Supplementary Information for:

Operando Raman probing of electrocatalytic biomass oxidation on gold nanoparticle surfaces

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Chemicals used: Gold nanoparticles (AuNPs), 28 nm in diameter, were purchased from US Research Nanomaterials, Inc. Nafion dispersion in water, D521, was obtained from Alfa Aesar. Carbon Cloth with MPL, W1S1005, was purchased from Graphite Store. TIMCAL Graphite & Carbon Super P® Conductive Carbon Black was purchased from MTI corporation. 5-Hydroxymethyl-2-furaldehyde (HMF) was purchased from TCI Chemicals and stored as a 500 mM stock in deionized water. Otherwise, all chemicals were used as received.

Electrode fabrication: AuNPs (10 mg) were combined with carbon black (0.5 mg) in a 50:50 (vol:vol) ethanol:water mixture. Nafion was added in to attain ~3% wt. relative to the amount of AuNPs used. The mixture was sonicated for 60 minutes, then stirred overnight. Following this, the AuNP mixture was drop-cast onto the carbon cloth to generate a loading of ~1 mg/cm². The electrode was dried at ambient conditions and subsequently investigated for catalysis. Gold dendrites/nanoneedles were electrodeposited onto carbon paper at -1.2V vs. Ag/AgCl for 300 seconds in a 0.5M HCl and 100 mM HAuCl₄ solution. AuNPs of 15 nm in size were synthesized by heating a 100 mL aqueous solution of 0.5mM HAuCl₄ until boiling at 1000 rpm stirring, then adding citric acid, dissolved in 1 mL water, to reach 5mM concentration in the reactor. The yellow Au solution subsequently turned reddish purple and was heated for 15 more minutes. The 15 nm AuNPs were then washed by centrifugation in water, then ethanol prior to drop casting them on the carbon electrode.

Electrochemistry: Electrocatalytic experiments were performed in a custom-built, two-compartment electrochemical cell. A Ag/AgCl reference electrode and graphite rod counter electrode were employed. A Biologic SP-150 potentiostat was utilised to conduct experiments. The electrolyte was composed of deionized water, adjusted to pH 12 through the addition of potassium hydroxide. HMF was added moments prior to electrochemical experiments from a 500 mM aqueous stock. Reaction products were analysed with a Bruker AV-300 NMR in a deuterium oxide solvent with 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) as an internal standard. Each run for product quantification was carried out with 10 mL electrolyte in the working electrode compartment and 1 cm^2 of the working electrode exposed to the solution.

Raman spectroscopy: Raman spectroscopy was performed with a Renishaw Invia Raman system. A 633 nm laser was utilised for all experiments. A 50X long working distance (8.5mm) objective was used for *operando* measurements and the distance between sample and objective was ~8.5 mm. A custom-build one-compartment Teflon electrochemical cell was utilised, which featured the same working electrode, but a Pt wire counter electrode and 2mm-diameter dri-ref Ag/AgCl electrode (World Precision Instruments). The same potentiostat and software was used for Raman experiments. Spectra were collected either in open circuit conditions or during a chronoamperometric run, after the system was allowed to first stabilize for 5 minutes at each potential.



Figure S1: TEM image of commercially purchased surfactant-free AuNPs used in this work with an average diameter of 28 nm.



Figure S2: Cyclic voltammogram of AuNPs in the absence of HMF in a pH 12 KOH electrolyte



Figure S3: Electrochemical impedance spectroscopy of AuNPs in pH 12 KOH with 100 mM HMF shows a decreasing charge-transfer resistance with increasingly positive voltage alongside a diffusion element growing in. (a) and (b) illustrate different magnifications of the data.



Figure S4: Cyclic voltammetry illustrated increasing catalytic current with increasing pH. In this work, pH 12 was chosen for in-depth studies because HMF may not be stable in strongly alkaline solutions and the aldehyde group may undergo reactions in solution through the Cannizzaro reaction. (a), (b), and (c) display different magnifications of the data.



Figure S5: Representation of the HMF molecule and the assignment of bands in the solution Raman spectra. The solution consisted of 500 mM HMF in pH 12 KOH. The close match of the Raman spectra with previous reports indicates that HMF is stable in these conditions.



Figure S6: Electrolysis at 1.2 V shows evidence for a full oxide layer formation on AuNPs from a wide band at $\sim 600 \text{ cm}^{-1}$ that is present only in the absence of HMF.



Figure S7: SERS spectra of HMF reduction at -1.0V vs. Ag/AgCl, in comparison to spectra at open circuit and of HMF in solution.



Figure S8: Electrocatalytic performance of Au dendrites. Enhanced currents were seen in the cyclic voltammogram (a), and DFF was the primary product detected after 24 hrs of electrolysis at 1.2 V vs. Ag/AgCl (b).



Figure S9: Raman spectra of HMF in solution and adsorbed on AuNPs (straight line) vs. on Au dendrites (dashed line) at open circuit and at 1.2V vs. Ag/AgCl.



Figure S10: Electrocatalytic performance of 15 nm AuNPs. The enhancement in current upon HMF addition only began at ~0.6V (a). The DFF was only detected in very small quantities after 24 hrs of electrolysis at 1.2V vs. Ag/AgCl.



Figure S11: *Operando* SERS spectra of 15 nm, citrate capped AuNPs. The spectra are dominated by the citrate ligands adsorbed onto the Au surfaces. Only at potentials of >0.6V, the main bands of HMF can be seen as the ligand bands decrease in intensity. This points to the surface-blocking effects of citrate ligands as primarily responsible for the materials' worse performance as compared to the other two systems studied in this work.