

Supplementary Information

Nanoscale electrochemical 3D deposition of cobalt with nanosecond voltage pulses in an STM

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1 Experimental

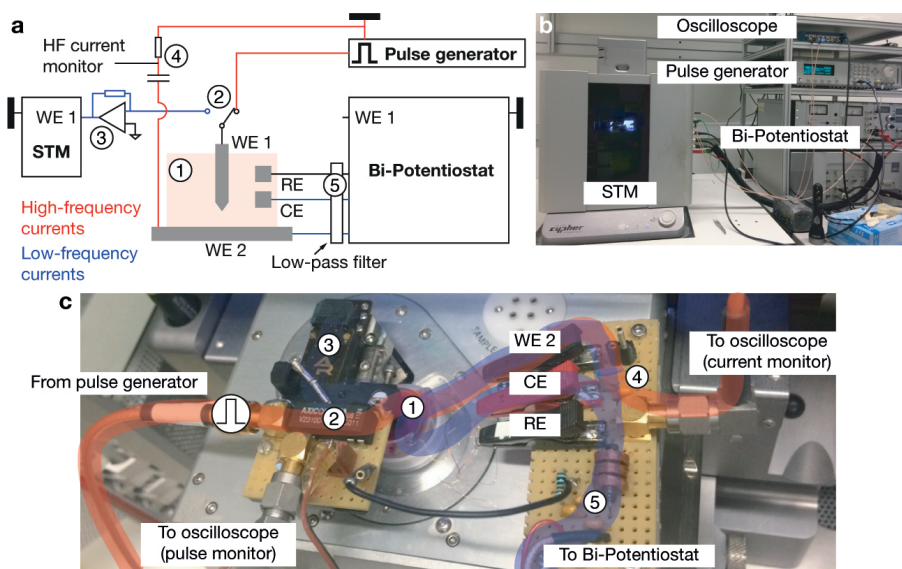


Fig. S1 Setup for local deposition in an electrochemical STM. a, Schematic of the home-built setup and corresponding photographs of b, the three sub-systems that were joined and c, the electrochemical cell with corresponding STM and filter electronics. The main components are: STM tip (WE 1) and substrate (WE 2) are immersed in an electrolyte solution contained in an electrochemical cell (1). The surface potentials of WE 1 and 2 are controlled by a bi-potentiostat. The tip is either connected to the current input of the STM (3) or the output of the pulse generator and is switched between the two with a mechanical relay (2). A high-pass filter (4) and low-pass filters (5) separate the high-frequency (red) and the low-frequency (blue) current circuits.

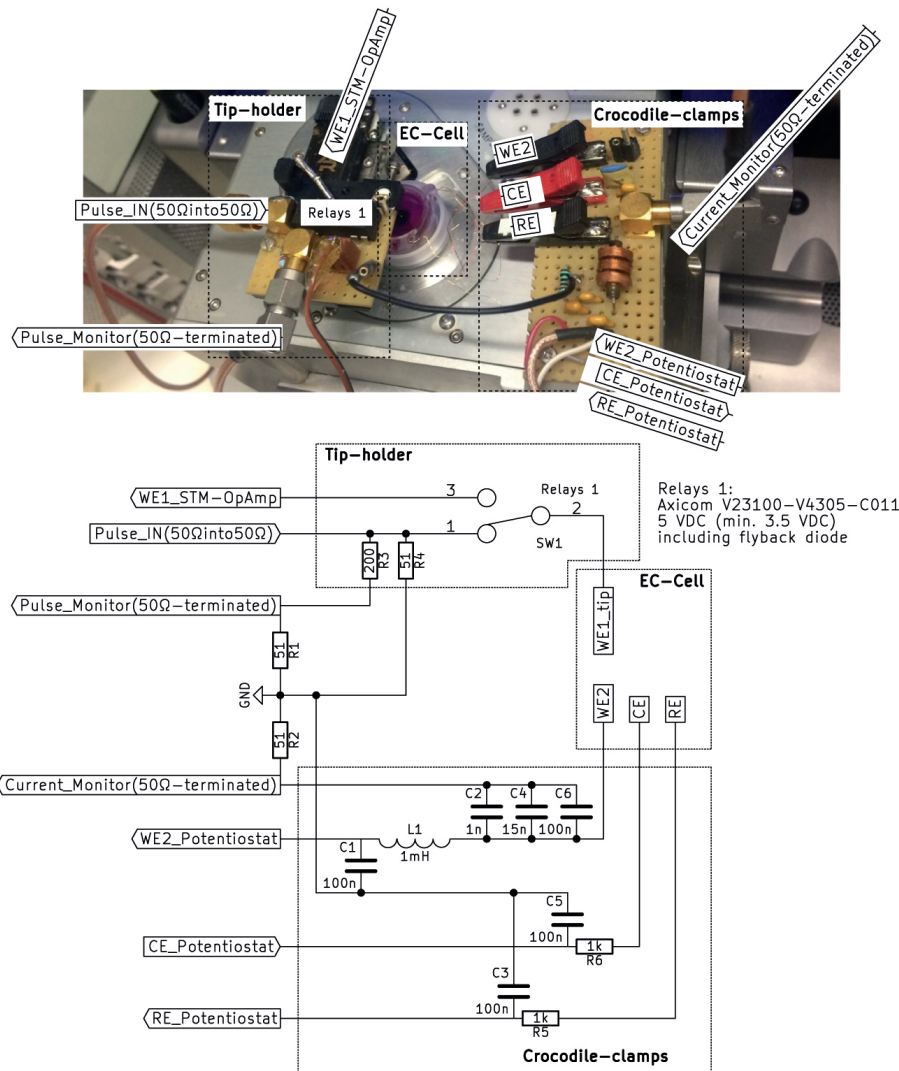


Fig. S2 Circuit diagram of the electronic components that couple the nanosecond pulses into the electrochemical cell and separate the high- and low-frequency currents. Main in- and outputs as well as some key components are labelled in the photograph.

2 Results

2.1 Reproducibility of smallest feature size

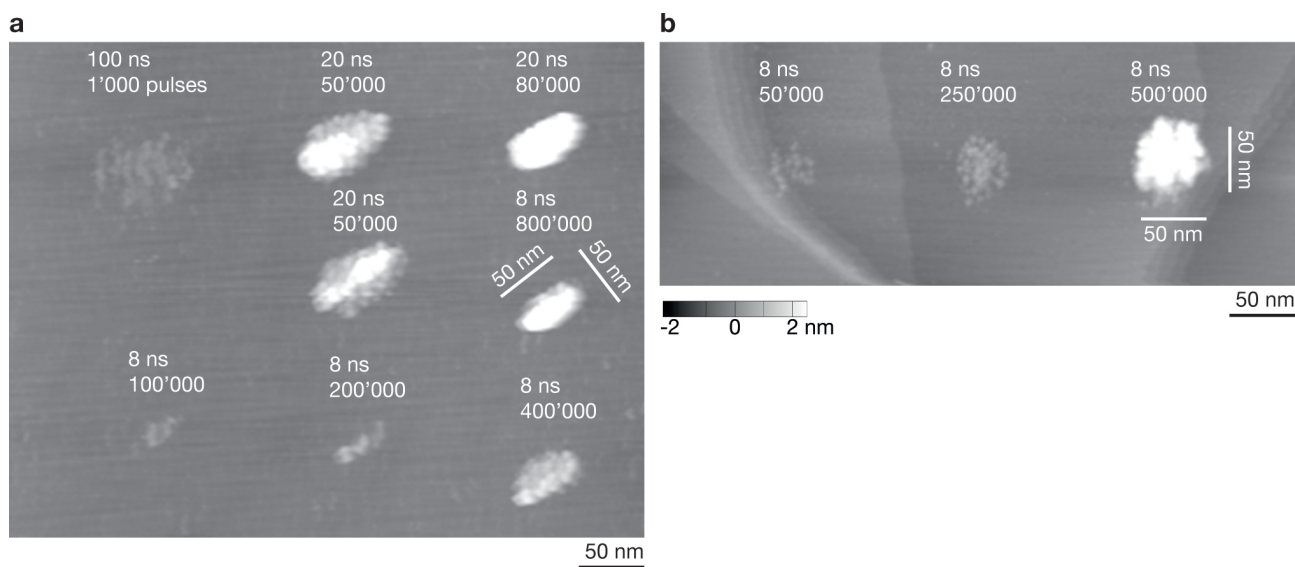


Fig. S3 Reproducible deposition of smallest feature size $\leq 50\text{ nm}$. Feature size as a function of pulse length and number of pulses per deposit. Experiments (a) and (b) were performed on different days, using different tips and electrolyte solutions. Deposition parameters. Electrolyte: 1 M CoSO_4 in DMSO; pulse length: as stated in the images; pulse amplitude: 6 V; duty cycle: 0.01; pulses per point: as stated; dwell distance: 10 nm; tip: Au.

2.2 Scanning electron microscopy analysis

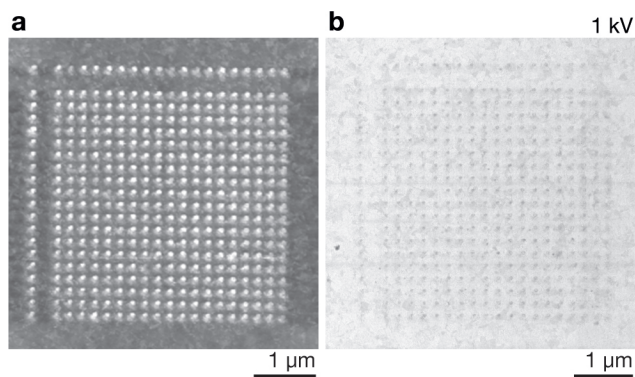


Fig. S4 SEM micrograph of a 2D grid. a, STM scan and b, 1 kV SEM micrograph of a grid (same as in Figure 2c). SEM EDX analysis of printed 2D patterns is not possible, as they are electron-transparent at acceleration voltages needed for analysis. Deposition parameters. Electrolyte: 1 M CoSO_4 in DMSO; pulse length: 100 ns; pulse amplitude: 6 V; duty cycle: 0.01; pulses per point: 3000; dwell distance: 10 nm.

2.3 Influence of total pulse number per deposit

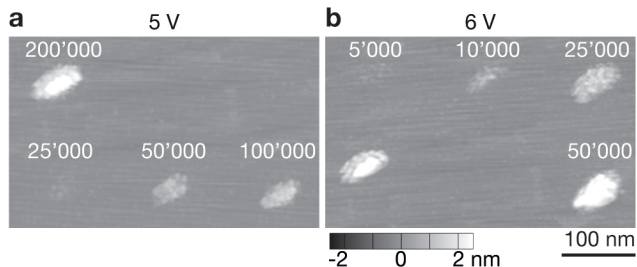


Fig. S5 Influence of total pulse number per deposit. Deposits grown with increasing number of pulses (as stated in the images) but otherwise identical parameters, for a pulse amplitude of a, 5 V and b, 6 V. At initial stages of deposition, with low numbers of pulses, the lateral diameter increases with the amount of pulses. For larger numbers of pulses, the lateral size of the deposits is approximately constant (compare 25000 and 50000 pulses in b), while its height increases. Note that the bottom-left deposit in (b) corresponds to the top-left deposit in (a). Deposition parameters. Electrolyte: 1 M CoSO_4 in DMSO; pulse length: 20 ns; pulse amplitude: as stated; duty cycle: 0.01; pulses per point: as stated; dwell distance: 10 nm.

2.4 Insufficient stability of Au STM tips

Negative values of the growth curves in Figure 3e indicate either the tip crashing into the substrate, a hole being milled into the substrate, or degradation of the tip. Post-deposition STM scans of the substrate exclude any subtractive machining of the substrate. Repeated tip crashes are also unlikely, as post-deposition SEM analysis of tips do not show any bending of the tip. However, a comparison of a Au STM tip before and after its use in multiple deposition experiments confirms removal of material from the tip apex (Figure S6a), presumably due to anodic dissolution of Au.

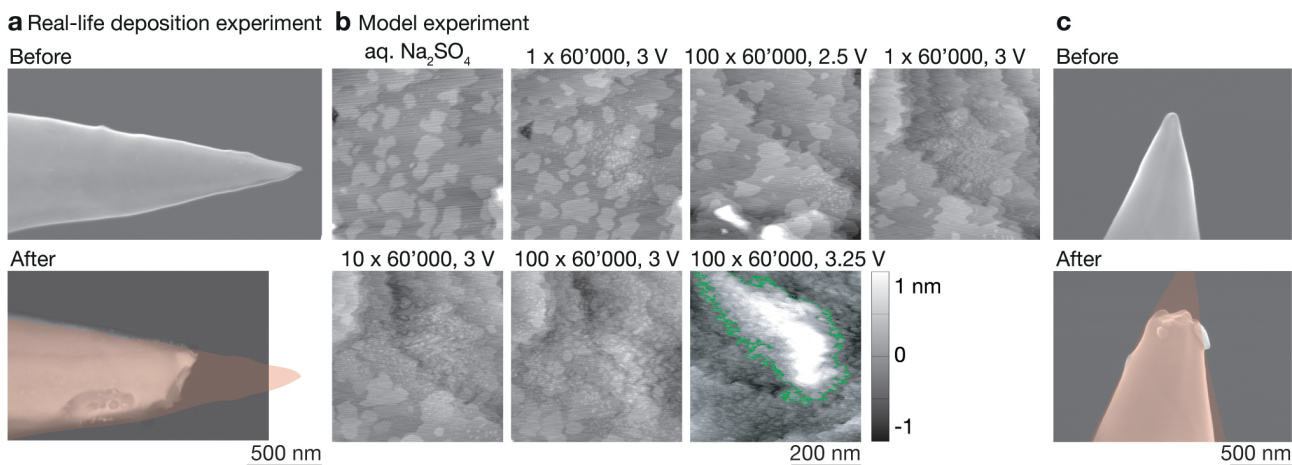


Fig. S6 Anodic degradation of Au tips. a, SE SEM micrographs of a Au STM tip before (left) and after (right) its use as a local electrode for multiple deposition experiments. A length of >500 nm of the original tip apex is missing after experiments. The red shading in the right micrograph indicates the dimensions of the original tip. b, c, A model experiment confirms substantial loss of tip material upon pulsing in aq. 0.25 M Na_2SO_4 . As the electrolyte solution is bare of metal cations that could be deposited on the substrate, the deposited material in must originate from the STM tip. b, STM scans of a Au surface before (first scan) and after pulsing the Au STM tip in 0.25 M aq. Na_2SO_4 using the parameters stated in the panels (Pulse width: 20 ns; duty cycle: 0.01; dwell distance: 50 nm). The location of scans 3–7 is different from 1–2. The volume of the outlined deposit in the last scan is $6.3 \times 10^4 \text{ nm}^3$. c, SEM micrograph of the Au tip used in (a) before (left) and after (right) the deposition experiments. The estimated volume of the tip material missing after deposition is $\approx 2 \times 10^7 \text{ nm}^3$.

To verify the loss of tip material upon anodic pulsing, we designed a straightforward model experiment based on the assumption that any material that is dissolved from the tip would redeposit on the substrate. Pulse experiments are conducted in supporting electrolyte solutions containing no metal cations that could be deposited (typically 0.25 M aq. Na_2SO_4). Consequently, all material grown on the substrate after a deposition event must originate from the tip. The used STM tips are imaged prior to and after deposition experiments. Indeed, these experiments confirm loss of tip material (Figure S6b, c). Thus, the following assumption is made and applied to the rest of the result section. Any material deposited in Co^{2+} -ion-free electrolyte solutions originates from the utilized tip and thus indicates the tip's degradation. However, this is no quantitative relation, as not all material dissolved from the tip transfers to the substrate. In Figure S6b, c, the estimated volume removed from the tip is $\approx 2 \times 10^7 \text{ nm}^3$, compared to only $\approx 6 \times 10^4$ –max. $1 \times 10^5 \text{ nm}^3$ for the largest deposit in (b).

2.5 Sufficient stability of Pt and Pt-Ir STM tips

The anodic instability of Au under typical deposition conditions necessitates an alternative tip material. A comparison of pulse experiments of Au and Pt tips in a Co^{2+} -free supporting electrolyte suggest a higher stability of Pt (**Figure S7**). While first clear signs of Au tip degradation, *i.e.*, deposited material below the tip, are detected after 1×60000 pulses, similar deposition of Pt is only observed after 100×60000 pulses (although there is minor deposition already after 10×60000 pulses).

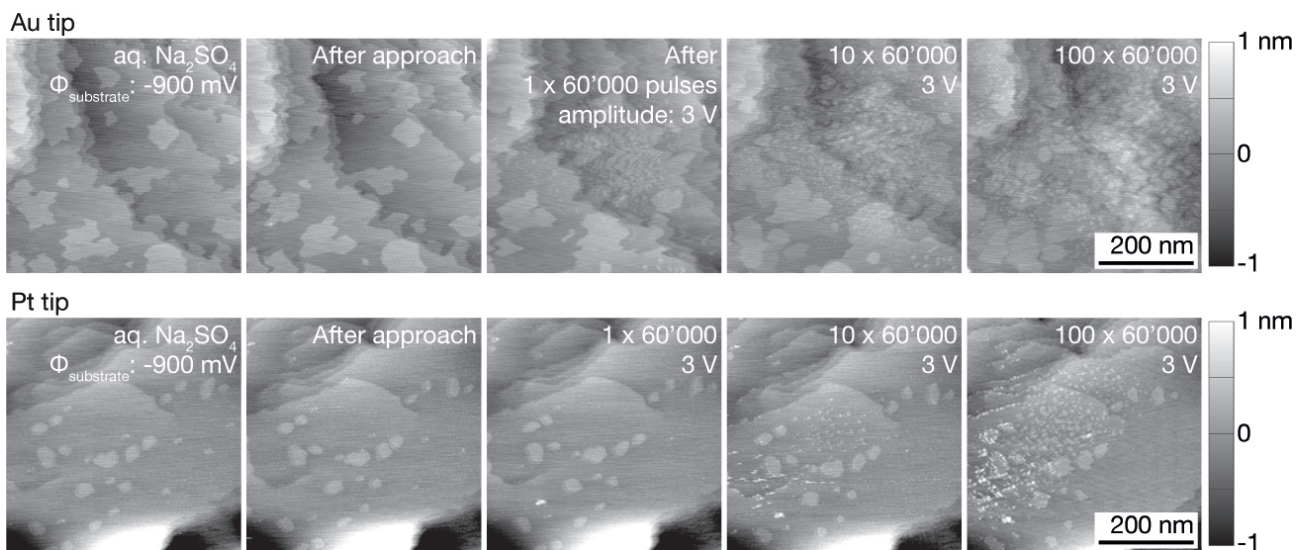


Fig. S7 Anodic stability of Au versus Pt tips. STM scans of a Au surface before and after $1 \times$, $10 \times$ and 100×60000 voltage pulses applied to either a Au (top row) or a Pt tip (bottom row) in 0.25 M aq. Na_2SO_4 . For the Au tip, deposition is evident already after 1×60000 pulses, indicating dissolution of the tip. In contrast, a similar amount of deposition from the Pt tip is only observed for 100×60000 pulses, suggesting a higher resistance of Pt against anodic oxidation. The label OFF indicates a simple tip approach without pulses. Deposition parameters. Pulse width: 20 ns; pulse amplitude: 3 V; duty cycle: 0.1; dwell distance: 50 nm; $\Phi_{\text{substrate}}$: -900 mV; Φ_{tip} : -700 mV vs. Au.

The deposition of Pt tip material onto the substrate is minimized if the pulse amplitude is decreased to 2.5 V (**Figure S8a**). This suggests a sufficient stability of the tip for Co deposition when compared to typical deposition parameters in Co^{2+} -containing electrolyte solutions. Indeed, a deposition experiment in 0.25 M aq. CoSO_4 yielded pronounced deposition already at 1×60000 pulses (**Figure S8b**)—a total polarization time that does not deposit any tip material in 0.25 M aq. Na_2SO_4 (a). Additionally, first signs of deposition are already evident after 5000 pulses. Lifting the surface potential to $\Phi_{\text{substrate}} > \Phi_{\text{Co} \rightarrow \text{Co}^{2+}}$ (-200 mV vs. Au), the deposit instantaneously dissolves and only some residues remain (**Figure S9a**). Smaller dots grown with a lower total polarization time dissolve completely (**Figure S9b**), indicating no co-deposition of Pt during pulsing.

The increased stability of Pt and Pt-20at.%Ir tips suggests the potential for stable and controlled deposition. However, as preliminary results show, the tips' inertness is only guaranteed in a narrow process window. Growth curves recorded for a Pt-20at.%Ir tip in aq. CoSO_4 suggest an increased process stability compared to Au tips—single deposits reach heights of $1\text{--}3 \mu\text{m}$ after 150×30000 pulses (3 V), and the number of growth curves that contain drops is decreased compared to experiments with Au tips (**Figure S10**). Nonetheless, abrupt collapses still occur with Pt-20at.%Ir tips. These instabilities seem to be a function of pulse amplitude: a pulse amplitude of 2.75 V results in continuous growth, while growth curves for larger voltages are less smooth and feature the well-known drops (**Figure S10c**). A comparison of pre- and post-deposition micrographs of the utilized tip's apex still indicates loss of material, as expected from the growth curves (**Figure S10a, d**). It is still to be shown that Pt or Pt-20at.%Ir tips do not degrade with appropriate process parameters.

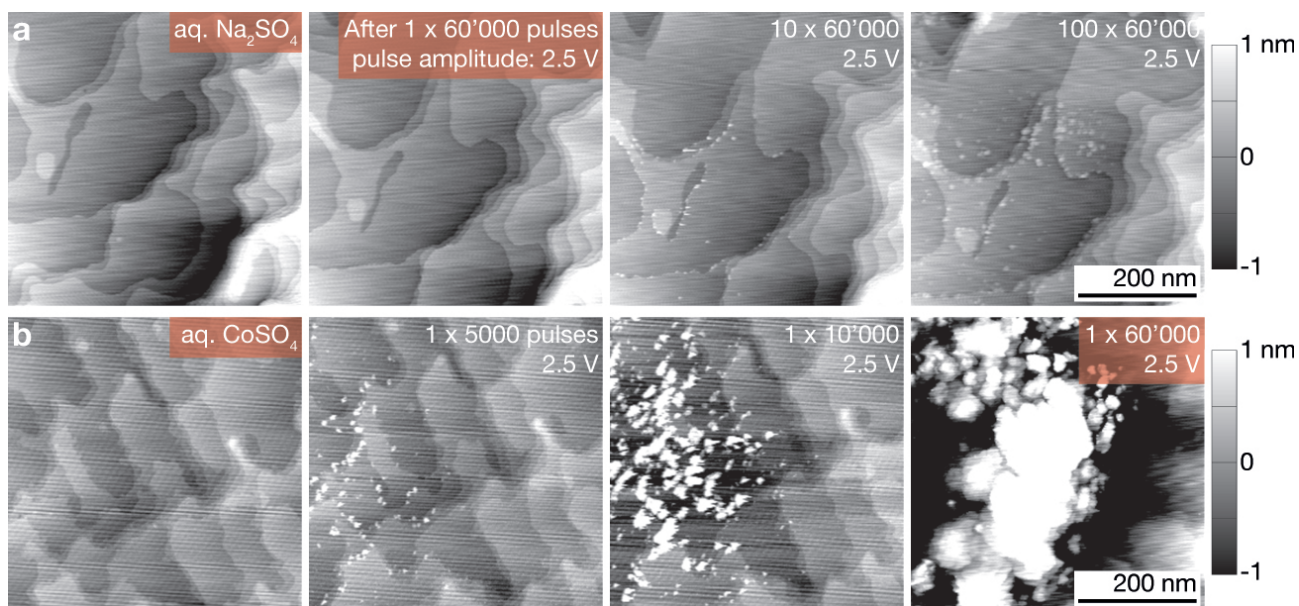


Fig. S8 Deposition with Pt tips in aq. Na_2SO_4 and CoSO_4 solutions. A comparison between deposition experiments in Co^{2+} -free and Co^{2+} -containing electrolytes suggest sufficient stability of Pt tips for Co deposition: STM scans of a Au surface before and after deposition with stated number of pulses in a, 0.25 M aq. Na_2SO_4 and b, 0.25 M aq. CoSO_4 . In the Co^{2+} -containing solution, a significant amount of material is deposited after 1×60000 pulses. In contrast, no deposition is detected with equal parameters in the Co^{2+} -free solution, and only minor deposition is observed after 100×60000 pulses. Note: the deposition in the rightmost scan of (b) was initiated on a previously clean surface, while the deposit in the third scan was grown on top of the one in the second scan. Deposition parameters, Pulse width: 20 ns; pulse amplitude: 2.5 V; duty cycle: 0.1; dwell distance: 50 nm; $\Phi_{\text{substrate}}$: -900 mV (a), -1000 mV (b); Φ_{tip} : -700 mV; tip: Pt.

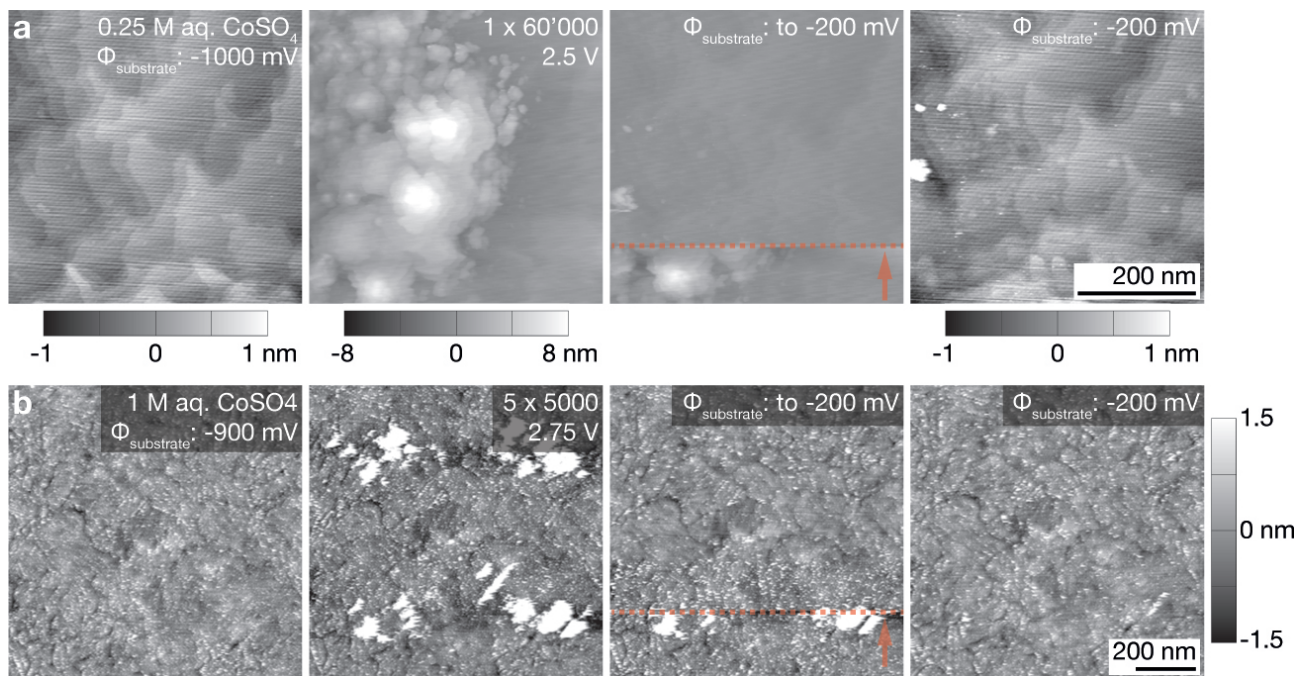


Fig. S9 Complete dissolution of deposits. a, STM scans of a Au surface before (first scan) and after deposition in 0.25 M aq. CoSO_4 (second scan, same deposit as in Figure S8b). Stepping $\Phi_{\text{substrate}}$ to -200 mV vs. Au (dashed line in the third scan). The arrow denotes the scan direction) results in the instantaneous dissolution of the deposits. Note the different gray scales of the individual panels. b, Scans of the surface of a Au thin film before and after the deposition of four dots (only 5×5000 pulses) and after their complete dissolution at -200 mV vs. Au. Deposition parameters. Pulse width: 20 ns; pulse amplitude: 2.5 V (a), 2.75 V (d); duty cycle: 0.1; dwell distance: 50 nm; Φ_{tip} : -700 mV. tip: Pt (a), Pt-20at.%Ir (b).

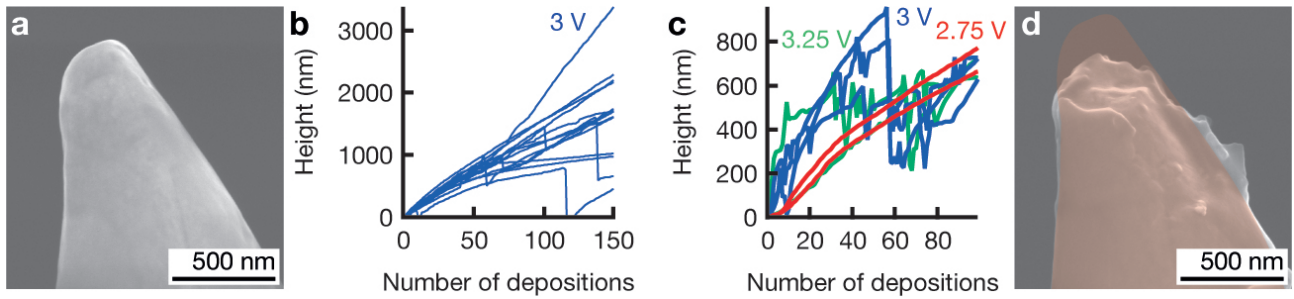


Fig. S10 Out-of-plane growth curves with Pt-20at.%Ir tips. a, d, Pre- and post-experiment SE micrograph of the tip used in (b) and (c). b, Growth curves recorded with a Pt-20at.%Ir tip. While stable growth up to a height of 2–3 μm can be achieved, the growth curves are not free of instabilities. c, Growth curves recorded for pulse amplitudes of 2.75, 3 and 3.25 V. Low amplitudes enable continuous growth, while larger voltages cause growth instabilities. Deposition parameters. Electrolyte: 1 M aq. CoSO_4 ; pulse width: 20 ns; pulse amplitude: 3 V (a), 2.75–3.25 V (b); duty cycle: 0.1; pulses per deposition event: 30000 (a), 10000–30000 (b); dwell distance: 50 nm; dwell time: 0.5 s; tip: Pt-20at.%Ir.