Supporting information for:

Environment effects upon electrodeposition of thin film copper oxide nanomaterials

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Table S4. Table of data for quantitative nanocube analysis

Pt *vs* Cu wire counter electrode on electrodeposition

The effect of using a Pt counter *vs* Cu counter was investigated on the 30 cycle $t_O > t_R$ deposition in 5 mM $Cu(Cl)_2$, 5 mM NaCl system. The quantitatively measured nanocube size and nanocube concentration is displayed below.

Table S1. Table of data showing the difference in nanocube size and nanocube concentration with choice of counter electrode.

Counter electrode	Nanocube size / nm	Nanocube concentration ($\times 10^8$) / cm^{-2}
Cu	134 ± 15	3.1 ± 0.2
Pt	188 ± 18	1.3 ± 0.6

EIS analysis of altering electrolyte concentration

Table S2. Table of data for Electrochemical Impedance Spectroscopic analysis of 5 mM $Cu(Cl)_2$ in the presence of either 5 mM NaCl or 50 mM NaCl.

Copper System (electrolyte)	R_S / Ω	R_{ET} / Ω
$CuCl_2$ + 5 mM NaCl	614 ± 5	790 ± 13
$CuCl_2$ + 50 mM NaCl	253 ± 2	580 ± 9

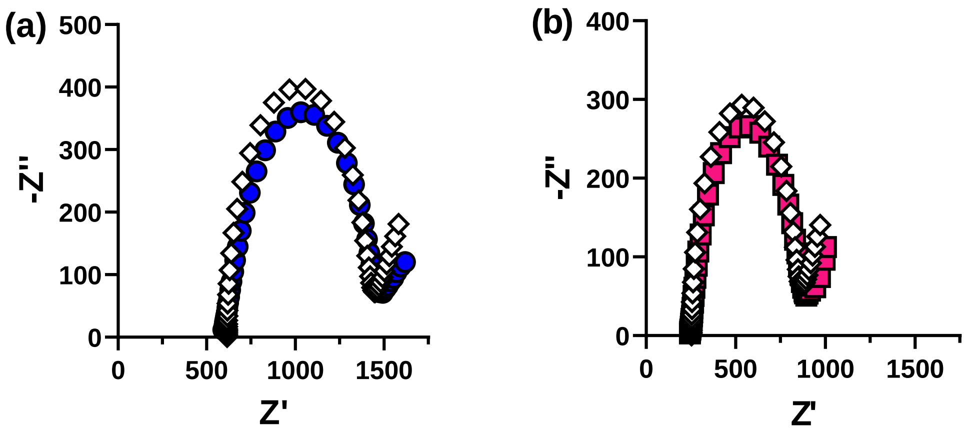


Figure S1 – Electrochemical Impedance Spectra of 5 mM $CuCl_2$ in the presence of (a) 5 mM and (b) 50 mM NaCl on ITO-coated glass substrate working electrode using a Cu wire counter and a Ag/AgCl (3 M NaCl) reference electrode.

Deposition data for 5 mM $CuCl_2$ with either 5 mM or 50 mM NaCl

5 mM $CuCl_2$ and 5 mM NaCl

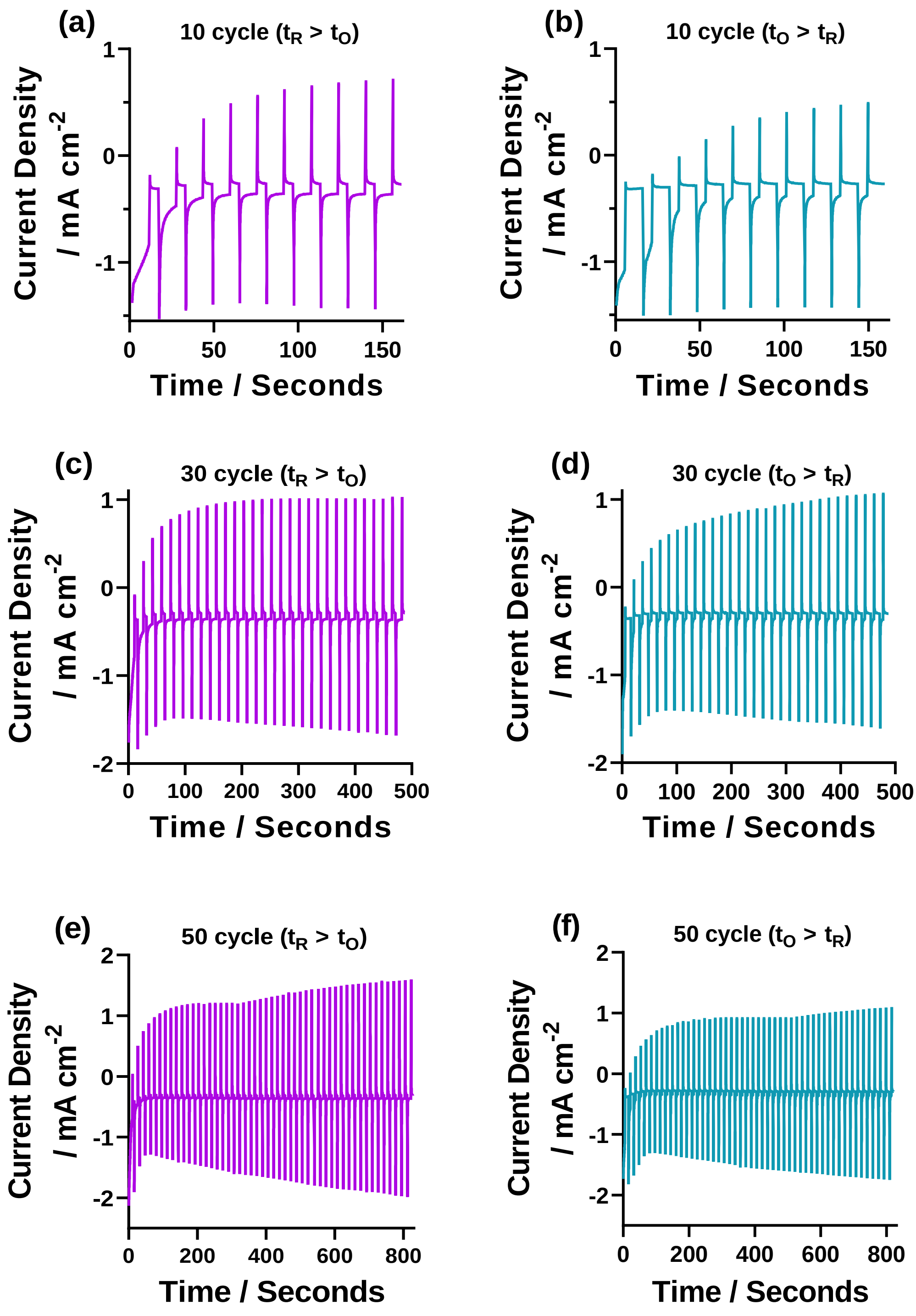


Figure S2 – Electrochemical deposition of Cu thin film for the 5 mM $Cu(Cl)_2$ with 5 mM NaCl system. Deposition was performed using chronoamperometry with -0.8 V (reducing potential) and -0.15 V (oxidising potential) *vs* ag/AgCl, with a 10 s : 5 s ratio of deposition time, where t_R

> t_O corresponds to a t_R = 10 s and t_O = 5 s and t_O > t_R corresponds to t_R = 5 s and t_O = 10 s for (a, b) 10 cycles, (c, d) 30 cycles and (e, f) 50 cycles for (a, c, e) t_R > t_O and (b, d, f) t_O > t_R.

5 mM $CuCl_2$ and 50 mM NaCl

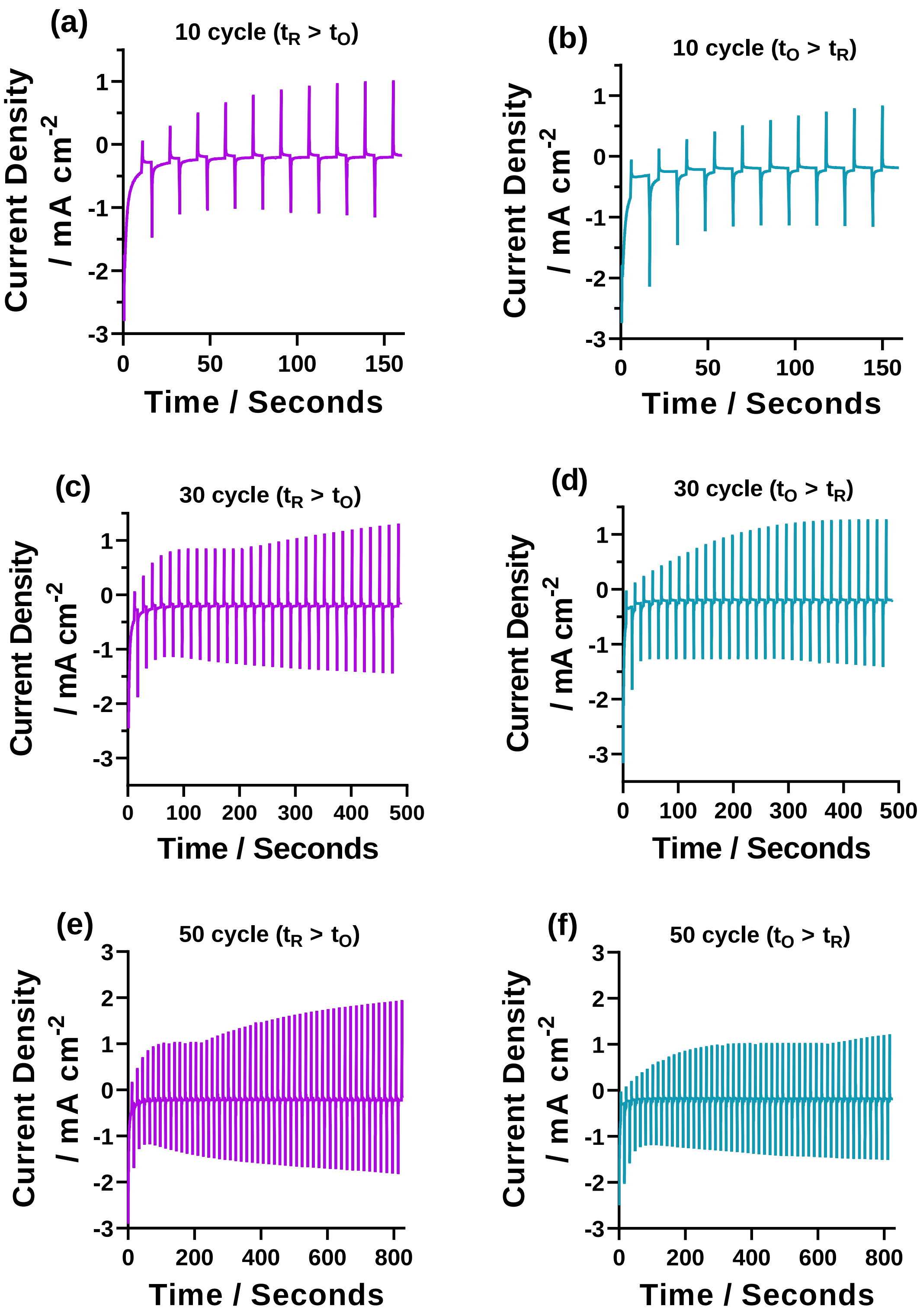


Figure S3 - Electrochemical deposition of Cu thin film for the 5 mM $Cu(Cl)_2$ with 50 mM NaCl system. Deposition was performed using chronoamperometry with -0.8 V (reducing potential) and -0.15 V (oxidising potential) *vs* ag/AgCl, with a 10 s : 5 s ratio of deposition time, where t_R

> t_O corresponds to a t_R = 10 s and t_O = 5 s and t_O > t_R corresponds to t_R = 5 s and t_O = 10 s for (a, b) 10 cycles, (c, d) 30 cycles and (e, f) 50 cycles for (a, c, e) t_R > t_O and (b, d, f) t_O > t_R.

Analysis of thin film Cu-nanomaterial deposition

pXRD

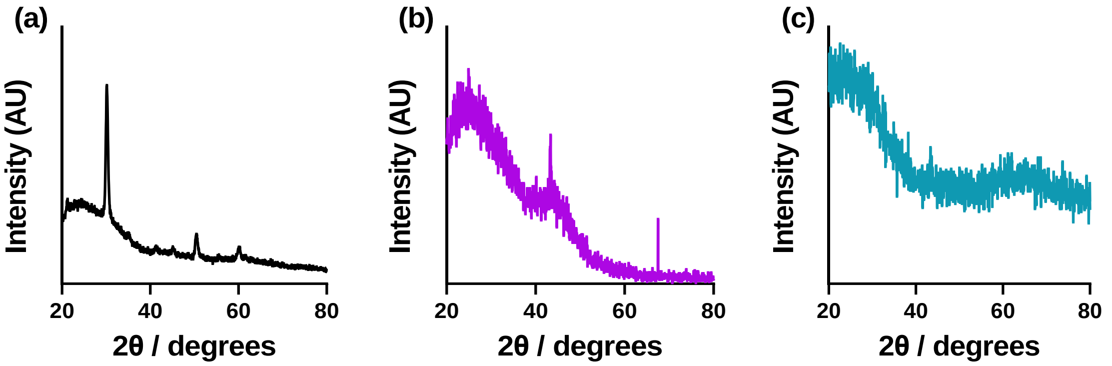


Figure S4. Figure showing the pXRD patterns for (a) bare ITO-coated glass electrodes and after electrodeposition of (b) 30 cycle t_R > t_O and (c) 30 cycle t_O > t_R.

Raman Spectroscopy

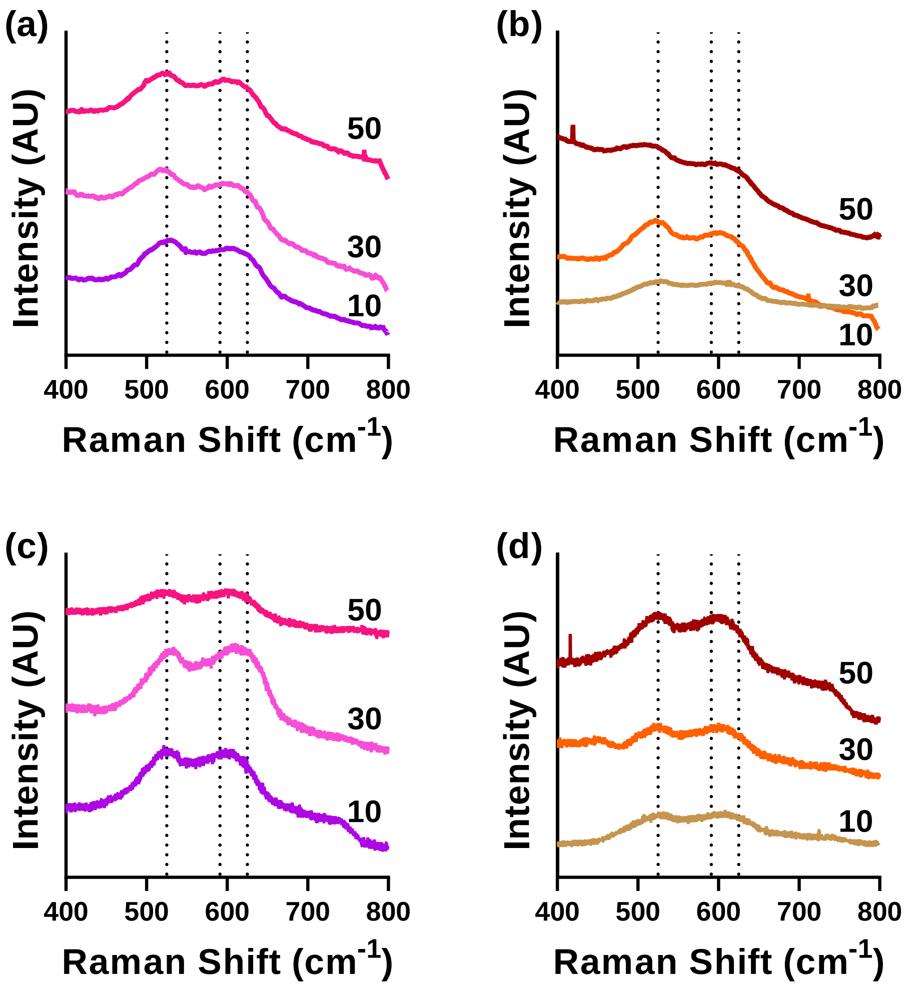


Figure S5 – Raman spectra measured for 5 mM $CuCl_2$ with (a, b) 5 mM NaCl and (c, d) 50 mM NaCl where (a, c) are t_R 10 s and t_O 5 s and (b, d) t_O 10 s and t_R 5 s for either 10, 30 or 50 cycles as shown. Recorded using a 633 nm wavelength laser at 50 x magnification and 25 % power (note the y-axis has been manually offset and is not representative of recorded intensity). Ticked lines are 525 and 625 which have been previously reported for Cu_2O.[1]

Cross-section SEM

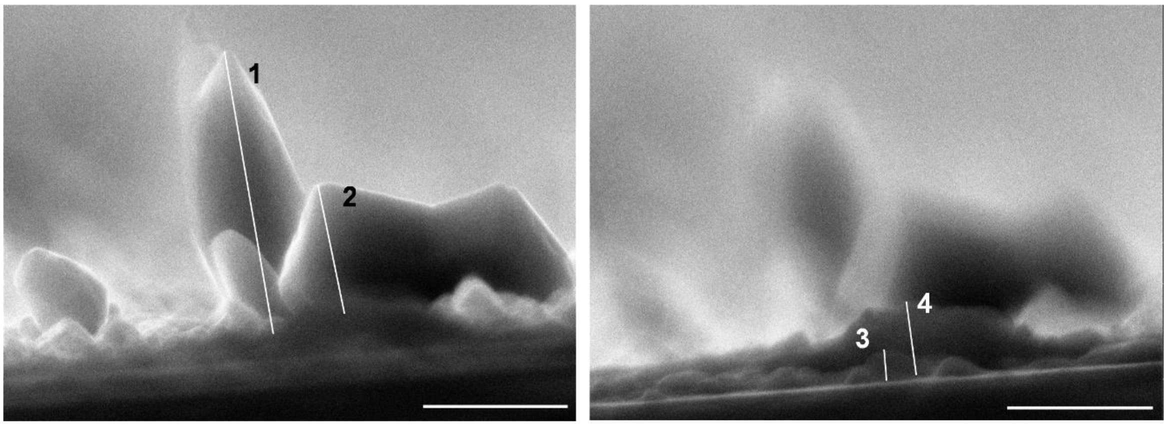


Figure S6. Cross section SEM images of the 30 cycle $t_O > t_R$ deposition in 5 mM $Cu(Cl)_2$, 5 mM NaCl system. Where the scale bars are 1 μm and the measured distances 1 = 1.98 μm, 2 = 0.90 μm, 3 = 218 μm and 4 = 532 μm.

100 cycle deposition

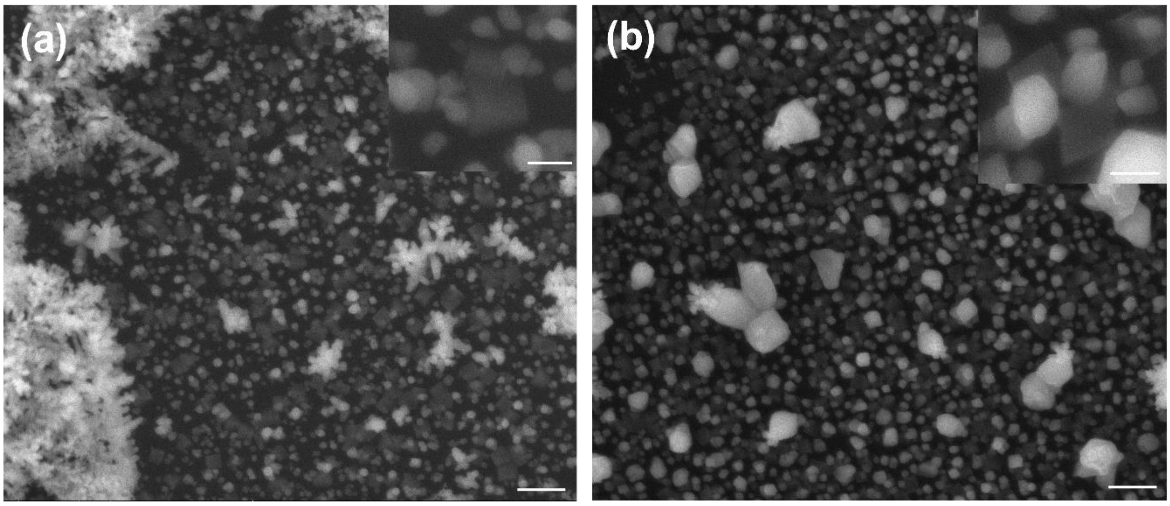


Figure S7. Figure showing representative secondary electron SEM images of electrodeposited copper electrodes from the 5 mM $CuCl_2$ and 5 mM NaCl solution with 100 cycles of (a) $t_R > t_O$ and (b) $t_O > t_R$. Scale bars for main images represent 1 µm, inset scale bars 250 nm.

SEM analysis of the 5 mM $CuCl_2$, 50 mM NaCl system

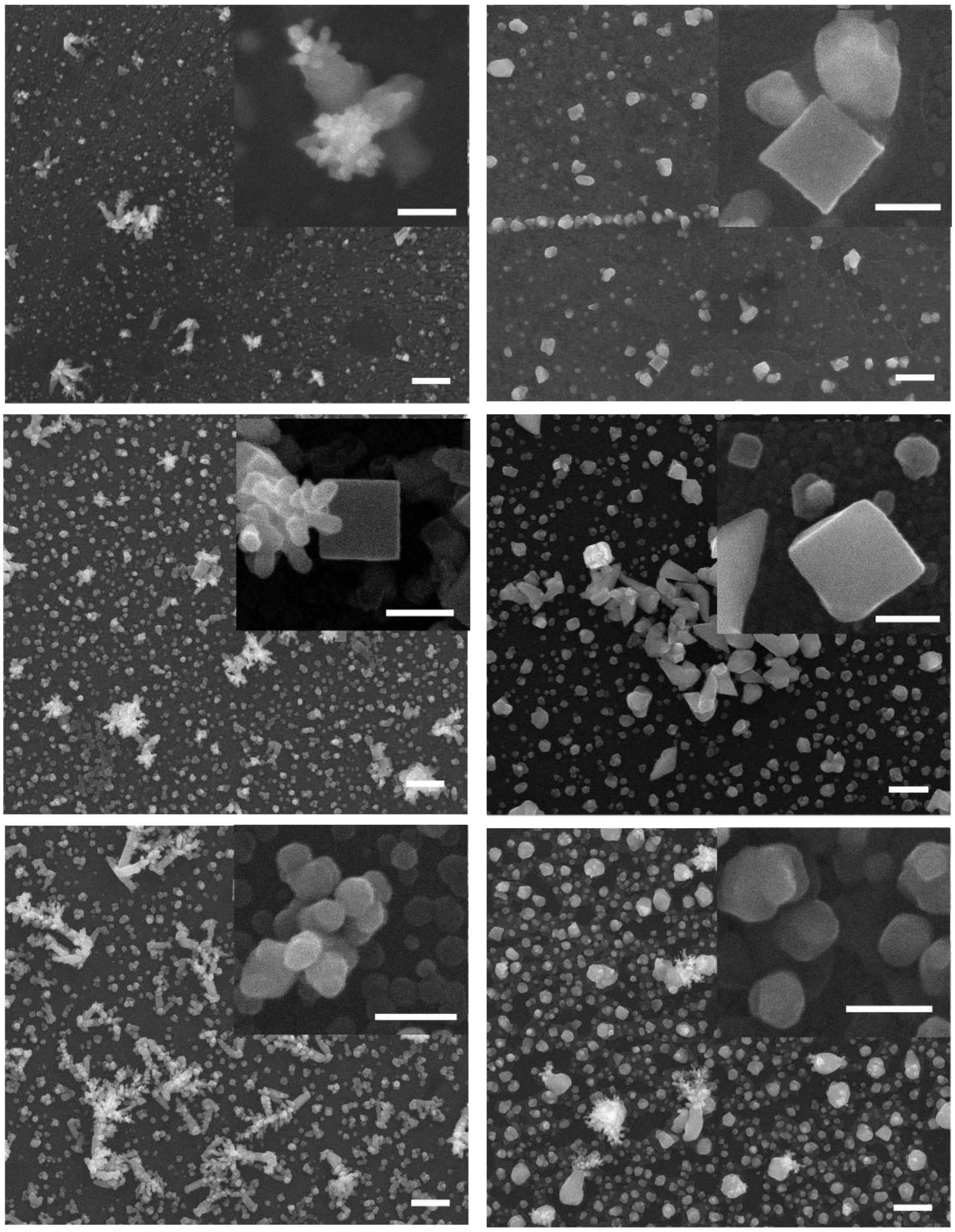


Figure S8. Figure showing representative secondary electron SEM images of electrodeposited copper electrodes from the 5 mM $CuCl_2$ and 50 mM NaCl solution with (a, b) 10 cycles, (c, d) 30 cycles and (e, f) 50 cycles where (a, c, e) $t_R > t_O$ and (b, d, f) $t_O > t_R$. All scale bars of the images represent 1 µm, insets 250 nm.

Mimicking the high resistance environment with the high concentration system

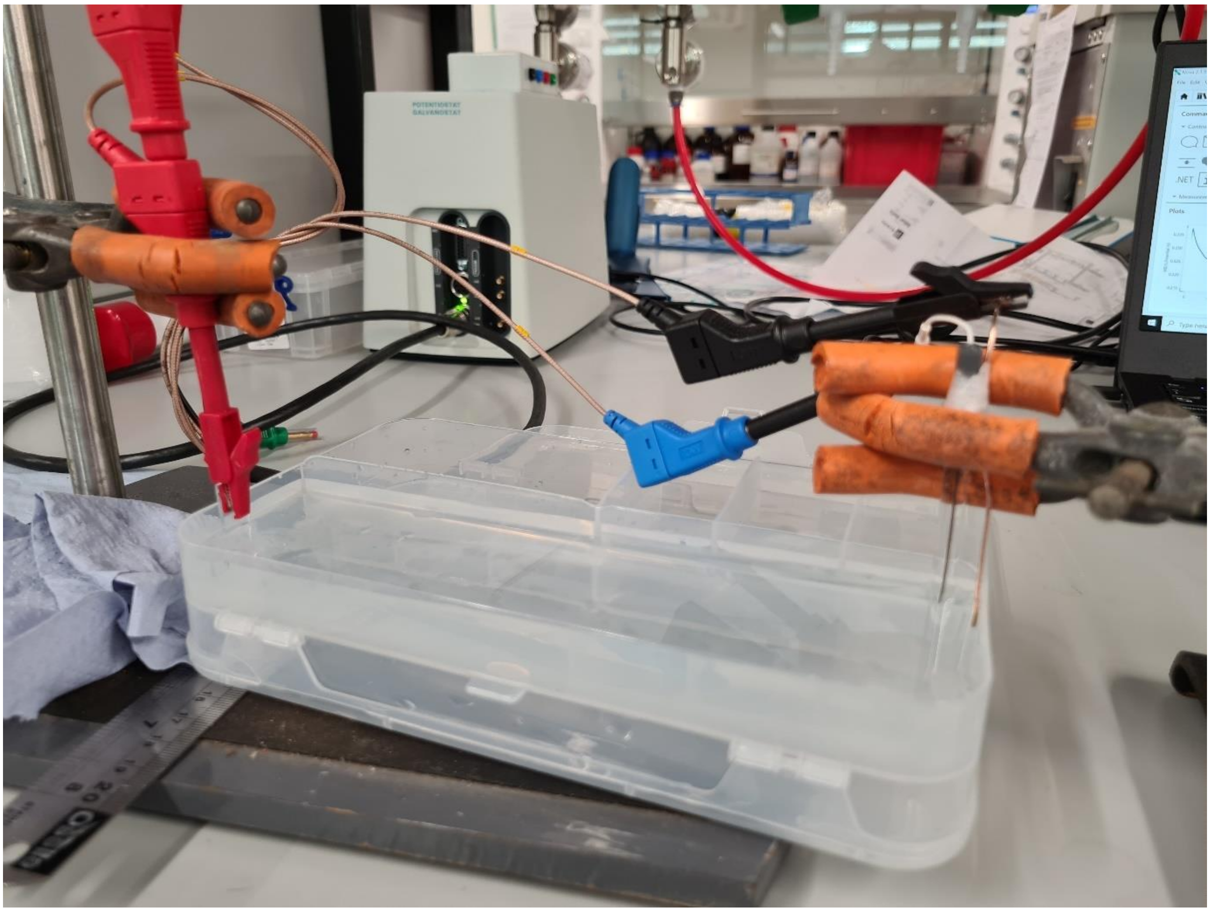


Figure S9. Photograph of the setup where increasing inter-electrode separation was measured.

Electrochemistry of increasing inter-electrode separation

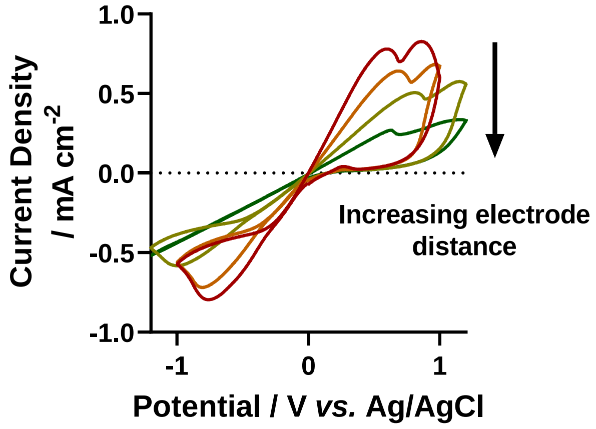


Figure S10. Cyclic voltammograms (CVs) of 5 mM $CuCl_2$ in the presence of 50 mM when increasing inter-electrode separation between the ITO-coated glass substrate working electrode, and the copper wire counter electrode and Ag/AgCl (3 M NaCl) reference electrode. Here red is 2 cm, brown is 5 cm, light green is 10 cm and dark green is 20 cm. CVs were recorded with a scan rate of 50 mV s^{-1}.

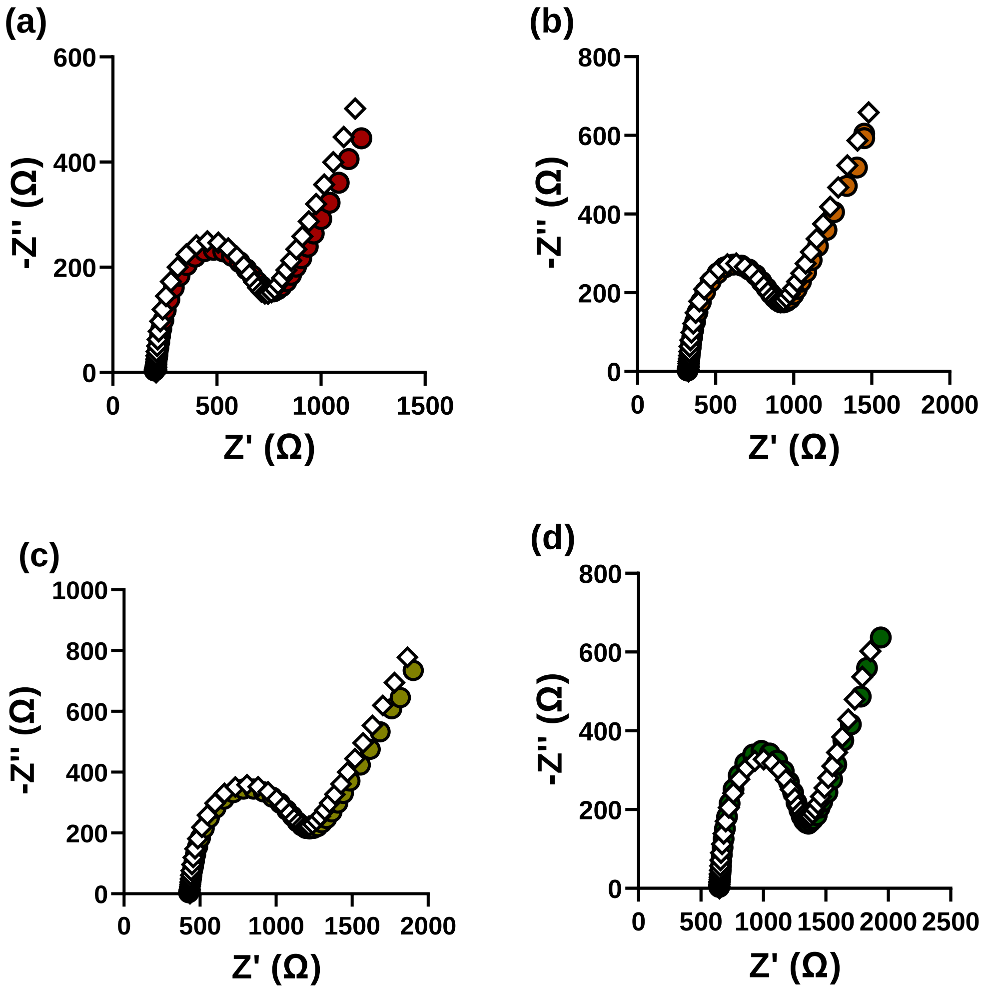


Figure S11. Electrochemical Impedance Spectra fitting for 5 mM $CuCl_2$ in the presence of 50 mM NaCl with increasing inter-electrode distance for (a) 2 cm, (b) 5 cm, (c) 10 cm and (d) 20 cm. Using ITO-coated glass substrate working electrode, a Cu wire counter, and a Ag/AgCl (3 M NaCl) reference electrode.

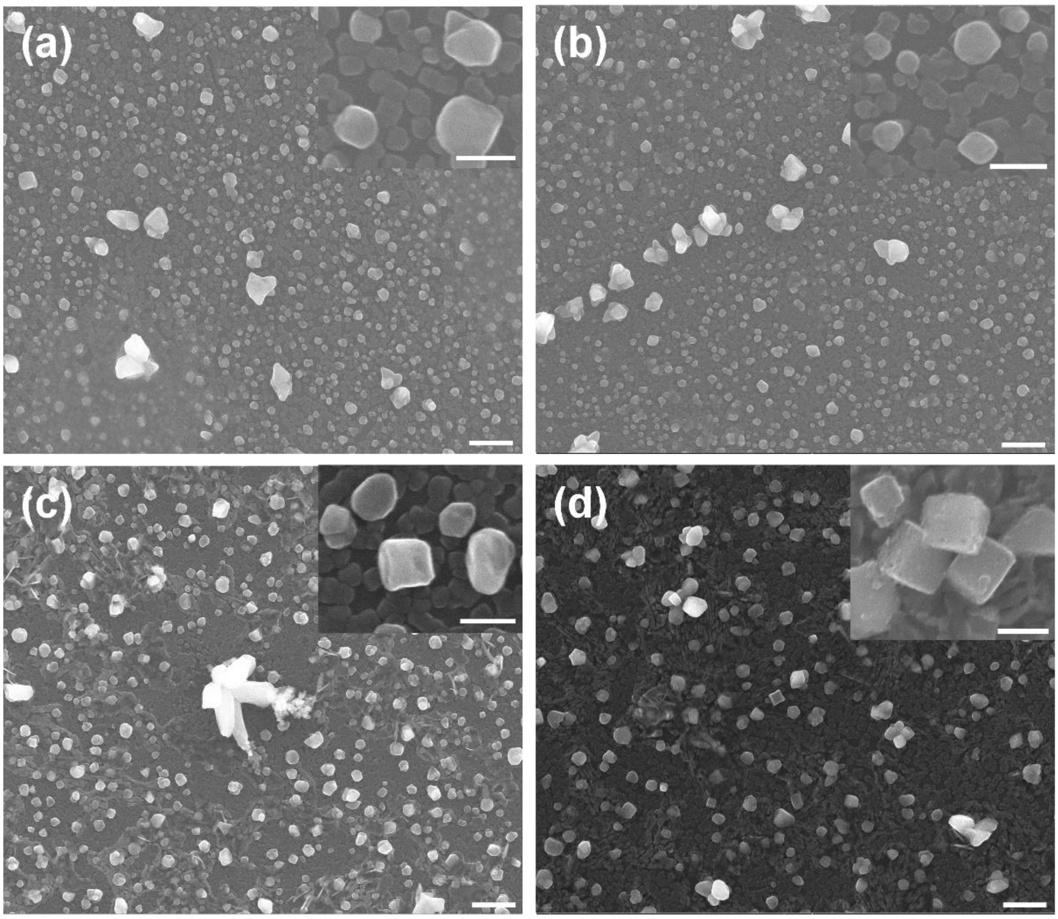


Figure S12. Representative SEM images of the 5 mM $CuCl_2$, 50 mM NaCl system with increasing inter-electrode separation between the working and counter and reference electrodes of (a) 2 cm, (b) 5 cm, (c) 10 cm and (d) 20 cm.

EIS fitting for the mixed anion systems

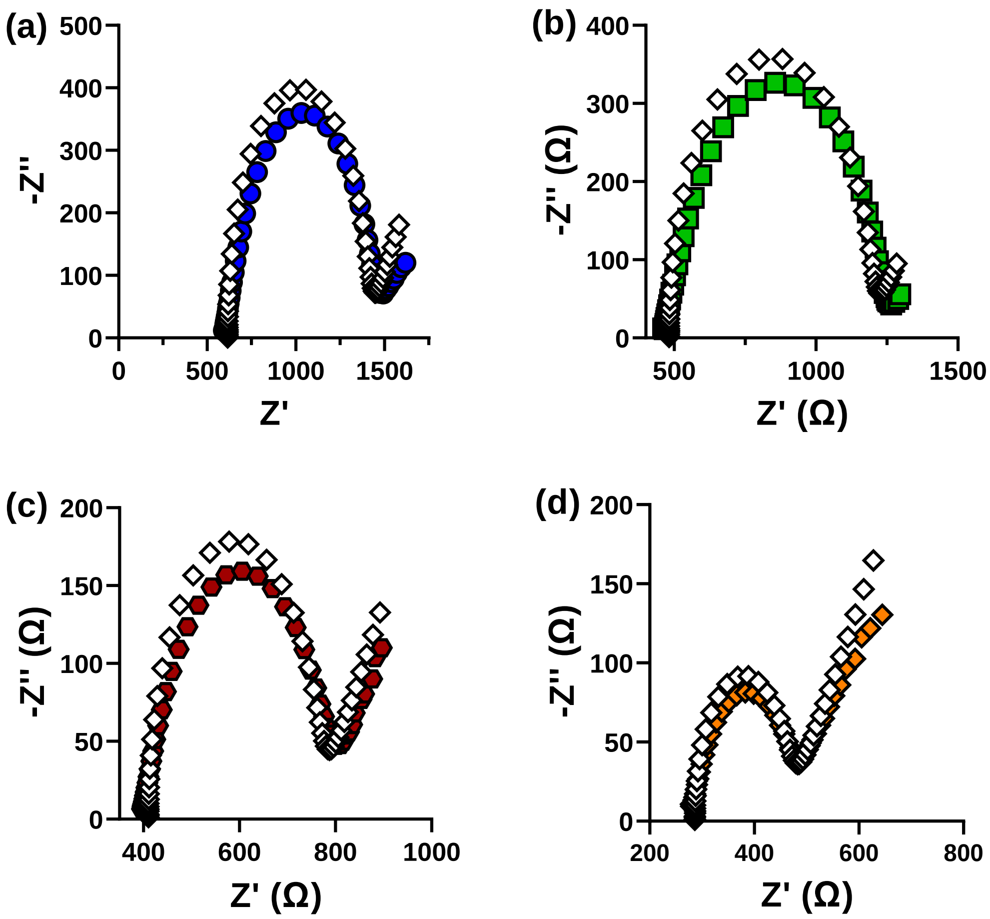


Figure S13. Electrochemical Impedance Spectra fitting for (a) 5 mM $CuCl_2$ (b) 5 mM $Cu(CH_3CO_2)_2$, (c) 5 mM $Cu(NO_3)_2$ and (d) $Cu(SO_4)$, in the presence of 5 mM NaCl (and 5 mM Na_2SO_4 in the $CuSO_4$ case). Using ITO-coated glass substrate working electrode, a Cu wire counter, and a Ag/AgCl (3 M NaCl) reference electrode.

Raman of mixed anion environment

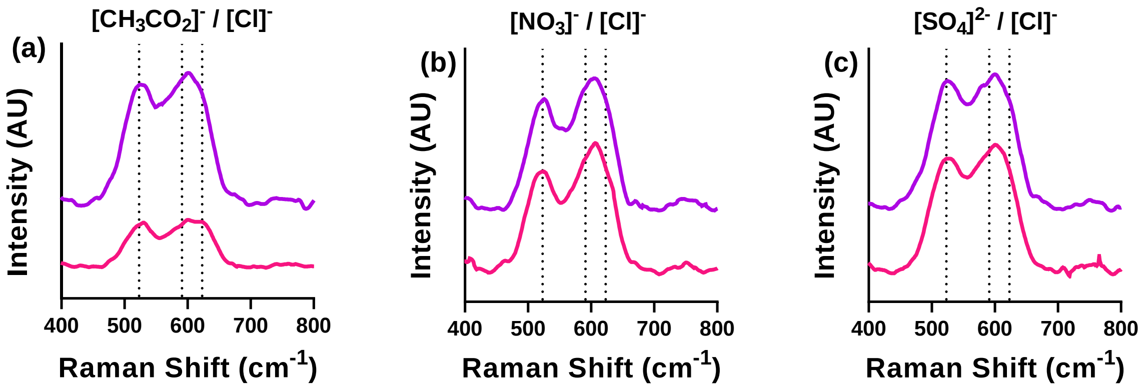


Figure S14. Raman spectra measured for (a) 5 mM $Cu(Cl)_2$ with 5 mM NaCl, (b) 5 mM $Cu(CH_3CO_2)_2$ with 5 mM NaCl, (c) 5 mM $Cu(NO_3)_2$ with 5 mM NaCl and (d) 5 mM $Cu(SO_4)$ with 5 mM NaCl and 5 mM Na_2SO_4. These films were deposited using either t_R 10 s and t_O 5 s (purple) or t_O 10 s and t_R 5 s (pink) for 30 cycles. Recorded using a 633 nm wavelength laser at 50 x magnification and 25 % power (note the y-axis has been manually offset and is not representative of recorded intensity). Ticked lines are 525 and 625 which have been previously reported for Cu_2O.[1]

X-ray photoelectron spectroscopy of mixed anion environments

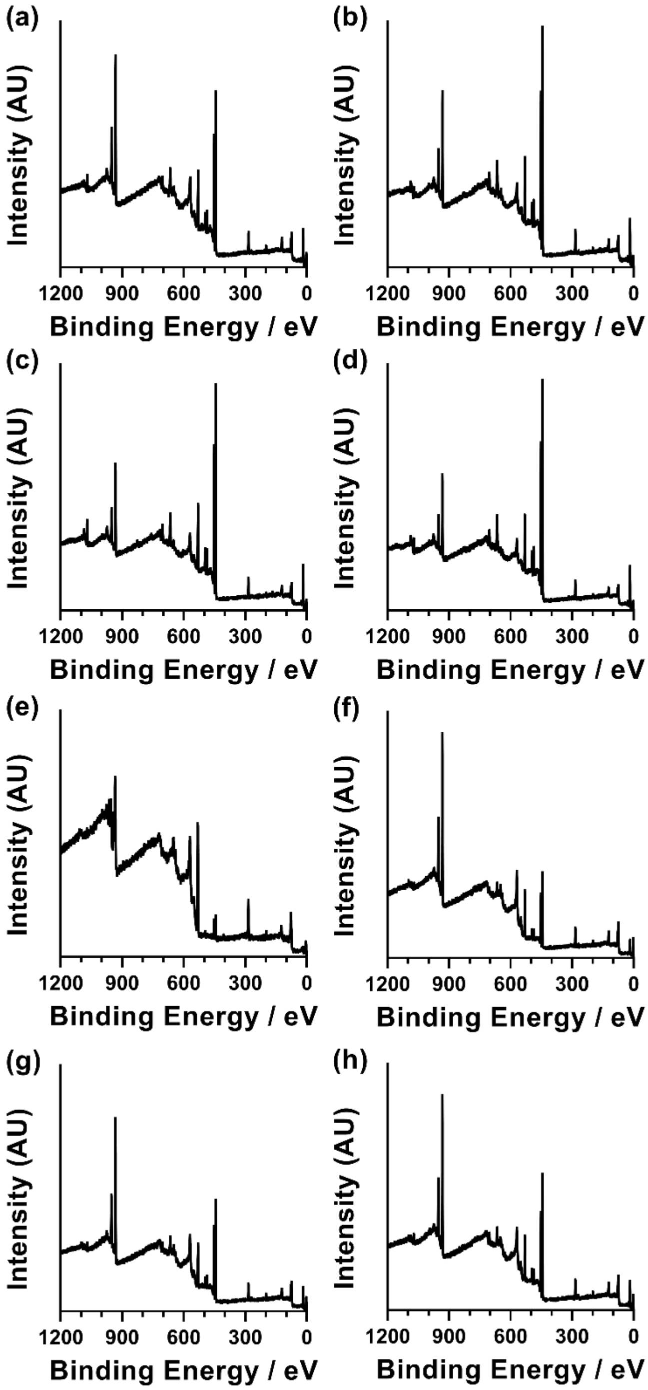


Figure 15. Figure showing the XPS survey spectra for thin film copper nanomaterial deposited using (a, b) $CuCl_2$, (c, d) $Cu(CH_3CO_2)_2$, (e, f) $Cu(NO_3)_2$ and (g, h) $CuSO_4$ salts, all in the presence of 5 mM NaCl. These depositions were through a 30-cycle step where (a, c, e, g) are t_R = 10 s and t_O = 5 s and (b, d, f, h) are t_R = 5 s and t_O = 10 s.

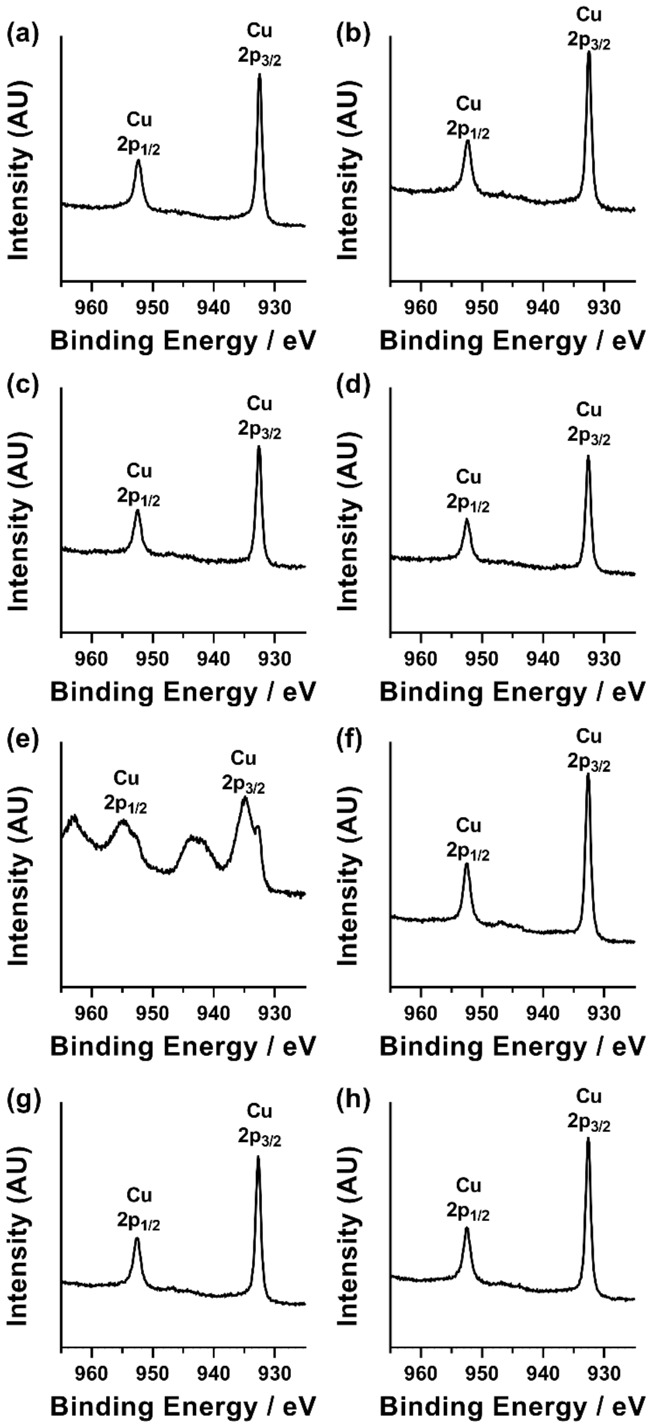


Figure 16. Figure showing the XPS Cu 2p spectra for thin film copper nanomaterial deposited using (a, b) $CuCl_2$, (c, d) $Cu(CH_3CO_2)_2$, (e, f) $Cu(NO_3)_2$ and (g, h) $CuSO_4$ salts, all in the presence of 5 mM NaCl. These depositions were through a 30-cycle step where (a, c, e, g) are t_R = 10 s and t_O = 5 s and (b, d, f, h) are t_R = 5 s and t_O = 10 s.

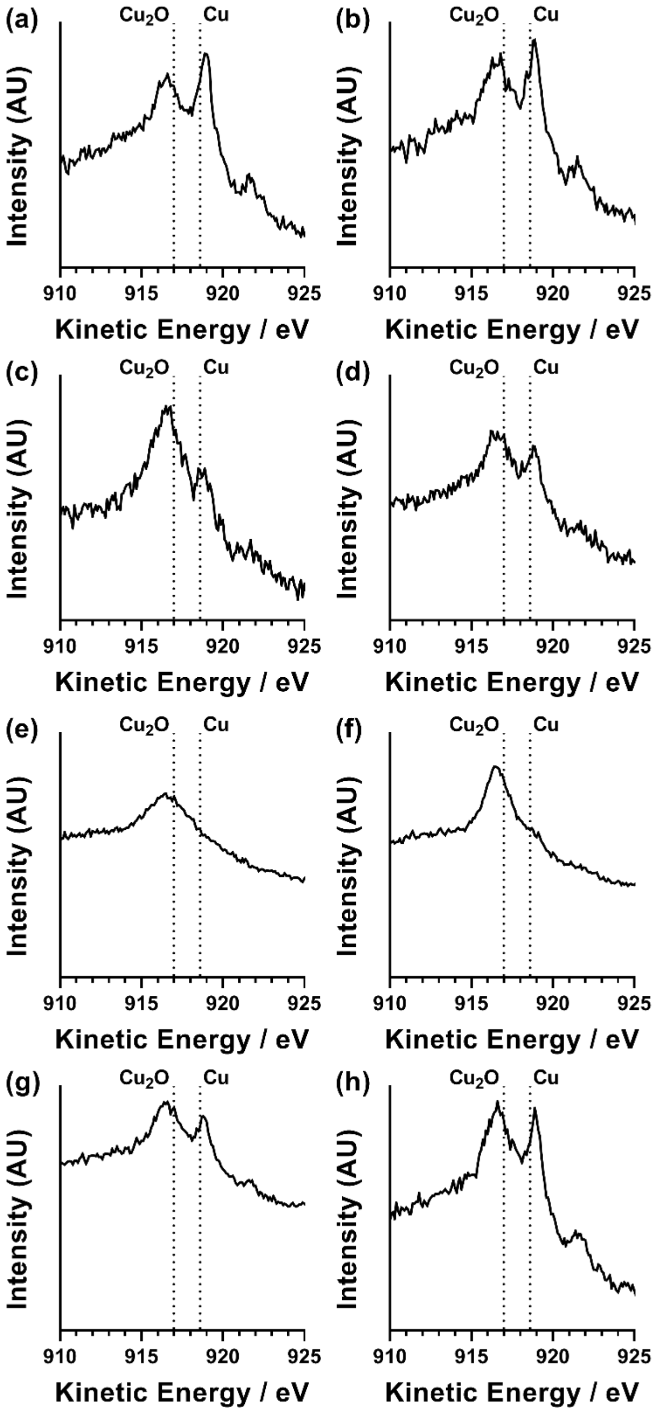


Figure 17. Figure showing the LMM Auger spectra for thin film copper nanomaterial deposited using (a, b) $CuCl_2$, (c, d) $Cu(CH_3CO_2)_2$, (e, f) $Cu(NO_3)_2$ and (g, h) $CuSO_4$ salts, all in the presence of 5 mM NaCl. These depositions were through a 30-cycle step where (a, c, e, g) are t_R = 10 s and t_O = 5 s and (b, d, f, h) are t_R = 5 s and t_O = 10 s.

EIS Fitting for mono-anionic environment electrochemical analysis

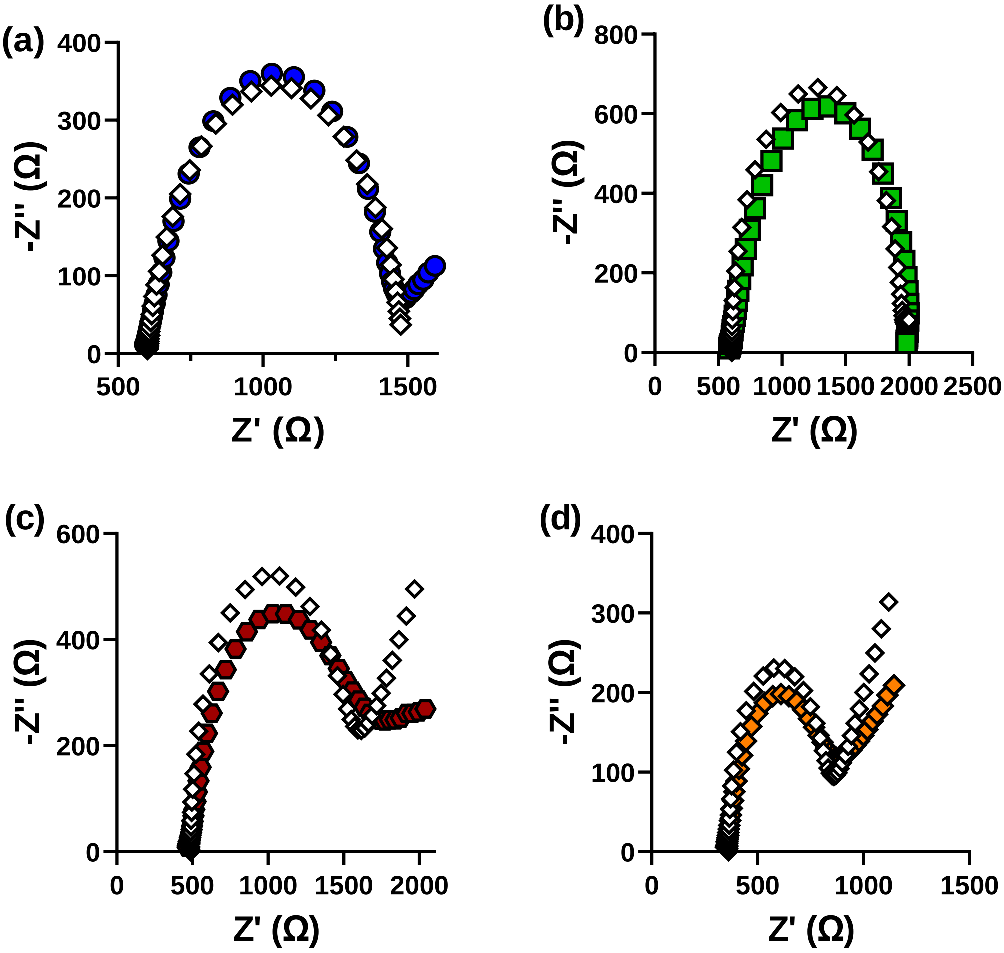


Figure S18. Electrochemical impedance spectroscopy (EIS) of 5 mM of various Cu salts (a) blue $Cu(Cl)_2$, (b) $Cu(CH_3CO_2)_2$, (c) $Cu(NO_3)_2$ and (d) $CuSO_4$ in the presence of 5 mM Na[A] where [A] represents the anion of the corresponding copper salt.

Raman analysis of mono-anionic environment depositions

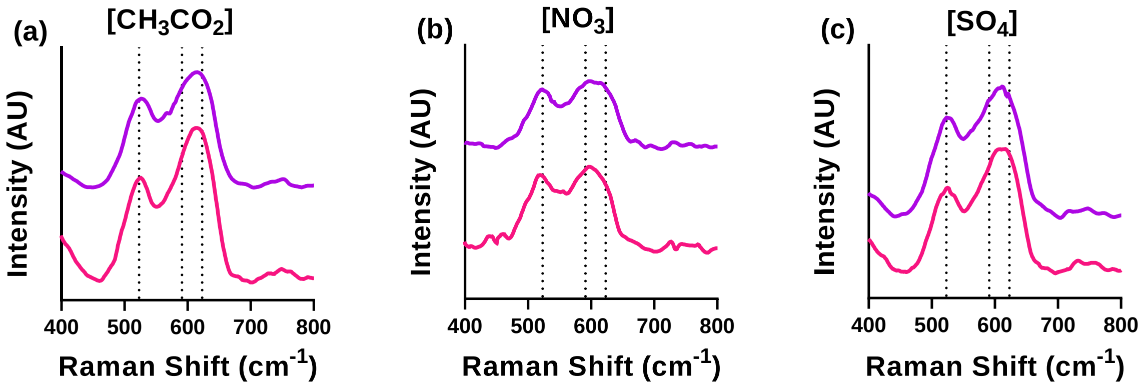


Figure S19. Raman spectra measured for 5 mM Cu[A] with 5 mM Na[A] mono anionic environments where (a) [A] = [CH_3CO_2], (b) 5 mM Cu(CH_3CO_2)$_2$ with 5 mM NaCl, (c) 5 mM Cu(NO_3)$_2$ with 5 mM NaCl and (d) 5 mM Cu(SO_4) with 5 mM NaCl and 5 mM Na_2SO_4. These films were deposited using either t_R 10 s and t_O 5 s (purple) or t_O 10 s and t_R 5 s (pink) for 30 cycles. Recorded using a 633 nm wavelength laser at 50 x magnification and 25 % power (note the y-axis has been manually offset and is not representative of recorded intensity). Ticked lines are 525 and 625 which have been previously reported for Cu_2O.[1]

X-ray Photoelectron Spectroscopy of mono-anionic environment depositions

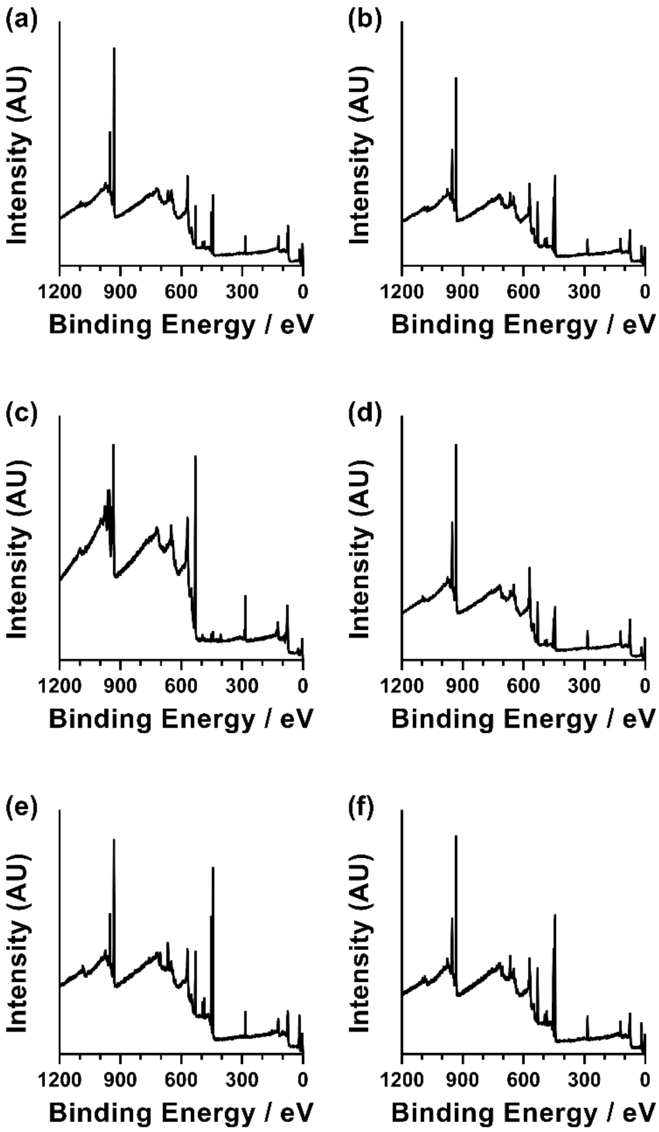


Figure S20. Figure showing the XPS survey spectra for thin film copper nanomaterial deposited using (a, b) $Cu(CH_3CO_2)_2$ + $NaCH_3CO_2$, (c, d), $Cu(NO_3)_2$ + $NaNO_3$ and (e, f) $CuSO_4$ + Na_2SO_4. These depositions were through a 30-cycle step where (a, c, e) are t_R = 10 s and t_O = 5 s and (b, d, f) are t_R = 5 s and t_O = 10 s.

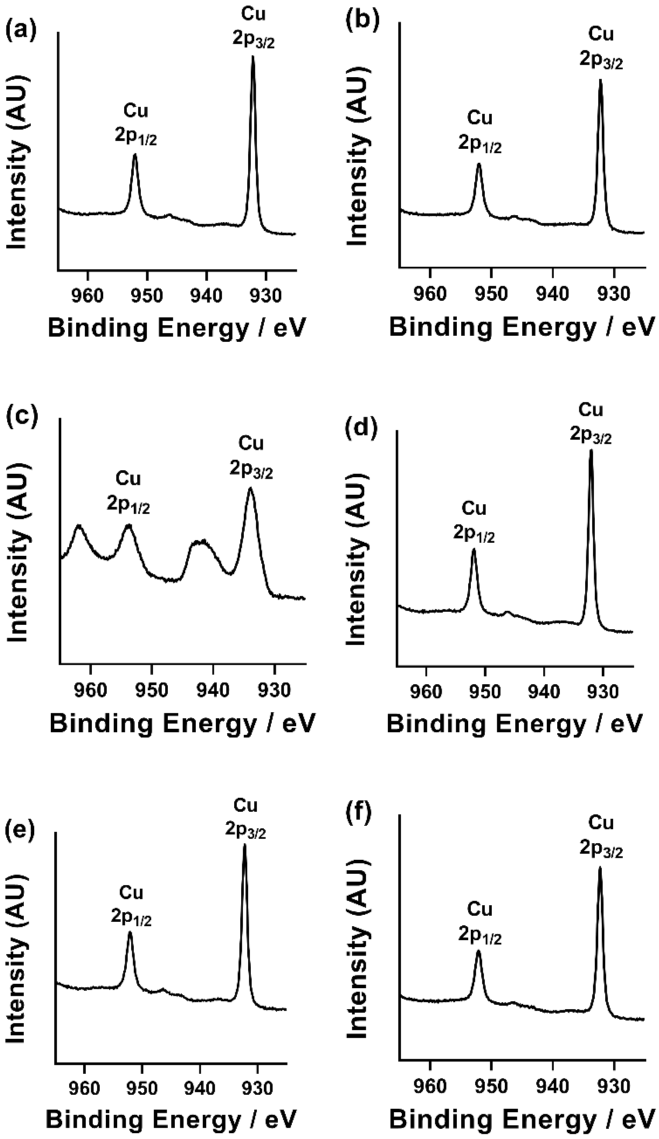


Figure S21. Figure showing the XPS Cu 2p spectra for thin film copper nanomaterial deposited using (a, b) $Cu(CH_3CO_2)_2$ + $NaCH_3CO_2$, (c, d), $Cu(NO_3)_2$ + $NaNO_3$ and (e, f) $CuSO_4$ + Na_2SO_4. These depositions were through a 30-cycle step where (a, c, e) are t_R = 10 s and t_O = 5 s and (b, d, f) are t_R = 5 s and t_O = 10 s.

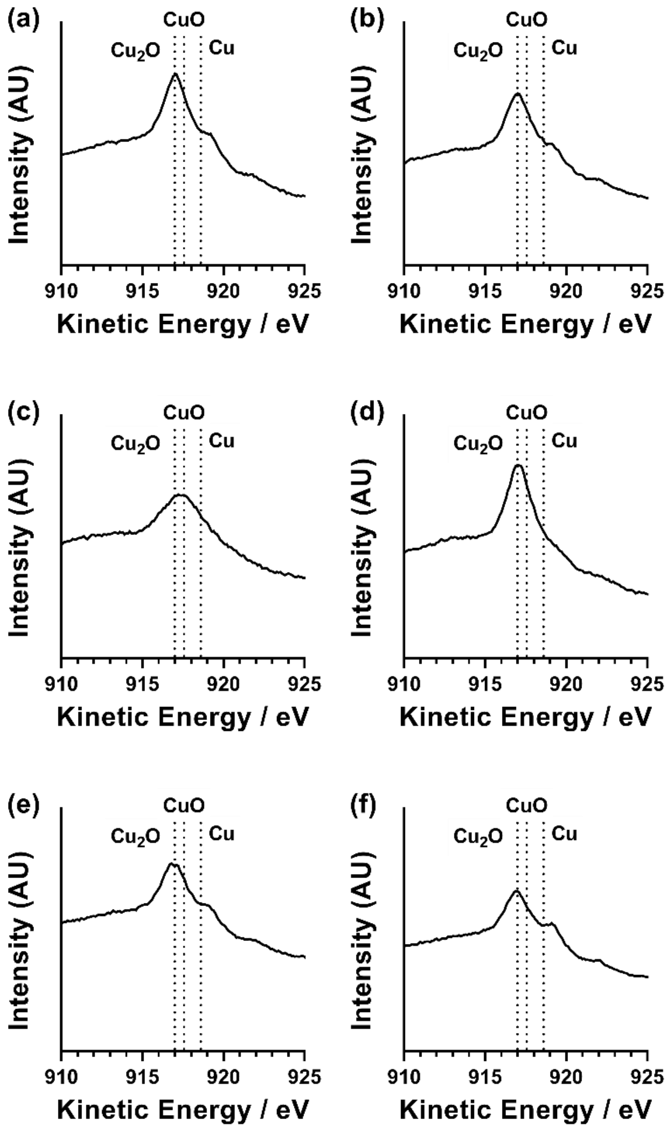


Figure S22. Figure showing the LMM Auger spectra for thin film copper nanomaterial deposited using (a, b) $Cu(CH_3CO_2)_2$ + $NaCH_3CO_2$, (c, d), $Cu(NO_3)_2$ + $NaNO_3$ and (e, f) $CuSO_4$ + Na_2SO_4. These depositions were through a 30-cycle step where (a, c, e) are t_R = 10 s and t_O = 5 s and (b, d, f) are t_R = 5 s and t_O = 10 s.

UV-Vis spectra

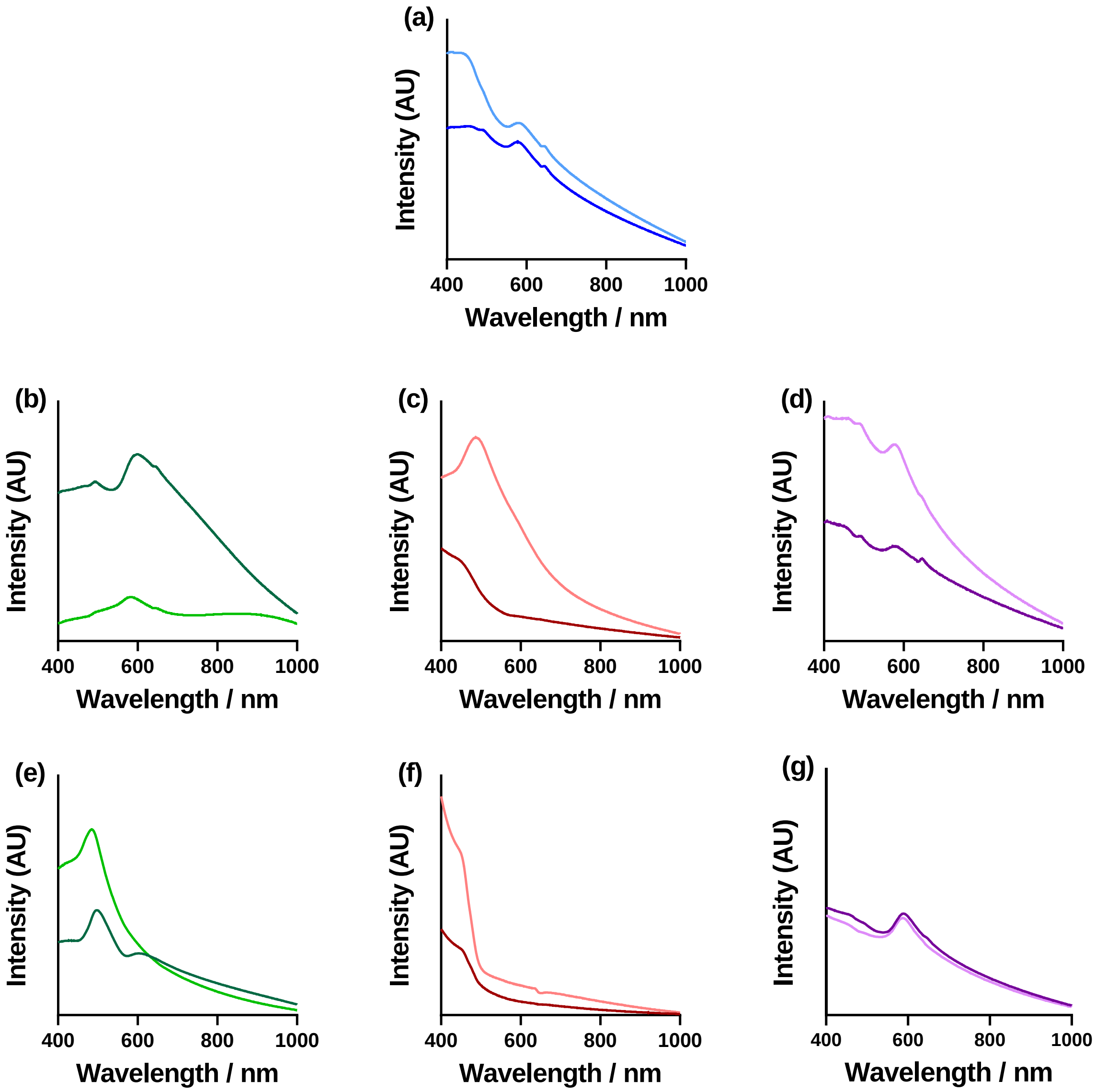
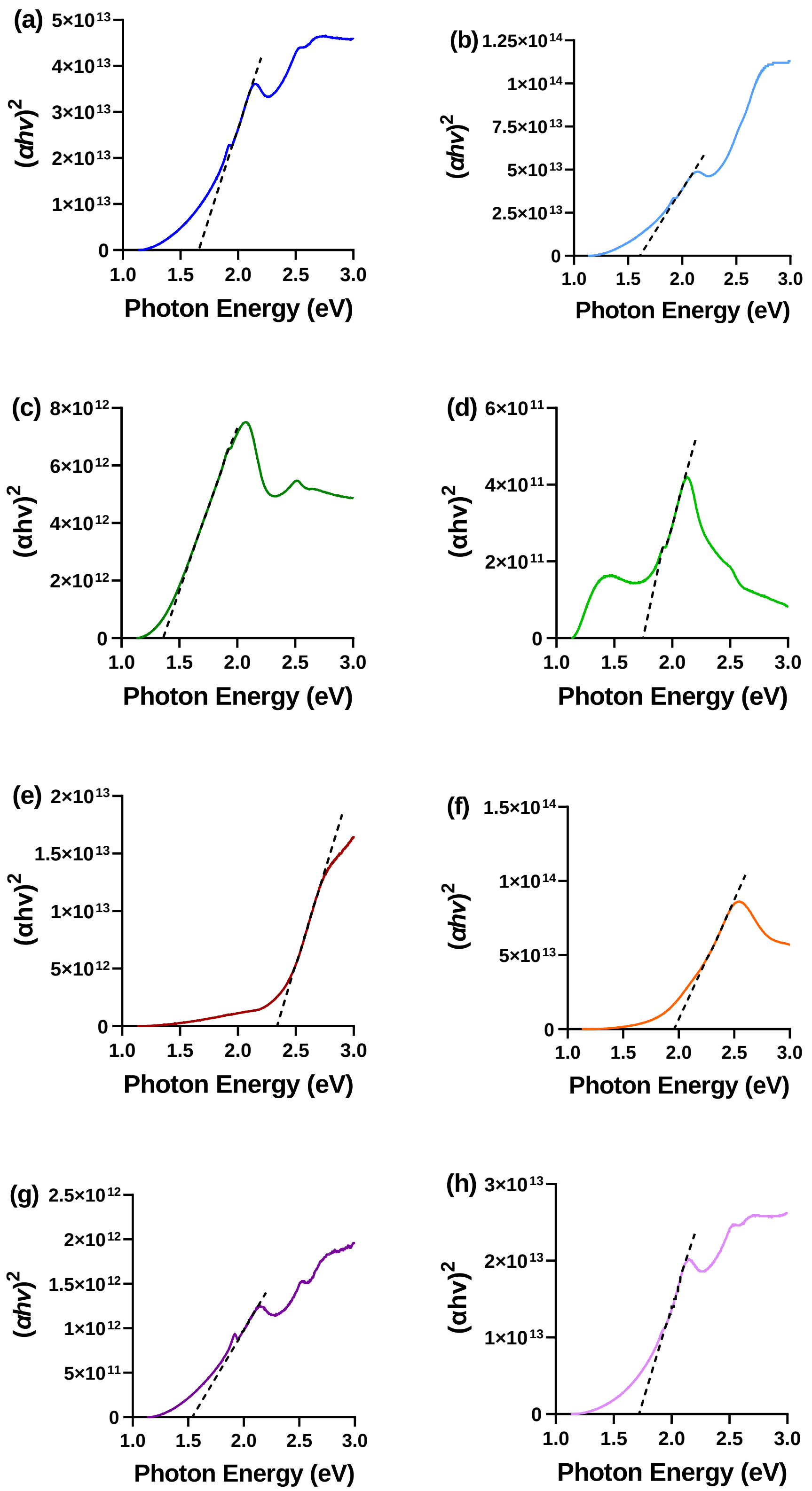


Figure S23. Figure showing measured UV-Vis spectra for thin films deposited through (dark) $t_R > t_O$ and (light) $t_O > t_O$ for (a) $CuCl_2$ + NaCl, (b) $Cu(CH_3CO_2)$ + NaCl, (c) $Cu(NO_3)$ + NaCl, (d) $CuSO_4$ + NaCl + Na_2SO_4, (e) $Cu(CH_3CO_2)$ + $NaCH_3CO_2$, (f) $Cu(NO_3)$ + $NaNO_3$ and (g) $CuSO_4$ + Na_2SO_4.

Band gap Tauc analysis



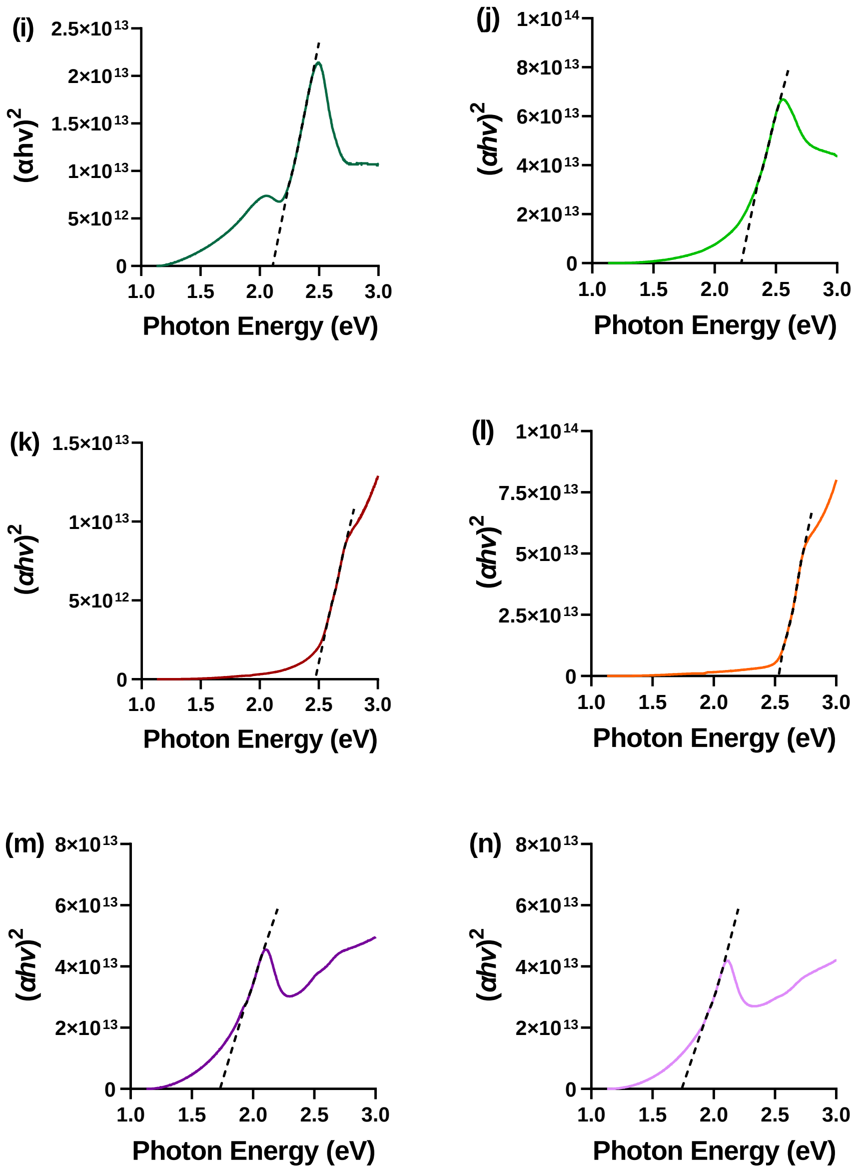


Figure S24. Tauc plots of all investigated systems where (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l), (m), (n).

Tables of data for all investigated systems

Table S3. Table of data for Ionic Strength, pH, Conductivity, V_{OCP}, R_S, R_{ET}, j_p, thin film resistance, thin film conductivity and thin film E_g

System	Ionic Strength* / mM	pH	Conductivity / mS cm^{-1}	V_{OCP} / mV *vs* Ag/AgCl	R_S / Ω cm^{-2}	R_{ET} / Ω cm^{-2}	j_p / mA cm^{-2}		Resistance† / Ω		Conductivity / S cm^{-1}		E_g / eV	
							(t_R > t_O)	(t_O > t_R)	(t_R > t_O)	(t_O > t_R)	(t_R > t_O)	(t_O > t_R)	(t_R > t_O)	(t_O > t_R)
$CuCl_2$ 5 mM NaCl	25	5.32	1.24	213 ± 6	614 ± 5	790 ± 13	1.03	1.06	91 ± 2	118 ± 18	813 ± 20	630 ± 94	1.66	1.60
$CuCl_2$ 50 mM NaCl	115	5.41	5.16	264 ± 3	253 ± 2	580 ± 9	1.31	1.25	156 ± 3	111 ± 1	476 ± 9	667 ± 4	-	-
$Cu(CH_3CO_2)_2$ 5 mM $CuCl_2$	25	5.85	1.07	155 ± 3	482 ± 4	712 ± 13	0.65	0.64	142 ± 13	140 ± 10	180 ± 16	183 ± 13	1.36	1.74
$Cu(NO_3)_2$ 5 mM NaCl	25	5.57	1.71	170 ± 9	410 ± 3	352 ± 6	0.81	0.84	127 ± 2	114 ± 5	390 ± 06	436 ± 18	2.34	1.96
$CuSO_4$ 5 mM NaCl 5 mM Na_2SO_4	60	5.53	2.06	176 ± 3	286 ± 2	178 ± 2	1.00	0.94	151 ± 7	115 ± 7	329 ± 30	430 ± 26	1.54	1.72
$Cu(CH_3CO_2)_2$ 5 mM $NaCH_3CO_2$	25	6.01	0.38	123 ± 6	605 ± 5	1325 ± 24	0.53	0.48	99 ± 11	164 ± 3	257 ± 27	156 ± 3	2.11	2.19
$Cu(NO_3)_2$ 5 mM $NaNO_3$	25	5.44	1.65	129 ± 3	488 ± 5	1004 ± 27	0.55	0.62	-	103 ± 1	-	482 ± 6	2.47	2.53
$CuSO_4$ 10 mM Na_2SO_4	80	5.73	2.62	119 ± 3	363 ± 3	446 ± 10	0.95	0.92	98 ± 1	120 ± 2	505 ± 7	412 ± 6	1.73	1.74

* Assuming full ionic dissociation
† Note this is absolute resistance and not resistance density in Ω / sq.

Table S4. Table of data for quantitative Cu_2O nanocube analysis

System	Average size of ($t_R > t_O$) nanocubes / nm	Average size of ($t_O > t_R$) nanocubes / nm	Coverage of ($t_R > t_O$) nanocubes / cm^{-2}	Coverage of ($t_O > t_R$) nanocubes / cm^{-2}
$CuCl_2$ 5 mM NaCl*	136 ± 21	134 ± 15	2.01 x10^8 ± 5.56 x10^7	3.10 x10^8 ± 1.83 x10^7
$CuCl_2$ 50 mM NaCl	/	/	/	/
$Cu(CH_3CO_2)_2$ 5 mM $CuCl_2$	392 ± 55	/	5.73 x10^7 ± 2.92 x10^6	/
$Cu(NO_3)_2$ 5 mM NaCl	/	202 ± 52	/	6.29 x10^8 ± 4.53 x10^7
$CuSO_4$ 5 mM NaCl 5 mM Na_2SO_4	/	/	/	/
$Cu(CH_3CO_2)_2$ 5 mM $NaCH_3CO_2$	/	/	/	/
$Cu(NO_3)_2$ 5 mM $NaNO_3$	/	181 ± 2	/	1.13 x10^9 ± 1.00 x10^8
$CuSO_4$ 10 mM Na_2SO_4	/	104 ± 14	/	7.28 x10^8 ± 7.29 x10^7

- All Cu salts are 5 mM concentration

* The size and coverage were calculated from the 30-cycle deposition