Supplementary Information (SI) for Nanoscale.

Supporting Information

The fate of nanoparticle surface chemistry during reductive electrosynthesis in aprotic media

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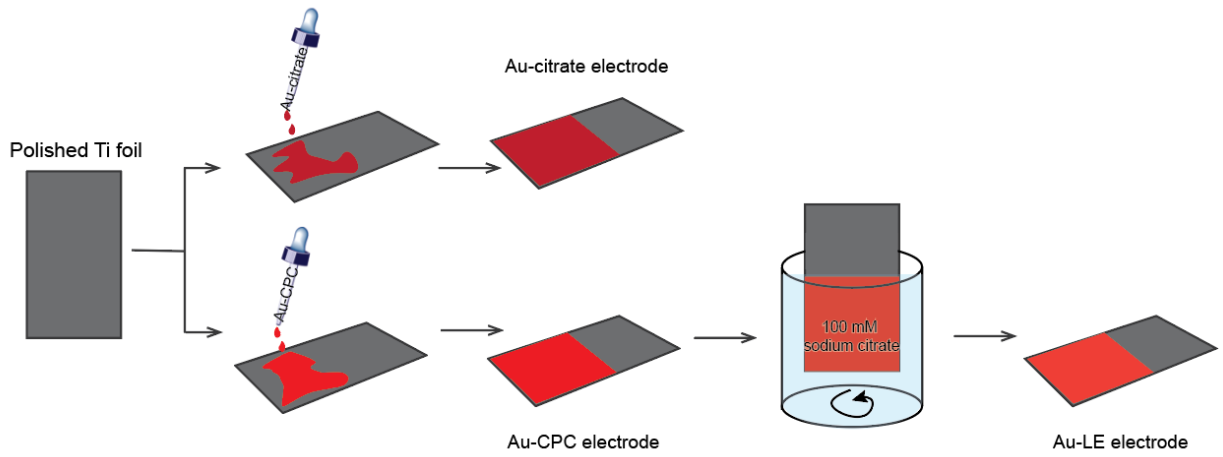


Fig. S1: Au electrode preparation and ligand exchange schematic.

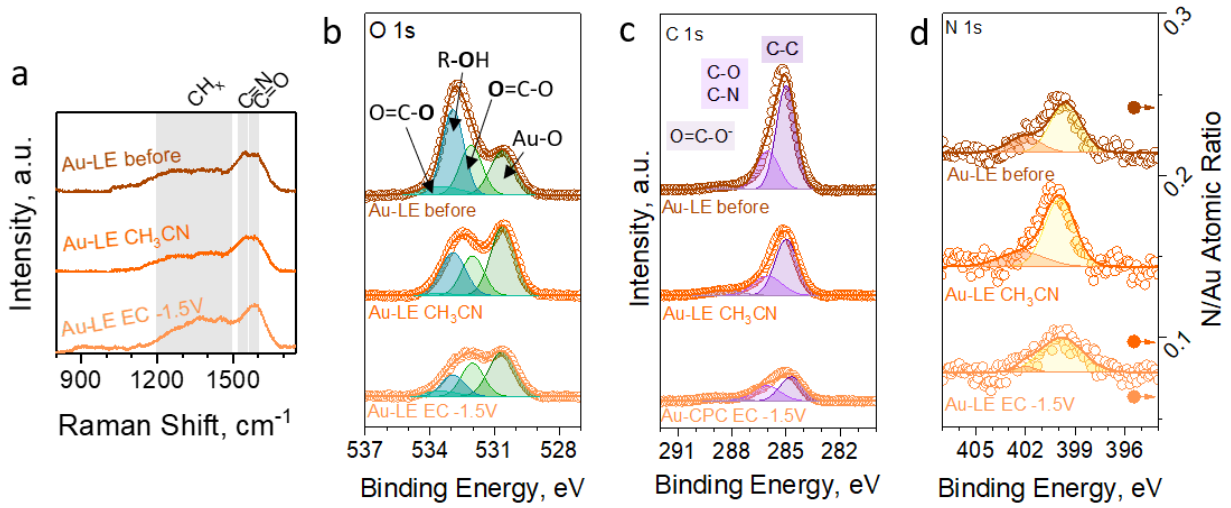
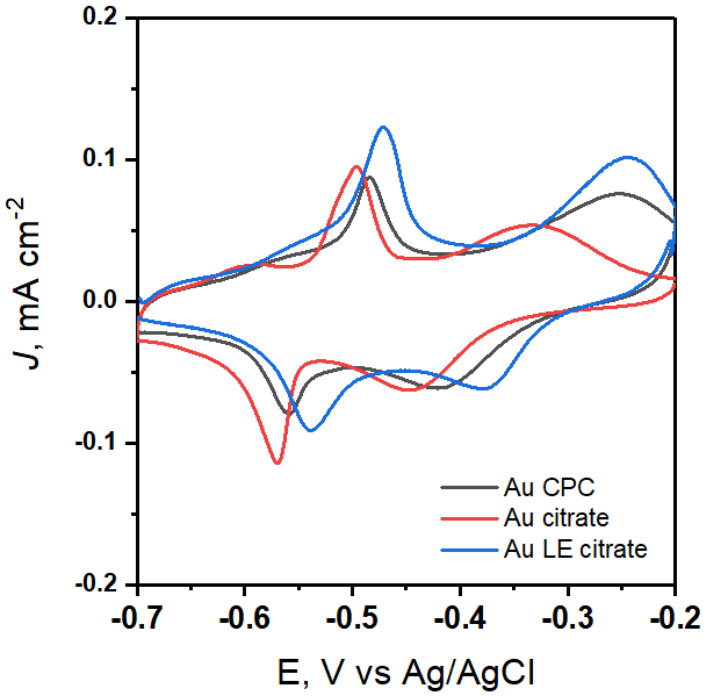


Fig. S2: Assessment of the Au-LE surface chemistry. Raman spectra (a) and XPS for O 1s (b), C 1s (c), and N 1s (d). Brown traces correspond to as prepared Au-LE, bright orange traces correspond to Au-LE extensively washed with acetonitrile, and light orange traces correspond to the Au-LE surface after EC for 1 h at -1.5 V vs Ag/Ag+.



	Au CPC	Au LE citrate	Au citrate
Q, µC	**1360**	**1320**	**847**
ECSA[a], cm^2	**4.95**	**4.81**	**3.09**

[a]ECSA was calculated using an arbitrary charge of 274 µC cm^{-2}

Fig. S3: Pb_{UPD} of Au nanoparticle electrodes with a loading of 1 mg cm^{-2} and the corresponding electrochemically active surface area (ECSA). Au-CPC (black trace), Au-citrate (red trace), and Au-LE (blue trace). CV was recorded in 0.1 M NaOH with the addition of 1 mM $Pb(NO_3)_2$ at a scan rate of 20 mV s^{-1}.

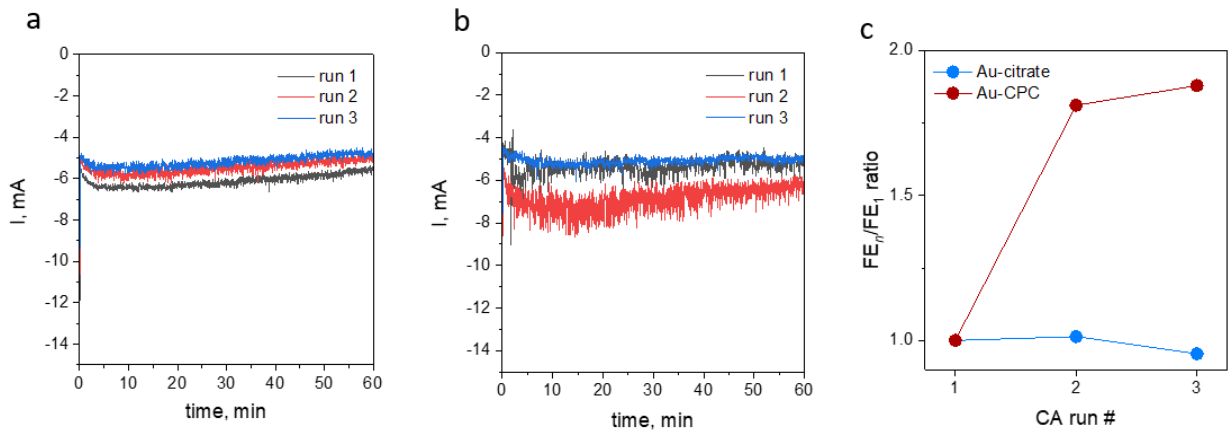


Fig. S4: Electrode stability in EC during short term electrolysis. (a,b) Consecutive 1h CAs under typical EC conditions at -1.5 V vs Ag/Ag^+ for Au-CPC electrode (a) and Au-citrate electrode(b). (c) Carboxylate FE change upon the electrode repeated use.

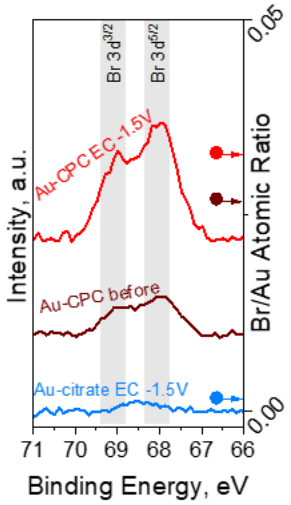
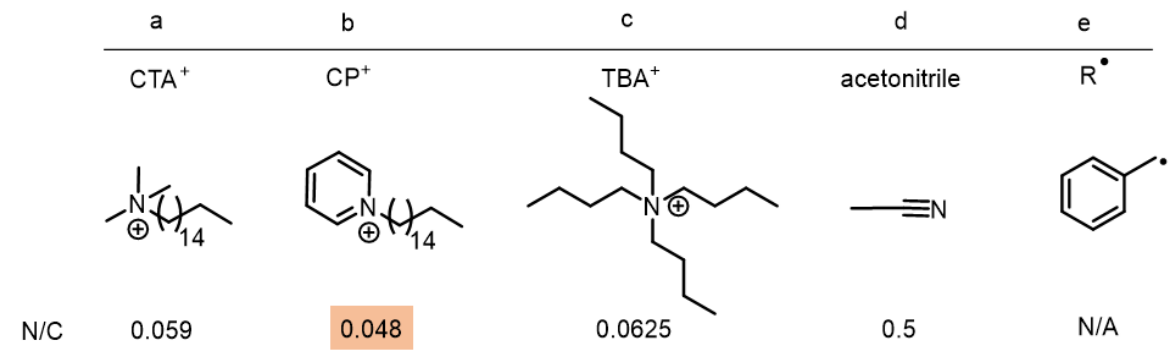


Fig. S5: XPS evaluation of adsorbed Br based on the Br 3d peak for Au-CPC and Au-citrate electrodes.



Au-CPC	C/Au	N/Au	N/C
before	3.02	0.15	0.05
CH_3CN	1.3	0.059	0.045
EC at -1.5V	1.04	0.026	0.025

$$\frac{C_{\not N}}{Au} = \left(\frac{C}{Au}\right)XPS - \frac{\left(\frac{N}{C}\right)XPS}{\left(\frac{N}{C}\right)calculated} \times \left(\frac{C}{Au}\right)XPS$$

N/C ratios for ***Au-CPC before*** and ***Au-CPC CH_3CN*** are close to that in CP^+ (0.048, highlighted orange) meaning most of the C source in these samples come from CPC. For ***Au-CPC EC -1.5 V*** N/C ratio is drastically decreased to 0.025 and pyridinium N mostly disappears from XPS (Figure 3g). As new N source is most likely coming from TBA^+ with higher N/C ratio of 0.0625 we can approximate C/Au ratio for non-N containing organic molecules on the surface being **0.624** using the equation on the left. Thus, that C is coming from the EC precursor and intermediates (e.g. **e**)

Fig. S6: Description of XPS evaluation of adsorbed organic molecules for Au-CPC.

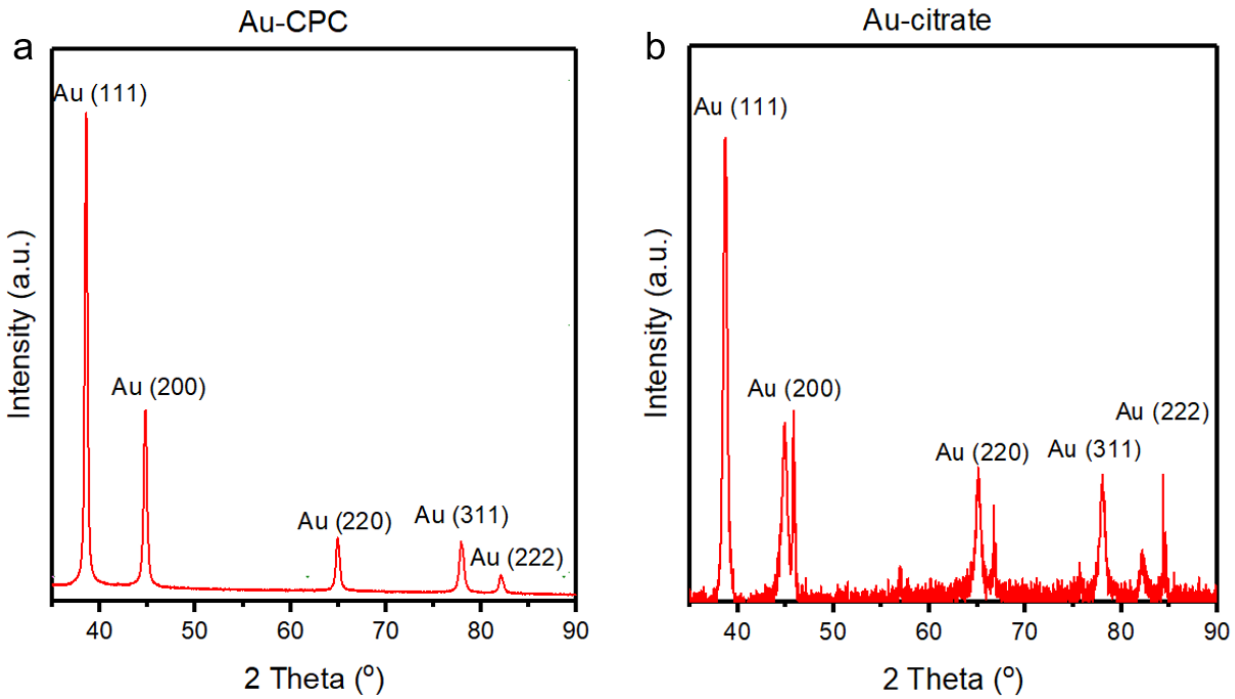


Fig. S7: XRD evaluation of Au-CPC (a) and Au-citrate (b) crystallinity. Au-CPC showing narrow representative peaks of single crystalline Au, while Au-citrate showing broadened peaks with bands characteristic of polycrystalline Au materials.