

Supporting information

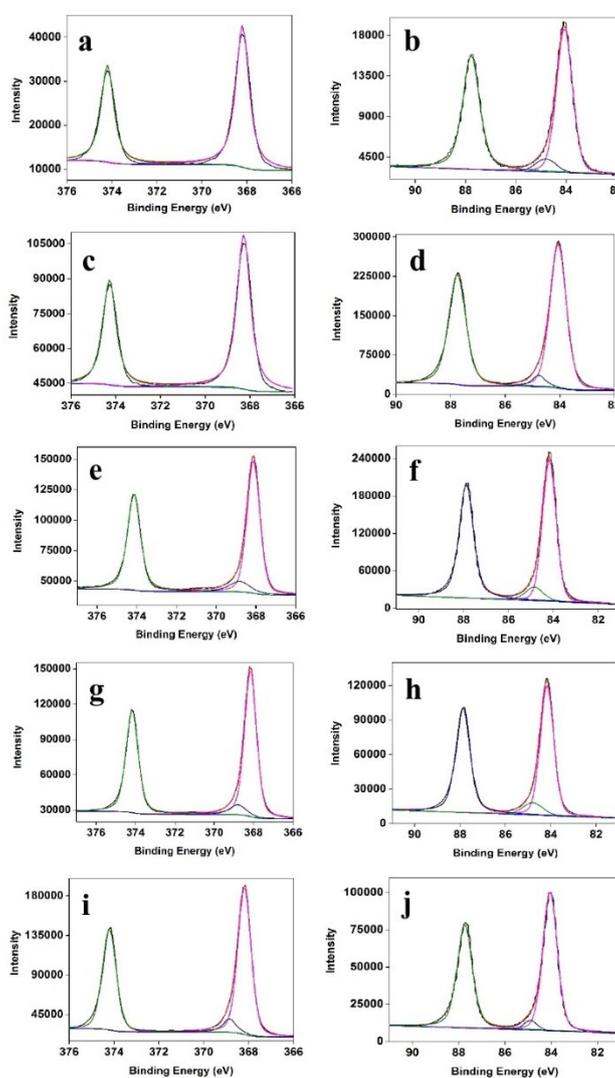


Fig. S1 XPS data. Ag 3d_{5/2} spectra for a) AuAg c) Au15 e) Au15_100 g) Au15_300 i) Au15_600 Au 4f_{7/2} spectra for b) AuAg d) Au15 f) Au15_100 h) Au15_300 j) Au15_600.

X-ray photoelectron spectroscopy (XPS) was utilized to analyse surface composition of the catalysts prepared under different conditions. 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 peaks are assigned to Au(0) and Au(I) respectively. On the other hand, the Ag 3d_{5/2} peak for all samples is located at 368.2 eV and this is typical of pure metallic Ag(0). 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. Ag(I) elemental concentration was between 10-14% in the 3 samples (Table 2). Presence of Ag(I) is attributed to the adsorption of O atoms on undercoordinated surface Ag atoms when the samples were exposed to air.²⁰ 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.²¹ Furthermore, annealing was carried out under argon gas which precludes the oxidation of Ag.

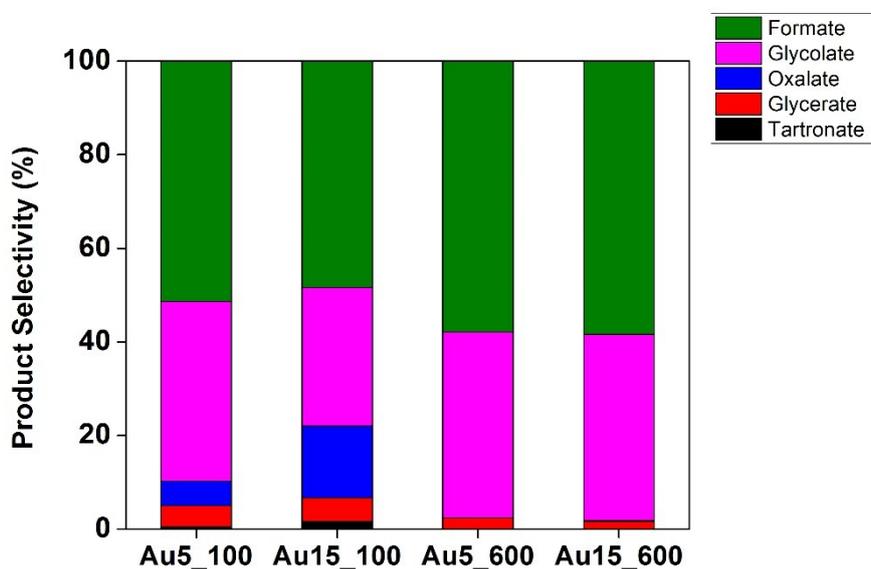


Fig. S2 Product selectivity of samples which were a) dealloyed for 5 min, annealed at 100 °C b) dealloyed for 15 min, annealed at 100 °C c) dealloyed for 5 min, annealed at 600 °C d) dealloyed for 5 min, annealed at 600 °C.

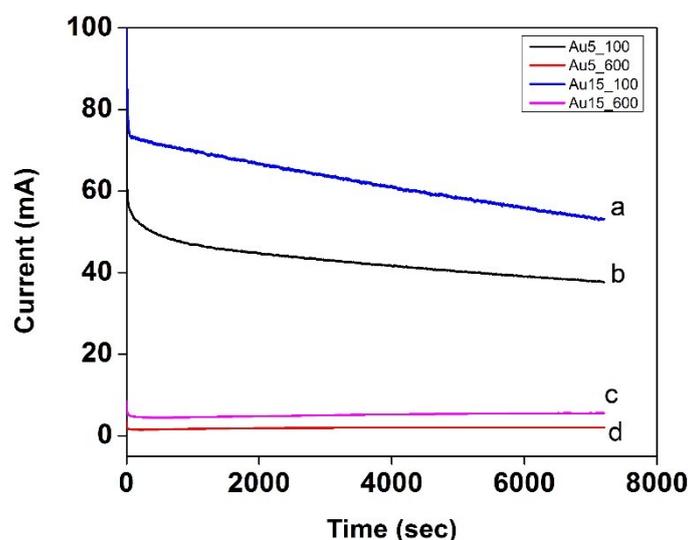


Fig. S3 Chronoamperograms of samples which were a) dealloyed for 15 min, annealed at 100 °C b) dealloyed for 5 min, annealed at 100 °C c) dealloyed for 15 min, annealed at 600 °C d) dealloyed for 5 min, annealed at 600 °C.

AuAg sheets were first etched for 5 and 15 min in concentrated HNO₃ before the dealloyed sheets were respectively annealed at 100 or 600 °C in argon gas for 2h. The resulting Ag containing, porous Au structures were then tested for glycerol electro-oxidation. Their comparative selectivity and electrochemical activities are presented in fig S1 and S2 respectively. Formate was the dominant product generated in all cases and thus, product selectivity is not significantly influenced by treatment method (Fig. S1). In comparison, electrochemical activity is strongly influenced by both etching time and annealing temperature (Fig. S2). At the same annealing temperature, samples which were etched for 15 min (Fig. S2a and S2c) generated a higher current than those which were only etched for 5 min (Fig. S2b and S2d). Furthermore, samples which were annealed at 100 °C exhibited markedly higher electrochemical activities compared to those annealed at 600 °C. As such, 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 further varying annealing temperature to further optimize our results.