset potential	0.98 V	0.98 V
	Current density	-5.50 mA/cm ²	-5.98 mA/cm ²
0.715 mg/cm ² (60 μl)	Onset potential	0.98 V	0.98 V
	Current density	-5.29 mA/cm ²	-5.89 mA/cm ²

Among these strained samples, the one with a mass loading of 20 μl presents the most efficient catalytic performance on ORR, even though the sample with a double loading (40 μl) has a relatively slight negative shift on the diffusion limiting current density (around 10%). Generally, increasing mass loading of samples on the surface of electrode bring a rise on the formation of intermediates which might lower the specific activity on ORR because of the generation of the passivation layer and raise the mass activity due to the increasing mass loading⁸. Moreover, crystal defects (i.e. dislocations, stacking faults and twin crystals) could decrease the production of intermediates and further release more surface active sites for an increased ORR performance.

The polarization curves of Ag NWs with different durations of sonication are shown in **Figure 4.9c**, which are measured in 0.1 M oxygen-saturated KOH with a rotating speed of 1600 rpm. After different durations of 0 min, 1 min, 5 min and 15 min sonication, the diffusion limiting current density are tested to be -5.41 mA/cm², -5.91 mA/cm², -5.07

mA/cm^2 and $-5.76 \text{ mA}/\text{cm}^2$ respectively. The most negative diffusion limiting current density attributes from sample with 1 min duration of sonication, however, the onset potential of it is almost the same as the onset potential of samples sonicating for 0 min and 5 mins. The 15 mins LSV curve has a more negative onset potential 0.92 V and a higher diffusion limiting current density of $-5.76 \text{ mA}/\text{cm}^2$ comparing with the original sample because the samples are rendered into low aspect ratio nanowires with plenty of deformations after a long duration of sonicating. Based on the polarization curves of samples sonicating for 1 min and 5 mins, the decreasing aspect ratio of nanowires leads to a diminution of the diffusion limiting current density, which means a drop on the performance of ORR. The negative shift of the onset potential of sample with sonication for 15 min is possibly because of the breakage of original Ag NWs. The enhancement on the electrocatalytic performance on ORR is likely on account of the induced strain⁷.

Figure 4.9. (a) Polarization curves of original samples with different catalysts loading in O_2 saturated 0.1 M KOH solution with the rotating speed of 1600 rpm . (b) Polarization curves of strained Ag NWs with different mass loading of catalysts in O_2 -saturated 0.1 M KOH solution with the rotating speed of 1600 rpm . (c) Polarization curves of strained Ag NWs with different mass loading of catalysts in O_2 -saturated 0.1 M KOH solution with the rotating speed of 1600 rpm . (d) Normalized current (%) versus Time (s) for Original and Deformed samples.

KOH solution with the rotating rate of 1600 rpm, (c) Polarization curves of 20 μL Ag NWs with duration of sonication varying from 0 min, 1 min to 5 mins and 15 mins at the rotating speed of 1600 rpm, (d) Chrono amperometry test for the stability of strained and original samples in O_2 saturated 0.1 M KOH solution with the rotating speed of 1600 rpm.

Another key evaluation in ORR is the stability of electrocatalytic materials. The CA curves conducted in an 0.1 M oxygen-saturated KOH electrolyte are presented in **Figure 4.9d**, which are tested for 15000s at the voltage of +0.7 V vs RHE with a rotating speed at around 1600 rpm. In contrast to catalysts for commercialization⁹, both the original sample (85.3%) and the strained sample (82.7%) indicate higher stability according to the higher current density after a long-time duration. More than 20% enhancement on the stability of ORR is shown with silver catalysts comparing to Pt/C.

4.4 Conclusions

In conclusion, sonication is introduced as an easy and high-efficient method to induce strain in Ag NWs. Around the necking region, mismatch and plastic deformations such as dislocations, stacking faults and twin crystals can be found through TEM images and analysis of the corresponding FFT and IFFT patterns. Due to the drop of the adsorption energy towards the intermediates formed during ORR process, which is attributed from the induction of strain, the passivation layer produced by the reaction between the silver catalysts and the intermediates is halted. Therefore, more surface active sites are released to participated in the catalytic reaction comparing with the original sample. After viewing the results and analysis of the electrochemical tests, the strained sample with 1 min sonication and mass loading of 40 μL presents the best ORR performance with a more negative diffusion limiting current density. Thus, the improvement on ORR and the stability enhancement presented in this work could be concluded to be the effect of the induction of strain.

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Chapter 5 Catalysis of Laser Irradiated Ag NWs on ORR

This chapter shows the catalysis results of Ag NWs after subject to laser irradiation. The microstructure analysis using SEM and TEM reveals the morphological and lattice distortion of Ag NWs due to the plastic deformation induced by the laser ablation. Many defects such as dislocations and stacking faults are visible and the surface of Ag NWs is determined to expose along high index crystalline lattice plane. These unique atomic structures demonstrate the significant improvement of ORR performance, which is presented in this chapter. The property dependence on the deformed structure of Ag NWs is discussed and further clarified by the calculation of the electron transfer numbers of ORR process using Koutecky-Levich plots based on the LSV data.

5.1 Preparation of Laser Irradiated Ag NWs

100 μ l Ag NWs ink was dropped on a glass slide for laser irradiating (1064nm wavelength Fiber Laser) at first. The parameters for laser irradiation were shown in the table below. After laser irradiation treatment (Details of laser irradiation are given in **Table 5.1**), the treated ink was mixed with 250 μ l DI water and 2 μ l Nafion (5 wt%) as the prepared sample (0.00234 mg/ μ l). Afterwards, 40 μ l ink was dropped onto GCE with a one hundred percent coverage and then dried at about 60 °C.

Table 5.1: Parameters for laser irradiation

Loop Count	Speed (mm/s)	Power %	Frequency (KHz)	Q Pulse Width (ns)
1	100	5	610	12

5.2 Morphology and Crystallography of Laser Irradiated Ag NWs

Figure 5.1a is a low magnified SEM image of original Ag NWs observed to have a length of about 30 μ m and a diameter of around 30 nm. **Figure 5.1b** presents a zoom-in Ag NWs before laser irradiation where the nanowires are apparently observed to be straight with no plastic deformation. In comparison, Ag NWs after laser irradiation are viewed very differently in morphology as shown in **Figure 5.1c**, which shows more clearly in **Figure 5.1d**, a zoomed-in SEM image of **Figure 5.1c**. Bending and necking in large regions occur on the almost every single nanowire. It is apparent that the energy deposition from laser beam is responsible for this deformation.

Figure 5.1: SEM images of original and laser irradiated samples (a) original samples before laser irradiations with high magnification, (b) a zoom-in image of image (a), (c) laser irradiated Ag NWs, (d) a zoom-in image of image (c).

Figure 5.2 displays a TEM image of the original Ag NWs taken at a low magnification. The FFT pattern (inset of **Figure 5.2a**) indicates that original Ag NWs were observed along the zone axis of $[1\ 1\ 1]$ of the FCC lattice. Likewise, a low magnified TEM image of strained Ag NWs is displayed in **Figure 5.2b**. **Figure 5.2c** is the corresponding FFT pattern of the red square area in **Figure 5.2b** which is indexed to be oriented along the zone axis of $[1\ 1\ 1]$. The FFT pattern of the yellow square area in **Figure 5.2b** is displayed in **Figure 5.2d** indicating that points are diffracted along the zone axis of $[1\ 1\ 5]$. **Figure 5.2e** is a

HRTEM image of showing the arrangement of Ag atoms after the deformation of Ag NWs. It consists of two different phase structures as demonstrated from its corresponding reciprocal image (**Figure 5.2f**), where two sets of diffraction patterns are identified. These two diffraction patterns are determined to be imaged along the zone axis of $[1\ 1\ 5]$ and $[1\ 1\ 6]$, respectively. The analysis suggests that laser deformed Ag NWs are oriented with the surface exposure of $(1\ 1\ 5)$ and $(1\ 1\ 6)$ lattice planes. These planes are considered be high index facets, which contributes high surface energy^{1, 2, 3} and easy and fast absorption of oxygen molecules⁴, in more favour of the catalytic activity of ORR in contrast of the original silver nanowires with laser irradiation free.

Figure 5.2: TEM images of laser irradiated samples (a) A low magnified image of laser irradiated Ag NWs (inset: FFT pattern), (b) A TEM image with low magnification presenting the necking area of the laser irradiated Ag NWs, (c) FFT pattern of the laser irradiated samples taken from the selected red square area in image (b), (d) FFT pattern of

the laser irradiated Ag NWs taken from the selected yellow square area in image (b), (e) a high-magnification STEM-ADF image of laser irradiated Ag NWs (inset: a low-magnification image of image (e)), (f) FFT pattern of image (e).

The models of the low-index lattice plane such as (1 1 1) and high-index planes including (1 1 5) and (1 1 6) are shown in **Figure 5.3**. **Figure 5.3(a-c)** is the plan-viewed these lattice planes which are perpendicular with the corresponding indices of crystal planes. **Figure 5.3a** displays the model of crystal lattice belonging to the original Ag NWs with a typical atom arrangement of the (1 1 1) lattice plane. **Figure 5.3b-c** exhibits the models of silver lattice planes after laser irradiation which could be set to be (1 1 5) and (1 1 6) planes. It could be observed that there are obvious differences of the arrangement of atoms. Through the comparison of the side-view models in Figure 5.3d-f, rotations from the original (1 1 1) plane could be found in both (1 1 5) and (1 1 6) lattice planes, meanwhile, there is a slightly difference of the rotation angle between those two high-index planes, a rotation angle of 71° is generated on the converting from the surface of (1 1 1) plane to the surface of (1 1 5) plane and a rotation angle of 68° could be observed on the surface of (1 1 6) plane after a rearrangement of atoms on (1 1 1) plane. Therefore, it might be able to be concluded that the rotation of crystal lattice could be caused by laser irradiation. After irradiating, high optical energy might be absorbed by Ag NWs, the huge amount of power could promote the thermal motion of silver atoms. The lattice planes might be rearranged due to the excited atoms which is presented as high-index planes. Meanwhile, it can be found that there are more atoms exposed on the surface of high-index facets comparing with original (1 1 1) plane. Thus, there could be more active sites on (1 1 5) and (1 1 6) planes resulting in a higher catalytic performance on ORR.

Figure 5.3: different viewing angles of lattice planes on original Ag NWs and laser irradiated Ag NWs. (a-c) top-view of the (1 1 1), (1 1 5) and (1 1 6) planes, (d-f) side-view of the (1 1 1), (1 1 5) and (1 1 6) planes.

There are also some defects like dislocation existing after laser irradiation which are shown in **Figure 5.4**. **Figure 5.4a** is a low magnified image of deformed region on Ag NWs induced by laser irradiation. Dislocations are found on almost every facets of the deformed surface area which are given in **Figure 5.4b-d**. The necking region might be generated by the strong laser ablation. As discussed in the last chapter, defects on the surface indicates that strains are induced and improve the surface energy and lower the binding energy between intermediates like OH species and oxygen molecules which weaken the adsorption of reactant on the surface of catalysts and release the active sites which could be blocked if the adsorption was too strong, thus, the catalytic performance could be improved because the large surface energy promoting the reaction and the increased surface active sites⁵.

Figure 5.4: TEM images of defects on laser irradiated silver nanowires (a) low magnification image of the necking area on silver nanowires (inset: FFT pattern), (b-d) The IFFT images performed across the $(-2\ 0\ 2)$, $(-2\ 2\ 0)$ and $(0\ 2\ -2)$ lattice planes of the yellow square region in image (a).

5.3 Electrochemical performance of Laser Irradiated Ag NWs

Figure 5.5a shows the cyclic voltammetry (CV) of ORR with laser irradiated Ag NWs as catalysts at powers of 0 W, 2 W, 4 W, 6 W, 8 W. The oxidation peak located at around

1.25 V contributes to the formation of the monolayer Ag_2O ⁶ and another oxidation peak at about 1.4 V is due to the generation of bulk Ag_2O and AgOH ⁷. The 4 W curve perform the lowest peak of forming bulk Ag_2O and AgOH comparing with the other curves, thus, the 4 W laser irradiated Ag NWs could have the less blockage of the silver oxides generated on the surface of the catalysts. The high intensity peaks positioned at around 1 V is the reduction peak of Ag oxides. The other reduction peak located at 0.8 V represents the reduction intensity of ORR performance. It could be found that the 4 W shows the most negative current density correlating with the best ORR activity among all those samples⁸.

Figure 5.5: LSV curves and CV curves of ORR catalysed by the original and laser irradiated Ag NWs in O_2 -saturated 0.1 M KOH (a) CV curves of laser irradiated Ag NWs with different powers, (b-f) Polarization curves of laser irradiated samples with powers of 0 W, 2 W, 4 W, 6 W, 8 W at various rotating speeds.

Figure 5.5b-f demonstrate the polarization curves with different power at various rotation speeds. At a higher rotating speed, the diffusion limiting current density would be more negative attributed to a higher ORR kinetics, which is due to the thickness of the diffusion layer of oxygen decrease with the rising of the rotating speed, therefore, the oxygen can diffuse faster to the surface of the RDE and provide abundant reactants via improving rotating speed⁹. Those polarization curves display the onset potential and the diffusion

limiting current density platform shift due to laser irradiation, the detail of these shifts is listed in **Table 5.2**. The data from the table shows that the ORR performances are all improved after laser irradiation with a trend of increasing ORR performance with increasing power of laser irradiation before the power reaches to 4 W, afterwards, the ORR performance decrease with the increasing of power of the laser irradiation. With the contrast of the original silver nanowires, laser irradiated samples show a positive shift of the onset potential from 0.8 V vs RHE and a negative shift of the diffusion limiting current density from 4.7 mA/cm². Based on those data, the positive shift of onset potential represents the decrease of the over potential, meanwhile, the negative shift of the diffusion limiting current density means an improved ORR kinetics. They both contribute to the enhancement of the ORR performance. Among all these tested samples, 4 W laser irradiation perform the largest shifts of onset potential (about 0.034 V) and diffusion limiting current density (26%), thus, 4 W could be the most suitable power for the ORR enhancement.

Table 5.2: The onset potential and diffusion limiting current density (J_L) of Ag NWs at different laser powers.

Power	0W	2W	4W	6W	8W
Onset Potential (V vs RHE)	0.891	0.896	0.925	0.918	0.895
J_L (mA/cm ²)	4.70	5.24	5.92	5.16	4.89

Figure 5.6a-c have shown the K-L plots of various laser power, tested at 0.15 V, 0.2 V and 0.25 V respectively which are utilized to calculate the electron-transfer numbers via Koutecky-Levich equations.

Figure 5.6d is a summary of the electron-transfer number of all these laser irradiated samples at different potentials. It could be clearly discovered that the sample with 4 W laser power has the highest electron-transfer number and the average number calculated is

3.65 for original Ag NWs and sample with 2 W laser irradiation, 4.2 for the sample with 4 W laser irradiation, 3.75 and 3.83 for laser irradiated Ag NWs with 6 W and 8 W laser powers. It could be concluded that almost all samples have an increasing of the electron-transfer number, especially the sample with 4 W laser irradiation which indicates a faster ORR kinetics and higher output of fuel cells.

Figure 5.6: (a-c) K-L plots of the laser irradiated Ag NWs at 0.15 V, 0.2 V and 0.25 V, (d) numbers of Electron transfer with power from 2 W to 8 W at different potentials.

5.4 Conclusions

The results indicate that the laser irradiation on silver nanowires could create reorganization of lattice structures which induces high-index facets such as (1 1 5) and (1 1 6). The existence of high-index facets might enhance the surface energy on the surface

of silver nanowires. Meanwhile, there are necking phenomena discovered via physical characterization. Moreover, defects like dislocations are observed around the necking region which could result in the improvement of the diffusion limiting current density. Comparing with original silver nanowires, the ORR performances of laser irradiated catalysts are improved with a more positive onset potential and a more negative diffusion limiting current density. Among these samples, 4 W laser irradiated sample has the best ORR performance. Therefore, laser irradiation could be an effective way to enhance the electrocatalytic performance of silver on ORR.

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Chapter 6 Conclusions and Recommendations

Sonication has been proved to be able to induce strain inside the Ag NWs and enhance the ORR performance due to improved surface energy around the deformed area. The reaction kinetics of the sonicated sample is calculated to be a close to 4-electron pathway. It has been figured out that laser irradiation could generate high-index facets like (1 1 5) and (1 1 6) with a enhanced ORR performance. Strains could be observed through TEM physical characterization. The electron transfer numbers have been calculated by K-L equations, accordingly, the 4 W laser irradiated sample performed a best ORR kinetics. However, the change of the absorption energy towards intermediates like OH, O species is unknown after laser irradiated. Therefore, DFT calculations are needed to correlate the improved ORR performance and the induction of high-index facets. Moreover, the mechanism of the occurrence of the high-index planes is still not clear. Hence, further research are required to be done to figure out how the high-index facets appears.

6.1 General Discussions

The main ORR performances are summarized below in **Table 6.1**, it clearly shows the enhancement on onset potential and diffusion limiting current density caused by sonication and laser irradiation. It indicates that deformation induce by these two methods both could increase the catalytic performance of Ag NWs.

Table 6.1: The onset potential and diffusion limiting current density (J_L) of Ag NWs with different methods including sonication and laser irradiation.

Methods	Parameters	Onset Potential	J_L (mA/cm ²)
		(V vs RHE)	
Sonication	0 min	0.95	5.50
	1 min	0.98	5.98
Laser Irradiation	0 W	0.891	4.70
	2 W	0.896	5.24
	4 W	0.925	5.92
	6 W	0.918	5.16
	8 W	0.895	4.89

6.1.1 Discussions on Sonicated Ag NWs

Electrochemistry tests have indicated that the sonicated Ag NWs have 17% improvement of electrocatalytic performance than the original Ag NWs. This is probably because defects induced by sonication increases the surface energy. According to the CV curves, the oxidation peaks attributed to the formation of AgOH decrease after sonication, it means

that sonication could reduce the production of intermediates which might block the active sites on the surface. Thus, not only surface energy but absorption of the intermediates results in the improvement of electrocatalytic performance of silver on ORR.

Additionally, loading and aspect ratio also play an impact role on the ORR performance. As mentioned in Chapter 4, the onset potential shift positively with the increasing of sample loading and the diffusion limiting current density move to negative direction as the aspect ratio increase. Moreover, a higher ORR kinetics via 4-electron transfer is brought by these methods.

Meanwhile, stability tests of both original and sonicated Ag NWs show a high steady performance comparing with Pt.

6.1.2 Discussions on Laser Irradiated Ag NWs

Laser irradiation could induce high-index facets like Ag (1 1 5) and Ag (1 1 6) on silver nanowires. High-index perform a higher surface energy than the original low-index facets such as Ag (1 1 1). Meanwhile, laser irradiated Ag NWs show a promoted performance on oxygen reduction reaction due to those new-generated facets. With different powers of laser, high-index facets could be observed on almost all samples through TEM. Especially for 4 W laser irradiated sample, the FFT pattern of the area with structure reorganization display a combination of the FFT pattern of Ag (1 1 5) facets with lower brightness and Ag (1 1 6) facets with higher brightness. Correlate with the STEM image of the structure reorganization area, only atoms of (1 1 6) facets could be found which means the main reorganization of lattice structure occurs on the surface of silver nanowires is the generation of (1 1 6) facets, (1 1 5) facets might show up in the core area of the silver nanowires which is too thick to be seen through physical characterizations. Therefore, the high-index facets and this kind of structure might contribute to the strongest positive shift of the onset potential. Meanwhile, there are plastic deformations appears which could promote the negative shift of the diffusion limiting current density.

6.2 Outstanding Questions

6.2.1 Improvement on ORR Stability with Ag-based catalysts

Although the ORR stability of the sonicated Ag NWs is way better comparing with Pt, there are a slightly decrease of the stability comparing with it of the original ultralong nanowires. Therefore, a requirement for enhancing the stability of the sonicated Ag NWs shows up which could be realized via alloying with elements like Cu, Co and Ni according to literatures.

6.2.2 Mechanism of Laser Irradiation on Generating High-Index Facets

High-index facets has been proved to be able to increase the surface energy, however, the DFT calculation of the generated new facets in this research is still needed to be studied to further identify this reorganization of lattice structure is high-index facet via calculating the surface energy. In addition, the process of this reorganization of this lattice structure is not clear for now. Thus, it is quite important to figure out how the lattice structure transfer from facets on the original sample to high-index facets on the laser irradiated sample which makes the research on ORR more complete and systematic.

6.2.3 Combination of Approaches

The electrocatalytic activities of Ag NWs has been enhanced by either laser irradiation and sonication to induce strain and high-index planes. A combination of both methods could be expected to further enhance the electrochemical performance on ORR. Based on literatures review, pure silver nanowires could be replaced by silver-based alloy nanostructures, which could not only bring a higher performance-cost ratio but also figure out the problems mentioned above via alloying and combing these methods.

In conclusion, the research works in this project have conclude that the induction of strain and high index planes could bring a higher surface energy and more active sites, which provide great contributions to the enhancement of nanostructured silver in the

electrocatalytic performance on ORR. The outcomes highly proved the hypothesis stated at the beginning of this thesis.

APPENDIX

Research papers as first or co-first author:

1. **Wang, Z.**; Cao, X.; Peng, D.; Lu, Y.; Zhang, B.; Huang, K.; Zhang, T.; Wu, J.; Huang, Y., *The Journal of Physical Chemistry Letters* **2021**, 12, 2029-2035.