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

Larissa Thia,^{†‡} Mingshi Xie,[‡] Zhaolin Liu,[§] Xiaoming Ge,[§] Yizhong Lu,[‡] Wenmei Eileen

Fong,[¶] Xin Wang^{*‡}

[†] Residues & Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute, Interdisciplinary Graduate School, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

[‡] School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore

[§] Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Republic of Singapore 138634

[¶] School of Materials Science and Engineering, 50 Nanyang Avenue, Singapore 639798

* Corresponding author. Email: WangXin@ntu.edu.sg. Phone: (65) 6316 8866. Fax: (65) 6794 7553.

ABSTRACT

C3 selectivity of carbon supported Au nanoparticles for glycerol electro-oxidation was significantly enhanced via Au interaction with electro-deposited Cu species. Notably, C3 selectivity of supported Au nanoparticles doubled after it underwent 90 minutes of Cu electrodeposition at +0.015 V. This result was obtained when glycerol electro-oxidation was carried out at +0.1 V for 2h. The most selective catalysts contained an Au^+ species which was generated via interaction between Au and electro-deposited Cu_2O . Presence of Au^+ increased selectivity to glycerate and tartronate while simultaneously suppressing C-C bond cleavage to glycolate and formate.

Keywords: glycerol electro-oxidation, selectivity, Cu electro-deposition, gold nanoparticles

1. Introduction

Utilization of glycerol for fuel cell applications is attractive due to its ability to cogenerate electricity and value-added chemicals. Glycerol is advantageous as a fuel as it is economical, easily purified and stored, non-volatile and environmentally friendly.^[1] Glycerol can also be used as feedstock for the production of valuable 3 carbon (C3) oxygenated derivatives.^[2] However, C-C bond cleavage of these C3 intermediates is unavoidable. As such, C2 and C1 side products are usually present in the reaction mixture.^[3] The diverse range of possible products gives rise to significant challenges in trying to control product selectivity whilst maintaining high catalytic activity. To this end, much effort has been expended to design catalysts that are both active and selective for glycerol oxidation.

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^[4] and high MA selectivity^[5] could be independently obtained. On the other hand, Kwon and co-workers investigated the ability of adatoms – Bi,^[6] Sn, Sb, In, As, Pb^[7] – 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.^[8] 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.^[9]

The use of bimetallic nanocomposites is also a commonly employed strategy to improve the performance of Au nanoparticles.^[10] 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.^[11] 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.

2. Experimental

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

1 ml 1% HAuCl₄·3H₂O 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% NaBH₄ 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.

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.

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.

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.

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

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 $^{\circ}\text{C}$. 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 curves.

3. Results and discussion

Fig. 1. 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. 1. 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 Cu₂O are observed. Cu_{+0.015V, 60min}-Au/C and Cu_{+0.015V, 90min}-Au/C displayed additional diffraction peaks at ~36.7 ° and ~42.6 ° and ~61.6 °, which are assigned to the (111), (200) and (220) planes of the Cu₂O phase (JCPDS 78-2076) respectively.

Fig. 2. XRD pattern of a) Au/C b) Cu_{-0.1V, 30min}-Au/C c) Cu_{+0.015V, 30min}-Au/C d) Cu_{+0.1V, 30min}-Au/C e) Cu_{+0.3V, 30min}-Au/C. Carbon peak at ~26° was eliminated for greater clarity.

Fig. 2 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 Cu_{V, 30min}-Au/C where by V indicates the Cu electro-deposition potential. Au was present in all the samples investigated. Besides the Au(111) peak, Cu_{+0.1V, 30min}-Au/C and Cu_{+0.3V, 30min}-Au/C displayed additional peaks at ~44.1 °, ~64.5 ° and ~77.5 °, which are assigned to the (200), (220) and (311) planes of the Au phase respectively. Moreover, in comparison to Cu_{+0.015V, 30min}-Au/C, Cu_{+0.1V, 30min}-Au/C contained both CuO and Cu₂O. Cu_{+0.1V, 30min}-Au/C displayed additional diffraction peaks at ~35.6 °, ~48.8 °, ~53.2 ° and ~61.3 °, which are assigned to the (111), (-202), (020) and (-113) planes of the CuO phase (JCPDS 48-1548) respectively.

Table 1
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

Various Cu species were obtained from the different electrochemical reactions that occurred at different applied potentials. Cu_{-0.1V, 30min}-Au/C contained mainly Cu(0) and Cu₂O, as its XRD spectra is similar to that of Cu_{+0.015V, 90min}-Au/C (Fig. 2b). Overall, Cu²⁺ reduction (from CuSO₄ stock solution) to Cu was the dominant reaction. As the reaction proceeded, electro-deposited Cu was then oxidized to Cu₂O owing to low reduction potential of the reaction (Eq 2, Table 1). This accounts for the presence of Cu₂O in all the samples except for Cu_{+0.3V, 30min}-Au/C. Furthermore, when Cu electro-deposition occurred at +0.1 V (E=+0.289

V vs. RHE), 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. 2d). 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.^[12] Small amounts of CuO were also observed in XRD spectra of $\text{Cu}_{+0.015\text{V}, 60\text{min}}\text{-Au/C}$, $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ and $\text{Cu}_{-0.1\text{V}, 30\text{min}}\text{-Au/C}$. As with $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$, $\text{CuO}(-111)$ peak in these samples existed as a shoulder peak alongside $\text{Cu}_2\text{O}(111)$ at $\sim 36.2^\circ$ (Fig. S1). Yoneda-XAFS and theoretical calculations showed that a duplex type structure consisting of an outer CuO and an inner Cu_2O layer were formed on top of metallic Cu thin films after its exposure to air.^[13] Hence, surface oxidation of Cu_2O also accounts for the presence of CuO . Lastly, high applied potential of +0.3 V ($E=+0.498$ V vs. RHE), meant that only miniscule amounts of Cu was deposited onto Au/C (Fig. 3a). XRD spectra of $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$ is essentially identical to Au/C (Fig. 2e).

Fig. 3. Chronoamperograms for a) $\text{Cu}_{+0.3\text{V}, 30\text{mins}}\text{-Au/CB}$ b) $\text{Cu}_{+0.1\text{V}, 30\text{mins}}\text{-Au/CB}$ c) $\text{Cu}_{+0.015\text{V}, 30\text{mins}}\text{-Au/CB}$ d) $\text{Cu}_{-0.1\text{V}, 30\text{mins}}\text{-Au/CB}$ e) $\text{Cu}_{-0.3\text{V}, 30\text{mins}}\text{-Au/CB}$

Table 2

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 1 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. 4), which is typical of pure metallic Au(0) species.^[14] 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.^[15]

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. 4b-4e respectively). This peak is assigned to the Au⁺ species.^[14a, 16] 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 S1) 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. 3b). 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 ($\Delta E = +2.06$ V).^[17] Au^+ has also been observed in other types of Cu_2O -Au nanocomposites such as heterodimers, core-shell particles and hollow spheres.^[18] Additionally, Au nanoparticles supported on CeO_2 (Au/CeO_2) and Au nanoparticles partially covered with very small NiO_x (NiO_x/Au) segments also reported the presence of Au^+ species after electron transfer occurred between $\text{Au}(0)$ and CeO_2 ^[19] and Ni_2O_3 ^[20] respectively. In comparison, CuO is more stable due to its higher reduction potential and Au^+ species are not commonly observed in Au - CuO nanocomposites.^[21]

Fig. 4. XPS curve fitting of the Au4f photoelectron peak for 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) $\text{Cu}_{+0.015\text{V}, 90\text{min}}\text{-Au/C}$ e) $\text{Cu}_{+0.1\text{V}, 30\text{min}}\text{-Au/C}$ f) $\text{Cu}_{+0.3\text{V}, 30\text{min}}\text{-Au/C}$

Fig. 5. 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. 5a. 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.^[22] 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 2). 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.^[23] 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 2). 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. 5b). 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.

Table 3

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

Catalyst	Product Selectivity (%)					
	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 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. Cu_{+0.015V, 30min}-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,^[24] water-gas shift reaction,^[25] and formaldehyde oxidation,^[26] 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 2). 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 2). 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 $\text{Cu}_{-0.3\text{V}, 30\text{min}}\text{-Au/C}$ showed the smallest increment (~5%) relative to Au/C. Correspondingly, $\text{Cu}_{-0.3\text{V}, 30\text{min}}\text{-Au/C}$ 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 S1). 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. 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.^[1, 27]

Fig. 6. 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. 6. 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-Cu₂O 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 2). 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. 7. 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. 7 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.^[1, 28] 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 Cu_{+0.015V, 90min}-Au/C decreased by more than half from ~60% to ~26%.

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 Cu₂O. Extending electro-deposition time to 90 min at +0.015 V, further increased Au⁺ content by three times. As such, Cu_{+0.015V, 90min}-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 tartronate were thus trapped at the catalyst layer for longer periods of time and C-C bond breaking to glycolate and formate was enhanced.

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Supplementary data

Supporting information includes detailed XRD characterization of products, chronoamperograms obtained during the Cu electro-deposition process and the Nernst equation used.

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Fig. S1. Expanded XRD patterns derived after Cu electro-deposition at A) Cu_{-0.1V, 30min}-Au/CB
B) Cu_{+0.015V, 60min}-Au/CB and Cu_{+0.015V, 90min}-Au/CB

Table S1

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 used to take into account differences in reaction condition

$$E = E^{\circ} + 0.0592 (\text{pH}_{\text{solution}})$$

Fig. S2. Cyclic voltammogram (CV) of Au-CB on carbon cloth electrode in 0.1 M NaOH at a scan rate of 50mV/s.

Fig. S3. 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

Fig. S3. shows the typical cyclic voltammogram of Cu-Au/C electrocatalysts when scanned in 0.1 M NaOH at a scan rate of 50mV/s. After Cu electro-deposition, copper species cover the carbon cloth electrode surface and partially obscure the observation of the Au/C peaks in the CV. Herein, the cathodic peak C2 at -0.17 V corresponds to the reduction of Cu(II) to Cu(0) while cathodic peak C3 represents -0.52 V results from the combination of two processes: reduction of Cu(I) to Cu(0) and also the reduction of Cu(II) to Cu(0).¹ On the other hand, the anodic peak A2, at -0.28 V and A1 at 0.1V correspond to the oxidation of Cu(0) to Cu(I) and Cu(I) to Cu(II) respectively.

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