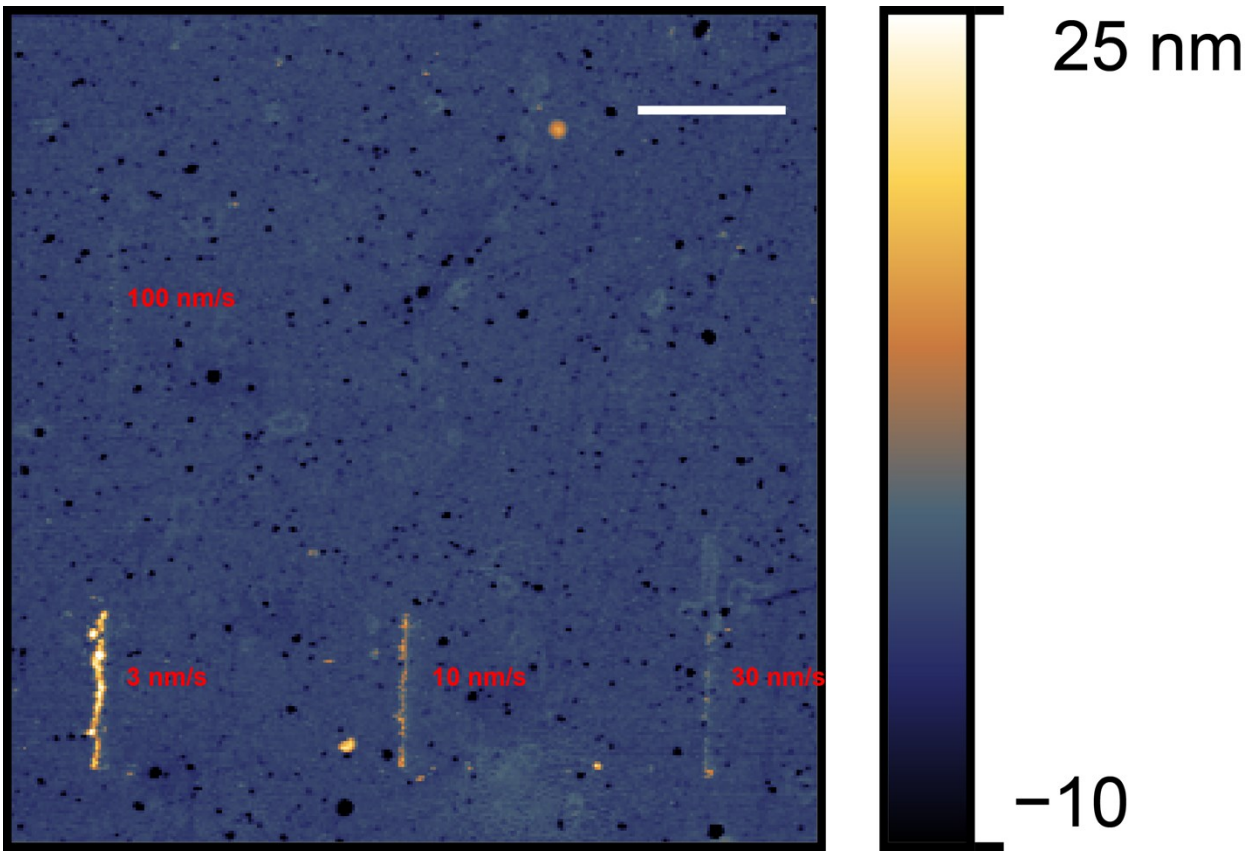
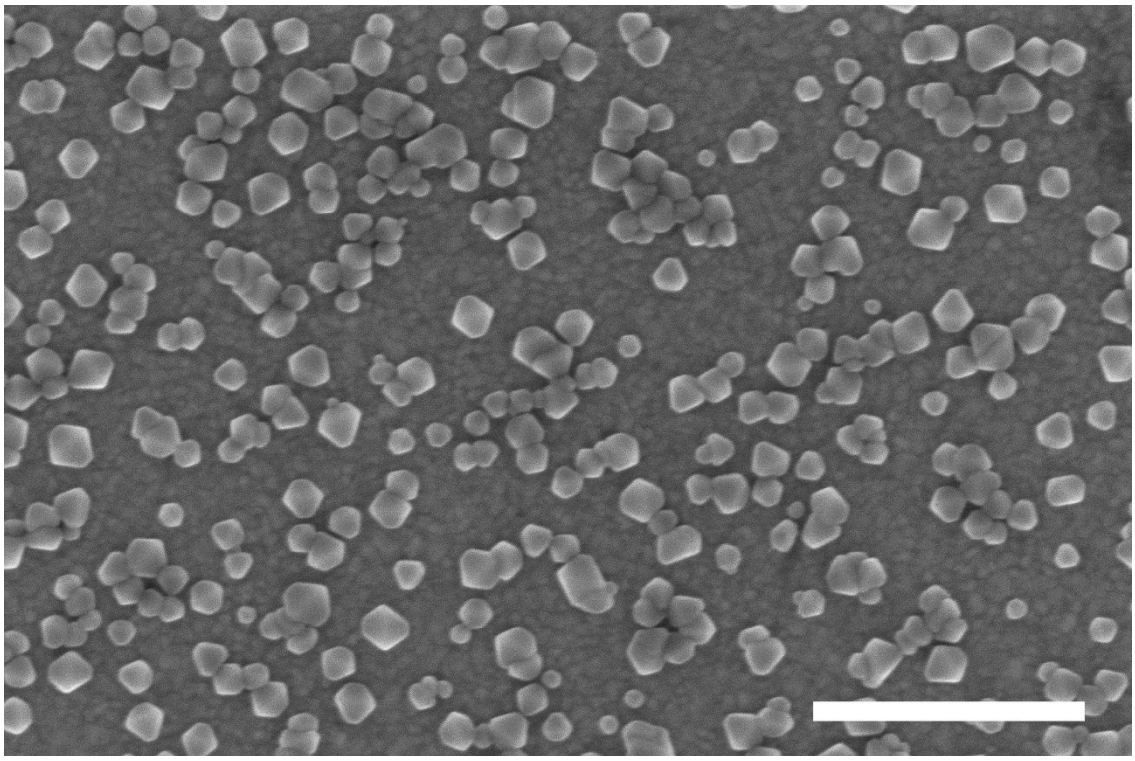
Electronic Supplementary Material (ESI) for CrystEngComm.

SI-1. Nanoscale deposition as a function of tip translation speed.

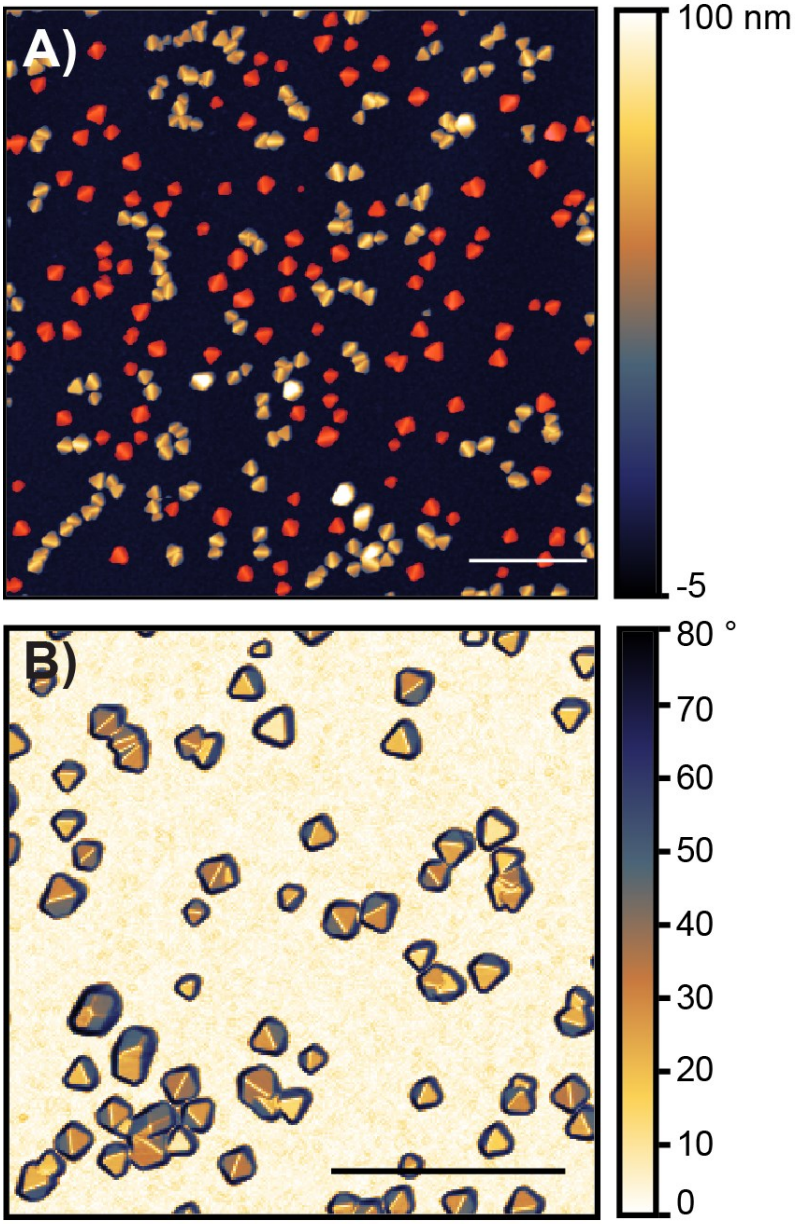


Supplementary Figure 1-1.
AFM topography image, obtained ex-situ with a ScanAsyst-Air tip, of written copper lines for the determination of the projected area and deposited volume as reported in Figure 1 in the main text. The lines were written by translating the AFM nano-electrode along a 1 μm long path, while applying a bias potential. Each line was written at a different translation speed, 3, 10, 30, and 100 nm/s respectively.
The raw image was treated to obtain a height of 0 nm for the flat surface. A mask on the image was applied with a height threshold value of 2 nm, and the projected area and volume were then determined for each copper line using the statistical quantities tool in the Gwyddion software. The scalebar is 1 μm.

SI-2. Copper deposition from 100 mM $CuSO_4$ (aq)



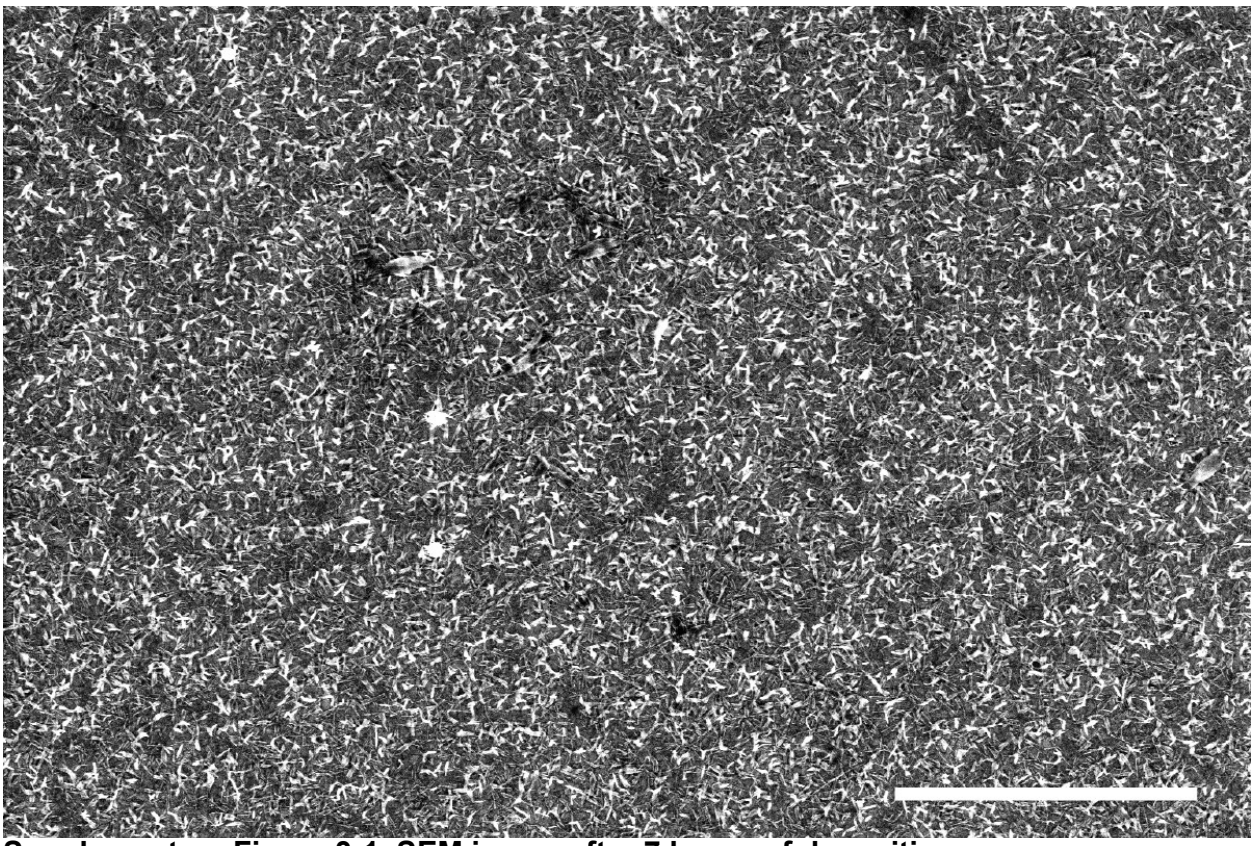
Supplementary Figure 2-1. SEM image of copper islands grown from 100 mM $CuSO_4$
SEM image of the copper islands grown for 10 seconds on a gold substrate at -50 mV vs. a copper wire reference electrode, as used for the XRD spectra in Figure SI 1-2. The scale bar is 500 nm.



Supplementary Figure 2-2. In-situ AFM of copper islands grown from 100 mM $CuSO_4$ (aq)

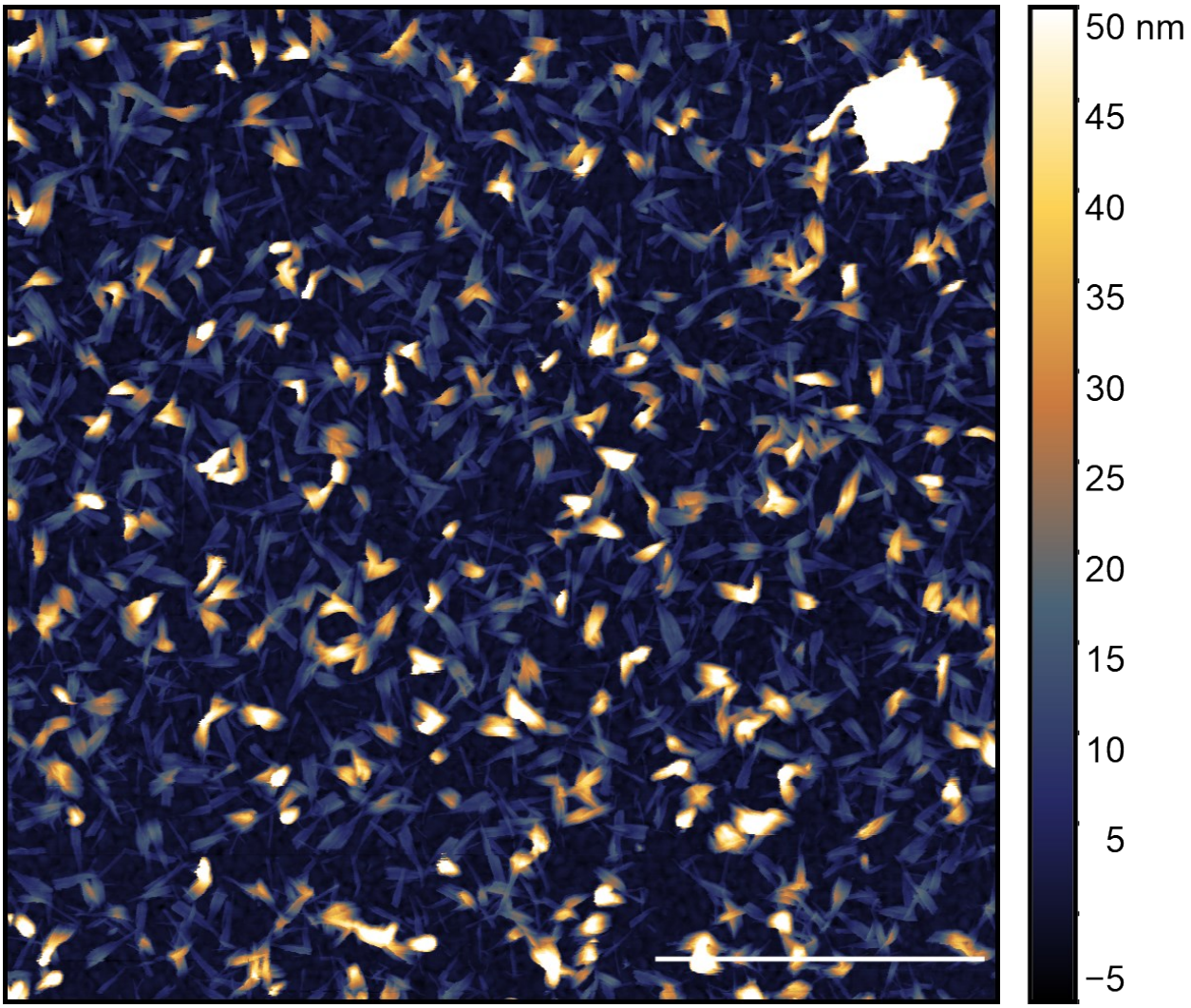
A) *in-situ* AFM topography (5 μm^2) of copper islands grown for 6 seconds on a gold substrate at -50 mV vs. a copper wire reference electrode from 100 mM $CuSO_4$ (aq). The mask is indicated as used to obtain the data for Figure 3 in the main text. A height threshold of 10 nm was used and grains that are overlapping or not fully within the scan area are eliminated. **B)** The lower right quadrant of image *a)* but transformed to represent the local inclination θ rather than the topography ($\theta(x,y) = \tan^{-1}\sqrt{\frac{dz_2}{dx} + \frac{dz^2}{dy}}$). The crystal facets are now clearly displayed as equi-angle planes. The scale bar is 1 μm in both images.

SI-3. nondirected copper deposition from 1μM $CuSO_4$ (aq)



Supplementary Figure 3-1. SEM image after 7 hours of deposition

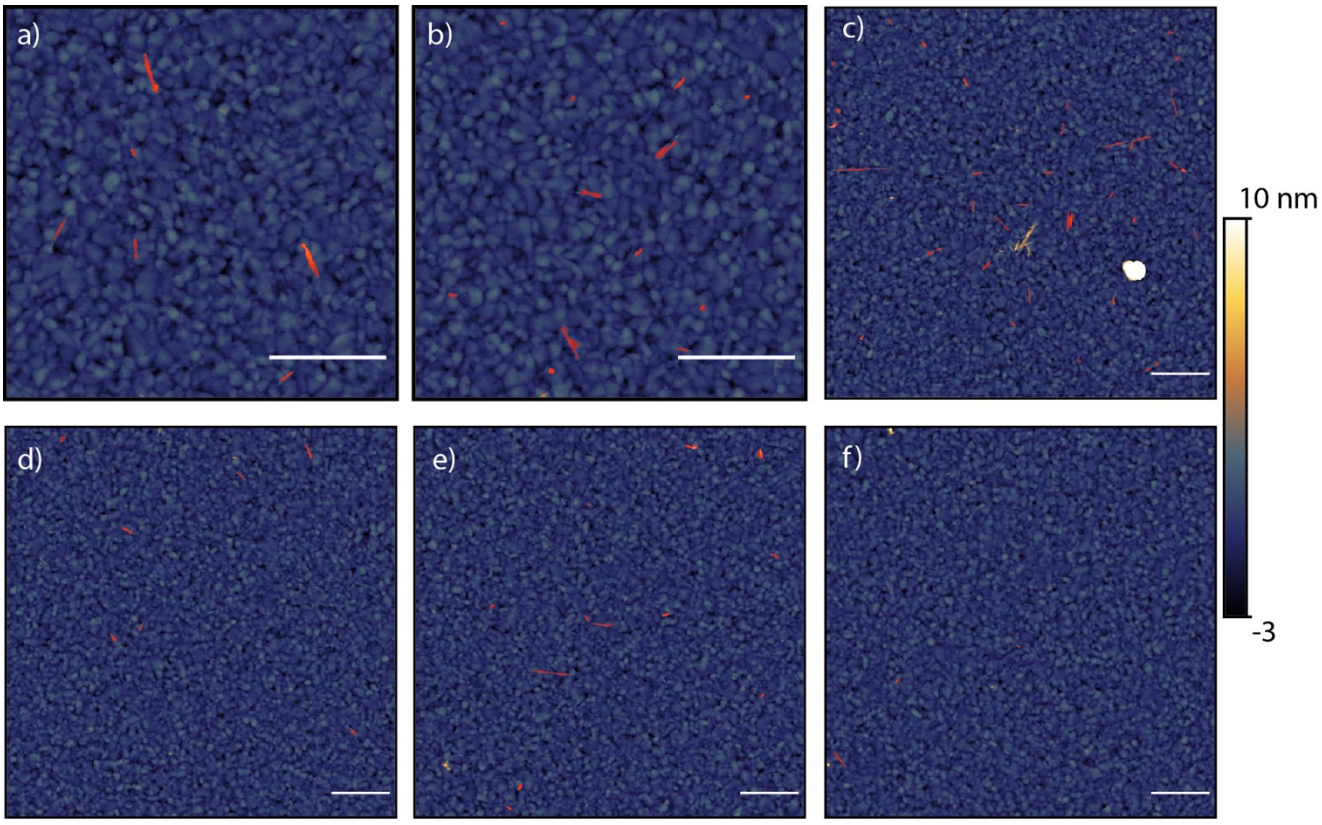
SEM image of a high coverage of overlapping ‘nanoneedles’ deposited from 1 μM $CuSO_4$ (aq) as outlined in the methods for a period of **25000 s** at -1V vs. a Cu quasi reference electrode. The scalebar is 2 μm.



Supplementary Figure 3-2. AFM topography after 7 hours of deposition

AFM image of a high coverage of overlapping 'nanoneedles' deposited from 1 μM $CuSO_4$ (aq) as outlined in the methods for a period of **25000 s** at -1V vs. a Cu quasi reference electrode. The scalebar is 1 μm.

Coverage is high in this case, and many particles overlap. Particles that can be identified as single rods are limited to ~ 10 nm in height, with larger clusters going up to ~50 nm. Considering the clearly progressive nucleation (compared to SI 3-3, and Figure 2b in the main text), these individual particles could either be limited in their growth or nucleated at later times, compared to the clusters.

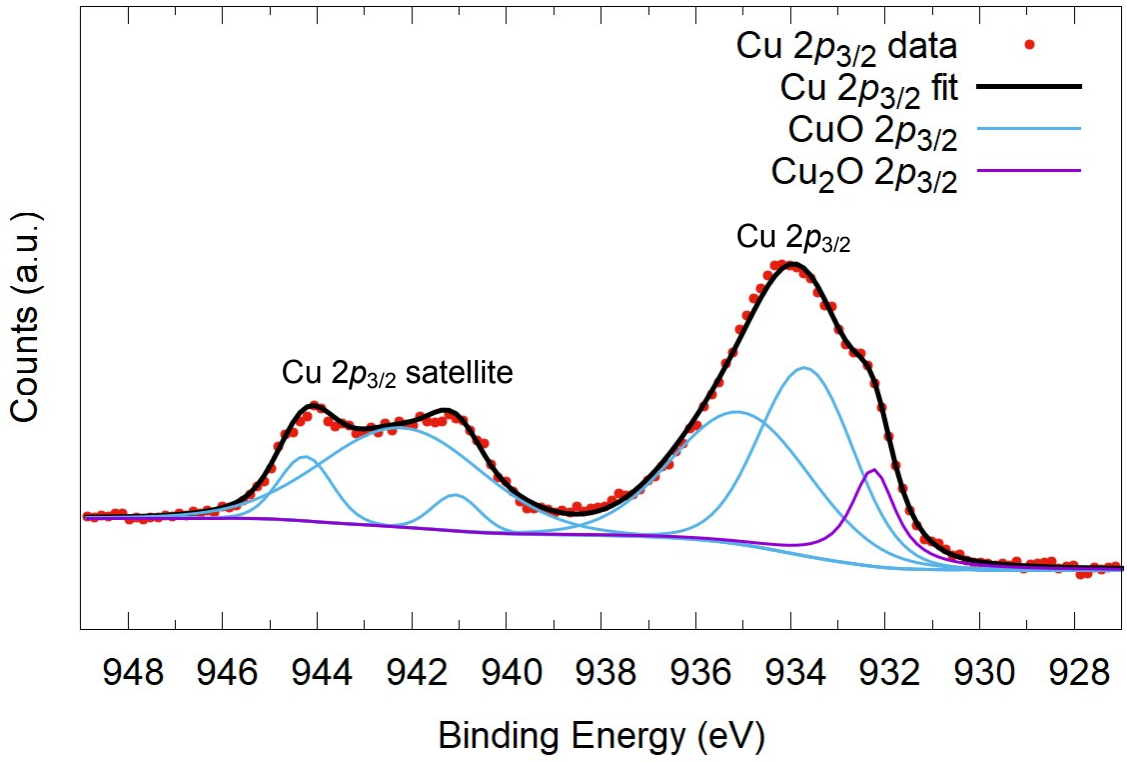


Supplementary Figure 3-3. AFM images used for geometric analysis

AFM images of non-directed growth for the Area-Volume and ellipticity plots in Figure 3 of the main text. The mask as used for the analysis in Figure 3 of the main text was obtained by drawing it manually over the grains and then combining this with a 1.5-2 nm height threshold (~2x the substrate roughness) sometimes combined with a threshold value for the grains footprint in cases where parts of the substrate were erroneously identified.

The final mask is indicated in red, totaling 83 grains in these images.

These islands were deposited from 1 μM $CuSO_4$(aq) as outlined in the methods for a period of **1000 s**. This shorter deposition time yields a much lower coverage, allowing us to identify many more individual islands than was possible on samples grown for 3000 s (main text Figure 2b) or 25000 s (SI X-1). The images **a)** and **b)** are 1 μm^2, and **c), d), e)** and **f)**, are 2 μm^2. All scalebars are 300 nm.



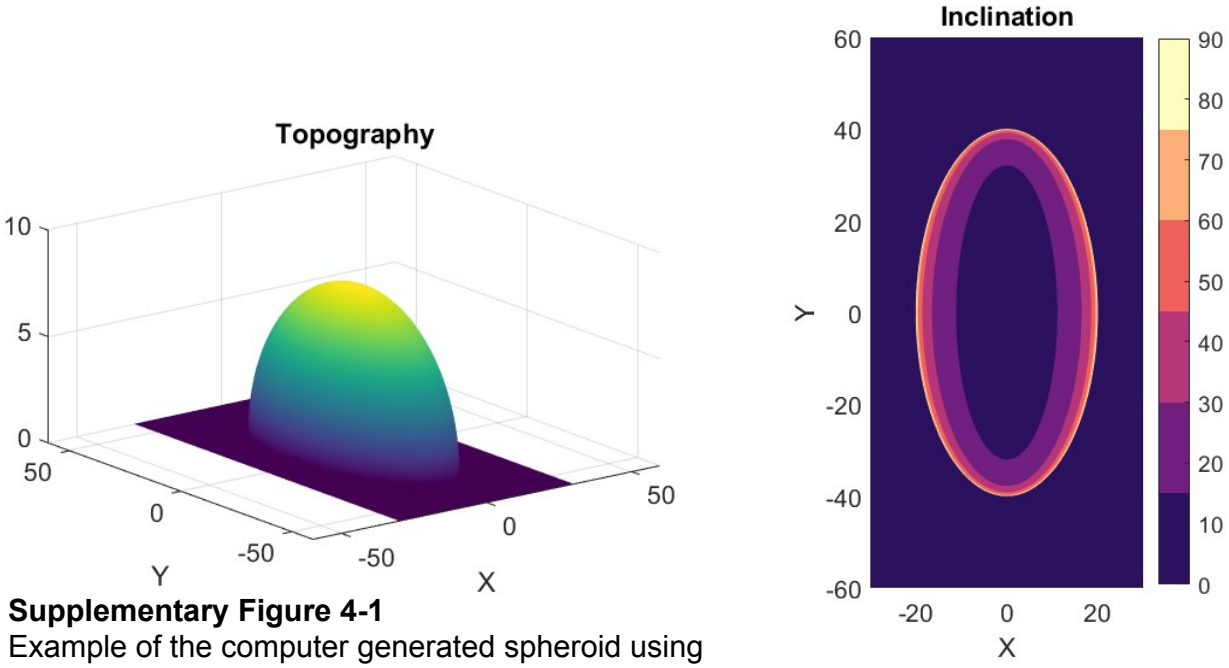
Supplementary Figure 3-4. XPS measurements of nondirected copper deposition from 1µM $CuSO_4$ (aq)

Deconvoluted X-ray photoelectron spectroscopy (XPS) spectrum of Cu $2p_{3/2}$ for a sample grown for **25000 s** (see SI 3-1). The oxidation state of copper is determined using the Cu $2p_{3/2}$ core level. At the higher binding energy the Cu $2p_{3/2}$ satellite is shown and at the lower binding energy the Cu $2p_{3/2}$ main peak is shown. The experimental values are shown as red dots, the peak fit envelope is shown in black, the CuO $2p_{3/2}$ peaks are shown in blue, and the Cu_2O $2p_{3/2}$ peak is shown in purple. The binding energy values are calibrated using the Au $4f_{7/2}$ peak of the gold substrate.

The predominant species is identified as CuO (blue line), based on the characteristic satellite peak for CuO species, its relative intensity, and the binding energy difference to the main peak. [1] A second species is required to fit the experimental data. It is identified as Cu_2O (purple line), based on the peak position of 932.2 eV. The lowest binding energy peak of the CuO peaks is measured at 933.7 eV, which is 0.6 eV higher than the literature value of 933.1 eV. This observation is attributed to the charging of the non-conductive CuO species. Based on the Cu $2p_{3/2}$ peak areas, 91% of the sample volume probed by XPS corresponds to CuO and 9% to Cu_2O.

[1] Biesinger, M.C., *Advanced analysis of copper X-ray photoelectron spectra,* Surface and interface analysis, **49**, 1325-1334 (2017).

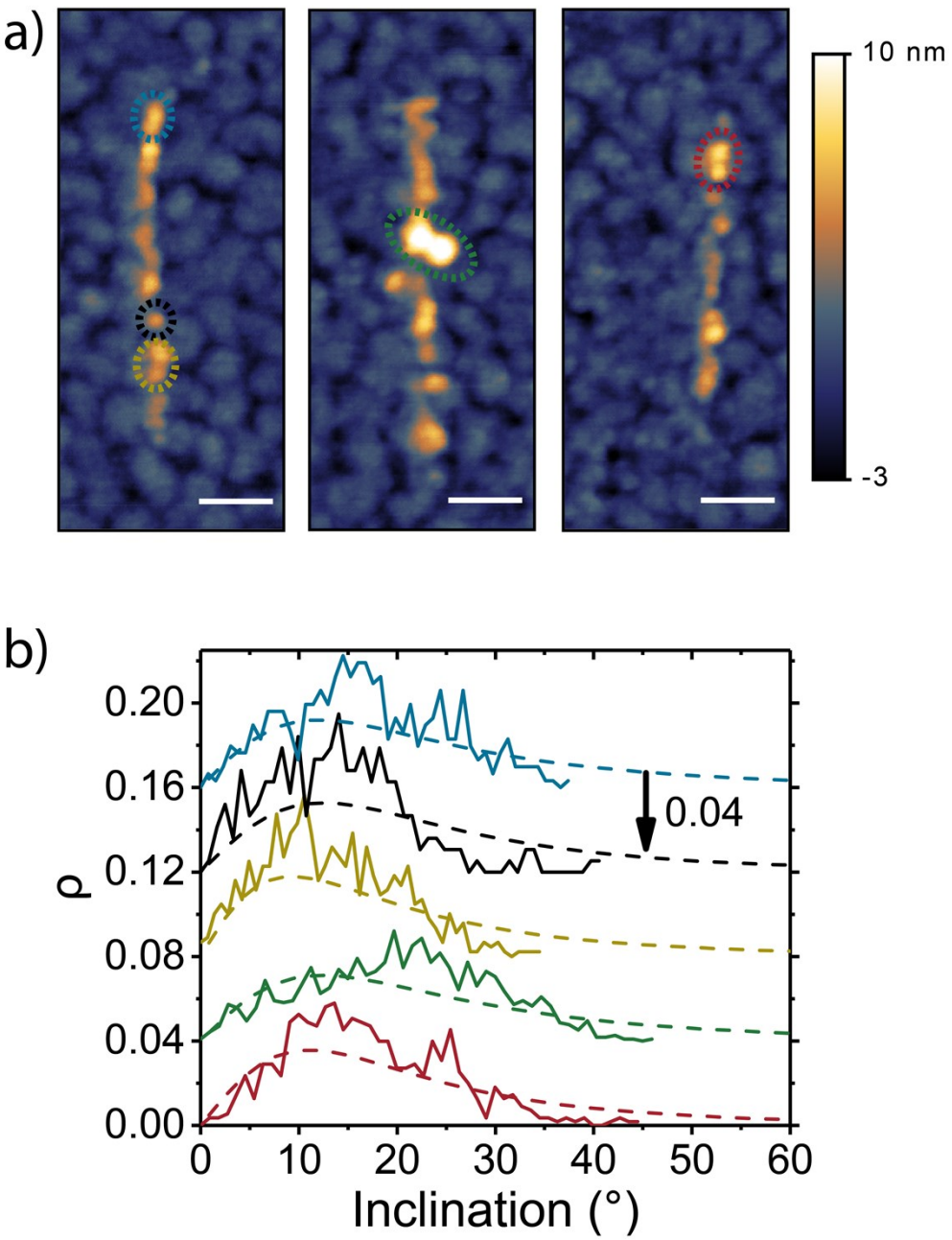
SI-4. Nanoscale islands and spheroidal shapes



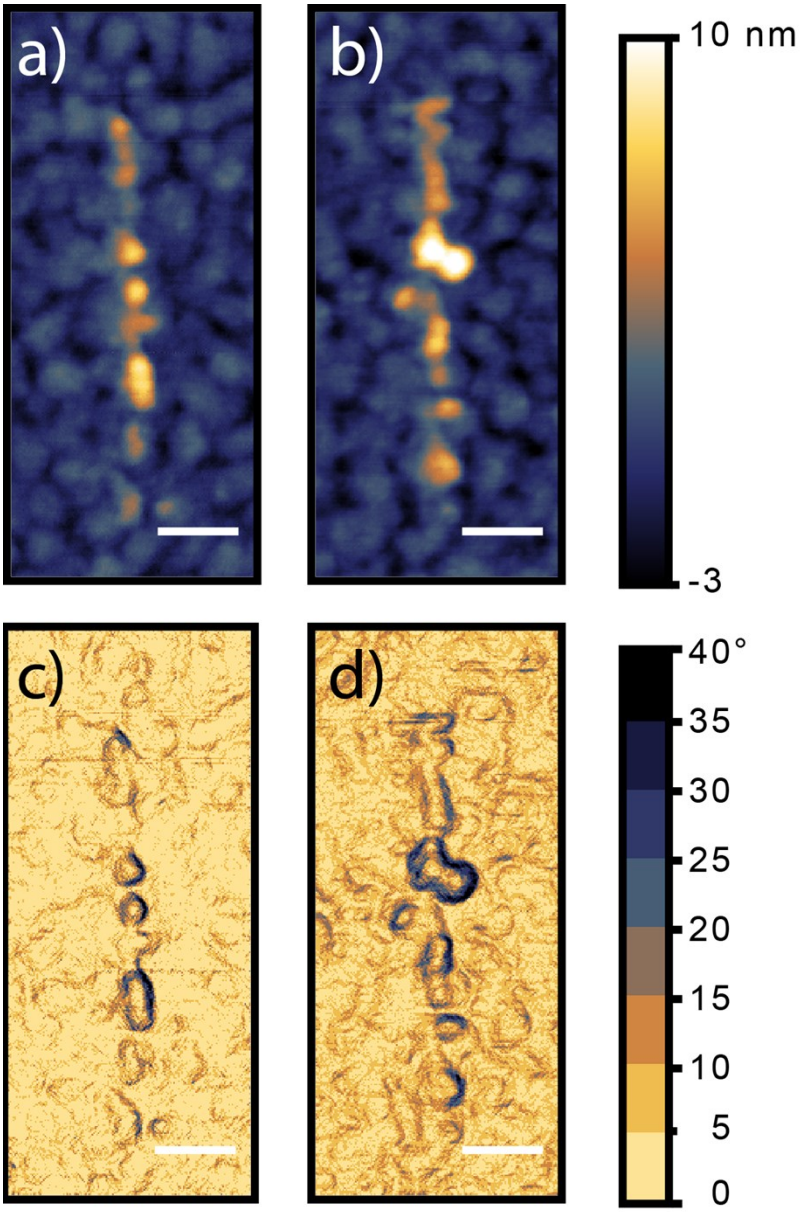
Supplementary Figure 4-1
Example of the computer generated spheroid using MATLAB, showing the topography (left) and inclination (right), as used for the histogram in the main text (Figure 2). The characteristic 'bulls-eye' for rounded shapes is visible, where the top has a large flatten base and the highest inclinations are found at the base.

The dimensions are based on section analysis on the AFM topography image (SI 4-3,45-4).

Image	Major Diameter	Minor Diameter	Height
Fig 2a (red)	80	40	8
Fig 2a (green)	100	32	5
Fig 2b (red)	60	8	6.4
Fig 2b (green)	50	9	3.2
SI 4-2 (blue)	27	16	7.2
SI 4-2 (black)	17	15	5.8
SI 4-2 (yellow)	37	17	7
SI 4-2 (green)	43.5	25	11.9
SI 4-2 (red)	30	23	8.3

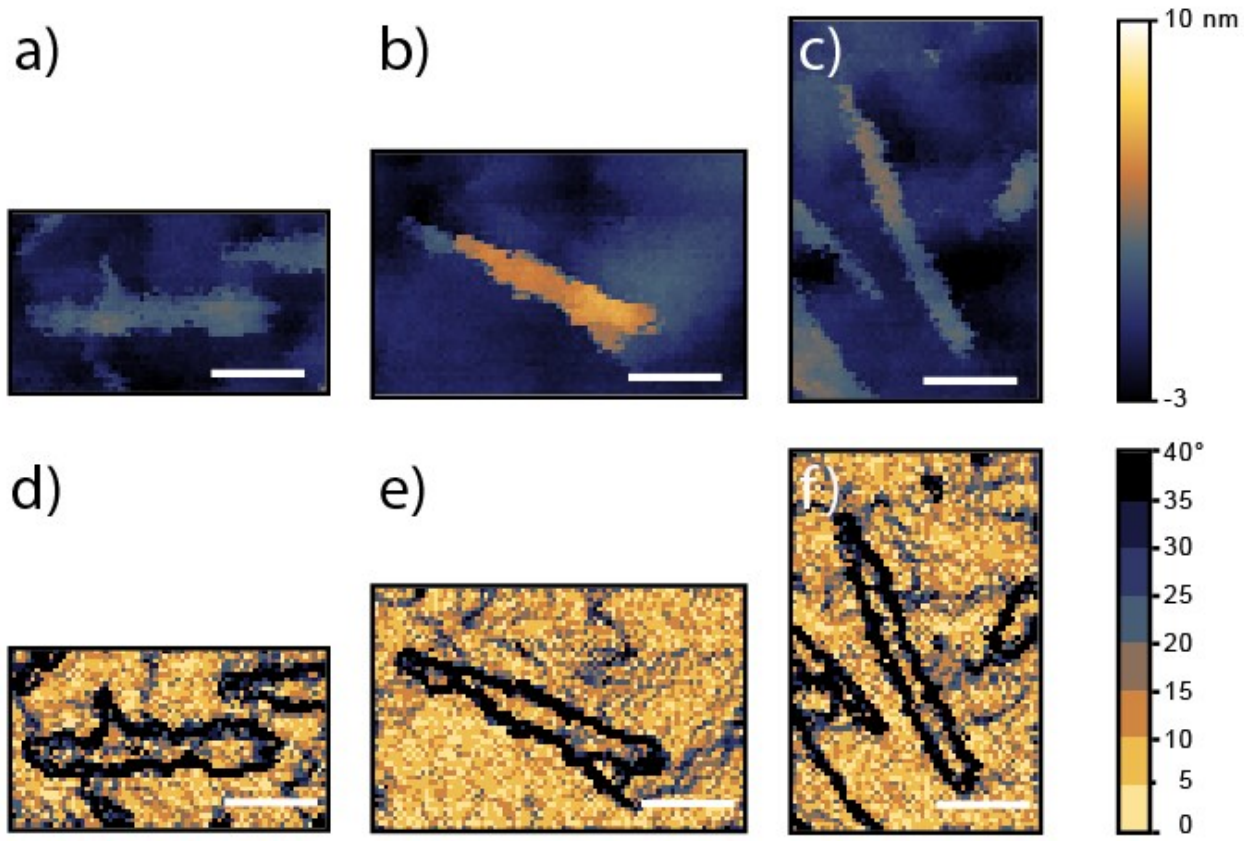


Supplementary Figure 4-2. Additional histograms of particles in directed copper growth in 1 μM $CuSO_4$ (aq)
a) AFM topography of additional individual lines deposited by directed electrodeposition from 1 μM $CuSO_4$. The scale bars are 100 nm. **b)** Inclination histograms (solid lines) of the particles indicated in *a).*The dashed lines correspond to the expected inclination distribution for a spheroidal shape with dimensions obtained from the topography images (see SI 4-1). The histograms are shifted vertically for clarity.



Supplementary Figure 4-3. Inclination map of directed copper growth in 1 µM $CuSO_4$ (aq)

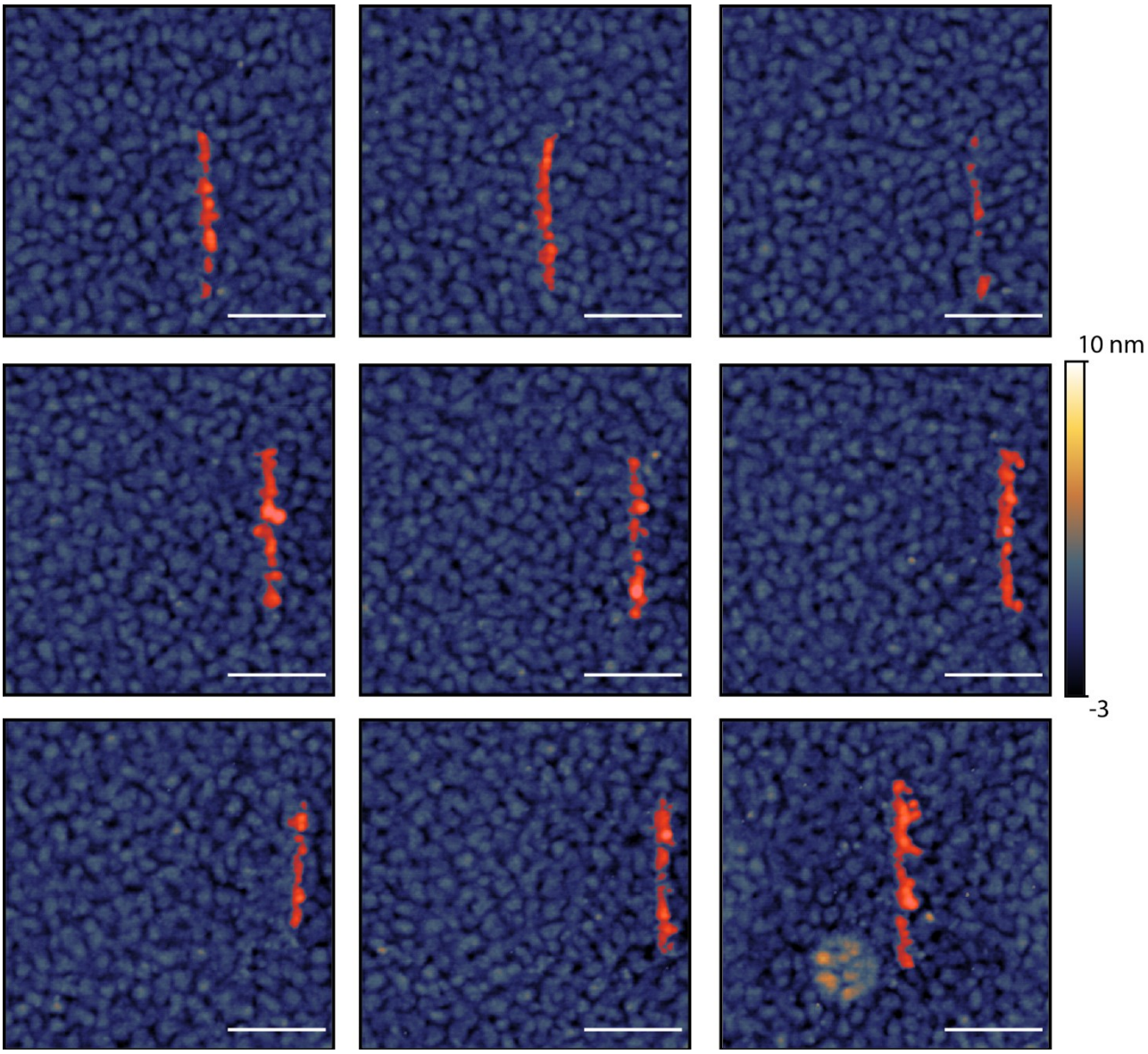
a),b), AFM topography of 2 individual lines from Figure 3b in the main text, deposited from 1 µM $CuSO_4$ (aq). **c),d),** corresponding inclination maps, obtained from the topography map ($\theta(x,y) = \tan^{-1}\sqrt{\frac{dz}{dx}^2 + \frac{dz}{dy}^2}$). The colorbar is discrete in steps of 5°. The highest angles are found at the edges, but the particles are typically surrounded by an area of lower angles going into the substrate. The scalebar is 100 nm in all images.



Supplementary Figure 4-4. Inclination map of nondirected copper growth in 1 μM $CuSO_4$ (aq)

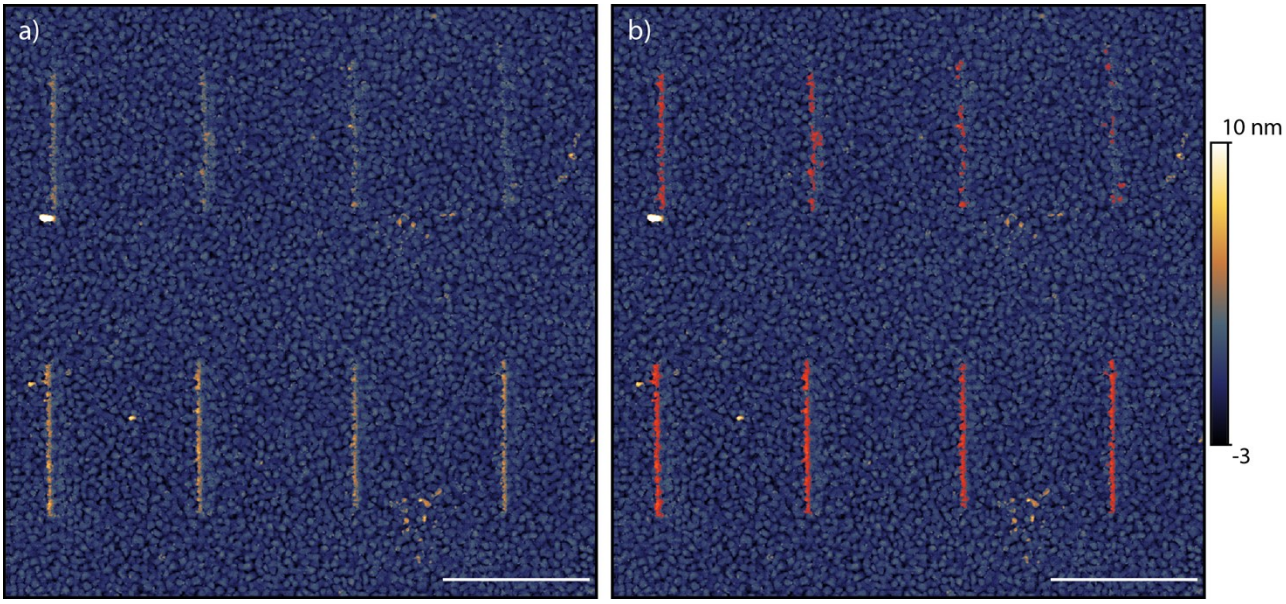
a),b),c), AFM topography of 3 individual islands from Figure 2b in the main text, deposited from 1 μM $CuSO_4$ (aq) as outlined in the methods for a period of **3000 s** at -1V vs. a Cu quasi reference electrode. a) and b) correspond to the green and red ellipse in the main text, respectively. **d),e),f)**, corresponding inclination maps, obtained from the topography map ($\theta(x,y) = \tan^{-1}\sqrt{\frac{dz_2}{dx} + \frac{dz^2}{dy}}$). The colorbar is discrete in steps of 5°, angles larger than 40°, as shown in the main text, are only observed at the edges. The scalebar is 20 nm in all images.

SI-5. Directed copper deposition from 1μM $CuSO_4$ (aq)



Supplementary Figure 5-1. AFM images of lines written with constant writing parameters.

AFM topography images of 9 lines used for Figure 3 in the main text. All lines are written with the same parameters (30 nN peakforce setpoint, 50 nm peakforce amplitude, translation speed 10 nm/s, 2.1 V between tip and sample (Aarts & Alarcon-llado, 2019)). The images shown are obtained with a Scanasyst-AIR tip ~ 1 year after deposition. The sample was kept in a nitrogen environment.The mask is defined by a 2 nm threshold value (~2x the substrate roughness) sometimes combined with a threshold value for the grains footprint in cases where single pixels were identified as grains. This yields a total of 34 grains. The scalebar is 300 nm.

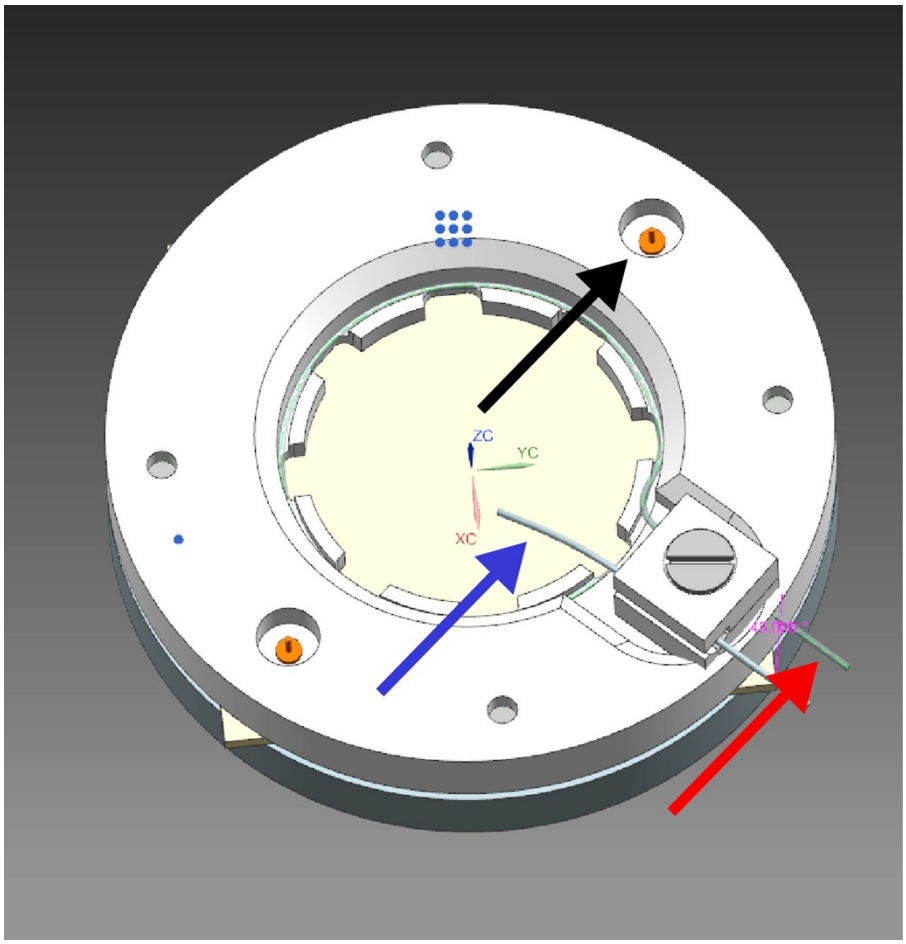


Supplementary Figure 5-2. AFM images of lines written with varying writing parameters.

a) AFM topography image of 8 lines used for Figure 3 in the main text, and **b)** the mask applied. The mask was defined by a 2 nm height threshold (~2x substrate roughness) around the lines combined with a minimum grain size of 30 pixels (~450 nm^2) to get rid of grains where parts of the substrate were erroneously identified. This yields a total of 62 grains.

Lines in both rows are written with varying current (5, 6.5, 8, 9.5 nA from left to right) and the 2 rows have a different peakforce setpoint (10 nN top, 30 nN bottom). The peakforce amplitude was 50 nm and the translation speed 10 nm/s for all lines (Aarts & Alarcon-llado, 2019).The scalebar is 1 μm.

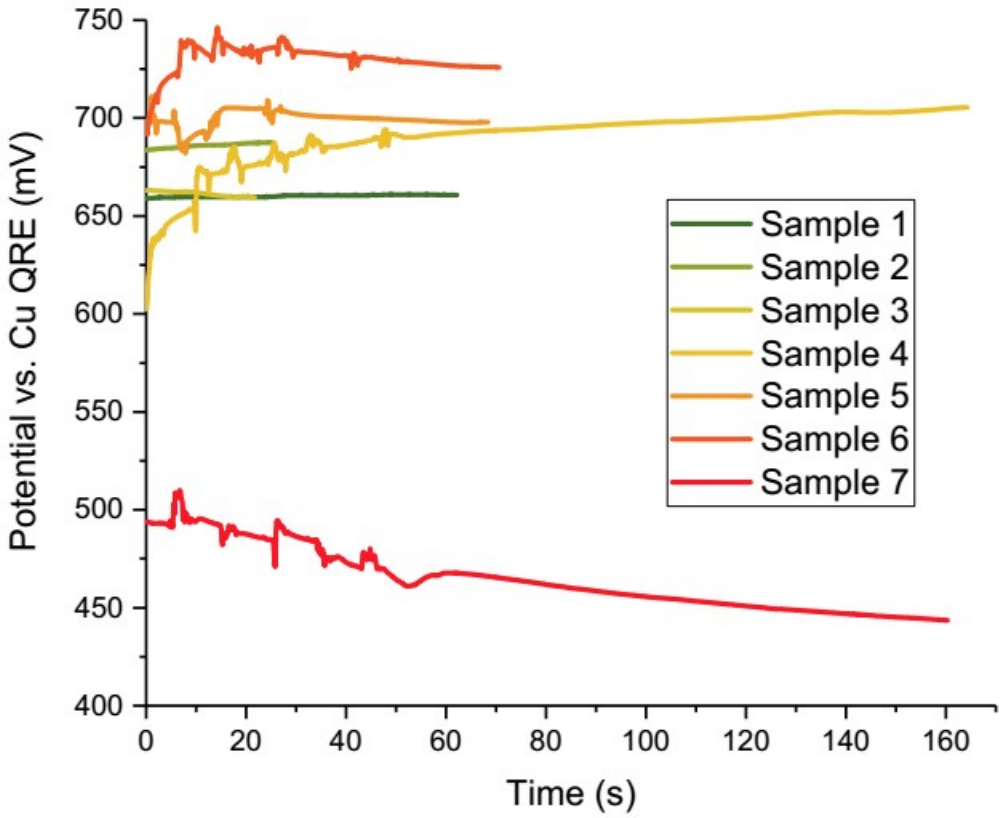
SI-6. Electrochemical Cell



Supplementary Figure 6-1. Schematic of the electrochemical cell

Drawing of the electrochemical cell used for the electrochemical AFM experiments. The cell has a rather large opening from the top as to fit the AFM scan head. The working electrode seals the cell and is contacted from the top with a spring loaded pin (black arrow). The counter electrode (red arrow) wraps around the perimeter of the cell to increase its surface area. The reference electrode is inserted into the liquid from the side (blue arrow).

SI-7. Open circuit potential in 1 μM $CuSO_4$



Supplementary Figure 7-1. Open circuit potential in 1 μM $CuSO_4$

Measured open circuit potential (OCP) values for all samples used for electrochemical deposition from 1 μM $CuSO_4$ (aq) in the macroscopic 3-electrode cell. The measurement is done prior to deposition, and the potential is measured against the copper quasi-reference electrode (QRE). The values mentioned in the main text are the mean and standard deviation of the values obtained from these measurements.