

Supporting Information for

Underpotential Co-deposition of Au-Cu Alloys: Switching the Underpotentially Deposited Element by Selective Complexation

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1. Experimental Section

Electrodeposition of Au-Cu alloy films. Two distinct electrolytes were developed to achieve Cu UPCD with Au and Au UPCD with Cu, respectively. The former electrolyte was based on Au-ethylenediamine, Au(EN)₂, and Cu-glycine complexes. Au(EN)₂ was synthesized according to the literature ^[1]; briefly, 0.5 mmol of HAuCl₄ was dissolved in 5ml of DI water (ultra-pure Milli-Q[®] water, resistivity 18.2 MΩ·cm), forming a brown precipitate; 2ml of 1M EN solution was then added, resulting in dissolution of the precipitate. After filtering, the solution concentration was adjusted to 0.025M Au(EN)₂. Cu glycinate complexes were obtained simply by successively adding CuSO₄ and glycine to the above solution. The final electrolyte consisted of 2 mM Au(EN)₂, 20 mM CuSO₄, 0.2 M glycine, 0.2 M Na₂SO₄ in MilliQ[®] water; the solution was brought to pH 7 with NaOH, resulting in a highly stable electrolyte.

In order to enable reverse UPCD a sulfite based electrolyte was used, prepared by first dissolving 2 mM CuSO₄ and 20 mM HAuCl₄ in water, followed by complexation with a large excess (0.168

M) of Na_2SO_3 to form monovalent complexes ($\text{Au}(\text{SO}_3)_2^{3-}$ for Au [2] and mainly Cu_2SO_3 for Cu [3]); pH was set at 8 by addition of H_2SO_4 to stabilize the complexes. This solution was stable for about two days before Au colloids would start to precipitate due to Au disproportionation: $3\text{Au}^+ \rightarrow 2\text{Au} + \text{Au}^{3+}$.

Electrochemical Characterization. The electrochemical behavior of the various solutions was investigated using a Princeton Applied Research electrochemical quartz crystal microbalance (EQCM, model QCM 922), which allows the simultaneous acquisition of current and mass data vs. electrode potential. The rate of mass increase dm/dt and the corresponding cyclic voltammetry data $j(V)$ were recorded at a Au coated quartz resonator (0.196 cm^2 working area) using a scan rate of 5mV/s ; during the measurement the solution was not stirred nor any deaeration was performed in order to minimize noise; solutions were however purged with nitrogen gas for 1h before starting each experiment.

Film growth. Electrodeposition of Au-Cu alloy films was performed in a three-electrode cylindrical cell with the electrodes in a vertical configuration. The counter-electrode was a Pt mesh, and the reference was a saturated $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ electrode (MSE). In this paper all potentials are referred to MSE ($E_{MSE}^0 = 0.650 \text{ V}_{\text{SHE}}$). The films were grown under potentiostatic conditions on 100 nm thick polycrystalline Ru films, sputter deposited onto a 5nm Ta adhesion layer on top of the native oxide of a Si (001) wafer. Just before deposition, the electrode was cleaned by successive immersion in pure methanol for 1 min, 0.1 M NaOH for 30s and 0.25 M H_2SO_4 for 30s, all at room temperature, then thoroughly rinsed in MilliQ[®] water.

Film Characterization. Film thickness was calculated from the EQCM growth rate data, and confirmed by optical profilometry (Veeco Wyto NT1100). Alloy composition was determined by

energy dispersive spectroscopy (EDS) using a detector attached to a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM). The Cu and Au fractions were determined at an accelerating voltage of 20 kV, using the K line for Cu and the M line for Au. Growth from the sulfite solution yields incorporation of sulfur (S) impurities in the alloy; the fraction of incorporated S was evaluated using the K line. Film morphology was investigated using the FE-SEM described above. Crystal structure was determined by X-ray diffraction, using a Panalytical X'Pert diffractometer with Cu K α radiation ($\lambda=1.5418\text{\AA}$) in the $\theta/2\theta$ geometry. Peak positions and the corresponding full width at half maximum (FWHM) were quantified by using a double Voigt function to deconvolute the (111) peaks from the background; these data were then used to calculate the lattice parameter and grain size.

2. Results

2.1. Electrochemical Equilibria

Table S1. Equilibria and stability constants

Complexing agent		Equilibrium equations	Equilibrium constants(Log)	Equation No.
NH ₂ CH ₂ COO H (short for HL)		$H^+ + L^- \Leftrightarrow HL$	$K = 9.7$	1 [4]
	Dissociation	$HL + H^+ \Leftrightarrow H_2L^+$	$K = 2.46$	2 [4]
		$Cu^{2+} + L^- \Leftrightarrow [CuL]^+$	$K_1 = 8.11$	3 [4]
	Association with Cu ²⁺	$Cu^{2+} + 2L \Leftrightarrow [CuL_2]$	$\beta_2 = 14.43$	4 [4]
		$[CuL]^+ + H^+ \Leftrightarrow [CuHL]^{2+}$	$\beta = 2.92$	5 [5]

Table S1 shows the relevant equilibria for glycine and its complexes with Cu²⁺ that have been considered in the determination of the free Cu²⁺ concentration as well as the published stability constants.

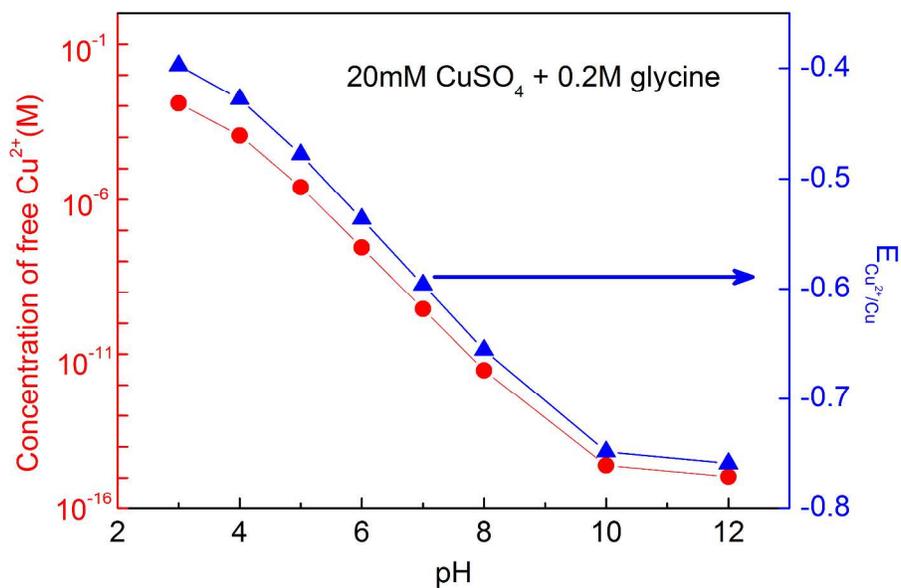
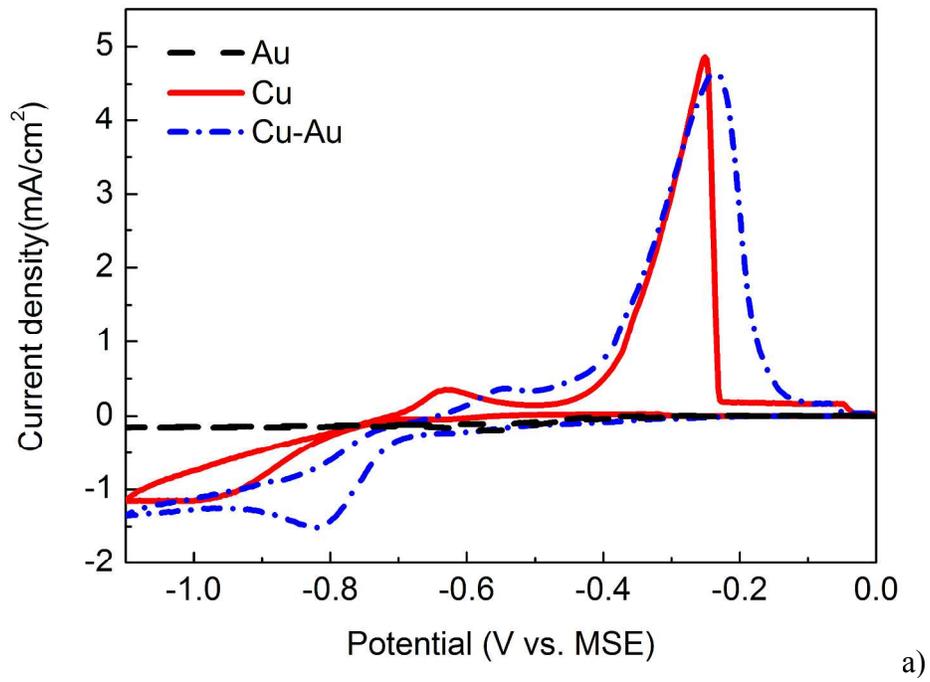


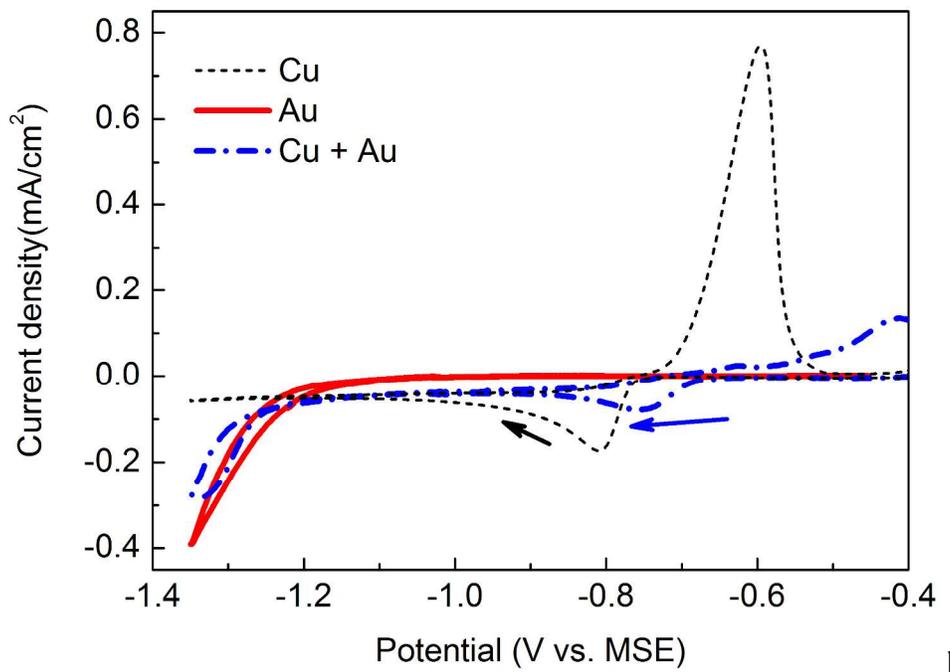
Figure S1. Concentration of free Cu²⁺ and corresponding redox potential as a function of pH in a solution containing 20mM CuSO₄ + 0.2M glycine.

Figure S1 shows the concentration of [Cu²⁺] and the corresponding calculated redox potential for the redox reaction Cu²⁺/Cu as a function of pH in an electrolyte containing 20mM CuSO₄ and 0.2M glycine. As can be seen, the redox potential can be controlled by manipulating pH.

Figure S2 below shows the cyclic voltammetry data for the two electrolytes used in this paper; these data complement the EQCM data shown in Figures 1a) and 2a) in the paper.



a)



b)

Figure S2. CV data (current density vs. potential) for: a) EN electrolyte; b) sulfite electrolyte.

References

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