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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**STRATEGIES TO TUNE THE SELECTIVITY OF GOLD FOR
GLYCEROL ELECTRO-OXIDATION**

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**Interdisciplinary Graduate School
NEWRI-Residues & Resource Reclamation Centre**

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A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of
Doctor of Philosophy

2016

To my parents, with gratitude.

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Abstract

The research work presented in this thesis aims to develop a unified strategy to tune the selectivity of carbon supported Au nanoparticles towards different products in the glycerol electro-oxidation pathway, under alkaline conditions.

Enhanced selectivity towards C3 products, glycerate and tartronate, could be achieved by simple electro-deposition of Cu onto Au nanoparticles. Our initial studies showed that the most selective catalysts were obtained when Cu electro-deposition occurred at -0.1 V and +0.015 V for 30 min. Enhancement in C3 selectivity is attributed to the presence of an Au^+ species that was generated as a result of electron transfer between Au and electro-deposited Cu_2O . Furthermore, Au^+ content tripled when Cu electro-deposition took place at +0.015 V for 90 min. As a result, C3 selectivity obtained by the resulting catalyst doubled with respect to pure carbon supported Au nanoparticles. However, beyond these optimal conditions, little to no Au^+ species were observed and C3 selectivity decreased.

Electro-deposition of Ni onto Au nanoparticles also gave rise to enhanced C3 selectivity. The most selective catalysts were obtained when Ni electro-deposition occurred at -0.3 V for 40 min. Au^+ species was similarly identified post Ni electro-deposition and it was generated due to electron transfer between Au and NiOOH species. When Ni electro-deposition occurred at more negative potentials, the resultant thick Ni surface layer partially shielded Au from the reaction medium thus reduced access of glycerol molecules to the Au active sites. As such, C3 selectivity of the Ni-Au/CB catalysts prepared under these conditions were relatively similar to that of pure Au/CB. Any possible synergistic effect between Au and Ni was thus nullified by the thick Ni surface coverage.

Lastly, we prepared residual Ag containing porous Au structures which were electrochemically active for glycerol electro-oxidation and highly selective towards C-C bond breaking products, glycolate and formate. Porous Au catalysts were prepared by etching alloyed AuAg sheets in

concentrated nitric acid. However, etching does not completely remove all traces of Ag, hence small amounts are still present. Low temperature annealing of the porous Au structures enhanced selectivity and product conversion. Annealing caused atomic rearrangement on the catalyst surface such that all atoms present necessarily participated in oxidizing glycerol. In this way, glycerol molecules were more likely evenly adsorbed onto the metal surface and this gave rise to the higher product conversion.

Keywords: glycerol electro-oxidation, Cu electro-deposition, Ni electro-deposition, porous Au, Au nanoparticles

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- 2) Wang, H.; Thia, L.; Li, N.; Ge, X.; Liu, Z.; Wang. X. *Applied Catalysis. B*, 2015, 166-167, 25-31.
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- 3) H. Wang.; M. Xie.; L. Thia.; A. Fisher.; and X. Wang. *The Journal of Physical Chemistry Letters*, 2014, **5**, 119-125.
- 4) L. Tao.; H. Wang.; M. Xie.; L. Thia.; W. N. Chen.; and X. Wang. *Chemical Communications*, 2015, **51**, 12170-12173.

Chapter 1

Introduction and Scope of Thesis

1.1. Introduction

Scheme 1. Transesterification of vegetable oils and fats yielding biodiesel, and glycerol as a by-product. Reprinted with permission from ref 1. Copyright Royal Society of Chemistry.

The progressively rapid depletion of fossil fuels has driven the search for alternative energy sources that are based on renewable raw materials. In line with this, the Directive on the Promotion of the use of biofuels and other renewable fuels for transport (2003/30/EC) was enforced within the European Union (EU) in 2003 to promote the use of biofuels for transport and reduce dependency on petroleum. Biodiesel is conventionally produced via the transesterification of vegetable oils or animal or waste fats. The homogeneous process is catalysed by a strong base which simultaneously cleaves fatty acids from the glycerol backbone and transforms them into methyl esters, leaving glycerol behind as a by-product (Scheme 1).^[1] Consequently, global production of glycerol from biodiesel has increased sharply in the past decade. Between 2003 and 2012, global glycerol production was ramped up by more than ten times from 200,000 tonnes in 2003 to more than 2 million tonnes in 2012.^[2]

1.2. Rationale: the need to valorise glycerol via electro-oxidation

Although glycerol is widely employed in a variety of industries, the current biodiesel production boom has flooded the market with a large excess of glycerol which classical industries have struggled to absorb. As such, new strategies to valorise glycerol are necessary in order to absorb this surplus.

The highly functionalized glycerol molecule can be used as a platform chemical for the production of new polymers, fine chemicals and pharmaceuticals. Amongst the available methods, electrochemical oxidation of glycerol in direct alcohol fuel cells (DAFCs) is extremely attractive, owing to its ability to co-generate electricity and valuable chemicals. As a fuel, glycerol is a viable alternative to methanol and ethanol, which are the two classical fuels for liquid fuel cells. Energy density for glycerol is 5.0 kWh kg^{-1} , which is comparable to that of methanol and ethanol at 6.1 and 8.0 kWh kg^{-1} respectively.^[3] Glycerol also has a lower fuel cross-over and is less toxic and volatile. More importantly, converting surplus glycerol to high value added chemicals helps offset the cost of biodiesel production and enables the process to be more economical.

Glycerol oxidation occurs either by the primary or secondary oxidation pathway. The primary oxidation pathway produces glyceric acid (GLYA), tartronic acid (TA) and mesoxalic acid (MA) as the principle C3 oxidation products while the secondary oxidation pathway generates dihydroxacetone (DHA) and hydroxyacetic acid (HYPA) as the main products. While GLYA is the dominant product generated under most experimental conditions tested, it has yet to find any practical applications. Nevertheless, it is a crucial intermediate for the production of TA and MA. TA is a very expensive reagent ($1564 \text{ US\$/g}$). Owing to its high costs, TA is primarily utilized in the treatment of osteoporosis and obesity.^[4] TA also has potential as an anti-corrosive protective agent that can be employed for high temperature applications.^[5] Similarly, MA, the direct oxidation product of TA, is also an expensive fine chemical ($156 \text{ USD\$/g}$). It has potential applications as a complexing agent and is a precursor in the synthesis of 4-chlorophenylhydrazonated mesoxalic acid, which is a demonstrated anti-HIV agent.^[6] The calcium or potassium salt of MA can also be used in the treatment of diabetes.^[7] On the other hand, DHA ($150 \text{ USD\$/kg}$), the secondary oxidation product, is the active ingredient in sunless tanning agents. Currently, DHA is commercially produced via fermentation, which is

necessitated given the strict quality requirements for cosmetic grade DHA. However, the conventional fermentation process is not very efficient owing to the low concentration of starting material used.

Despite their potential to be utilized for a wide variety of applications, C3 products derived from partial oxidation of glycerol are currently limited to high value applications such as for medicine due to their high cost. Yet, the significantly higher commercial value of these oxidation products compared to crude and purified glycerol (less than 0.3 US\$/kg and about 0.6 US\$/kg respectively), provides motivation to optimize the glycerol oxidation process such that these chemicals can be selectively produced in high concentrations. However, the glycerol oxidation pathway is highly complex and the ability to tune the oxidation pathway to produce specific products selectively remains challenging. In addition to the above mentioned C3 products, a variety of C2 and C1 products such as oxalic acid, glycolic acid, formic acid and CO₂ are typically generated during the reaction. These C1 and C2 products also lend themselves to a large number of industrial applications. For example, glycolic acid is also widely used in textile dyeing, leather tanning and personal care products while major applications of formic acid include silage and animal feed preservation.

1.3. Scope of thesis

1.3.1 Objectives

The goal of this study is to develop a general strategy to tune the selectivity of carbon supported Au nanoparticles (Au/C) towards specific products during glycerol electro-oxidation. Specifically, this work aims to investigate the ability of electro-deposited Cu, Ni and Ag to influence the selectivity of Au/C. To date, a general strategy to tune the selectivity of Au/C towards specific products in the glycerol electro-oxidation pathway has yet to be proposed.

1.3.2. Hypothesis

Presence of electro-deposited transition metals may influence the catalytic performance of the Au/C through the following ways (i) synergistic interaction between the two metals (ii) electronic modification of Au/C via electron transfer (iii) ability of the electro-deposited species to alter the glycerol oxidation pathway on Au/C. A thicker catalyst layer will result post electro-deposition and this will likely be favourable for the formation of deeper oxidation products. Hence, this thesis aims to determine if the electro-deposition of transition metals will influence the selectivity of Au/C for glycerol electro-oxidation and the underlying factors which drive these changes.

The detailed scope of this thesis is as follows:

Chapter 1: gives a short introduction on why there is a surplus of glycerol in the market and rationalizes the need to valorise surplus glycerol via electro-oxidation. The objectives and hypothesis of our research work as well as the scope of this thesis is also outlined.

Chapter 2: provides a detailed literature review on the various catalytic systems which have been studied for both glycerol oxidation and electro-oxidation. In particular, we highlight the various strategies that have been employed to improve the catalytic performance of metal catalysts. We also discuss the glycerol electro-oxidation mechanism when the reaction takes place over gold and platinum electrode under different pH conditions.

Chapter 3: evaluates the ability of electro-deposited Cu species to influence the selectivity of Au/C. C3 selectivity of the resulting catalysts were significantly enhanced due to synergistic interaction between Au and the electro-deposited Cu species. Furthermore, extent of improvement in C3 selectivity was dependent on deposition time and potential, with the highest improvement obtained after Cu electro-deposition occurred for 90 minutes at +0.015 V. Presence of electro-deposited Cu led to electronic modification of Au/C and the generation of an Au^+ species in the catalyst. Au^+ was formed as a result of electron transfer between Au and

electro-deposited Cu_2O . Catalysts containing the Au^+ species observed increased selectivity to glycerate and tartronate while simultaneously suppressing C-C bond cleavage to glycolate and formate.

Chapter 4: evaluates the ability of electro-deposited Ni to influence the selectivity of Au/C. C3 selectivity of Au/C for glycerol electro-oxidation was enhanced after Ni electro-deposition. Au/C underwent electronic modification as a result of interaction with the electro-deposited Ni species. The most selective catalysts contained an Au^+ species which was generated via interaction between Au and NiOOH species.

Chapter 5: investigates the ability of electro-deposited Ag to influence the selectivity of Au/C. Presence of electro-deposited Ag heightens C-C bond cleavage of glycerol and the resulting catalysts are highly selective to glycolate and formate when electro-oxidation takes place in alkaline conditions. Additionally, 100% selectivity to formate could be obtained when glycerol electro-oxidation was carried out under high applied potentials, in the absence of base. Our results revealed that very small amounts of Ag were sufficient to attain high selectivity towards glycolate and formate,

Chapter 6: examines the ability of porous Au structures containing residual Ag to achieve high selectivity towards glycolate and formate. Porous Au structures were obtained by etching AuAg sheets in concentrated nitric acid. However, the etching process could not completely dealloy Ag and residual amounts still remained embedded within the porous 3D framework. Residual Ag tuned the product distribution towards glycolate and formate when glycerol electro-oxidation occurred under alkaline conditions. Heat treatment of the catalysts after dealloying resulted in further improvements in selectivity as annealing caused residual Ag to diffuse and precipitate onto the surface of the porous framework. Presence of greater amounts of exposed Ag was the driving factor for improved selectivity to glycolate and formate.

Chapter 7: provides a summary of this thesis and gives recommendations for future work.

Chapter 2

Literature Review

2.1. Introduction

Heterogeneous catalytic oxidation of glycerol can be carried out using inexpensive oxidizing agents such as air and oxygen or via electrochemical methods. Glycerol oxidation is usually carried out in an autoclave or glass reactor under elevated temperature and pressure, using water as a solvent. Glycerol is also a potential fuel for direct alcohol fuel cells (DAFC). Utilization of glycerol as a fuel in DAFCs is advantageous as it enables the co-generation of electricity and valuable chemicals. Applied potential can also be used as means to further tune catalytic selectivity during the reaction.

Most studies investigating the catalytic (electro)-oxidation of glycerol have focused on using supported Pd, Pt, Au noble metal catalysts since non-noble metal catalysts tend to perform poorly. Hence, this chapter will provide an overview of the catalytic performance of Au, Pt and Pt based catalysts under both electro-catalytic and oxidative conditions. In particular, we will highlight the various strategies that have been undertaken in order to improve innate performance of these noble metal catalysts.

2.2. Glycerol Oxidation

2.2.1. Platinum group catalysts

Platinum group based catalysts (Pt and Pd) have been widely explored as potential candidates for glycerol oxidation^[8]. Supported Pt and Pd catalysts produce glyceric acid as the main oxidation product when glycerol oxidation occurs under base free and basic conditions^[9]. The employment of Pt catalysts is particularly attractive owing to their high activity under base free conditions. Consequently, oxidation products generated do not need to undergo additional neutralization and acidification steps in order to obtain the free acid. In general, small Pt/C nanoparticles (<6nm) are more active for glycerol oxidation under base free conditions.

Although activity decreases sharply when particles are larger than 6nm, selectivity to glyceric acid increases.^[10]

2.2.1.1. Influence of morphology

Influence of morphology on the catalytic performance of Pt based catalysts have been evaluated. Notably, Li and co-workers prepared carbon nanotube supported, highly faceted Pt nanocrystals (HFNC/CNT) for glycerol oxidation under base free conditions.^[11] The highly faceted nanocrystals possessed many exposed Pt(111) facets and also a large number of atomic steps. These unique structural features enabled HFNC/CNT to attain remarkably high selectivity to glyceraldehyde (~80%) while Pt/C was selective to glyceric acid (~47%), the thermodynamically stable product. However, HFNC/CNT was less active than Pt/C and exhibited a lower TOF. Zaera and Li also showed that improved activity observed with Pt/C catalysts having higher metal loadings was associated with the increase in number of terrace steps present.^[12] They posited that this arises due to the need for large surface ensemble sites for optimum glycerol adsorption. In agreement with the results reported by Li's group, Zaera and Li also determined that catalytic activity does depend on the shape of the Pt nanoparticles, in particular, their exposed facets. However, in their system, the (100) planes of Pt nanoparticles appeared more active for glycerol oxidation than the (111) terraces as higher activities were observed with cuboctahedral rather than tetrahedral shaped Pt nanoparticles.

2.2.1.2. Effect of support

Catalytic stability is an important factor for liquid phase reactions as leaching and reconstruction of the active phase causes deactivation. Stability can be improved by forming strong metal-support interactions or by confinement effect. In particular, ability of the highly porous triazine framework to improve stability of Pd nanoparticles for glycerol oxidation was investigated (Fig. 2.1).^[13]

Fig. 2.1. Reaction scheme of the dynamic trimerization of terephthalonitrile leading to the formation of a 2D framework. At 400 °C, an organized triazine network is formed whereas at 600 °C an amorphous network is obtained. Reprinted with permission from ref 13. Copyright ACS Publications.

When prepared via impregnation method, the triazine framework enabled the in-situ formation of a PdH_x species ($\sim 2.6\text{nm}$) which were stabilized within its pores ($\sim 2.7\text{nm}$). Confinement of PdH_x within CTF resulted in a highly stable catalyst which maintained its high catalytic activity even after being reused 9 times. On the other hand, when Pd/CTF was prepared via sol-immobilization, the particles having an average diameter of $\sim 3.1\text{nm}$ were too large to fit into the pores of CTF. However, Pd/CTF still demonstrated improved stability, catalytic activity and C3 selectivity relative to Pd/AC . In this case, enhanced stability of the Pd/CTF was attributed to the strong interaction between Pd and the nitrogen functionalities present in CTF.^[14]

Meanwhile, the performance of mesoporous carbon nitride (MCN) supported Pt catalysts (Pt/MCN) for glycerol oxidation was investigated.^[15] Compared to CTF, the MCN supports appear to be less stable after repeated recycling and glycerol conversion decreased. Specifically, N-concentration within the MCN support decreased after recycling, suggesting that leaching had occurred. This in turn led to the growth of Pt nanoparticles as the N containing species served as anchor sites for Pt. Furthermore, the ordered mesoporous structure collapsed over time. MCN was also unable to prevent the over oxidation of Pt which resulted in its eventual deactivation.

Similar to mesoporous carbon nitride supports, nitrogen groups incorporated into carbon nanotubes (N-CNTS) can also function as active sites to anchor metal nanoparticles. This in turn improves nanoparticle dispersion on the support.^[16] Different nitrogen functionalities including quaternary (graphitic), pyridinic, pyrrolic nitrogen, and nitrogen oxides can be incorporated into CNTS. Presence of nitrogen groups on CNTS 1) provides versatile reactive sites for a robust interface; (2) lowers the work-function for facile charge injection and redox reaction; (3) modifies the charge transfer characteristics with excessive electrons; (4) offers permanent dipoles that can activate catalytic activity and surface reactivity; and (5) can alter the surface acid/base properties of CNTs by functionalization via amination.^[17]

Catalysts composed of metal nanoparticles supported on N-CNTS have been applied to glycerol oxidation.^[18] N-CNTS supported metal nanoparticles showed improved catalytic activity compared to those supported on purely acid treated CNTS. Presence of electron donating N containing functionalities typically resulted in: smaller nanoparticles with narrower size distribution, improved dispersion, higher loading and improved electrochemical activity.^[19] Improvements in catalytic activity was also co-related to the amount of N-content incorporated.^[19a] Hou and co-workers gleaned this observation when glycerol oxidation was carried out over Pt nanoparticles supported on N-doped CNTS (Pt/N-CNTS) under base free conditions.^[20] Moderate N-content gave rise to the largest increase in glycerol conversion and highest TOF. On the other hand, N-CNTS possessing high N content exhibited poor catalytic performance owing to reduced specific surface area which restricted active site accessibility. Furthermore, Pt/N-CNTS and Pt/CNTS gave rise to higher glycerol conversions compared to Pt/AC and oxide (SiO_2 , TiO_2 , Al_2O_3) supported Pt. However, product distribution was relatively similar. Notably, interaction of Pt nanoparticles with the nitrogen groups on CNTS retarded their deactivation due to over-oxidation and enabled continuous glycerol conversion even after 6 h.^[19a] The type of N functionality present also influenced the extent to which

catalytic performance was enhanced since different N functionalities possess different electronic properties.^[21] For example, graphitic and pyridinic nitrogen act as electron donors and electron acceptors, respectively.^[18b, 21d, 22] Thus the type of N functionality present influences the direction of charge transfer between support and catalyst. This in turn alters electronic properties of the resulting catalyst, and leads to differences catalytic performance.^[19b]

2.2.1.3. Disadvantages

Employment of platinum group catalysts in liquid phase oxidation reactions poses a few disadvantages. Catalyst deactivation due to Pt surface oxidation is the biggest obstacle in the large-scale application of Pt based catalysts. High temperatures and a low partial pressure of oxygen are usually required in order to stabilize the catalytically active zero valent Pt species and prevent oxygen poisoning.^[23] Platinum group based catalysts are also highly susceptible to poisoning either by by-products or adventitious species.^[23b] In addition, strongly coordinated products generated in-situ may lead to reversible metal dissolution–precipitation which in turn increases mobility of metal atoms at the catalyst surface. Increased mobility results in particle growth leading to a decrease in specific surface area and consequently turnover frequency (TOF). On the other hand, irreversible dissolution results in loss of catalyst as it is leached into solution.^[24]

2.2.2 Gold based catalysts

2.2.2.1. Advantages

Au based catalysts are more stable, more resistant to oxidation^[25], and exhibit high tolerance towards poisoning chemical groups such as aliphatic and aromatic amines. This is due to the high electrode potential ($E^0 = +1.69$ V) of Au which is responsible for its inert nature. Indeed, bulk Au displays little to no catalytic activity. However, Haruta, in his groundbreaking work, discovered that supported Au in the nanoscale region (typically with diameters below 10nm) is surprisingly active, especially at low temperatures.^[26] Additionally, Au based catalysts tend

to be more selective than Pt/Pd based catalysts as they are able to discriminate between different chemical groups and geometrical positions, leading to superior yields of desired products. Among many examples, glycols can be selectively oxidised to monocarboxylates^[27] and unsaturated alcohols can be fully converted to unsaturated aldehydes^[28] when their respective reactions are catalysed by Au nanoparticles. As such, the discussion in the following chapter mainly revolves around the catalytic performance of Au catalysts for glycerol oxidation under alkaline conditions and the factors which influence its performance.

2.2.2.2. Size Effect

Catalytic performance of Au based catalysts for glycerol oxidation is significantly influenced by the size of the Au nanoparticles.^[27] ^[29] In general, smaller Au nanoparticles (average diameter <20 nm) exhibited turnover frequencies (TOFs) that were about an order of magnitude higher than larger Au nanoparticles (average diameter ≥ 20 nm). However, the latter demonstrated higher selectivity for glyceric acid. On average, selectivity to glyceric acid was about 10% higher with larger Au nanoparticles. Moreover, extending Au particle size beyond 20 nm resulted in catalytic performance similar to bulk Au. Judicious selection of Au particle size carried out in conjunction with careful tuning of reaction conditions led to significant improvements in glyceric acid selectivity.^[30] 100% selectivity to glyceric acid was achieved when glycerol oxidation was carried out over 1% Au/charcoal or 1% Au/graphite catalysts, under mild conditions (60°C, 3 h, and water as solvent).

Ideal particle size for optimal catalytic performance is also dependent on the support used.^[31] Carbon supported Au nanoparticles with an average diameter of 7-8 nm display optimal activity. However, catalytic performance improved with decreasing particle size for oxide supported Au nanoparticles. Au nanoparticles smaller than 8 nm tend to lie deep in the carbon support and are less accessible to glycerol during the reaction. As such, catalytic activity declines when particle size decreases beyond a certain threshold. Presumably, the shielding of smaller Au

nanoparticles does not exist when they are deposited on oxide supports. Hence catalytic activity continued to increase with decreasing particle size.

2.2.2.3. Effect of Preparation methods

Fig. 2.2. High resolution HAADF STEM images of single Au atom and Au₂ cluster. Reprinted with permission from ref 33. Copyright ACS Publications.

Preparation methods influence the size and dispersion of the resulting catalysts and this in turn affects their catalytic performance.^[32] Supported Au nanoparticles are typically prepared via sol-immobilization or incipient-wetness methods. The sol-immobilization method consists of reducing the aqueous metal precursors in the presence of stabilizers followed by immobilizing the pre-formed sols onto a support. The incipient-wetness method involves impregnating the support with appropriate amounts of aqueous metal precursor. After which, the catalyst is then dried and calcined to activate it before employment. Sol-immobilization is more effective for preparing catalysts that possess the following characteristics: smaller nanoparticles, narrower size dispersion, good surface exposition and high dispersion. On the other hand, the classical incipient wetness method tends to result in larger particles (average particle diameter >10 nm) which have a tendency to aggregate. As such, activated carbon supported Au nanoparticles prepared by sol-immobilization were generally more active and consequently less selective for

glyceric acid. In comparison, catalysts prepared by the incipient wetness method exhibited lower activity but higher selectivity to glyceric acid due to their larger sized nanoparticles.

Wells and co-workers also demonstrated that the sol-immobilization method can be modified in order to generate Au catalysts with improved catalytic performances and durability.^[33] Herein, the sols generated under different conditions were subsequently immobilized onto a TiO₂ support (Au/TiO₂) and tested for glycerol oxidation. In general, Au sols prepared with the same solvent system, experienced a decrease in average size when reaction temperature was reduced. Additionally, changing the solvent environment by decreasing the water/ethanol ratio lead to increasing larger particles as PVA protecting agent is insoluble in ethanol. Au/TiO₂ catalysts prepared in water (Au/TiO₂-water), at 1 °C, exhibited the highest activity for glycerol oxidation. Its TOF was also about 10 times higher than that observed for a similarly sized catalyst, which was prepared using a 50/50 ethanol/water ratio at 0 °C. The superior activity of Au/TiO₂-water was associated with the presence of ultra-small Au clusters (1-5 atoms) in the catalyst (Fig. 2.2). Au/TiO₂-water was also highly durable and catalytic activity only decreased slightly after 10 successive recycling tests. The decline in catalytic performance was attributed to aggregation of the very small Au clusters. Notably, even though different reaction conditions gave rise to Au nanoparticles with the same average size, their resultant catalytic performance varied. Hence, interaction between PVA and the solvent system appeared to affect the catalytic performance of Au/TiO₂. This interaction could be modulated by the temperature and the solvent system in which the Au nanoparticles were generated in.

2.2.2.4. Influence of protecting agent

In line with the observations made by Wells and co-workers discussed above, Prati and co-workers observed that TOF suffered a drastic decrease when PVA was completely removed from the Au nanoparticle surface.^[34] Furthermore, this decrease was not commensurate with the corresponding increase in particle size. This observation suggested that PVA not only

functions as a stabilizing agent but is also actively involved during the reaction. In addition, PVA appeared to mediate selectivity as well since C3 selectivity increased with increasing amounts of PVA. That is, C3 selectivity increased with decreasing particle size. Improvement in C3 selectivity was attributed to the ability of PVA to direct the adsorption mode of glycerol. PVA arrangement on Au nanoparticles surface created a sort of porous structure that directed the adsorption of glycerol to the Au active sites by interacting with their OH groups (Fig. 2.3)

Fig. 2.3. Mode of glycerol adsorption on Au nanoparticles (a) in the presence of PVA, (b) on its free surface. Reprinted with permission from ref 34. Copyright Royal Society of Chemistry.

In another work, Prati's group determined how the nature of protective agent, or lack thereof, influenced catalytic performance.^[35] AuPd alloys were prepared by immobilizing protected Au seeds onto activated carbon support followed by addition of Pd. Au seeds protected with steric stabilizer such as PVA (Pd@Au_{PVA}/AC), resulted in small, highly dispersed and homogeneously alloyed nanoparticles. However, Au seeds protected with electronic stabilizer such as THPC resulted in particles that experienced considerable agglomeration. THPC protected AuPd (Pd@Au_{THPC}/AC) were also not uniformly alloyed and bigger particles tended to be richer in Au. These structural differences lead to differences in catalytic activities. As expected, Pd@Au_{PVA}/AC was most active while Pd@Au_{THPC}/AC was less active compared to its monometallic counterparts. Hence, choice of protecting agents can exert some degree of influence on the resultant catalytic performance.

2.2.2.5. Influence of other metals on catalytic performance of Au

Many groups have also prepared bimetallic catalysts^[36] to understand how other metals, namely Pd and Pt, influence the catalytic performance of Au for glycerol oxidation. In general, bimetallic catalysts (typically in the form of alloys or core-shell structures) observed significant improvements in catalytic activity compared to monometallic catalysts.^[37] Selectivity, on the other hand, was influenced to a greater extent by the nature of support, preparation method and reaction conditions rather than the catalyst constituents.

Most research has focused on the catalytic performance of supported AuPd alloys owing to the synergistic interaction that results when both metals are alloyed.^[38] For example, single phase activated carbon supported AuPd catalysts (AuPd/AC) were about 6-7 times more active for glycerol oxidation compared to Au/AC and Pd/AC.^[39] Catalytic performance of supported AuPd alloys was also affected by the Au to Pd ratio.^[40] Activity improved with increasing Au to Pd ratio until a maximum is reached. Poor catalytic activity of Pd rich AuPd alloys was likely due to Pd deactivation during the reaction. However, selectivity to glycerate was relatively similar for all AuPd alloys.

Nature of the support and catalyst preparation method affected the catalytic performance of supported AuPd alloys.^[41] TiO₂ improved catalytic activity of AuPd alloys to a larger extent compared to carbon supports when both catalysts were prepared by impregnation method. Lower activity of the carbon supported catalyst was due to its wider size distribution which consisted of a significant proportion (ca. 20%) of particles that are larger than 20nm. However, it must be noted that TiO₂ supported AuPd consisted of core-shell structures whilst carbon supported AuPd existed mainly as alloys with some degree of Pd enhancement on its surface. Furthermore, carbon and TiO₂ supported AuPd alloys prepared by the sol-immobilization (AuPd_{SI}) were more active than those prepared by wet impregnation (AuPd_{IW}), even though both methods produced similarly sized alloys. These differences were attributed to variations

in relative proportions of Pd^0 and Pd^{2+} present in the alloy. Given that AuPd_{SI} was more active for glycerol oxidation, this suggested that surfaces of the nanoparticles require both Au and Pd atoms to be accessible and that the Pd should be in the metallic state.

Alternatively, Davis and co-workers prepared carbon supported AuPd (AuPd/C) bimetallic catalysts by depositing Au onto the surface of commercially purchased 3-nm supported Pd particles.^[42] They also prepared carbon supported AuPd via sol-immobilization (AuPd-sol/C) for comparison. Au did not uniformly cover the Pd surface in AuPd/C and some Pd was exposed on the surface. In contrast, Pd was nearly completely covered by Au in AuPd-sol/C . AuPd/C was significantly more selective to glycerate due to the presence of surface Pd which aided in the decomposition of H_2O_2 formed on the Au surface.

Wong and co-workers prepared carbon supported AuPd bimetallic structures (Pd-on-Au/AC) with varying Pd surface coverages.^[43] Bimetallic catalysts were significantly more active for glycerol oxidation compared to monometallic Au and Pd. Higher activity of Pd-on-Au/AC was attributed to them having lower activation energies for the $\beta\text{-C-H}$ bond cleavage rate limiting step compared to Au/AC . The presence of Pd on Au lowered activation energy by about 5 kJ mol^{-1} . Furthermore, Pd-on-Au/AC catalysts weakened adsorption strength for the glycerolate intermediate and this also contributed to its higher activity and enhanced selectivity to glyceric acid. Catalytic activity exhibited a volcano dependence on Pd surface coverage. That is, catalytic activity increased with increasing Pd surface coverage, until maximum activity was reached at 80% Pd surface coverage. At Pd surface coverages greater than 80%, catalysts became more susceptible to deactivation either by CO poisoning or by adsorbate fouling. Additionally, these catalysts were also more prone to undergoing oxidation and subsequent deactivation during the reaction. Glyceric acid selectivity was also dependent on Pd surface coverage.

Fig. 2.4. Possible electron transfer from starch ligand to alloy PtAu–Starch NPs and from Au Atoms to adjacent Pt atoms. Reprinted with permission from ref 44. Copyright ACS Publications.

Ebitani and co-workers prepared hydrotalcite supported PtAu alloyed catalysts (PtAu-starch/HT) using starch as a stabilizing and reducing agent.^[44] Compared to Au/HT, PtAu-starch/HT exhibited significantly enhanced catalytic performance when glycerol oxidation occurred under mild, base free conditions. Catalytic performance was dependent on the ratio of Pt to Au within the alloys. Activity increased with increasing Pt to Au ratio while conversely, glyceric acid selectivity decreased. Notably, alloying Pd with Au inhibited the over-oxidation of glycerol oxidation intermediates to CO₂ and 100% mass balance could be attained. Enhanced catalytic performance of PtAu-starch/HT was due to both geometric and electronic changes that were brought about by alloy formation and the use starch as a protecting agent (Fig. 2.4). First, both Pt and Au atoms gained negative charges from the starch ligand. Excess electrons on the Au atoms were also transferred to the Pt atoms. The negatively charged Pt atoms likely enhanced oxygen absorption and generated anionic O₂ species such as superoxo or peroxo oxygen that initiated the polyol oxidation catalytic cycle. Furthermore, replacement of active Pt atoms with inactive Au atoms changed the geometry of the Pt surface and this could have contributed to the enhanced performance of the AuPt-starch/HT catalysts.

Other types of bimetallic structures have also been investigated for glycerol oxidation. Notably, Tomishige and co-workers reported that carbon supported Pd-Ag (Pd-Ag/C) catalysts exhibited exceptionally high selectivity (up to 85%) towards dihydroxyacetone (DHA).^[45] Alloying Pd with Ag thus altered the inherent selectivity of Pd/C. Although, catalytic activity of the Pd-Ag/C catalysts was relatively low, it could be improved with pre-treatment. Alternatively, alloying Pt with Cu significantly improved stability of Pt which is prone to deactivation.^[46] PtCu/C catalysts maintained its catalytic performance during recycling and was more selective to glyceric acid compared to Pt/C catalysts having the same Pt loading. Thus, presence of Cu in Pt suppressed C-C bond cleavage and decreased selectivity to C1 side products.

Recently, Hutchings and co-workers prepared TiO₂ supported Au-Pt-Pd trimetallic catalysts (Au-Pt-Pd/ TiO₂) for glycerol oxidation.^[47] Au-Pt-Pd/TiO₂ performed poorly under base free conditions, even at high temperatures. However, catalytic performance improved under basic conditions. In the presence of base, Au-Pt-Pd/TiO₂ was more active compared to bimetallic catalysts (Au-Pt/TiO₂, Pd-Pt/TiO₂ and Au-Pd/TiO₂) at short reaction times of 0.5h. However, when the reaction was extended to 4h, the glycerol conversion attained by Au-Pt-Pd/TiO₂ was not significantly higher than that of Au-Pd/TiO₂ and Pd-Pt/TiO₂. In terms of selectivity, Au containing catalysts displayed higher C3 selectivity compared to Pd-Pt/TiO₂.

2.2.3. Effect of support

2.2.3.1 Carbon supports

Although unsupported Au nanoparticles may be able to achieve high catalytic activity for glycerol oxidation,^[48] there are certain advantages to be realized when nanoparticles are immobilized onto a support. Supported nanoparticles have longer catalyst lives and can be recycled. Thus, they are more economical for industrial applications. Supported nanoparticles are also more stable compared to their respective sols and undergo a smaller degree of agglomeration during catalysis and storage. This is particularly important for structure sensitive

reactions such as glycerol oxidation, as catalytically active species need to maintain their highly dispersed states in order to ensure that high catalytic activity is sustained throughout the reaction. Lastly, the properties of nanoparticles may be altered as a result of metal-support interactions. Tuning the metal-support interaction may therefore be a way to mediate catalytic performance of supported nanoparticles.^[49]

Support selection is based on a series of desirable characteristics: inertness, stability under reaction, regeneration conditions, adequate mechanical properties, appropriate physical form for the given reactor, high surface area, porosity and chemical nature.^[50]

For glycerol oxidation, carbon based supports have proven to be an enduring choice as they give rise to comparatively better catalytic activity than oxide supports.^[27, 51] Nature of the carbon support affects the activity of Au nanoparticles but has little influence on its selectivity.^[51c] Selectivity is more dependent on the size and nature of catalytic entities employed.^[32c] For instance, Au supported on activated carbon (Au/AC) achieved an estimated 6 times increase in TOF compared to Au supported on titanium dioxide (Au/TiO₂). However, no significant improvements in selectivity was observed. Fraction of micropores present in the carbon support and their structure could exert some influence over the resulting catalytic activity.^[51b] Activated carbon supports possessing a lower fraction of micropores exhibited higher activity for glycerol oxidation. This may be due to the shielding effect experienced by smaller nanoparticles as a result of being embedded within the micropores. Additionally, micropore structure might also play a role in determining catalytic activity.

Degree of graphitization^[52] and crystallinity^[53] are other key considerations that should be taken into account when selecting a carbon support. A high degree of graphitization provides many anchor sites for the formation of small, highly dispersed Au nanoparticles while high crystallinity ensures that a large fraction of these graphitic edges are exposed in an orderly manner. Hence, Au supported on highly crystalline supports such as graphite (Au/G)

demonstrated higher glycerol oxidation activity than when supported on poorly crystalline carbon supports like activated carbon (Au/AC) and carbon nanofibers (Au/CNFS). Additionally, significant nanoparticle agglomeration was observed in Au/CNFS. Au/G was also more selective towards C3 oxidation products (glyceric acid and hydroxypyruvic acid) while Au/CNFs and Au/AC exhibited high selectivity towards glycolic acid.^[54] On the other hand, while carbon nanospheres (CNS) possessed even poorer crystallinity compared to CNF, Au/CNS exhibited comparable performance with Au/G. CNS consists of graphene sheets in the form of waving flakes that follow the curvature of the sphere. These graphitic flakes in turn provide reactive “dangling bonds” which have been proposed to enhance surface reactions.^[55]

Fig. 2.5. Aberration-corrected HRTEM images of Au particles supported on highly graphitized CNF support. a) A representative 2–4 nm particle with (111) surface epitaxially parallel to the graphitic layer of CNF. b) Structure model derived from the image in part a. Reprinted with permission from ref 56. Copyright John Wiley and Sons.

Crystallinity of CNFS may determine the orientation in which Au nanoparticles are immobilized onto the support and this in turn impacts its catalytic performance.^[56] Highly ordered graphitic layers on the CNF surface (Au/CNFs-LHT) led to preferential immobilization of Au on its (111) plane, exhibiting more facet area (Fig. 2.5). In comparison, disordered CNF surfaces (Au/CNFs-PS) led to random orientation of supported nanoparticles. Au/CNFs-LHT and Au/CNFs-PS had similar particle sizes and thus exhibited similar TOF values. However, Au/CNFs-LHT was 34% less selective to glyceric acid and 20% more selective to formic acid compared to Au/CNFs-PS and Au/C, both of which shared similar product distributions.

Hence the poor glyceric acid selectivity of Au/CNFs-LHT suggests that exposure of low index Au surfaces in Au/CNFs-LHT likely promoted C-C bond cleavage.

2.2.3.2. Oxide Supports

2.2.3.2.1. Influence of basic/acidic nature of oxide supports

As aforementioned, oxide supported nanoparticles tend to exhibit poorer catalytic activity for glycerol oxidation compared to carbon supported nanoparticles. However, the use of oxide supports has engendered significant improvements in C3 selectivity even under base free conditions. Furthermore, product distribution and/or C3 selectivity of oxide supported nanoparticles could be tuned by modifying the acidic/basic nature of the oxide supports. In general, basic supports tend to result in higher catalytic activity compared to acidic supports under base free conditions. Glycerol oxidation proceeds via oxidative dehydrogenation and basic supports enhance β -hydride abstraction, which is the rate limiting step. In comparison, employment of acidic supports usually resulted in higher C3 selectivity and a distinctly different product distribution under base free conditions. More specifically, acidic supports favoured high selectivity towards glyceraldehyde whilst basic supports promoted its sequential oxidation to glyceric acid, tartronic acid and other C2 and C1 side products. For example, AuPt nanoparticles supported on basic MgO (AuPt/MgO) showed moderate catalytic activity and exceptionally high selectivity to glyceric acid even when glycerol oxidation occurred under ambient temperature and neutral conditions.^[57] However, basic sites probably bind strongly to the glycerol oxidation products and prevented desorption until their complete conversion to CO₂.^[58] As such, basic supports also observed lower mass balance. Notably, sequential oxidation of glyceric acid to tartronic acid and other over oxidation products can be restrained by doping the strongly basic sites with a weak base.^[58]

In addition, Prati and co-workers investigated how the acidic nature and strength of different oxide supports (SiO₂, MCM-41, H-mordenite, sulfated ZrO₂ (S-ZrO₂)) influenced the catalytic

performance of supported AuPt nanoparticles for glycerol oxidation under base free conditions.^[59] Total acid strength was the most significant factor in governing catalytic activity. More acidic supports resulted in lower catalytic activity. However, only Bronsted acid sites contributed to total acid strength while Lewis acid sites did not. On the other hand, selectivity to glyceraldehyde was enhanced with weakly acidic supports. Successive transformation of glyceraldehyde to glyceric acid proceeds via an acid catalyzed geminal diol formation and its dehydrogenation to a carboxylic acid. Weaker acids only enable this process to a limited extent and favour the formation of glyceraldehyde. On another note, C3 selectivity of Au/H-mordenite and Pt/H-mordenite were significantly higher than Au/AC and Pt/AC respectively.^[60] Employment of H-mordenite resulted in a marked decrease in H₂O₂ production and thus C-C bond scission was inhibited.

Ebitani and co-workers investigated the use of the basic hydrotalcite (HT) compound as a support for glycerol oxidation.^[44, 61] Both Au/HT and Pt/HT showed 100% glycerol conversion when the reaction occurred under base free conditions. Moreover, catalytic performance of Pt/HT was linked to the degree of basicity of HT which influenced Pt nanoparticle size and thus, its final oxidation state. Basic strength of HT could be tuned by varying its Mg/Al ratio.^[62] Higher Mg/Al ratios led to more basic supports and larger Pt⁰ nanoparticles.^[62d] Larger Pt⁰ nanoparticles are less susceptible to oxidation when exposed to air and are better able to maintain their zero valent state. Since effective glycerol oxidation required more than 35% of the nanoparticles to exist as Pt⁰, HT supports with higher basicity promoted enhanced catalytic activity. Similarly, C3 selectivity of Au nanoparticles could also be tuned by varying the Al/Mg ratios of crystalline MgAl₂O₄ spinel supports.^[63] In general, MgAl₂O₄ supports possessing higher Al/Mg ratios were more selective to glycolic acid whilst those having lower Al/Mg ratios were more selective to glyceric acid. Supports with similar Al/Mg ratios resulted in similar C3 selectivity, even if their Au particle sizes differed.

2.2.3.2.2. Nickel oxide supports

While nickel based catalysts have been extensively investigated for glycerol steam reforming^[64], their catalytic application towards glycerol oxidation is limited owing to poor catalytic performance^[65]. However nickel oxide (NiO) based materials have shown some promise as supports for Au nanoparticles^[66] during glycerol oxidation. In particular, Au nanoparticles supported on NiO nanoparticles (Au/nNiO) and NiO-TiO₂ mixed oxide supports (Au/NiO-TiO₂) demonstrated high catalytic performance for glycerol oxidation.^[67] Amongst all the catalysts tested, Au/nNiO demonstrated the highest activity for glycerol oxidation under basic conditions. Although presence of TiO₂ in the support decreased activity by up to 3 times, there was a corresponding 20% improvement in selectivity to glyceric acid. Au was found to be preferentially deposited onto NiO in the NiO-TiO₂ supports. This indicated that the NiO nano-crystalline thin sheets anchored and stabilized the Au nanoparticles. Improved glyceric acid selectivity presented by Au/NiO-TiO₂ was attributed to changes in its interaction with glycerol as opposed to changes in electronic structure of either oxide support or Au nanoparticles. Preferential confinement of Au on NiO likely introduced new interfaces in close proximity to the TiO₂. This in turn influenced diffusion and binding of reactants during the reaction.

2.2.3.2.3. Copper oxide supports

Importantly, Xu and co-workers demonstrated that CuO supported Au nanoparticle (Au/CuO) catalyst was extremely selective for dihydroxyacetone under base free conditions.^[68] Furthermore, by tuning the reaction conditions, 100% selectivity towards DHA could be obtained. However, glycerol conversion was only 1% under these conditions. Glycerol conversion improved significantly while maintaining high dihydroxyacetone selectivity when reaction conditions were further optimized. These results are significant as this is the first report demonstrating that supported Au catalysts can selectively oxidize the secondary alcohol group

under base free conditions. In contrast, when glycerol oxidation was carried out over Au/CuO in alkaline conditions, glyceric acid was once again the main oxidation product and dihydroxyacetone was not produced.

2.2.4. Influence of reactor design

Most of the experimental investigations discussed in this chapter were conducted in stainless steel autoclaves (semi-batch reactors)^[69] or in glass reactors under optimized conditions. However, the results of these preliminary, small scale investigations might not translate well when the reaction is conducted under actual industrial conditions. In view of this, catalytic testing was carried out in alkaline membrane fuel cells and fixed bed reactors, which enable a more realistic simulation of actual industrial conditions.^[70]

Selectivity is significantly influenced by the type of reactor employed. For example, supported PtBi catalysts gave rise to higher glycerol conversions and DHA selectivity when glycerol oxidation took place in a fixed bed reactor instead of a semi-batch reactor. Using a fixed bed reactor, Kimura obtained 80% DHA selectivity at 80% conversion with PtBi nanoparticles supported on granular coal.^[71] When reaction took place in a semi-batch reactor, selectivity to DHA decreased with increasing glycerol conversion.^[72] As such, even though high initial DHA selectivity of ~80% could be attained, final selectivity declined sharply to 37% at 70% conversion.^[73]

Catalysts also need to exhibit long term stability so as to ensure that their catalytic activity is maintained throughout the long on stream time. Catalytic stability can be maintained by embedding the nanoparticles within resin matrix. Au nanoparticles supported on commercial weak basic anion resin (Dowex M-43) maintained its high selectivity to glyceric acid and tartronic acid when tested in both semi-batch and fixed bed reactors.^[74] Furthermore, Au/DowexM-43 was stable for up to 22h in the fixed bed reactor without undergoing significant particle aggregation, growth or deactivation. Similarly, well-dispersed AuPd

nanoparticles stabilized in commercial ion-exchange resin^[75] were tested for glycerol oxidation in both batch type and fixed bed flow reactors, under alkaline conditions. Interestingly, selectivity to TA increased by about 3 times in the fixed bed reactor compared to the batch type reactor. Davis and co-workers previously suggested that the disparities in diacid (TA and OA) selectivities between semi-batch and fixed bed reactors was due to differences in reactor configuration.^[76] During the reaction, glyceric acid (or other monoacid species) could function as a chelating agents^[77] which co-ordinate with Au/C and inhibit its activity. Catalytic inhibition is less likely in a flow reactor which operates at a stationary state such that the monoacid products generated are continuously removed by the flowing fluid stream. In contrast, there is sufficient time and fluid volume in a semi-batch reactor. Glyceric acid produced is thus able to convert to an inhibitory by-product species that adsorbs onto the catalyst and inhibits it. Kim and co-workers also ascertained that Pt/C exhibited significantly better catalytic performance when glycerol oxidation was carried out in a continuous flow electro-catalytic reactor instead of an electro-catalytic batch reactor.^[78] TOF obtained by Pt/C was nearly ten times higher in the former case. Pt/C also achieved higher selectivity to glyceric acid at lower glycerol conversion when in the continuous flow reactor. Compared to conventional batch reactors, electro-catalytic reactors are advantageous as they enable glycerol oxidation to take place in the absence of stoichiometric oxidants i.e. without pressurized oxygen gas. Catalytic performance of Pt/C in electro-catalytic reactors also far surpassed that in conventional batch reactors.

Catalytic performance of gold on carbon coated monolith (Au/CM) was evaluated in a continuous flow structured reactor and mesoscale structured down flow slurry bubble columns (SBCR) under mild conditions.^[79] SBCR enabled faster glycerol conversion compared to the monolith reactor. Nonetheless, catalytic activity was one order of magnitude higher in the monolith reactor and two orders of magnitude higher in SBCR compared to the autoclave

reactor. Differences in reactor configuration also gave rise to differences in product distribution. Au/CM demonstrated high selectivity to GLYA when the reaction took place in the monolith and autoclave reactors. On the other hand, SBCR yielded approximately equal quantities of DHA and GLYA under similar conditions. The ability to generate DHA was indicative of higher oxygen availability and thus faster oxygen transport within SBCR compared to the autoclave and monolith reactors. Furthermore, particle-bubble interaction and mesoscale structuration also contributed appreciably to the different product selectivity observed in SBCR. Placing Au/CM in a meso-scale structured environment which structured gas–liquid–solid reacting flows in thin channels or capillaries brought about enhanced interaction between bubbles and particles. This in turn enhanced transport and reaction rates within SBCR and eventually gave rise to the differences in product selectivity observed.

2.2.5. Copper based catalysts

Catalytic performance of copper (Cu) based materials as catalysts or supports have been investigated for glycerol oxidation. Cu nanoparticles are attractive owing to their ability to catalyse glycerol oxidation under base free conditions. For example, Cu(0) nanoparticles (15–20nm) supported on ordered mesoporous cobalt monoxide (Cu/CoO) managed 86% glycerol conversion in the absence of base.^[80]

Cu has also been utilized as an additive to improve the catalytic performance of other materials. For example, catalytic performance of MgAl layered double hydroxides (LDH) for glycerol oxidation improved after the addition of Cu.^[81] Catalytic performance of CuMgAl was tuned by varying the amount of Cu. Increasing Cu content generally improved glycerol conversion and selectivity to glyceric acid until a maximum was reached. Moreover, calcination of CuMgAl was crucial to its high catalytic performance. This is due to differences in active species present in the calcined and uncalcined samples. In the uncalcined sample, Cu existed as Cu(OH)₂. However, after calcination Cu(OH)₂ was oxidized to CuO. Since the calcined

sample was more active than the uncalcined sample, it follows that Cu^{2+} existing in the form of $\text{Cu}(\text{OH})_2$ was less active than Cu^{2+} present in the calcined mixed oxide sample.

Similarly, CuNiAl hydrotalcites (HT) were also active and selective for glycerol oxidation under basic conditions.^[82] Furthermore, catalytic performance significantly improved after HT was functionalized with an amino group. In particular, amino modified CuNiAl HT ($\text{CuNiAl-C}_5\text{H}_{10}\text{N}_2\text{H}_3$) was 14% more selective to glyceric acid compared to Au/C. $\text{CuNiAl-C}_5\text{H}_{10}\text{N}_2\text{H}_3$ also proved to be very stable and maintained its catalytic performance for an additional 6 catalytic runs. Interestingly, while $\text{CuNiAl-C}_5\text{H}_{10}\text{N}_2\text{H}_3$ only managed 8% glycerol conversion in the absence of base, it remained highly selective for glyceric acid and selectivity even increased to 85%. Synergistic effect of the Cu species, Lewis base sites and Bronsted base sites present on the hydrophobic surface of the $\text{CuNiAl-C}_5\text{H}_{10}\text{N}_2\text{H}_3$ catalysts all contributed to its noteworthy catalytic performance.

Recently, AuCu alloys supported on niobium oxide ($\text{AuCu/Nb}_2\text{O}_5$) were investigated for glycerol oxidation.^[83] There appeared to be very limited synergistic effect between Au and Cu, when the alloy was supported on Nb_2O_5 . Glycerol conversion attained by the bimetallic structure was only 11% higher than that of $\text{Au/Nb}_2\text{O}_5$ when the reaction was carried out at 60°C. At higher reaction temperatures of 90°C, both catalysts obtained comparable glycerol conversion. Furthermore, glyceric acid selectivity exhibited by $\text{AuCu/Nb}_2\text{O}_5$ was 20% and 30% lower than that of $\text{Au/Nb}_2\text{O}_5$ at 60°C and 90°C respectively.

2.3. Glycerol electro-oxidation

2.3.1. Mechanism

Scheme 2. The glycerol oxidation mechanism on Au and Pt electrodes in alkaline media under different pH conditions. Reprinted with permission from ref 84. Copyright John Wiley and Sons.

Koper and co-workers studied the mechanism of glycerol oxidation when the reaction was carried over Au and Pt electrodes under different pH conditions (Scheme 2).^[84] Their studies were carried out by using a combination of cyclic voltammetry (CV) and high performance liquid chromatography (HPLC) that adopted a rapid online sample collection process with a modified micrometer-sized sample collecting tip.^[85] All potentials reported for this work were measured with respect to the reversible hydrogen electrode (RHE).

The Pt electrode was active over the entire pH range. Furthermore, the glycerol oxidation pathway taken over the Pt electrode is essentially the same, regardless of pH. Pt electrode was most active under alkaline conditions and least active under acidic conditions. In terms of selectivity, glyceraldehyde was the dominant oxidation product generated over the Pt electrode. It was first obtained at low applied potentials and continued to be present throughout the entire potential range. Glyceraldehyde was subsequently converted to glyceric acid then glycolic acid,

formic acid and CO_2 as the applied potentials increased.^[86] Interestingly, the PtO_x surface generated at high applied potentials appeared to be active for glycerol oxidation under neutral and acidic conditions but not in alkaline media. In neutral conditions, the PtO_x surface continued to generate glyceraldehyde even at higher applied potentials. However, the selectivity of PtO_x to glyceraldehyde was less than that of the clean Pt surface as glyceraldehyde was subsequently oxidized to glyceric acid and other side products. Under acidic conditions, the PtO_x surface facilitated high selectivity to formic acid and CO_2 at high applied potentials. Formic acid and CO_2 were generated via C-C bond breakage of glyceric acid and glycolic acid. To account for these observations, Koper and co-workers suggested that either the Pt surface at these high potentials was not fully oxidized to PtO_x in the presence of glycerol or that the high anodic potential makes PtO_x catalytically active. The secondary alcohol oxidation pathway was also observed at the Pt electrode over the entire pH range. Dihydroxyacetone and its corresponding oxidation product, hydroxypyruvic acid, were both detected in the reaction solutions. In addition, the acidic media was observed to be particularly favourable for secondary alcohol oxidation and under these conditions, the highest concentration of DHA was attained.

In contrast, the Au electrode was highly active for glycerol oxidation in alkaline media, especially at higher applied potentials, but inactive under acidic conditions. Under basic conditions, current density of the Au electrode at high applied potentials was nearly 10 times that of the Pt electrode. The higher activity of Au could be ascribed to its delayed surface oxidation compared to Pt; onset potential was 0.4 V and 0.8 V for Pt and Au respectively in alkaline media. Having said that, the Pt electrode was more active than the Au electrode in the potential region in which both electrodes were not covered by an oxide layer. Product distribution over the Au electrode was also significantly influenced by its onset potential. Glyceric acid instead of glyceraldehyde was detected as the main product. The acid

intermediate was then actively oxidized to glycolic acid and formic acid each with about 45% selectivity when applied potential was greater than 0.8 V. In contrast, only a small amount of glycolic acid and formic acid were observed over the Pt electrode in alkaline media; the main oxidation product derived from Pt was glyceric acid. These differences in product distribution and selectivity was ascribed to the wider potential range available for further oxidation over the Au electrode.

Pt was more active than Au for glycerol oxidation under neutral conditions and it exhibited a significantly higher current density. However, reaction kinetics for both electrodes are generally more sluggish under neutral conditions compared to alkaline conditions. The current density of glycerol oxidation on Pt and Au electrodes under neutral conditions was, respectively, 10 and 50 times lower than under alkaline conditions. These observations strongly suggest that OH^- promotes the glycerol oxidation and plays an important role of a proton acceptor or a reaction mediator, especially on an Au electrode.^[87] Furthermore, glyceraldehyde was the only product observed over the Au electrode under neutral conditions. Small amounts of CO_2 were later detected by online electrochemical mass spectrometry. This indicated that some glycolic acid and formic acid were also produced but not detected. In line with these observations, Koper and co-workers subsequently showed that the presence of OH^- in solution accelerated C-C bond cleavage of glyceric acid to glycolic acid and formic acid, even in the absence of catalyst.^[88] This stemmed from their observation that glyceraldehyde could independently convert to a range of products including glyceric acid, glycolic acid and formic acid, under alkaline conditions in the absence of Au (Fig. 2.6). The role that OH^- plays during the selective oxidation of alcohols in aqueous phase over supported metal catalysts was first investigated by Davis and co-workers (Fig. 2.7) Theoretical calculations revealed that the presence of surface bound hydroxide intermediates facilitated O-H bond activation of the alcohols via proton transfer in much the same way as it occurs in solution.

Fig. 2.6. Decomposition of (a) glyceraldehyde and (b) glycolaldehyde, the primary oxidation products of glycerol and ethylene glycol, respectively, in a nondeaerated O₂-containing 0.1 M NaOH solution in the absence of gold, as determined by HPLC. Reprinted with permission from ref 88. Copyright ACS Publications.

Calculated activation barrier for the deprotonation process is very high and O-H bond activation by the metal alone is unlikely. However, the presence of adsorbed hydroxyl groups on the surface of Pt and Au significantly reduces the activation energy required for this rate limiting step. For instance, the calculated activation barriers for the dissociative adsorption of ethanol over the Au(111) and Pt(111) surfaces in water are 204 and 116 kJ mol⁻¹ respectively. However, the presence of adsorbed hydroxyl intermediates was calculated to have lowered the activation barrier to 22 and 18 kJ mol⁻¹ for Au(111) and Pt(111) respectively. The resulting ethoxy anion species resulting from deprotonation is a highly reactive species and consequently forms the acetaldehyde product with ease.^[89]

Fig. 2.7. Reaction scheme for the oxidation of alcohols to acids over Au surface in water at high pH. Reprinted with permission from ref 90. Copyright Nature Publishing Group.

Koper and co-workers later proved that the rate limiting deprotonation step is base catalysed and is facilitated solely by the added OH^- without the involvement of Au (Fig. 2.6).^[88] Moreover, the amount of base required to form the alkoxide intermediate is dependent on the pKa of the alcohol. Reactivity of the alcohol and its pKa share a Hammett type relationship such that alcohols with lower pKa values are more reactive. Glycerol and other sugar alcohols proved to have high oxidation activity at pH=11, corresponding to their low pKa values. In contrast, alcohols with a high pKa, such as isopropanol and isobutanol, were significantly less active. Both Koper and Davis's studies posited that the Pt and Au electrodes investigated only became involved during the β -hydride elimination step to form the aldehyde intermediate. The adsorbed hydroxide intermediates continued to lower the activation barrier for the subsequent activation of the C-H bond of the ensuing alkoxide intermediate to form the aldehyde over Au. However, for Pt, this step already has a very low barrier and it does not require further assistance from the adsorbed OH. Taking into account that OH^- in solution can independently facilitate further oxidation and C-C bond cleavage of glyceraldehyde to glyceric acid, glycolic acid and formic acid, it is possible to conclude that Au plays a limited role during the alcohol oxidation process. Having said that, importance of the interaction between Au and the adsorbed

hydroxyl intermediates during β -hydride elimination cannot be undermined. Some interaction of the alkoxide with the (hydroxylated) gold surface is still mandatory (Fig. 2.7).

2.3.2. Factors affecting catalytic performance

2.3.2.1. Effect of metal-support interactions

Fig. 2.8. The schematic drawing of the loading of Au NPs on P4P/rGO and P4P/G. Reprinted with permission from ref 91. Copyright Elsevier Publications.

Our group investigated the use of modified graphene supports to improve the catalytic performance of Au and Pd nanoparticles for glycerol electro-oxidation. In the first report, we prepared Au nanoparticles supported on poly(m-aminophenol) (Au-PmAP/G) and poly(4-vinylpyridine) (Au-P4P/G) functionalized graphene and compared their performance for glycerol oxidation against that of Au/C (Fig. 2.8).^[91] Au-P4P/G possessed the highest electro-catalytic activity and current density. Our results demonstrated that metal-support interactions changed the electronic properties of Au nanoparticles and this in turn altered its C3 selectivity. In particular, Au-P4P/G was notably more selectivity to glyceric acid than Au-PmAP/G and Au/C, regardless of the applied potential used for glycerol electro-oxidation. High C3 selectivity observed with Au-P4P/G was attributed to the electron enrichment experienced by Au as a result of its interaction with the strongly electron donating pyridine groups present in the P4P chains. Conversely, the weakly electron donating $-N=$ groups in PmAP brought about

weaker metal-support interaction. Thus, electronic enhancement experienced by Au was less significant and PmAP was not as effective in tuning Au selectivity.

Next, Pd nanoparticles were supported on carbon nitride (Pt/CN_x) and carbon nitride modified graphene (Pd/CN_x-G). Catalytic performance of Pt/CN_x and Pd/CN_x-G for glycerol electro-oxidation were compared against Pd/C reference catalyst.^[92] Once again, metal-support interactions played a central role in governing the selectivity of Au nanoparticles. Pd/CN_x-G gave rise to the highest C3 selectivity, possibly owing to the comparatively smaller Pd nanoparticles (~4.4nm) present on the support. On the other hand, despite its larger particle size, Pd/CN_x exhibited higher C3 selectivity than Pd/C. Interaction between Pd nanoparticles and nitrogen atoms present on CN_x likely altered the electronic properties^[93] of the former and weakened its absorption ability to C3 products, especially glyceric acid.

2.3.2.2. Advanced carbon materials as supports

Graphene^[94] and carbon nanotubes^[95] (CNTS) based materials have emerged as a new class of carbon materials in recent years. Owing to their physicochemical and electrochemical properties par excellence, graphene and CNTS have been widely applied as catalysts and supports for many reactions.^[96] When employed as supports for glycerol oxidation^[97], graphene and carbon nanotubes (CNTS) based catalysts resulted in higher current densities and improved catalytic performance than when supported on other types of carbon materials such as carbon black and activated carbon.^[98] The superior electro-catalytic activity of the former is due to its good electrical conductivity and large electrochemical active surface areas which allows for better catalyst utilization. Furthermore, the edges and defects on graphene and CNTS as well as their large surface areas enabled these supports to effectively anchor the metal nanoparticles and stabilize them. As a result, the as-prepared catalysts typically consist of small, uniformly dispersed nanoparticles which demonstrate high catalytic activity when applied to glycerol oxidation.^[99] The robust nature of these carbon supports also suggests that their high

performance can be maintained even under harsh conditions, rendering them suitable for industrial applications.^[100]

Extensive research has also been carried out to modify graphene and CNTS in order to further improve catalytic performance. With respect to glycerol electro-oxidation, metal nanoparticles supported on multi-walled CNTS (MWCNTS) performed significantly when MWCNTS were functionalized with -COOH (MWCNT-COOH) rather than -SO₃H (MWCNTS-SO₃H). Higher activity of MWCNT-COOH was due to its ability to form uniformly dispersed, small nanoparticles. MWCNT-COOH also possessed a higher electrochemically active surface area (EASA) than MWCNTS-SO₃H.^[101]

San's and Shen's groups made use of the intrinsic properties of these carbon supports to immobilize CeO₂^[102] nanoclusters onto MWCNTS (CeO₂-MWCNTS)^[103] and graphene nanosheets (CeO₂-GNS)^[104] respectively. Immobilization helped stabilize the CeO₂ nanoclusters which have a tendency to agglomerate during preparation^[105] and when subjected to electrochemical conditions^[106]. Formation of CeO₂-MWCNTS and CeO₂-GNS enabled the subsequent deposition of small, uniformly dispersed Au and Pt nanoparticles respectively as the CeO₂ nanoclusters functioned as anchor site for the metal nanoparticles. Both Au/CeO₂-MWCNTS and Pt/CeO₂-graphene exhibited higher current density and significantly improved durability when applied to glycerol electro-oxidation as compared to Au/MWCNTS and Pt/GNS respectively.

2.3.3. Effect of non-noble metals on Pt and Pd based catalysts

Co-catalysts are often used to improve the catalytic performance of noble metal catalysts for glycerol electro-oxidation. Employment of a co-catalyst, typically a non-noble metal, generally leads to significant improvements in electrochemical activity.^[107] In line with this, the promotional effect of Ni on the electrochemical activity of Pd and Pt has been previously reported. PdNi/C experienced improved reaction kinetics relative to Pd/C at low potentials.^[108]

This was attributed to a bifunctional mechanism involving the transfer of OH^- species from the Ni(OH)_2 surface towards the adsorbed organic molecules close to the Pd surface where the reaction takes place. Furthermore, the large forward peak current density and a higher real surface activity, exchange current density, and i_f/i_r ratio was exhibited by $\text{Pt}_2\text{Ni/C}$ relative to Pt/C . These enhanced electrochemical activities was attributed to the following characteristics in $\text{Pt}_2\text{Ni/C}$ (1) modified lattice parameter of the Pt-Ni alloy might structurally favour the reaction (2) electronic modification with an increased Pt 5d band vacancy would electronically promote the reaction.^[109]

When Pt was alloyed with Sb, the resulting PtSb/C catalyst was highly selectivity towards DHA (61.3% selectivity) at high conversion rates of 90.3% when the reaction was carried out under acidic conditions in an electro-catalytic reactor system.^[110] In contrast, under the same conditions, Pt/C is highly selective to glyceraldehyde and glyceric acid. Little to no DHA was produced by Pt/C . PtSb/C was also significantly more active compared to Pt/C . Presence of Sb in Pt results in fewer intermediate residues accumulating on the catalyst surface during glycerol electro-oxidation. For Pt based catalysts, adsorption and accumulation of carbonaceous intermediates on the Pt surface is a common problem that eventually leads to catalyst deactivation. As such, presence of a co-catalyst not only altered the reaction pathway but also prevented the active sites on Pt from being blocked. Similarly, the synergistic effect of Ru and Sn on PtRuSn ternary catalyst enabled complete oxidation of CO or CO-like poisonous species on Pt sites and prevented catalyst deactivation.^[111] Addition of Ru and Sn also facilitated C-C bond cleavage and formic acid was the dominant product. Geometric environment of the fcc Pt crystallites was altered as a result of Ru and Sn addition. In particular, incorporation of larger Sn atoms into the PtRu lattice led to elongation of crystal structure, which in turn likely facilitated C-C and C-H cleavage. Additionally, Sn addition modifies the electronic environment of PtRuSn/C via electron transfer to Pt. This electronic modification weakens the

bond between carbon atoms and surface Pt atoms. Furthermore, Sn oxides supply sufficient oxygen containing species of OH which facilitates removal of the adsorbed carbonaceous species.

Fig. 2.9. Glycerol electro-oxidation over Pt (favours the primary oxidation pathway) and Pt containing reversibly adsorbed Bi (favours the secondary oxidation pathway). Reprinted with permission from ref 112. Copyright ACS Publications.

Inaya, Tsuto and their co-workers were the first to observe that the presence of Bi on the Pt nanoparticle surface greatly improved selectivity towards dihydroxyacetone (DHA).^[72c] When the reaction was carried out in a semi-batch reactor, a maximum of 20% DHA selectivity could be obtained with 1%Bi-5%Pt/C catalyst at 30% glycerol conversion. Conversely, 5%Pt/C only managed ~5% DHA selectivity at 40% conversion. The authors posited that the Bi adatoms function as site blockers on Pt(111) and their presence orientated the adsorbed glycerol molecule in such a way that the secondary –OH group was positioned favourably for oxidation. In extension of this work, Koper and co-workers examined the relationship between Pt and Bi under electro-catalytic conditions (Fig. 2.9).^[112] Specifically, they were interested in determining whether the irreversible or reversible adsorption of Bi onto Pt was more effective in achieving high DHA selectivity under acidic conditions. Reversibly adsorbed Bi on Pt/C was more effective in directing the reaction onto the secondary oxidation pathway, especially at low applied potentials; 100% selectivity to DHA was obtained at ~0.6V vs RHE (reversible hydrogen electrode). At higher applied potentials, Bi underwent oxidative desorption from the

electrode. High Bi surface coverage was necessitated for enhanced selectivity to DHA, failing which a significant increase in glyceric acid selectivity was observed. The interaction between Bi and the two primary alcohol groups on glycerol might play a role in increasing DHA selectivity. However, the presence of Bi in solution for reversible adsorption lowered current density and activities relative to Pt/C.

Kim and co-workers also examined the catalytic performance of carbon supported PtBi alloys in an electro-catalytic reactor, under acidic conditions with heating.^[110] They determined that product distribution was highly dependent on the electrode potential and nature of the catalyst. In particular, applied potential influenced the nature of the species present on the catalyst surface and altered its catalytic activity. PtBi/C was highly selective to DHA at low potentials. However, at higher applied potentials, selectivity to DHA decreased as Bi oxidized to form Bi oxide/hydroxide species, which are not selective to DHA.

Subsequently, Koper and co-workers extended their study to determine the effect of antimony (Sb), tin (Pb), lead (Sn) and indium (In) adatoms on Pt/C.^[113] Irreversible adsorption of Sb onto Pt/C achieved 80% DHA selectivity at lower potentials (0.35–0.55V vs RHE). Yet despite its promising performance, Sb was still less efficient than Bi bringing about 100% DHA selectivity.

In contrast, Pb, Sn and In did not manage to steer the reaction pathway from primary to secondary oxidation. Glyceric acid was the main oxidation product obtained. Poor DHA selectivity was attributed to their incomplete adsorption onto Pt/C. As mentioned above, high surface coverage of the adatom is a necessary pre-condition for high activity.

2.3.4. Effect of non-noble metals on Au based catalysts

The promotional effect of co-catalysts on the catalytic performance of Au has also been reported. For instance, the effect of RuO₂ on Au was studied by dispersing Au onto preformed RuO₂/C.^[114] However, there appears to be limited synergistic interaction between RuO₂ and

Au. Although RuO₂ promoted Au catalyst was more stable than the un-promoted catalyst, RuO₂ reduced the electrochemically active surface area of Au and also decreased maximum current density. Furthermore, presence of RuO₂ also did not alter the product distribution and glycerol conversion values of Au/C.

In comparison, C-C-C bond breakage was favoured when Au was alloyed with Ag (AgAu/C). favoured the formation of formic acid.^[115] The impact of Ag on the glycerol electro-oxidation over AuAg/C was likely driven by electronic modifications and Ag segregation on the catalysts surface. Presence of Ag also enhanced the electrochemical activity of Au/C, resulting in decreased onset potential and higher current density during chronoamperometry.^[115b]

2.3.5. Glycerol electro-oxidation in alkaline membrane fuel cells

Fig. 2.10. Schematic illustration of the anion exchange membrane-based fuel electro-catalytic flow reactor. Reprinted with permission from ref 116. Copyright Elsevier Publications.

Catalytic performance of supported Au^[116-117], Pd^[118] and Pt^[70] based catalysts for glycerol oxidation in direct alcohol alkaline membrane fuel cells (DAFC) was extensively investigated by Li and co-workers (Fig. 2.10). Catalytic performance is generally dependent on the following (1) applied potential (2) catalyst loading (3) concentration of base (4) concentration of glycerol (5) catalyst preparation method. Most importantly, high selectivity to either mesoxalic acid^[100b] or tartronic acid^[117a] could be achieved by when glycerol oxidation was carried out in DAFCs. For example, 69.3% selectivity to tartronic acid could be attained at

89.2% glycerol conversion when glycerol oxidation is carried out over Au/C catalysts in DAFC for 12 h. 1527 J of energy was released during this process.

Selectivity to mesoxalic acid and tartronic acid could be further optimized by tuning the applied potential. Furthermore, a thick electrode layer is particularly favourable for the generation of TA and MA. Electrode thickness alters the rate at which reactants and products diffuse out of the catalyst layer. This in turn affects the concentration profiles of reactants and reaction intermediates available inside the electrocatalytically active region. Thicker porous electrodes likely facilitate deeper oxidation of the intermediates by holding them within the confined electrolyte volume for longer periods of time. At the same time, glycerol is held outside of the electrocatalytically active region. Electrode thickness can be tuned by adjusting the metal loading or by changing the catalyst amount. Notably, Au/C catalysts with loadings of 5 mg cm^{-2} afforded 46% selectivity to mesoxalic acid at an applied potential of 0.3 V (anode overpotential of 0.531 V). In comparison, when catalyst loading was reduced to 1 mg cm^{-2} , Au/C was more selective to tartronic acid (39% selectivity) but less selective to mesoxalic acid (19% selectivity), at the same applied potential. These results are significant because despite strong commercial interest, mesoxalic acid has never been reported as a major product from the direct oxidation of glycerol, when the reaction was carried out in half cells or semi-batch reactors.^[119] Currently, the most effective way to derive MA from glycerol is via a 2 step oxidation method using 2 different catalysts. Glycerol is first converted to TA before it is further oxidized to MA, typically using a conventional Pt-Bi based catalyst. As such, DAFCs thus represent a highly promising route to sustainable electro-catalytic conversion of biorenewable intermediates to chemicals along with electricity cogeneration.

Chapter 3

Cu modified carbon supported Au nanoparticles as highly selective catalysts for glycerol electro-oxidation in alkaline solution

3.1. Introduction

Several strategies have been developed to improve catalytic selectivity during glycerol oxidation. One approach is via the use mediators and adatoms. For instance, when Ciriminna and co-workers employed radical TEMPO catalyst (2,2,6,6- tetramethylpiperidine-1-oxyl) for glycerol oxidation under different conditions, moderate DHA selectivity^[120] and high MA selectivity^[6] could be independently obtained. On the other hand, Kwon and co-workers investigated the ability of adatoms – Bi,^[112] Sn, Sb, In, As, Pb^[113] – to mediate the selectivity of Pt/C catalysts for glycerol oxidation. Reversibly adsorbed Bi on Pt/C was most effective in completely blocking the active sites for primary alcohol oxidation. Presence of reversibly adsorbed Bi in conjunction with electrochemical control, resulted in 100% DHA selectivity over Pt/C.

Another approach is via tuning the nature of support.^[58-59, 61, 63, 67] Nature of support influences the metal-support interaction which in turn affects catalytic performance. For example, our group observed that Pd nanoparticles generated on carbon nitride/graphene support (Pd-CN_x/G) showed improved C3 selectivity relative to Pd/C and Pd-CN_x due to smaller Pd particle sizes obtained during synthesis. Additionally, strong interaction between Pd and nitride groups on the CN_x surface likely altered the electronic properties of Pd and weakened its adsorption ability toward C3 products, especially glyceric acid.^[92]

The use of bimetallic nanocomposites is also a commonly employed strategy to improve the performance of Au nanoparticles.^[36] In particular, synergistic interaction between Au and Cu or Cu oxides has resulted in catalysts that are highly activity and/or selective for glycerol electro-oxidation.^[68, 81, 83] However, in those reports, glycerol oxidation was carried out in autoclave reactors under high pressure and temperature.

Herein, we demonstrate that the C3 selectivity of carbon supported Au nanoparticles (Au/C) for glycerol electro-oxidation under alkaline conditions is enhanced by the presence of electro-deposited Cu species on the Au surface. To the best of our knowledge, this is the first article showing that the selectivity of Au nanoparticles for glycerol electro-oxidation can be improved by its interaction with electro-deposited metal and/or metal oxide species present on the Au surface. C3 selectivity could be further tuned by optimizing Cu electro-deposition potential and time.

3.2. Experimental

3.2.1. Synthesis of 4nm Au nanoparticles supported on carbon black

1 ml 1% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was added to 100 ml DI water and the solution was stirred vigorously for 1 min before adding 1 ml 1% sodium citrate solution. After an additional 1 min of vigorous stirring, 1 ml freshly prepared, ice cold 0.075% NaBH_4 in 1% sodium citrate was quickly added and the solution stirred for another 5 min before storage at 4 °C. Then, an appropriate amount of aqueous carbon black dispersion and Au nanoparticle solution were mixed under ultrasonication for 1 h and stirred overnight. After 24 h, pH of the solution was adjusted to below 2 by using 0.2 M HCl and the further stirred for another hour. Finally, the product was filtered, washed three times with copious amounts of DI water and methanol then dried below 80 °C.

3.2.2. Electrochemical Characterization

All electrochemical tests were carried out at room temperature in a conventional three-electrode cell using a Princeton Applied Research VMP2 multichannel potentiostat. Our three electrode cell consisted of Pt wire counter electrode, Ag/AgCl (sat KCl) reference electrode and carbon cloth (CC, $1.5 \times 1.5 \text{ cm}^2$, Gashub) working electrode. All applied potentials are reported with respect to the Ag/AgCl reference electrode.

3.2.3. Preparation of CC working electrode

~2.4 mg of the catalyst was dispersed in 1 mL of ethanol and 0.5 mL of 0.05 wt.% Nafion solution via ultrasonication. This dispersion was drop cast onto CC to prepare a sample with a loading of $\sim 1.07 \text{ mg cm}^{-2}$. The electrodes were dried overnight under ambient conditions.

3.2.4. Cu electro-deposition process

Au/C was first cycled 20 times in 0.2 M NaOH to improve wettability of the hydrophobic carbon cloth. The electrodes were then immersed in a stock solution containing 50 mM $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 0.1 M Na_2SO_4 and held under constant potential. The electrodes were then rinsed thoroughly in DI water before being cycled 30 times in 0.2 M NaOH solution to ensure catalytic stability. The as-prepared electrodes were tested for glycerol electro-oxidation by placing them in 26 mL of 0.5 M NaOH + 0.5 M glycerol solution under constant potential for 2 h. Subsequently, 1 mL of the solution was collected for high-performance liquid chromatography (HPLC) analysis.

3.2.5. Characterization with XPS and XRD

X-ray photoelectron spectroscopy (XPS) data were collected with a Theta Probe electron spectrometer (ESCA-Lab-200i-XL, Thermo Scientific). X-ray diffraction (XRD) patterns were collected by Bruker D2 Phaser. The as prepared carbon cloth electrodes were directly utilized for XPS and XRD analysis without further modification

3.2.6. Chromatographic Analysis of Products

The obtained products were analysed using a Biorad HPX-87H Aminex column for high-performance liquid chromatography (HPLC, Agilent 1260 Infinity). The eluent was 4 mM sulfuric acid. During the test, 20 μL of the sample was injected into the column which was maintained at 65 °C. Eluent flow rate was 0.2 mL min^{-1} . Both refractive index (RID) and UV-VIS detectors were used to analyze the results. Standard solutions of the various oxidation products were also analysed under the same conditions to produce the calibration

3.3. Results and Discussion

3.3.1. TEM Characterization

Fig. 3.1. TEM images of a) Au/C b) Cu_{-0.1V, 30min}-Au/C c) Cu_{+0.015V, 30min}-Au/C d) Cu_{-0.015V, 90min}-Au/C e) Cu_{+0.1V, 30min}-Au/C f) Cu_{+0.3V, 30min}-Au/C and their corresponding size distribution.

Fig. 3.1 shows the TEM images of the various catalysts after Cu electro-deposition was carried out at various potentials and for different time lengths. The Cu-Au/C catalysts are all larger than Au/C and this indicates that Cu species have been successfully deposited onto Au/C.

However, there is no discernible trend in size distribution possibly due to Cu species not being evenly coated onto the Au/C surface. Having said that, our catalytic results (see below) demonstrated that size effect did not influence resulting catalytic selectivity.

3.3.2. XRD Characterization

Fig. 3.2. XRD pattern of a) $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$ b) $\text{Cu}_{+0.015\text{V}, 60\text{min}}\text{-Au/C}$ c) $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$.

XRD data derived after Au/C nanoparticles underwent Cu electro-deposition at +0.015 V for varying time lengths is shown in Fig. 3.2. The catalysts are denoted as $\text{Cu}_{+0.015\text{V}, t\text{min}}\text{-Au/C}$, where t represents the length of electro-deposition process. Au is present in all samples, as observed from the sharp diffraction peak at $\sim 38.5^\circ$, which is assigned to the (111) plane of the Au phase (JCPDS 65-2870). Length of the Cu deposition process influenced the type of Cu species deposited. $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$ contained only Cu(0), as determined by the diffraction peaks at $\sim 43.7^\circ$ and $\sim 50.7^\circ$ and $\sim 74.4^\circ$, which are assigned to the (111), (200) and (220) planes of the Cu(0) phase (JCPDS 04-0836) respectively. Cu(111) diffraction peak also coincided with the Au(200) peak which occurs in the same region. However, when Cu electro-deposition occurred for at least 60 min, both Cu(0) and Cu_2O are observed. $\text{Cu}_{+0.015\text{V}, 60\text{min}}\text{-Au/C}$ and $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ displayed additional diffraction peaks at $\sim 36.7^\circ$ and $\sim 42.6^\circ$ and $\sim 61.6^\circ$,

which are assigned to the (111), (200) and (220) planes of the Cu_2O phase (JCPDS 78-2076) respectively.

Fig. 3.3. XRD pattern of a) Au/C b) $\text{Cu}_{-0.1\text{V}, 30\text{min}}\text{-Au/C}$ c) $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$ d) $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ e) $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$. Carbon peak at $\sim 26^\circ$ was eliminated for greater clarity.

Fig. 3.3 shows the XRD patterns derived after Cu electro-deposition was carried out over Au/C for 30 min at various applied potentials. The resulting catalysts are denoted as $\text{Cu}_{\text{V}, 30\text{min}}\text{-Au/C}$ where by V indicates the Cu electro-deposition potential. Au was present in all the samples investigated. Besides the Au(111) peak, $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ and $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$ displayed additional peaks at $\sim 44.1^\circ$, $\sim 64.5^\circ$ and $\sim 77.5^\circ$, which are assigned to the (200), (220) and

(311) planes of the Au phase respectively. Moreover, in comparison to $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$, $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ contained both CuO and Cu_2O . $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ displayed additional diffraction peaks at $\sim 35.6^\circ$, $\sim 48.8^\circ$, $\sim 53.2^\circ$ and $\sim 61.3^\circ$, which are assigned to the (111), (-202), (020) and (-113) planes of the CuO phase (JCPDS 48-1548) respectively.

Fig. 3.4. Expanded XRD patterns derived after Cu electro-deposition at a) $\text{Cu}_{-0.1\text{V}, 30\text{min}}\text{-Au/C}$ b) $\text{Cu}_{+0.015\text{V}, 60\text{min}}\text{-Au/C}$ and c) $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$.

Table 3.1. Nernst potential calculated for the respective Cu electro-deposition potentials.

Cu electro-deposition potential (V) vs. Ag/AgCl	Calculated Nernst potential (V) vs. RHE
+0.3	+0.498
+0.1	+0.298
+0.015	+0.213
-0.1	+0.098
-0.3	-0.102

Nernst Equation was used to take into account differences in reaction conditions:
 $E = E^{\circ} + 0.0592(\text{pH}_{\text{solution}})$

Table 3.2. Possible electrochemical reactions in the reaction system.

Eq	Electrochemical reaction	Nernst Potential (V) (vs. RHE)
1	$\text{CuSO}_4 + 2\text{e}^- \rightleftharpoons \text{Cu} + \text{SO}_4^{2-}$	+0.34
2	$\text{Cu}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu} + 2\text{OH}^-$	+0.054
3	$\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cu}_2\text{O} + 2\text{H}^+$	+0.61
4a	$\text{CuO}(\alpha) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O}$	+0.25
4b	$\text{CuO}(\beta) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O}$	+0.33
5	$\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}$	+2.11

Various Cu species were obtained from the different electrochemical reactions that occurred at different applied potentials. $\text{Cu}_{-0.1\text{V}, 30\text{min}}\text{-Au/C}$ contained mainly Cu(0) and Cu_2O , as its XRD spectra is similar to that of $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ (Fig. 3.2). Overall, Cu^{2+} reduction (from CuSO_4 stock solution) to Cu was the dominant reaction. As the reaction proceeded, electro-deposited Cu was then oxidized to Cu_2O owing to low reduction potential of the reaction (Eq 2, Table 3.2). This accounts for the presence of Cu_2O in all the samples except for $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$. Furthermore, when Cu electro-deposition occurred at +0.1 V ($E=+0.289$ V vs. RHE, Table 3.1), the applied potential was sufficiently high such that Cu_2O underwent further oxidation to CuO. As such, both Cu_2O and CuO was observed in $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ (Fig. 3.3d). These observations are in line with previous reports which examined the Cu electro-deposition process with X-ray and UV-photoelectron spectroscopy (XPS and UPS) and X-ray reflectivity

measurements.^[121] Small amounts of CuO were also observed in XRD spectra of Cu_{+0.015V}, 60min-Au/C, Cu_{+0.015V}, 90min-Au/C and Cu_{-0.1V}, 30min-Au/C. As with Cu_{+0.1V}, 30min-Au/C, CuO(-111) peak in these samples existed as a shoulder peak alongside Cu₂O(111) at $\sim 36.2^\circ$ (Fig. 3.3). Yoneda-XAFS and theoretical calculations showed that a duplex type structure consisting of an outer CuO and an inner Cu₂O layer were formed on top of metallic Cu thin films after its exposure to air.^[122] Hence, surface oxidation of Cu₂O also accounts for the presence of CuO. Lastly, high applied potential of +0.3 V ($E=+0.498$ V vs. RHE, Table 3.1), meant that only miniscule amounts of Cu was deposited onto Au/C (Fig. 3.5a). XRD spectra of Cu_{+0.3V}, 30min-Au/C is essentially identical to Au/C (Fig. 3.3e).

Fig. 3.5. Chronoamperograms for a) Cu_{+0.3V}, 30mins-Au/C b) Cu_{+0.1V}, 30mins-Au/C c) Cu_{+0.015V}, 30mins-Au/C d) Cu_{-0.1V}, 30mins-Au/C e) Cu_{-0.3V}, 30mins-Au/C.

3.3.3. XPS Characterization

Table 3.3. Relative chemical composition of catalysts prepared at different Cu electro-deposition potentials. Elemental concentrations are expressed as atomic percentage (at. %).

Sample	Au4f (element concentration, at. %)		Cu2p (element concentration, at. %)		Au/Cu _x O _y atomic ratio
	Au ⁰	Au ⁺	Cu ⁺ / Cu	Cu ²⁺	
Cu _{-0.1V, 30min} -Au/C	89.33	10.67	81.38	18.62	2.65/97.35
Cu _{+0.015V, 30min} -Au/C	90.51	9.49	60.77	39.23	3.84/96.16
Cu _{+0.015V, 90min} -Au/C	72.48	27.52	61.02	38.98	2.24/97.76
Cu _{+0.1V, 30min} -Au/C	96.18	3.82	63.68	36.32	3.13/96.87
Cu _{+0.3V, 30min} -Au/C	100	0	100	0	54.03/45.97

X-ray photoelectron spectroscopic (XPS) was used to analyse surface composition of the catalysts prepared at different Cu electro-deposition potential and time. Table 3.3 summarizes their respective elemental surface compositions (atom%). All binding energies were referenced to the adventitious C1s line at 284.8 eV. Au4f_{7/2} peak for all 5 samples was located at a BE of 84.4 eV (Fig. 3.6), which is typical of pure metallic Au(0) species.^[123] Our samples are thus composed of binary nanocomposites instead of Au-Cu alloys since alloy formation is typically accompanied by a shift of the Au4f peak relative to pure Au nanoparticles.^[124]

An additional Au4f peak at 85.7 eV was present when Cu electro-deposition was carried out between -0.1 V and +0.1 V (Fig. 3.6b-e respectively). This peak is assigned to the Au⁺ species.^[123a, 125] Au⁺ content was highest in Cu_{+0.015V, 90min}-Au/C (27.52%) after an extended oxidation period of 90 min and lowest in Cu_{+0.1V, 30min}-Au/C (3.82%). When Cu electro-deposition occurred at +0.1 V, its Nernst potential at +0.298 V (Table 3.1) was very close to the equilibrium potential of Cu²⁺ reduction reaction. Hence, smaller amounts of Cu species were deposited onto Au/C at +0.1 V (Fig. 3.5b). This in turn decreased Au-Cu oxide interaction

and reduced the amount of Au^+ species generated. Au^+ was generated via electron transfer from Au to the electro-deposited Cu_2O present on its surface. Consequently, Cu_2O was reduced to Cu. This redox process is thermodynamically favourable and spontaneous owing to the relatively large difference in their reduction potentials ($\Delta E = +2.06 \text{ V}$).^[126] Au^+ has also been observed in other types of Cu_2O -Au nanocomposites such as heterodimers, core-shell particles and hollow spheres.^[127] Additionally, Au nanoparticles supported on CeO_2 (Au/CeO_2) and Au nanoparticles partially covered with very small NiO_x ($\text{NiO}_x\text{@Au}$) segments also reported the presence of Au^+ species after electron transfer occurred between $\text{Au}(0)$ and CeO_2 ^[128] and Ni_2O_3 ^[129] respectively. In comparison, CuO is more stable due to its higher reduction potential and Au^+ species are not commonly observed in Au-CuO nanocomposites.^[130]

Fig. 3.6. XPS curve fitting of the Au4f photoelectron peak for a) Au/C b) Cu_{-0.1V}, 30min-Au/C c) Cu_{+0.015V}, 30min-Au/C d) Cu_{+0.015V}, 90min-Au/C e) Cu_{+0.1V}, 30min-Au/C f) Cu_{+0.3V}, 30min-Au/C.

Fig. 3.7. a) Typical XPS Cu2p photoelectron peak after deconvolution b) XPS Cu2p peak for Cu+0.3V, 30min-Au/C.

A typical Cu2p XPS spectra is shown in Fig. 3.7a. Cu2p_{3/2} BE cannot be used to distinguish between Cu⁺ and Cu⁰ as they are essentially identical. Nevertheless, XPS shows that Cu⁺/Cu and/or Cu²⁺ are present in all samples. Cu2p spectra typically shows 2 major components at BE ~934 eV and ~935 eV, which correspond to Cu⁺ and/or Cu and Cu²⁺ respectively.^[131] In line with XRD results, Cu⁺/Cu are the dominant species. Cu⁺ generally contributes between 60-80 atom% while Cu²⁺ contributes between 40-20 atom% (Table 3.3). As mentioned previously, the presence of CuO is due, in part, to surface oxidation of Cu₂O.

Discrepancy exists between the XRD and XPS analysis of Cu+0.015V, 30min-Au/C. Namely that metallic Cu was the sole species observed in the XRD spectrum but XPS also identified the minor presence of Cu²⁺. A similar inconsistency was reported when comparing the XRD and XPS spectra of Cu₂O nanoplatelets supported on few layer graphene.^[132] Only Cu and Cu₂O diffraction peaks were present in their XRD spectrum. However, both Cu⁺ and Cu²⁺ were identified in the XPS Cu2p spectra, with the latter being dominant. Different natures of both techniques can account for the inconsistencies observed. XPS exclusively probes the outermost layers of nanoparticles while XRD provides phase identification of the sample and determines its average bulk composition. As such, different contents of the same species are observed in XRD and XPS.

XPS also confirmed that Au is the major species on the surface of $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$ (Table 3.3.). Moreover, the atomic proportion of Au on $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$ is about 18% more than the other samples. XPS also evidenced the presence of Cu species in $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$ which were not observed in XRD (Fig. 3.7b). Cu^+ was the sole Cu species observed. As expected, the intensity of its Cu2p peaks were significantly lower than those obtained for other samples. The notably lesser amount of Cu_2O deposited resulted in little to no CuO being observed in the XPS spectra.

3.3.4. Voltammetric characterization of catalysts

Fig. 3.8. Cyclic voltammogram (CV) of Au-C on carbon cloth electrode in 0.1 M NaOH at a scan rate of 50mV/s.

Fig. 3.9. A typical cyclic voltammogram (CV) of Au/C post Cu electro-deposition for 30 mins in 0.1 M NaOH at a scan rate of 50mV/s.

Due to high catalyst loading of $2\text{mg}/\text{cm}^2$, catalytic activity was observed to be more sluggish. In particular, the Au peaks were not observed after Cu electro-deposition likely due to the presence of Cu species on the surface of Au/C.

3.3.5. Catalytic activity for glycerol electro-oxidation

Table 3.4. Glycerol electro-oxidation in alkaline medium using catalysts prepared at different Cu electro-deposition potentials.

Catalyst	Tartronate (%)	Glycerate (%)	Oxalate (%)	Glycolate (%)	Formate (%)	C3 Selectivity (%)
Au/C	7.68	22.06	3.08	43.98	23.20	29.74
$\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$	17.56	28.89	16.00	12.69	24.87	46.45
$\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$	11.93	27.07	8.23	20.73	32.04	39.00
$\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$	14.55	39.03	3.77	17.59	25.06	53.58
$\text{Cu}_{-0.1\text{V}, 30\text{min}}\text{-Au/C}$	12.35	34.73	7.65	20.07	25.21	47.07
$\text{Cu}_{-0.3\text{V}, 30\text{min}}\text{-Au/C}$	7.95	26.86	4.51	25.85	34.83	34.81

Carbon cloth electrodes containing Au/C underwent Cu electro-deposition at various potentials for 30 min. The as-prepared catalysts were then investigated for glycerol electro-oxidation which was carried out at 0.1 V for 2 h in alkaline medium. Table 3.4 evidences that the presence of electro-deposited Cu species improved the innate C3 selectivity (glycerate and tartronate) of Au/C. C3 selectivity of all Cu-Au/C samples were higher than that of pure Au/C. Presence of electro-deposited Cu species increased C3 selectivity while simultaneously suppressing C-C bond breaking, as observed from the significantly lower glycolate selectivity exhibited by the Cu-Au/C samples. Having said that, the type of Cu species present on Au/C does affect the extent to which its C3 selectivity was improved. Highest improvement in C3 selectivity occurred when Cu electro-deposition took place at +0.015 V. $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$ increased C3 selectivity by ~24% relative to Au/C.

C3 selectivity obtained by Cu-0.1V, 30min-Au/C was relatively similar to that of Cu+0.015V, 30min-Au/C selectivity due to their similar Au⁺ content (~10%). As mentioned above, Au⁺ is commonly observed in Au/CeO₂ catalysts. Furthermore, when Au/CeO₂ was applied to CO oxidation,^[133] water-gas shift reaction,^[134] and formaldehyde oxidation,^[135] Au⁺ was identified as the dominant catalytic species as catalysts containing higher amounts of Au⁺ exhibited higher activity. Similarly, we posit that presence of Au⁺ was the main driving force for increased selectivity to glycerate and tartronate. Yet, C3 selectivity of Cu-0.1V, 30min-Au/C was still ~6% lower than that of Cu+0.015V, 30min-Au/C. Slightly elevated C-C bond breakage occurred over the former and resulted in higher selectivity to glycolate and oxalate. As observed from XPS analysis, Cu-0.1V, 30min-Au/C contains ~20% more Cu⁺ species on its surface as compared to Cu+0.015V, 30min-Au/C (Table 3.3). The higher composition of Cu₂O species likely generated a catalyst that favoured C-C bond breaking over deeper oxidation. Additionally, when Cu electro-deposition occurred at -0.1 V, more Cu species were deposited onto Au/C. The slightly thicker Cu coating would have hindered diffusion of the oxidation products away from the catalyst layer, thus leading to slight decrease in C3 selectivity.

C3 selectivity generally decreased when Cu electro-deposition was carried out at applied potentials more positive than +0.015 V. C3 selectivity of Cu+0.1V, 30min-Au/C decreased by about 14% compared to Cu+0.015V, 30min-Au/C due to its comparatively lower Au⁺ content (Table 3.3). Nonetheless, C3 selectivity of Cu+0.1V, 30min-Au/C was still about 10% higher than that of Au/C. Although no Au⁺ was observed in Cu+0.3V, 30min-Au/C, its C3 selectivity was slightly higher than that of Cu+0.1V, 30min-Au/C. This was mainly contributed by an increase in tartronate selectivity. Fig. 5b shows that only Cu₂O was deposited onto Au/C. The Cu₂O species present likely interacted with Au in such a way that deeper oxidation of glycerate to tartronate was favoured. C3 selectivity of Cu-0.3V, 30min-Au/C showed the smallest increment (~5%) relative to Au/C. Correspondingly, Cu-0.3V, 30min-Au/C was the most selective to formate. When Cu electro-

deposition occurred at +0.3 V, the Nernst potential of the reaction was -1.02 V (Table 3.1). The highly negative applied potential provided a very large driving force for CuSO_4 reduction to Cu and likely precluded further oxidation of Cu to Cu_2O . As such, Au^+ was not present in the system. Furthermore, the rapid reduction of Cu^{2+} onto Au/C also means that considerably more Cu was deposited at -0.3 V (Fig. 3.4). The thicker Cu coating on Au/C hindered the diffusion of glycerate and tartronate away from the catalyst layer after being formed. The intermediates thus remained trapped within the catalyst layer and continued to undergo further oxidation until they were released as formate or carbon dioxide. In the same vein, Li and co-workers determined that a thick electrode layer facilitated deeper oxidation of glycerate to tartronate or mesoxalate as the former was held within the confined electrolyte volume for longer periods of time. This was observed when glycerol electro-oxidation was carried out in a direct alcohol alkaline membrane fuel cell.^[100b, 116]

Fig. 3.10. Product selectivity during glycerol electro-oxidation over catalysts prepared at +0.015 V, with different time lengths.

Using +0.015 V as the optimal applied potential, we then investigated how electro-deposition time influenced catalytic selectivity. The catalysts were denoted as $\text{Cu}_{+0.015\text{V}, t_{\text{min}}}\text{-Au/C}$ where t indicates the length of the electro-deposition process. C3 selectivity of the as-prepared catalysts

for glycerol electro-oxidation at +0.1 V is summarized in Fig. 3.11. C3 selectivity increased with increasing deposition time until it reached a maximum at 90 min. $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ achieved C3 selectivity of ~60%, which was double that of Au/C. Herein, $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ doubled selectivity to both glycerate and tartronate whilst C-C bond breakage to glycolate and formate was suppressed to a largest extent. As established previously, presence of Au^+ species generated from Au- Cu_2O interaction is the main contributing factor towards the relatively higher C3 selectivity of this group of catalysts. Importantly, XPS analysis shows that when Cu electro-deposition was extended to 90 min, the proportion of Au^+ present in $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ (27.5%) was almost 3 times higher than that in $\text{Cu}_{+0.015\text{V}, 30\text{min}}\text{-Au/C}$ (9.5%) (Table 3.3). The significantly higher proportion of Au^+ species accounts for the superior C3 selectivity exhibited by $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$. However, when Cu electro-deposition was extended to 120 min, C3 selectivity observed a sharp decrease ~16% relative to $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$. The longer deposition time resulted in more Cu species being deposited onto Au/C. As with $\text{Cu}_{-0.3\text{V}, 30\text{min}}\text{-Au/C}$, a thicker catalyst layer is detrimental for C3 selectivity. Nevertheless, C3 selectivity of $\text{Cu}_{+0.015\text{V}, 120\text{min}}\text{-Au/C}$ was still ~15% higher than that of Au/C. This again evidences the synergistic relationship between Au and Cu and/or Cu_2O .

Fig. 3.11. Comparing C3 selectivity of $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ with that of pure Au/C over a range of potentials.

Finally, we investigated how selectivity of $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ was affected by the applied potential at which glycerol electro-oxidation occurred. Fig. 3.12 shows that C3 selectivity obtained by $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ was higher than that of Au/C across the entire potential range tested. Highest C3 selectivity achieved by $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ was ~60% and this was obtained when glycerol electro-oxidation was carried out at 0 V and 0.1 V. Moreover, at 0 V and 0.1 V, C3 selectivity of $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ was about 1.7 and 2 times higher than that of Au/C respectively. In line with previous reports, C3 selectivity decreased with increasing applied potential.^[91, 100] C-C bond breaking is accelerated at higher potentials and glycerate is converted to glycolate and formate with greater ease. As such, C3 selectivity of $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ decreased when glycerol electro-oxidation occurred at applied potentials higher than 0.1 V. For example, when glycerol electro-oxidation took place at 0.3 V instead of 0.1 V, C3 selectivity obtained by $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ decreased by more than half from ~60% to ~26%.

3.4. Conclusion

Herein, we have demonstrated that electro-deposition of Cu species onto Au/C significantly enhanced C3 selectivity of Au nanoparticles during glycerol electro-oxidation. Cu electro-deposition at -0.1 V and +0.015 V resulted in the most selective catalysts. High selectivity was attributed to the presence of an Au^+ species which was generated as a result of Au interaction with electrodeposited Cu_2O . Extending electro-deposition time to 90 min at +0.015 V, further increased Au^+ content by three times. As such, $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ displayed the highest C3 selectivity amongst all the catalysts investigated. Beyond these optimal conditions, little to no Au^+ species were observed and C3 selectivity decreased. Furthermore, longer deposition times (120 min) and too negative deposition potentials (-0.3 V) were detrimental to catalytic selectivity. Under these conditions, thick Cu and/or Cu oxide layers built up over Au/C and impeded diffusion of intermediates from the catalyst surface after oxidation. Glycerate and

tartrate were thus trapped at the catalyst layer for longer periods of time and C-C bond breaking to glycolate and formate was enhanced.

Chapter 4

Ni modified carbon supported Au nanoparticles as highly selective C3 catalysts for glycerol electro-oxidation

4.1. Introduction

In the previous chapter, we examined the ability of electro-deposited Cu species to influence the selectivity of Au/C catalysts for glycerol electro-oxidation. Au and electro-deposited Cu shared a synergistic relationship such that the resulting catalysts exhibited enhanced C3 selectivities. In particular, an Au^+ species was observed in the most selective catalysts. Au^+ was likely generated as a result of electron transfer between Au and Cu_2O . Given these positive results, we then extended our investigation to the electro-deposited Ni species on the C3 selectivity of carbon black supported Au nanoparticles (Au/C) for glycerol electro-oxidation. Ni was chosen based on reports evidencing the high electro-catalytic activity of pure nickel catalysts for glycerol electro-oxidation under alkaline conditions.^[65, 136] Cyclic voltammetry (CV) studies identified NiOOH as the active catalytic species as glycerol electro-oxidation occurred in tandem with the conversion of $\beta\text{-Ni(OH)}_2$ to NiOOH. Subsequently glycerol was oxidized at the NiOOH surface, while NiOOH was simultaneously reduced and reformed $\beta\text{-Ni(OH)}_2$. However, HPLC analysis of bulk solution revealed that formic acid and glycolate were the major products generated.

4.2. Experimental

4.2.1. Ni electro-deposition process

Au/C was prepared and treated according to the experimental procedure listed in Chapter 3. The electrodes were then immersed in a stock solution containing 50 mM nickel (II) nitrate hexahydrate ($\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and held under constant potential. Following that, the electrodes were rinsed thoroughly in DI water before being cycled 30 times in 0.2 M NaOH solution. The as-prepared electrodes were then tested for glycerol electro-oxidation by placing them in 26

mL of 0.5 M NaOH + 0.5 M glycerol solution and holding under constant potential for 2 h. Subsequently, 1 mL of the solution was collected for high-performance liquid chromatography (HPLC) analysis.

4.3. Results and Discussion

4.3.1. XPS characterization

Fig. 4.1. Typical XPS Ni2p photoelectron peak after deconvolution.

Table 4.1. Relative Au composition of catalysts prepared at different Ni electro-deposition potentials. Elemental concentrations are expressed as atomic percentage (at.%).

Sample	Au4f (element concentration, at. %)		Au/Ni _x O _y atomic ratio (%)
	Au ⁰	Au ⁺	
Ni _{-0.3V,40min} -Au/C	89.95	10.05	7.29/92.71
Ni _{-0.6V,40min} -Au/C	0	100	0.51/99.49
Ni _{-0.8V,40min} -Au/C	0	100	0.37/99.63
Ni _{-1.2V,40min} -Au/C	0	100	0.43/99.57

Table 4.2. Binding energies of Au4f and Ni2p peaks and their corresponding species.

Sample	Au4f (eV)	Ni2p (eV)
Ni _{-0.3V} -Au/C	84.41 (Au ⁰) 85.00 (Au ⁺)	852.58 (Ni ⁰) 853.40 (NiO) 854.30 (NiOOH) 856.77 (Ni(OH) ₂)
Ni _{-0.6V} -Au/C	0	852.70 (Ni ⁰) 853.75 (NiO) 854.70 (NiOOH) 856.00 (Ni(OH) ₂)
Ni _{-0.8V} -Au/C	0	852.60 (Ni ⁰) 854.60 (NiOOH) 856.60 (Ni(OH) ₂)
Ni _{-1.2V} -Au/C	0	852.35 (Ni ⁰) 854.50 (NiOOH) 856.60 (Ni(OH) ₂)

X-ray photoelectron spectroscopy (XPS) was used to analyse surface composition of the samples prepared with different Ni electro-deposition potentials. Each sample was held at the indicated potential for 40 min and the samples are denoted as Ni_{V,40min}-Au/C whereby V represents the applied potential at which Ni electro-deposition took place. Table 4.1 summarizes their respective elemental surface compositions (atom%) while the individual binding energies of the deconvoluted peaks are listed in Table 4.2. All binding energies are referenced to the adventitious C1s line at 284.8 eV.

Fig. 4.1 depicts the typical Ni2p spectra obtained from each sample after deconvolution. Overall, Ni²⁺ reduction to metallic Ni was the dominant electrochemical reaction across the entire applied potential range tested (Table 4.4) In line with this, the Ni⁰ peak at ~852 eV was the dominant peak. Furthermore, additional peaks at ~853 eV, ~854 eV and ~856.02 eV were also identified in the Ni2p spectra. These peaks can be ascribed to the NiO,^[137] Ni(OH)₂,^[138] and NiOOH species^[139] which were generated post electro-deposition, when the carbon cloth electrodes were cycled between -0.8 V to 1.0 V for 30 cycles in 0.2 M NaOH solution. As previously reported, when carbon supported Ni catalysts (Ni/C) were cycled in alkaline media,

surface oxidation of Ni/C occurs in two or more steps as illustrated by the following equations:^[136b, 140]

1) Ni⁰ is first oxidized to α -Ni(OH)₂ at lower potentials ($-0.61 \leq E \leq -0.11$ V vs. Ag/AgCl):

2) At higher potentials ($-0.11 \leq E \leq 0.79$ V vs. Ag/AgCl), α -Ni(OH)₂ is converted to β -Ni(OH)₂ which is the less hydrated, more stable and thermodynamically favored Ni hydroxide species.

3) When $E > 0.79$ V vs. Ag/AgCl, β -Ni(OH)₂ is further oxidized to the β -NiOOH

Fig. 4.2. XPS spectra of Au4f in (a) Ni-0.3V, 40min-Au/C (b) Ni-0.6V, 40min-Au/C (c) Ni-0.8V, 40min-Au/C (d) Ni-1.2V, 40min-Au/C.

Fig. 4.2 shows the Au4f XPS spectra of the 4 samples. Au4f spectra of Ni_{-0.3V, 40min}-Au/C was fitted well to double groups of peaks, corresponding to Au4f_{7/2} and Au4f_{5/2}. Additionally, its Au4f_{7/2} peak consisted of 2 components at 84.41 and 85.0 eV, which correspond to Au⁰ (89.95%) and Au⁺ (10.05%) respectively. Au⁺ was generated when electron transfer occurred between Au nanoparticles and the highly oxidized NiOOH species.^[129, 141] In contrast, the characteristic doublet peak pattern of Au4f was not observed in the spectra of Ni_{-0.6V, 40min}-Au/C, Ni_{-0.8V, 40min}-Au/C and Ni_{-1.2V, 40min}-Au/C. Instead, these 3 samples only exhibited one broad, low intensity peak centred around 85 eV. When Ni electro-deposition occurred at applied potentials more negative than -0.3 V, large amounts of Ni and Ni (hydro)oxide species were deposited onto Au/C. The thick Ni layer in turn obscured detection of Au during XPS analysis. Similarly, the C1s peaks of Ni_{-0.6V, 40min}-Au/C, Ni_{-0.8V, 40min}-Au/C and Ni_{-1.2V, 40min}-Au/C (Fig. 4.3) could not be observed as well. These results indicate that the surface of the Ni_{-0.6V, 40min}-Au/C, Ni_{-0.8V, 40min}-Au/C and Ni_{-1.2V, 40min}-Au/C are composed mainly of Ni species and little to no Au is exposed.

Fig. 4.3. C1s spectra obtained after Ni electro-deposition was carried out at (a) -0.3V (b) -0.6V (c) -0.8V (d) -1.2V.

4.3.2. TEM characterization

Fig. 4.4. TEM images obtained from (a) Au/C (b) Ni-0.3V, 40min-Au/C (c) Ni-0.6V, 40min-Au/C (d) Ni-1.2V, 40min-Au/C.

Fig. 4.4 shows the TEM images obtained from pure Au/C, Ni-0.3V, 40min-Au/C, Ni-0.6V, 40min-Au/C and Ni-1.2V, 40min-Au/C. Pure Au/C consisted of spherical particles which are well dispersed on the C support (Fig. 4.4a). An analysis of 200 particles determined that the Au nanoparticles exhibited a narrow size distribution centred around 3 nm. Au nanoparticles continued to maintain their spherical shape even after undergoing Ni electro-deposition. Interestingly, thin crumpled Ni oxide sheets were observed in the TEM images of Ni-0.6V, 40min-Au/C and Ni-1.2V, 40min-Au/C (Fig. 4.4c and d), with the latter possessing a significantly greater quantity of these sheet like structures. Furthermore, the carbon support cannot be clearly seen in the TEM image

of Ni-1.2V, 40min-Au/C, which thus indicates that an extremely thick Ni layer was deposited onto Au/C when the applied potential was -1.2 V. This observation is further confirmed by the fact that the C1s XPS peak of Ni-1.2V, 40min-Au/C was not detected during measurement (Fig. 4.3d). Ni(OH)₂ sheet like structures possessing rough and wrinkled surface features were previously synthesized when Ni electro-deposition was carried out over zinc oxide nanorods (ZnO).^[142]

4.4. Catalytic activity for glycerol electro-oxidation

Fig. 4.5. Product and C3 selectivity achieved when glycerol electro-oxidation was carried out over (a) Au/C (b) Ni-0.3V, 40min-Au/C (c) Ni-0.6V, 40min-Au/C (d) Ni-0.8V, 40min-Au/C (e) Ni-1.2V, 40min-Au/C.

Carbon cloth electrodes containing Au/C underwent Ni electro-deposition at various applied potentials for 40 min. The as-prepared catalysts were then investigated for glycerol electro-oxidation, which was carried out at +0.3 V for 2 hours in 0.5 M glycerol + 0.5 M NaOH solution. Fig. 4.5 shows the relative product distribution and overall C3 selectivity obtained by each catalyst. Highest improvement in C3 selectivity occurred when Ni electro-deposition took place at -0.3 V. C3 selectivity achieved by Ni-0.3V, 40min-Au/C (~45%) was about twice as high as that of pure Au/C (~23%). Ni-0.3V, 40min-Au/C enabled enhanced conversion to glycerate and tartronate whilst simultaneously suppressing formate production. Au⁺ species present in Ni-0.3V, 40min-Au/C likely contributed to its enhanced C3 selectivity. In the same vein, Au⁺ species are

commonly generated in CeO₂ supported Au nanoparticles (Au/CeO₂). Furthermore, Au⁺ was determined to be the active species in these catalyst. When Au/CeO₂ was applied to CO oxidation^[133], water-gas shift^[134] and formaldehyde oxidation^[135a] reactions, catalysts with higher Au⁺ content gave rise to higher activity. The presence of a relatively thin Ni layer also facilitated ease of diffusion of the oxidation products away from the catalyst layer and thus limited the extent of over-oxidation.^[100b, 116] In contrast, when Ni electro-deposition occurred at applied potentials more negative than -0.3 V, C3 selectivity of the resulting catalysts experienced a marked decrease relative to Ni_{-0.3V, 40min}-Au/C. C3 selectivity attained by Ni_{-0.6V, 40min}-Au/C, Ni_{-0.8V, 40min}-Au/C and Ni_{-1.2V, 40min}-Au/C ranged between 23-26% which is relatively similar to that obtained by pure Au/C (Fig. 4.5). The poorer C3 selectivity exhibited by this group of catalysts is due to their significantly higher Ni surface coverage, which in turn shielded the active Au species from the reactant media and severely limited their activity. On the other hand, the highly oxidized NiOOH was previously identified as the active species when carbon supported nickel nanoparticle catalysts (Ni/C) were tested for glycerol,^[136c, 136d] sugar^[143] and alcohol^[144] (methanol and ethanol) electro-oxidation in alkaline media. However, in our system, it is apparent that the NiOOH catalytic sites were significantly less active than the catalytic sites present on Au nanoparticles. The thicker Ni surface coverage also hindered diffusion of the oxidation products away from the catalyst layer and thus encouraged over-oxidation to C1 and C2 side products.

Fig. 4.6. Product and C3 selectivity achieved when glycerol electro-oxidation was carried out (a) Au/C (b) Ni_{-0.3V, 5min}-Au/C (c) Ni_{-0.3V, 20min}-Au/C (d) Ni_{-0.3V, 40min}-Au/C (e) Ni_{-0.3V, 80min}-Au/C.

Using -0.3 V as the optimal applied potential, deposition time was then varied between 5 and 80 min to determine its effect on the C3 selectivity. The resulting catalysts are denoted as Ni_{-0.3V, tmin}-Au/C where t represents the length of time which electro-deposition was carried out for. C3 selectivity with increased with increasing deposition time until it reached a maximum of 45% after Ni electro-deposition occurred for 40 min (Fig. 4.6). However, when Ni electro-deposition was carried out for an additional 40 min, C3 selectivity of Ni_{-0.3V, 80min}-Au/C decreased slightly to 39%. The longer electro-deposition time resulted in a thicker Ni layer on Au/C which was detrimental to C3 selectivity. Nonetheless, C3 selectivity of Au/C improved post Ni deposition and this is indicative of the synergistic effect between Au and the electro-deposited Ni species.

Table 4.3. Comparing C3 selectivity obtained from Au/C and Ni_{-0.3V, 40min}-Au/C when glycerol electro-oxidation was carried out at different applied potentials.

Applied Potential (V)	Sample	Product Selectivity (%)					C ₃ /(C ₂ +C ₁) selectivity (%)
		Tartronate (%)	Glycerate (%)	Oxalate (%)	Glycolate (%)	Formate	
0.1	Au/C	6.33	20.36	6.36	28.66	38.29	36.41
	Ni _{-0.3V, 40min} -Au/C	15.87	27.88	4.20	35.23	16.82	77.78
0.2	Au/C	4.20	16.84	5.52	33.34	40.11	26.65
	Ni _{-0.3V, 40min} -Au/C	7.97	25.49	2.85	25.36	38.34	50.28
0.3	Au/C	2.72	15.87	3.27	43.12	35.02	22.84
	Ni _{-0.3V, 40min} -Au/C	7.82	23.15	2.36	41.04	25.63	44.86
0.4	Au/C	1.55	14.36	2.10	43.84	38.16	18.92
	Ni _{-0.3V, 40min} -Au/C	6.05	17.51	2.36	42.91	31.17	30.82

Fig. 4.7. Comparing the C3 selectivity of Ni_{-0.3V, 40min}-Au/C with that of pure Au/C over a range of potentials.

Lastly, C3 selectivity of Ni_{-0.3V, 40min}-Au/C was determined when glycerol electro-oxidation was carried out at different applied potentials. Table 4.3 lists the product distribution and C3 selectivity obtained by Au/C and Ni_{-0.3V, 40min}-Au/C at each applied potential tested. In general, selectivity decreased with increasing applied potential due to accelerated C-C bond cleavage

at higher potentials (Fig. 4.7). Nevertheless, C3 selectivity of Ni-0.3V, 40min-Au/C was higher than that of Au/C across the entire potential range tested. C3 selectivity of Ni-0.3V, 40min-Au/C was highest when glycerol oxidation was carried out at 0.1 V. At this potential, C3 selectivity of Ni-0.3V, 40min-Au/C was 78% and was about twice as high as that obtained by Au/C (36.41%). Notably, C3 selectivity obtained by Ni-0.3V, 40min-Au/C continued to be twice as high as that of Au/C over the entire potential range tested (Table 4.3).

4.5. Conclusion

Electro-deposition of Ni species onto Au/C enhanced its C3 selectivity for glycerol electro-oxidation. Optimal C3 selectivity was obtained when Ni electro-deposition was carried out for 40 min at -0.3 V. Au⁺ species generated under these conditions likely contributed to the higher selectivity of this catalyst. Furthermore, at this potential, the Ni layer derived was sufficiently thin such that the oxidation products could easily diffuse away from the catalyst layer after being generated. In contrast, when Ni electro-deposition occurred at applied potentials more negative than -0.3V, significantly larger amounts of Ni were deposited onto Au/C. The thicker Ni surface coverage partially shielded the Au nanoparticles from the glycerol solution and thus severely limited their activity. C3 selectivity of the Ni-Au/C catalysts prepared under these conditions were relatively similar to that of pure Au/C. Any possible synergistic effect between Au and Ni was thus nullified by the thick Ni surface coverage.

Chapter 5

Ag containing porous Au structures as highly selective catalysts for glycolate and formate

5.1. Introduction

Formic acid is an important chemical feedstock that is mostly used as a synthetic precursor or as a commercial product in the leather, agriculture and dye industries.^[145] Formic acid is also a potential starting material for hydrogen production and also has the potential to power fuel cells to generate electricity.^[146] Currently, formic acid is produced from toxic carbon monoxide and water through the carbonylation of NaOH at elevated pressures and temperatures. Production of formic acid from glycerol thus represents an environmentally friendly and cost efficient way to generate formic acid.

A small number of studies have demonstrated that silver (Ag) facilitates C-C bond breaking of glycerol and favours the formation of formic acid. When glycerol electro-oxidation was carried out over polycrystalline Ag electrode in alkaline medium, glycerate, glycolate and formate were the main products.^[147] However, glycerol oxidation was hindered at electrode potentials higher than 1.13 V vs RHE after the first monolayer of Ag₂O forms on the electrode surface. Surface Ag₂O prevents adsorption of glycerol and OH⁻ species and thus the subsequent oxidation of glycerol.

In comparison, Tremiliosi-Filho and co-workers carried out glycerol electro-oxidation over carbon supported AuAg alloys (AuAg/C) in alkaline medium.^[115a, 148] FTIR studies confirmed that C-C-C bond breaking was favoured and formate was formed selectively. Notably, AuAg/C exhibited an onset potential that was 120 mV lower than that of Au/C. Improved electrochemical activity was attributed to the ligand effect as presence of Ag altered the electronic properties of Au by reducing the Au density of states close to the Fermi level. This in turn tuned the adsorption strength of adsorbates on the Au surface and thus increased energy

efficiency during catalysis. On the other hand, current density obtained by AuAg/C during glycerol electro-oxidation was nearly 10 times lower than that of Au/C. This is due to the segregation of Ag on the surface of the alloys which reduced the amount of available Au for catalysis. In fact, Ag/C nanoparticles were independently shown to be very poor catalysts for promoting glycerol oxidation while Au was the active species in the alloy that dictated the rate of reaction. Hence, in order to take advantage of high formic acid selectivity that Au-Ag based catalysts afford whilst maintaining high catalytic and electrochemical activity, it is important to design Ag containing catalysts which possess Au rich surfaces.

In this chapter, we examined the ability of Ag containing, porous Au structures to tune the glycerol oxidation pathway towards formate and glycolate whilst maintaining high electrocatalytic activity. 3D porous Au structures were obtained by etching alloyed AuAg sheets in concentrated nitric acid solution. However, dealloying did not completely remove Ag and residual amounts remained embedded within the 3D framework. Our catalyst thus consisted of a porous Au rich framework that possessed residual amounts of Ag within its pores. When tested for glycerol oxidation, the Ag containing porous Au catalyst exhibited high selectivity towards formate as well as high electrochemical activity. Catalytic performance of surface Ag rich porous structures was also examined. Surface Ag content was altered by annealing the porous Au structures at various temperatures. Annealing caused residual Ag to diffuse and precipitate onto the surface of the framework and the porous structures became increasingly Ag rich as annealing temperatures increased. Surface Ag rich structures exhibited significantly poorer electrochemical activity compared to surface Au rich structures however selectivity to formate improved.

5.2. Experimental

5.2.1. Materials

Alloyed silver-gold (AuAg) sheets were purchased from Changhong Metals Ptd Ltd, China. The sheets were 0.1 mm thick, with both gold and silver possessing 99.99% purity. 1g of alloy was composed of 42 wt% Au and 58 wt% Ag.

All electrochemical reactions were conducted in a three electrode cell which comprised of a stainless steel working electrode, Pt wire counter electrode and Ag/AgCl reference electrode. All potentials are reported with respect to the Ag/AgCl reference electrode.

5.2.2. Methods

5.2.2.1. Preparation of Au porous structures

The etching process consisted of floating the AuAg sheets (~0.5 cm x 1 cm) in concentrated nitric acid (69%) for a given amount of time. The sheets were then removed from the nitric acid solution (HNO_3) and thoroughly rinsed with DI water before oven drying at 80 °C for 30 min.

Following this, the dealloyed sheets were annealed for 2 h under argon atmosphere at a prescribed temperature. The as prepared catalysts were then tested for glycerol electro-oxidation by placing them in 15 ml of 0.5 M NaOH + 0.5 M glycerol solution under constant potential for 2 h. Subsequently, 2 mL of the solution was collected for high-performance liquid chromatography (HPLC) analysis.

5.2.2.2. Preparation of Ag/C reference catalyst

Ag/C was prepared via direct electro-deposition of Ag onto carbon cloth electrode (1.5 cm x 1.5 cm). The carbon cloth electrodes were immersed into stock solution containing 50 mM AgNO_3 dissolved in 1 M NH_4OH (28% NH_3 in H_2O). Ag electro-deposition was carried out at -0.2 V for 30 min. Following which the electrodes were rinsed thoroughly with water and tested for glycerol oxidation under the conditions mentioned above.

5.3. Results and discussion

5.3.1. Effect of catalyst pre-treatment and etching time on morphology

The most common way to generate porous structures with different porosities is to vary etching time.^[149] Etching usually occurs by simply soaking the AuAg sheets in concentrated HNO₃ solution. However, long etching times result in coarsened structures due to fast diffusion of gold in the electrolyte. Hence, in order to fabricate porous Au structures with ligament sizes less than 6 nm, AuAg sheets are etched in concentrated HNO₃ under applied anodic potential.^[150] Erlebacher and co-workers report that Ag is completely removed from the alloyed sheet after etching for 5 mins and the resulting framework contains pores centred around 8 nm. Furthermore, 15 mins of etching generated 15-20 nm sized pores while continued immersion caused the porosity length scale to approach the thickness of their original membrane (about 100 nm).^[149a] However, longer immersion times led to significant coarsening and the eventual collapse of the 3D structure into a 2D one. The porous framework also became more brittle. Alternatively, porous Au structures with varying porosities can be attained by annealing the sheets under argon atmosphere after etching.^[151] Li and Sieradzki reported that heating the dealloyed samples between 100-900 °C resulted in a more than 2 orders of magnitude spread in the length scales of the microstructures. Furthermore, some studies also report heat treating the AuAg sheets before dealloying so as to relieve the sheets of residual stresses that may have developed during the cutting operation.^[151b, 152]

Given the different treatment methods reported in the literature, preliminary studies were conducted in order to determine the effect of treatment method on the morphology of the resulting porous structures. Influence of heat treatment prior to the etching process was examined by annealing the samples either at 800 °C for 2 h or at 900 °C for 12 h under argon atmosphere. Following this, the AuAg sheets were then etched in concentrated HNO₃ for either 5 or 60 mins to further examine if there was any effect of etching time on morphology and

catalytic performance. The resultant catalysts were then dried and tested for glycerol electro-oxidation. FESEM images of the spent catalysts which were subjected to the treatment methods described above are shown in Fig. 5.1. The typical random porous 3D structure is observed in all the samples. As such, annealing the AuAg sheets prior to etching does not have a significant effect on the resultant morphology. Fig. 5.2a and c show the samples which were dealloyed for 5 min but annealed prior at 800 °C for 2 h and 900 °C for 12 h respectively. Both samples contained pores which were up to 4 nm in length. Pore size increased with etching time. The extent of increase was also influenced by annealing conditions. Pores were mainly between 10-20 nm when the samples were annealed at 800 °C for 2 h followed by etching for 60 min (Fig. 5.2b). On the other hand, when the AuAg sheets were pre-heated at 900 °C for 12 h before being etched for 60 min, the resulting sample consisted of interconnected, elongated pores which were tens of nm in length, with some pores reaching up to 100 nm. However, long etching times in both cases caused the samples to become extremely brittle and fragmented easily upon handling. Hence, tuning porosity by varying etching time and is not a feasible way to generate samples that can be easily handled for catalytic testing.

Fig. 5.1. FESEM images of porous Au samples annealed at 900 °C for 12 h before dealloying for 60 min.

Fig. 5.2. FESEM images of porous Au samples that were heat treated at 800 °C for 2 h before dealloying for a) 5 min b) 60 min. FESEM images of porous Au samples that were heat treated at 900 °C for 2 h before dealloying for c) 5 min d) 60 min.

5.3.2. Effect of etching-annealing method on morphology and catalytic performance

Next, we attempted to vary porosity using the etching – annealing method. Etching time was initially kept at 5 min and subsequent annealing took place at either 100 °C or 600 °C for 2 h, under argon atmosphere. The as-prepared samples were then tested for glycerol electro-oxidation. Fig. 5.3 shows the FESEM images of spent catalysts prepared under the conditions described above. The silver coloured AuAg alloyed sheets became copper coloured after floating in concentrated HNO_3 solution. As observed in fig 5.3b, 5 min of dealloying followed by annealing at 100 °C for 2 h generated pores in the range of 20-30 nm. In comparison, the

samples which were only etched for 5 min possessed pores that reached a maximum of 4 nm. Elevating annealing temperature to 600 °C caused extensive morphological changes in the sample. The 3D random porous structure that was observed in all the previous samples was noticeably absent. Instead of being perforated with numerous small pores, the surface of 3D structure was largely flat but divided by deep gorges and a few large pores. (Fig. 5.4). This was likely due to extensive fusion of the Au ligaments during heating at such high temperatures. Pores generated at 600 °C were significantly larger than those generated at 100 °C; the 4 pores featured in fig 5.3c range between 300-450 nm. On another note, samples prepared by this etching-annealing method became more ductile instead of brittle after treatment. Consequently, the sheets did not easily fragment even when handled with tweezers. Given the ease of product handling and the ease of generating samples with varying porosity, we carried out further variations of this method in order to optimize our results.

Fig. 5.3. FESEM images of the porous Au structure that was etched for 5 min followed by heating at a-b) 100 °C and c-d) 600 °C.

Fig. 5.4. FESEM image evidencing the deep gorge present in the sample that was prepared by etched for 5 min followed by annealing at 600 °C for 2 h.

Subsequently, etching was carried out for 15 min followed by annealing at 100 °C or 600 °C. These catalysts were then tested for glycerol electro-oxidation and their catalytic performance was compared vis-à-vis samples that were dealloyed for 5 min but annealed at the same temperature. FESEM results of catalysts prepared under these conditions are presented and discussed below. The samples are labelled with the general formula Au(t)_tempt where t indicates the etching time and tempt represents the annealing temperature.

HPLC studies show that formic acid was the dominant product generated in all cases (Fig. 5.5). Given that catalysts prepared under different annealing conditions have distinctly different morphologies, these results are indicative that product selectivity is not controlled by the morphology or porosity. Notably, increasing annealing temperature from 100 °C to 600 °C resulted in almost 100% conversion to glycolic acid and formic acid. On the other hand, electrochemical activity was strongly influenced by annealing temperature and thus catalyst morphology. Samples which were annealed at 100 °C exhibited markedly higher electrochemical activities compared to those annealed at 600 °C. For example, the glycerol oxidation current obtained by Au15_100 (53.2 mA) was nearly 10 times higher than that generated by Au15_600 (5.53 mA). Furthermore, samples which were etched for 15 min were generally more active than those which were only etched for 5 min. Taken together, these 2 results indicate that glycerol electro-oxidation activity is dependent on Au content and surface area of exposed Au. Samples with higher Au content (longer etching time) and greater exposed Au surface area (lower annealing temperature) are more active for glycerol electro-oxidation. Hence for our subsequent investigations, we fixed etching time at 15 min whilst varying annealing temperature to further optimize our results.

Fig. 5.5. Product selectivity of samples which were a) dealloyed for 5 min, annealed at 100 °C b) dealloyed for 15 min, annealed at 100 °C c) dealloyed for 5 min, annealed at 600 °C d) dealloyed for 5 min, annealed at 600 °C.

Fig. 5.6. Chronoamperograms of samples which were a) dealloyed for 5 min, annealed at 100 °C b) dealloyed for 15 min, annealed at 100 °C c) dealloyed for 5 min, annealed at 600 °C d) dealloyed for 5 min, annealed at 600 °C.

5.3.3. Effect of annealing temperature on morphology

For the samples discussed herein, etching time was fixed at 15 min whilst annealing temperature was varied between 100-900 °C to further investigate the effect of annealing temperature on catalytic performance. Annealing was carried out for 2 h under argon atmosphere. FESEM images of freshly prepared catalysts are presented in Fig. 5.7.

3D random porous structure was generated after 15 min of etching and most pores fall in the range of 10-20 nm (Fig. 5.7a). After etching the initially silver coloured AuAg sheets became copper coloured and this is in line with the observations made by Erlebacher and co-workers.^[149a] There were no significant changes in pore size when the sample was annealed at 100 °C and pores remained in the range of 10-20 nm (Fig. 5.7b). Further increasing annealing temperature to 300 °C caused pore size to increase significantly and most pores were few hundreds of nm in length. Additionally, small, well dispersed particles were observed on the surface of the porous framework (Fig. 5.7c, indicated by red arrows). The copper coloured dealloyed sheets reverted back to being silver coloured after annealing occurred at 600 °C and 900 °C. FESEM shows that annealing at 600 °C caused extensive fusion of the Au ligaments in the porous framework (Fig. 5.7f). The sample appeared to be devoid of the 3D random porous architecture observed in the 15 min dealloyed sample (Fig. 5.7a). Instead, it consisted of very large Au ligaments with pores in the micrometre length scale (Fig. 5.1e). Notably, the 3D structure was maintained even after annealing at such high temperatures. Similar to the 600 °C annealed sample, the surface of the 900 °C annealed sample was also covered with numerous, well dispersed particles (Fig. 5.7). The nature of these particles are subsequently determined with EDX and XPS. On the other hand, both the pure AuAg sheet and the sample annealed at 900 °C exhibited poor conductivity and we were unable to properly image the samples using FESEM. High temperature heating at 900 °C likely caused extensive melting of the Ag containing porous Au sheets and realloying of Au with residual Ag.

Fig. 5.7. FESEM images of the samples obtained after etching for 15 min in concentrated nitric acid and subsequent annealing at a) no annealing b) 100 °C c-d) 300 °C e-f) 600 °C.

5.3.4. EDX and XPS Analysis

Energy dispersive x-ray spectroscopy (EDX) was used to analyze the bulk composition of the spent catalyst. Table 5.1 to 5.4 and their corresponding SEM figures present the average Ag and Au atomic and mass ratios for each sample. The samples are notated in the form Au(t)_tempt, where t represents the dealloying time in mins and tempt represents the annealing temperature in degrees celsius.

1 g of the as purchased AuAg alloy consisted of 42.0 wt% Au and 58.0 wt% Ag, as specified by the manufacturer. Au content increased significantly after the AuAg sheet was etched for 15 min in concentrated HNO₃. EDX shows that relative mass of Au increased to 92.9% in Au15 while Ag mass content decreased to 7.06% (Table 5.1). However, annealing caused Ag content to increase relative to Au even though Au was still the dominant species in the catalyst. Mass of Ag increased to 14.81% after annealing at 100 °C while mass of Au decreased slightly to 85.19% (Table 5.2). When annealing temperature increased to 600 °C, relative mass of Ag doubled by 2.5 times and reached 37.47%. Consequently, relative Au mass decreased to 62.53%.

X-ray photoelectron spectroscopy (XPS) was utilized to analyse surface composition of the catalysts prepared under different conditions. Fig. 5.12 presents the deconvoluted Ag and Au peaks for the respective samples. All binding energies were referenced to the adventitious C1s line at 284.8 eV. Au4f_{7/2} peak for all 5 samples, including the AuAg alloy, could be deconvoluted into 2 peaks located at binding energy (BE) of 84.0 eV and 84.8 eV. These 2 peaks are assigned to Au(0) and Au(I) species respectively. On the other hand, the Ag 3d_{5/2} peak for is located at 368.2 eV for all the samples and this is typical of pure metallic Ag(0) species. Additionally, an oxidized Ag(I) species was generated after the annealing process and an additional peak around 368.8 eV was observed in Au15_100, Au15_300 and Au15_600 (Fig. 6.12 e, g and i respectively). Ag(I) elemental concentration was between 10-14% in the 3

samples (Table 5.5). Presence of Ag(I) is attributed to the adsorption of O atoms on undercoordinated surface Ag atoms when the samples were exposed to air.^[153] Oxidation of Ag(0) to Ag(I) did not occur during annealing due to the low thermal stability of Ag₂O, which thermally reduces back to Ag(0) at high temperatures.^[154] Furthermore, annealing was carried out under argon gas which precludes the oxidation of Ag.

More importantly, our XPS and EDX results are in agreement with each other. XPS also shows that the sample surface becomes more Ag rich as annealing temperature increases. Table 5.5 summarizes the respective elemental surface compositions (atom%) of each sample. Ag/Au atomic ratio of the AuAg alloy was 1.92. After etching, the Ag/Au atomic ratio for Au15 decreased significantly to 0.26. Thus, Au15 is composed of an Au rich surface, with small amounts of residual Ag. However, Ag/Au atomic ratio of the annealed samples increased with increasing annealing temperature. Ag/Au atomic ratio of Au15_100 increased slightly to 0.51 while the atomic ratio for Au15_600 was 1.68. This indicates that Au15_100 still possessed a relatively Au rich surface even though some amounts of Ag had deposited onto the sample surface during low temperature annealing. In comparison, Au15_600 was overwhelmingly Ag rich and its Ag/Au atomic ratio was relatively close to that of AuAg alloy.

Taken together, our EDX and XPS results evidence that residual Ag which was initially embedded within the porous structure melted during annealing and precipitated onto the surface of the porous framework. As annealing temperature increased, more Ag precipitated onto the surface of the framework and resulted in higher Ag/Au atomic ratios.

Fig. 5.8. SEM-EDX obtained from 5 different areas on Au15.

Table 5.1. Mass (%) and atomic (%) ratios of Au15.

Au15	Mass (%)		Atom (%)	
	Ag L	Au M	Ag L	Au M
1	7.32	92.68	12.60	87.40
2	10.34	89.66	17.40	82.60
3	7.05	92.95	12.16	87.84
4	3.93	96.07	6.95	93.05
5	6.64	93.36	11.50	88.50
Average	7.06	92.94	12.12	87.88

Fig. 5.9. SEM-EDX for Au15_100.

Table 5.2. Mass (%) and atomic (%) ratios of Au15_100.

Au15_100	Mass (%)		Atom (%)	
	Ag L	Au M	Ag L	Au M
1	16.51	83.49	26.53	73.47
2	13.90	86.10	22.76	77.24
3	16.26	83.74	26.18	73.82
4	15.46	84.54	25.03	74.97
5	11.90	88.10	19.78	80.22
Average	14.81	85.19	24.06	75.94

Fig. 5.10. SEM-EDX for Au15_300.

Table 5.3. Mass (%) and atomic (%) ratios of Au15_300.

Au15_300	Mass (%)		Atom (%)	
	Ag L	Au M	Ag L	Au M
1	23.45	76.55	35.87	64.13
2	24.60	75.40	37.34	62.66
3	19.11	80.89	30.13	69.87
4	25.58	74.42	38.56	61.44
5	22.62	77.38	34.81	65.19
Average	23.07	76.93	35.34	64.66

Fig. 5.11. SEM-EDX for Au15_600.

Table 5.4. Mass (%) and atomic (%) ratios of Au15_600.

Au15_600	Mass (%)		Atom (%)	
	Ag L	Au M	Ag L	Au M
1	40.17	59.83	55.07	44.93
2	39.04	60.96	53.90	46.10
3	30.42	69.58	44.39	55.61
4	41.20	58.80	56.13	43.87
5	36.51	63.49	51.22	48.78
Average	37.47	62.53	52.14	47.86

Fig. 5.12. XPS data. Ag 3d_{5/2} spectra for a) AuAg c) Au15 e) Au15_100 g) Au15_300 i) Au15_600; Au 4f_{7/2} spectra for b) AuAg d) Au15 f) Au15_100 h) Au15_300 j) Au15_600.

Table 5.5. Relative Au and Ag concentrations for samples prepared under different conditions. Elemental concentrations are expressed as atomic percentage (at.%).

Sample	Ag (element concentration, at. %)		Au (element concentration, at. %)		Ag/Au atomic ratio (%)
	Ag ⁰	Ag ⁺	Au ⁰	Au ⁺	
AuAg	100	0	90.46	9.54	1.92
Au15	100	0	92.46	7.54	0.26
Au15_100	86.20	13.80	87.93	12.07	0.51
Au15_300	90.41	9.59	88.59	11.41	1.07
Au15_600	90.06	9.94	94.49	5.51	1.68

5.3.5. Voltammetric characterization of porous Au-Ag alloys

Fig. 5.13. CV obtained when the AuAg alloyed sheet was cycled in 1 M NaOH.

Fig. 5.14. CV obtained after the AuAg sheet was etched for 15 min. The sample was cycled in 1 M NaOH.

Characteristic voltammetric behaviour of the AuAg sheet when cycled in 1 M NaOH is presented in Fig. 6.8. Shape of the cyclic voltammogram (CV) generated by the AuAg sheet is similar to that reported for polycrystalline Ag electrodes^[147] or supported Ag nanoparticles^[155] when cycled under alkaline conditions. Three anodic peaks are observed at 0.22 V (a1), 0.32 V (a2) and 0.42 V (a3) vs Ag/AgCl. Peak a1 is associated with Ag dissolution and the formation of a surface monolayer of Ag₂O films while a2 and a3 are attributed to bulk phase formation of AgOH and Ag₂O respectively.^[156]

Surface oxidation of the Ag from Ag(0) to Ag(I) (peak a2) and the reduction of Ag₂O to Ag(0) (c2) coincides with the redox peaks of polycrystalline Au electrode. When polycrystalline Au electrode is cycled in alkaline media, it generates a pair of redox peaks at 0.3 V and 0.08 V (vs. SCE). The former peak is associated with surface oxidation of Au(0) to Au(I) oxides during the anodic scan while the latter peak is associated with the subsequent reduction of Au(I) back to Au(0) during the cathodic scan. It is likely that the redox peaks associated with the oxidation and reduction of Au were shielded by the redox peaks of Ag species as they possessed higher peak currents. Hence, redox peaks typically associated with polycrystalline Au electrodes cannot be clearly distinguished from the Ag redox peaks in the CV.^[157]

Selective dissolution of Ag resulted in great changes in the CV profile, even though the etching time was only 15 min (Fig. 6.9). Shape of the CV obtained for the 15 min dealloyed sample resembles that of the polycrystalline Au electrode.^[157]

5.3.6. Catalytic activity for glycerol electro-oxidation

Fig. 5.15. Glycerol electro-oxidation in alkaline medium using catalysts prepared at different conditions.

Table 5.6. Total concentration of oxidation products obtained for the different catalysts.

Sample	Total concentration of products (mM)
AuAg	7.12
Au15	44.53
Au15_100	74.48
Au15_300	25.29
Au15_600	8.59

As-prepared Ag containing porous Au structures were tested for glycerol electro-oxidation. Fig. 5.15 shows the product selectivity obtained by the respective catalysts when glycerol electro-oxidation was carried out in 15 ml of 0.5 M glycerol + 0.5 M NaOH solution at 0.1 V for 2 h. Formate and glycolate were the dominant products generated in all cases despite significant differences in catalysts morphologies. This is indicative that product distribution and selectivity are not controlled by catalyst morphology. Instead, amount of surface Ag drives changes in product distribution and catalytic activity.

AuAg alloyed sheet was highly selective to formate and glycolate, with product selectivity being 59.31% and 34.72% respectively. Correspondingly, AuAg was poorly selective to

glycerate (4.8% selectivity) and oxalate (1.2% selectivity) while no tartronate was observed in the HPLC chromatograms. Product distribution achieved by AuAg was similar to that of polycrystalline Ag electrode, which also produced glycerate, glycolate and formate as the main products under alkaline conditions.^[147] However, electrochemical activity of AuAg was extremely poor and current attained at the end of the 2 h run was only 1.4 mA (Fig. 5.17e). Dealloying AuAg for 15 min resulted in a 23% increase in selectivity to oxalate. Glycerate selectivity also increased marginally to 8.5% and 4.7% selectivity to tartronate was obtained. However, glycolate and formate selectivity decreased 13% and 18% vis-à-vis AuAg and this decrease corresponds to a significant increase in Au content in Au15 (Table 5.1 and 5.5). As established earlier, Ag is selective towards C-C bond breaking of glycerol and its reduced content in Au15 resulted in poorer selectivity to glycolate and formate compared to AuAg. Nevertheless, presence of residual Ag embedded within the catalyst layer still managed to exert a significant control over the reaction pathway and relatively high selectivity to formate and glycolate could still be achieved. Additionally, electrochemical activity was significantly enhanced after etching and current increased to 42 mA (Fig. 5.17b). This is due to the Au rich nature of Au15 whereby surface content of Au is roughly 7.5 times more than that of AuAg. In line with this, glycerol conversion also increased in tandem and total product concentration obtained by Au15 was around 6 times higher than that of AuAg (Table 5.6).

Annealing Au15 at increasing temperatures from 100 °C to 600 °C led to a gradual increase in glycolate and formate selectivity and a corresponding decrease in glycerate, tartronate and oxalate selectivity. Au15_100 achieved 48.38% and 29.59% selectivity to formate and glycolate respectively and this represents an 8% increase relative to Au15 for both products (Fig. 5.15). Concentration of products attained by Au15_100 was also 1.7 times higher than that of Au15 (Table 5.6). Improved product conversion was due to the rearrangement of Au and Ag atoms on the catalyst surface during annealing. Ag/Au atomic ratio of Au15 and

Au15_100 is 0.26 and 0.51 respectively. This means that for Au15, there is 1 Ag atom for every 4 Au atoms while for Au15_100, there is 1 Ag atom for every 2 Au atoms (Fig. 5.16). On the other hand, the atomic radius of Au and Ag are 1.79 Å and 1.75 Å respectively while the C-C bond length is 1.54 Å. Each glycerol molecule thus adsorbs onto a set of 3 Au and/or Ag atoms on the catalyst surface. Given the higher proportion of Au atoms in Au15 and its higher activity compared to Ag, glycerol would strongly favour adsorption onto sets of Au triplets instead of those containing Ag atoms. This might lead to the isolation of Ag containing sites on the catalyst surface in the adsorption process which in turn reduces its overall catalytic activity since not all surface atoms are being utilized. In comparison, for Au15_100, each triplet set necessarily includes an Ag atom due to its higher Ag surface content. In this way, glycerol molecules are more likely evenly adsorbed onto the metal surface and this gives rise to the higher product conversion obtained.

Fig. 5.16. Schematic drawing of Au and Ag atomic arrangement on the surface of a) Au15 and b) Au15_100.

Further annealing Au15 at 600 °C enabled a 18% increase in both glycolate and formate selectivity relative to Au15. However, electrochemical activity exhibited by Au15_600 (Fig. 5.17d) was only marginally better than AuAg and product concentration was similarly low. Changes in product distribution exhibited by the annealed samples are attributed to the gradual increase in Ag/Au atomic ratio from 0.26 in Au15 to 1.68 in Au15_600 as determined by XPS (Table 5.5). As such, Ag exerted an increasingly larger influence over the reaction pathway in the annealed samples and this gave rise to higher glycolate and formate selectivity. However, we also note that even small amounts of residual Ag that was embedded within the pores of

Au15 and Au15_100 was sufficient to steer the selectivity of Au towards the C-C bond breaking products.

Interestingly, oxalate selectivity increased measurably after dealloying. Oxalate selectivity obtained by AuAg and Au15 was 1.17% and 24.71% respectively. However, selectivity decreased by 8% when the sample was annealed at 100 °C while little to no oxalate was observed with Au15_300 and Au15_600. Collectively, these results indicate that Au is responsible for the further oxidation of glycerate to tartronate as well as the subsequent oxidation of glycolate to oxalate while Ag controls C-C bond breaking of glycerate to glycolate and formate.

Fig. 5.17. Chronoamperograms of a) Au15_100 b) Au15 c) Au15_300 d) Au15_600 e) AuAg sheet.

5.4. Conclusions

In this article, we present porous Au catalysts that demonstrates highly selectivity towards glycolate and formate due to the presence of residual Ag embedded within its porous network. Unlike AuAg alloys, our optimized catalyst also exhibited extremely high electrochemical activity due to its Au rich surface. As such, we have successfully circumvented the problem of low electro-catalytic activity that usually plagues Ag containing catalysts, owing to the inherently poor conductivity of Ag. Low temperature annealing at 100 °C improved selectivity

and electrochemical activity relative to the dealloyed sample. However, annealing at higher temperatures of 300 °C and 600 °C caused electrochemical activity to decrease sharply due to the enhancement of Ag content on the catalyst surface. Formate and glycolate selectivity improved marginally with increased surface Ag content. The dealloyed sample that was annealed at 100 °C gave rise to the best overall catalytic performance as it managed to achieve high electrochemical activity coupled with high selectivity to both formate and glycolate.

Chapter 6

Conclusions and recommendations for future work

6.1. Conclusions

Au based catalysts are one of the most extensively investigated catalytic systems for glycerol electro-oxidation. A variety of products including, glycerate, tartronate, glycolate, oxalate and formate were generated when glycerol electro-oxidation was carried out over Au based catalysts under our experimental conditions. A diverse range of catalytic systems have been developed in order to improve the selectivity of Au toward specific products during catalysis. Alternatively, reaction conditions such as applied potential and catalyst loading can be optimized in order to achieve improved selectivity. However, as yet, there has been no unified system which enables one to easily steer selectivity of Au towards different products in the oxidation pathway.

In this thesis, we investigated whether the simple electro-deposition of transition metal species onto Au/C could alter the selectivity of Au towards different products in the glycerol oxidation pathway. We determined that electro-deposition of Cu and Ni onto Au/C effectively tuned selectivity towards glycerate and tartronate. Moreover, we synthesized residual Ag containing porous Au structures which exhibited both high catalytic activity and selectivity to formate. More specifically, our major findings are:

- 1) Cu electro-deposition onto Au/C led to significant improvements in C3 selectivity.

Greatest enhancement in C3 selectivity was observed when Cu electro-deposition occurred at -0.1 V and +0.015 V. High selectivity is attributed to the presence of an Au^+ species which was generated when Au interacted with electrodeposited Cu_2O . Furthermore, when electro-deposition occurred at +0.015 V for 90 min, Au^+ content

- increased by three times. This in turn enabled $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ to double C3 selectivity relative to Au/C when glycerol electro-oxidation occurred at 0.1 V.
- 2) Ni electro-deposition onto Au/C also led to improvements in C3 selectivity. Similarly, high selectivity is attributed to the presence of an Au^+ species that was identified in the most selective catalysts. In this case, Au^+ was generated when Au interacted with NiOOH , which was generated when the electro-deposited Ni species was cycled in NaOH post electro-deposition.
 - 3) Ni electro-deposition onto Au/C is optimized at -0.3 V. When electro-deposition occurs at applied potentials more negative than -0.3 V, a significantly thicker Ni layer is deposited onto Au/C. The thicker Ni surface partially shielded the Au nanoparticles from the glycerol solution and thus severely limited their activity. C3 selectivity of the Ni-Au/CB catalysts prepared under these conditions are relatively similar to that of pure Au/CB. Any possible synergistic effect between Au and Ni was thus nullified by the thick Ni surface coverage.
 - 4) Ag is known to favour C-C bond breaking of glycerol. However, Ag-Au based catalysts such as AuAg alloys also typically exhibit low electro-chemical activity due to the poor conductivity of Ag. It is thus necessary to develop Ag containing catalysts that possessed an Au rich surface in order to achieve high electrochemical activity whilst maintaining high selectivity.
 - 5) We developed residual Ag containing porous Au structures as highly active and selective catalysts for glycerol electro-oxidation. Porous Au structures possessed an Au rich surface which enabled high electro-catalytic activity. Furthermore, presence of residual amounts of Ag embedded deep within the porous structure lead to high selectivity towards glycolate and formate.

6) Low temperature annealing of the porous Au structure led to further improvements in formate selectivity and conversion. Formate selectivity improved due to the higher surface Ag content. On the other hand, annealing also resulted in atomic rearrangement on the catalyst surface, which subsequently improved conversion. The dealloyed only sample was Au rich and this led to the isolation of Ag sites on the catalyst surface. However, after annealing, Au and Ag atoms were rearranged such that all atoms present on the catalyst surface necessarily participated during the reaction. In this way, glycerol molecules were more likely evenly adsorbed onto the metal surface and this gave rise to the higher product conversion.

6.2. Recommendations for future work

We have established that the simple electro-deposition of Cu and Ni onto Au/C tuned its selectivity towards glycerate and tartronate. Yet, it is difficult to control the electro-deposition process such that all particles are evenly coated with the desired species. On the other hand, electro-deposition can only be used as means to provide surface coverage onto Au/C. It cannot be used to deposit transition metals selectively onto specific facets of the Au particle. As such, our future work can involve designing and synthesizing Au nanoparticle catalysts which have specific facets covered or replaced with transition metal species. Through this, the catalytic performance of Au/C can be further tuned and the specific interaction between transition metal species and Au/C be understood in greater depth.

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