Nanowires and their morphology induced catalytic properties

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**NANOWIRES AND THEIR MORPHOLOGY INDUCED
CATALYTIC PROPERTIES**

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**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2018

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CATALYTIC PROPERTIES**

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INTERDISCIPLINARY GRADUATE SCHOOL

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in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

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

06-08-2018

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Abstract

Overall, this thesis aims to investigate the mechanism behind one dimensional nanostructure synthesis and catalytic performance, which hopes to contribute towards optimizing of catalytic process. More specifically, we planned to exploit the recent advances in one dimensional nanostructures synthesis, which we limits the scope to nanowires synthesis, and investigate the growth mechanism of the nanowires (NWs) synthesis if it was still not well understood. Next, with this understanding in synthesis mechanism, we hoped to create novel NWs structures, especially hybrid NWs structures, and apply them for photocatalysis and electrocatalysis. Besides that, we hoped to observe and identified specific advantages in catalysis arises from specific nanostructure, or in other words, morphology induced properties.

TiO₂ nanowires had outstanding performance as light absorbing materials, and its large scale synthesis had been reported. However, there were not enough study done on the large scale synthesis mechanism, resulting in poor length and diameter control. We had demonstrated that large scale TiO₂ NWs synthesized via molten salt method adopts seed-assisted growth mode, with ripening as the main growth mechanism in chapter 2. Rutile NPs not only able act as seed to control the diameter of the resulting NWs, but also able to act as feedstock, where the selectivity comes from its own size. We had also identified the key to grow hybrid TiO₂ NWs was to control the rate of ligand adsorption and TiO₂ deposition in Chapter 3. We had tried various methods to increase ligand adsorption speed and decrease TiO₂ deposition rate. However, all the attempts had failed to control the lateral growth or the NWs obtained was not TiO₂. As we had exhausted all possible means but was unsuccessful to obtain the desired nanostructure, the project was halted.

Ultrathin metal nanowires array was also an interesting system with great potential in catalysis. Although its synthesis mechanism is well studied, there had not been enough research conducted on the catalysis part. We have

demonstrated that by simply changing the morphology of electrocatalyst from nanoparticles to aligned nanowire arrays, the catalytic activity can be improved dramatically by providing more electrochemical active surface for electrocatalysis, one-dimensional channels for improved mass transport and better conductivity in Chapter 4. Our approach provides a new and simple means to enhance the electrocatalytic activity, reduce the size of electrode for miniaturization of portable devices and improve the effectiveness of existing and emerging electrochemical technologies. We had proposed an EOR mechanism on Pd surface in Chapter 5, where OH^- ions act as the main inhibitor that poison the Pd surface. We had discussed in details of the processes that might be happening in different part of the EOR CV. This understanding had helped us to identified the limiting factors of EOR mechanism and thus possible to suggest methods on improving the EOR activity and stability in DEFCs devices. A part from that, we had discovered that reservoir plays important role in determining the performance of Pd in EOR. The reservoir effect on our long and dense Au@Pd NWs array structure, proven to be a morphology induced property, might also be a contributing factor for its high performance in EOR.

In addition, we had also shown that the present of two Pd facets on our Au@Pd NWs might be responsible for different ethanol oxidation product formation as proposed in our hypothesis through the studies conducted in Chapter 6. Pd (200) and (220) facets each have different affinity towards OH^- species, which results in different ethanol oxidation pathway on each facet, where Pd (200) facets responsible for the formation of acetic acid, and Pd (220) forms acetaldehyde. It was also discovered that some ligands bind specifically to one of the facets, which might served as a means to control ethanol oxidation product selectivity in the future.

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Abbreviations

4MBA	4-Mercaptobenzoic Acid
APTES	(3-Aminopropyl)triethoxysilane
CV	Cyclic Voltammetry
DMF	Dimehtylformamide
EDS	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EOR	Ethanol Oxidation Reaction
HPLC	High Performance Liquid Chromatography
HRTEM	High Resolution Transmission Electron Microscopy
NBs	Nanobelts
NPs	Nanoparticles
NRs	Nanorods
NTs	Nanotubes
NWs	Nanowires
PVP	Polyvinylpyrrolidone
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
TiO ₂	Titanium dioxide
XRD	X-ray Diffraction

Chapter 1

Introduction

Nanomaterials had a variety of usages, especially in the field of catalysis due to their unique physical and chemical properties as compared with bulk materials. However, there were still some major challenges faced in the field of nanocatalysis, which includes the lack of large scale synthesis methodology, poor morphology control due to insufficient synthesis mechanistic understanding and difficulties in optimization due to inadequate catalytic mechanism knowledge. One dimensional nanostructure had special optoelectronic as compared to other structure, which was more preferred in electrochemical and photoelectrochemical catalysis. Out of all, TiO₂ nanowires had outstanding performance as light absorbing materials, and its large scale synthesis had been reported. However, there were not enough study done on the large scale synthesis mechanism, resulting in poor length and diameter control. Apart from that, ultrathin metal nanowires array was also an interesting system with great potential in catalysis. Although its synthesis mechanism is well studied, there had not been enough research conducted on the catalysis part. We aim to use these two systems as model to study the mechanism behind one dimensional nanostructure synthesis and catalytic performance, which hopes to contribute towards optimizing of catalytic process.

1.1 Nanomaterials and Their Usage in Catalysis

Nanomaterials were defined as solid of any shape, whether they were elementals, alloys, compounds or composites, with one of its dimension in the range of nanometre (nm). Nanomaterials had been a key focus of research and had contributed to the advances of science and technologies for the past decades^{1,2}. Nano-scale materials have very different physical and chemical properties as compared with their bulk counterpart, primarily due to their large surface to volume ratio^{1,2}. Their small sizes not only provide larger surface area per unit mass, but also increase the ratio of low-coordination atoms on surfaces³. These low-coordination atoms are of greatest important for catalysis, due to their high affinity to bond with absorbed molecules¹. Thus, atoms on the corner of nanomaterials were the most active as they were the least saturated in terms of coordination, followed by those on the edge and those in plane surface⁴.

Figure 1.1 Graph illustrating the evolution of dispersion F (fraction of atoms at the surface) with n for the cubic clusters (where n is the number of atoms along an edge of cubic and N is the total number of atoms in a cube). The cubic structure for $n=2$ to $n=5$ was displayed along with the graph. Reprinted with permission from ref. [4]. Copyright © PCCP Owner Societies.

Another physical property which was heavily affected by size was the melting point. Due to the low coordination of the surface atoms of nanomaterials, they were relatively unstable, which results in lower lattice energy, thus lower melting point compared to their bulk counterpart. For example, the melting point of gold nanoparticles (NPs) with the size of 2.5 nm was reported to be 930 K⁵, which was much lower than melting point of bulk gold at 1336 K. Generally, smaller sizes nanomaterials have much lower melting point as compared with bulk materials, and this correlation was clearly illustrated in Figure 1.2⁶.

Figure 1.2 Graph illustrated the change in melting temperature (T_m) of indium metal confined in porous glass of different pore size (d). The dashed line represent melting point of bulk indium metal. Reprinted with permission from ref. [6]. Copyright © 1993, American Physical Society.

As mentioned previously, the higher surface to volume ratio of nanomaterials had induced a higher ratio of surface atoms which has low coordination, thus affect the electroaffinity, work function and Hamiltonian of the nanomaterials, which in turns affect any other properties depending on these⁷. Some of the examples include quantum-confinement, phase transition, diffusivity, chemical reactivity, mechanical strength and thermal stability⁷. A part from that, nanomaterials also exhibits some novel phenomena not observed in bulk, such as superparamagnetism³.

Nanomaterials had played an important role in catalysis, especially in the field of photocatalysis and electrocatalysis. In the vast choices of nanomaterials, application of metal nanoparticles in catalysis were among one of the most well studied, due to their high reactivity and selectivity in various heterogeneous catalytic reaction⁸. For examples, metals such as platinum (Pt), palladium (Pd) and rhodium (Rh) had been used as catalyst in the production of

polymer and dyes, where they were used to catalyse the coupling and hydrogenation reaction⁹. A part from that, metal nanostructure also provides high turnover frequency, such as Pt NPs supported on silica catalyzed ethylene hydrogenation had a turnover frequency of 3.8 s^{-1} at 10 torr C_2H_2 , 100 torr H_2 and 298 K ¹⁰. The high surface area, high reactivity and high turnover frequency provided by metal nanomaterials had proved that they were able to perform at a higher efficiency compared to their bulk counterpart, which means that less catalyst was needed to perform the reaction. This will reduce the cost of production significantly, making nanomaterials a more preferred catalyst in industrial process.

In addition, the catalytic properties of metal nanoparticles (NPs) can be tuned by modifying its neighbouring atom or molecules, which was called ligand effect¹¹. The influence of ligand on the catalytic activity was mostly attributed to the change in electronic structure of metal nanocluster¹². One of the ways to alter catalytic behaviour of metal NPs through ligand effect was by changing the support of the metal NPs. It was found that simply by replacing of the manganese oxide (MgO) support with aluminium oxide ($\gamma\text{-Al}_2\text{O}_3$) was able to alter the catalytic activity of alkene hydrogenation by tenfold¹². Organic molecules that bind onto the surface of metal NPs will also affect their catalytic activity through ligand effect. For example, Pt NPs functionalized with triphenylphosphine triphosphonate, $\text{P}(\text{C}_6\text{H}_4\text{PO}_3\text{H}_2)_3$ ligand had shown a huge decrease in oxygen reduction reaction catalytic activity compared to those without the ligand¹³.

As nanomaterials provided advantages such as unique physical and chemical properties, high efficiency, low cost and tunable catalytic activity, they were used in a wide range of applications, such as in the field of heterogeneous catalysis, electrocatalysis and photocatalysis. Benzyl alcohol oxidation was among the most well studied in heterogeneous catalysis by metal NPs. One of such catalysts was gold-palladium (Au/Pd) NPs, which has a high turnover frequency (TOF) of $35,404 \text{ h}^{-1}$ under milder reaction condition of

120 °C¹⁴. Another well established reaction was carbon monoxide (CO) oxidation, where supported Au NPs shown extraordinary high catalytic activity¹⁵⁻¹⁷. Iron (Fe), cobalt (Co) and nickel (Ni) NPs supported on carbon nanotubes were also shown to be effective catalyst for organic pollutant removal¹⁸.

Besides oxidation reaction, metal NPs were also effective heterogeneous catalyst in reduction reactions. Hydrogenation of phenol, quinoline, nitriles, alkyne and alkene by Pd NPs as catalyst had well been reported¹⁹. Pd was chosen as hydrogenation catalyst mostly due to its ability to dissociate hydrogen gas effectively¹⁹. Reduction of 4-nitrophenol (4-NP) was also an important reaction in industrial to obtain 4-aminophenol(4-AP)²⁰. Nickel (Ni), gold (Au), silver (Ag) and palladium NPs had been reported to catalyse the reduction of 4-NP²¹, where Pd-Ag nanodendrites had shown to have impressive reduction rate constant of $39.1 \times 10^{-3} \text{ s}^{-1}$ (Figure 1.3)²².

Figure 1.3 Pd-Ag dendrites catalytic performance in 4-NP reduction. A. Time lapsed UV-vis absorption spectra of 4-NP reduction catalysed by Pd-Ag dendrites in the present of sodium borohydride (NaBH_4), where the insert shows the absorbance changes at 400 nm used to calculate catalytic rate constant. B. Rate constant calculated for 4-NP reduction catalysed by various nanodendrites. Reprinted with permission from ref. [22]. Copyright © 2010 American Chemical Society.

Nanomaterials also play an important role in the field of electrocatalysis, among which, fuel cell reactions were most studied²³. Some of the examples of fuel cell reactions include oxygen reduction reaction (ORR), which was utilized in hydrogen fuel cell²⁴ and metal-air batteries²⁵⁻²⁶; hydrogen evolution reaction (HER), which was used to produce hydrogen gas for feedstock of hydrogen fuel cell²⁷; and hydrazine oxidation, where hydrazine (H_2N_2) was a potential fuel for future fuel cells²⁸⁻²⁹. Pt NPs as electrocatalyst for ORR had been very well studied³⁰, and various effort had been made to further improve the ORR activity on Pt NPs. One of such examples were the attempts to synthesize Pd NPs with high index planes³¹⁻³³, as ORR activity on Pt were heavily influenced by the orientation of the steps and terraces on the NPs surfaces³³. Other attempts to improve ORR performance of Pt NPs involved the alloying of Pt NPs with various metals at different ratio. For example, alloying Pt with gallium (Ga) in the ratio of 6 to 1 (Pt_6Ga_1) had successfully increase the ORR current by 5 times as compared with Pt NPs³⁴. Another major research approach in ORR was to develop non noble metal based catalyst or even metal free catalyst³⁵, in an attempt to lower the cost of catalyst. Fe- and Co-based catalysts were the most common replacement for Pt in ORR catalysis and had been studied in fuel cell system³⁶⁻³⁹, where one of the Fe-based catalyst was able to achieve a peak power of 0.56 W/cm^2 in hydrogen-oxygen (H_2/O_2) fuel cell⁴⁰.

Similar to ORR, Pt NPs was the most effective catalyst for HER, with a low overpotential and able to generate high current density⁴¹. However, due to high cost and rarity of platinum, recent development of HER catalyst was pushed towards non noble metal base catalyst⁴²⁻⁴⁴. Noble metal free catalyst was invented based on the structure of nitrogenase and hydrogenase, which were present in nature for large scale production of hydrogen gas⁴². This includes but not limited to transition metal sulphites⁴⁵⁻⁴⁷, selenides⁴⁸⁻⁴⁹ and phosphides⁵⁰⁻⁵². One of such examples, were molybdenum sulphite (MoS_2) nanosheets, which exhibits excellent current density (15 mA/cm^2 with overpotential of -0.25 V) and high stability⁵³. A part from transition metal

nanomaterials, carbon based nanomaterials was also utilized in HER. Carbon materials were usually inert, hence they were heavily used as current collector, and chemical modification was needed before they can be used for catalysis⁴². Nitrogen (N), sulphur (S) and phosphorus (P) were often doped into carbon nanomaterial in HER catalysis⁵⁴⁻⁵⁶. As shown in Figure 1.4, the overpotential of HER had been dramatically improved with the introduction of dopant, as reported by Y. Zheng⁵⁷.

Figure 1.4 Potential polarization curves of HER catalyzed by N- and P-doped graphene. Reprinted with permission from ref. [57]. Copyright © 2015, Royal Society of Chemistry.

Nanomaterials had also been used widely in photocatalysis field. However, instead of metal nanomaterials, semiconductor nanomaterials were the focus in photocatalysis or photoelectrocatalysis, as semiconductors were the ones that were able to absorb solar photon to drive redox reaction⁵⁸. The key reactions in photocatalysis were water splitting, which generates hydrogen gas (H_2) and oxygen gas (O_2) that can be used as fuel⁵⁹⁻⁶⁰; and degradation process, where reactive oxygen species (ROS) was used to breakdown organic pollutant and waste⁶¹⁻⁶². For application in water splitting, the most common photocatalyst was made up of a light harvesting semiconductor nanomaterials, with metal or oxide NPs or nanocluster attached to it as hydrogen or oxygen evolution catalyst⁶². For example, TiO_2 coupled with Pt or Au nanocluster had found to improve HER in water splitting effectively⁶³.

Photocatalytic degradation process, consist of multiple organic reactions, such as oxidation, reduction, isomerizations and condensations process⁵⁸. As semiconductor photocatalyst was unselective towards a wide range of toxic and non-biodegradable organic pollutant, they were a great choice for pollution or waste treatment⁶⁴. Some of the common organic reaction investigated includes alcohols oxidation⁶⁵⁻⁶⁶ and glucose oxidation⁶⁷⁻⁶⁸. For examples, methanol was selectively oxidised to formic acid, which then reacts with methanol to give the ester methyl formate with up to 91 % yield when anatase TiO_2 NPs was used as photocatalyst⁶⁹. Catalyst for glucose photo-oxidation, was normally transition metal doped TiO_2 NPs supported on zeolite, which shows high selectivity towards glucaric acid and gluconic acid as product⁷⁰, such as shown in Figure 1.5, chromium doped TiO_2 (Cr- TiO_2) supported on zeolite shows a product selectivity of 99.7 % towards glucaric acid and gluconic acid after illuminated for 10 minutes with a 125 W mercury lamp⁷¹.

Figure 1.5 Selectivity and conversion results of glucose photo-oxidation with Cr-TiO₂ supported on zeolite. Reprinted with permission from ref. [71]. Copyright © 2013 Elsevier B.V.

From the discussion above, it can be established that the usage of nanomaterials in catalysis is crucial and will continue to be relevant for the next few decades. However, even with such a huge effort pouring into this field, there were still some challenges faced in nano-based catalysts. One of the key bottleneck was that there were lacked of new direction in the nano-based catalyst. Up to this day, almost all available, common chemical compounds had been screen through for catalysis. Fine tuning of chemical composition to obtain a better catalyst had become increasingly harder, as the search for new material had now pushed towards combining three or more elements together (example, usage of Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} nanowires as catalyst for ethanol oxidation⁷²). With such a large amount of combinations in terms of elements and their ratios, the probability of getting a correct combination for catalysis had become much slimmer. Of course, there were other approaches available to improve the catalyst, such as by facets control. Nevertheless, most of the common and stable facets had been screened through and well characterized,

and others were almost impossible or without the proper knowledge to be produced, especially the high index plane. One of the least searched area were the effect of morphology of nanomaterials on catalyst. Some might already recognized the potential that nanocatalysts' morphology can offer, but the lack of methodology to synthesize these nanostructure had limit their research.

A part from that, scalable nanomaterial synthesis had also been a challenge in nano-based catalysis. The end goal of developing various nanocatalysts was to employed them in real world, with the hoped to achieved higher efficiency with a smaller amount of catalysts, thus lowering the cost of production. A lot of nanomaterials had proven themselves to be highly efficient catalyst, but one of the main roadblock that prevent them from being commercialized was the inability to scale up the synthesis. When research was conducted in laboratory, the amount of nanomaterials used was relatively small, often in milligram (mg) or even microgram (μg) scale. Furthermore, most of the synthesis will only provide nanomaterials in the scale of mg, or at most, gram (g). However, to apply the catalyst in industry, we need to be able to synthesize the nanomaterials in the scale of kilogram (Kg). As nanosynthesis was a delicate process, we could not scale up the synthesis simply by scaling up all the reactants and a new methodology often need to be developed. Thus, scalable nanosynthesis remains a huge challenge in the field of nano-based catalysis.

Besides that, the lacked of mechanistic understanding, in both nanosynthesis and nano-based catalysis was also a major problem faced. As discussed previously, the understanding in nanosynthesis mechanism had become more and more important in the search for new materials for catalysis. Many researchers had conducted stimulations, which narrow down the scope to screen for new materials, facets or morphology that was optimum for a particular reaction. Despite their success in obtaining the optimum nanomaterial as catalyst through stimulations, the lack of knowledge in nanosynthesis mechanism means that there were no means for them to synthesize this catalyst. In addition to that, without understanding on the synthesis mechanism,

morphology control on the nanomaterials cannot be performed. Without the understanding of how a particular nanostructure was formed, fine tuning of the nanostructure cannot be achieved, and optimization of the nanosynthesis cannot be done.

Furthermore, the lacked of mechanistic understanding in nano-based catalysis had also prevent the proper optimization of the reaction conditions and the catalyst itself. Some researchers were only interested in performance of the catalyst, and pay less amount of attention on the reasons behind the caused this excellent performance. The lacked of mechanistic knowledge, in particular on those reaction with special catalytic conditions, had made it difficult to improve the catalytic performance. Without proper understanding on the catalytic mechanism, it was hard to identify which were the limiting factors in the catalytic reaction, and what aspect had been improved by a particular catalyst. The combination of all the above had made it very difficult for optimization of nano-based catalysis.

1.2 Advantages of One Dimensional Nanostructures

It had already been well recognized that the morphology of the nanomaterials have a huge effect on their catalytic performances. However, these difference in catalytic performance were often attributed to different active site or facets which was exposed, rather than the unique shape the nanomaterials processes. One of such examples was shown by platinum nanocrystal (Pt NCts) in electro-oxidation of light oxygenates, where tetrahedral shaped Pt NCts has higher performance than octahedral Pt NCts due to the exposure of high index planes such as (730) , (520) and (210)⁷³. Although sometimes it was hard to differentiate, facets induced properties were not the focus of discussion here, as we were more interested in morphology induced properties, which arise from the unique shape of the nanostructure and general among nanomaterials with the same shape regardless of their chemical composition.

We have focus our studies on one dimensional (1-D) nanomaterials, due to the unique properties that they offered. 1-D nanomaterials are structures with high aspect ratio (normally more than 10) with at least one of its dimension in the nanometre range. 1-D nanomaterials can take a lot of forms, such as nanobelts (NBs), nanorods (NRs), nanotubes (NTs) and nanowires (NWs). 1-D nanostructures had gain a lot of interest especially in the field of electrocatalysis and photocatalysis as they not only inherit all the properties of their zero dimension (0-D) counterparts (nanoparticles), but also exhibits new properties which were beneficial for catalysis. One of such examples was that 1-D nanostructure often contains less surface defects as compared with 0-D NPs⁷⁴. Defect sites were less favourable in catalysis as the difference in local coordination often made the site inactive. The reason that 1-D nanostructure have less surface defects arise from their morphology, as the growth in one direction allows the exposure of preferred lattice planes with fewer lattice

boundaries⁷⁵, thus 1-D nanostructures often consist of pristine surfaces with long portion of crystalline plane as compared with their 0-D counterparts⁷⁶.

Apart from having less surface defects, the growth of 1-D nanostructures with fewer lattice boundaries also means that it offers a direct pathway for charge transport, resulting in faster charge transport and which was favourable for electrocatalysis. Some of the 1-D nanostructure even exhibits ballistic transport, where the charge experience less resistivity due to scattering, as in the case of graphene nanoribbon⁷⁷. Additionally, 1-D nanostructure also displayed better mechanical properties than their 0-D counterpart, where they had shown to have high flexibility and elasticity⁷⁸. For examples, nickel nanowires was shown to have an impressive elastic strain of 34.6 %⁷⁹. Another advantage of 1-D nanostructures was that they were harder to be aggregated together. In the case of 0-D nanostructures, when they were concentrated and loaded onto electrode, they were able to come together and become closely pack due to their morphology, which results in loss of surface available of catalysis and possibly material diffusion problem. On the other hand, the high aspect ratio 1-D nanostructure had caused it to be difficult for them to pack closely when concentrated, resulting in lesser loss in catalytic surface and a better material diffusion.

With all the advantages stated above, it was not hard to imagine 1-D nanostructure out-perform 0-D NPs in electrocatalysis. It had been reported that cerium oxide (CeO_2) NWs and NRs have a higher carbon monoxide (CO) conversion rate as compared with CeO_2 NPs as shown in Figure 1.6 below⁸⁰. Another example was on platinum-cobalt (Pt-Co) alloy NWs, where its specific current in methanol oxidation exceeds those of the NPs⁸¹.

Figure 1.6 The change of carbon monoxide conversion rate with reaction temperature by various CeO_2 catalyst. Reprinted with permission from ref. [80]. Copyright © 2009 Elsevier B.V.

Figure 1.7 Cyclic voltammety curves of methanol oxidation with Pt–Co alloy nanowires de-alloyed for 30 min, 2 h, and 15 h as catalyst. Reprinted with permission from ref. [81]. Copyright © 2009 American Chemical Society.

1-D nanostructures had offered unique advantages in electrocatalysis over 0-D nanostructures. Still, 1-D nanostructures were even more useful in photocatalysis due to their additional optical properties. One of its advantages was that 1-D nanostructures were able to increase the light absorption up to 15 times as compared with 0-D nanostructure⁸². In particular, 1-D nanostructure array provide large surface area for light absorption through their long axis, yet convenient separation of photogenerated charge carries through their short radial distance, which decrease the loss of charge carrier through recombination and offer charge-carrier transport in the direction perpendicular to the charge collecting substrates⁸³⁻⁸⁵.

Also, 1-D nanostructure has low reflectance of light, which was induced by light scattering and trapping within the 1-D nanostructure array, assisting in

light absorption of 1-D nanostructure⁸⁶⁻⁸⁷. The radial diameter of 1-D nanostructure was highly related to some important physical parameters in photocatalysis, such as the exciton Bohr radius, the wavelength of light, the phonon mean free path and the excitation diffusion length⁸⁸. Thus, simply by adjusting the length, diameter and material composition, the physical parameters of 1-D nanostructure was highly tunable, making it possible for them to meet special conditions needed for some photoredox processes^{83-85,89}.

The main disadvantage of 1-D nanostructure as compared with 0-D nanostructure was the lower surface to volume ratio. Nevertheless, approaches had been taken to enlarge the surface area of 1-D nanostructure without losing its overall morphology, thus maintaining its unique properties as 1-D nanomaterials and overall photocatalytic performance. One of such approaches was to increase the surface roughness, generally through etching process, or deposits NPs of the same material uniformly on the surface of 1-D nanostructure, which will greatly increase the specific surface area⁹⁰.

There had been various photocatalytic activities which utilised 1-D nanostructures. For examples, titanium oxide (B) phase, TiO₂(B)-anatase core-shell NWs was used for photocatalysis of pollutant degradation⁹¹. Zinc oxide, ZnO NTs and NWs had also been used for photocatalytic degradation of azobenzene-containing polymer and rhodamine B(RhB)⁹². Besides that, ZnO NRs also reported to have higher photocatalytic conversion rate and better selectivity towards oxidation of alcohol to aldehydes as compared to commercially available ZnO NPs⁹³. The result for benzyl alcohol conversion was shown in Figure 1.8.

Figure 1.8 Photocatalytic performances of ZnO NRs as compared with commercial ZnO NPs on benzyl alcohol oxidation. A. Photocatalytic conversion timeline. B. Selectivity towards benzaldehyde. Reprinted with permission from ref. [93]. Copyright © 2013, Royal Society of Chemistry.

1-D nanostructures had also been heavily used in energy related reaction, such as hydrogen evolution reaction (HER), where hydrogen might be a source of fuel. For examples, branched TiO_2 NRs had produced a much higher photocurrent as compared with its NPs counterpart as shown in Figure 1.9⁹⁴. 1-D nanostructure had also been utilised in photocatalytic water splitting, such as the titania-silicone (TiO_2 -Si) segmented NWs array reported by P. Yang et al., where TiO_2 part act as photoanode to produce oxygen (O_2) gas and Si part act as photocathode to produce hydrogen (H_2) gas⁹⁵. Apart from oxides, other 1-D materials, such as tantalum nitride (Ta_3N_5) NRs, had also been reported as catalyst for photoelectrocatalytic (PEC) water splitting⁹⁶.

Figure 1.9 Photoelectrochemical properties of TiO₂ NPs, TiO₂ NRs and TiO₂ branched NRs. A. Schematic illustration of the samples. B. Curves of photocurrent density produced vs potential (J-V curve) under solar simulator of 100mW/cm². C. Incident photon-to-current conversion efficiency (IPCE) curves measured at 0.6 V vs RHE. Reprinted with permission from ref. [94]. Copyright © 2011, American Chemical Society.

In conclusion, 1-D nanostructures have very unique electronic and optical properties, making them suitable for a wide range of applications such as catalysis, chemical sensing, medical diagnostics, nanoelectronics and optoelectronics devices, which makes them very interesting research topics. In

this thesis, we focus our exploration in two directions. The first research direction focus on synthetic mechanistic studies behind a large scale synthesis of 1-D nanostructure, in an attempt to develop large scale synthesis methodology of hybrid 1-D nanostructure for catalytic purposes. The second research direction focus on catalytic mechanistic studies of 1-D nanostructure array, to pin-point the origin of enhanced catalytic performance and identified factors crucial for optimization of catalytic conditions, while evaluate the possibility of present of any morphology-induced properties.

1.3 Titanium Dioxide (TiO₂) One-Dimensional Nanostructures

Titanium dioxide, or titania (TiO₂) had been a star materials in research and in industry with a wide range of applications. Ever since its ability in photocatalytic water splitting was discovered in 1972⁵⁹, and its usage in water remediation in 1977⁹⁷, TiO₂ had been heavily investigated for the past few decades. TiO₂ processes a lot of advantages compared to other semiconductor, such as having high chemical stability, abundant, low cost, high photoreactivity and resistant to photo-corrosion, making it a suitable photocatalyst⁹⁸⁻¹⁰⁰. TiO₂ had been used in photocatalytic degradation of pollutant¹⁰¹⁻¹⁰², photocatalytic reduction of carbon dioxide (CO₂)¹⁰³⁻¹⁰⁴, water splitting¹⁰⁵⁻¹⁰⁶, supercapacitors¹⁰⁷⁻¹⁰⁸, dye-sensitized, quantum dot-sensitized or perovskite solar cells¹⁰⁹⁻¹¹¹, lithium-ion batteries¹¹²⁻¹¹³, biomedical devices¹¹⁴⁻¹¹⁵ and gas sensors¹¹⁶.

In addition to its photocatalytic activity, TiO₂ was also applied in a wide range of commercial product, primarily due to its strong white colour and ability to breakdown organic compounds. TiO₂ had been used as a pigment in formulations of paints¹¹⁷⁻¹¹⁸, toothpaste and sunscreen¹¹⁹⁻¹²⁰. TiO₂ was also used in applications such as self-cleaning¹²¹⁻¹²², sterilisation¹²³, anti-fogging¹²⁴, lithography¹²⁵ and metal corrosion prevention¹²⁶⁻¹²⁷. For examples, TiO₂ has been used in air purifiers and self-cleaning windows in Japan for years¹²⁸⁻¹²⁹.

Although TiO₂ was considered an optimum material for photocatalysis or photoelectrocatalysis, there were still some problem and challenges faced. Bare TiO₂ can only make use of around 5 % of the incident solar light, due to its huge band gap of 3.0 eV¹³⁰⁻¹³¹. Thus, methods had been developed to improve light utilization ability and charge separation simultaneously. Some of the approaches adopted include doping, deposition of metal NPs on TiO₂ surface to construct heterojunction and alkali modification. The band gap of TiO₂ can be reduced by non-metal anions doping, such as nitrogen, carbon, boron, fluorine, phosphorus, sulphur and iodine. For example, nitrogen, N-

doped TiO_2 nanotubes (NTs) had shown improved performance in photocatalytic degradation of methylene blue¹³². Metal doping of TiO_2 had also been performed, such as copper cations doped TiO_2 NRs array had shown a 40 % increase in methylene blue degradation efficiency¹³³.

Figure 1.10 Photocatalytic degradation of methylene blue with N-doped TiO_2 NTs. Reprinted with permission from ref. [132]. Copyright © 2008, Royal Society of Chemistry.

Alkali modification of TiO_2 surface was also common, in particular in CO_2 reduction reaction. As CO_2 were acidic oxide molecules, their absorption on TiO_2 can be improved via introduction of alkaline sorbents. For example, sodium hydroxide (NaOH) modified TiO_2 can greatly enhance CO_2 molecules absorption on TiO_2 surface, thus the photocatalytic activity of CO_2 reduction was much higher than bare TiO_2 ¹³⁴.

Additionally, another effective approach to enhance TiO_2 light absorption was by decorating the surface of TiO_2 with metal NPs, which

utilized the surface plasmon resonance (SPR) effect of metal NPs. Some examples of metal NPs used was gold (Au), silver (Ag), platinum (Pt) and palladium (Pd), which basically focus on NPs that can be optically excited in the visible light region. On top of increase light absorption, introduction of metal NPs can also reduce charge recombination, thus enhancing photon to electron conversion rate. For example, Au NPs decorated TiO₂ NTs had shown increased hydrogen evolution from photocatalytic oxidation of ethanol/water mixture¹³⁵. Ag NPs decorated TiO₂ NRs also shown to have better performance in organic solar cells as compared with bare TiO₂ NRs as shown in Figure 1.11¹³⁶.

Figure 1.11 Performance of AgNPs decorated TiO₂ NRs in organic solar cells. The curves of photocurrent density produced vs potential (J-V curve) were measured under solar stimulator of 100mW/cm². Reprinted with permission from ref. [136]. Copyright © 2013, American Chemical Society.

The advantages of utilising 1-D TiO₂ nanostructure in photocatalytic and photoelectrocatalytic had been shown clearly above. Thus, it was important to go through different synthesis method that was used to produce these TiO₂ 1-D structures. The synthesis method of 1-D TiO₂ nanostructure can generally be divided to four types: solution-based approaches, vapour-based approaches, template growth and top-down fabrication techniques¹³⁷. Out of all the above, solution-based approaches were the most common. Solution-based synthesis has the advantages of low cost, simple processing and good reproducibility¹³⁸⁻¹³⁹. However, morphology control and optimization remains a huge challenge¹³⁷. Solution-based approaches can further be divided to methods such as hydrothermal or solvothermal methods, sol-gel methods, surfactant-assisted methods and microwave assisted methods. Various titanium (Ti) precursor can be used in hydrothermal and solvothermal methods to obtain 1-D nanostructure, such as titanium isopropoxide (TTIP, Ti[OC₃H₇]₄) and titanium chloride (TiCl₄)¹⁴⁰⁻¹⁴¹. This was due to the high temperature and high pressure conditions used.

Sol-gel method for synthesizing 1-D nanostructure typically required spatial confinement or guidance, such as titanium acetate complex formed by TTIP and acetic acid, which converted to TiO₂ nanofibers upon heating, where the organic groups were removed¹⁴². Surfactant-assisted synthesis was also a common strategy, where the surfactant acts as capping agents that control the growth direction. One of such examples was the synthesis of TiO₂ NRs via hydrolysis of TTIP with oleic acid as surfactant¹⁴³. Microwave assisted methods were mostly coupled with hydrothermal methods, where microwave served as alternative heating source. TiO₂ NRs can be produced via a TiCl₄ and water system using microwave as source of heating¹⁴⁴.

Figure 1.12 Transmission electron microscope (TEM) images of TiO₂ NRs synthesized via hydrothermal method. Reprinted with permission from ref. [141]. Copyright © 2006, American Chemical Society.

Vapour-based approaches have several advantages as compared with solution based approaches, which includes high quality and crystallinity of product obtained and delicate control and the composition and dimension of the 1-D nanostructure obtained. However, as vapour-based approaches often conducted in vacuum and at high temperature, it suffers drawback such as high production cost, and was only suitable for small-scale production¹³⁷. Vapour-based approaches can be further divided into chemical or physical vapour deposition (CVD) method, atomic layer deposition-related (ALD) method and pulsed laser deposition method. Out of the above, CVD was the most popular method, where vertically aligned TiO₂ NRs can be grown on sapphire substrates with very uniform height and diameter, using TTIP as precursor¹⁴⁵. Surface reaction-limited pulsed chemical vapour deposition (SPCVD), was a method derived from ALD process, where pulsed of TiCl₄ and H₂O were injected into the CVD growth chamber separated by inert gas purging at 600 °C to obtain TiO₂ NRs¹⁴⁶. Pulsed laser deposition method utilised high power laser as

heating source, which vapourises the Ti sources and cause it to deposit on substrate and form TiO_2 NWs¹⁴⁷.

Figure 1.13 Scanning electron microscope (SEM) images of TiO_2 NRs synthesized via CVD method. Reprinted with permission from ref. [145]. Copyright © 2008, Institute of Physics Science.

Template method consists of different pore-filling techniques which were chosen based on the physical and chemical properties of the template as well as the target. This method was in particularly useful for design of nanostructure which goes against the preferences of the material lattice structure. However, the fabrication process was always complicated, and there was always risk of contamination of the 1-D nanostructure during synthesis or possible damage to the nanostructure during template removal¹³⁷. Different template methods were available for the synthesis of 1-D nanostructures, such as sol-gel template method and suspended molecular template. Sol-gel method was often used to create 1-D nanostructure using anodic aluminium oxide (AAO) as template. As the diameter of the channel was often too large and it was hard to completely fill them, TiO_2 NTs, instead of TiO_2 NWs, was often obtained as product¹⁴⁸. However, this can be improved by increasing the reaction temperature and immersion time period, which allowed the AAO template to be filled completer, results in TiO_2 NWs¹⁴⁹. Suspended molecular template utilized a 1-D nanostructure, such as wire-shaped organic molecules as

template, which were suspended in solution or dispersed on a substrate, which the target material was directly deposited on them. For examples, cobalt, Co-doped TiO_2 NWs had been obtained by sputtering on a poly(3,4-ethylenedioxythiophene) (PEDOT) NWs as suspended template¹⁵⁰.

Figure 1.14 Scanning electron microscope (SEM) images of TiO_2 NTs synthesized via sol-gel template method. Reprinted with permission from ref. [148]. Copyright © 2009, American Chemical Society.

In addition to all the method above, 1-D TiO_2 nanostructures can also be synthesized via top-down fabrication techniques. This usually involved the selective etching and oxidation of bulk Ti foil. In the presence of suitable organic vapour such as ethanol, and at high temperature, bulk Ti can be oxidised directly to TiO_2 NWs¹⁵¹. TiO_2 NTs can also be formed via electrochemical anodisation of Ti foils, which selectively etched the Ti foils¹⁵²⁻¹⁵³. This top down fabrication approaches was able to produce a large quantity of uniform 1-D TiO_2 nanostructure with uniform morphology. Nevertheless, there was lack of morphology control flexibility, such as in terms of length, diameter and cross-section shape of nanostructure¹³⁷.

Figure 1.15 Cross section SEM images of TiO_2 NWs grown on bulk Ti. Reprinted with permission from ref. [151]. Copyright © 2007, Elsevier.

Figure 1.16 SEM images of TiO_2 NWs obtained via large scale molten salt synthesis. Reprinted with permission from ref. [154]. Copyright © 2013, American Chemical Society.

As discussed above, there were a lot of synthesis methods developed to produce 1-D TiO_2 nanostructures. However, we were still lacked of a synthesis

methodology that can allowed for large scale production, and at the same time provide enough flexibility in controlling the morphology of the nanostructure, such as length and diameter. Solution-based approaches and top-down fabrication were both scalable; however, they were either lacked of uniformity, or flexibility in nanostructure morphologies. Recently, a large scale synthesis of high quality, uniform and single crystalline TiO_2 NWs via molten salt method had been reported¹⁵⁴. This method had a high potential of becoming the ideal large scale synthesis method for TiO_2 NWs, with controllable length and diameter. Hence, in Chapter 2, we exploit the mechanism behind the formation of TiO_2 NWs via molten salt method, which we hoped to acquire knowledge to tune both the length and diameter of TiO_2 NWs. Next, we try to control the morphology of this TiO_2 NWs in Chapter 3, where we hoped to create a new hybrid structure, and intended to use the new morphology for photocatalytic applications. However, after exhausted all possible means, the desired morphology was not obtained, and the project was halted.

1.4 Ultrathin Gold Nanowires Array

Gold in nano-scale, had proved its usefulness in various catalysis and electrocatalysis field, and also as co-catalyst in photocatalysis as discussed previously in section 1.2 and 1.3. A part from these, one dimensional (1-D) gold (Au) nanostructure, especially vertically aligned 1-D nanostructures, had also shown unique usages especially in field of detection. Gold nanowires (Au NWs) array is a stable field emitters¹⁵⁵ and can be used for surface enhanced raman scattering (SERS) detection¹⁵⁶. Au NWs array had also been reported as a biosensor for glucose¹⁵⁷, thrombin protein¹⁵⁸ and nucleic acid detection¹⁵⁹.

Among all the methods to synthesize Au NWs array or forest, electrochemical deposition with anodic aluminium oxide (AAO)¹⁶⁰⁻¹⁶² or polycarbonate polymer¹⁶³⁻¹⁶⁴ as template was the most common method. However, similar to other template-assisted synthesis, this synthesis method suffers from the risk of introducing contaminant to the NWs array, and also the risk of damaging the NWs array during template removal¹³⁷. A part from that, Au NWs created with this method often have diameter in the range of tens of nanometre (nm) to hundreds of nm, where ultrathin NWs (<10 nm) had not been reported.

Figure 1.17 Scanning electron microscopy (SEM) images of Au NWs array. Reprinted with permission from ref. [165]. Copyright © 2013, American Chemical Society.

Recently, J. He et.al. had reported a unique solution growth of ultrathin Au NWs array under ambient conditions¹⁶⁵. This method had reported that Au NWs growth from substrate-bound seeds in polar solvent using a strong ligand. Previously, only a limited number of seeded growth of ultrathin metal NWs had been discovered¹⁶⁶⁻¹⁶⁸, which might be the reason the solution based substrate-bound NWs rarely been reported. Besides that, normally weak ligands such as oleyamine¹⁶⁹⁻¹⁷¹, hexadecyltrimethylammonium bromide (CTAB)¹⁷²⁻¹⁷⁴ and polyvinylpyrrolidone (PVP)¹⁷⁵⁻¹⁷⁷ was used in solution based growth, and strong ligand was less preferred, which made this synthesis method very unique.

Figure 1.18 Illustration on the growth of Au NWs forest on substrate. A. Synthesis methodology of Au NWs on silicon or silica substrate. B. Illustration on Au deposition on Au-substrate due to present of strong ligand on Au seed. Reprinted with permission from ref. [165]. Copyright © 2013, American Chemical Society.

Figure 1.18 illustrates the conditions used for Au NWs growth on substrate¹⁶⁵. The first step involved the immobilization of Au seed onto substrate surface with 3-aminopropyltriethoxysilane (APTES). Next, in the present of a strong ligand, 4-mercaptobenzoic acid (4MBA), Au precursor, chloroaurate acid (HAuCl₄) was reduced by L-ascorbic acid (AA) and grows into NWs. The growth method seems to be similar to that of vapour-liquid-solid

(VLS) growth in chemical vapour deposition (CVD), but careful examination had reveal that this was not the case. The difference between this Au NWs growth and VLS growth will be discussed shortly after.

The growth mechanism of this Au NWs forest was heavily dependent on the present of strong ligand, 4MBA. The role of 4MBA here was not to induce any specific facets, but the fact that it bonds strongly to Au surface is crucial for this synthesis¹⁶⁵. As 4MBA binds onto the Au seed, the newly reduced Au cannot deposited on the surface of Au seed. Thus, the fresh Au can only deposited at the Au-substrate interface, as this was the only place where 4MBA cannot binds effectively. The freshly formed Au surface was quickly binds by 4MBA again, limiting the growth on the perimeter, thus forcing Au to deposit continuously on the Au-substrate interface, pushing the Au upwards into NWs. This selective deposition of Au was the key to NWs formation here as shown in Figure 1.18b.

There were a few unique characteristics of the Au NWs forest synthesis reported by J. He¹⁶⁵. One of the most notable characteristic was that this type of NWs can only grow from substrate-bound seeds, but cannot grow from colloidal seeds under similar conditions. This might be due to the lack of Au-substrate interface where 4MBA cannot bind effectively and fresh Au can selectively deposit on. In colloidal seeds case, the Au seed simply grew larger in size¹⁶⁵. Secondly, the NWs only grow from one side of the seed, and the diameter of the Au NWs was independent of the size of Au seed used. The diameter of Au seed was controlled by the concentration of 4MBA ligand present, where higher ligand amount leads to smaller NWs diameter, which means that the diameter of the Au NWs was highly tunable.

This characteristic had distinguish this Au NWs growth from other solution based synthesis, as the seeds were often the nucleation centres in colloidal synthesis, and the nanocrystals grown around the seeds, which always results in diameter larger than the seed¹⁷⁸. Whereas in VLS growth, the entire molten seed acts as catalyst in the synthesis, thus the size of the NWs produced

was often similar or slightly larger than that of the seed¹⁷⁹. As the author had demonstrated the ability to grow NWs with smaller diameter than Au seed, the Au NWs growth here was clearly different from VLS growth.

In addition, growth of the Au NWs was always originated from the Au-substrate interface, which pushed the seed away from the substrate. In contrast, the materials always selectively deposit at the seed and NWs interface in VLS growth, where the NWs was always pushed away from the seed¹⁷⁹. If the seed was immobilized on a substrate surface, the NWs will seem to grow from the seed, where the seed will still remain on the substrate surface even after NWs was formed. A part from that, as the seed was required to be molten in VLS growth, the reaction temperature was always very high, which is a huge difference from the ambient condition used in this Au NWs forest synthesis. Therefore, we can conclude that the Au NWs forest growth mode was different than those of the VLS growth.

Besides the simplicity and robust in preparation, this Au NWs forest synthesis method also offered high flexibility, in terms of substrate choice, diameter, length of NWs, and even materials for the NWs. It was already been demonstrated that apart from silicon wafer, the Au NWs forest can be prepared on trumpet shells¹⁶⁵. The Au NWs growth had also been demonstrated on glass fibers, where it was used as fixed-bed catalysis for reduction of 4-nitrophenol¹⁸⁰. This had shown that it was also possible to grow Au NWs on electrode such as fluorine-doped tin oxide (FTO) glass, and apply them for electrocatalysis. Subsequently, the materials used for synthesis of the NWs were not limited to Au itself. Similar method can be used to grow silver (Ag) and palladium (Pd) NWs, or even hybrid NWs such as Au-Pd di-block NWs¹⁸¹. The choice of materials, combined with the tunability in terms of diameter and length, had made this NWs array a suitable system for testing of electrochemical catalysis in various reactions, which was explored in Chapter 4. Next, we would like to determine if the vertically aligned NWs array structure will have any impact on the catalysis mechanism or pathway, which was investigated in Chapter 5 and 6.

1.5 Research Motivation and Scientific Contribution

Overall, this thesis aims to investigate the mechanism behind one dimensional nanostructure synthesis and catalytic performance, which hopes to contribute towards optimizing of catalytic process. More specifically, we planned to exploit the recent advances in one dimensional nanostructures synthesis, which we limits the scope to nanowires synthesis, and investigate the growth mechanism of the nanowires (NWs) synthesis if it was still not well understood. Next, with this understanding in synthesis mechanism, we hoped to create novel NWs structures, especially hybrid NWs structures, and apply them for photocatalysis and electrocatalysis. Besides that, we hoped to observe and identified specific advantages in catalysis arises from specific nanostructure, or in other words, morphology induced properties.

We strongly believed that there is still a huge window left in synthesis mechanistic understanding and the possibility to create more complex nanostructures. We had chosen to use titanium dioxide (TiO_2) NWs as the model study system due to its wide usage in photocatalysis and the lack of understanding behind molten salt synthesis mechanism. We proposed that the synthesis of TiO_2 NWs in molten salt follows a seed assisted growth mode, which was investigated in Chapter 2. With understanding on the synthesis mechanism, we determined that the key to construct hybrid TiO_2 NWs was to control the rate between ligand binding and TiO_2 deposition, which was discussed in Chapter 3. We had planned to use the hybrid TiO_2 NWs for photocatalytic application, but after exhaust all means, the desired nanostructure was not obtained, thus the project was halted. Nevertheless, we still contributed to the science society by working out the detail TiO_2 NWs molten salt growth mechanism which can be used to fine tune the morphology such as diameter and length of NWs.

We were also interested in a metal NWs array system, where the synthesis mechanism was already well studied, but there were only limited amount of application studies conducted. We see a huge potential of this metal

NWs array in electrocatalysis, which had not been performed thus far. We proposed that this ultrathin metal NWs array was able to provide advantages such as huge surface area, high conductivity and mass transport, which was crucial in electrocatalysis. We had choose ethanol electro-oxidation reaction as the model reaction to demonstrate our point, which was explored in Chapter 4. From our study, we had discovered that there were not enough studies conducted on the ethanol oxidation on palladium (Pd) surface, which prevent us from optimizing our metal NWs array. We had investigate the ethanol oxidation mechanism on Pd in Chapter 5, where we proposed that hydroxide species was the main inhibitor which was highly influence by applied potential. We had also discovered reservoir effect as a morphology induced properties, which has caused some unique behaviour in our NWs array catalyst system.

In Chapter 6, we also investigated different ethanol oxidation pathway adopted by different facets of Pd. Our hypothesis was that Pd (200) facets and (220) facets have different ethanol oxidation pathway, which leads to different product being produced. All the knowledge from studies in ethanol oxidation mechanism on Pd surface and reservoir effect will contribute to further design and optimization of catalyst in electro-oxidation of ethanol.

References:

- [1] E. Roduner. *Chem. Soc. Rev.* **2006**, 35, 583–592.
- [2] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides. *Chem. Rev.* **2005**, 105, 1103–1169.
- [3] K. D. Gilroy, A. Ruditskiy, H. C. Peng, D. Qin, Y. Xia. *Chem. Rev.* **2016**, 116, 10414–10472.
- [4] E. Roduner. *Nanoscope Materials: Size-Dependent Phenomena*, The Royal Society of Chemistry, Cambridge, **2006**.
- [5] K. Koga, T. Ikeshoji, K. Sugawara. *Phys. Rev. Lett.* **2004**, 92, 115507.
- [6] K. M. Unruh, T. E. Huber, C. A. Huber. *Phys. Rev. B: Condens. Matter*, **1993**, 48, 9021-9027.
- [7] Chang Q. *Prog. Solid State Chem* **2007**, 35, 1-159.
- [8] J. Zhang, M. Chaker, D. Mac. *J. Colloid Interface Sci.* **2017**, 489, 138–149.
- [9] F. Zereini, C.L.S. Wiseman. *Platinum Metals in the Environment*, Springer-Verlag: Berlin, Heidelberg, **2015**.
- [10] H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang, G. A. Somorjai. *J. Am. Chem. Soc.* **2006**, 128, 3027–3037.
- [11] H.L. Jiang, Q. Xu. *J. Mater. Chem.*, **2011**, 21, 13705 – 13725.
- [12] A. M. Argo, J. F. Odzak, F. S. Lai, B. C. Gates. *Nature*, **2002**, 415, 623-626.
- [13] D. S. Gatewood, T. L. Schull, O. Baturina, J. J. Pietron, Y. Garsany, K. E. Swider-Lyons, D. E. Ramaker *J. Phys. Chem. C* **2008**, 112, 4961-4970.
- [14] D. O. Grigoriev, H. Möhwald and D. G. Shchukin, *Phys. Chem. Chem. Phys.*, **2008**, 10, 1975-1982.
- [15] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima. *J. Catal.* **1989**, 115, 301–309.

- [16] M. Haruta. *Catal. Today* **1997**, 36, 153–166.
- [17] M. Haruta, T. Kobayashi, H. Sano, N. Yamada. *Chem. Lett.* **1987**, 16, 405–408.
- [18] Y. Yao, C. Hao, L. Chao, F. Wei, D. Zhang, G. Wu, B. Chena, S. Wang. *J. Hazard. Mater.* **2016**, 314, 129–139.
- [19] Y. Gong, M. Li, H. Li and Y. Wang. *Green Chem.* **2015**, 17, 715–736.
- [20] B. Chen, U. Dingerdissen, J. G. E. Krauter, H. Rotgerink, K. Mobus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke and H. Trauthwein. *Appl. Catal. A* **2005**, 280, 17–46.
- [21] H. Hu, J. H. Xin, H. Hu, X. Wang, D. Miao, Y. Liu. *J. Mater. Chem. A* **2015**, 3, 11157–11182.
- [22] J. Huang, S. Vongehr, S. Tang, H. Lu, X. Meng. *J. Phys. Chem. C* **2010**, 114, 15005–15010.
- [23] S. E. F. Kleijn, S. C. S. Lai, M. T. M. Koper, P. R. Unwin. *Angew. Chem. Int. Ed.* **2014**, 53, 3558 – 3586.
- [24] M. K. Debe. *Nature* **2012**, 486, 43 – 51.
- [25] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke. *J. Phys. Chem. Lett.* **2010**, 1, 2193 – 2203.
- [26] M. Armand, J. M. Tarascon, *Nature* **2008**, 451, 652 – 657.
- [27] P. C. K. Vesborg, B. Seger, I. Chorkendorf. *J. Phys. Chem. Lett.* **2015**, 6, 951–957.
- [28] V. Rosca, M. T. M. Koper. *Electrochim. Acta* **2008**, 53, 5199 – 5205.
- [29] B. Alvarez-Ruiz, R. Gomez, J. M. Orts, J. M. Feliu. *J. Electrochem. Soc.* **2002**, 149, D35 – D45.
- [30] N. M. Markovic, T. J. Schmidt, V. Stamenkovic, P. N. Ross. *Fuel Cells* **2001**, 1, 105–116.
- [31] B. Y. Xia, H. B. Wu, X. Wang, X. W. Lou, *Angew. Chem. Int. Ed.* **2013**, 125, 12563–12566.
- [32] T. Yu, D. Y. Kim, H. Zhang, Y. Xia. *Angew. Chem. Int. Ed.* **2011**, 50, 2773–2777.

- [33] X. Huang, Z. Zhao, J. Fan, Y. Tan, N. Zheng. *J. Am. Chem. Soc.* **2011**, 133, 4718–4721.
- [34] I. E. L. Stephens, A.S. Bondarenko, U. Gronbjerg, J. Rossmeisl, I. Chorkendorff. *Energy Environ. Sci.* **2012**, 5, 6744–6762.
- [35] K. N. Wood, R. O’Hayre, S. Pylypenko. *Energy Environ. Sci.* **2014**, 7, 1212–1249.
- [36] F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J. -P. Dodelet, G. Wu, H. T. Chung, C. M. Johnston, P. Zelenay. *Energy Environ. Sci.* **2011**, 4, 114–130.
- [37] C. W. B. Bezerra, L. Zhang, K. Lee, H. Liu, A. L. B. Marques, E. P. Marques, H. Wang, J. Zhang. *Electrochim. Acta* **2008**, 53, 4937–4951.
- [38] D. S. Su, G. Sun. *Angew. Chem., Int. Ed.* **2011**, 50, 11570–11572.
- [39] D. C. Higgins, Z. Chen. *J. Chem. Eng.* **2013**, 91, 1881–1895.
- [40] A. Serov, K. Artyushkova, P. Atanassov. *Adv. Energy. Mater.* **2014**, 4, 1301735.
- [41] W. Zhou, J. Jia, J. Lu, L. Yang, D. Hou, G. Li, S. Chen. *Nano Energy* **2016**, 28, 29–43.
- [42] M. Zeng, Y. Li. *J. Mater. Chem. A* **2015**, 3, 14942–14962.
- [43] J. Deng, P. Ren, D. Deng, L. Yu, F. Yang, X. Bao. *Energy Environ. Sci.* **2014**, 7, 1919–1923.
- [44] C.G.M. Guio, L.A. Stern, X. Hu. *Chem. Soc. Rev.* **2014**, 43, 6555–6569.
- [45] J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont and T. F. Jaramillo. *ACS Catal.* **2014**, 4, 3957–3971.
- [46] M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin. *J. Am. Chem. Soc.* **2013**, 135, 10274–10277.
- [47] Z. Wu, B. Fang, Z. Wang, C. Wang, Z. Liu, F. Liu, W. Wang, A. Alfantazi, D. Wang and D. P. Wilkinson. *ACS Catal.* **2013**, 3, 2101–2107.
- [48] X. Zou, J. Jiang, T. Ding, J. Zhang, B. Pan, J. Zuo, Q. Yang, *Nanoscale* **2014**, 6, 11046–11051.

- [49] H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, N. Liu, Y. Cui. *Nano Lett.* **2013**, 13, 3426–3433.
- [50] E. J. Popczun, J. R. Mckone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak. *J. Am. Chem. Soc.* **2013**, 135, 9267–9270.
- [51] E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak. *Angew. Chem., Int. Ed.* **2014**, 53, 5427–5430.
- [52] Y. Xu, R. Wu, J. Zhang, Y. Shi, B. Zhang. *Chem. Commun.* **2013**, 49, 6656–6658.
- [53] Y. Yan, B. Xia, N. Li, Z. Xu, A. Fisher, X. Wang. *J. Mater. Chem. A*, **2015**, 3, 131–135.
- [54] J. Duan, S. Chen, M. Jaroniec, S. Z. Qiao. *ACS Nano* **2015**, 9, 931–940.
- [55] Y. Zhao, F. Zhao, X. Wang, C. Xu, Z. Zhang, G. Shi, L. Qu. *Angew. Chem. Int. Ed.* **2014**, 53, 13934–13939.
- [56] Y. Ito, W. Cong, T. Fujita, Z. Tang, M. Chen. *Angew. Chem. Int. Ed.* **2015**, 54, 2131–2136.
- [57] L. Wei, H. E. Karahan, K. Goh, W. Jiang, D. Yu, O. Birer, R. Jiang, Y. Chen. *J. Mater. Chem. A* **2015**, 3, 7210–7214.
- [58] J. C. Colmenares, R. Luque. *Chem. Soc. Rev.* **2014**, 43, 765–778.
- [59] A. Fujishima, K. Honda. *Nature* **1972**, 238, 37–38.
- [60] J. A. Turner. *Science* **2004**, 305, 972–974.
- [61] M. Fagnoni, D. Dondi, D. Ravelli, A. Albini. *Chem. Rev.* **2007**, 107, 2725–2756.
- [62] Y. Qu, X. Duan. *Chem. Soc. Rev.* **2013**, 42, 2568–2580.
- [63] A. Kubacka, M. Fernandez-Garcia, A. Colon. *Chem. Rev.* **2012**, 112, 1555–1614.
- [64] A. Di Paola, E. Garcia-Lopez, G. Marcı, L. Palmisano. *J. Hazard. Mater.* **2012**, 211–212, 3–29.
- [65] P. R. Harvey, R. Rudham, S. Ward. *J. Chem. Soc., Faraday Trans. 1* **1983**, 79, 2975–2981.

- [66] F. J. Lopez-Tenllado, A. Marinas, F. J. Urbano, J. C. Colmenares, M. C. Hidalgo, J. M. Marinas, J. M. Moreno. *Appl. Catal. B* **2012**, 128, 150-158.
- [67] J. C. Colmenares, A. Magdziarz, A. Bielejewska. *Bioresour. Technol.* **2011**, 102, 11254-11257.
- [68] J. C. Colmenares, A. Magdziarz. *J. Mol. Catal. A: Chem.* **2013**, 366, 156-162.
- [69] H. Kominami, H. Sugahara, K. Hashimoto. *Catal. Commun.* **2010**, 11, 426-429.
- [70] J. C. Colmenares, A. Magdziarz, O. Chernyayeva, D. Lisovytskiy, K. Kurzydłowski, J. Grzonka. *ChemCatChem* **2013**, 5, 2270-2277.
- [71] J. C. Colmenares, A. Magdziarz, K. Kurzydłowski, J. Grzonka, O. Chernyayeva, D. Lisovytskiy. *Appl. Catal., B* **2013**, 134–135, 136-144.
- [72] M. Carmo, R. C. Sekol, S. Ding, G. Kumar, J. Schroers, A. D. Taylor. *ACS Nano*, **2011**, 5, 2979 - 2983.
- [73] N. Tian, Z. Y. Zhou, S. G. Sun , Y. Ding, Z. L. Wang. *Science* **2007**, 316, 732-735.
- [74] M. C. Williams. *Fuel Cells* **2001**, 1, 87–91.
- [75] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, G. Gates, Y. Yin, F. Kim, H. Yan. *Adv. Mater.* **2003**, 15, 353–389.
- [76] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, G. Gates, Y. Yin, F. Kim, H. Yan. *Adv. Mater.* **2003**, 15, 353–389.
- [77] M. Koch, F. Ample, C. Joachim, L. Grill. *Nature Nanotechnology* **2012**, 7, 713–717.
- [78] S. Wang, Z. Shan, H. Huang. *Adv. Sci.* **2017**, 4, 1600332.
- [79] L. Wang, P. Liu, P. Guan, M. Yang, J. Sun, Y. Cheng, A. Hirata, Z. Zhang, E. Ma, M. Chen. *Nat. Commun.* **2013**, 4, 2413.
- [80] N. Ta, M. L. Zhang, J. Li, H. J. Li, Y. Li, W. Shen. *Catal. Today* **2009**, 148, 179–183.
- [81] L. Liu, E. Pippel, R. Scholz, U. Gosele. *Nano Lett.* **2009**, 9, 4352–4358.

- [82] P. Krogstrup, H. I. Jørgensen, M. Heiss, O. Demichel, J. V. Holm, M. Aagesen, J. Nygard, A. F. Morral. *Nature Photonics* **2013**, 7, 306–310.
- [83] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang. *Nat. Mater.* **2005**, 4, 455–459.
- [84] Z. Fan, H. Razavi, J. W. Do, A. Moriwaki, O. Ergen, Y.L. Chueh, P. W. Leu, J. C. Ho, T. Takahashi, L. A. Reichertz, S. Neale, K. Yu, M. Wu, J. W. Ager, A. Javey. *Nat. Mater.* **2009**, 8, 648–653.
- [85] J. Tang, Z. Huo, S. Brittman, H. Gao, P. Yang. *Nat. Nanotechnol.* **2011**, 6, 568–572.
- [86] J. L. Xie, C. X. Guo, C. M. Li. *Energy Environ. Sci.* **2014**, 7, 2559–2579.
- [87] B. Weng, S. Liu, Z. R. Tang, Y. J. Xu. *RSC Adv.*, **2014**, 4, 12685–12700.
- [88] S. Liu, Z. R. Tang, Y. Sun, J. C. Colmenares, Y. J. Xu. *Chem. Soc. Rev.* **2015**, 44, 5053–5075.
- [89] R. K. Joshi, J. J. Schneider. *Chem. Soc. Rev.* **2012**, 41, 5285–5312.
- [90] J. Tian, Z. Zhao, A. Kumar, R.I. Boughton, H. Liu. *Chem. Soc. Rev.* **2014**, 43, 6920–6937.
- [91] B. Liu, A. Khare, E. S. Aydil. *ACS Appl. Mater. Interfaces* **2011**, 3, 4444–4450.
- [92] J. Bae, J. B. Han, X. M. Zhang, M. Wei, X. Duan, Y. Zhang, Z. L. Wang. *J. Phys. Chem. C* **2009**, 113, 10379–10383.
- [93] Z. R. Tang, X. Yin, Y. Zhang, Y. J. Xu. *RSC Adv.* **2013**, 3, 5956–5965.
- [94] I. S. Cho, Z. Chen, A. J. Forman, D. R. Kim. *Nano Lett.* **2011**, 11, 4978–4984.
- [95] C. Liu, J. Tang, H. M. Chen, B. Liu, P. Yang. *Nano Lett.* **2013**, 13, 2989–2992.
- [96] Y. Li, T. Takata, D. Cha, K. Takanabe, T. Minegishi, J. Kubota, K. Domen. *Adv. Mater.* **2013**, 25, 125 - 131.
- [97] S. N. Frank, A. J. Bard. *J. Am. Chem. Soc.* **1977**, 99, 303–304.
- [98] Z. Zhao, J. Tian, Y. Song, A. Cobot, H. Liu. *Adv. Mater.* **2015**, 27, 2557–2582.

- [99] R. Fagan, D. E. McCormack, D. D. Dionysiou, S. C. Pillai. *Materials Science in Semiconductor Processing* **2016**, 42, 2–14.
- [100] H. Xu, S. Ouyang, L. Liu, P. Reunchan. *J. Mater. Chem. A* **2014**, 2, 12642–12661.
- [101] M. Y. Wang, J. Ioccozia, L. Sun, C. J. Lin, Z. Q. Lin. *Energy Environ. Sci.* **2014**, 7, 2182-2202.
- [102] Y. K. Lai, J. Y. Huang, Z. Q. Cui, M. Z. Ge, K. Q. Zhang, Z. Chen, L. F. Chi. *Small* **2016**, 12, 2203-2224.
- [103] L. L. Tan, W. J. Ong, S. P. Chai, A. R. Mohamed. *Appl. Catal. B* **2015**, 166, 251-259.
- [104] O. K. Varghese, M. Paulose, T. J. LaTempa, C. A. Grimes. *Nano Lett.* **2009**, 9, 731-737.
- [105] W. G. Yang, Y. H. Yu, M. B. Starr, X. Yin, Z. D. Li, A. Kvit, S. F. Wang, P. Zhao, X. D. Wang. *Nano Lett.* **2015**, 15, 7574-7580.
- [106] L. P. Zhang, P. Cui, H. B. Yang, J. Z. Chen, F. X. Xiao, Y. Y. Guo, Y. Liu, W. N. Zhang, F. W. Huo, B. Liu. *Adv. Sci.* **2016**, 3, 1500243.
- [107] H. L. Tang, M. Xiong, D. Y. Qu, D. Liu, Z. J. Zhang, Z. Z. Xie, X. Wei, W. M. Tu, D. Y. Qu. *Nano Energy* **2015**, 15, 75-82.
- [108] X. H. Lu, M. H. Yu, G. M. Wang, T. Zhai, S. L. Xie, Y. C. Ling, Y. X. Tong, Y. Li. *Adv. Mater.* **2013**, 25, 267-272.
- [109] M. D. Ye, D. J. Zheng, M. Y. Wang, C. Chen, W. M. Liao, C. J. Lin, Z. Q. Lin. *ACS Appl. Mater. Interfaces* **2014**, 6, 2893-2901.
- [110] M. D. Ye, X. K. Xin, C. J. Lin, Z. Q. Lin. *Nano Lett.* **2011**, 11, 3214-3220.
- [111] M. D. Ye, D. J. Zheng, M. Q. Lv, C. Chen, C. J. Lin, Z. Q. Lin. *Adv. Mater.* **2013**, 25, 3039-3044.
- [112] Y. X. Tang, Y. Y. Zhang, W. L. Li, B. Ma, X. D. Chen. *Chem. Soc. Rev.* **2015**, 44, 5926-5940.
- [113] Y. Y. Zhang, Y. X. Tang, S. Y. Yin, Z. Y. Zeng, H. Zhang, C. M. Li, Z. L. Dong, Z. Chen, X. D. Chen. *Nanoscale* **2011**, 3, 4074-4077.

- [114] H. Q. Li, Y. K. Lai, J. Y. Huang, Y. X. Tang, L. Yang, Z. Chen, K. Q. Zhang, X. C. Wang, L. P. Tan. *J. Mater. Chem. B* **2015**, 3, 342-347.
- [115] Y. K. Lai, L. X. Lin, F. Pan, J. Y. Huang, R. Song, Y. X. Huang, C. J. Lin, H. Fuchs, L. F. Chi. *Small* **2013**, 9, 2945-2953.
- [116] J. Gong, Y. Li, Z. Hu, Z. Zhou, Y. Deng. *J. Phys. Chem. C* **2010**, 114, 9970–9974.
- [117] N.S. Allen, M. Edge, A. Ortega, G. Sandoval, C.M. Liauw, J. Verran, J. Stratton, R. B. McIntyre. *Polym. Degrad. Stab.* **2004**, 85, 927-946.
- [118] N.S. Allen, M. Edge, A. Ortega, C.M. Liauw, J. Stratton, R.B. McIntyre. *Polym. Degrad. Stab.* **2002**, 78, 467-478.
- [119] M. Buchalska, G. Kras, M. Oszajca, W. Łasocha, W. Macyk. *J. Photochem. Photobiol. A Chem.* **2010**, 213, 158-163.
- [120] A. Weir, P. Westerhoff, L. Fabricius, K. Hristovski, N. von Goetz. *Environ. Sci. Technol.* **2012**, 46, 2242-2250.
- [121] R. Fateh, A. A. Ismail, R. Dillert, D. W. Bahnemann. *J. Phys. Chem. C* **2011**, 115, 10405-10411.
- [122] S. Banerjee, D. D. Dionysiou, S. C. Pillai. *Appl. Catal. B Environ.* **2015**, 176–177, 396-428.
- [123] J. W. MacFarlane, H. F. Jenkinson, T. B. Scott. *Appl. Catal. B Environ.* **2011**, 106, 181-185.
- [124] K. Hashimoto, H. Irie, A. Fujishima. *Jpn. J. Appl. Phys.* **2005**, 44, 8269-8285.
- [125] T. Tatsuma, W. Kubo, A. Fujishima. *Langmuir* **2002**, 18, 9632-9634.
- [126] Y. Ohko, S. Saitoh, T. Tatsuma, A. Fujishima. *J. Electrochem. Soc.* **2001**, 148, B24-B28.
- [127] T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima. *Chem. Mater.* **2001**, 13, 2838-2842.
- [128] H. Honda, A. Ishizaki, R. Soma, K. Hashimoto, A. Fujishima. *J. Illum. Eng. Soc.* **1998**, 27, 42–49.

- [129] K. Sunada, T. Watanabe, K. Hashimoto. *Environ. Sci. Technol.* **2003**, 37, 4785–4789.
- [130] S.G. Kumar, L.G. Devi. *J. Phys. Chem. A* **2011**, 115, 13211–13241.
- [131] C. U. G. Silva, R. Juárez, T. Marino, R. Molinari, H. Garcia. *J. Am. Chem. Soc.* **2010**, 133, 595–602.
- [132] Z. Jiang, F. Yang, N. Luo, B. T. T. Chu, D. Sun, H. Shi, T. Xiao, P. P. Edwards. *Chem. Commun.* **2008**, 47, 6372–6374.
- [133] O. Kerkez, I. Boz. *J. Phys. Chem. Solids* **2014**, 75, 611–618.
- [134] X. Meng, S. Ouyang, T. Kako, P. Li, Q. Yu, T. Wang, J. Ye. *Chem. Commun.* **2014**, 50, 11517–11519.
- [135] N. T. Nguyen, M. Altomare, J. Yoo, P. Schmuki. *Adv. Mater.* **2015**, 27, 3208–3215.
- [136] Q. Lu, Z. Lu, Y. Lu, L. Lv, Y. Ning, H. Yu, Y. Hou, Y. Yin. *Nano Lett.* **2013**, 13, 5698–5702.
- [137] X. Wang, Z. Li, J. Shi, Y. Yu. *Chem. Rev.* **2014**, 114, 9346–9384.
- [138] H. Yu, W. E. Buhro. *Adv. Mater.* **2003**, 15, 416–418.
- [139] Y. Chang, M. L. Lye, H. C. Zeng. *Langmuir* **2005**, 21, 3746–3748.
- [140] P. D. Christy, N. Melikechi, N. S. Nirmala Jothi, A. R. Baby Suganthi, P. Sagayaraj. *J. Nanopart. Res.* **2010**, 12, 2875–2882.
- [141] M. N. Tahir, P. Theato, P. Oberle, G. Melnyk, S. Faiss U. Kolb, A. Janshoff, M. Stepputat, W. Tremel. *Langmuir* **2006**, 22, 5209–5212.
- [142] R. Sui, A. S. Rizkalla, P. A. Charpentier. *J. Phys. Chem. B* **2006**, 110, 16212–16218.
- [143] P. D. Cozzoli, A. Kornowski, H. Weller. *J. Am. Chem. Soc.* **2003**, 125, 14539–14548.
- [144] K. L. Lin, F. D. Mai, Y. C. Chan, J. C. Chung, K. M. Lin, C. C. Yu, M. Y. Liao, F. Y. Li. *J. Chin. Chem. Soc.* **2012**, 59, 603–613.
- [145] C. A. Chen, Y. M. Chen, A. Korotcov, Y. S. Huang, D. S. Tsai, K. K. Tiong, *Nanotechnology* **2008**, 19, 075611.
- [146] J. Shi, C. Sun, M. B. Starr, X. Wang. *Nano Lett.* **2011**, 11, 624–631.

- [147] J. H. Noh, J. H. Park, H. S. Han, D. H. Kim, B. S. Han, S. Lee, J. Y. Kim, H. S. Jung, K. S. Hong. *J. Phys. Chem. C* **2012**, 116, 8102-8110.
- [148] T. S. Kang, A. P. Smith, B. E. Taylor, M. F. Durstock. *Nano Lett.* **2009**, 9, 601-606.
- [149] B. B. Lakshmi, P. K. Dorhout, C. R. Martin. *Chem. Mater.* **1997**, 9, 857-862.
- [150] Y. H. Lee, J. M. Yoo, D. H. Park, D. H. Kim, B. K. Ju. *Appl. Phys. Lett.* **2005**, 86, 033110.
- [151] S. Daothong, N. Songmee, S. Thongtem, P. Singjai. *Scr. Mater.* **2007**, 57, 567-570.
- [152] S. P. Albu, A. Ghicov, J. M. Macak, R. Hahn, P. Schmuki. *Nano Lett.* **2007**, 7, 1286-1289.
- [153] D. Kuang, J. Brillet, P. Chen, M. Takata, S. Uchida, H. Miura, K. Sumioka, S. M. Zakeeruddin, M. Gratzel. *ACS Nano* **2008**, 2, 1113-1116.
- [154] B. Liu, H. M. Chen, C. Liu, S. C. Andrews, C. Hahn, P. Yang. *J. Am. Chem. Soc.* **2013**, 135, 9995-9998.
- [155] A. Apte, P. Joshi, P. Bhaskar, D. Joag, S. Kulkarni. *Applied Surface Science* **2015**, 355, 978-983.
- [156] A. La Porta, M. Grzelczak, L. M. Liz-Marzan. *ChemistryOpen* **2014**, 3, 146 - 151.
- [157] T. Tian, J. Dong, J. Xu. *Microchim Acta* **2016**, 183, 1925-1932.
- [158] L. Shi, Z. Chu, Y. Liu, W. Jin. *J. Mater. Chem. B* **2015**, 3, 3134-3140.
- [159] T.S. Ramulu, R. Venu, B. Sinha, B. Lim. *Biosens. Bioelectron.* **2013**, 40, 258-264.
- [160] Y. Kanno, T. Suzuki, Y. Yamauchi, K. Kuroda. *J. Phys. Chem. C* **2012**, 116, 24672-24680.
- [161] G. E. Fernandes, J. H. Kim, Z. Liu, J. Shainline, R. Osgood III, J. Xu. *Optical Materials* **2010**, 32, 623-626.
- [162] S. H. Yoo, S. Park. *Adv. Mater.* **2007**, 19, 1612-1615.

- [163] A. Dangwal, C. S. Pandey, G. Muller, S. Karim, T. W. Cornelius, C. Trautmann. *Appl. Phys. Lett.* **2008**, 92, 063115.
- [164] M. Yang, F. Qu, Y. Li, Y. He, G. Shen, R. Yu. *Biosens. Bioelectron.* **2007**, 23, 414-420.
- [165] J. He, Y. Wang, Y. Feng, X. Qi, Z. Zeng, Q. Liu, W. S. Teo, C. L. Gan, H. Zhang, H. Chen. *ACS Nano* **2013**, 7, 2733-2740.
- [166] D. Azulai, E. Cohen, G. Markovich. *Nano Lett.* **2012**, 12, 5552–5558.
- [167] Y. G. Sun, Y. D. Yin, B. T. Mayers, T. Herricks, Y. N. Xia. *Chem. Mater.* **2002**, 14, 4736–4745.
- [168] F. Kim, K. Sohn, J. Wu, J. Huang. *J. Am. Chem. Soc.* **2008**, 130, 14442–14443.
- [169] Z. Huo, C. K. Tsung, W. Huang, X. Zhang, P. Yang. *Nano Lett.* **2008**, 8, 2041–2044.
- [170] C. Wang, Y. Hu, C. M. Lieber, S. Sun. *J. Am. Chem. Soc.* **2008**, 130, 8902–8903.
- [171] A. Halder, N. Ravishankar. *Adv. Mater.* **2007**, 19, 1854–1858.
- [172] K. Critchley, B. P. Khanal, M. Y. Górzny, L. Vigderman, S. D. Evans, E. R. Zubarev, N.A. Kotov. *Adv. Mater.* **2010**, 22, 2338–2342.
- [173] F. Kim, K. Sohn, J. Wu, J. Huang. *J. Am. Chem. Soc.* **2008**, 130, 14442–14443.
- [174] O. Krichovski, G. Markovich. *Langmuir* **2007**, 23, 1496–1499.
- [175] L. Hu, H. S. Kim, J. Y. Lee, P. Peumans, Y. Cui. *ACS Nano* **2010**, 4, 2955–2963.
- [176] X. Huang, N. Zheng. *J. Am. Chem. Soc.* **2009**, 131, 4602–4603.
- [177] Y. Wang, Q. Wang, H. Sun, W. Zhang, G. Chen, Y. Wang, X. Shen, Y. Han, X. Lu, H. Chen. *J. Am. Chem. Soc.* **2011**, 133, 20060–20063.
- [178] S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai, P. Yang. *Nat. Mater.* **2007**, 6, 692–697.
- [179] M. Law, J. Goldberger, P. D. Yang. *Annu. Rev. Mater. Res.* **2004**, 34, 83–122.

- [180] J. He, W. Ji, L. Yao, Y. Wang, B. Khezri, R. D. Webster, H. Chen. *Adv. Mater.* **2014**, 26, 4151–4155.
- [181] J. He, Y. Wang, Z. Fan, Z. Lam, H. Zhang, B. Liu, H. Chen. *Nanoscale*, **2015**, 7, 8115–8121.

Chapter 2

Synthesis and Mechanism Study of Single Crystalline Titanium Dioxide Nanowires.

Titanium dioxide (TiO₂) had numerous roles in photocatalysis and electrocatalysis, such as its usage as charge collector in dye-sensitized solar cells (DSCs) and as photocatalyst for water-splitting, due to its low price and abundance, apart from being resistant to photo-corrosion, non-toxic and easy to handle. Recently, large scale synthesis of single crystalline rutile TiO₂ NWs with uniform diameter through molten salt method had been reported, however, the growth mechanism was unclear. We had demonstrated that TiO₂ NWs synthesized via molten salt method adopts seed-assisted growth mode, with ripening as the main growth mechanism. A part from acting as seed that control the diameter of the resulting NWs, rutile NPs also acts as feedstock, where the selectivity comes from its own size, which is common with ripening as main growth mechanism. As TiO₂ NWs adopt seed-assisted growth mode, it is now possible for us to create segmented hybrid TiO₂ NWs.

2.1 Introduction

Titanium dioxide (TiO₂) had numerous roles in photocatalysis and electrocatalysis, such as its usage as charge collector in dye-sensitized solar cells (DSCs) and as photocatalyst for water-splitting¹⁻², due to its low price and abundance, apart from being resistant to photo-corrosion, non-toxic and easy to handle³⁻⁷. However, to obtain high quality, single crystalline, rutile phase TiO₂ nanowires for catalysis purposes, multi washing step, long reaction time (more than 72 hours for hydrothermal synthesis) and further annealing is often required, not to mention the use of strongly corrosive concentrated hydrochloric acid⁸⁻¹⁰.

Out of all the synthesis methods, molten salt synthesis method seems to be one of the more promising methods for production of high quality TiO₂ nanowires (NWs). Molten salt synthesis offers a more robust and less time consuming alternative to the traditional hydrothermal method for TiO₂ nanowires synthesis. Molten salt synthesis involves the usage of molten state salt as reaction medium as opposed to the traditional liquid medium¹¹. More than often, a mixture of salts at their eutectic salt composition is used to lower down the reaction temperature to bring the salt into molten state. In TiO₂ synthesis, sodium chloride (NaCl) and sodium phosphate dibasic (Na₂HPO₄) is often used, with their eutectic point going as low as 725 °C when the weight ratio of NaCl:Na₂HPO₄ is 4:1¹¹, while Na₂HPO₄ also acts as catalyst that helps to convert anatase phase TiO₂ to rutile phase simultaneously. Apart from that, as molten salt synthesis reaction temperature is high, the TiO₂ nanowire obtained is often single crystalline, eliminates the need to further anneal the product after synthesis, which greatly shortens the synthesis time.

Besides the advantages mentioned above, molten salt synthesis also readily scale-up, unlike the conventional hydrothermal method. Using of cheap precursor such as NaCl and Na₂HPO₄ also decreases the production cost of TiO₂ nanowires, which is an important factor for commercialization of this method.

Recently, B. Liu et al. had further improved the molten salt synthesis method to obtain uniform, high quality and single crystalline rutile TiO₂ NWs in large scale¹². By using commercial P25 nanoparticles (P25 NPs) as TiO₂ precursor, single crystalline TiO₂ nanowires with uniform diameter of 100 nm and length between 5 to 40 μm were obtained after reacting in NaCl:Na₂HPO₄ at 825 °C for 8 hours¹². B. Liu et al. had also shown that it was possible to dope these TiO₂ nanowires simply by mixing transition metal ions in nitrate salt form together with the salt and P25 NPs mixture before heating, further improving the photocatalytic properties of TiO₂ nanowires¹².

Figure 2.1 SEM images, atomic lattice of single crystalline TiO₂ NWs synthesized by molten salt method, and the UV-Vis absorption of transition metal doped TiO₂ NWs. Reprinted with permission from reference [12]. Copyright © 2013 American Chemical Society.

The molten salt synthesis mechanism had been proposed, where Na₂HPO₄ act as catalyst that convert anatase nanoparticles to rutile phase, which then formed NWs. The mechanism of conversion is as follow¹¹⁻¹²:

At around 200 °C, Na₂HPO₄ loses water to form sodium pyrophosphate tetrabasic (Na₄P₂O₇), which is the active catalyst. At 650 °C, Na₄P₂O₇ combined with anatase nanoparticles to form Na₄TiP₂O₉ complex, which decomposed on further heating to produce rutile and give back Na₄P₂O₇ catalyst. However, the mechanism that was proposed still fails to explain why NWs was formed instead of other structures such as NPs.

Despite all the advances achieved thus far in molten salt synthesis of rutile TiO₂ NWs, there were still some difficulties faced in TiO₂ nanowires production. One of the major problems is the lack of controllability in the morphology and diameter of nanowires produced. The length and diameter of TiO₂ nanowires produced is often random and uncontrollable, with the exception where P25 NPs was used as TiO₂ precursor. Hence, it will be beneficial to study and understand the mechanism behind nanowires formation from P25 NPs in molten salt to pin-point the critical factor that control length and diameter of nanowires produced. In addition, the modification or doping done on the TiO₂ nanowires were often simple. As shown in many cases, present of p-n junction is essential for various device applications such as single nanowire solar cells and transistor. With more understanding on the growth mechanism, we will be able to create more complex hybrid structure, such as multiple transition metal ions doping to create controllable p-n junction on a single TiO₂ NWs.

Here in, we would like to report a seeded growth mechanism of TiO₂ NWs in molten salt. The diameter of TiO₂ NWs obtained were controlled by the initial size of rutile nanoparticles that act as seed, with ripening as the main growth mode.

2.2 Results and Discussion

2.2.1 Initial Hypothesis – Seeded Growth Mode

The growth of nanomaterials was heavily influenced by the growth environment. Without present of external influences, nanomaterials will preferred to adopt shapes that enable them to minimize their surface energy¹³. Thus, most nanomaterials form under this condition will adopt either spherical shape (lowest surface energy) or cubic or hexagonal-like structure (single crystalline nanoparticles influence by its lattice structure). Therefore, nanomaterial formed was often highly symmetrical, which imply that anisotropic structure, such as the growth of nanowire, must involve the application of external forces¹³. There were a few methods that can be used for the formation of nanowires, such as template, screw dislocation and ligand. In the case of molten salt synthesis, template method can be ruled out as there were nothing that can act as template of nanowires in molten state. From the atomic lattice image of TiO₂ NWs in Figure 2.1, it can be observed clearly that there were no indications of screw dislocation. Thus, the growth of TiO₂ NWs in molten salt can only be supported by ligand, which selectively stabilized the sides' surfaces, limiting its growth and forcing the nanowires to grow in only one direction¹⁴. In our case, NaCl acted as the ligand that stabilised the {100} facets, limiting the growth on the side of NWs. The effect of NaCl on TiO₂ NWs had been demonstrated by R. Babasri et. al., without the present of NaCl, only TiO₂ nanoparticles was formed¹⁵.

We had hypothesized that TiO₂ NWs synthesized using molten salt method adopts seeded growth mode, where rutile nanoparticles (NPs) act as seed. This initial hypothesis was proposed based on the different morphology of TiO₂ NWs obtained when different TiO₂ precursor was used. As shown in results obtained by B. Liu et al In Figure 2.2, when pure rutile NPs was used as precursor, no NWs were obtained¹². In fact, rutile NPs remain almost

unchanged after the synthesis, which was a strong proof, that rutile NPs act as seed. When P25 NPs (which consists of both rutile and anatase NPs) was used as precursor, TiO₂ NWs of uniform diameter was obtained. Presumably, rutile NPs in P25 act as seed which control the diameter of the NWs, while anatase NPs grow on it. This hypothesis was further proof by irregular NWs that were obtained when pure anatase NPs was used as precursor without the present of rutile NPs as seed.

Figure 2.2. SEM images of TiO₂ NWs synthesized from different precursors. A. P25 B. Pure rutile nanoparticles C. Pure anatase nanoparticles Reprinted with permission from reference [12]. Copyright © 2013 American Chemical Society.

However, our hypothesis cannot completely explain the growth phenomena observed. In P25 NPs, the ratio of rutile to anatase is roughly 1: 5. If all rutile NPs act as seed and all anatase NPs grow on them, then the TiO₂ NWs obtained will only be of 5 or 6 times the length of its original size. In reality, as shown in Figure 2.2, the NWs obtained were of very high aspect ratio, which proof that the growth in the longitudinal direction (length) was much more than in lateral direction (diameter). This had give us hope that it might be possible to create hybrid NWs structure with different segment doped with different transition metal ions.

To prove our hypothesis, our strategy is to use other oxide NPs to replace the role of rutile NPs in the molten salt synthesis. As oxide can easily grown on other oxide, we aspect TiO₂ can grow easily on other oxide seed as

well. Then, we can use imaging techniques such as electron microscopy and element mapping to visualize the position of oxide seed in TiO₂ NWs formed.

Overall, the mechanistic studies of TiO₂ NWs growth will be highly dependant on images obtained from electron microscopy before and after synthesis. The primary reason was due to the fact that molten salt synthesis used to produce TiO₂ NWs was conducted at extremely high temperature, it was hard to perform any in-situ characterization during the synthesis, and we also did not have equipment with such capability available. However, we believed that we were able to deduce enough information based on the electron microscopy images to hypothesize what might happen during the synthesis process.

2.2.2 Testing of Seeded Growth Hypothesis

We had hypothesized that TiO₂ NWs synthesized using molten salt method adopts seeded growth mode, where rutile nanoparticles (NPs) act as seed. Our strategy is to replace rutile seed with other oxide NPs, which was chosen to be SiO₂ and Fe₂O₃ in this case.

Figure 2.3. TiO₂ NWs obtained by using different oxides nanoparticles as seed. A & B. SiO₂ nanoparticles as seed. C & D. Fe₂O₃ as seed.

As shown in Figure 2.3, the product were not similar to P25 produced TiO₂ NWs, which was not what we had expected. For the case where SiO₂ NPs were used as seed, the TiO₂ NWs obtained were of various diameters, ranging from 0.1 to 1 μm, which indicates that, nothing act as seed to control the diameter of the NWs. For the case where Fe₂O₃ NPs were used as seed, particles of various shapes, instead of NWs, were observed. This is most likely

due to Fe ions from Fe₂O₃ NPs had heavily doped into TiO₂ at high temperature of synthesis, which alter the morphology of TiO₂ product produced. In both cases, the original seeds (SiO₂ or Fe₂O₃ NPs) cannot be observed or determined from the SEM images, which shown that this is a bad approach. Therefore, instead of pure oxides NPs, heavy metal NPs (gold, Au in this case) was chosen for the huge contrast with oxides under TEM, due to the difference in atomic number. As it is difficult for TiO₂ to grow directly on Au surface, usage of pure AuNPs as seed is not suitable in the synthesis. Instead, oxides coated gold nanoparticles (Au@SiO₂ and Au@TiO₂) were used as seed to facilitate the growth of TiO₂ on them.

Figure 2.4 TiO₂ NWs obtained by using oxides coated gold nanoparticles as seed. A & B. Au@TiO₂ used as seed. C& D. Au@SiO₂ used as seed.

However, the product we obtained is still not as what we had expected. Although TiO₂ NWs were successfully formed, we did not observe any Au NPs trapped within TiO₂ NWs, which can act as a direct proof for seeded growth mechanism. As shown in Figure 2.4, when Au@TiO₂ was used as seed, Au NPs were found to aggregate together, where the TiO₂ shell had disappeared. This might be due to the TiO₂ shell, which is amorphous, get transformed to rutile by the Na₂HPO₄ catalyst present, and deposited as a part of the rutile TiO₂ NWs. On the other hand, when Au@SiO₂ NPs were used as seed, TiO₂ did not deposit on the SiO₂ shell as predicted. Instead, the presence of Au@SiO₂ NPs seems not to affect the formation of TiO₂ NWs. The NWs formed were of various diameter and length, similar to the case where pure anatase was used as precursor (case where no seed is present). Au@SiO₂ NPs which had aggregated together can still be seen mixed together with the TiO₂ NWs product. The above cases had clearly shown that oxide NPs were not a good candidate as seed, as TiO₂ will not deposit on them in the molten salt growth process. Apart from that, amorphous TiO₂ NPs will be a bad candidate as they will act as feedstock to the NWs and disappear. Hence, single crystalline, short rutile nanorods (NRs) had been chosen as seed for our assessment. As these NRs were already in the most stable rutile stage, they will not be dissolved away and converted to feedstock for NWs, and the growth can be easily determined by assessing the change in diameter and length of the resulting NRs or NWs.

In order for us to achieve our purpose, it is important for us to find a way to produce large quantity, pure, single crystalline rutile NRs with very narrow range of diameter and length, so that subsequent growth in any direction can be easily distinguished. After much consideration, we had decided to use back the original molten salt method to synthesize these rutile NRs. With this, we were able to not only obtain rutile NRs in high quality and large scale, but also eliminate any possible influence from other chemicals, as the exact same chemicals and conditions were used. One of the key points to synthesize rutile NRs instead of NWs is to alter the ratio between P25 NPs precursor and

Na₂HPO₄. When the ratio of P25 to Na₂HPO₄ increases, more rutile NPs were present to act as seed. With the increasing amount of seed, the feedstock needs to be shared within more seed, resulting in shorter NRs as product instead of NWs. This happens because the amount of anatase that can be transformed into rutile (feedstock) is the same given that the amount of catalyst (Na₂HPO₄) did not change. Hence, despite the present of more precursor (anatase NPs in P25), they cannot be transform into rutile fast enough as the amount of Na₂HPO₄ did not change, making them become "idle" and not act as feedstock, producing a temporary situation where more seed is present while the amount of feedstock remains. The weight ratios of reactant which was used to produce short NRs and long NWs were summarized as below:

Table 2.1 Recipes for synthesis of long TiO₂ nanowires and short TiO₂ nanorods

Product	P25	NaCl	Na ₂ HPO ₄
TiO ₂ NWs (Long)	1	4	1
TiO ₂ NRs (Short)	4	4	1

The TiO₂ NRs synthesized (1st growth) were then used as seed in subsequent NWs growth, which was referred to as 2nd growth. To get a clearer picture of the growth mode, the product obtained from 2nd growth was then used as seed in the 3rd growth. All the growth (2nd growth and 3d growth) use the short NRs recipe instead of the long NWs recipe, as the NWs recipe often give very long NWs, making it difficult to determine if the NWs comes from growth on NRs or newly form NWs(from anatase NPs). With this method, any growth on the NRs will be enhanced and shown a huge difference in any changes in length or diameter of the initial TiO₂ NRs seed.

Figure 2.5 TiO₂ NRs/NWs obtained for 1st, 2nd and 3rd growth. A & B. 1st growth; C& D. 2nd growth; E & F. 3rd growth.

Table 2.2 Diameter and length of TiO₂ NWs obtained during 1st, 2nd and 3rd growth.

TiO ₂	Diameter (nm)			Length (μm)		
	Range	Average	Standard Deviation	Range	Average	Standard Deviation
1 st Growth	58 – 157	99.1	21.5	0.49 – 1.25	0.78	0.23
2 nd Growth	90 – 1570	298.4	298.9	0.70 – 8.45	3.27	1.61
3 rd Growth	1040 – 6410	2735.7	1078.6	8.20 – 28.13	16.82	3.92

Figure 2.6 Graph showing the change in diameter and length of TiO₂ NWs with 1st, 2nd and 3rd growth.

As shown in Figure 2.5 and Table 2.2, the TiO₂ NRs obtained using P25 nanoparticles as precursor were 99.1 nm in diameter and 0.78 μm in length averagely, with a very small variation in length and diameter (standard deviation were 21.5 nm and 0.23 μm respectively as shown in Table 2.2). During the 2nd growth, there was already an observable change in the diameter of TiO₂ NWs, where there was a 201.1 % increase in diameter and 319.2 % increase in average length. 3rd growth shown an even larger change in the diameter and length of TiO₂ NWs obtained. The diameter of NWs increased dramatically by 816.8 % to 2735.7 nm and the length of NWs increased 414.4 % to 16.82 μm as compared to those from the 2nd growth. The change in length and diameter were summarized in the chart as shown in Figure 2.6, with error bar included. From these observations, we can firmly assure that the TiO₂ NWs do indeed adopt a seeded-growth mode, as shown in the consistent increase in length and diameter of TiO₂ NWs in each growth. As the same short NRs recipe is used, we can safely assume that any product form directly from precursor

will have similar length and diameter as the product in 1st growth. However, it was shown clearly especially in the 3rd growth, that the range of diameter and length of the product obtained deviates very far from those obtained in 1st growth. This is strong evidence that the TiO_2 precursor only grow on the seed present, which show that our NWs adopt seeded-growth mode.

Figure 2.7 SEM image of TiO_2 NWs doped with various transition metal ions. Reprinted with permission from reference [12]. Copyright © 2013 American Chemical Society.

Although we had obtained satisfying evidences that seeded-growth mode is indeed the reason that leads to thicker and longer NWs formed in 2nd and 3rd growth, we had to rule out other factors that might also affect the morphology of TiO_2 NWs obtained. As shown from the results of B. Liu et. al. in Figure 2.7, TiO_2 NWs that was doped with transition metal ions seems to become much thicker, which suggest that present of contaminant will affect the diameter and length of TiO_2 NWs formed. We had identified two most possible contaminants in our system, which is water and iron (Fe). The water was introduced from the washing steps between each round of synthesis. Although water should already been fully evaporated before reaching the reacting temperature, a trace amount might still be trapped in salt crystal. Fe might be introduced from experiment

apparatus such as spatula which was used to transfer the reacting mixture and product. Hence, control experiment had to be performed to eliminate the effect of contaminant.

Figure 2.8 SEM images of TiO₂ NWs obtained in the control experiments. A. Fe ions (10 wt %) added. B. Water added.

The results of the control experiments were shown in Figure 2.8. As shown above, presence of Fe ions does influence the morphology of the TiO₂ NWs formed, causing them to become thicker. However, the amount of Fe ions to cause this change is huge, which was 10 wt% of TiO₂. Such a large amount of Fe ions present will alter the colour of TiO₂ and salt mixture used, making the reacting mixture appear to be yellowish in colour rather than the original pure white colour. This change in colour was not observed in our case. Apart from this, another reason to eliminate influence of Fe ions contamination is the increase in diameter during the 2nd growth is already much larger than those in Figure 2.8. Hence, we can safely eliminate any effect of contamination from Fe ions in our system. On the other hand, addition of water did not affect the morphology of TiO₂ NWs obtained. Therefore, we can confirm that the growth observed in 2nd growth and 3rd growth were not influenced by presence of contaminant, thus strengthening our hypothesis that TiO₂ NWs obtained from molten salt synthesis method adopt seeded growth mode, making the synthesis of hybrid NWs structure possible.

2.2.3 Evaluate Criteria of Seed

We had proven that TiO₂ NWs synthesized via molten salt method indeed adopted seeded growth mode, but we have little understanding regarding the criteria of the seed. From our previous results, we had established that only rutile nanomaterial, whether in NPs or NRs form, were able to act as seed in the synthesis. to further test this hypothesis, we had mixed rutile NPs of different size with anatase NPs, and compared the product obtained with those using P25 NPs as precursor.

Figure 2.9 TEM and SEM images of rutile precursors and their product. A. & D. Pure rutile NPs and its resulting TiO₂ NWs. B. & E. P25 NPs and its resulting TiO₂ NWs. C. & F. Pure rutile macroparticles and its resulting TiO₂ NWs.

As shown in Figure 2.9, the diameter of TiO₂ NWs formed seems to be determined by the size of the initial rutile NPs or seed. Similar to P25 NPs case, when small rutile NPs was used as precursor, the NWs produced has a very small diameter as well. The average diameter of obtained from rutile NPs as seed was 106 nm, which is very close to those obtained from P25 NPs (125 nm).

On the other hand, the NWs obtained when rutile macroparticles was used as seed was much thicker, with an average diameter of 660 nm. This result is consistent with our hypothesis that rutile NPs acts as seed in the seeded growth mode, hence it was expected that the size of the seed also plays a role in influencing the diameter of TiO₂ NWs produced.

However, there is still some problem that cannot be solved with our understanding on rutile seed. Commercially used P25 NPs consist of roughly 33 % rutile NPs and 67 % anatase NPs¹. If all rutile NPs act as seed, the NWs will only be able to grow to a length 3 times of its own diameter, which was clearly not the case.

Figure 2.10 SEM images of product obtained when: A. pure rutile macroparticles; B. pure rutile NPs was used as precursor.

Similar to what that had been demonstrated by B. Liu et. al., when pure rutile macroparticles was used as precursor, no NWs was produced. Instead, the rutile macroparticles just retained its morphology after molten salt synthesis. However, contradicted to what we had expected, when smaller size rutile NPs was used as precursor, NWs can be produced. This has shown that rutile NPs not only act as seed, but also able to act as feedstock and grow on other rutile NPs to form NWs. This observation helps to explain why NWs using P25 NPs as precursor can grow into such a long NWs, some of the rutile NPs in P25 NPs

must have also acted as feedstock just like those anatase NPs. Although the aspect ratio problem of NWs produced by P25 NPs can now be explained, this gives rise to a new question: how do the rutile NPs know if they should act as seed or feedstock? From our observation in Figure 2.10, we believed that this selectivity arises from the size of rutile NPs. At such a high reacting temperature of 825 °C, we believed that some smaller rutile NPs will be dissolved in the NaCl and Na₂HPO₄ eutectic salt mixture. Depending on their sizes, smaller NPs might be completely dissolved and larger NPs will be taking longer to completely dissolve, thus only resulting in a slight decrease in size. These dissolved, smaller NPs then act as feedstock, which deposited on undissolved, larger rutile NPs to form NWs. In the case of rutile macroparticles, a similar process might have also occurred, but since the size of these rutile macroparticles were so huge, the size changes caused by dissolving and re-deposit were only marginal and thus not observable, leaving the macroparticles seemingly unchanged before and after molten salt synthesis.

Since rutile NPs were able to act both as seed and feedstock depending on their size during molten salt synthesis, the amount of rutile NPs that were able to act as seed must be less than what we had expected. Hence, it will be interesting to push to the limit and investigate the amount of rutile NPs that act as seed in a molten salt synthesis. This amount will be hard to quantify using normal methods, as we were not able to separate rutile NPs that act as seed from those that act as feedstock easily. Nevertheless, we can still get a good approximation by decreasing the ratio of rutile NPs to anatase NPs in a synthesis. As demonstrated before, the diameter of TiO₂ NWs produced will be fairly uniform with the presence of seed, decreasing the rutile NPs ratio to a point where the diameter of NWs is no longer uniform can help us determine the amount of seed present in a synthesis.

Figure 2.11 SEM images of TiO₂ NWs obtained by mixing different ratio of rutile NPs to anatase NPs as precursor. A. Rutile : Anatase = 1 : 50. B. Rutile : Anatase = 1 : 100.

By mixing pure rutile NPs with pure anatase NPs together, we can easily obtained a TiO₂ precursor mixture with the ratio of rutile to anatase NPs as we desired. The NWs produced still maintain a uniform diameter despite the ratio of rutile : anatase had been decrease to 1 : 100 as shown in Figure 2.11. This was consistent with our prediction that a very small amount of rutile NPs present was enough to act as seed and control the diameter of NWs produced through molten salt synthesis. Hence, it was safe to assume that majority of the rutile NPs in P25 actually act as feedstock, which contribute to the growth of these long TiO₂ NWs with high aspect ratio.

Figure 2.12 SEM images of TiO_2 NWs using $\text{Ti}(\text{OH})_x$ as precursor. A. Without addition of rutile NPs as seed. B. Addition of 2.5 wt% of rutile NPs as seed.

The growth mechanism can be applied to other TiO_2 precursors as well. One of the examples was shown in Figure 2.12 above, where titanium hydroxide, $\text{Ti}(\text{OH})_x$ was used as TiO_2 precursor instead of rutile or anatase NPs. The TiO_2 NWs produced have similar behaviour as those of rutile or anatase NPs. In the absence of seed (only $\text{Ti}(\text{OH})_x$ was used), the NWs produce have a wide range of diameter. When a small amount of rutile NPs was added, TiO_2 NWs with a very uniform diameter was obtained. Hence, it can be concluded that other TiO_2 precursors also adopted seeded-growth mechanism using molten salt synthesis.

2.2.4 Ripening as Main Growth Mode

Our previous experiment results had raised the possibility that rutile NPs in P25 actually act as both seed and feedstock, depending on its size. This size selectivity arise from the proposal that smaller size rutile NPs actually dissolved faster than those of larger size. This is a common phenomena observed in ripening of NPs in solution, which give rise to the possibility that ripening might also happens to our molten salt synthesis method.

Figure 2.13 SEM images of TiO₂ NWs obtained with different TiO₂ precursor and Na₂HPO₄ catalyst weight ratio. A. TiO₂ : Na₂HPO₄ = 2 : 1. B. TiO₂ : Na₂HPO₄ = 1 : 1. C. TiO₂ : Na₂HPO₄ = 1 : 2. D. TiO₂ : Na₂HPO₄ = 1 : 4

It was well known that Na₂HPO₄ catalyst plays important role in converting anatase phase NPs to rutile NPs, and it do so by reacting with

anatase phase NPs to form Na₄TiP₂O₉, and then release TiO₂ in rutile phase. This behaviour of Na₂HPO₄ had also implied that Na₂HPO₄ was able to "dissolve" TiO₂ at high temperature. However, we know that at the weight ratio of TiO₂ : Na₂HPO₄ = 1 : 1, Na₂HPO₄ was not able to dissolve all TiO₂, which was the basic principle where short TiO₂ NRs can be produced simply by increasing the weight ratio of TiO₂ to TiO₂ : Na₂HPO₄ to 4 : 1. In this control experiment, we would like to do the direct opposite of that, which was to decrease the weight ratio of TiO₂ in the molten salt synthesis. This was done to check the amount of TiO₂ that will be completely dissolved by Na₂HPO₄. To prove that ripening occurred in the molten salt synthesis method, we must first prove that TiO₂ can be dissolved by Na₂HPO₄. Unlike in the case of metal ions in water, the dissolution of TiO₂ in Na₂HPO₄ cannot be observed easily, hence we made use of the fact that a small amount of rutile NPs was sufficient to act as seed in our NWs. The point where the TiO₂ NWs produced no longer have uniform diameter only happens if all the rutile NPs disappeared, where they were completely dissolved by Na₂HPO₄.

Figure 2.13 shown that changing the weight ratio of TiO₂: Na₂HPO₄ did affect the resulting length of TiO₂ NWs, however, no clear change in diameter had been observed up to ratio of 1:2. When the TiO₂: Na₂HPO₄ weight ratio was of 1:4 (Figure 2.12D), the diameter of TiO₂ NWs produced had very wide range, similar to the case where no TiO₂ seed was used to control the diameter, despite the fact that there is still rutile NPs in P25 that can act as seed. This observation indicates that all TiO₂ precursors, including the rutile NPs, had completely dissolved in Na₂HPO₄. With this, we had successfully proof that TiO₂ can be dissolved in Na₂HPO₄ at high temperature, thus it will be possible that ripening process did occurred in our molten salt synthesis system.

Figure 2.14 X-ray powder diffraction (XRD) spectrum of molten salt synthesis product obtained at different time using: A. P25 NPs; B. anatase NPs as precursor.

Results obtained from X-ray powder diffraction (XRD) spectrum had also served as evidence that support the ripening mechanism. XRD test was conducted for product of different TiO₂ precursor to check the conversion rate of anatase to rutile. As shown in Figure 2.14, when P25 NPs was used as precursor, almost all anatase had converted to rutile within 8 minutes of reaching 825 °C. However, in the case where anatase NPs was used as precursor, only a very small amount of anatase was converted to rutile within 8 minutes of 825 °C. If ripening process had occurred during molten salt synthesis of TiO₂ NWs, it will not be hard to imagine that rutile phase material only grow on rutile and anatase phase material only grow on anatase. This can explain the difference of anatase to rutile conversion rate between P25 NPs and anatase NPs as precursor. In the case of P25 NPs, once anatase NPs was dissolved in Na₂HPO₄ at high temperature, it can choose to either grow on rutile

NPs or another anatase NPs. Since rutile is the more stable phase of both, there is a higher tendency of it to deposit on rutile rather than on anatase NPs. As only anatase can be converted to rutile but not the other way round, and rutile phase only ripen on rutile, the size of rutile NPs increases, making them much harder to be dissolved, and anatase NPs become smaller and lesser. As the existing rutile NPs in P25 act as a platform for dissolved TiO₂ to grow on, the conversion of anatase phase to rutile phase becomes much faster. On the other hand, even though rutile is a more stable phase, there is no rutile NPs to act as growing platform when pure anatase NPs was used as precursor. Hence, most of the dissolved TiO₂ can only grow on anatase NPs, increasing its size, making it even harder to be ripened and convert to rutile phase. The lack of rutile phase in the first 8 minutes of synthesis when anatase NPs was used as precursor had provide direct evidence that anatase phase only grow on anatase, which is crucial evidence for the ripening mechanism proposed.

2.3 Conclusion

In summary, we had demonstrated that TiO₂ NWs synthesized via molten salt method adopts seed-assisted growth mode, with ripening as the main growth mechanism. Rutile NPs not only able act as seed to control the diameter of the resulting NWs, but also able to act as feedstock, where the selectivity comes from its own size, which is common with ripening as main growth mechanism. As TiO₂ NWs adopt seed-assisted growth mode, it is now possible for us to create hybrid TiO₂ NWs with different segment doped with transition metal ions via molten salt synthesis, which will be discussed in the next chapter.

2.4 Detailed Experimental Section

Materials and Characterization:

All chemicals were used as purchased without further purification. Anatase TiO₂ nanoparticles (TiO_{2(A)}), 4-mercaptobenzoic acid (4MBA), 11-mercaptoundecanoic (MUA), P25 nanoparticles (P25), polyvinylpyrrolidone (PVP), sodium chloride (NaCl) and sodium phosphate dibasic (Na₂HPO₄) were purchased from Sigma-Aldrich, hydrogen tetrachloroaurate (III) hydrate (HAuCl₄), iron (III) chloride hexahydrate (FeCl₃·6H₂O), sodium citrate tribasic (citrate) and tetraethyl orthosilicate (TEOS) were purchased from Alfa Aesar, ammonia (NH₃·H₂O) and sodium hydroxide (NaOH) were purchased from Sinopharm, 2-propanol (i-PrOH) was purchased from Fisher Scientific, titanium tetrafluoride (TiF₄) was purchased from STREM, hydrochloric acid (HCl) was purchased from MSR and ethanol (EtOH) was purchased from Merck. Transmission electron microscopy images were collected using a JEM-1400 Transmission Electron Microscope (JEOL) operated at 120 kV. Copper specimen grids (200 meshes) with formvar/carbon support film (TEM grids) used were purchased from Beijing XXBR Technology Co. Field emission scanning electron microscope (FE-SEM) images were collected on a JEOL JSM-6700F Scanning Electron Microscope. Acetone, deionized water and ethanol treated silicon wafer of 1 cm × 1 cm were used to prepare SEM samples.

TiO₂ Nanowires Synthesis:

Following molten salt method from B. Liu¹², the rutile TiO₂ nanowires were synthesized by mixing P25, NaCl and Na₂HPO₄ in 1:4:1 weight ratio. The mixture was then grinded with mortar and pestle to form a homogeneous mixture. Then, the mixture was placed in a boat shaped crucible and heated at 825° C for 8 hours in a tube furnace. Next, the mixture was cooled to room temperature. Next, the mixture was transferred to a round bottom flask and dispersed in large amount of distilled water (around 200 mL for every 1 g of

mixture), then heated at 90 °C for 1 hour with vigorous stirring to remove soluble salt. This washing step was skipped in some experiments. For synthesis of short TiO₂ nanorods, the ratio between P25, NaCl and Na₂HPO₄ was changed to 4:4:1. For some experiments, P25 was replaced by various “seed” (examples: SiO₂, Fe₂O₃ and Au@SiO₂) and anatase TiO₂ nanoparticles in 1:8 ratio by weight.

Synthesis of SiO₂ Nanoparticles

The silica nanoparticles (SiO₂ NPs) were synthesized using Stöber method reported by T. Pham¹⁶. 300 µL NH₃·H₂O and 150 µL of TEOS were added into 5 mL of EtOH and stirred vigorously for 14 hours. The SiO₂ NPs were then purified by centrifugation and re-dispersed in EtOH.

Synthesis of Fe₂O₃ Nanoparticles

The iron oxide nanoparticles (Fe₂O₃ NPs) were synthesized by using the method described by L. Rossi¹⁷. 100 mL of FeCl₃·6H₂O (2.0 M, H₂O) was prepared and transferred to a round bottom flask. Next, 90 mL of NaOH (6.0 M, H₂O) was added slowly into the round bottom flask under stirring, and then 10 mL of water was added into the gel-like mixture and stirred for another 10 minutes. The mixture was left undisturbed at 100 °C for 10 days. Then, the nanoparticles was washed by centrifugation and re-dispersed in water.

Synthesis of Au Nanoparticles (AuNPs)

The 60 nm gold nanoparticles (AuNPs) were synthesized by citrate reduction method reported by Y.J. Wong¹⁸. Firstly, 40 nm AuNPs were prepared by adding 50 mL of water, 250 µL of HAuCl₄ (29.4 mM, H₂O) and 375 µL of citrate (34.0 mM, H₂O) into a round bottom flask. Next, 50 mL of water, 50 µL of NaOH (0.2 mM, H₂O), 250 µL of citrate and 250 µL of HAuCl₄ were added in sequence and the mixture was refluxed at 110 °C for 20 minutes. This step was repeated for 3 times, and then 100 µL of NaOH, 500 µL of citrate and 500

μL of HAuCl₄ were added in sequence and reflux for 20 minutes at 110 °C. This subsequent step was repeated for 6 times, and AuNPs of 60 nm diameter was obtained.

Synthesis of Au@SiO₂ Nanoparticles

The silica coated gold nanoparticles were synthesized by modified Stöber method reported by Y. J. Wong¹⁸. 3 mL of 60 nm citrate stabilised AuNPs was centrifuged and concentrated to 20 μL, and then re-dispersed in 480 μL of water. Next, the solution was added into 2.5 mL of 2-propanol, and subsequently 20 μL of MUA (2 mM, ethanol) was added. The solution was stirred vigorously for 10 minutes, and then 600 μL of TEOS (11.2 mM, H₂O) and 90 μL of NH₃·H₂O was added. The solution was stirred vigorously for 14 hours, and then centrifuged and re-dispersed in ethanol.

Synthesis of Au@TiO₂ Nanoparticles

The titanium oxide coated gold nanoparticles (Au@TiO₂ NPs) were synthesized by modified method described by H. Sun¹⁹. Firstly, 5 μL of 4MBA (3mM, EtOH) was added into 1 mL of citrate stabilised AuNPs and incubated at 60 °C for 2 hours. Next, TiF₄ powder was dissolved in HCl solution of pH 2 to make a 0.04 M TiF₄ solution, and incubated for 1 hour. Then, the AuNPs were centrifuged and re-dispersed in 1.38 mL of EtOH, 0.07 mL of H₂O, 0.13 mL of PVP (200 mM, H₂O), followed by addition of 0.1 mL of TiF₄ (0.04M). The mixture was sonicated for 10 s and incubated at 65 °C for 3 hours.

References

- [1] B. Liu, E.S. Aydil. *J. Am. Chem. Soc.* **2009**, 131, 3985- 3990.
- [2] A. Fujishima, K. Honda. *Nature* **1972**, 238, 37-38.
- [3] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R.C. Fitzmorris, C. Wang, J.Z. Zhang, Y. Li. *Nano Lett.* **2011**, 11, 3026 – 3033.
- [4] I. S. Cho, Z. Chen, A. J. Forman, D. R. Kim, P. M. Rao, T. F. Jaramillo, X. Zheng. *Nano Lett.* **2011**, 11, 4978-4984.
- [5] S. K. Mohapatra, M. Misra, V. K. Mahajan, K. S. Raja. *J. Phys. Chem. C* **2007**, 111, 8677- 8685.
- [6] S. Y. Noh, K. Sun, C. Choi, M. Niu, M. Yang, K. Xu, S. Jin, D. Wang *Nano Energy* **2013**, 2, 351 – 360.
- [7] Y. Lin, G. Yuan, R. Liu, S. Zhou, S.W. Sheehan, D. Wang. *Chem. Phys. Lett.* **2011**, 507, 209 – 215.
- [8] Q. Jia. *J. Nanosci. Nanotechnol.* **2011**, 11, 9846-9850.
- [9] S. S. Amin, A. W. Nicholls, T. T. Xu. *Nanotechnology* **2007**, 18, 445609.
- [10] J. M. Wu, H. C. Shih, W. T. Wu, *Nanotechnology* **2005**, 17, 105 - 109.
- [11] B. Roy, S. P. Ahrenkiel, P. A. Fuierer. *J. Am. Ceram. Soc.* **2008**, 91, 2455-2463.
- [12] B. Liu, H. M. Chen, C. Liu, S. C. Andrews, C. Hahn, P. Yang. *J. Am. Chem. Soc.*, **2013**, 135, 9995 – 9998.
- [13] Y. Wang, J. He, W. H. Chong, H.Chen, *Angew. Chem. Int. Ed.* **2015**, 54, 2022 – 2051.
- [14] Y. Feng, Y. Wang, H. Wang, T. Chen, Y. Y. Tay, L. Yao, Q. Yan, S. Li, H. Chen, *Small* **2012**, 8, 246 – 251.
- [15] B. Roy, S.P. Ahrenkiel, P.A. Fuierer. *J. Am. Ceram. Soc.*, **2008**, 91, 2455 – 2463.
- [16] T. Pham, J. B. Jackson, N. J. Halas, T. R. Lee. *Langmuir*, **2002**, 18, 4915 – 4920.

- [17] L. Rossi, S. Sacanna, W. T. M. Irvine, P. M. Chaikin, D. J. Pine, A. P. Philipse. *Soft Matter*, **2011**, 7, 4139 – 4142.
- [18] Y. J. Wang, L. Zhu, W. S. Teo, Y. W. Tan, Y. Yang, C. Wang, H. Chen. *J. Am. Chem. Soc.* **2011**, 133, 11422 – 11425.
- [19] H. Sun, J. He, J. Wang, S.Y. Zhang, C. Liu, T. Sritharan, S. Mhaisalkar, M. Y. Han, D. Wang, H. Chen. *J. Am. Chem. Soc.* **2013**, 135, 9099 – 9110.

Chapter 3

Synthesis of Multiple Transition Metal Doped Hybrid Titanium Dioxide Nanowires

Hybrid materials had been focus of research due to their wide usage in electronic sector. Arrays of hybrid NWs, whether they were in the form of radial junction or axial junction, provide advantages such as strain relaxation, improved light adsorption and charge separation in solar cells. We had identified the key to grow hybrid TiO₂ NWs was to control the rate of ligand adsorption and TiO₂ deposition. Various methods had been adopted to increase ligand adsorption speed and decrease TiO₂ deposition rate. However, all the attempts had failed to control the lateral growth, and the most promising NWs structure obtained was not TiO₂. As we had exhausted all possible means but was unsuccessful, the project was halted.

3.1 Introduction

Hybrid materials had been focus of research due to their wide usage in electronic sector. One of the most important characteristics of hybrid material is the formation of p-n junction, which is the basic for creation of various electronic and photonic devices such as transistor, capacitor, diodes, LEDs, laser, electro-optic modulators and optoelectronic devices¹⁻³. Hybrid materials can adopts a number of morphology, but much interest had been given to hybrid nanowires (NWs), especially since the discovery of its usage in solar cells⁴. Arrays of hybrid NWs, whether they were in the form of radial junction or axial junction, provide advantages such as strain relaxation, improved light adsorption and charge separation in solar cells⁴.

The p-n junction in hybrid nanowires can be created via two methods: introduction of another material or doping. In the first method, p-n junction was created by joining two substrates together, which were normally an organic-inorganic combination, such as gold NWs with carbon nanotubes (Au NWs-CNT)⁵ and cadmium sulphite-polymer NWs (CdS-Pol NWs)⁶, while combination of two semiconductor are also very common, such as zinc oxide and copper oxide (ZnO-CuO)⁷⁻⁹. However, this method required the joining of two very different materials, which is often difficult and less tuneable. Besides that, the method developed to synthesize this type of hybrid NWs are mostly case specific with little to no generality.

The second method to create p-n junction in hybrid NWs is via doping, where one side of the NWs was doped with p-type dopant and the other side with n-type dopant. Sometimes, the middle part of the NWs was left un-doped, creating a p-i-n junction instead of a normal p-n junction¹⁰⁻¹¹. Doping method allows the tunings of doping concentration to control the conductivity, and are often more general, where a variety of dopants can be selected and doped into NWs using the same method to shift the energy bands relative to the Fermi level¹², which cannot be easily achieved in the previous method.

Our idea of creating hybrid TiO₂ NWs is through doping different segment of NWs with different transition metal ions. There were a variety of dopants reported for TiO₂, which generally can be divided into metal and non-metal dopant. Examples of non-metal dopant include nitrogen and carbon¹³, and metal dopant were normally transition metal such as iron (Fe), vanadium (V), copper (Cu) and manganese (Mn)^{12,14-15}, but doping with rare earth metal had been reported as well¹⁶. Most TiO₂ doping methods involved the incorporation of dopant during the synthesis step, but these methods were not ideal for creation of hybrid TiO₂ nanostructure, in which the doped part and un-doped part of TiO₂ had to undergo different growth mechanism. However, although doping via post treatment of TiO₂ is easier for creation of hybrid TiO₂ NWs, they normally involved high temperature and long annealing time, and only the surface of TiO₂ nanostructure was doped.

Here, we would like to develop a method to create hybrid TiO₂ NWs, where dopants were incorporated during the synthesis step. As reported by B. Liu et.al, they had successfully incorporated various transition metal dopants uniformly through the whole NWs, which include vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), niobium (Nb), molybdenum (Mo) and rhodium (Ru). With our studied on TiO₂ NWs growth mechanism as shown in previous chapter, we had gain enough understanding on growth of TiO₂ NWs and we think that it will be possible for us to create single or even multi-junction hybrid TiO₂ NWs via a 2 steps growing method, where controlling the growth rate of TiO₂ as the key strategy. Our initial synthesis design of multi-junction hybrid TiO₂ NWs was shown in Figure 3.1 below.

Figure 3.1 Synthesis scheme of multi-junction hybrid TiO₂ NWs via 2-step growth using molten salt method.

3.2 Results and Discussion

3.2.1 Identifying Problem and Solving Strategy

Before we attempt to synthesis hybrid TiO₂ NWs, it was important to identify the key challenge faced and develop a method for solving the problem. We had decided to use 2-step growth method to create hybrid TiO₂ NWs. However, from our study in previous chapter, we found that the TiO₂ NWs not only grow longer, but also grow thicker during the 2nd growth, as demonstrated in Figure 2.5. Hence, it will be important for us to identify what is the reason that caused the NWs to grow thicker, and how we can control it.

We think that the key point that controls the growth direction of TiO₂ NWs in molten salt is the competition between the absorption of ligand (sodium chloride, NaCl in this case) and deposition of TiO₂ on TiO₂ seed surface. The role of sodium chloride in the formation of TiO₂ NWs had been demonstrated by R. Babasri et. al., without the present of NaCl, only TiO₂ nanoparticles was formed¹⁷. As screw dislocation had been ruled out by atomic lattice image of NWs in Figure 2.1, and it was unlikely that NaCl act as template in molten state, it was highly possible that NaCl selectively stabilized the sides surfaces, limiting the nanowire growth on the side and forcing the nanowire to grow in only one direction. This behaviour was highly similar with the role of ligands in normal colloidal synthesis, thus NaCl can also be considered as ligand in this particular molten salt synthesis. It had been determined from the sharp selected area electron diffraction (SAED) patterns that the sides of the TiO₂ NWs was bounded by four {100} facets¹⁸. As the {011} facets that was observed at the tips of the nanowires was formed to minimize the total surface energy along with the {100} facets¹⁹, it can be concluded that NaCl binds preferentially to the {100} facets, which was the sides of NWs.

On a fresh TiO₂ surface, there is always a possibility for ligand to adsorb, or for new TiO₂ to deposit on it. If ligand adsorb onto fresh TiO₂ surface first,

the TiO₂ NWs will only grow longer, as NaCl ligand preferentially binds to {100} facets, which limits the growth in TiO₂ NWs diameter. However, if TiO₂ deposition happens before ligand adsorbs onto TiO₂ surface, the NWs will not only grow longer, but also grow thicker. This growth behaviour was illustrated in Figure 3.2 below.

Figure 3.2 Illustration showing how the competition between ligand adsorption and TiO₂ deposition affect the final morphology of TiO₂ NWs.

To solve the problem where TiO₂ NWs becomes thicker in 2nd growth, we need to suppress the lateral growth during synthesis, and controlling the speed of either or both the ligand binding and TiO₂ deposition is the key strategy. The suppression of lateral growth on TiO₂ NWs can be achieved either by increasing the adsorption speed of NaCl ligand on TiO₂ surface or decreasing the deposition speed of TiO₂, or the combination of both. Hence, our initial studies will focus on identifying factors or modification to tune the speed for both the process mentioned above.

3.2.2 Increase Ligand Adsorption Rate

We had identified that increase ligand (NaCl) adsorption speed and decrease TiO₂ deposition speed is the key point in controlling lateral growth in TiO₂ NWs (NWs becomes thicker). Of all method, we think that the easiest was to use un-washed TiO₂ nanorods (NRs) as the precursor. Freshly synthesized TiO₂ NRs surface will still be covered with NaCl ligand before undergoing washing step. Using un-washed TiO₂ NRs as precursor will decrease the chance of lateral growth as NaCl ligand already adsorbed on its surface, making TiO₂ deposition on the four sides of NRs impossible. As TiO₂ can only deposit on the tips, the NRs will only grow longer and not thicker.

Figure 3.3 SEM image of TiO₂ NWs obtained from 2nd growth using un-washed TiO₂ NRs as precursor.

Unfortunately, things did not work out as our prediction. As shown in Figure 3.3, the NWs still become thicker when un-washed TiO₂ NRs was used as precursor. This might be due to the binding strength of NaCl ligand on TiO₂

surface was weaker than we expected. In ideal case, NaCl which act as ligand should continue to adsorb on TiO₂ surface in the synthesis process. However, our product had indicates that the ligand detached from TiO₂ NRs surface during synthesis, might happen even before reaching the reaction temperature. This is due to the fact that eutectic salt pair (NaCl-Na₂HPO₄) melts at 750 °C, while TiO₂ ripening (or growth) happens around 800 °C.

Since our first attempt to increase ligand adsorption speed had fail, we had proposed to alter the mixing method to provide better mixing between the reactants. Previously we had been using mortar and pestle to mix the reactants; however, this is not an effective mixing method, especially for nano-size materials. The inhomogeneous mixing might results in some TiO₂ NRs precursor had limited access to NaCl ligand, and without any ligand blocking the side surface, the NWs continue to grow thicker and thicker. Hence, we think that by changing the mixing method from mortar and pestle to sol mixing, we can ensure that all TiO₂ NRs precursor was surrounded by NaCl ligand uniformly, and we can rule out the possibility that 2nd growth product was formed from inhomogeneous mixing.

Figure 3.4 SEM image of 2nd growth TiO₂ NWs obtained from using sol mixing method.

The sol mixing method involved the addition of a very small amount of water into the mixture of TiO₂ NRs, NaCl and Na₂HPO₄, where they form a very thick, white paste. The paste was then mixed excessively using a glass rod to achieve a homogeneous mixing of the reactant. Next, the resulting white paste was dried in oven before heated in furnace. Despite our effort, the resulting TiO₂ NWs still grow thicker as shown in Figure 3.4, which indicates to us that TiO₂ NRs precursor had sufficient access to NaCl ligand, and mixing was not a key factor in controlling ligand adsorption speed.

From our previous attempts, it seems that NaCl was not a very strong ligand and did not adsorb onto TiO₂ NRs surface fast enough. Hence, we had decided to tune the ligand binding strength and absorption speed by replacing NaCl with other types of salt, where we hoped to find a ligand which is strong enough and adsorb onto TiO₂ surface fast enough to suppress lateral growth in 2nd growth product. There were a few criteria which were considered when selecting replacement for NaCl. The first and most important criteria are that

the replacement salt must be able to withstand the high reaction temperature, where the salt cannot decompose upon long heating at 825 °C. A part from that, it was preferable that the replacement salt have close or lower melting temperature as NaCl. This is to ensure that molten salt state can be achieved at reaction temperature of 825 °C. From the safety and ease of handling view point, the replacement salt should not be corrosive or release any toxic gas or compound upon heating. Using these criteria, we had selected 13 types of salt, and we had first tested if any TiO₂ NWs can be formed using these salts. The results obtained were as followed:

Figure 3.5 SEM images of TiO₂ NWs obtained when different salt was used to replace NaCl. A. NaCl (control). B. KCl C. MgSO₄. D. Na₂MoO₄. E. NaF. F. NaBr. G. Na₂SO₄. H. K₂SO₄.

Figure 3.6 SEM images of product obtained when the following salt was used to replace NaCl: A. Na₂WO₄. B. Na₂TeO₃. C. Na₂SiO₃. D. Na₂CO₃. F. K₂CO₃. G. NaOAc.

Figure 3.5 illustrated TiO₂ NWs obtained when NaCl was replaced by potassium chloride (KCl), magnesium sulphate (MgSO₄), sodium molybdate (Na₂MoO₄), sodium chloride (NaF), sodium bromide (NaBr), sodium sulphate (Na₂SO₄) and potassium sulphate (K₂SO₄). These salts, where we named as NWs forming salt, were generally group 1 salt, with the exception of MgSO₄. Some of these were expected to form NWs, as they have similar chemical component as NaCl, thus they were expected to interact similarly with TiO₂ as NaCl. Some of the examples were KCl, NaF and NaBr; all were a combination of group 1 cations and group 17 anions, just like NaCl, where the TiO₂ NWs obtained from each of these salts only differ in diameter and length. A part from that, sulphate salt seems to be working as well, although the NWs formed from these sulphate salts were much shorter compared to those of NaCl. From our experiments, most oxometalate salt did not give TiO₂ NWs or NRs as product, with the exception of Na₂MoO₄. This might be due to molybdenum as a second row transition metal its resulting oxometalate ion was much smaller than other oxometalate ions tested, and were able to come closer together, which might result into more effective binding on (110) surface to form NRs.

On the other hand, not all group 1 salt was able to give NWs as product. Sodium tungstate (Na₂WO₄), sodium tellurite (Na₂TeO₃), sodium silicate (Na₂SiO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃) and sodium acetate (NaOAc) were all group 1 salt, but no NWs was observed as product. As mentioned in previous paragraph, oxometalate salts were not NWs forming salt, possibly due to their large ionic size. Silicate and acetate salts might not be good as well, most likely due to their weak ionic strength which was not strong enough to binds on TiO₂ surface; similar case with carbonate salt as well. The NWs forming salt and non-NWs forming salt was summarized in the Table 3.1 below.

Table 3.1 Summary of NWs forming and non-NWs forming salt.

NWs Forming Salt	Non-NWs Forming Salt
Group 1 halides <ul style="list-style-type: none"> • NaCl • KCl • NaF • NaBr 	Group 1 carbonates <ul style="list-style-type: none"> • Na₂CO₃ • K₂CO₃
Group 1 sulphates <ul style="list-style-type: none"> • Na₂SO₄ • K₂SO₄ 	Sodium oxometalates <ul style="list-style-type: none"> • Na₂WO₄ • Na₂TeO₃
Group 2 sulphates <ul style="list-style-type: none"> • MgSO₄ 	Sodium silicates <ul style="list-style-type: none"> • Na₂SiO₃
Sodium oxometalates <ul style="list-style-type: none"> • Na₂MoO₄ 	Sodium acetates <ul style="list-style-type: none"> • NaOAc

After we had determined salts which will give NWs, we can proceed to the next stage which is testing the salt adsorption speed in 2nd growth, where we hoped to observe less growth in lateral direction of the TiO₂ NWs formed. We had chosen NaBr, NaF, MgSO₄ and K₂SO₄.

Figure 3.7 SEM images for product obtained in 2nd growth when NaCl was replaced with other NWs growing salt. A. NaBr. B. NaF. C. MgSO₄. D. K₂SO₄.

As shown in Figure 3.7, when NaCl was replaced with NaBr and NaF, the resulting NWs grew much longer and thicker during the 2nd growth. This results was expected as TiO₂ NWs obtained from NaBr and NaF were much thicker compared with those obtained from NaCl as shown in Figure 3.5. Hence, it was not surprising the 2nd growth products obtained from these salts will be somewhat similar in length and diameter as those obtained in 1st growth (Figure 3.5). On the other hand, high expectation was placed on MgSO₄ and K₂SO₄ product as these salts give rather thin NWs previously in 1st growth (Figure 3.5). However, irregular shaped particles were obtained as product. This might be due to both sulphate salts were not fast enough to absorb on TiO₂ surface to block it before TiO₂ deposition, which results in random growth of TiO₂ at all direction, thus forming these irregular shaped particles.

All our attempts to increase NaCl ligand binding speed to prevent growth in lateral direction, such as using un-washed precursor, changing mixing method and replacing NaCl salt in synthesis had all failed. Hence, we decided to move on to developing methods to slow down TiO₂ deposition speed instead.

3.2.3 Decrease TiO₂ Deposition Rate

Our strategy to decrease TiO₂ deposition speed during 2nd growth focused on modifying the TiO₂ precursor. We wanted a TiO₂ precursor which is harder to convert to rutile phase, so as to decrease the deposition of TiO₂ on the seed TiO₂ NRs, which give time for the NaCl to bind onto the surface first and suppress lateral growth.

Figure 3.8 SEM images of TiO₂ NWs obtained when Ti(OH)_x was used as precursor for 2nd growth.

We had change the TiO₂ source of 2nd growth from the normal P25 NPs to titanium hydroxide [Ti(OH)_x]. This is based on the fact that Ti(OH)_x need to be converted to TiO₂ in amorphous phase first, before converting to rutile phase and deposit onto TiO₂ NRs which act as seed in 2nd growth, hence giving time for NaCl to absorb onto TiO₂ NRs surface first. However, the TiO₂ NWs obtained still shown significant lateral growth, resulting in very thick NWs, which indicates that the TiO₂ deposition speed is still not slow enough.

To counter this, we had switch to another way of modifying TiO₂ precursor. We decided to use TiO₂ NPs pre-heated with NaCl and Na₂HPO₄ salt mixture as precursor, where the TiO₂ source is now Na₄P₂TiO₉ rather than TiO₂ NPs. This design was based on previous literature, where Na₄P₂TiO₉ crystal structure will slightly change when cooled down, which we depict this as the

inactive form (cannot provide TiO₂ material). Our assumption is that once Na₄P₂TiO₉ crystal was cooled down and become inactive, it will take some time for it to change back to the active form even at high temperature, thus slowing the TiO₂ deposition speed onto TiO₂ NRs. If our assumption is correct, this should give enough time for NaCl ligand to bind onto TiO₂ NRs seed, and we should be observed less growth occurred on the lateral direction.

Figure 3.9 Illustration depicting how switching to Na₄P₂TiO₉ precursor will influence the final TiO₂ NWs product.

For comparison, we had prepared three types of Na₄P₂TiO₉ to be used as TiO₂ precursor in 2nd growth, which was rutile NPs, P25 NPs and anatase NPs preheated with NaCl and Na₂HPO₄ respectively. The morphology of preheated precursors mostly remain as NPs, with the exception of preheated P25 NPs, which form short NRs as shown in Figure 3.10.

Figure 3.10 SEM images of preheated TiO₂ with salts precursors and their respective 2nd growth product. A. Preheated rutile NPs. B. Preheated P25 NPs. C. Preheated anatase NPs. D. 2nd growth product from preheated rutile NPs. E. 2nd growth product from preheated P25 NPs. F. 2nd growth product from preheated anatase NPs.

As shown in Figure 3.10, the 2nd growth product obtained from preheated P25 NPs and anatase NPs were similar to those obtained when normal P25 NPs was used as precursor. However, preheated rutile NPs precursor gives product which consist of high aspect ratio NWs. This means that the growth in longitudinal direction was far more dominant compared to the growth in lateral direction. Although the NWs still become thicker, which means growth in lateral direction was not completely suppress, the fact that growth in longitudinal direction was much more indicates that the deposition rate of TiO₂ had slow down significant enough, where the competition between ligand absorption and TiO₂ deposition had becomes much greater. This provides a direction for us to further fine tune and control the TiO₂ deposition rate.

Figure 3.11 X-ray diffraction (XRD) spectrum of NWs product obtained from 2nd growth using preheated rutile NPs as precursor as compared with XRD spectrum of pure rutile and anatase.

Before further optimization was done, the NWs product obtained from 2nd growth of TiO₂ NRs using preheated rutile NPs and salt mixture as precursor was characterized with X-ray diffraction (XRD) spectroscopy to make sure that the product was indeed TiO₂, preferentially still in rutile phase. However, as shown in Figure 3.11, the XRD spectrum of our product only partially overlapped with the XRD spectrum of pure rutile, and did not overlapped at all with XRD spectrum of pure anatase, which suggests the product we obtained were not TiO₂. In fact, the XRD spectrum of our product match perfectly to those of Na₂Ti₆O₁₃, which had made our previous discovery useless as the high aspect ratio of NWs, originates from a change in chemical structure rather than lowering of TiO₂ deposition rate as we had expected.

3.3 Conclusion

In summary, we had identified the key to grow hybrid TiO₂ NWs was to control the rate of ligand adsorption and TiO₂ deposition. We had tried various methods to increase ligand adsorption speed, such as using un-washed precursor, changing mixing method and replacing NaCl salt, and modifying TiO₂ precursors to decrease TiO₂ deposition rate. However, all the attempts had failed to control the lateral growth or the NWs obtained was not TiO₂. As we had exhausted all possible means but was unsuccessful, the project was halted.

3.4 Detailed Experimental Section

Materials and Characterization:

All chemicals were used as purchased without further purification. Anatase TiO₂ nanoparticles (TiO_{2(A)}), magnesium sulphate (MgSO₄), P25 nanoparticles (P25), rutile TiO₂ NPs (TiO_{2(R)}), sodium acetate (NaOAc), sodium bromide (NaBr), sodium chloride (NaCl), sodium carbonate (Na₂CO₃), sodium fluoride (NaF), sodium molybdate (Na₂MoO₄), sodium phosphate dibasic (Na₂HPO₄), sodium silicate (Na₂SiO₃), sodium sulphate (Na₂SO₄), sodium tungstate (Na₂WO₄), sodium tellurate (Na₂TeO₃), potassium carbonate (K₂CO₃), potassium chloride (KCl) and potassium sulphate (K₂SO₄) were purchased from Sigma-Aldrich, titanium tetrafluoride (TiF₄) was purchased from STREM and sodium hydroxide (NaOH) were purchased from Sinopharm. Field emission scanning electron microscope (FE-SEM) images were collected on a JEOL JSM-6700F Scanning Electron Microscope. Acetone, deionized water and ethanol treated silicon wafer of 1cm × 1cm were used to prepare SEM samples.

TiO₂ Nanorods (NRs) Synthesis:

Following molten salt method from B. Liu¹⁸, the rutile TiO₂ nanorods were synthesized by mixing P25, NaCl and Na₂HPO₄ in 4:4:1 weight ratio. The mixture was then grinded with mortar and pestle and put into crucible, heated at 825° C for 8 hours in a tube furnace. After the mixture was cooled to room temperature, the nanorods were washed with boiling water and dried before used in further synthesis.

Ti(OH)_x Synthesis:

200 g of TiCl₄ was added into 1L of NaOH solution (10 M) at 30 °C. The solution was stirred and heated at 70 °C for 5 hours. After that, the resulting white precipitate was filter out, washed with water and dried in air.

Preheated TiO₂ NPs Preparation:

P25 NPs was mixed with NaCl and Na₂HPO₄ in 8:9:2.25 weight ratio. The mixture was mixed with mortar and pestle, and heated at 825 °C for 10 minutes. Then, the mixture was cooled down rapidly to avoid further reaction. Preheated rutile and anatase precursor can be prepared via the same method by replacing P25 NPs with rutile NPs or anatase NPs of the same weight.

2nd growth of TiO₂ NWs:

TiO₂ NRs seed: P25 NPs weight ratio of 1:8 was prepared. Then, this TiO₂ material was mixed with NaCl and Na₂HPO₄ in 4:4:1 weight ratio using mortar and pestle. The mixture was then heated to 825°C for 8 hours. After that, the mixture was cooled to room temperature and washed with boiling water. For some experiments, the NaCl in the synthesis was replaced by other salt such as NaBr, NaF, KCl etc. In some case, the P25 NPs was replaced with Ti(OH)_x. In the case where preheated TiO₂ NPs were used, TiO₂ NRs was added into the preheated mixture, making sure the weight ratio of TiO₂ NRs: TiO₂ NPs present was 1:8 (Weight ratio of TiO₂ NRs: preheated mixture = 1:19.25)

In the case where unwashed TiO₂ NRs was used, the amount of NaCl and Na₂HPO₄ present along with the NRs was deduced by back calculating their respective weight ratio (Assumption: all P25 NPs had reacted to form NRs) (Example: if 900 mg of unwashed TiO₂ NRs was weighted, 400 mg will be TiO₂ NRs, 400 mg will be NaCl and 100 mg will be Na₂HPO₄). After the actual amount of TiO₂ NRs was determined, the weight ratio between TiO₂ NRs: P25 was weighted to be 1:8, and the total weight of TiO₂: NaCl: Na₂HPO₄ present was adjusted to be in 4:4:1 weight ratio. After that, all procedure followed.

References

- [1] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang. *Chem. Soc. Rev.* **2014**, 43, 5234-5244.
- [2] Y. P. Yuan, L. W. Ruan, J. Barber, S. C. J. Loo, C. Xue. *Energy Environ. Sci.*, **2014**, 7, 3934-3951.
- [3] P. Krogstrup, H. I. Jørgensen, M. Heiss, O. Demichel, J. V. Holm, M. Aagesen, J. Nygard, A. F. i Morral. *Nature Photonics* **2013**, 7, 306-310.
- [4] E. C. Garnett, M. L. Brongersma, Y. Cui, M. D. McGehee. *Annu. Rev. Mater. Res.* **2011**, 41, 269–295.
- [5] N. Chopra, J. Wu, P. Agrawa. *J. Nanomater.* **2015**, 2015, 125970.
- [6] N. Kumar, V. Dutta. *J. Colloid Interface Sci.* **2014**, 434, 181-187.
- [7] S. Das, V. C. Srivastava. *Materials Science in Semiconductor Processing*, **2017**, 57, 173-177.
- [8] K. Vijayalakshmi, K. Karthick. *J. Mater. Sci. - Mater. Electron.* **2014**, 25, 832 - 836.
- [9] R. Saravanan, S. Karthikeyan, V.K. Gupta, G. Sekaran, V. Narayanan, A. Stephen. *Mater. Sci. Eng., C* **2013**, 33, 91-98.
- [10] J. Yoo, B. M. Nguyen, I. H. Campbell, S. A. Dayeh, P. Schuele, D. Evans, S. T. Picraux. *ACS Nano*, **2015**, 9, 5154–5163.
- [11] P. Zhang, P. Liu, S. Siontas, A. Zaslavsky, D. Pacifici, J. Y. Ha, S. Krylyuk, A. V. Davydov. *J. Appl. Phys.* **2015**, 117, 125104.
- [12] M. Ge, C. Cao, J. Huang, S. Li, Z. Chen, K. Q. Zhang, S. S. Al-Deyab, Y. Lai. *J. Mater. Chem. A*, **2016**, 4, 6772–6801.
- [13] A. Yu, G. Wu, F. Zhang, Y. Yang, N. Guan. *Catal Lett* **2009**, 129, 507–512.
- [14] W. Li, X. Liu, H. Li. *J. Mater. Chem. A*, **2015**, 3, 15214–15224.
- [15] M. Xu, P. Da, H. Wu, D. Zhao, G. Zheng. *Nano Lett.* **2012**, 12, 1503–1508.

- [16] H. Liu, L. Yu, W. Chen, Y. Li. *J. Nanomater.* **2012**, 2012,235879.
- [17] B. Roy, S.P. Ahrenkiel, P.A. Fuierer. *J. Am. Ceram. Soc.*, **2008**, 91, 2455 – 2463.
- [18] B. Liu, H.M. Chen, C. Liu, S.C. Andrews, C. Hahn, P. Yang. *J. Am. Chem. Soc.* **2013**, 135, 9995 – 9998.
- [19] M. Ramamoorthy, D. Vanderbilt, R.D. Kingsmith, *Phys. Rev. B* 1994, 49, 16721 – 16727.

Chapter 4

Noble Metal Nanowires Array as a Novel Class of Electrocatalyst

Ethanol oxidation had gain a lot of attention due to its used in direct ethanol fuel cells (DEFCs). Well-aligned noble metal (NM) nanowire arrays were grown on conductive electrodes based on a seeded solution growth method. The nanowire arrays simultaneously provide high electrochemical active surface for electrocatalysis, facilitate the diffusion of reactants and products, and improve the electronic charge transport. Our best nanowire arrays exhibited much enhanced electrocatalytic activity, achieving 38.0 times increase in specific activity over the commercial catalysts for ethanol electrooxidation. These noble metal nanowire array catalysts provide a new direction to enhance the electrocatalytic activity and reduce the size of electrode for miniaturization of portable electrochemical devices.

4.1 Introduction

The growth of gold nanowires (Au NWs) array or “forest” on substrate surface had been reported by J. He¹. This growing method was unconventional as the vertically align Au NWs only growth from gold seed (Au NS) bounded onto substrate surface (Figure 4.1). The advantages of this Au NWs growth method were they can be grow in large scale of up to tens of cm² and ambient conditions, unlike vapour-liquid-solid (VLS) growth method that required high temperature. A part from that, the diameter of this Au NWs was independent from the size of the Au NS, which implied a highly tunable NWs diameter via changing the ligand 4-mercaptobenzoic acid (4MBA) concentrations. Besides that, the length of Au NWs can be easily tuned by controlling the reaction time. These characteristics makes Au NWs forest a good candidate as fixed-bed catalyst or electrocatalyst. Furthermore, the Au NWs were shown to be able to grow on various substrate surfaces such as glass, seashell, plastic and paint, not just limited to silica wafer. The ability for the Au NWs to grow on conductive substrates also makes it easier to handle for electrocatalysis testing.

Figure 4.1 Au NWs forest growth illustrated in literature. Reprinted with permission from ref. [1]. Copyright © 2013, American Chemical Society.

However, before these Au NWs forest can be utilised as electrocatalyst, there were a few challenges that needed to be solved first. As Au NWs cannot stand on its own, the platform at which electrocatalyst can be performed becomes a very important factor. A part from being conductive, the platform should also have large surface area to fully utilise the capacity of our NWs. Besides that, as the conditions to catalyse each reactions were different, the types of reaction that we hoped to utilise our NWs forest system should be determined first so that the electrocatalyst can be optimized accordingly. Another challenge faced was the mechanical strength and stability of the Au NWs forest. Although fairly stable when dried, the Au NWs grown on silica wafer as demonstrated by the author can be scratched away easily when the wafer was wet, hence the mechanical stability of Au NWs must be improved to be used as electrocatalyst, which will be in contact with electrolyte solution most of the time. Other than the problems mentioned above, the material of the NWs forest itself might also be an issue. Gold is only an active catalyst in limited reactions such as carbon monoxide oxidation; hence Au NWs might not be a good choice for electrocatalysis. Therefore, there is a need to develop a method to coat other materials such as metals and oxides evenly on Au NWs, not just to increase the catalytic performance, but also to widen the range of reactions where our NWs forest system can be utilised.

Here, we would like to report the usage of our noble metal NWs forest as electrocatalyst for ethanol oxidation reaction (EOR). Our NWs forest not only provides a high electrocatalytic active surface area (ECSA), but also improves mass transport and conductivity of the catalyst, which results in tremendous increase in EOR catalytic activity.

4.2 Design Principle

Fuel cells have higher fuel conversion and electrical efficiencies as compared with conventional combustion or power generation technologies²⁻³. Liquid fuels such as methanol or ethanol are of particular interest because of their high volumetric energy density and ease of handling as compared with other fuels such as hydrogen, apart from being less toxic and renewable, leading to the development of direct alcohol fuel cells (DAFCs)³. DAFCs rely on reactions between the fuel (methanol or ethanol) at the anode and the oxidant (molecular oxygen) at the cathode³. Both anode and cathode require efficient catalysts to lower the electrochemical overpotential for high energy conversion efficiency. So far, platinum (Pt) is still the best anode catalyst, but the usage has been greatly limited by its prohibitive cost⁴⁻⁵. Compared with Pt, palladium (Pd) is more abundant and has good catalytic activity for alcohol oxidation; it works under basic condition which is more amenable for device fabrication; however its catalytic activity is inferior to Pt⁶⁻⁷. Therefore, how to improve the catalytic activity of Pd for alcohol oxidation to match that of Pt has attracted increasing interest.

Various approaches have been proposed to improve the performance of Pd electrodes. For example, facet engineering⁸⁻⁹ or alloying, either with transition metal¹⁰⁻¹¹ or oxide¹²⁻¹³, was found to positively influence the catalytic activity of Pd. To increase the electrochemical active surface area (ECSA) while maintaining good electrode conductivity and mass transport properties, Pd electrocatalysts were grown into one-dimensional nanostructure¹⁴⁻¹⁵ or loaded onto high aspect ratio supports, such as carbon nanotubes¹⁶⁻¹⁷, oxide nanotubes¹⁸ or graphene¹⁹⁻²⁰. However, all of the previous efforts only made marginal improvements in the electrocatalytic activity of Pd towards alcohol oxidation.

Our noble metal (NM) nanowire arrays offer the advantages to simultaneously improve all factors that govern the electrocatalytic performance.

The nanowire arrays synthesized via seeded solution growth method were able to provide high electrochemical active surface for electrocatalysis, while at the same time facilitate the diffusion of reactants and products, and improve the electronic charge transport. These improvements collectively lead to superior catalytic activity by more than one order of magnitude as compared to the state-of-the-art commercial catalysts for electrochemical applications. The synthesis of nanowire arrays can be readily scaled up to make electrodes up to square meters, which should provide a new direction to enhance the electrocatalytic activity and reduce the size of electrode for miniaturization of portable electrochemical devices.

4.3 Results and Discussion

4.3.1 Selection Criteria and Initial Results

Before the start of any electrocatalysis, we had to select a suitable support or substrate to grow the Au NWs array on. The support must be conductive for our Au NWs to function as an electrocatalyst. Apart from that, unlike other electrocatalysts which were loaded onto the substrate or support, considering the fact that our Au NWs will grow directly on the substrate, it will be hard to completely clean and reuse the substrate. Hence, supports or electrodes meant to be reused such as glassy carbon electrode which cost quite a lot might not be a good choice in our case. Instead, cheap and disposable support such as fluorine doped tin oxide (FTO) glass or indium doped tin oxide (ITO) glass might be a more suitable choice. However, this type of support might not be optimum to be utilised in devices and meant to be used for preliminary screening only. It was hoped that we were able to further enhance the advantages offered by our NWs array in three dimensional supports such as carbon cloth and nickel foam.

After the support had been decided, it was now important to improve the mechanical strength, more specifically, the binding between Au NWs and FTO glass surface. As mentioned previously, Au NWs only bind weakly to silica wafer surface and can be scratched away easily in wet condition. Similar phenomena had been observed for Au NWs on FTO glass surface. Some of the Au NWs can be observed to peel off from FTO glass surface during Au NWs synthesis and washing steps, even by using naked eyes, indicating a significant amount of Au NWs were lost. We had identified that the problem might lie in the uneven spreading of 3-(aminopropyl)triethoxysilane (APTES) which was used to help the adsorption of Au NWs on FTO glass surface. As APTES was not spread evenly, the FTO glass surface has an uneven amount of APTES. Those parts with less APTES have weaker binding strength of Au NWs, which results

in Au NWs easily peeled off from FTO surface. To improve the mechanical stability of Au NWs on FTO glass, we had treated the FTO glass surface with oxygen plasma, which not only clean the FTO surface free of any contaminant, but also improve the hydrophilicity of FTO glass. After the plasma treatment, APTES can be spread evenly onto FTO glass surface, which improve the binding between APTES and glass surface, thus improve the binding between Au NWs and glass surface as well. Apart from that, it was also observed that introducing a protective layer was able to improve the mechanical stability of the Au NWs. Generally, Au NWs with a layer of coating, whether with metals or oxides, were less likely to peel off from FTO glass. This might be due to the coating materials not only coat on Au NWs, but at the same time some might deposits on FTO glass surface and joint with those coated on Au NWs, which might provide extra binding force with the support, thus resulting in more mechanical stable NWs array.

Due to the nature of our NWs array and its synthesis method, it might not be suitable to be use as electrocatalyst in some of the reactions. One of such examples is reactions involving gas, or more specifically, reactions that produce large amount of gas. These gas products will form air bubbles around the Au NWs array. When they were released from the catalyst surface, the capillary force produced was enough to tear the Au NWs array apart, causing them to peel off from FTO glass surface. Therefore, it was not possible to use our NWs as electrocatalyst for reaction such as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). A part from that, we have to exclude any reactions conducted under acidic conditions, as present of acid will destabilise APTES which was used to bind the Au NWs with FTO glass surface, which results in peeling off of the NWs array. Therefore, until we can find a replacement of the binding chemical APTES, we can only stick to reaction conducted under neutral or basic conditions.

Figure 4.2 SEM images of Au NWs with different length.

The Au NWs synthesized was characterized using scanning electron microscopy (SEM). As shown in Figure 4.2, the Au nanowires stand densely and vertically on the substrate. The diameter of the Au nanowires is around 3 – 5 nm while the length can be simply tuned by changing the growth time. The entire growth process took less than 2 hours at room temperature, making this a fast and easy method to growth NWs array.

Figure 4.3 Electrocatalytic properties of Au NWs. A. CV curves of Au NWs, Au NPs and detached Au NWs catalysts measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s. Insert shows the zoom in CV curves of Au NPs and detached Au NWs. B. Chronoamperometry graph measured at 1.07 V vs. RHE. C. CV curves of for Au NWs, Au NPs and detached Au NWs measured in solution of 0.5 M H₂SO₄ at a scan rate of 50 mV/s. D. Specific current and current density comparison of Au NWs, Au NPs and detached Au NWs.

The electrocatalytic properties of as-prepared NM nanowire arrays were evaluated and compared to the state-of-the-art nanoparticle (NP) electrocatalysts. Figure 4.3A displays the cyclic voltammetry (CV) curves, which show that the Au nanowire arrays exhibit significantly higher catalytic activity towards ethanol electrooxidation as compared with the gold nanoparticles (Au NPs), which can be clearly observed from the forward oxidation peak at 1.3 V vs. RHE. The maximum mass specific current of Au nanowire arrays reaches 1345.0 A/g, which is 11.6 times higher than that of the

Au NPs (115.7 A/g). Additionally, the Au nanowire arrays also exhibit excellent electrocatalytic durability throughout 1 hour of continuous electrochemical operation. It is well-known that pure Au is not a good electrocatalyst for ethanol oxidation. Even so, our Au nanowire arrays were able to display significantly enhanced catalytic performance, not just matching, but exceeding the performance of the commercially available, state-of-the-art palladium on carbon (Pd/C) catalyst by 7.8 times.

4.3.2 Coating of Au NWs Array with Metals

To further improve the catalytic performance of our Au NWs array, we had decided to coat Au NWs array with a layer of metal, especially noble metal such as Pd or Pt which had proven to be effective catalyst for ethanol oxidation reaction. Hence, we need to develop a method which was able to coat a layer of metal evenly on the surface of Au NWs array.

Figure 4.4 TEM images of Au NWs coated with various metal. A. Au@Bi NWs. B. Au@Cd NWs. C. Au@Co NWs. D. Au@Cu NWs. E. Au@Ni NWs. F. Au@Pd NWs.

First, we had tried to coat Au NWs with the solution based hydrazine reduction method reported by P.R Sajanlal and T.Pradeep⁴⁹. This method reduce metal in the form of chloride salt at high temperature via hydrazine, in the present of sodium hydroxide (NaOH) and cetyltrimethylammonium bromide (CTAB) as protecting ligand. We had tried to coat nickel (Ni) and cobalt (Co) as illustrated in the literature, and then extended the method to other salt such as bismuth (Bi), cadmium (Cd), copper (Cu) and palladium (Pd). The

results obtained were shown in Figure 4.4. With the exception of Bi and Cd, a clear shell layer can be observed in all the samples. Even so, we had assumed that all the coating was successful as both NWs that underwent Bi and Cd had become thicker. Although this method had successfully coated Au NWs with various metals, including our target metal Pd, the coating was thick and uneven. This will not be beneficial to our dense NWs array as such uncontrollable coating often results in fusing of neighbouring NWs into a thick film, which make us lost all the advantages offered by our NWs array. Hence, we need to find a more controllable method to coat metal, especially Pd onto Au NWs.

Figure 4.5 SEM images depicting different Pd coating that was obtained by tuning the surface energy between Au and Pd. A. Au NWs covered with an even layer of Pd shell. B. Au NWs covered with bumpy and uneven Pd shell. C. Au NWs with uneven Pd coating and a huge Pd lump at the root. D. Au NWs with teeth-like Pd island on surface. E. Au NWs with Pd concentrating on the tip. F. Au NWs decorated with Pd NPs.

To obtain an even Pd shell on Au NWs, we had decided to switch to another solution based, ascorbic acid reduction method. This coating method make use of our knowledge of tuning the surface energy between Au and Pd to achieve a controllable, even coating of Pd on Au NWs. Freshly prepared Au

NWs surface was covered with 4-mercaptobenzoic acid (4MBA) ligand. These 4MBA ligands interact with each other through strong π - π stacking, increasing the surface energy of Au, making it almost impossible for anything to coat on it. Hence, Au NWs decorated with Pd nanoparticles (NPs) such as those in Figure 4.5f was obtained, where the Pd NPs might not be physically bonded to the Au surface. However, this problem can be solved by removing the 4MBA ligand from Au surface. As there is only a small lattice mismatch between Au and Pd (less than 5%), when a slow reduction method such as ascorbic acid reduction was used, there is a high chance of Pd to deposit on Au, forming an even layer of Pd shell on Au NWs as illustrated in Figure 4.5a. The thiol functional group of 4MBA bonded very strongly to Au surface, and our strategy to remove it was to replace 4MBA with another thiol containing small molecules at high temperature, which can then be washed away easily due to its small size and weak intermolecular interaction. The thiol molecule we had chosen in this case was mercaptoacetic acid (MAA).

Furthermore, to illustrate our point of tuning interfacial energy with ligand, we had also perform the ligand exchange step in various solvent and temperature, to produce situations which either favour 4MBA or MAA ligand on Au NWs surface, and observed if there was any change in Pd shell morphology. As our prediction, in situations where 4MBA is preferred to stay on Au NWs surface, such as using solvent where 4MBA has a low solubility (cyclohexane), only a small amount of Pd was deposited on the tip of Au NWs (Figure 4.5e). In another situation where ligand exchange step was performed at room temperature, there was not enough energy to drive the exchange of 4MBA with MAA, hence a fair amount of 4MBA still remain on Au surface, resulting in uneven Pd coating with Pd lumps present on the tip or the root of Au NWs (Figure 4.5c). Another point to note was that simply washing the Au NWs without ligand exchange cannot remove the 4MBA ligand effectively. Even when the Au NWs was treated in ethanol solvent where 4MBA was very soluble in and with high temperature, the removal of 4MBA is still not

complete, results in Pd island formation on Au NWs (Figure 4.5d), indicating that ligand exchange was essential in this coating step. Due to the importance of this ligand exchange step, it was crucial to find a solvent where both 4MBA and MAA ligand can dissolve fairly well. We had found that the best solvent for ligand exchange was dimethylformamide (DMF), where an even Pd shell can be obtained consistently, although other solvent such as ethanol and hexane work as well. However, some solvent such as tetrahydrofuran (THF) give Pd shell with an uneven or bumpy surface (Figure 4.5b), probably due to interaction of left over solvent molecule with Pd surface.

Figure 4.6 Physical characterization of vertically aligned Au and Au@Pd nanowire forest. A & B. Large area SEM image of Au and Au@Pd NWs. C. TEM image of Au NWs. D. HRTEM image of Au NWs. E. TEM image of Au@Pd NWs. F. HRTEM image of Au@Pd NWs. G & H. HRSTEM image of Au@Pd NWs showing clear core-shell nanostructure. I & J. Electron energy loss spectroscopy (EELS) mapping of a single Au@Pd NW as displayed in H &

K. Energy dispersive X-ray spectroscopy (EDX) line scan along the cross-section of a single Au@Pd NW as shown in H.

After optimizing the ligand exchange condition (MAA in DMF solvent, 65°C) to obtain an even Pd shell on Au NWs, physical characterization was performed to confirm the present of uniform Pd shell on Au NWs surface. After coating Pd on Au nanowires (Au@Pd NWs), the nanowires can be seen to remain vertically aligned but their diameters slightly increase to 5 – 8 nm, and the thickness of Pd shell is tunable simply by varying the Pd precursor concentration and/or Pd coating time (Figure 4.6b and e). The crystal structure was examined by transmission electron microscopy (TEM). Both Au and Au@Pd nanowires are quasi-single-crystalline (Figure 4.6d and f). Energy-dispersive X-ray spectroscopy line scan and electron energy loss spectroscopy (EELS) elemental mapping were conducted to investigate the Pd distribution in Au@Pd nanowires (Figure 4.6g to k), from which, it is clear that Pd has been successfully enwrapped on the outer surface of Au nanowires to form a core-shell nanoarchitecture (Figure 4.6g and h).

Figure 4.7 A digital photograph showing the bare FTO glass, FTO glass with Au NWs, and FTO glass with Au@Pd NWs.

Figure 4.8 Electrocatalytic properties of Au@Pd NWs. A. CV curves of Au@Pd NWs, Pd/C and detached Au@Pd NWs catalysts measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s. Insert shows the zoom in CV curves of Pd/C and detached Au@Pd NWs. B. Chronoamperometry graph measured at 0.87 V vs. RHE. C. CV curves of for Au@Pd NWs, Pd/C and detached Au@Pd NWs measured in solution of 0.5 M H₂SO₄ at a scan rate of 50 mV/s. D. Specific current and current density comparison of Au@Pd NWs, Pd/C and detached Au@Pd NWs.

NWs arrays including Au and Au-core-Pd shell were grown on conductive FTO substrates for electrocatalysis (Figure 4.7). Pd was known to be an effective electrocatalyst for ethanol oxidation reaction (EOR) in basic condition. Hence, when Au nanowires were coated with a thin layer of more effective ethanol oxidation catalyst – Pd, we expect the EOR performance to increase. In fact, the electrocatalytic activity was immediately doubled. The forward oxidation peak mass specific current of Au@Pd NWs arrays at 1.0 V vs. RHE increases to 2237.7 A/g, which is an astonishing 12.9 times higher

than that of the commercially available, state-of-the-art Pd/C (172.6 A/g), making this the highest among all reported Pd-based electrocatalysts (Figure 4.8a).

4.3.3 Origin of Nanowires Array Astonishing Performance

Before proceed on any investigation on the performance of our Au@Pd NWs, we had to first rule out any possible synergistic effect caused by the Au-core and Pd-shell, as we had been comparing our Au@Pd NWs performance with a pure Pd catalyst (Pd/C).

Figure 4.9 CV curves of Pd NPs and Au@Pd NPs measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s.

As shown in the CV curves of Figure 4.9, there is only a slight difference in the specific current for palladium nanoparticles (Pd NPs) and gold-core palladium-shell nanoparticles (Au@Pd NPs) of the same size (15 nm), ruling out the enhancement effect from the Au@Pd synergy in our system. The performance of our Au@Pd NWs were astonishing even when compared to Au@Pd NPs, with an 37.2 times enhancement in mass specific current. This observation was enough to prove that the enhancement in catalytic performance did not originate from Au-Pd synergistic effect.

Figure 4.10 CV curves for Au@Pd NWs, Pd/C and detached Au@Pd NWs measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

To probe the origin of enhanced electrocatalytic activity, ECSA of Au@Pd nanowires and Pd/C was determined from palladium oxide (PdO) reduction, which is 110.1 and 43.3 m^2/g , respectively, as shown in Figure 4.10. Clearly, Au@Pd nanowires could provide more catalytic sites per unit mass of catalyst for ethanol electrooxidation as compared to the state-of-the-art Pd/C. It is important to note that such a high ECSA cannot be achieved simply by stacking Pd/C to the same thickness as the height of nanowire arrays (Table 4.1), which offers a huge advantage when the size of electrode is limited.

Figure 4.11 The ability to grow noble metal nanowire forest on three-dimensional conductive electrode was demonstrated on carbon fiber cloth. A-C. SEM images of bare carbon cloth. D-F, SEM images of Au NWs grown on conducting carbon cloth. G-I, SEM images of Au@Pd NWs grown on conducting carbon cloth.

As the high ECSA can already be achieved on a planar FTO glass electrode, it will not be hard to imagine how much more active sites can be provided by our nanowire arrays in a highly porous, three-dimensional electrode. The seeded solution growth method of NM nanowire arrays makes it possible for nanowires to be grown on arbitrary conductive supports (e.g., carbon fiber cloth, Figure 4.11), increasing the possibility to produce electrode with ultra-high ECSA.

Figure 4.12 The mass transport of nanowire arrays and nanoparticle catalyst layers were assessed by comparing their electrocatalytic active surface area (ECSA) at different length or thickness. A. CV curves for Au@Pd NWs and B. Pd/C of different length or thickness measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s. C. A comparison plot of ECSA against thickness of catalyst between Au@Pd NWs and Pd/C.

Table 4.1 ECSA measured in 0.5 M H_2SO_4 solution for Au@Pd NWs, Pd/C and Au@Pd NPs at different length/thickness.

Au@Pd NWs length (nm)	ECSA (m^2/g)	Pd/C thickness (nm)	ECSA (m^2/g)
130	109.1	150	73.8
250	110.1	300	64.4
360	100.4	730	52.1
600	106.9	1500	28.9
920	37.5		

Apart from high ECSA, the aligned nanowire catalyst is also expected to facilitate diffusion of reactants and products, owing to the aligned one-

dimensional channels. The diffusion properties were accessed by measuring the ECSA of nanowire arrays with different nanowire lengths. The ECSA of Au@Pd NWs remains almost constant up to 600 nm in length (Figure 4.12, Table 4.1), indicating that the active surface area of nanowires increases proportionally with their mass. This is a good indication that diffusion should not be a limiting factor in submicron nanowire arrays. On the other hand, Pd/C showed a progressive decrease in ECSA with increasing electrode thickness (Figure 4.12, Table 4.1), suggesting that diffusion is indeed a problem in nanoparticle-based electrocatalyst.

Table 4.2 Ethanol diffusion coefficient estimated from the Randles-Sevcik method. The length of Au@Pd NWs and thickness of Pd/C were kept to around 200 nm.

Au@Pd NWs			Pd/C		
Scan rate, v (V/s)	Peak current, I_p (A)	Diffusion coefficient, D (cm ² /s)	Scan rate, v (V/s)	Peak current, I_p (A)	Diffusion coefficient, D (cm ² /s)
0.001	3.0×10^{-3}	2.8×10^{-14}	0.001	4.9×10^{-4}	2.9×10^{-16}
0.002	5.0×10^{-3}		0.002	4.1×10^{-4}	
0.005	8.0×10^{-3}		0.005	7.8×10^{-4}	
0.010	1.0×10^{-2}		0.010	9.9×10^{-4}

Figure 4.13 Plot of peak current against square root of scan rate for Au@Pd NWs and Pd/C.

The conclusion where material diffusion is harder in NPs system as compared with NWs is further confirmed via comparing the ethanol diffusion coefficient in the Au@Pd NWs and Pd/C electrodes estimated from Randles-Sevcik method (Figure 4.13, Table 4.2), where the diffusion coefficient in the Au@Pd NWs ($2.8 \times 10^{-14} \text{ cm}^2/\text{s}$) is about two orders of magnitude larger than that in Pd/C ($2.9 \times 10^{-16} \text{ cm}^2/\text{s}$). The details of calculation and assumptions made were included in Section 4.4.

Figure 4.14 Schematic illustration showing different electron and material transport pathways adopted by nanoparticles and nanowire arrays. A. Pd/C. B. Au@Pd NWs.

Besides, electronic conductivity of nanowire arrays is also expected to be better than the nanoparticle-based counterpart. As electrons adopt ballistic transport while travelling through aligned nanowires which results in less resistivity via scattering, nanowire arrays provide a perfect channel to transport electrons. On the other hand, when catalyst-loaded support particles pack into a film, such as Pd/C, electrons face not only scattering, but also multiple junctions among the layers of particles as illustrated in Figure 4.14. These junctions contribute significantly to the high resistance; thereby severely decrease the electronic conductivity of nanoparticle film. As a result, conductivity of nanowires²¹ is at least one order magnitude higher than their nanoparticles counterpart²².

Additionally, the orientation of nanowires was found to greatly influence the electrochemical performance. Once Au or Au@Pd nanowires were detached from the substrate, the electrocatalytic activity dropped drastically to nearly the same level as that of the respective nanoparticles, highlighting the importance of nanowire alignment (Figure 4.3 and 4.8). We measured the ECSA of both

aligned and detached nanowires ($110.1 \text{ m}^2/\text{g}$ and $81.8 \text{ m}^2/\text{g}$ respectively for Au@Pd NWs, Figure 4.10) and noticed that there was only less than 30% decrease in ECSA after detaching the nanowires. Based on the previous studies, the metallic junction could increase the resistivity of metal nanostructures by a few orders of magnitude²³. Thus, the decrease in activity by detaching nanowires from substrate could be mainly attributed to the greatly increased difficulty in charge transport. In the case of nanowire arrays, the direct contact of individual nanowires with the conductive substrate ensures good electronic conductivity. This high electrode conductivity, together with the facilitated reactant and product diffusion and large ECSA renders nanowire arrays with unprecedented electrochemical performance. Hence, it is not surprising that the previous efforts of loading catalysts onto nanowire supports and CNTs could not achieve the same level of performance as our nanowire forest.

Figure 4.15 Optimization of electrocatalytic properties. A. CV curves of Au NWs with different Pd:Pt ratios, commercial Pd/C and Pt/C measured in solution of 1.0 M NaOH and 1.0 M ethanol at a scan rate of 50 mV/s. Insert shows the zoom in CV curves of Pd/C and Pt/C. B. Chronoamperometry graph measured at 0.87 V vs. RHE. Insert shows the zoom in chronoamperometry graph for Pd/C and Pt/C.

The electrocatalytic activity of nanowire arrays can be further optimized by coating the nanowires with catalysts having higher intrinsic catalytic activities. Previously, we have demonstrated the Au@Pd core-shell nanowires for ethanol oxidation. If we add Pt into the Pd shell, the electrocatalytic activity can be further enhanced as shown in Fig. 4. Among which, the Au@Pd_{2.2}Pt₁ (Table S3) core-shell nanowire arrays show the highest activity, achieving a peak mass specific current of as high as 6568.1 A/g, which is 2.9 times higher

than that of the Au@Pd nanowire arrays, and 38.0 times higher as compared with Pd/C (Figure 4.15). We also compared the performance of Au@Pd_{2.2}Pt₁ NWs with the commercially available Pt/C (platinum on Vulcan XC-72), which demonstrated an astonishing 20.0 times enhancement in the mass specific current (Figure 4.15).

4.4 Conclusion

In summary, we have demonstrated that by simply changing the morphology of electrocatalyst from nanoparticles to aligned nanowire arrays, we can dramatically improve the catalytic activity by providing more electrochemical active surface for electrocatalysis, one-dimensional channels for improved mass transport and better conductivity. Our approach provides a new and simple means to enhance the electrocatalytic activity, reduce the size of electrode for miniaturization of portable devices and improve the effectiveness of existing and emerging electrochemical technologies.

4.5 Detailed Experimental Section

Materials:

Ascorbic acid (AA), (3-aminopropyl)triethoxysilane (APTES), bismuth (III) chloride (BiCl_3), cetyltrimethylammonium bromide (CTAB), dimethylformamide (DMF), ethanol (EtOH), chloroauric acid (HAuCl_4), chloropalladous acid (H_2PdCl_4), chloroplatinic acid (H_2PtCl_6), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), methacrylic acid (MAA), 4-mercaptobenzoic acid (4-MBA), nafion solution (Nafion), nickel (II) chloride (NiCl_2), polyvinylpyrrolidone (PVP), palladium on activated charcoal (Pd/C), sodium borohydrate (NaBH_4), sodium citrate tribasic dihydrate, and fluorine doped tin oxide (FTO) glass were all purchased from Sigma-Aldrich. Cobalt (II) chloride (CoCl_2), copper (II) chloride (CuCl_2) and sodium citrate tribasic (citrate) were purchased from Alfa Aesar, sodium hydroxide (NaOH) was purchased from Sinopharm and cadmium (II) chloride (CdCl_2) was purchased from ACROS Organic. Platinum on Vulcan XC 72 was purchased from Premetek. All chemicals were used as received without further purification.

Structural Characterization:

The surface morphologies of Au NWs and Au@Pd NWs were characterized by field emission scanning electron microscope (SEM, JEOL JSM-6700F), transmission electron microscopy (TEM, JEOL, operated at 100 kV) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010EX, operated at 200 kV). Atomic resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) experiments were carried out on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope (JEOL, JEM-2100F) with high-angle annular dark-field (HAADF) detector operated at 200 kV. The mass and chemical composition of Au NWs and Au@Pd NWs were determined using inductively

coupled plasma mass spectrometry (ICP-MS, Agilent 7700 Series, MicroMist nebulizer, Quartz spray chamber, 3 channel peristaltic pump).

Electrochemical Characterization:

The electrochemical properties were studied in a standard three-electrode cell. The cyclic voltammetry and chronoamperometry measurements were conducted using a CHI 660D electrochemical workstation. The reference electrode used is saturated calomel electrode (SCE) and the counter electrode is Pt foil. As both Au NWs and Au@Pd NWs were growth directly on substrate, no additional treatment was needed when applied as the working electrode. The controls used in this experiment, Pd/C, Pt/C and Au NPs were prepared using drop-cast method, and then were covered with a thin layer of Nafion (5 μL , 5 wt%) before electrochemical measurement. The Pd loading on Au@Pd NWs and Pd/C catalyst were $17.6 \mu\text{g}/\text{cm}^2$. The Au loading on Au NWs and Au NPs were $13.9 \mu\text{g}/\text{cm}^2$. The working electrode surface area was limited to 0.28 cm^2 . The cyclic voltammograms were measured at a scan rate of 50 mV/s. The chronoamperometry curves for ethanol oxidation were measured at 0.87 V vs. RHE for Pd and 1.07 V vs. RHE for Au. For both cyclic voltammograms and chronoamperometry measurements, the electrolyte used was 1.0 M ethanol with 1.0 M NaOH aqueous solution. The electrolyte was purged with N_2 gas for 30 minutes prior to all electrochemical measurements. All electrochemical measurements were carried out at 25 $^\circ\text{C}$.

Au NWs Synthesis:

Au NW arrays were synthesized following method reported by J. He¹. Firstly, gold seed (Au NSs) solution was prepared by adding 100 μL of aqueous HAuCl_4 solution (17 mg/mL), 160 μL of sodium citrate (1 wt%, H_2O) and 620 μL of NaBH_4 (3.8 mg/mL) into 20 mL of deionized H_2O while stirring. Next, FTO glass (around 2 cm^2) was treated in APTES solution (1 $\mu\text{L}/\text{mL}$, EtOH: H_2O = 1:1) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then incubated in gold seed solution prepared previously for 1

hour. After that, the gold seed immobilized FTO glass was rinsed in water twice, and then incubated in growth solution for 15 minutes. The growth solution was made up of 150 μL of HAuCl_4 (17 mg/mL, H_2O), 600 μL of 4-MBA (10 mM, EtOH), 900 μL of AA (20mM, H_2O) and 2.1 mL of EtOH as solvent. Finally, the FTO glass covered with Au NWs was rinsed with EtOH and H_2O , and then stored for further use. All of the above procedures were carried out at room temperature.

Coating of metal shell on Au NWs via hydrazine reduction method:

The coating of metal shell was adopted from simple overgrowth method reported by P. R. Sajanlal⁴⁹. The FTO glass with AuNWs grown on it was soaked in CTAB solution (25 mM, H_2O) for one hour, and then rinsed with H_2O . The FTO glass was then placed in a bikar, and for each cm^2 of FTO glass, 1 mL of H_2O was added. Next, for every 1 mL of H_2O , 10 μL of metal chloride (NiCl_2 , CoCl_2 , CdCl_2 , CuCl_2 , BiCl_3 , or PdCl_2 , 0.25 M), 100 μL of NaOH (0.1M) and 360 μL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was added into the AuNPs or AuNWs solution at 80 $^\circ\text{C}$ for 5 minutes. The mixture was then allowed to cool to room temperature and stored in the reacting mixture before used.

Coating of metal shell on Au NWs via ascorbic acid reduction method:

Pd was coated by incubating the as-prepared Au NW arrays in MAA solution (1 $\mu\text{L}/\text{mL}$, DMF) at 60 $^\circ\text{C}$ for 2 hours, then rinsed with water. Subsequently, the FTO glass with Au NWs was incubated in Pd growth solution at room temperature. The Pd growth solution was made up of 200 μL of H_2PdCl_4 (20 mM, H_2O), 40 μL of PVP (20 mg/mL, H_2O), 400 μL of AA (10 mM, H_2O) and 2 mL of H_2O as solvent. The synthesized Au@Pd NWs were rinsed with H_2O and stored for further use. In some experiments, the solvent for MAA solution was replaced with cyclohexane, ethanol, hexane and tetrahydrofuran. The incubation temperature was also lower to room temperature in some experiments; in another experiment, no MAA was added to act as control.

Calculation to obtain ECSA for Au material:

Figure 4.16 CV curves for Au NWs, Au NPs and detached Au NWs measured in solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

To obtain the electrochemical active surface area (ECSA) of Au NWs and Au NPs, cyclic voltammetry measurements were carried out in 0.5 M H_2SO_4 at a scan rate of 50 mV/s. ECSA was calculated using the following equation:

$$\text{ECSA} = Q_{\text{H}}/0.45*[\text{Au}]$$

where Q_{H} is the charge resulting from gold oxide (Au_2O_3) reduction (around 1.15 V vs. RHE), 0.45 mC cm^{-2} is the electrical charge associated with Au_2O_3 reduction and $[\text{Au}]$ is the loading amount of Au on the working electrode. The ECSA value of Au NWs, Au NPs and detached Au NWs are 50.8 m^2/g , 10.2 m^2/g and 35.6 m^2/g , respectively.

Calculation to obtain ECSA for Pd material:

Figure 4.10 CV curves for Au@Pd NWs, Pd/C and detached Au@Pd NWs measured in solution of 0.5 M H₂SO₄ at a scan rate of 50 mV/s (Repeat).

To obtain the electrochemical active surface area (ECSA) of Au@Pd NWs and Pd/C, cyclic voltammetry measurements were carried out in 0.5 M H₂SO₄ at a scan rate of 50 mV/s. ECSA was calculated using the following equation:

$$\text{ECSA} = Q_{\text{PdO}} / 0.405 \cdot [\text{Pd}]$$

where Q_{PdO} is the charge resulting from palladium oxide (PdO) reduction (around 0.70 V vs. RHE), 0.405 mC cm⁻² is the electrical charge associated with PdO reduction and [Pd] is the loading of Pd on the working electrode. The ECSA value of Au@Pd NWs, Pd/C and detached Au@Pd NWs are 110.1 m²/g, 43.3 m²/g and 81.8 m²/g, respectively.

Assumption and calculation made for Randles-Sevcik equation:

The consumption of reactants (ethanol) on the catalyst surface is instantaneous, reactants will be depleted at the catalyst surface if a potential is suddenly applied and there will be a concentration gradient that drive diffusion of reactants (ethanol molecules) from bulk of solution to the surface of catalyst. In both cases (Au@Pd NWs and Pd/C), the diffusion of ethanol towards the electrode can be divided into two parts: the diffusion of ethanol from bulk to the surface layer of catalyst, and the diffusion of ethanol inside the catalyst layer. The two diffusion steps were lumped together and difficult to be decoupled. Here, we treat both Au@Pd NWs and Pd/C electrodes with same catalyst layer thickness as the planar electrodes, the overall ethanol diffusion coefficient for the Au@Pd NWs and Pd/C electrodes was estimated using the Randles-Sevcik equation as shown below:

$$I_p = 0.4463 nFAC \left(\frac{nFvD}{RT} \right)^{\frac{1}{2}}$$

where I_p is the peak current, n is the number of electrons involved in ethanol oxidation, F and R is faraday constant and gas constant, respectively, A is the electrode surface area, C is the bulk concentration of ethanol, v is the scan rate, T is temperature and D is the diffusion coefficient. Following this equation, the diffusion coefficient can be estimated by plotting the peak current against square root of scan rate. The results were presented in Figure 4.13 and Table 4.2.

Loading Amount of Au, Pd and Pt:

Table 4.3 The gold (Au), palladium (Pd) and platinum (Pt) loading amounts of various nanowires on FTO as measured from ICP-OES.

Sample	Loading amount on FTO (mg/cm ²)		
	Au	Pd	Pt
Au NWs	0.019	0	0
Au@Pd NWs	0.018	0.017	0
Au@Pd_{13.3}Pt₁ NWs	0.018	0.017	0.001
Au@Pd_{5.2}Pt₁ NWs	0.018	0.016	0.003
Au@Pd_{2.2}Pt₁ NWs	0.017	0.011	0.005
Au@Pt NWs	0.022	0	0.001

References

- [1] J. He, Y. Wang, Y. Feng, X. Qi, Z. Zeng, Q. Liu, W. S. Teo, C. L. Gan, H. Zhang, H. Chen. *ACS Nano* **2013**, 7, 2733-2740.
- [2] M. Winter, R. J. Brodd. *Chem. Rev.* **2004**, 104, 4245-4270.
- [3] E. H. Yu, U. Krewer, K. Scott. *Energies* **2010**, 3, 1499-1528.
- [4] V. R. Stamenkovic B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C.A. Lucas, G. Wang, P. N. Ross, N. M. Markovic. *Nat. Mater.* **2007**, 6, 241-247.
- [5] M. K. Debe. *Nature* **2012**, 486, 43-51.
- [6] C. Bianchini, P. K. Shen. *Chem. Rev.* **2009**, 109, 4183-4206.
- [7] M. Z. F. Kamarudin, S. K. Kamarudin, M. S. Masdar, W. R. W. Daud. *Int. J. Hydrogen Energy* **2013**, 38, 9438-9453.
- [8] C. L. Lu, K. S. Prasad, H. L. Wu, J. A. A. Ho, M. H. Huang. *J. Am. Chem. Soc.* **2010**, 132, 14546-14553.
- [9] N. Tian, Z. Y. Zhou, N. F. Yu, L. Y. Wang, S. G. Sun. *J. Am. Chem. Soc.* **2010**, 132, 7580-7581.
- [10] S. T. Nguyen, H. M. Law, H. T. Nguyen, N. Kristian, S. Wang, S. H. Chan, X. Wang. *Appl. Catal.*, **2009**, B 91, 507-515.
- [11] S. Y. Shen, T. S. Zhao, J. B. Xu, Y. S. Li. *J. Power Sources* **2010**, 195, 1001-1006.
- [12] P. K. Shen, C. W. Xu, *Electrochem. Commun.* **2006**, 8, 184-188.
- [13] C. W. Xu, Z. Q. Tian, P. K. Shen, S. P. Jiang. *Electrochim. Acta* **2008**, 53, 2610-2618.
- [14] F. Ksar, G. Surendran, L. Ramos, B. Keita, L. Nadjo, E. Prouzet, P. Beaunier, A. Hagege, F. Audonnet, H. Remita. *Chem. Mater.* **2009**, 21, 1612-1617.
- [15] A. L. Wang, H. Xu, J. X. Feng, L. X. Ding, Y. X. Tong, G. R. Li. *J. Am. Chem. Soc.* **2013**, 135, 10703-10709.

- [16] N. Mackiewicz, G. Surendran, H. Remita, B. Keita, G. Zhang, L. Nadjio, A. Hagege, E. Doris, C. Mioskowski. *J. Am. Chem. Soc.* **2008**, 130, 8110-8111.
- [17] F. Hu, X. Cui, W. Chen. *J. Phys. Chem. C* **2010**, 114, 20284-20289.
- [18] F. P. Hu, F. W. Ding, S. Q. Song, P. K. Shen. *J. Power Sources* **2006**, 163, 415-419.
- [19] X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie, X. Wang. *J. Am. Chem. Soc.* **2011**, 133, 3693-3695.
- [20] L. Gao, W. Yue, S. Tao, L. Fan. *Langmuir* **2013**, 29, 957-964.
- [21] S. De, T. M. Higgins, P. E. Lyons, E. M. Doherty, P.N. Nirmalraj, W. J. Blau, J. J. Boland, J. N. Coleman. *ACS Nano* **2009**, 3, 1767-1774.
- [22] Y. Wu, Y. Li, B. S. Ong. *J. Am. Chem. Soc.* **2006**, 128, 4202-4203.
- [23] L. Hu, H. S. Kim, J.-Y. Lee, P. Peumans, Y. Cui. *ACS Nano* **2010**, 4, 2955-2963.
- [24] R. Sajanlal, T. Pradeep. *J. Phys. Chem. C* **2010**, 114, 16051-16059.

Chapter 5

Study of Ethanol Oxidation Reaction Mechanism on Palladium Surface

Renewable energy is currently one of the hottest research areas as it is seen to be a critical way to achieve a sustainable development of future energy. One of such renewable energy sources is ethanol that can be produced from agriculture feedstock, which leads to the development in direct ethanol fuel cells (DEFCs). Our noble metal aligned nanowires (NWs) arrays had achieved 38.0 times increase in specific activity on ethanol oxidation reaction (EOR) over the commercial catalysts palladium on activated carbon (Chapter 4), but further optimization could not be performed due to lack of understanding in detail catalytic mechanism. We had proposed an EOR mechanism on Pd surface with OH⁻ ions as the main inhibitor that poison the Pd surface and the details process occurred in different part of the EOR CV, which helped to identified the limiting factors of EOR mechanism and thus possible to suggest methods on improving the EOR activity and stability in DEFCs devices. A part from that, we had also discovered that reservoir plays important role in determining the performance of Pd in EOR. The reservoir effect on our long and dense Au@Pd NWs array structure might also be a contributing factor for its high performance in EOR.

5.1 Introduction

Renewable energy is currently one of the hottest research areas as it is seen to be a critical way to achieve a sustainable development of future energy¹. One of such renewable energy sources is ethanol that can be produced from agriculture feedstock, which leads to the development in direct ethanol fuel cells (DEFCs)². Ethanol oxidation reaction (EOR), which occurred on the anode side of DEFCs, was focus of our current research. As shown in previous chapter (Chapter 4), our noble metal aligned nanowires (NWs) arrays can dramatically improve the catalytic activity of ethanol oxidation reaction by providing more electrochemical active surface for electrocatalysis, one-dimensional channels for improved mass transport and better conductivity, where the best catalyst achieved 38.0 times increase in specific activity over the commercial catalysts palladium on activated carbon. Our approach provides a new and simple means to enhance the electrocatalytic activity and reduce the size of electrode for miniaturization of portable devices.

The next step of our project was to optimize our palladium coated gold nanowires (Au@Pd NWs) arrays catalyst for assembly of DEFCs device. One of such attempts was to grow our NWs array on a three dimensional support which provides a large surface area as compared with planar fluorine-doped tin oxide (FTO) glass, further enhancing the current density generated by our NWs array. However, despite the increase in support surface area, the current density from EOR did not increase proportionally. When shifting from FTO glass substrate to carbon clothes, we were expecting a large increase in current density as the substrate surface area had increased by at least 20 folds. As shown in Figure 5.1, the EOR current density seems to increase tremendously at the first glance, but careful inspection had shown that this was not the case. Insert had shown that at potential of 0.9 V vs RHE, the current density only shown a 7.0 times increase, which is much lower than our expectation and became a huge challenge for our optimization. A part from that, the stability of

our catalyst is still a huge problem that needed to be solved before proceeding to fuel cells testing. As shown in previous chapter (Figure 4.15b), the specific current was left with roughly 20 % after only one hour, which makes them clearly not suitable to act as anode in fuel cells.

Figure 5.1 Cyclic Voltammetry (CV) graphs of Au@Pd NWs grown on FTO and carbon cloth substrate respectively, measured in 1 M EtOH and 1 M NaOH electrolyte at a scan rate of 50 mV/s. Insert shows the zoom in CV of FTO.

The obstacles faced in optimization of our NWs array system as illustrated above was mainly due to our lack of understanding in EOR mechanism. Without any knowledge in EOR mechanism, it was hard to determine the cause behind the problem we faced, and optimization of electrode cannot proceed properly. However, unlike the case of EOR mechanism on platinum (Pt) catalyst which was very thoroughly studied³, the EOR mechanism on palladium (Pd) surface were not so well defined. There had been attempts to study EOR mechanism, such as by T. Shen⁴, and also Y.Y. Yang⁵. However,

these mechanisms were lacked of details (Figure 5.2 and 5.3), such as factors that limit current production, which did not provide enough information to help solving the problems we faced. Hence, there is a need to study the detail mechanism of ethanol oxidation pathway on Pd before we can proceed with optimization of our NWs array catalyst.

Figure 5.2 Scheme illustrating the general ethanol oxidation mechanism on Pd surface proposed by T. Shen. Reprinted with permission from ref. [4]. Copyright © 2014, American Chemical Society.

Figure 5.3 Ethanol oxidation pathways on Pd surface in alkaline solution proposed by Y.Y. Yang⁵. Reprinted with permission from ref. [5]. Copyright © 2014, American Chemical Society.

Our general strategy to study the ethanol oxidation mechanism was to gather as much information as possible by diversified the reaction conditions, and analysing the trends observed during data collection. The information we gather will primarily be in the form of electrochemical data, such as cyclic voltammetry (CV) and amperometric i-t curve (I-t). For examples, we will examine behaviour of different Pd catalyst under different reaction condition, and take notes of any situation which will influence the resulting EOR current observed. Besides that, we would be taking reference from the well studied EOR mechanism on Pt, due to the similarity in catalysis behaviour between Pd and Pt.

Figure 5.4 EOR pathways on Pt electrode proposed by S.C.S. Lai⁶. The solid arrow denote pathway in acidic condition, while the dotted arrow denote pathway in basic condition. Reprinted with permission from ref. [6]. Copyright © 2010, Elsevier.

Figure 5.5 Detailed EOR mechanisms on Pt surface in alkaline solution proposed by P.A. Christensen⁷. Reprinted with permission from ref. [7]. Copyright © 2013, Royal Society of Chemistry.

As shown in Figure 5.4 and 5.5, the ethanol oxidation mechanism on Pt surface had been fairly well studied. As discussed by both S.C.S. Lai⁶ and P.A. Christensen⁷, the ethanol oxidation pathway was fairly different in alkaline condition than those in acidic condition. One of the key difference between Pt and Pd as catalyst was that the main oxidation product for Pd was acetate (or acetic acid)⁸, which might indicate the inability of Pd to catalyse breaking of C-C bond in ethanol. With that in mind, we tried to work out the details of ethanol oxidation mechanism on Pd surface mainly based on the C2 pathway of those on Pt (Figure 5.4).

Here in, we would like to propose an ethanol oxidation mechanism on Pd surface, with hydroxide ions (OH^-) as the main inhibitor that poison the Pd surface. A part from that, we would also like to report a reservoir effect observed in our Au@Pd NWs array system, which might helped to explain some behaviour displayed only by our NWs array.

5.2 Results and Discussion

5.2.1 Hydroxide Species as Main Inhibitor on Palladium Surface

Before we tried to propose any ethanol oxidation mechanism on Pd, it was very critical to determine the main inhibitor, which is the species responsible for poisoning of Pd surface. With more understanding on the inhibition mechanism, we hoped we will be able to pin-point the factor that limits the current density in our three dimensional electrode, and also improves the stability of our Au@Pd NWs. To resolve this, we began with observing how the current density and inhibition potential changes when the concentration of reactants were altered. As there were only two reactants that involved and will absorbed on Pd surface during ethanol oxidation, the main inhibitor must be originates from either of these two reactants or intermediates produced from these reactants during ethanol oxidation, which we term ethoxi species (partially oxidised ethanol product such as CH_3CO^*) and hydroxi species (OH^* or O^* from hydroxide ions). By changing the concentration of ethanol (EtOH) and sodium hydroxide (NaOH), we will be able to observe the changed in inhibition behaviour and will be able to pin-point which species was more likely to be responsible for Pd surface inhibition.

Figure 5.6 CV graphs showing EOR on Pd plate at different EtOH concentration. The concentration of NaOH was kept at 1.0 M and the scan rate used was 50mV/s.

Figure 5.7 CV graphs showing EOR on Pd plate at different NaOH concentration. The concentration of EtOH was kept at 1.0 M and the scan rate used was 50mV/s.

For the purpose to study possible inhibitor of EOR on Pd surface, we would like to keep the electrocatalyst as simple as possible. Hence, we had chosen to use Pd plate as the working electrode to avoid any interference that might arise from structure or morphology of the electrocatalyst. In a typical EOR CV, both forward and reverse scan will result in an oxidation peak (positive current). The focus on analysis here will be on the forward oxidation peak (at around 0.9 – 1.1 V vs RHE), where the decrease in current indicates that the Pd surface was inhibited or poisoned. As shown in Figure 5.6, when the EtOH concentration increase while the NaOH concentration was kept at 1.0 M, the inhibition occurred at a much higher potential, meaning that it was now harder to inhibit or poison the Pd surface. From this trend, it was clear that ethoxi species might not be responsible for the inhibition of Pd surface. If any species originates from EtOH was responsible for inhibition, whether they were

partial oxidation product like CH_3CO^* or ethanol itself, increasing of the EtOH concentration in the system will result in more ethoxi species being produced. With the limited amount of Pd surface and more ethoxi species present, the inhibition should occurred faster and hence should result in lower inhibition potential. However, the trend observed was totally opposite of that, which indicates that present of ethoxi species actually slow down the inhibition process, thus they should not be the main inhibitor.

On the other hand, when the concentration of NaOH was increased while the concentration of EtOH was kept at 1.0 M, the inhibition had occurred at a more negative potential. This observation had indicates that the present of excess NaOH actually speed up the inhibition process on Pd surface, which suggests that NaOH might be linked to the poisoning or inhibition of Pd surface in EOR. As it will be fairly unlikely for the sodium ions (Na^+) of NaOH to interact with Pd, hydroxide ions (OH^-) or hydroxi species shall be responsible for poisoning of Pd surface.

Figure 5.8 CV curves of different EtOH and KOH concentration reported by Z.X. Liang where Pd disk was used as electrode and the scan rate used was 20 mV/s. A. CV of different EtOH concentration while KOH concentration was kept at 1.0 M. B. CV of different KOH concentration when EtOH concentration was kept at 1.0 M. Reprinted with permission from ref. [9]. Copyright © 2008, Elsevier.

Similar results had also been reported before, such as those by Z.X. Liang⁹. The trend of inhibition potential observed was exactly the same as what we observed (Figure 5.8), although differences was not as huge as ours. The inhibition potential was more positive when the concentration of EtOH increases, and more negative when the concentration of OH⁻ increases. This had shown that the trend we observed was not unique and should be able to apply to all Pd system, where hydroxi species was responsible for poisoning of Pd surface.

5.2.2 Ethanol Oxidation Reaction Mechanism on Palladium

From our studies in previous section, a part from identifying that hydroxi species were responsible for inhibition or poisoning of Pd surface, we also noticed that increasing the EtOH concentration or amount of ethoxi species had postponed the inhibition of Pd to higher potential. This observation had indicates that there was a competition exist between EtOH and OH⁻ on the surface of Pd surface during the electro-oxidation, and we think the competition between these two species was the main factor that control the current produced at each potential.

Figure 5.9 Ethanol oxidation reaction equations in alkaline electrolyte which was generally agreed and accepted, proposed by Z.X. Liang⁹.

As shown in Figure 5.9, the EtOH molecules that absorbed onto Pd surface, which undergo a two stage oxidation process with OH⁻ absorbed on Pd as well. With our hypothesis that OH⁻ as the inhibitor, we proposed that EOR oxidation will continue on Pd surface as long as both EtOH species and OH⁻ species present, which is the part where the current continue to increase in the forward CV scan. Once OH⁻ start to dominate on Pd surface, the current will drop as there were not enough EtOH molecules to react with, and the current decreases until a point where the Pd surface were fully covered with absorbed OH⁻, the Pd surface was inhibited and no more EOR happens, result in zero current produced. With reference from the EOR process on Pt surface, we proposed the EOR mechanism as shown in Figure 5.10 below.

Figure 5.10 Illustration of ethanol oxidation mechanism on Pd surface proposed.

As depicted in Figure 5.10, the EOR mechanism was proposed based on a two stage oxidation process. In the first stage, EtOH molecule reacts with three OH^- ions to give an ethoxi species, CH_3CO^* , which then reacts with another OH^- ions at the second stage and release from Pd surface to give acetic acid, or more possibly acetate ions as the electrolyte was in alkaline condition, deprotonation was most likely to occur. It was found that during the studies of ethanol oxidation on platinum (Pt) surface, the breaking of alpha-hydrogen was found to have the lowest reaction barrier (0.64 eV), thus it was the most favourable process during the first step of ethanol oxidation¹⁰. Similarly, the breaking of alpha-hydrogen was also calculated to have the lowest reaction barrier (0.29 eV) among all the processes¹¹. Given that the alpha-carbon was adsorbed onto palladium (Pd) surface instead of the oxygen of the alcohol group, it was highly possible that the initial steps of ethanol adsorption involved removal of one of the alpha-hydrogens.

We had believed that the absorption of ethanol molecules and OH^- ions on Pd surface were heavily influenced by the potential applied. Both species were influenced by the applied potential in the same way, the more positive the applied potential, the higher their affinity toward Pd. However, as OH^- was a negatively charged ion, its affinity towards Pd was influenced more by applied

potential. Hence, at higher applied potential, there was a higher chance of OH^- ions to absorb onto Pd surface as compared with EtOH molecules, as OH^- has a much higher affinity towards Pd at this point, which might be the cause for the inhibition of Pd surface.

Figure 5.11 CV curve of ethanol oxidation reaction conducted on Pd plate in 1.0 M EtOH and 1.0 M NaOH at a scan rate of 50mV/s. The CV curve was divided into 7 parts and each part was highlighted with different colour.

We had proposed that there were competition between the EtOH and OH^- on Pd surface, and their affinity toward Pd were influenced by applied potential, thus controlling the current produced at different potential range or different stage in a CV curve. Thus, we had divided the EOR CV curve of Pd plate into seven parts, and we tried to deduce what happens on the surface of Pd during these different potential range.

Figure 5.12 Illustration on the first part of EOR CV curve of Pd plate.

Initially, when the applied potential was low, the Pd surface was predominantly covered with absorbed EtOH molecules or ethoxi species (CH_3CO^*). At low potential (<0.4 V vs RHE), the affinity of ethanol towards Pd were much stronger than those of OH^- ions. Thus, these absorbed EtOH will absorbed first and blocked the Pd surface, preventing OH^- ions from absorbing. As EOR required both EtOH and OH^- to be present on Pd surface simultaneously, at this stage, there was little or no current at all being produced. We had proposed the domination of EtOH molecule at low potential were based on the following observation.

Figure 5.13 CV curves showing the absorption potential of EtOH and OH⁻ on Au@Pd NWs. Absorption of OH⁻ ion was measured in 1 M NaOH solution at a scan rate of 50 mV/s. Absorption of EtOH molecules was measured in dimethylformamide (DMF) solvent, with 1.0 M of EtOH and 0.1M tetrabutylammonium tetrafluoroborate (nBu₄-BF₄) at a scan rate of 50 mV/s. Control was also carried out to eliminate absorption peak of DMF (0.1 M nBu₄-BF₄ in DMF, scan rate 50 mV/s).

Figure 5.14 CV curves of Pd disk electrode in the present and absent of EtOH in 1.0 M of KOH, reported by Z.X. Liang⁹. Reprinted with permission from ref. [9]. Copyright © 2008, Elsevier.

As shown in Figure 5.13, the EtOH absorption peak on Pd occurred at a lower potential (0.25 V vs RHE) as compared with OH⁻ absorption peak (0.70 V vs RHE). This indicates that at low potential EtOH molecules will absorb first onto Pd surface. Another observation made by Z.X. Liang⁹ (Figure 5.14) was that OH⁻ absorption peak disappeared in the present of EtOH, which not just indicates that EtOH absorbed first, but also suggests that OH⁻ was not able to replace EtOH at low potential, hence the OH⁻ absorption peak disappear completely instead of being pushed to a higher potential. With the observations above, it was safe to assume that at low potential, EtOH molecules dominate on Pd surface.

Figure 5.15 Illustration on the second part of EOR CV curve of Pd plate.

As the CV scan continues, the affinity of both EtOH molecules and OH⁻ ions towards Pd increases, due to the positive potential applied on the Pd plate working electrode which attracts negatively charged ions and polar molecules. However, although OH⁻ affinity towards Pd increased more than EtOH, but overall EtOH affinity towards Pd was still stronger. Hence, majority of the OH⁻ ions will react with EtOH molecules to give CH₃CO*_(abs) instead of being adsorbed on the Pd surface as illustrated in Figure 5.15, which gives rise to the oxidation current. Still, this does not mean that no OH⁻ ions will be adsorbed on the Pd surface; a small amount of OH⁻ ions will be adsorbed on the Pd surface, which react with CH₃CO*_(abs) to give acetic acid or acetate ions as products and leave the Pd surface, opening up more Pd surface to keep the EOR going. If there were absolutely no OH⁻ ions adsorbed on the Pd surface, the EtOH molecules would be finished oxidised to CH₃CO* in a short amount of time, then the EOR reaction would be quenched and there would be zero current, which was clearly not the case.

Figure 5.16 Illustration on the third part of EOR CV curve of Pd plate.

As the CV scan continues, the applied potential became higher, and the affinity of EtOH and OH⁻ towards Pd further increases. At this part of CV scan, the affinity of EtOH and OH⁻ towards Pd were fairly similar, but EtOH still was slightly higher. As more OH⁻ absorbed on Pd surface, more acetic acid or acetate ions were produced and left Pd surface, opened up more active site on Pd surface for more EtOH or OH⁻ to absorb on. Thus, more electrons was produced and more current was produced at a higher rate. Thus, the current in part 3 will be slightly steeper than those in part 2.

Figure 5.17 Illustration on the forth part of EOR CV curve of Pd plate.

As the CV scan continues, it will reach a point where the affinity of OH⁻ toward Pd exceeds those of EtOH. It was not that the affinity of EtOH towards Pd was not affected by the higher applied potential, but the increase in OH⁻ was much more, probably due to its smaller size and its negative charge. OH⁻ will start dominating the Pd surface, leaving less active site for EtOH to absorb onto. A part from that, we believed that once an OH⁻ ion absorbed onto a Pd site, it will affect its neighbouring Pd site, making them more susceptible to receive OH⁻ ions as illustrated in the insert of Figure 5.17. Hence, once the OH⁻ start to dominant on Pd surface, other OH⁻ ions will quickly absorbed onto the remaining Pd site, fully covering all Pd surface in a concerted process. This process happens so fast that no EtOH molecules can compete with OH⁻ ions for the Pd site, and with the inability of EtOH to replaced OH⁻ that already absorb on Pd surface, the Pd surface was blocked and no EOR can happens. The current drop to near zero and inhibition of Pd surface had occurred. It was worth noticing that inhibition happens so fast that the current almost drop instantaneously, which suggests that the inhibition process is a concerted and cascading process. After inhibition had occurred, continue to increase the

applied potential might result in a stronger Pd-OH bond, or Pd might be oxidised to palladium oxide (PdO).

Figure 5.18 CV curves of Pd plate with different scanning range. A. CV curves of Pd plate start from 0.45 V and end between 1.15 V to 1.65 V in 1 M EtOH and 1 M NaOH, with a scan rate of 50 mV/s. B. CV curves of Pd plate start from 0.45 V and end between 1.15 V to 1.65 V in 1 M NaOH, with a scan rate of 50 mV/s.

To investigate the bonding strength between Pd-OH, a series of CV scan was performed where the range was gradually increase from 1.15 V to 1.65 V, way pass the inhibition potential but before oxygen evolution reaction (OER) occurred. This means that all Pd surface was already covered with absorbed OH⁻, hence changing the CV range should have little to no effect on a fully inhibited surface. However, as observed in Figure 5.18, this was not the case. Apparently, the higher the CV range, the more negative the position of reverse peak. The reverse peak was the point where the inhibited surface was

"refreshed", where the inhibitor OH^- was released from Pd surface and EOR can occurred once again. Hence, the potential where the "release" occurred give an indication on the relative Pd-OH bond strength, the stronger the bond, the "release" happens slower, and thus the reverse peak becomes more negative as more energy was required to break the bond.

Figure 5.18a had shown that the further the CV scan went during the forward scan, the more negative the reverse peak, indicating that there was a strengthening of Pd-OH bond. Furthermore, it was shown in Figure 5.18b that the further the CV scan went during the forward scan, the Pd reduction peak (between 0.7 to 0.9 V vs RHE) shifted to more negative potential, and the shape of the peak change from broad, double peak to a single, sharp peak. The information provided here was that in smaller CV range, two oxidised form of Pd exist, one was easier to be reduced than the other, and thus the Pd reduction peaks were more positive overall. In larger CV range, only one oxidised form of Pd exists, and it was harder to be reduced, resulting in a sharp, more negative Pd reduction. We had suspected the species that was harder to be reduced here might be PdO, while the two Pd reduction peaks which was easier to be reduced might arise from mixture of Pd-OH and PdO.

At smaller CV scan range, majority of Pd surface exist as Pd-OH, with smaller ratio of PdO. During the reverse scan Pd-OH bond was broken first (OH^- desorbed from Pd surface) resulting in the first broad reduction peak (0.95 V), then PdO was reduced back to Pd (second, smaller reduction peak at 0.80 V). As the forward CV scan proceeds to higher potential, more Pd-OH was oxidised to PdO, hence the first Pd reduction peak becomes smaller and the second reverse peak become larger. Finally, the forward CV scan proceed to such a high potential where all Pd-OH on the Pd surface were oxidised to PdO, resulting in only one Pd reduction peak at 0.70 V. Our observation seems to suggest that there were a two-stage inhibition process that occurred on Pd, where the first stage was where OH^- fully absorbed on Pd surface which was a weak inhibition and can be remove easier; the second stage was where Pd-OH

was oxidised to PdO, which was a stronger inhibition and harder to be "removed" or reduced back to Pd.

Figure 5.19 Illustration on the fifth part of EOR CV curve of Pd plate.

When the CV curve continues with the reverse scan, the current remain zero as the Pd surface still remain inhibited by the absorbed OH⁻. As the reverse scan continue the affinity of EtOH and OH⁻ towards Pd become weaker with the decreasing applied potential. However, at this potential range, the affinity of OH⁻ towards Pd is still stronger than EtOH, thus EtOH cannot kick out or replace the absorbed OH⁻ from Pd surface. Hence, Pd surface remains inhibited.

Figure 5.20 Illustration on the sixth part of EOR CV curve of Pd plate.

The applied potential continue to decrease until a point where the affinity of OH⁻ towards Pd drops below EtOH, coupled with the potential where OH⁻ start to desorbed from Pd surface (Figure 5.20), the bond between Pd-OH was broken and OH⁻ was release from Pd surface, providing a fresh surface for EOR to happen again, thus EOR current was observed. As the inhibition of Pd surface by OH⁻ was a concerted process, the release of OH⁻ from Pd surface must be a concerted process as well. Once a OH⁻ was released, the neighbours were also affected and the release process happens at a very fast rate, where almost all OH⁻ was released from Pd simultaneously. Thus, there was a spike in EOR current, as almost all Pd surface was available for EOR reaction simultaneously.

Figure 5.21 Illustration on the seventh part of EOR CV curve of Pd plate.

As the applied potential decreased, EOR continue to happen, where both EtOH and OH⁻ continues to absorb onto Pd surface. However, the current continue to decrease due to the amount of OH⁻ absorbed onto Pd surface had become lesser, as their affinity towards Pd continue to decrease. This process continue until a point where OH⁻ affinity to Pd was so weak that they can no longer compete with EtOH for a spot on Pd surface, EtOH became dominant on Pd surface once again. However, without the present of absorbed OH⁻ on Pd surface, the EOR cannot progress, thus the current drops to zero.

Figure 5.22 Stability data of Pd plate measured in 1 M EtOH and 1 M NaOH hold at a certain potential during a CV scan. A. Pd plate held at different potential during the forward CV scan before reaching inhibition potential. B. Pd plate held at different potential during the forward CV scan after inhibition potential. C. Pd plate held at different potential during the reverse CV scan before reaching release potential. D. Pd plate held at different potential during the reverse CV scan after release potential.

The competition between EtOH and OH^- can be seen more clearly when the CV scan was paused and held at that particular potential for some time. During the forward scan, it can be observed clearly that as the applied potential increase, the initial current become higher, but the stability become worst, meaning the drop in current become faster (Figure 4.22a). This had indicated that there was higher chance of OH^- ions being absorbed on Pd surface as the potential increases, thus it become easier for OH^- to accumulate on Pd surface and inhibit the surface. This was especially clear at 0.95 V which was very close to the inhibition potential, the current dropped almost instantaneously to

zero within 10s of second. When the CV scan was paused at potential higher than the inhibition potential, there was a small current initially which dropped very fast to zero (Figure 4.22b). This might be due to the release of some OH^- inhibitor from Pd surface during the switch from CV to stability test, where there might be split second where no potential was applied on Pd plate, thus some surface was available for EOR. However, once the potential was applied, these surfaces were quickly inhibited again by OH^- , hence the current dropped back to zero.

When the CV was paused during the reverse scan, the current generally remain as zero, although a small initial current was observed (Figure 4.22c), probably caused by the switching of electrochemical technique as explained above. However, when the CV was paused at a potential very close to the release potential (0.85 V), it can be seen the current jumped up, and then decay again. This was due to at this potential, the affinity of OH towards Pd had become so weak that it was not enough to kept them on Pd surface, and some EtOH had start to replace the OH inhibitor. This had caused a cascading event where almost all the OH^- was release from Pd surface, which resulted in the jump in current. After the release potential, the stability data was generally similar to those of the forward scan, although a slightly higher initial current can be observed. This was actually expected as seen in EOR CV, at lower potential range, the reverse scan generally have higher current than the forward scan (comparing part 7 and part 2 in Figure 5.11).

Figure 5.23 CV curves of Pd plate with different scan range, measured in 1 M EtOH and 1 M NaOH at a scan rate of 50 mV/s.

A part from that, when the forward CV scan ends at a potential where inhibition had not occurred fully, the reverse oxidation peak potential were observed to shift to more positive side (Figure 5.23). This is due to the fact that when Pd surface was not fully covered by inhibitor OH^- (the applied potential was decreased too fast), there will still be some surface which was accessible by EtOH molecule. When an EtOH absorbed on Pd surface, the neighbouring absorbed OH^- can be removed easily via EOR reaction that happened, causing a weaker Pd-OH bond overall. Thus, it had become easier to remove OH^- from Pd surface, needing less energy and the release happen at more positive potential, causing the reverse peak to shift positively.

With this, we had illustrated the process that happens at each stage of a CV scan, where the EOR current was mainly controlled by the competition between EtOH and OH^- on Pd surface. Nevertheless, there were still some

phenomena that had not been explained, such as why the reverse peak has higher current than its forward scan counterpart under the same potential, which will be explain in the next section: reservoir effect.

5.2.3 Reservoir Effect

Although we had proposed a EOR mechanism that can explain what had happened at each stage of a CV scan, this mechanism was not complete as we still lacked of hypothesis that was able to explain some phenomena observed, such as the current which was always higher in reverse scan than those in forward scan at low potential range.

Figure 5.24 CV curve of Pd plate measured in 1 M EtOH and 1 M NaOH at a scan rate of 50 mV/s, where the insert table shown the total amount of charge that pass through during forward and reverse scan.

Our first intuition about this phenomenon was that there were same amount of charge (electrons) that pass through during the forward and reverse scan, as the reverse oxidation peak has a smaller potential range, its current become much higher than those of the forward peak. However, as shown in the measurement in Figure 5.24 above, this was not the case as the amount of charge that was produced during the forward scan was still much larger than the

reverse scan. Thus, we had to propose other hypothesis to explain this phenomenon.

Figure 5.25 Illustration on how a reservoir was formed right after inhibitor, OH^- was release from Pd surface.

We had imagined the scenario at release potential during the CV reverse scan, where the OH^- inhibitor had just release from Pd surface in a cascading and concerted manner. At this point of time, there must be a populated amount of OH^- near the surface of Pd as compared with the bulk. We had to be reminded at this potential, the affinity of EtOH towards Pd surface is actually higher than those of OH^- , and the consumption of OH^- was huge, as 4 OH^- was needed to oxidise one EtOH to acetic acid (or 5 to acetate ion), which indicates that there will be a deficiency of OH^- on Pd surface. At this potential, the rate of reaction was limited by the amount of OH^- present near or on the Pd surface and how fast they can be replenished. Thus, these OH^- ions reservoir acts as the key to keep the EOR going by replenishing the OH^- on Pd surface, giving more time for other OH^- ions in the bulk solution to diffuse to Pd surface, slowing EtOH from dominating on Pd surface which will decrease the reaction rate, thus lowering the current produced.

Figure 5.26 Stability of Pd plate, held at 0.82 V vs RHE during forward and reverse scan of a CV, measured in 1.0 M EtOH and 1.0 M NaOH.

As shown in Figure 5.26, when the CV was paused and held at 0.82 V (release potential) during the forward and reverse scan, the initial current of stability data from the reverse scan were seem to be higher than those of forward scan (Figure 5.26). However, after around 100 s, both stability data from the forward and reverse scan overlapped with each other. This observation had illustrated that the high initial current of reverse scan was provide by the OH^- reservoir present, which kept the "gate" for EOR opened by providing more absorbed OH^- . However, this phenomenon was only temporary as the amount of OH^- reservoir present was limited. Once the OH^- reservoir was finished being consumed, the rate of reaction drop back to its original state, thus the current from reverse scan will overlapped with those from forward scan eventually, in this case, after about 100 s.

We had demonstrated that the possibility of a reservoir might be present for a small amount of time on Pd plate. However, we felt that this phenomenon

of temporary trapping of ions should not be unique to the Pd plate system, as most Pd based electrocatalyst system shown similar forward and reverse peak shape during an EOR CV scan. Since a reservoir of OH^- ions can exist, the same should happen to EtOH molecules as well. Furthermore, the reservoir effect should be more prominent in our NWs array system, as the long vertical NWs should be able to trap more ions as compared with the flat Pd plate. Generally, the reservoir effect, or the phenomena of temporary trapping of EtOH or OH^- ions near catalytic surface, should be more prominent in nanostructure with diffusion problem, such as those with very long and dense NWs structure, branched nanostructure or rough surface.

Figure 5.27 CV curve of EOR for long Au@Pd NWs as compared with Pd plate measured in 1 M EtOH and 1 M NaOH at a scan rate of 50 mV/s.

One of the key evidence for the existent of reservoir comes from our long Au@Pd NWs array. In a normal Pd based electrocatalyst system, inhibition of Pd surface occur around 1.0 V, and oxygen evolution reaction

(OER) happens around 1.7 V as shown by Pd plate in Figure 5.27. The occurrence of OER was most easily spotted as oxygen gas produced will form gas bubbles on surface of electrocatalyst. However, in our long Au@Pd NWs array, no gas bubbles were observed to form on the surface of electrode way pass 1.7 V. In fact, gas bubbles start to appear only after 3.2 V. The absent of gas bubbles had indicates that no OER had occurred between 1.7 V and 3.2 V, which seems impossible as first glance as the potential a reaction occurred was determined by its activation energy and should remain roughly similar when the same material was used as catalyst. We believed that the delay in OER occurrence was caused by EtOH reservoir which was trapped by our long NWs array.

Figure 5.28 Illustration on how present of EtOH reservoir postponed the EOR inhibition and oxygen evolution reaction.

The EtOH reservoir had kept the EOR going on Pd surface by preventing OH⁻ ions domination on Pd surface. Supposedly, at the applied potential of 1.0V, the affinity of OH⁻ ions towards Pd should already exceed

EtOH, they should have a higher chance to absorb onto Pd surface and inhibition should occur. However, the EtOH molecules which had accumulated within the NWs array during the lower potential prevent this from happening by continue to replenish EtOH that already oxidised on Pd surface, and giving more time for EtOH molecules from bulk to reach Pd surface before EOR was shut down by absorbed OH^- ions. Thus, the EtOH reservoir act as a key to keep the "door" of EOR opened, and inhibition cannot happen until this reservoir was run out, as illustrated in Figure 5.28. During this process, it was not impossible for two OH^- ions to absorb on neighbouring spot, especially given the concerted nature of the OH^- absorption process, and OER could have occurred. Nevertheless, EOR had a lower cost in energy, as the onset potential of EOR was at 0.4 V. Thus, between EOR and OER, it was less energy costly and more efficient to catalyse EOR, and until EOR was completely turned off, no OER actually occurred.

Figure 5.29 EOR CV curves of Au@Pd NWs measured in 1 M EtOH and 1 M NaOH at a scan rate of 50 mV/s. A. CV curves of Au@Pd NWs of different length. B. CV curve of Au@Pd NWs of different density.

As mentioned before, the reservoir effect, or the phenomena of temporary trapping of EtOH or OH^- ions near catalytic surface, should be more prominent in nanostructure with diffusion problem, such as those with very long and dense NWs structure. As seen in Figure 5.29a, we had observed that

the inhibition potential shifted towards the positive side as the NWs length increases. This was due to longer NWs should have more diffusion problem, thus a better ability to trap EtOH molecules between the NWs, as it was more difficult for the molecules to diffuse out. Hence, longer NWs with larger EtOH reservoir can keep the EOR going on for a longer time before the Pd surface was inhibited by absorbed OH^- ions. Thus inhibition occurred at a later time and the inhibition potential of longer NWs was shifted positively.

Similarly, the density of NWs also influences the amount of EtOH reservoir present, which was reflected in the inhibition potential (Figure 5.29b). As the density of our Au@Pd NWs array was heavily influenced by the amount of Au seed that present in the initial steps of the synthesis, using diluted Au seed solution will results in sparser NWs array being formed. In comparison, denser NWs will have more material diffusion problem, resulting in a larger amount of EtOH reservoir being held within the NWs layer. Larger EtOH reservoir will postpone the inhibition of Pd surface as these EtOH reservoirs prevent OH^- ions from dominating on Pd surface, resulting in higher inhibition potential. So far, the observations presented above were consistent with what we expected in systems with higher reservoir effect.

Figure 5.30 CV curve of Au@Pd NWs conducted in 1 M EtOH and 1 M NaOH. A. CV curve of Au@Pd NWs at different scan rate. B. CV curve of Au@Pd NWs stopped at different potential under the scan rate of 100 mV/s.

A part from that, in the case of Au@Pd NWs array, it was observed that for different scan rate, even though the forward oxidation peaks shifted accordingly, there seems to be less change in reverse oxidation peak, especially in terms of current (Figure 5.30a). In the forward CV scan, the inhibition occurred at higher potential at higher scan rate mainly due to the higher scan rate had exceed the time scale where inhibition happened. For example, the actual potential for inhibition to happen was at 1.0 V vs RHE, and the time taken for inhibition to complete was around 0.5 s. In lower scan rate, the changed in potential were slower, hence the time taken for inhibition to complete and reflected on CV curve did not results in a huge difference in potential. However, at higher scan rate such as 500 mV/s, this 0.5 s time difference means that when the inhibition was completed and reflected on the CV, the potential already increased by 0.25 V. Thus, it will appear as if the inhibition potential was larger at a higher scan rate.

However, things seem to be very different during the reverse CV scan. While the small shift in reverse oxidation peak position seems to suggest that the release of inhibitor seems to occur much faster than the inhibition process, the peak current of the reverse oxidation peak seems to remain roughly similar despite the increase in scan rate. It might be possible that this reverse oxidation

peak current might be directly correlated with the surface area available for EOR. Since there were only so many surfaces available on the Au@Pd NWs array, there was only limited amount of EOR that can occurred and a limited amount of current that can be generated, despite the change in the scan rate of CV. Thus, the reverse peak currents remain roughly similar.

It can also be observed that the decay of reverse oxidation peak's current was much faster in CV curve with lower scan rate than those of higher scan rate. This was related to the OH^- reservoir that present. As all the CV curves were measured from the same sample, the same amount of OH^- reservoir should be present. Nevertheless, we had to keep in mind that this OH^- reservoir is only a temporary trapping of OH^- ions within the NWs layer, not only that they get consumed over time, but they might also diffuse out of the NWs layer if given enough time, which was exactly what happens at lower scan rate. As the CV proceeds with a lower scan rate, the time taken to change from one potential to another had increased. This longer time period had gave time for the OH^- ions which was temporary trapped near Pd surface to diffuse out and reach equilibrium with the OH^- ions in the bulk solution, thus decreasing the amount of OH^- reservoir present. Hence, there were not enough OH^- reservoirs to sustain the EOR reaction and the current decayed faster at lower scan rate. Note needs to be taken that it was not that the OH^- reservoir was consumed much faster at lower scan rate. If that was the case, there should be more EOR going on and higher current should be observed, which clearly not observed here.

It can also been seen that when the CV scan stopped at the point before inhibition had complete (partially inhibited CV curves), the reverse oxidation shifted positively and the peak current remain roughly similar (Figure 5.30b). The shift in reverse peak potential had been explained in previous section using Pd plate as example, which was due to weaker overall Pd-OH bond formed by incomplete inhibition, resulting in easier and earlier release potential. However, it can be observed clearly that as compared with Pd plate (Figure 5.23), the

reverse oxidation peak current in Au@Pd NWs system did not have a huge change. The peak current did drop slightly, but in the case Pd plate, the reverse peak current had dropped by half. We think that this might be due to the larger amount of OH^- reservoir that present in Au@Pd NWs as compared with Pd plate. Even if the inhibition did not complete, there were already sufficient amount of OH^- ions that was attracted near the Pd surface and was trapped inside the NWs array, and it was hard for them to diffuse out due to the confined space within the NWs array. These OH^- reservoirs had ensures that there were enough OH^- near Pd surface for EOR to continue on Pd surface, unlike the case of Pd plate. Even if the OH^- ions were drawn near to the Pd surface on Pd plate, they can diffuse away easily as there was no confinement. Without enough OH^- reservoirs to sustain EOR on the Pd plate, the reverse oxidation peak current dropped hugely.

Figure 5.31 Stability data of Au@Pd NWs with different length in 1 M EtOH and 1 M NaOH. The current was normalised for easy comparison.

The reservoir effect induced by our nanowire array also had a significant impact on the stability of catalyst during ethanol oxidation. As reservoir was induced by structure with diffusion problem, the longer the nanowires, the more severe was the diffusion problem, and more ethanol reservoir can be "collected" within the nanostructure. From our hypothesis, the main inhibitor on Pd catalyst in ethanol oxidation is hydroxyl species, thus the larger amount of ethanol reservoir present that will prevent the hydroxyl species from completely poisoning the surface, the longer it takes for the current to decrease, the better the stability. The experimental result was consistent with our hypothesis. As shown in Figure 5.31, longer nanowires do have a slower decrease in current, resulting in better stability overall. Therefore, the presence of reservoir induced by nanowire forest had a beneficial effect on the stability of ethanol oxidation using Pd as catalyst.

5.3 Conclusion

In summary, we had proposed an EOR mechanism on Pd surface with OH^- ions as the main inhibitor that poison the Pd surface. We had discussed in details of the processes that might be happening in different part of the EOR CV. This understanding had helped us to identified the limiting factors of EOR mechanism and thus possible to suggest methods on improving the EOR activity and stability in DEFCs devices. A part from that, we had discovered that reservoir plays important role in determining the performance of Pd in EOR. The reservoir effect on our long and dense Au@Pd NWs array structure might also be a contributing factor for its high performance in EOR.

5.4 Detailed Experimental Section

Materials:

Ascorbic acid (AA), (3-aminopropyl)triethoxysilane (APTES), dimethylformamide (DMF), ethanol (EtOH), chloroauric acid (HAuCl_4), chloropalladous acid (H_2PdCl_4), methacrylic acid (MAA), 4-mercaptobenzoic acid (4-MBA), polyvinylpyrrolidone (PVP), palladium on activated charcoal (Pd/C), sodium borohydrate (NaBH_4), sodium citrate tribasic dihydrate, and fluorine doped tin oxide (FTO) glass were all purchased from Sigma-Aldrich. Sodium citrate tribasic (citrate) were purchased from Alfa Aesar and sodium hydroxide (NaOH) was purchased from Sinopharm. All chemicals were used as received without further purification.

Structural Characterization:

The surface morphologies of Au NWs and Au@Pd NWs were characterized by field emission scanning electron microscope (SEM, JEOL JSM-6700F).

Electrochemical Characterization:

The electrochemical properties were studied in a standard three-electrode cell. The cyclic voltammetry and chronoamperometry measurements were conducted using a CHI 660D electrochemical workstation. The reference electrode used is saturated calomel electrode (SCE) and the counter electrode is Pt foil. No additional treatment was needed when Au@Pd NWs or the commercially available Pd plate were applied as the working electrode. The Pd loading on Au@Pd NWs catalyst were $17.6 \mu\text{g}/\text{cm}^2$. The working electrode surface area was limited to 0.28 cm^2 . The cyclic voltammograms were measured generally at a scan rate of 50 mV/s unless specified otherwise. For both cyclic voltammograms and chronoamperometry measurements, the electrolyte used was 1.0 M ethanol with 1.0 M NaOH aqueous solution. The electrolyte was purged with N_2 gas for 30 minutes prior to all electrochemical measurements. All electrochemical measurements were carried out at 25°C .

Au NWs Synthesis:

Au NW arrays were synthesized following method reported by J. He¹². Firstly, gold seed (Au NSs) solution was prepared by adding 100 μL of aqueous HAuCl_4 solution (17 mg/mL), 160 μL of sodium citrate (1 wt%, H_2O) and 620 μL of NaBH_4 (3.8 mg/mL) into 20 mL of deionized H_2O while stirring. Next, FTO glass (around 2 cm^2) was treated in APTES solution (1 $\mu\text{L}/\text{mL}$, $\text{EtOH}:\text{H}_2\text{O} = 1:1$) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then incubated in gold seed solution prepared previously for 1 hour. After that, the gold seed immobilized FTO glass was rinsed in water twice, and then incubated in growth solution for 15 minutes. The growth solution was made up of 150 μL of HAuCl_4 (17 mg/mL, H_2O), 600 μL of 4-MBA (10 mM, EtOH), 900 μL of AA (20mM, H_2O) and 2.1 mL of EtOH as solvent. Finally, the FTO glass covered with Au NWs was rinsed with EtOH and H_2O , and then stored for further use. All of the above procedures were carried out at room temperature.

Au@Pd NWs synthesis:

Pd was coated by incubating the as-prepared Au NW arrays in MAA solution (1 $\mu\text{L}/\text{mL}$, DMF) at 60 $^\circ\text{C}$ for 2 hours, then rinsed with water. Subsequently, the FTO glass with Au NWs was incubated in Pd growth solution at room temperature. The Pd growth solution was made up of 200 μL of H_2PdCl_4 (20 mM, H_2O), 40 μL of PVP (20 mg/mL, H_2O), 400 μL of AA (10 mM, H_2O) and 2 mL of H_2O as solvent. The synthesized Au@Pd NWs were rinsed with H_2O and stored for further use. In some experiments, the solvent for MAA solution was replaced with cyclohexane, ethanol, hexane and tetrahydrofuran. The incubation temperature was also lower to room temperature in some experiments; in another experiment, no MAA was added to act as control.

SEM images of Au@Pd NWs

Figure 5.32 SEM images of Au@Pd NWs. A. Normal Au seed concentration. B. Au seed diluted by 10 times.

References

- [1] J. Goldemberg *Science*, **2007**, 315, 808-810.
- [2] C. Bianchini, P. K. Shen. *Chem. Rev.* **2009**, 109, 4183 – 4206.
- [3] S. C. S. Lai, S. E. F. Kleijn et. al. *Catal. Today* **2010**, 154, 92-104.
- [4] T. Sheng, W. F. Lin, C. Hardacre, P. Hu. *J. Phys. Chem. C* **2014**, 118, 5762–5772.
- [5] Y. Y. Yang, J. Ren et al. *ACS Catal.* **2014**, 4, 798-803.
- [6] S. C. S. Lai, S. E. F. Kleijn et al *Catal. Today* **2010**, 154, 92-104.
- [7] P. A. Christensen, S. W. M. Jones, A. Hamnett. *Phys. Chem. Chem. Phys.* **2013**, **15**, 17268-17276.
- [8] Z. Y. Zhou, Q. A. Wang et al, *Electrochim Acta*, **2010**,55, 7995-7999.
- [9] Z. X. Liang, T. S. Zhao, J. B. Xu, L. D. Zhu *Electrochimica Acta* **2009**, 54, 2203–2208.
- [10] H.F. Wang, Z.P. Liu. *J. Am. Chem. Soc.* **2008**, 130, 10996 – 11004.
- [11] E.D. Wang, J.B. Xu, T.S. Zhao. *J. Phys. Chem. C* **2010**, 114, 10489 – 10497.
- [12] J. He, Y. Wang, Y. Feng, X. Qi, Z. Zeng, Q. Liu, W. S. Teo, C. L. Gan, H. Zhang, H. Chen. *ACS Nano* **2013**, 7, 2733-2740.

Chapter 6

Selectivity of Ethanol Oxidation Product via Potential and Facets Control.

Ethanol was deemed to be one of the clean and sustainable energy sources. One of its oxidation product, acetate ions (or acetic acid), has variety of usage in chemical, food and medical industries. Acetaldehyde, another oxidation product of ethanol, acts as precursor for variety of chemical compounds. The selectivity of ethanol oxidation product in palladium (Pd) based catalyst was towards acetate, which made up of more than 90 % of the total product. We had discovered that the presence of two Pd facets on our Au@Pd NWs might be responsible for different ethanol oxidation product. Pd (200) and (220) facets each have different affinity towards OH species, which results in different ethanol oxidation pathway on each facet, where Pd (200) facets responsible for the formation of acetic acid, and Pd (220) forms acetaldehyde. It was also discovered that some ligands bind specifically to one of the facets, which might serve as a means to control ethanol oxidation product selectivity in the future

6.1 Introduction

Ethanol was deemed to be one of the clean and sustainable energy sources. Apart from it was used as fuel in direct ethanol fuel cells (DEFCs), the oxidation product of ethanol was found to be useful as well. One of the oxidation product, acetate ions (or acetic acid), has variety of usage in chemical, food and medical industries. Acetic acid was used as precursor for the production of vinyl acetate monomer¹, which can be polymerised and used as important component in paints and adhesives². Ester produced from acetic acid was also used as solvents for inks, paints and coatings. Acetic anhydride, produced from the dehydration of two acetic acid molecules, were an acetylation agent used to make synthetic textile for photographic film³. Acetic acid itself was also a good solvent, it can be used for recrystallization to purify organic compound such as terephthalic acid (TPA)⁴.

A part from its application in industry sector, acetic acid was used as antiseptic against bacteria activity such as streptococco, staphylococci and pseudomonas⁵⁻⁶. It was also used as treatment for otitis externa⁷. Diluted acetic acid, or vinegar, was used as condiment in many food preparations, and also used in pickling of vegetables and fruits⁸.

Acetaldehyde, another oxidation product of ethanol, was used for industrial production of acetic acid. It also acts as precursor for variety of chemical compounds, such as pyridine and pentaerythritol⁹. Acetaldehyde was also used for commercial production of butadiene (synthetic rubber) in some country such as Japan¹⁰. Due to their wide usage, it will be beneficial to improve the selectivity of product during ethanol electro-oxidation.

Table 6.1 Product yield of ethanol oxidation on 20 wt% Pt/C, PtRu/C and Pt₃Sn/C in 0.1 M ethanol and 0.5 M sulphuric acid (H₂SO₄). Reprinted with permission from ref. [13]. Copyright © 2006, Elsevier.

Catalyst	Potential Scan Region (V)	Product Yield (%)		
		CO ₂	CH ₃ CHO	CH ₃ COOH
Pt/C	0.06 – 1.16	0.3	77	23
PtRu/C	0.06 – 0.70	0.4	74	26
Pt ₃ Sn/C	0.06 – 0.60	0.4	78	22

In the electro-oxidation of ethanol with platinum (Pt) based catalyst, a mixture of product was always obtained. Typically, the major product obtained was acetaldehyde, followed by acetate which usually made up of quarter of the total product, and around 1 % was fully oxidised to carbon dioxide (CO₂)¹¹⁻¹³. Nevertheless, trace amount of other products such as carbon monoxide (CO) and formate (HCOO⁻) had also been reported¹³. Compared with Pt, the selectivity in palladium (Pd) based catalyst was much better, where more than 90 % of the product was acetate (CH₃COO⁻), in some cases, the sole product¹⁴⁻¹⁵. However, at lower ethanol (EtOH) or hydroxide (OH⁻) concentration, trace amount of acetaldehyde (< 1 %) and CO² (< 2.5 %) had also been reported¹⁶⁻¹⁷.

Figure 6.1 EOR product obtained from Pd based catalyst. A. EOR products obtained via high performance liquid chromatography (HPLC) at various potential reported by A. Santasalo-Aarnio². Solid line represent potential sweep with sample collection for HPLC analysis and dashed line without. B. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of EOR products. Reprinted with permission from ref. [14]. Copyright © 2009, Elsevier.

So far, there had been no effective method to tune and control the selectivity of ethanol oxidation reaction (EOR) product. Herein, we would like to report a possible way to tune EOR product selectivity through facet control in our palladium coated gold nanowires (Au@Pd NWs) forest system.

6.2 Results and Discussion

6.2.1 Background Current and Multiple Reverse Peak

During the investigation on EOR mechanism on our Au@Pd NWs array, we noticed some strange electrochemical behaviour which was not observed in Pd plate system.

Figure 6.2 Typical CV curves of Au@Pd NWs measured in 1 M EtOH and 1 M NaOH with scan rate of 50 mV/s.

It was observed that in more than 60 % of the CV curves obtained, there was a huge background current that was produced simultaneously during EOR (Figure 6.2), which leads to the skewed baseline instead of the flat baseline observed in Pd plate system. Apart from that, it was observed that around 40 % of the CV curves obtained have multiple reverse oxidation peaks, which had never observed in Pd plate. These two observations had lead us to believe that

there might be another reaction that happens simultaneously with EOR during this potential range on our Au@Pd NWs surface.

Figure 6.3 CV curves of Au@Pd NWs measured in 1 M NaOH with scan rate of 50 mV/s, with or without EtOH.

It was unlikely that this huge background current was caused by capacitance. Nevertheless, it was still worth to conduct control experiment to rule out the capacitance current, as our Au@Pd NWs array had huge surface area and had demonstrated the ability to trap ions or molecules temporary (reservoir effect), their capacitance might also be huge. As shown in Figure 6.3, without the present of EtOH, the currents produced from OH⁻ absorption and also reduction of palladium oxide were very small, and capacitance current only contributed for roughly 1 mA/cm². Therefore, it was unlikely that this huge background current observed in our Au@Pd NWs array was contributed from capacitance.

Figure 6.4 CV curves of EOR on different Pd nanomaterials measured in 1 M EtOH and 1 M NaOH with scan rate of 50 mV/s. A. Commercial available Pd/C. B. Au@Pd NPs.

The observation of huge background current during EOR was not limited to our Au@Pd NWs. As shown in Figure 6.4, in some Pd nanomaterials such as commercial available catalyst Pd on activated charcoal (Pd/C) and palladium coated gold nanoparticles (Au@Pd NPs), a significant amount of background current can be observed during EOR. This study had suggested that the large background current might not be unique in our Au@Pd NWs forest system, but the huge enhancement in EOR catalytic activity provided by our NWs forest had also enhanced this reaction that leads to the production of this background current, which make it becomes much more significant in our NWs forest.

Figure 6.5 CV curves of EOR on Au@Pd NWs with different scan range measured in 1 M EtOH and 1 M NaOH with scan rate of 50 mV/s.

In the effort to investigate the origin of this background current, we had increase the potential range of CV. As shown in Figure 6.5, this background current seems to be a part of a new pairs of oxidation. Just as in the case of partially inhibited peaks investigated in previous chapter, before reaching the point of inhibition (or inhibition potential), there were no clear forward and reverse peak, but just a straight line going up and down. When the CV potential range was increased, a second inhibition process had occurred and a second forward oxidation peak appeared. When the reverse CV scan was performed, a second reverse oxidation peak also appeared. The appearance of these second sets of oxidation peaks had indicated two important things : the first one was that not all Au@Pd NWs surface were inhibited (or poisoned) at 1.1 V where normal EOR should ends, some of the surface remain un-inhibited and was able to catalyst reaction; the second fact was that a second oxidation reaction had occurred, given the simple electrolyte system, the second oxidation reaction

was most likely also EOR but undergo a different mechanism, which likely to give a different EtOH oxidation product.

Table 6.2 Various chemical test performed to determine ethanol oxidation product obtained at different potential.

Chemical Test	Sample A	Sample B
	Product from second sets of oxidation peaks (1.40 V, 15 hrs)	Product from first sets of oxidation peaks (0.85 V, 15 hrs)
Odour	Fruity Odour	Vinegar
Iodoform Test (Methyl Ketone)	Positive	Positive
NaHCO₃ (Carboxylic Acid)	Negative	Positive
Brady's Reagent (Aldehyde/Ketone)	Positive	Negative
Benedict Solution (Aldehyde)	Positive	Negative
Proposed Product	Acetaldehyde	Acetic Acid

As it was possible that the second set of oxidation peaks give rise to different ethanol oxidation product, chemical test of the product was carried out. Electrolysis was first carried out at 1.40 V for 15 hours, where normal EOR inhibition already happened and the current should only attributed to product of second oxidation peak. This product was term sample A. Control experiment was also performed at 0.85 V to check the product from normal EOR (first set of oxidation peaks), which was named sample B. The chemical test result was summarized in Table 6.2. Firstly, the product from electrolysis at 0.85 V (Sample B) has a sour vinegar smell, which suggests that the major product

should be acetic acid. Instead, the product from second sets of oxidation peaks (Sample A) has a sweat, slightly rotten fruit odour, which is a strong indication that indeed a different product was obtained.

From the iodoform test, both products give positive results, which indicates that both were methyl ketone. When sodium bicarbonate (NaHCO_3) was added to the products, only sample B gives effervescence indicates the present of acid that reacts with NaHCO_3 , which release carbon dioxide (CO_2) gas. No effervescence observed for sample A, which means sample A was not an acid. Addition of Brady's reagent give a positive test result for sample A and a negative for sample B, which indicates that sample A was most likely an a ketone or aldehyde. Furthermore, a positive result in Benedict's test had confirmed that sample A was indeed an aldehyde. Given the reaction condition, a only chemical that might undergo oxidation was EtOH , and it was unlikely that Pd can catalyse the breakage of C-C bond, thus the product from second oxidation peaks was most likely acetaldehyde.

Figure 6.6 HPLC data of product obtained from electrolysis at 1.40 V. The liquid phase used was 0.1 M H_2SO_4 , the flow rate of liquid phase was 1 mL/min and the column temperature was 40 °C

To confirm our hypothesis that the second set of oxidation peaks gives a different EOR product (acetaldehyde), a high performance liquid chromatography (HPLC) was performed. From the HPLC test, there were only two peaks observed, the first peaks was most likely from sodium sulphate (Na_2SO_4), which was formed when the electrolysis product containing sodium hydroxide (NaOH) was neutralised with sulphuric acid (H_2SO_4) before injected into HPLC column. The second peak, with a retention time of around 24.8 minutes, indicates that acetaldehyde indeed present and was the major product. (The retention time for acetic acid and ethanol was 18.4 and 32.8 minutes respectively.)

6.2.2 Different Surface Responsible for Different EOR Product

Previously we had confirmed that the two sets of oxidation peaks observed corresponded for different EOR product: the first set of oxidation peaks (1.0 V) give rise to acetic acid; the second set of oxidation peaks (1.3 V) produce acetaldehyde. Next, we would like to further investigate what give rise to these two sets of oxidation peaks.

Figure 6.7 HRSTEM image of Au@Pd NWs, with both (200) and (220) facets labelled.

Careful examination of high-resolution scanning transmission electron microscopy (HRSTEM) images of the Au@Pd NWs had revealed that there

were two major facets that exist on the surface of our Au@Pd NWs array. As shown in Figure 6.7, the Au@Pd NWs was made up of alternating crystal domain, with (200) and (220) facets exposed. The existence of these two types of facets might be the origin for the two sets of oxidation peaks. Our hypothesis was that each of these facets adopt a slight different pathway in EOR, resulting in different EOR product.

Figure 6.8 CV curves of highly twisted Au@Pd NWs synthesized in hexane and tetrahydrofuran (THF) solvent, measured in 1 M EtOH and 1 M NaOH at scan rate of 50 mV/s.

To rule out the contribution from defects, EOR had been conducted in highly twisted, ultrathin Au@Pd NWs, which have a high ratio of defects on their surfaces. Two types of highly twisted Au@Pd NWs were tested, which was synthesized in hexane and tetrahydrofuran (THF) solvent. However, as shown in Figure 6.8, none of the highly twisted NWs had exhibit the high

background current observed in our Au@Pd NWs array, which indicates that defects were not responsible for the second sets of oxidation peaks.

Our initial hypothesis was that Pd (200) surface was the more common surface, which was responsible for the production of acetic acid in EOR. This was the surface that was inhibited first, thus contribute to the first pair of oxidation peaks. On the other hand, Pd (220) surface was responsible for the production of acetaldehyde in EOR, which was harder to be inhibited and contributed for the second pair of oxidation peaks observed during EOR CV. The assumption of which Pd facets was initially based on the ratio of (200) to (220) on Au@Pd NWs surface and the ratio of current that give acetic acid as product to acetaldehyde. As observed in Figure 6.5, before the first inhibition happened, the current ratio of those that supposedly produce acetic acid was higher than current responsible for formation of acetaldehyde at all potential. Since the ratio of (200) surface as observed in HRSTEM images (Figure 6.7) was higher as compared to (220), we proposed that (200) was responsible for formation of acetic acid, thus (220) surface was responsible for formation of acetaldehyde.

Figure 6.9 Illustration on how acetaldehyde was formed on Pd surface.

In the terms ethanol oxidation mechanism, acetic acid (or acetate ions) was considered the incomplete oxidation form of ethanol molecules. However, given that Pd could not catalysed the breakage of C-C bond very well, acetic acid was the highest oxidation form that can be achieved on Pd surface. On the

other hand, acetaldehyde was always regarded as the intermediate species before the complete oxidation of ethanol molecules to acetic acid. Thus, it will be very interesting to find out that why the oxidation of ethanol stops at acetaldehyde instead of goes all the way to acetic acid. From the stoichiometric point of view, four OH^- ions was needed to oxidise one EtOH molecules to acetic acid (five to acetate ions), but only two OH^- ions was needed to oxidise EtOH to acetaldehyde. Since more OH^- ions were needed to completely oxidise EtOH to acetic acid, it might be possible that the oxidation stopped at acetaldehyde due to insufficient supply of OH^- ions as illustrated in Figure 6.9.

Figure 6.10 Voltammograms of the oxygen reduction reaction of Pd crystals with different facets using rotating disk electrode (rotating rate: 2000 rpm) in 0.1 M HClO_4 saturated O_2 with scan rate of 10 mV/s. Reprinted with permission from ref. [18]. Copyright © 2010, American Chemical Society.

As previously reported by S. Kondo et. al., different Pd facets give rise to a slight different onset potential in a oxygen reduction reaction¹⁸. It seems that Pd {100} facet has the earliest onset potential, while Pd {110} facet has the

latest onset (Figure 6.10). The difference in onset potential during oxygen reduction reaction might have been due to the different ability of these facets in absorbing oxygen species. Pd {110} facets (equivalence of Pd (220) facets) seems to have the weakest ability to attract or absorb oxygen species, making it harder for oxygen molecules to absorb on it, thus harder for the facets to catalyse oxygen reduction reaction, resulting in the later onset of reaction. On the opposite site, Pd {100} facets (equivalence to Pd (200) facets) seems to attract and absorb oxygen species easily, resulting in the early onset potential.

Figure 6.11 Characterization and electrochemical results of Pd octahedral (Pd Octs), Pd rhombic dodecahedral (Pd Rds) and Pd cubic nanocrystals (Pd NCs). A. X-ray diffraction (XRD) samples of the samples. B. CV curves of the samples measured in N_2 -saturated 0.1 M NaOH with scan rate of 50 mV/s. Reprinted with permission from ref. [19]. Copyright © 2016 Elsevier.

It was proposed that Pd (200) and Pd (220) facets might have different affinity towards oxygen species. Recently, the synthesis of Pd octahedral (Pd Octs), Pd rhombic dodecahedral (Pd Rds) and Pd cubic nanocrystals (Pd NCs) reported by J.S. Ye¹⁹, which might provide insight to our hypothesis. Through the XRD characterization, it was shown that Pd NCs surface majority made up of (200) facets, while Pd Rds consists more of (220) facets (Figure 6.11a)¹⁹. As shown in CV curves in Figure 6.11b, Pd NCs with majority (200) facets has a

clear OH^- absorption peak at -0.4 V vs Ag/AgCl, while OH^- absorption peak was almost invisible for Pd Rds with (220) facets¹⁹. This observation has prove that Pd (200) has much higher affinity towards OH^- ions as compared with (220) surface.

The understanding that different Pd facets have different affinity towards OH^- ions might help to explain why different Pd facets give rise to different EOR product. Pd (200) had higher affinity towards OH^- ions, was able to attract and absorb a huge amount of OH^- ions on its surface, providing enough OH^- ions to complete the oxidation of EtOH molecules, thus giving acetic acid (acetate ions) as product. Besides that, its higher affinity towards OH^- ions also meant that it can be inhibit easier by OH^- ions, which results in early inhibition at 1.1 V, giving raise to the first oxidation peak in the EOR CV curve of our Au@Pd NWs array. On the other hand, Pd (220) facets with lower affinity towards OH^- ions thus cannot attract and absorb enough OH^- ions to its surface. Without a sufficient supply of OH^- ions, ethanol cannot be oxidised completely, which was forced to stop half way, which give acetaldehyde as product. In addition, its lower affinity towards OH^- ions also meant that it was harder to be inhibited by OH^- ions, thus inhibition occurred at a higher potential of 1.4 V, which give raise to the second oxidation peak in the EOR CV curve of our Au@Pd NWs array. This explanation was consistent with our hypothesis that (200) facets was responsible for formation of acetic acid, and (220) facets was responsible for formation of acetaldehyde.

6.2.3 Different Functional Group Selectively Bond to Different Pd Facets

With the understanding that different Pd facets responsible for different EOR product, it was important now to figure out a way to control these facets, thus control the selectivity of product obtained. As it was hard to control the Pd facets on Au@Pd NWs array to consist of purely (200) or purely (220) facets, one of the easier approach was to shield one of the facets, leaving the other one for electrocatalysis of EOR. To achieve the selective shielding of Pd facets, we had investigate through a series of organic molecules which will act as ligand on Pd surface, and take note of any ligand that will selectively bond to one of the facets.

Figure 6.12 CV curves of Au@Pd NWs washed different times after APTES treatment, measured in 1 M EtOH and 1 M NaOH at 50 mV/s scan rate.

It was found that different washing intensity during Au@Pd NWs synthesis affect the ratio of background current present. This was particular obvious during the (3-Aminopropyl)triethoxysilane (APTES) treatment step. In a typical Au@Pd NWs synthesis, APTES was used to treat the surface of substrate to stick the gold seed on the substrate. As shown in Figure 6.12, the amount of washing performed after APTES treatment step had result in very different ratio of background current. It seems that the amount of APTES left over after the washing step was crucial to control the ratio of background current. The more washing was performed, the lesser amount of APTES left in synthesis, and this seems to lead to larger ratio of background current. This was only possible if APTES selectively binds to Pd (220) surface, which was responsible for the present of background current and production of acetaldehyde.

Figure 6.13 CV curves of Au@Pd NWs washed for 10 times after APTES treatment (control), then soaked in 2.5 mM of APTES solution for 15 minutes after synthesis, measured in 1 M EtOH and 1 M NaOH at 50 mV/s scan rate.

To confirm that APTES did selectively binds to Pd (220) surface on Au@Pd NWs array, thus suppressing the background current, we had purposely introduced APTES back into synthesis after excessive washing. In a sample that was washed 10 times after APTES treatment, the sample was soaked in 2.5 mM of APTES solution for 15 minutes after the whole Au@Pd NWs synthesis was complete. Indeed, after the re-introduced of APTES after synthesis, the background current was suppress completely when compared to the control sample (Figure 6.13). The fact the APTES was able to suppress background current in such a short amount of time (15 minutes) also proved that the suppression of background current was not due to facets directing effect of APTES during synthesis which influence the growth of Pd shell to produce more (200) surface. The only explanation for APTES to work so fast was that it selectively binds onto (220) surface of Pd, and the bonding was so strong that APTES molecules did not detached from Pd (220) surface during electrochemical test, thus suppressing the background current.

Figure 6.14 CV curves of Au@Pd NWs illustrating how each CV cycle changes before reaching stable state, measured in 1 M EtOH and 1 M NaOH at 50 mV/s scan rate.

The strong binding strength of APTES can be deduced by observing how the CV curves change with each cycle. In a sample of Au@Pd NWs with excessive washing after APTES treatment, the typical CV curves were shown in Figure 6.14. In this sample, the only ligand that is supposed to be on the Au@Pd NWs surface was polyvinylpyrrolidone (PVP), with a very small amount of APTES present. Judging from the CV curves, PVP was a weak ligand as compared with APTES, which was removed during the first CV cycle, indicated by the large peak at 1.2 V. After that, the second and third cycle proceed without any background current, indicating that the small amount of APTES present still shields the Pd (220) facets. However, as the scan proceeds, the APTES molecules can no longer hold strongly on the Pd surface and detach from the Au@Pd NWs, resulting in the appearance of background

current from forth cycle onwards, and reached a stable state around tenth cycle. It was likely that the APTES can shield the (220) surface more effectively if present in larger quantity, as APTES molecules can undergo hydrolysis to form a continuous network, which will act like a multi-dentate ligand, making it harder to be removed as shown in Figure 6.13.

Figure 6.15 CV curves of Au@Pd NWs soaked in different ligand after synthesis, measured in 1 M EtOH and 1 M NaOH at 50 mV/s scan rate. The concentration of ligand used was 2.5 mM and the soaking period was 15 minutes. The chemical structure of the ligands was shown in insert.

To check if there was any other ligand that selective binds to Pd (200) or (220) surface, Au@Pd NWs was soaked in some ligand with the concentration of 2.5 mM for a period of 15 minutes. If the background current disappeared, this means that the ligand must have binds onto one of the facets. The identity of Pd facets that was shield can be differentiate easily from the inhibition

potential, as Pd (220) has lower affinity towards OH^- , it will be inhibited at a higher potential. Thus, for the CV curves without background current, if the inhibition happened around 1.0 V, the ligand had selectively binds to (220) facets; if the inhibition happened after 1.3 V, the ligand had selectively binds to (200) facets. If no current was present, this means that the ligand binds strongly to both (200) and (220) surface.

As shown in Figure 6.15, out of the ligands tested, only (3-mercaptopropyl)trimethoxysilane (MPTMS) and polyethylenimine, ethylenediamine branched (PEE) had successfully suppress the background current, while 3-cyanopropyltriethoxysilane (CPTES) and tetraethyl orthosilicate (TEOS) shown no effect. Since the inhibition potential for both Au@Pd NWs treated with MPTMS and PEE were around 1.0 V, both the ligand had selectively binds to (220) surface, similar to APTES ligand, leaving the (200) surface for electrocatalysis of EOR. From these results, it can be concluded that ligand with amino functional group and mercapto functional group was more likely to bond selectively to Pd (220) facets.

6.3 Conclusion

In conclusion, we had shown that the presence of two Pd facets on our Au@Pd NWs might be responsible for different ethanol oxidation products. Pd (200) and (220) facets each have different affinity towards OH^- species, which results in different ethanol oxidation pathways on each facet, where Pd (200) facets are responsible for the formation of acetic acid, and Pd (220) forms acetaldehyde. It was also discovered that some ligands bind specifically to one of the facets, which might serve as a means to control ethanol oxidation product selectivity in the future.

6.4 Detailed Experimental Section

Materials:

Ascorbic acid (AA), (3-aminopropyl)triethoxysilane (APTES), 3-cyanopropyltriethoxysilane (CPTES), dimethylformamide (DMF), ethanol (EtOH), chloroauric acid (HAuCl_4), chloropalladous acid (H_2PdCl_4), hexane, methacrylic acid (MAA), 4-mercaptobenzoic acid (4-MBA), (3-mercaptopropyl)trimethoxysilane (MPTMS), nafion solution (Nafion), oleylamine (OA) palladium on activated charcoal (Pd/C), polyvinylpyrrolidone (PVP), polyethylenimine, ethylenediamine branched, sodium borohydrate (NaBH_4), sodium citrate tribasic dihydrate (citrate), sulphuric acid (H_2SO_4), tetraethyl orthosilicate (TEOS), tetrahydrofuran (THF) and fluorine doped tin oxide (FTO) glass were all purchased from Sigma-Aldrich. Sodium citrate tribasic (citrate) were purchased from Alfa Aesar and sodium hydroxide (NaOH) and triisopropylsilane (TIPS) was purchased from Sinopharm. All chemicals were used as received without further purification.

Structural Characterization:

The surface morphologies of ultrathin Au@Pd NWs were characterized by transmission electron microscopy (TEM, JEOL, operated at 100 kV). Atomic resolution scanning transmission electron microscopy (STEM) were carried out on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope (JEOL, JEM-2100F) with high-angle annular dark-field (HAADF) detector operated at 200 kV. High performance liquid chromatography (HPLC) was performed on a Shimadzu modular HPLC machine (Prominence). The samples were neutralized with H_2SO_4 before injected into the HPLC machine.

Electrochemical Characterization:

The electrochemical properties were studied in a standard three-electrode cell. The cyclic voltammetry and chronoamperometry measurements were conducted

using a CHI 660D electrochemical workstation. The reference electrode used is saturated calomel electrode (SCE) and the counter electrode is Pt foil. No additional treatment was needed when Au@Pd NWs array was applied as the working electrode. The Pd loading on Au@Pd NWs catalyst were $17.6 \mu\text{g}/\text{cm}^2$. For ultrathin, highly twisted Au@Pd NWs synthesized in hexane and THF, they were prepared using drop-cast method, and then were covered with a thin layer of Nafion ($5 \mu\text{L}$, 5 wt%) before electrochemical measurement. The working electrode surface area was limited to 0.28 cm^2 . The cyclic voltammograms were measured generally at a scan rate of 50 mV/s unless specified otherwise. For both cyclic voltammograms and chronoamperometry measurements, the electrolyte used was 1.0 M ethanol with 1.0 M NaOH aqueous solution. The electrolyte was purged with N_2 gas for 30 minutes prior to all electrochemical measurements. All electrochemical measurements were carried out at 25°C .

Au@Pd NWs Synthesis:

Au NW arrays were synthesized following method reported by He, J. T²⁰. Firstly, gold seed (Au NSs) solution was prepared by adding $100 \mu\text{L}$ of aqueous HAuCl_4 solution (17 mg/mL), $160 \mu\text{L}$ of sodium citrate (1 wt%, H_2O) and $620 \mu\text{L}$ of NaBH_4 (3.8 mg/mL) into 20 mL of deionized H_2O while stirring. Next, FTO glass (around 2 cm^2) was treated in APTES solution ($1 \mu\text{L/mL}$, $\text{EtOH}:\text{H}_2\text{O} = 1:1$) for 15 minutes. Then, the FTO glass was washed with H_2O for 5 times, which was then incubated in gold seed solution prepared previously for 1 hour. After that, the gold seed immobilized FTO glass was rinsed in water twice, and then incubated in growth solution for 15 minutes. The growth solution was made up of $150 \mu\text{L}$ of HAuCl_4 (17 mg/mL , H_2O), $600 \mu\text{L}$ of 4-MBA (10 mM , EtOH), $900 \mu\text{L}$ of AA (20 mM , H_2O) and 2.1 mL of EtOH as solvent. Finally, the FTO glass covered with Au NWs was rinsed with EtOH and H_2O . Pd was coated by incubating the as-prepared Au NW arrays in MAA solution ($1 \mu\text{L/mL}$, DMF) at 60°C for 2 hours, then rinsed with water. Subsequently, the FTO glass with Au NWs was incubated in Pd growth solution at room

temperature. The Pd growth solution was made up of 200 μL of H_2PdCl_4 (20 mM, H_2O), 40 μL of PVP (20 mg/mL, H_2O), 400 μL of AA (10 mM, H_2O) and 2 mL of H_2O as solvent. The synthesized Au@Pd NWs were rinsed with H_2O and stored for further use. In some experiments, the frequency of washing step was altered.

Highly twisted ultrathin Au@Pd NWs Synthesis (Hexane):

The highly twisted ultrathin Au@Pd NWs was synthesized using the method reported by H. Feng²¹. 3 mg of HAuCl_4 and 100 μL of OA was mixed into a 2.5 mL hexane solvent, followed by 150 μL of TIPS, and incubated at room temperature for 5 hours. After that, washing was conducted by addition of 8 mL EtOH into the mixture, and centrifuged at 4,500 rpm for 15 minutes. The dark red Au NWs precipitate obtained was re-dispersed in 2.5 mL of hexane. The washing step was repeated for two more times. The Au NWs was then re-dispersed in DMF solution, where 20 μL of H_2PdCl_4 (20 mM, H_2O) and 40 μL of AA (10 mM, H_2O) was added. The mixture was incubated for 5 hours, and centrifuged at 4,500 rpm for 15 minutes to remove the supernatant, then washed with DMF once and hexane once. After that, the Au@Pd NWs was re-dispersed in 2.5 mL of hexane containing 100 μL of OA and stored for further use.

Highly twisted ultrathin Au@Pd NWs Synthesis (THF):

The highly twisted ultrathin Au@Pd NWs was synthesized using the method reported by Y. Chen²². The synthesis step was exactly similar to those synthesized with hexane solvent, except that the hexane solvent was replaced by THF in this case.

TEM characterization

Figure 6.16 TEM images of ultrathin highly twisted Au@Pd NWs synthesized in: A. Hexane. B. THF.

High performance liquid chromatography (HPLC)

Figure 6.17 Retention time for HPLC of various samples using 0.1 M H₂SO₄ as mobile phase, flow rate of 1 mL/min and column temperature of 40 °C.

References

- [1] H. Cheung, R. S. Tanke, G.P. Torrence. "Acetic Acid", *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, **2005**. doi:10.1002/14356007.a01_045.pub2
- [2] G. Roscher. "Vinyl Esters", *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, **2005**. doi:10.1002/14356007.a27_419
- [3] H. Held, A. Rengstl, D. Mayer. "Acetic Anhydride and Mixed Fatty Acid Anhydrides", *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, **2005**. doi:10.1002/14356007.a01_065
- [4] M. Malveda, C. Funada. "Acetic Acid". *Chemicals Economic Handbook. SRI International*. **2003**, 602-5000.
- [5] V. L. Madhusudhan, *International Wound Journal*. **2015**, 13, 1129–1136.
- [6] H. Ryssel, O. Kloeters, G. Germann, T. Schäfer, G. Wiedemann, M. Oehlbauer. *Burns: Journal of the International Society for Burn Injuries*. **2009**, 35, 695–700.
- [7] B. S. Nagoba, S. P. Selkar, B. J. Wadher, R. C. Gandhi. *Journal of Infection and Public Health*. **2013**, 6, 410–415.
- [8] A. Bernthsen, J. J. Sudborough. *Organic Chemistry. London: Blackie and Son*. **1922**, 155-156.
- [9] M. Eckert. "Acetaldehyde" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2007**.
- [10] Research and Markets ltd. "Acetaldehyde – Global Business Strategic Report". Retrieved from <https://www.researchandmarkets.com/research/lc8hz5/acetaldehyde>
- [11] Q. Wang, G. Q. Sun, L. H. Jiang, Q. Xin, S. G. Sun, Y. X. Jiang, S. P. Chen, Z. Jusys, R. J. Behm. *Phys. Chem. Chem. Phys.* **2007**, 9, 2686 - 2696.

- [12] H. Wang, Z. Jusys, R. J. Dehm. *J. Phys. Chem. B* **2004**, 108, 19413 - 19424.
- [13] L. Colmenares, H. Wang, Z. Jusys, L. Jiang, S. Yan, G. Q. Sun, R. J. Behm. *Electrochim. Acta* **2006**, 52, 221-233.
- [14] C. Bianchini, V. Bambagioni, J. Filippi, A. Marchionni, F. Vizza, P. Bert, A. Tampusci. *Electrochem. Commun.* **2009**, 11, 1077–1080.
- [15] C. S. Stanley, M. T. M. Koper. *J. Phys. Chem. Lett.* **2010**, 1, 1122-1125.
- [16] J. Rasko, M. Domok, K. Baan, A Erdohelyi. *Appl. Catal., A* **2006**, 299, 202–211.
- [17] S. Y. Shen, T. S. Zhao, Q. X. Wu. *Int. J. Hydrogen Energy*, **2012**, 37, 575-582.
- [18] W. Niu, L. Zhang, G. Xu. *J. Phys. Chem C* **2009**, 113, 12625-12628.
- [19] J. S. Ye, S. Y. Hsu, C. L. Lee. *Electrochim. Acta* **2016**, 211, 1024-1032.
- [20] J. He, Y. Wang, Y. Feng, X. Qi, Z. Zeng, Q. Liu, W. S. Teo, C. L. Gan, H. Zhang, H. Chen. *ACS Nano* **2013**, 7, 2733-2740.
- [21] H. Feng, Y. Yang, Y.g You, G. Li, J. Guo, T. Yu, Z. Shen, T. Wu, B. Xing. *Chem. Commun.* **2009**, 0, 1984–1986.
- [22] Y. Chen, Y. Wang, J. Peng, Q. Xu, J. Weng, J. Xu. *ACS Nano* **2017**, 11, 2756-2763

Chapter 7

Conclusion and Outlooks

In conclusion, we had fulfilled our aim to explore the mechanism behind one dimensional nanostructure synthesis and catalytic performance, which contributes towards optimizing of catalytic process. We had investigated the growth mechanism for molten salt synthesized TiO₂ nanowires, and determined the key to grow hybrid TiO₂ NWs was to control the rate of ligand adsorption and TiO₂ deposition, although the desired hybrid structure was not obtained. We have demonstrated that by simply changing the morphology of electrocatalyst from nanoparticles to aligned nanowire arrays, we can dramatically improve the catalytic activity by providing more electrochemical active surface for electrocatalysis, one-dimensional channels for improved mass transport and better conductivity. We had explored the ethanol oxidation mechanism on Pd surface and discovered reservoir effect shown by nanowires array. We had also investigated the role of Pd facets on ethanol oxidation pathway and the effect on the product obtained.

7.1 Conclusion

In conclusion, we had fulfilled our aim to explore the mechanism behind one dimensional nanostructure synthesis and catalytic performance, which contributes towards optimizing of catalytic process. We had demonstrated that TiO_2 NWs synthesized via molten salt method adopts seed-assisted growth mode, with ripening as the main growth mechanism, which was consistent with our initial hypothesis in Chapter 2. Rutile NPs not only able act as seed to control the diameter of the resulting NWs, but also able to act as feedstock, where the selectivity comes from its own size, which is common with ripening as main growth mechanism. As TiO_2 NWs adopt seed-assisted growth mode, it is possible for the creation of hybrid TiO_2 NWs with different segment doped with transition metal ions via molten salt synthesis. We had identified the key to grow hybrid TiO_2 NWs was to control the rate of ligand adsorption and TiO_2 deposition, as proposed in our hypothesis. We had tried various methods to increase ligand adsorption speed, such as using un-washed precursor, changing mixing method and replacing NaCl salt, and modifying TiO_2 precursors to decrease TiO_2 deposition rate in Chapter 3. However, all the attempts had failed to control the lateral growth or the NWs obtained was not TiO_2 . As we had exhausted all possible means but was unsuccessful to obtain the desired nanostructure, which was hybrid TiO_2 NWs with different segment doped with transition metal ions, the project was halted.

In the case of nanowire array, we have demonstrated that by simply changing the morphology of electrocatalyst from nanoparticles to aligned nanowire arrays, we can dramatically improve the catalytic activity by providing more electrochemical active surface for electrocatalysis, one-dimensional channels for improved mass transport and better conductivity. The design and performance of electrocatalyst studied in Chapter 4 was consistent with what we had proposed before. Our approach provides a new and simple means to enhance the electrocatalytic activity, reduce the size of electrode for

miniaturization of portable devices and improve the effectiveness of existing and emerging electrochemical technologies. We had proposed an EOR mechanism on Pd surface in Chapter 5, where OH^- ions act as the main inhibitor that poison the Pd surface. We had discussed in details of the processes that might be happening in different part of the EOR CV. This understanding had helped us to identified the limiting factors of EOR mechanism and thus possible to suggest methods on improving the EOR activity and stability in DEFCs devices. A part from that, we had discovered that reservoir plays important role in determining the performance of Pd in EOR. The reservoir effect on our long and dense Au@Pd NWs array structure, proven to be a morphology induced property, might also be a contributing factor for its high performance in EOR.

We had shown that the present of two Pd facets on our Au@Pd NWs might be responsible for different ethanol oxidation product formation as proposed in our hypothesis through the studies conducted in Chapter 6. Pd (200) and (220) facets each have different affinity towards OH^- species, which results in different ethanol oxidation pathway on each facet, where Pd (200) facets responsible for the formation of acetic acid, and Pd (220) forms acetaldehyde. It was also discovered that some ligands bind specifically to one of the facets, which might served as a means to control ethanol oxidation product selectivity in the future.

7.2 Outlooks

Based on the observation and understanding in the mechanism of nanowires synthesis and electrocatalysis discussed in this thesis, several future directions can be explored.

7.2.1 Titanium Dioxide Nanowires with Radial Heterojunction.

Although we had failed to synthesize the desired nanostructure, which was hybrid titanium dioxide nanowires (TiO_2 NWs) with different segment doped with transition metal ions, our understanding in the growth mechanism of TiO_2 NWs in molten salt synthesis had allowed us to create TiO_2 NWs with radial heterojunction, where the core and shell of the NWs can be doped with different transition metal ions. This can be achieved via normal second growth, which was the typical “fail” product in the process of creating segmented TiO_2 NWs illustrated in Chapter 3. The transition metal dopant can be added easily by mixing the cations into the synthesis mixture during first or second growth.

TiO_2 NWs with radial heterojunction, or coaxial p-n junction, have a variety of photovoltaic applications, such as their usage in solar cells¹ or ultraviolet photodetector². TiO_2 NWs with radial heterojunction can also be used in devices such as field-effect transistors³. Bare TiO_2 itself was an n-type semiconductor, when doped with transition metal ions such as iron (Fe), manganese (Mn) and chromium (Cr), it can become a p-type semiconductor. Thus, by selectively doping the core or the shell of the TiO_2 hybrid NWs, we can easily create a coaxial p-n junction along the NWs. This type of structure allows for efficient charge separation, thus decreasing the loss of charge through recombination and increase the incident photon to current conversion rate (IPEC), which will be beneficial for photovoltaic applications. Apart from that, the band gap of TiO_2 NWs can be tuned by changing the dopant types and

doping concentration, which make it highly suitable for customization towards specific reactions.

Figure 7.1 TiO_2 NRs/NWs obtained for 1st, 2nd and 3rd growth. A. & B. 1st growth; C. D. 2nd growth; E.F. 3rd growth. Where 2nd growth can be used to create radial p-n junction in TiO_2 NWs.

7.2.2 Application of Au@Pd Nanowires as Anode in Direct Ethanol Fuel Cells.

We had shown in Chapter 4 that our gold core palladium shell nanowires (Au@Pd NWs) array had extraordinary electrochemical performance in ethanol oxidation reaction (EOR). Thus, it will be reasonable to test the performance of our catalyst in a real device, which was direct ethanol fuel cell (DEFCs) in this case. DEFCs, like all fuel cells and batteries, were made up of cathode and anode. The cathode side reaction was normally oxygen reduction reaction (ORR), while the anode side was ethanol oxidation reaction (EOR). We had planned to use our Au@Pd NWs array as the anode in EOR, and use a standard ORR catalyst at the cathode, such as platinum on carbon (Pt/C). We will evaluate the DEFCs performance based on parameters such as open circuit potential (V_{oc}), discharge current density, power output and stability of the device.

Before we assembly the devices, there were still a few challenges that need to solved. First, we needed to solve the current density problem as mentioned briefly in Chapter 5. As fluorine-doped tin oxide (FTO) glass was not a suitable electrode to be used in DEFCs, we had intended to change the substrate of Au@Pd NWs to three dimensional electrode such as carbon clothes, which will simultaneously increase the electrochemical active surface area and loading for the NWs. However, despite the change in substrate, the current density of the NWs in EOR did not increase proportionally, resulting in a lower than expected NWs. Through our understanding, we can now deduce that the current density was probably limited by the amount of ethanol and hydroxide (OH^-) ions present. For all testing conducted, the electrolyte used was 1 M ethanol and 1 M NaOH. Nevertheless, given the large surface and loading amount, the ethanol and OH^- ions were probably consumed too fast on the electrode, where the current density had now become limited by the diffusion of reactant from the bulk. Thus, this current density problem can most likely be solved by increasing the concentration of ethanol and NaOH used.

Another major challenge faced in the constructing DEFCs device was the stability. As shown in Chapter 4, the current stability test for Au@Pd NWs at 0.87V vs RHE was only 25 % left after only one hour due to poisoning of the Pd surface with inhibitor. This stability was clearly insufficient for performance of DEFCs as fuel cells were normally expected to last for days or even weeks. Therefore, we need to develop a method to improve the current stability of the Au@Pd NWs. One of the possible method might be through facet control, where Pd (220) facet had shown to have less affinity towards OH⁻ ions which will act as inhibitor, thus we might be able to improve the stability by tuning Au@Pd NWs surface to (220) facet. Another approached was through reservoir effect demonstrated by our Au@Pd NWs array. The present of large amount of ethanol reservoir might helped to improve the current stability, thus we should design the catalyst structure to be able to trap as much ethanol reservoir as possible. For example, making denser and longer NWs, creating branches on the NWs and increase the surface roughness of the NWs.

Besides that, another problem that we have to solve was the reactant selectivity. In normal half cell reaction, the electrolyte was often bubbled with nitrogen gas prior to the testing to avoid any interference from oxygen gas dissolved in the electrolyte. However, since in DEFCs, the cathode reaction was ORR, it was inevitable that some dissolved oxygen molecules might diffuse to the anode side despite the present of a membrane. Therefore, we need to determine the selectivity of our Au@Pd NWs towards EOR and the amount of changes caused by dissolved oxygen in our Au@Pd NWs array EOR before moving to device testing.

In additionally, we also have to consider the design of the DEFCs. Some of the point to take note of includes if we want to construct a flow cell, the operating temperature of DEFC and the electrolyte concentration used, and how these conditions will affect the EOR performance of our Au@Pd NWs array catalyst.

7.2.3 Other Electrocatalytic Applications of Nanowires Array.

Our Au@Pd NWs array had shown to be an effective ethanol electro-oxidation catalyst. However, we also felt that this NWs array might also be applied on other electrocatalytic reaction. For example, we think that our Au@Pd NWs array might also have great electrocatalytic performance in oxidation of longer chain alcohols. Pd was an active electrocatalyst not only for ethanol, but also for methanol. Thus we think that Pd might be a general catalyst for oxidation of alcohols, such as propanol, butanol, pentanol and hexanol. We would also like to explore the possibility of oxidising heavier and more complex alcohol (secondary and tertiary alcohol) such as benzyl alcohol, cyclohexanol etc. However, some of the problems that might be faced included the solubility of the reactant. As the molecular weight of the alcohols increased, their solubility in the aqueous solution decreases, due to the increasingly larger carbon chain which is hydrophobic. Therefore, modification needs to be made on the electrolyte, which was an aqueous solution in our case. One of the solutions was to change the aqueous electrolyte to a polar organic solvent, such as dimethylformamide (DMF) and acetonitrile. Still, doing so will give rise to another problem, where these organic solvent, even though they can dissolve the long chain alcohol, could not conduct ionic species effectively. This can be solved by adding some organic soluble salt as supporting electrolyte into the organic solvent. Example of such organic soluble salt was tetrabutylammonium tetrafluoroborate ($n\text{-Bu}_4\text{BF}_4$).

A part from alcohols, it might be possible to use our NWs array for other reaction such as carbon dioxide (CO_2) reduction, oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). As discussed previously in Chapter 4, our NWs array was stable in non-acidic conditions, thus it might be possible to apply them on all reactions which did not required acidic conditions. However, there might be a slight problem when dealing with system with the present of gas, such as oxygen evolution reaction, as the capillary effect caused

by the liquid and gas interface will tear the NWs array away from its substrate. This can be solved by increase the mechanical strength of the NWs array, such as by coating the NWs with a layer of mesoporous silica. Nevertheless, this method will decrease the contact between the metal NWs surface with the reactant, which will decrease the performance of the catalyst. A better approach for solving the peel off caused by capillary effect was to decrease the density of the Au@Pd NWs. When the NWs were sparser, it was harder for them to stick together, which will caused less capillary effect and they will not peel off all together.

Furthermore, there were still a lot of combinations of metal and oxide that can be coat on to the Au NWs array, which give a wider range for choices of reactions for electrocatalysis or photocatalysis. For examples, it was already shown in Chapter 3 that other transition metal such as nickel, cobalt and copper can be coated onto Au NWs surface. Besides that, the coating of alloy or bimetallic shell was also possible, which gives a wide tunability for our NWs array as catalysts. However, some of the metal coated, such as nickel and copper, were easily oxidised in air. Hence, there might be a need to introduce extra coating such as mesoporous silica or conductive polymer to reduce the contact of these metal NWs with oxygen in the air, thus decrease the risk of being oxidised.

7.3 Outstanding Questions

Despite the new knowledge developed on TiO₂ NWs molten salt synthesis in Chapter 2, we had still not discovered an effective method to control the ligand binding rate and TiO₂ deposition rate, which leads to failure to produce segmented hybrid NWs. This had seriously limited the morphology control of TiO₂ NWs on molten salt synthesis. The project was halted but should any other means of control had been proposed, it was still worth of giving a try.

In Chapter 5, we had discussed about the reservoir effect on the Au@Pd NWs array system and its impact on ethanol electro-oxidation. However, the investigation was not complete as the impact of reservoir effect on other electrochemical catalytic reactions had not been tested, which might ultimately be useful to other catalytic reactions as well.

In Chapter 6, although we had proposed that different Pd facets was responsible for different ethanol oxidation products, and we have some preliminary results that support our hypothesis, but this had not been proved beyond though. Further investigation was still needed and control experiments should still be performed on other Pd nanomaterials with similar facets to rule out if this observation was unique to the nanowires array system.

References

- [1] E. C. Garnett, P. Yang. *J. Am. Chem. Soc.***2008**, 130, 9224 – 9225.
- [2] T. D. Dao, C. T. T. Dang, G. Han, C. V. Hoang, W. Yi, V. Narayanamurti. *Appl. Phys. Lett.***2013**, 103, 193119.
- [3] V. Schmidt, H. Rien, S. Senz, S. Karg, W. Riess, U. Gosele. *Small***2006**, 2, 85-88.

List of Publications

- [1] Z. Lam, C. Liu, H. Tao, H. -Y. Wang, J. Chen, W. Xu, L. Zhang, Y. Zhu, L. Liu, Y. Han, B. Liu, H. Chen. Noble Metal Nanowire Forest as A Novel Class of Electrocatalyst, manuscript in preparation.

- [2] J. Chen, L. Zhang, Z. Lam, H. Tao, Z. Zeng, H. B. Yang, J. Luo, L. Ma, B. Li, J. Zheng, S. Jia, Z. Wang, Z. Zhu, B. Liu. Tunneling Interlayer for Efficient Transport of Charges in Metal Oxide Electrodes. J. Am. Chem. Soc. **2016**, 138(9), 3183 – 3189.

- [3] J. He, Y. Wang, Z. Fan, Z. Lam, H. Zhang, B. Liu, H. Chen. Substrate-Bound Growth of Au-Pd Diblock Nanowire and Hybrid Nanorod-plate. Nanoscale **2015**, 7(17), 8115 – 8121.