Electronic Supplementary Material (ESI) for Nanoscale Advances.

Mechanistic Control of the Galvanic Replacement Reaction of Gold on Cuprous Oxide

Supporting Information

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Materials characterization (SI Data): Scanning electron micrographs (SEM) were measured with a FEI Nova Nanolab SEM. Energy-dispersive X-ray (EDX) spectra were measured with a Bruker Quantax EDS spectrometer on the same SEM. Transmission measurements were performed using a UV-vis spectrometer with integrating sphere (V780, Jasco Inc.).

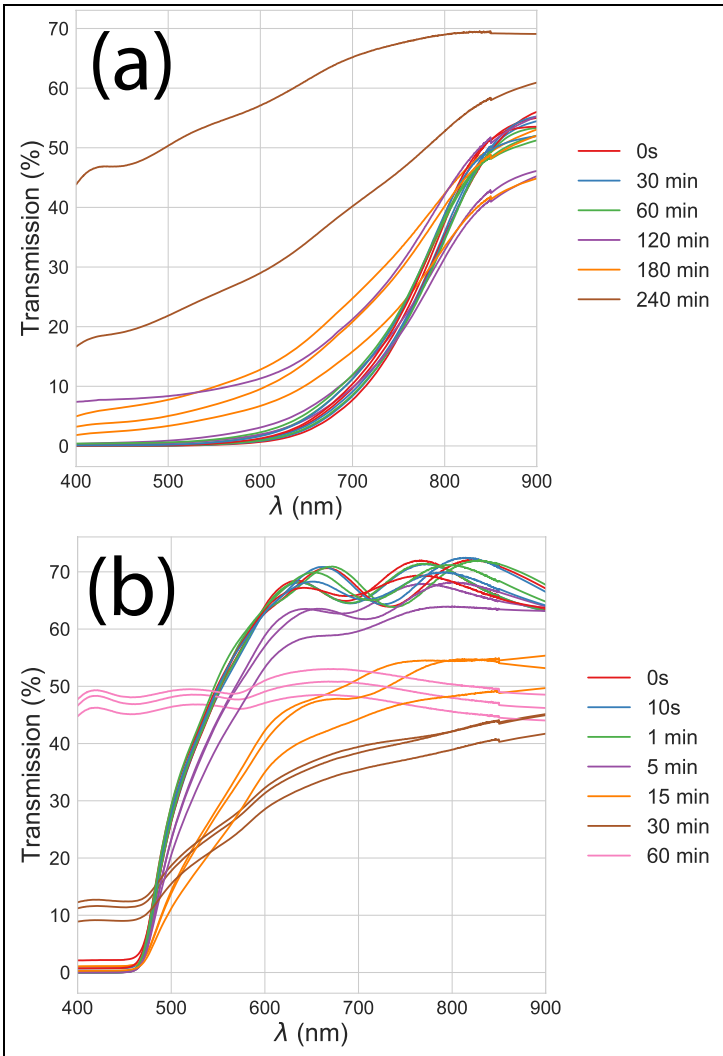

Figure S1 – UV-Vis transmission measurements of the dissolution of (a) CuO and (b) Cu_2O (experiments performed in triplicate) in a null solution of 10mM H_2SO_4 adjusted to pH 2.7 without the addition of NaAuCl4, or a 0mM GR solution. The increasing transmission for CuO demonstrates the slow dissolution of the film over the course of hours. The transmission spectra for Cu_2O shows a decrease in transmission below the band gap of Cu_2O and an increase in transmission above the band gap. This is an observation of the disproportionation of Cu_2O and the dissolution of the CuO, trapping the interface with opaque Cu metal.

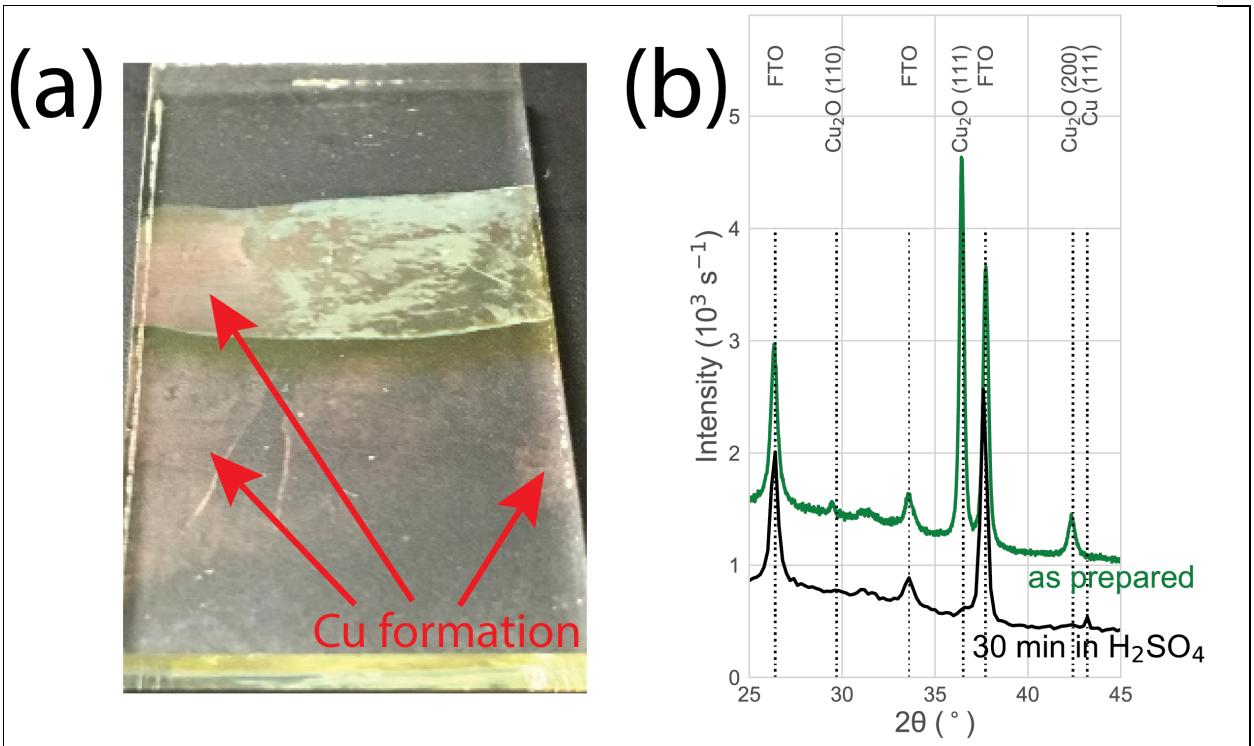

Figure S2 – (a) Cu formation on Cu_2O after 30 min in pH 2.7 H_2SO_4 without added NaAuCl4 (the null solution). (b) XRD measurements of as prepared Cu_2O (green) and the Cu_2O film exposed to the null solution for 30 min (black). The measurement indicates that the Cu_2O has been almost entirely dissolved and a small amount of metallic Cu has formed on the electrode surface. The Cu(111) Bragg reflection appeared only after the exposure to H_2SO_4.

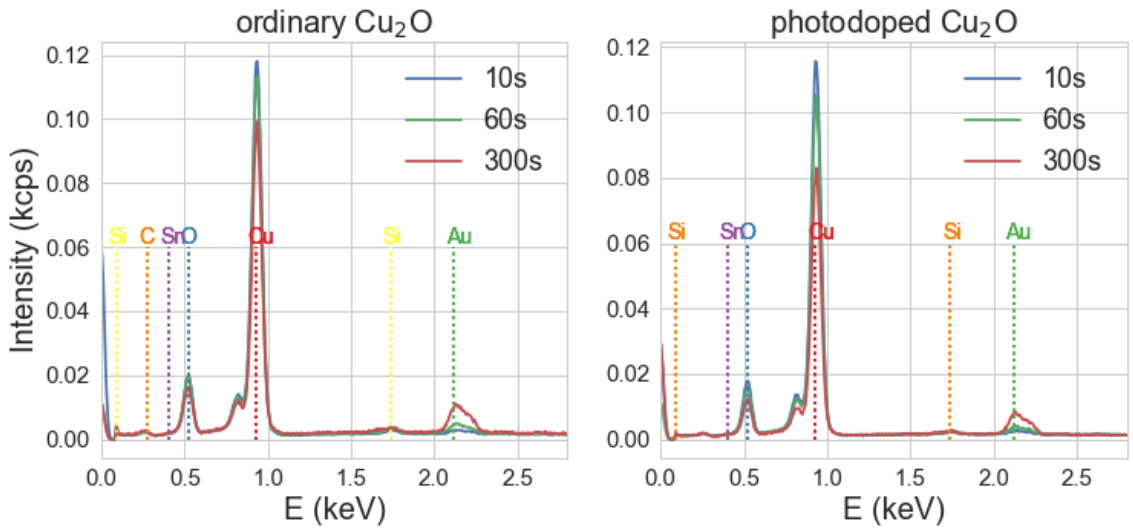

Figure S3 – EDX spectra of ordinary electrodeposited Cu_2O films (left) and photoelectrodeposited (400 mW cm^{-2} at 455 nm) Cu_2O films (right) on exposure to 1 mM $AuCl_4^-$ GR solution (pH 2.7) for 10 s, 60 s, and 300 s. Both show a strong increase in the presence of Au on the surface and a slight decrease in the total Cu and O signals with increasing GR solution exposure. This indicates that Au is depositing while the Cu_2O surface is dissolving.

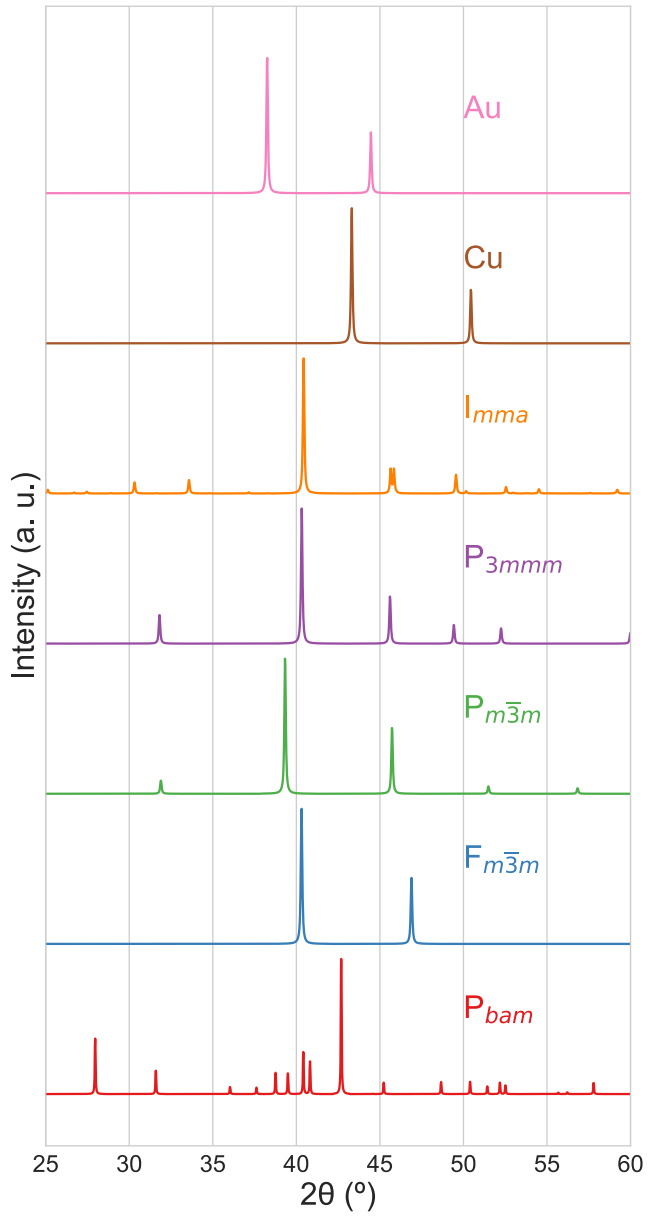

Figure S4– Reference XRD patterns for the P_{bam}, $F_{m\bar{3}m}$, $P_{m\bar{3}m}$, P_{3mmm}, and I_{mma} phases of Cu-Au alloys calculated from reference crystal structure data tables[1] using Mercury, a crystal structure analysis software package.[2] The Cu and Au patterns are also shown. The Au and Cu crystal structures belong to the $F_{m\bar{3}m}$ space group, so they mostly form substitutional alloys of the same or related space groups, where the position of Bragg reflections vary depending on the stoichiometry and of the alloy. The phase diagram of the Cu-Au intermetallic system shows a number of phases, even at room temperature.[3] The orthorhombic P_{bam} phase the only Cu-Au alloy phase with a Bragg reflection at the position ((120) reflection at 2θ=28.0°) observed in the powder XRD of the Au galvanic replacement reaction on Cu (Figure 3). The P_{bam} phase also has a number of Bragg reflections near the broad XRD feature observed in the range of 2θ=37.0°-41° at 50mM $AuCl_4^-$, though every Cu-Au alloy an intense Bragg reflection in that range. The P_{bam} phase is also notable as one with notably high Cu stoichiometry (~90%).[1]

1 P. Villars, L. D. Calvert and W. B. Pearson, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, Metals Park, Ohio, USA, 1985, vol. 2.
2 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J Appl Cryst*, 2006, **39**, 453–457.
3 H. Baker, *ASM handbook: Alloy phase diagrams*, ASM International, 1992.

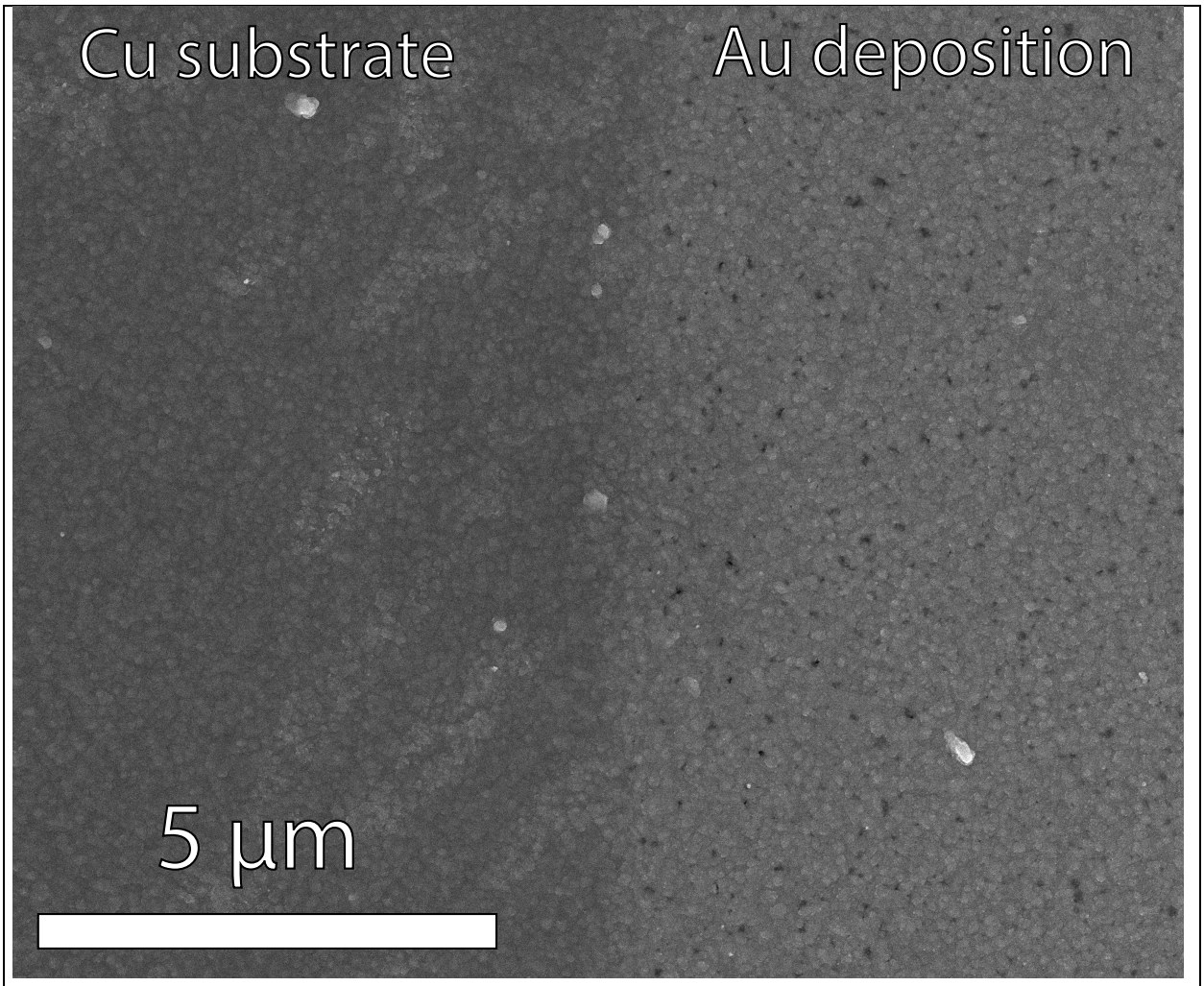

Figure S5 – The deposition at the GR solution level for 5mM $AuCl_4^-$ after a 60s exposure.

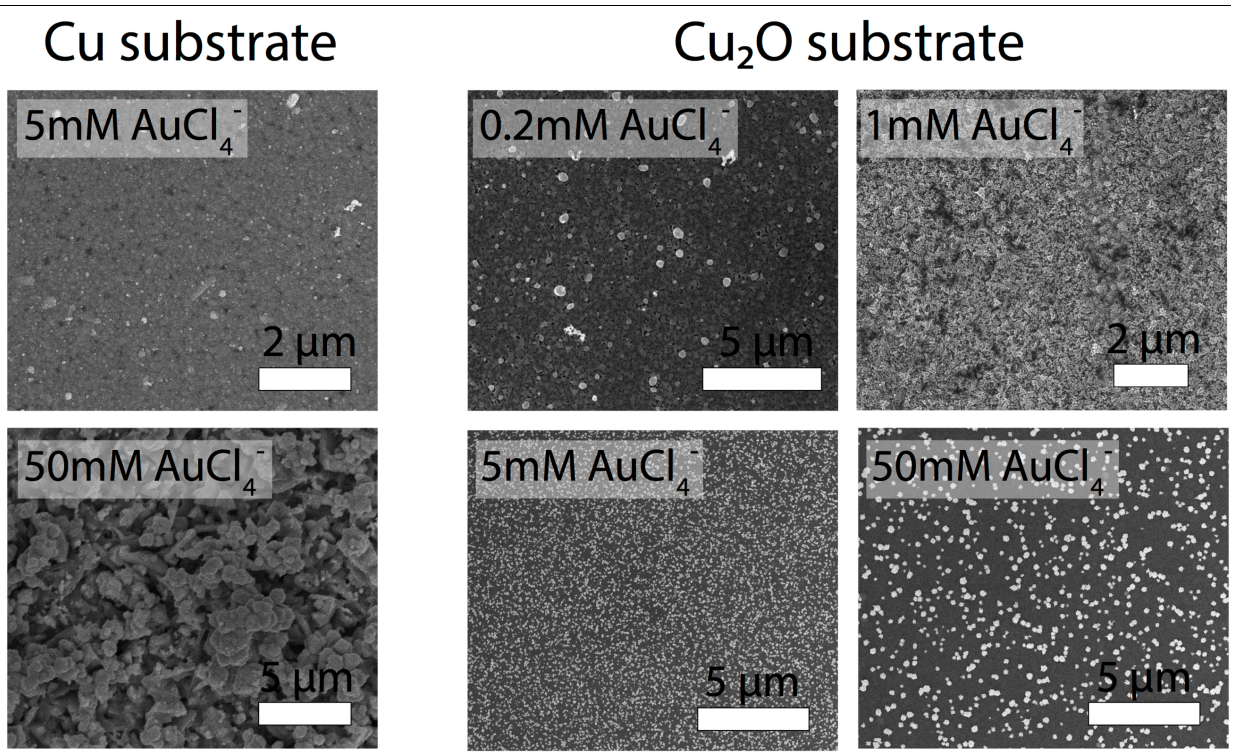

Figure S6– Micron-scale images of Au deposition on Cu and Cu_2O substrates (for comparison to Figure 4 in the main text).