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Selective electro-conversion of glycerol to glycolate on carbon nanotube supported gold catalyst†

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Glycerol is electro-converted to glycolate with 85% selectivity on carbon nanotube supported Au catalyst (Au/CNT) in alkaline electrolyte at 1.6 V (*vs.* SHE) under mild reaction conditions (room temperature, atmosphere pressure, water as solvent).

Glycolic acid has a broad range of cleanser applications due to its high acidity (pK_a 3.83) and chelation properties with metal ions.[1] It is also widely used in textile dyeing, leather tanning, personal care products, and the preparation of polyglycolic acid (PGA), which is a macromolecule for dissolvable sutures,[2] drug delivery materials[3] and gas barrier packaging materials.[4] Up to now, glycolic acid has mainly been produced by the acid-catalyzed reaction of formaldehyde and carbon monoxide,[5] or by hydrolysis of glycolonitrile (a production from formaldehyde and hydrogen cyanide),[1b,6] both of which involve highly toxic chemicals in the processes. In lab-scale synthesis, glycolic acid can be obtained from either the hydrolysis of monochoroacetic acid, or the Cannizzaro type reaction of glyoxal in alkaline media.[1a,7] Although these reactions involve less poisonous chemicals and milder reaction conditions, they are still based on traditional petroleum resources. It is urgent to develop more efficient, eco-benign, and renewable processes to produce glycolic acid.

Recently, glycerol attracts immense research interests as a bio-renewable chemical feedstock with a low price (US$0.3 kg^{-1}, crude glycerol),[8] Extensive research is devoted to the development of highly selective catalysts to efficiently convert glycerol to higher valued oxygenated chemicals.[1c,9] Compared to Pt and Pd catalysts, Au nanoparticles have demonstrated a unique catalytic ability in enhancing the glycerate selectivity in high pH media.[10] A glycerate selectivity of 100% was obtained under optimized conditions.[9c] Recently, we investigated the selective oxidation of glycerol in anion-exchange membrane fuel cell (AEMFC) reactors, and found that glycerol can be further oxidized to tartronate and mesoxalate with high selectivities on the Au/C catalyst under an anode overpotential of 0.4–0.7 V *vs.* SHE.[11] With the assistance of H$_2$O$_2$, glycolate has been detected as a main product from glycerol oxidation on Au nanoparticles

in a heterogeneous catalysis batch reactor.[1c,12] Under the favourable conditions, the highest selectivity to glycolate was reported to be 56% (at 100% glycerol conversion).[1c] However, the reaction requires the use of large amounts of H$_2$O$_2$ (H$_2$O$_2$/glycerol molar ratio 4 : 1), elevated temperature (120 °C), and high pressure (7 bar), which may still not be suitable for large-scale production.

Our recent research found that glycolate became an appreciable product from glycerol oxidation on highly polarized Au catalyst (at potentials >0.9 V) in an electrolysis cell reactor.[11] In this communication, we reported a glycolate selectivity of 85% in alkaline electrolyte on Au/CNT catalyst at a potential of 1.6 V. As the reaction takes place under mild conditions without any toxic or strongly oxidative reactants, it implies a more efficient alternative green approach to the current syntheses of glycolate.

CNT was used as an electro-catalyst support based on the considerations of its higher electric conductivity, and better durability under high potentials.[13] 40 wt% Au/CNT was synthesized through a modified solution phase reduction method.[11,14] As shown in Fig. 1(a) and S1,† the as-prepared Au nanoparticle (NP) was uniformly dispersed on CNT support with a size distribution of 2–6 nm, centered at 2.5 nm. The XRD pattern in Fig. 1(b) displayed a typical face-centered cubic (FCC) structure. The average metal crystal size of Au/CNT calculated from Au (220) diffraction peak is 2.6 nm, which is in close agreement with the TEM result.

The glycerol oxidation was investigated in an electro-catalytic reactor at room temperature as illustrated in Fig. S2.† The product distributions after 3 h of reaction at different applied potentials were summarized in Fig. 2 (the corresponding product concentration profile is shown in Fig. S3†) and clearly
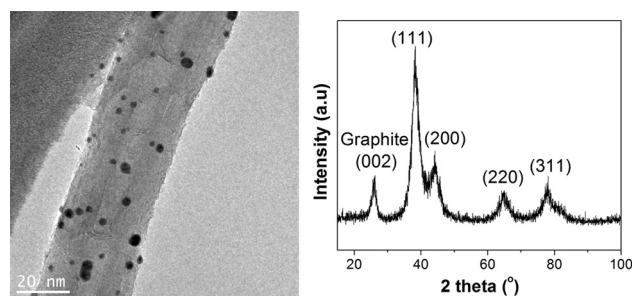
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Fig. 1 (a) TEM image and (b) XRD pattern of Au/CNT catalyst.

demonstrates that the selectivity to glycolate is heavily dependent on the applied potential. In general, higher selectivities to glycolate were observed at higher applied potentials. At the applied potential of 1.6 V, glycolate selectivity can reach up to 85%; while at 1.0 V, its selectivity is only 41%. On the contrary, the selectivity to tartronate gradually decreased with the applied potential increasing. The selectivity to glyoxylate, which is an oxidation product from tartronate,[11] also decreased. This observation is consistent with our previous AEMFC work. Under an alkaline electro-catalytic environment, glycerol was quickly oxidized to glycerate on the Au catalyst surface.[15] At lower potentials (*i.e.*, in AEMFC anode), glycerate is preferably oxidized to tartronate, which could be further oxidized to mesoxalate.[11] However, at higher potentials, the C–C bond cleavage reaction is predominant, resulting in higher selectivity to glycolate. Meanwhile, the carbon balance calculated by eqn (2) (see ESI†) slightly increased from 10% (at 1.0 V) to 13% (at 1.6 V), indicating more C_2 products (glycolate, glyoxylate, and oxalate) were oxidized to C_1 products (formate and carbonate). To elucidate this mechanism, 1.0 M glycolate was oxidized at 1.6 V for 3 h. The results (Fig. S4†) clearly shows the formation of formate, with selectivities of 62% and 73% in 2.0 and 1.0 M KOH electrolytes, respectively. In addition, the corresponding carbon balances were 15% and 16%, indicating that formate may be further oxidized to carbonate. We also considered the oxidation of oxalate in the electro-catalytic reactor. When 2.0 M

KOH + 1.0 M oxalate was employed, a stable anodic current and a carbon balance of 12% were observed after a 6 h reaction at 1.6 V, indicating that the C–C bond cleavage of oxalate also accounts for the formation of carbonate.

The concentration effects of KOH and glycerol were evaluated at 1.6 V for 3 h, and the results are summarized in Table 1. It is obvious that higher concentrations of KOH would enhance the reaction rate. As the KOH concentration increased from 0.5 M to 4.0 M, the glycerol conversion jumped from 16% to 43%, due to the promoted deprotonation of glycerol in a higher pH environment.[14b,16] Higher KOH concentration also facilitates the oxidation of hydroxyl groups in glycerol, leading to higher selectivities of tartronate and oxalate in the experiment with 4.0 M KOH. Meanwhile, the initial glycerol concentration also affects the product distribution. With a lower initial glycerol concentration of 0.5 M, more deeper-oxidized products (glycolate: 87% and oxalate: 5%) were obtained. When the initial glycerol concentration was increased to 2.0 M, more glycerate was observed instead. The observation is consistent with the reaction mechanism discussed above: at high applied potentials, the glycerol electro-oxidation on Au follows the reaction sequence of glycerol → glycerate → glycolate → oxalate. When a lower initial glycerol concentration is employed, more reaction intermediates will be adsorbed on the catalyst surface and be further oxidized, resulting in higher selectivities to glycolate and oxalate. It is noted that compared to the applied potentials, the initial concentrations of KOH and glycerol have only minor effects on the product distribution, which indicates that the product distribution is primarily governed by the applied potential.

Fig. 3 shows the results of 2.0 M KOH + 1.0 M glycerol oxidation carried out at 1.6 V for up to 12 h. It is apparent that the selectivity to each product kept almost constant during the whole reaction period, demonstrating that the reaction time has limited influences on the product distribution. This observation also indicates that the glycerol electro-oxidation product selectivity is strongly dependent on the applied potentials. The conversion of glycerol stabilized at 50% after 6 h reaction. However, small anodic currents were still recorded with the reaction time increasing, which may be attributed to the continuous generation of C_1 products. With the reaction time increasing from 6 to 12 h, the carbon balance gradually increased from 25% to 31%. At the same time, the concentration of each observed C_3 (glycerate and tartronate) and C_2 products gradually decreased with the reaction time increasing, which also demonstrated the decomposition of C_3 and C_2 products to C_1 products.
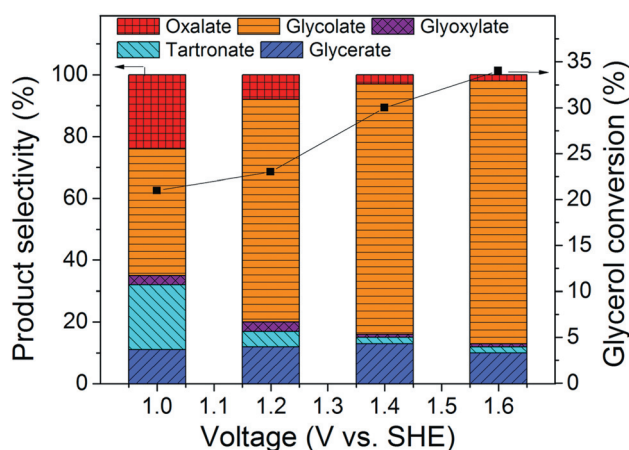

Fig. 2 Electro-oxidation of glycerol (2.0 M KOH + 1.0 M glycerol) on Au/CNT under different applied potentials, 3 h, room temperature.

Table 1 Electro-oxidation of glycerol on Au/CNT at 1.6 V, 3 h, room temperature

Entry	Selectivity[a] (%)					Glycerol conversion (%)	Carbon balance (%)
	GLY	TAR	GLO	GLC	OXA		
4.0 M KOH + 1.0 M Glycerol	4	8	0	80	8	43	9
2.0 M KOH + 1.0 M Glycerol	10	2	1	85	2	34	13
1.0 M KOH + 1.0 M Glycerol	14	2	1	81	2	26	19
0.5 M KOH + 1.0 M Glycerol	14	3	2	79	2	16	12
2.0 M KOH + 2.0 M Glycerol	16	2	2	78	2	19	10
2.0 M KOH + 0.5 M Glycerol	5	3	0	87	5	29	14

[a] GLY = glycerate; TAR = tartronate; GLO = glyoxylate; GLC = glycolate; OXA = oxalate.
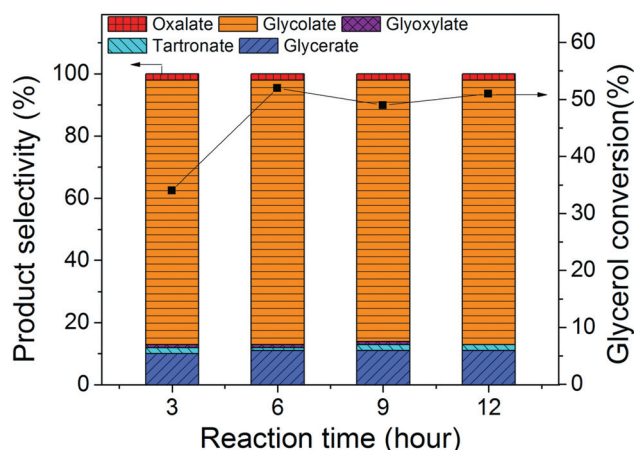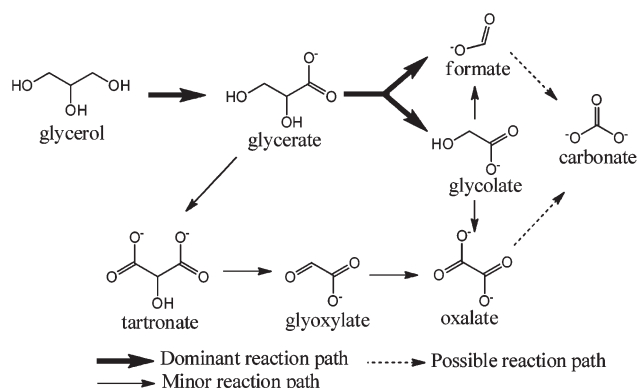
Fig. 3 Electro-oxidation of glycerol (2.0 M KOH + 1.0 M glycerol) on Au/CNT catalyst at 1.6 V for different reaction times, room temperature.

Scheme 1 Proposed reaction pathway for the electro-oxidation of glycerol on Au/CNT catalyst at high potentials.

It has been discovered that Au catalyst facilitates glycerol oxidation to tartronate, and further to mesoxalate in low applied potentials of 0.4–0.7 V under AEMFC reactor operation conditions.[11] In sharp contrast to the previous results, here we report a potential-regulated selective electro-oxidation of glycerol to glycolate, and the proposed reaction pathway for electro-oxidation of glycerol on Au/CNT is shown in Scheme 1. At high potentials (>1.2 V), glycerol is rapidly oxidized to glycerate, and then the C–C bond cleavage of glycerate proceeds dominantly, leading to a high selectivity to glycolate. Glycolate could be slowly oxidized to formate and oxalate, which may be further oxidized to carbonate. It is noted that when glycolate was used as substrate, no glyoxylate was observed in the products, which indicates that the small amount of glyoxylate in glycerol electro-oxidation products was from the C–C breakage of tartronate.

In conclusion, we successfully demonstrated a green electro-conversion approach to efficient synthesis of glycolate from the bio-renewable feedstock glycerol under mild reaction conditions. This investigation reveals that the selectivity to glycolate is strongly dependent on the applied potential. Under the optimized conditions, the glycolate selectivity can reach up to 85% at 50% glycerol conversion.

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