Supplementary File - Dynamic perturbation of the electrical double layer with an electrochemical AFM for confined metal electrodeposition

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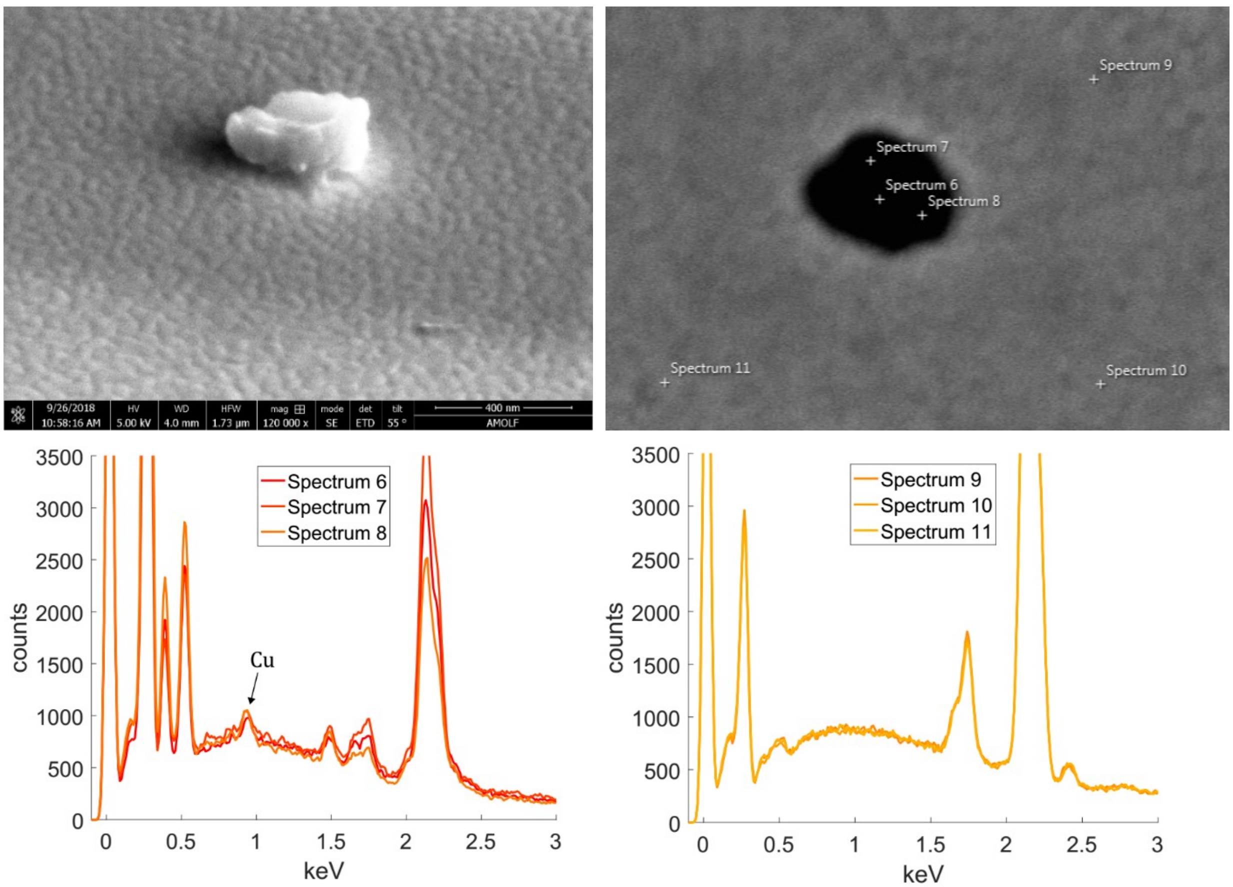
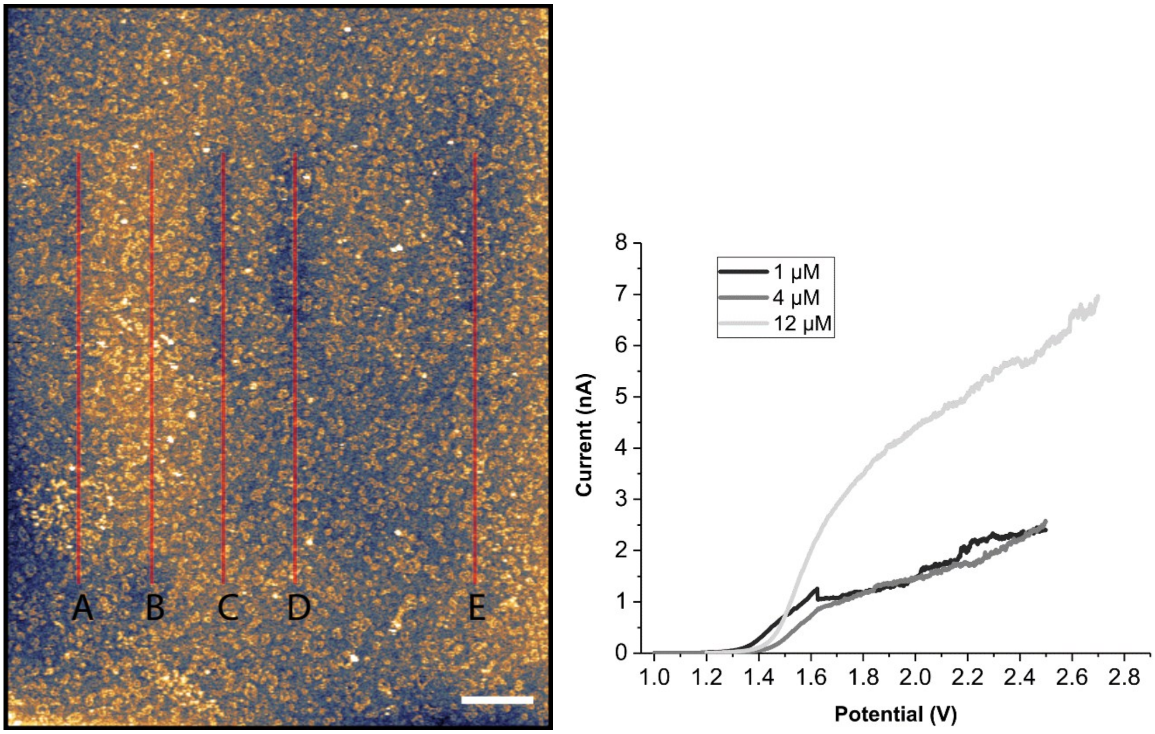
SI-1. Elemental characterization of a larger deposit using SEM-EDX



Supplementary Figure 1. Elemental characterization of a larger deposit using SEM-EDX

A larger structure (~500 nm radius and ~ 300 nm height as obtained from ex-situ AFM) was deposited with the tip stationary for an hour with a potential difference of 2 V between tip and substrate ***a)*** *Secondary electron SEM image of the deposit (55 degrees tilt).* ***B)*** *Backscatter electron image at normal incidence, displaying elemental contrast between the deposit and the substrate.* ***C,D)*** *EDX spectra of the points indicated on the deposit (C) and on the sides (D), as indicated in (B). A clear peak associated with copper is observed at ~ 0.94 keV, which is absent in the reference spectra. Peaks in the reference are associated with the substrate containing gold (2.13 keV) and silicon (1.74 keV), and carbon peaks (0.02, 0.27 keV). Additional peaks in the deposit include oxygen (0.52 keV), nitrogen (0.39 keV), and aluminum (1.49 keV), the last 2 of which we attribute to scattering inside the SEM chamber. Spectra were obtained with an acceleration voltage of 5 keV and a current of 800 pA.*

SI-2. Extended parameters space for deposition in 10 µM $CuSO_4$ and *I-V* characteristics as a function of ion concentration

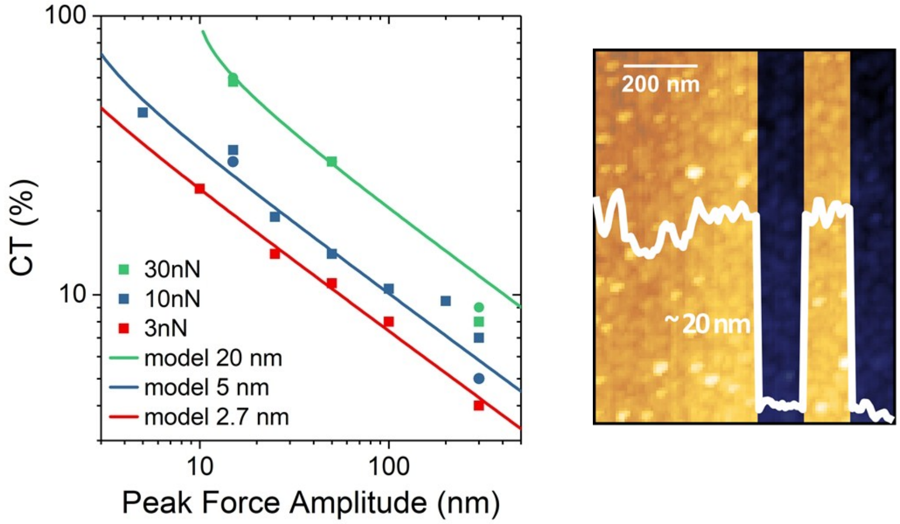


Supplementary Figure 2. Extended parameters space for deposition in 10 µM $CuSO_4$

Left panel) *Larger scan area for the highest concentration (12 µM) of the image shown in the main text in figure 1c. The tip is translated along the red lines (guide to the eye, bottom to top), while ramping the voltage at 1.25 or 2.5 mV/s, and using different force setpoints for the feedback while moving. The translation speed is 10 nm/s for line A (main text), and 20 nm/s for B through E. The force is varied in terms of the photodiode voltage (SI-6.), 0.1, 0.15, 0.1, 0.05, 0.05 V for line A through E, respectively. The voltage is ramped from 1.2 -> 2.7, 1.2 -> 1.9, 1.2 -> 2.7, 1.2 -> 2.7, 1 -> 2.5 V in the same order. No deposition is observed for any of the parameters in the vicinity of our experiment at this concentration. The scale bar is 2 µm.*

Right) *The current measured at the nanoelectrode while walking the paths as shown in figure 1d in the main text. The tip potential is swept from 1 -> 2.5 V for the 1, and 4 µM $CuSO_4$ (aq) solution, and from 1 -> 2.7 V for the 12 µM $CuSO_4$ (aq) solution. The path is walked over a period of 20 minutes with a sweep rate of 1.25 mV/s and a current sample interval of 1 mV.*

SI-3. Contact time and center of oscillation with AFM parameters



Supplementary Figure 3. Dependence of cantilever position on AFM parameters

The average gap size <z>, as referred to in the main text, is determined by integrating the tip position from the highest point up to the point of contact, divided by half the oscillation period.

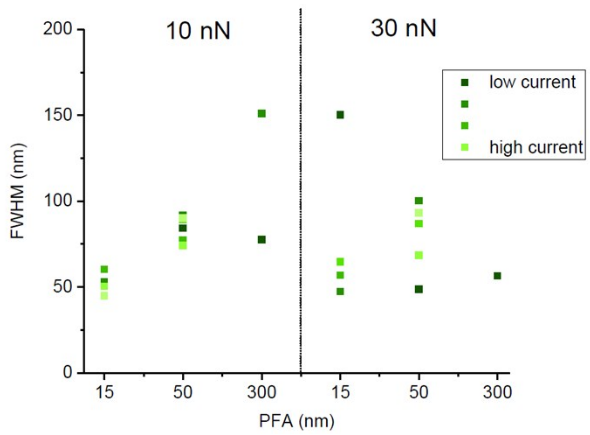
$$\frac{\int_0^{\frac{T-CT}{2}} PFA * cos\left(\frac{f}{2\pi}t\right)dt}{\frac{T}{2}}$$

, with CT the measured contact time, PFA the peakforce amplitude and using the frequency f = 2 kHz, and period T = 500 µs.

The figure illustrates the effect of peak force amplitude and peak force setpoint on the amount of time spent in contact with the sample. ***Left)*** *Contact time read out from the Nanoscope software for the contact time as a function of peakforce amplitude for different force setpoints (dots, squares). The center of the sinusoidal oscillation is expected to shift by the force setpoint divided by the spring constant, assuming no indentation of the sample. This gives a shift of 2, 6.7, and 20 nm for a setpoint of 3, 10, and 30 nN respectively, for the nominal spring constant of 1.5 N/m. The straight lines are a fit to the data calculated for a sinusoidal movement of the tip with the center of the oscillation given by the amplitude-x, yielding x = 2.7, 5, and 20 nm for the different forces, in good agreement with the expected shift.*

Right) *Raw AFM height sensor data when switching the peakforce setpoint from 3 nN -> 30 nN twice during the scan (slow scan axis in horizontal direction). The overlay shows the height profile, illustrating how the Z-piezo moves down (approximately 20 nm) due to the force setpoint, determined by the cantilever spring constant and indentation of the sample.*

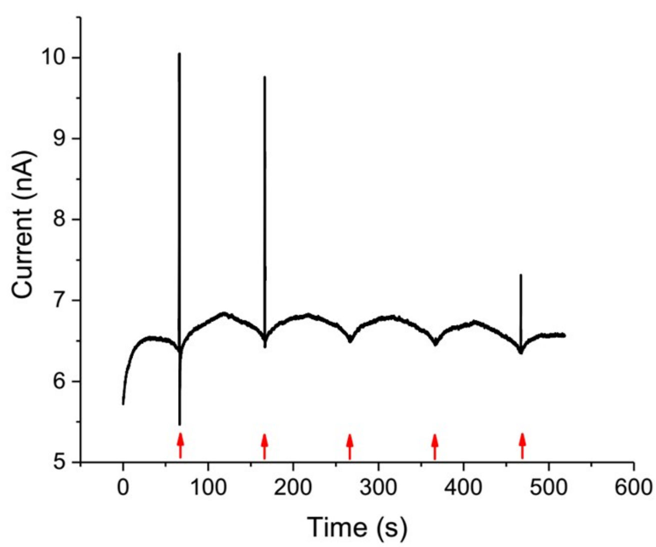
SI-4. Width of deposited lines



Supplementary Figure 4. FWHM of deposited lines from Figure 3b in the main text

The full width half maximum of the lines used for figure 3b in the main text. The individual datapoints for all currents are displayed, where the color ranges from dark to light green, for lower to higher currents, respectively (arbitrary scale). The amount of individual current datapoints varies for each set of oscillation parameters, as growth is not observed for all currents (see main text). While the width seems to increase slightly at the intermediate amplitude, no clear trends in the width are observed as a function of the applied current.

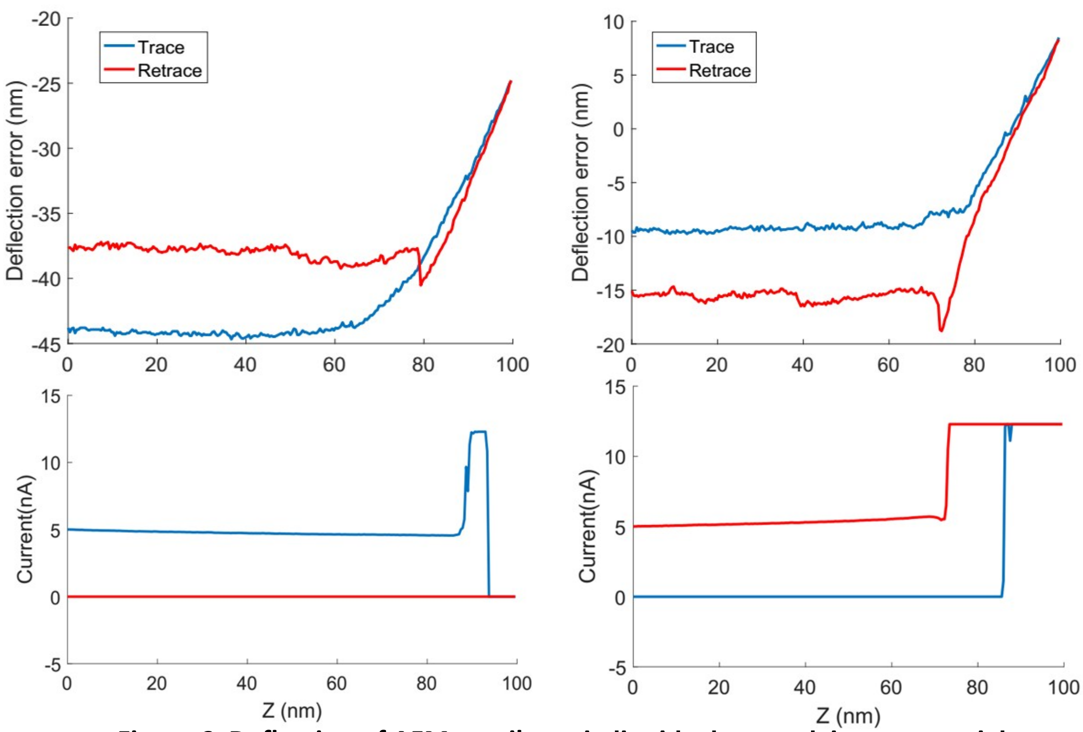
SI-5. Current response of the nanoelectrode in consecutive approach curves



Supplementary Figure 5. Current response of nanoelectrode during approach

Current response at the AFM nanoelectrode when executing 5 consecutive approaches with a tip potential of 1.7 V. The tip is approached and retracted over a distance of 1 µm with a frequency of 0.01 Hz (20 nm/s). These approach *curves show that the current decreases/increases as the tip approaches/retracts from the surface. At the point of contact (indicated by the red arrows), a short circuit current is observed. The current sampling rate is 20 Hz. The approach is terminated at an applied force of ~10 nN (deflection trigger of 8 nm with a spring constant of 1.25 N/m)*

SI-6. Electrostatic interaction between biased AFM-tip and substrate in liquid



Supplementary Figure 6. Deflection of AFM cantilever in liquid when applying a potential

Single approach curve of the AFM tip where the tip-substrate potential was manually turned off for the retrace during the contact(left panels), and turned on for the retrace during the contact (right panels), as seen in the current channel (bottom panels) that is measured simultaneously by the AFM software.

The applied potential is 2.1 V. In both cases a clear attractive force is seen in the deflection of the cantilever (top panels) when a potential is applied (as evidenced by the flow of current in the bottom panels). The difference in deflection of ~5 nm corresponds to ~4 nN for this spring constant.

The ramp size is 100 nm, at 0.01 Hz (2 nm/s), the force-trigger for the approach curve was set to ~15 nN (deflection trigger of 17 nm with a spring constant of 1.15 N/m).

SI-7. AFM parameters and cantilever resonance characteristics

Supplementary Table 1. AFM parameters used during the deposition process.

Data used in	Peakforce Amplitude (nm)	Peakforce setpoint (nN)	Translation speed (nm/s)
Fig 1b	50	30	3
Fig 1c	50	30	30 + 3 (consecutive)
Fig 1d	50	6.3†	10

Fig 2b	50	30	10
Fib 2c	50	30	3, 10, 30, 100
Fig 3b	15, 50, 300	10, 30	10
Fig 3c	10, 25, 50, 100, 300	3	10
S.1.	50	30	-
S.2.	50	2.1, 3.2, 6.3, 9.5†	10, 20
S.4.	15, 50, 300	10, 30	10

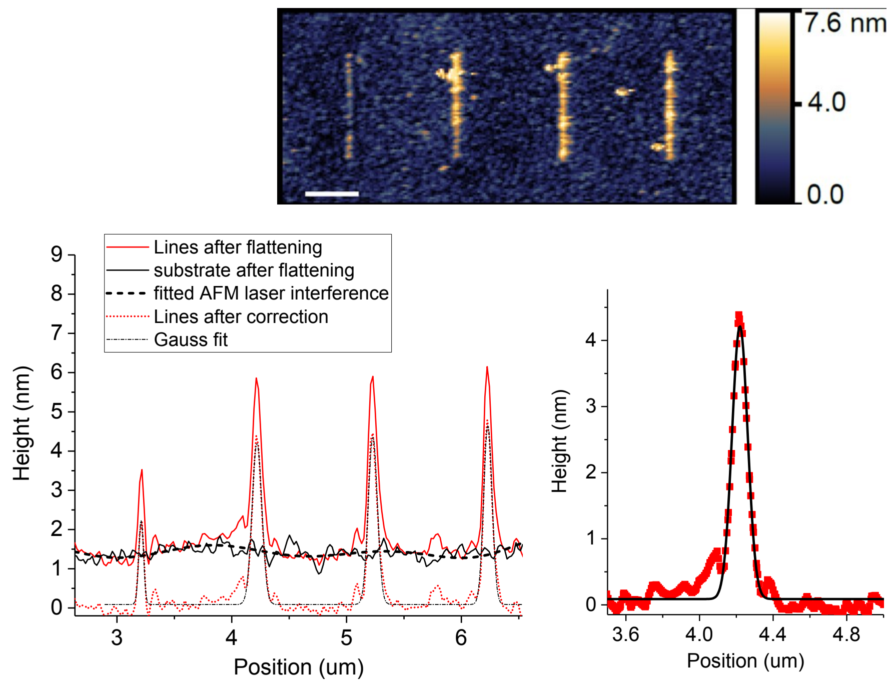
† The force was set in terms of the photodiode voltage. With a used deflection sensitivity of 35 nm/V and a spring constant that was later determined to be 1.8 N/m (see next table for the resonant behavior), this yields a force of 6.3 nN for the used setpoint voltage of 0.1 V.

Supplementary Table 2. Resonance characteristics and spring constants of all cantilevers used.**Data used in**	Frequency in air (kHz)	Q-factor in air	Used k (N/m)
Fig 1b	65.7†	208†	1.68
Fig 1c	32.6‡	-	1.80
Fig 1d	63.4†	214†	-
Fig 2	65.7†	208†	1.68
Fig 3b	58.3	195	1.41
Fig 3c	63.4†	210†	1.59
S.1.	51.3†	116†	0.88
S.2.	63.4†	214†	-
S.4.	58.3	195	1.41
S.5.	58.3	200	1.25
S.6.	52.1†	105†	1.15

† Frequency and Q-factor were obtained in air for that tip on a different day than the day of the measurement, the reported spring constant is the value used on the day of the measurement obtained in the electrolyte.

‡ Frequency was obtained with the tip immersed in the liquid rather than in air.

SI-8. Line profile fitting and analysis



Supplementary Figure 8. Illustration of the line profiles and fitting used for analysis

Top: *Representative AFM images used in the main text (fig 3b, 30 nN peakforce 50 nm peakforce amplitude, for different currents), scale bar 500 nm.* ***Bottom left:*** *Averaged profile of the lines along the vertical direction (solid red curve). The solid black curve is the average profile of the substrate outside the lines used to account for the laser interference (dashed black curve). The dotted red line is the background corrected average line profile. Thin dash-dotted line is the Gaussian fit to the four lines.* ***Bottom right:*** *zoom-in of the profile and fit for the line second from the left. The Gauss function in Origin 2017 was fitted,*

$$y = y_0 + \frac{A}{w\sqrt{(\frac{\pi}{2})}} + e^{-\frac{2(x-x_c)^2}{w^2}}$$

, with y_0 being the offset, x_c the center position, and w equal to $\sqrt{ln(4)}$ **the full width at half maximum.*