Electronic Supplementary Information for

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

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1. Experimental Section

1.1 Synthesis of Au/CNT catalyst.

0.5 mmol $AuCl_3$ (151.7 mg) was first dissolved in a mixture of 16 ml octadecene and 4 ml oleylamine under a nitrogen flow. The system was then rapidly heated to 80°C, followed by a quick injection of 1.5 ml $LiBEt_3H$. After holding the temperature for 10 min, the Au nanoparticles (NPs) were achieved by quickly cooling down the solution to room temperature and separated by centrifugation.

The as-prepared Au-NPs were then dispersed into 50 ml Hexanes and slowly dropped into an isopropanol solution of CNT (148.0 mg). The final product Au/CNT catalyst (40 wt%) was obtained after the filtration and washed with copious amounts of ethanol.

1.2 Electro-catalytic oxidation of glycerol.

The reaction was carried out in an electro-catalytic reactor, with two liquid diffusion electrodes (a Au/CNT based anode, 5.0 mg_{Au} cm^{-2}, and a Pt/C based cathode, 1.0 mg_{Pt} cm^{-2}), and a solid anion-exchange membrane (FAA, 110 μm). The reactor was assembled as the scheme shown in Fig S2, with an active cross-sectional area of 1 cm^2, and a Hg/HgO electrode in the anode chamber to control the anode overpotential. During each run, 8.0 ml of glycerol (or glycolate, oxalate) + KOH solution was introduced into a plastic vessel and pumped into the anode chamber through a closed loop by a peristaltic pump (Gilson minipuls 3). At the same time, a KOH solution (the same pH as the anode reactant solution) was cycled through the cathode chamber. The anode applied potential was controlled by potentiostats (Versastat, Princeton Applied Research) for a certain reaction time.

1.3 Products analysis.

The oxidation products were analyzed by high-performance liquid chromatography (HPLC, Agilent 1100), with a refractive index detector (RID, Agilent G1362A) and a variable wavelength detector (VWD, 220 nm, Agilent G1314A). An OA-1000 column (Alltech) was operated at 60°C, and an eluent of 5 mM aqueous sulfuric acid flowing at 0.3 ml min^{-1} was applied for the products separation. 20 μl of the sample was injected into the HPLC system. Products were identified by comparison with authentic samples.

For glycerol oxidation, the product selectivity is calculated as:

$$Selectivity = \frac{Moles\ of\ specific\ product\ forms}{Total\ moles\ of\ C_2\ and\ C_3\ products\ decteted} \times 100\% \quad (1)$$

The carbon balance is based on:

$$Carbon\ balance = \frac{3M_{G_i} - 3M_{C_3} - 2M_{C_2} - M_{C_1} - 3M_{G_f}}{3M_{G_i}} \times 100\% \quad (2)$$

If assuming that no C_2 products were further oxidized to C_1 products, then,

$$M_{C_2} = M_{C_1} \quad (3)$$

Therefore:

$$Carbon\ \ balance = \frac{M_{G_i} - M_{C_3} - M_{C_2} - M_{G_f}}{M_{G_i}} \times 100\% \quad (4)$$

Where M_{Gi} and M_{Gf} are the initial and final moles of glycerol in the electrolyte. M_{C3}, M_{C2}, and M_{C1} are the moles of C_3 products (glycerate and tartronate), C_2 products (glycolate, glyoxylate and oxalate), and C_1 products (formate and carbonate), respectively. A smaller carbon balance number indicates less C_2 chemicals were further oxidized to C_1 products.

For glycolate oxidation, the selectivity was calculated as follows:

$$Selectivity = \frac{Moles\ of\ specific\ product\ forms}{Total\ moles\ of\ C_1\ and\ C_2\ products\ decteted} \times 100\% \quad (5)$$

The carbon balance was based on:

$$Carbon\ balance = \frac{2M_{C_i} - 2M_{C_2} - M_{C_1} - 2M_{C_f}}{2M_{C_i}} \times 100\% \quad (6)$$

If assuming that no formate was further oxidized to carbonate (CO_2 combined with OH^- in high pH media) then,

$$M_{C_1} = M_{C_{FM}} \quad (7)$$

Therefore:

$$Carbon\ \ balance = \frac{M_{C_i} - M_{C_2} - 1/2M_{C_{FM}} - M_{C_f}}{M_{C_i}} \times 100\% \quad (8)$$

where M_{Ci} and M_{Cf} are the initial and final moles of glycolate in the electrolyte. M_{C2}, M_{C1}, and M_{CFM} are the moles of C_2 products (glyoxylate and oxalate), C_1 products (formate and carbonate), and formate respectively. A smaller carbon balance number indicates less formate was further oxidized to carbonate.

2. Supporting Figures.

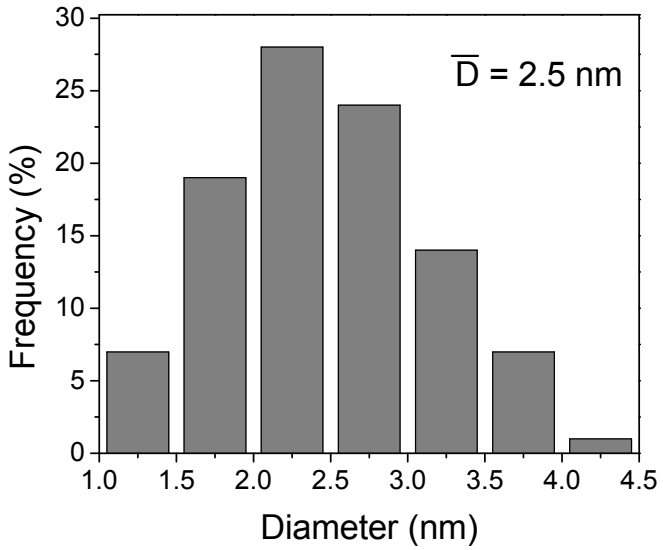

Fig. S1 Particle size distribution of Au/CNT, measured from >100 particles in arbitrarily chosen areas.

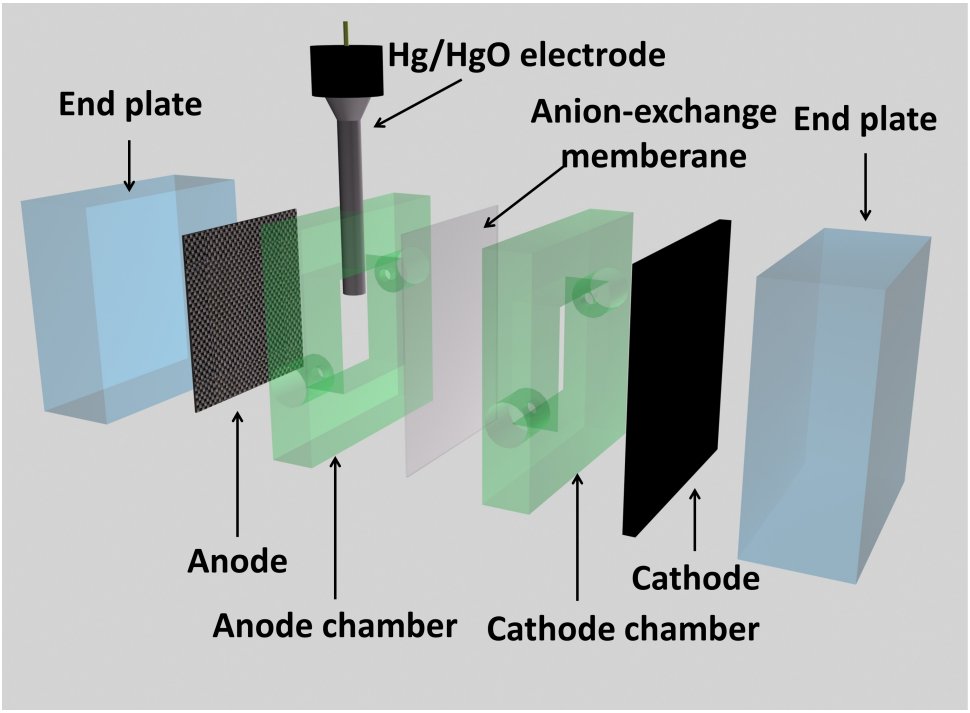

Fig. S2 Schematic illustration of the anion exchange membrane-based electro-catalytic reactor.

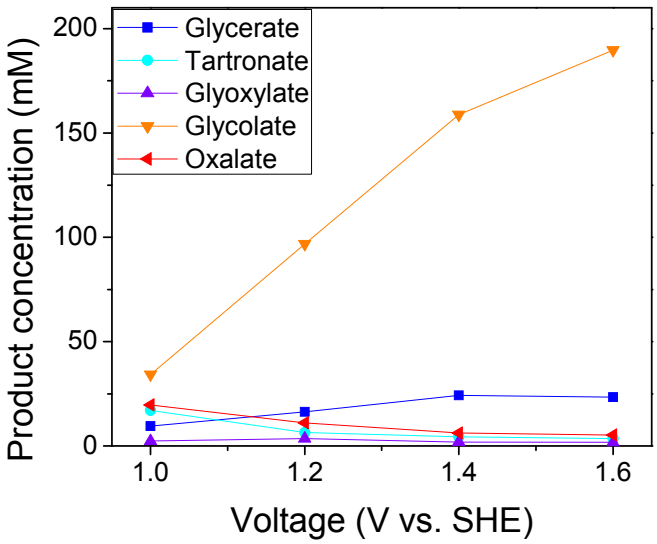

Fig. S3 Product concentrations for the electro-oxidation of 2.0 M KOH + 1.0 M glycerol on Au/CNT catalyst under different applied potentials at room temperature, 3 h.

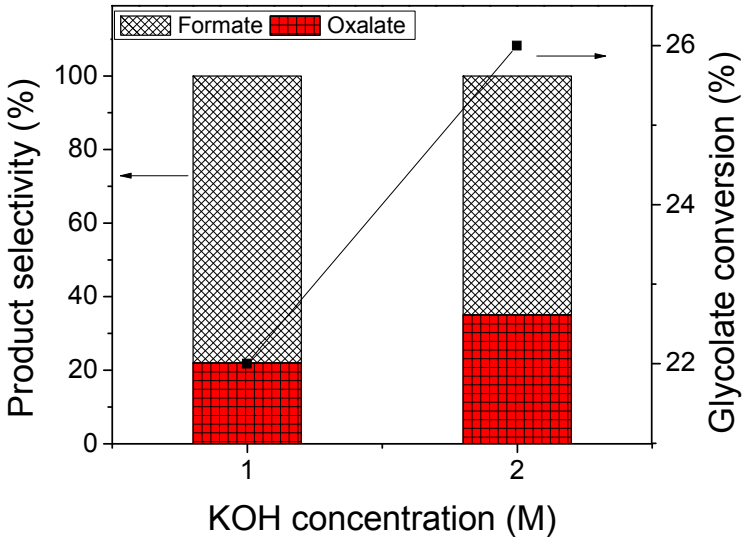

Fig. S4 Electro-oxidation of glycolate (1.0 M) on Au/CNT catalyst under different KOH concentration at room temperature, 3 h. The applied potential is 1.6 V vs. SHE.