

Supporting Information

Nanoscopic polypyrrole AFM-SECM probes enabling force measurements under potential control

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1. Ion-beam induced deposition (IBID) of platinum

For ion-beam induced deposition (IBID)^[1], it is important that the ion beam is perpendicular to the tip to ensure that the deposition mainly occurs at the exposed electroactive area. To avoid drifts due to charging, the ion beam acceleration voltage was reduced to 16 kV, and the cantilever was thoroughly grounded via a beryllium copper spring. The deposition therefore resulted in a tip-shaped cone. SEM imaging revealed that the corner facing towards the end of the needle showed a significantly higher deposition rate. This enables the formation of pyramidal-shaped platinum-carbon (Pt/C) tips with a diameter of 100 to 150 nm.

Initially, the deposition followed the selected rectangular pattern up to a height of approximately 200 nm; beyond 200 nm, the depositions predominantly proceeded closest to the location of the gas nozzle. At approximately the same level, partial milling of the previously deposited material at a position opposite of the injection needle started. Due to the small pattern, no shadowing effect of the gallium beam was observed, and hence, the entire process was controlled by the gas flow. Due to the continuous deposition process, less precursor gas reached the area opposite of the gas nozzle. Hence, the obtained structures were predominantly influenced by the angle and by the location of the gas nozzle (see Figure S1).

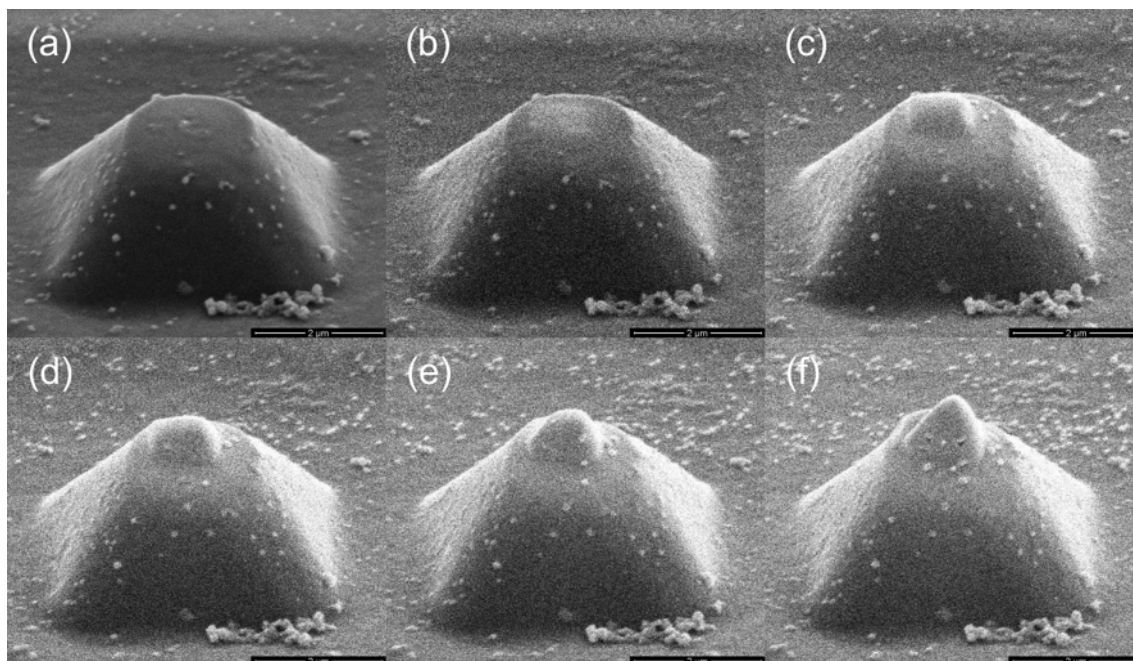


Figure S1: SEM images of a cantilever tip at different stages of the platinum deposition. (a) Before deposition; (b) first precipitation; (c) rectangular growth; (d) shadowed deposition; (e) milling of previously deposited material; (f) final Pt/C probe. Note: The images are extracted from a movie showing the stepwise deposition. The observed phenomena are more clearly evident in the associated video file.

2. Milling of Pt/C probes

The deposition resulted in Pt/C probes with tip radii in the range of approx. 50 – 80 nm. If needed, the tip radius may be further reduced by FIB milling. The milling steps depicted in Figure S2 C resulted in pyramidal-shaped tip with tip radii of less than 20 nm (Figure S2 A, B, D, E). Milling was performed at 30 kV using charge neutralization to avoid drifts. For cleaning purposes, single-pass milling was performed to remove any platinum deposited at the plateau beside the actual electrode (Figure S2 C).

Characterization in $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ of the re-sharpened tip showed the expected decrease in current due to the reduced electroactive area (Figure S2 F).

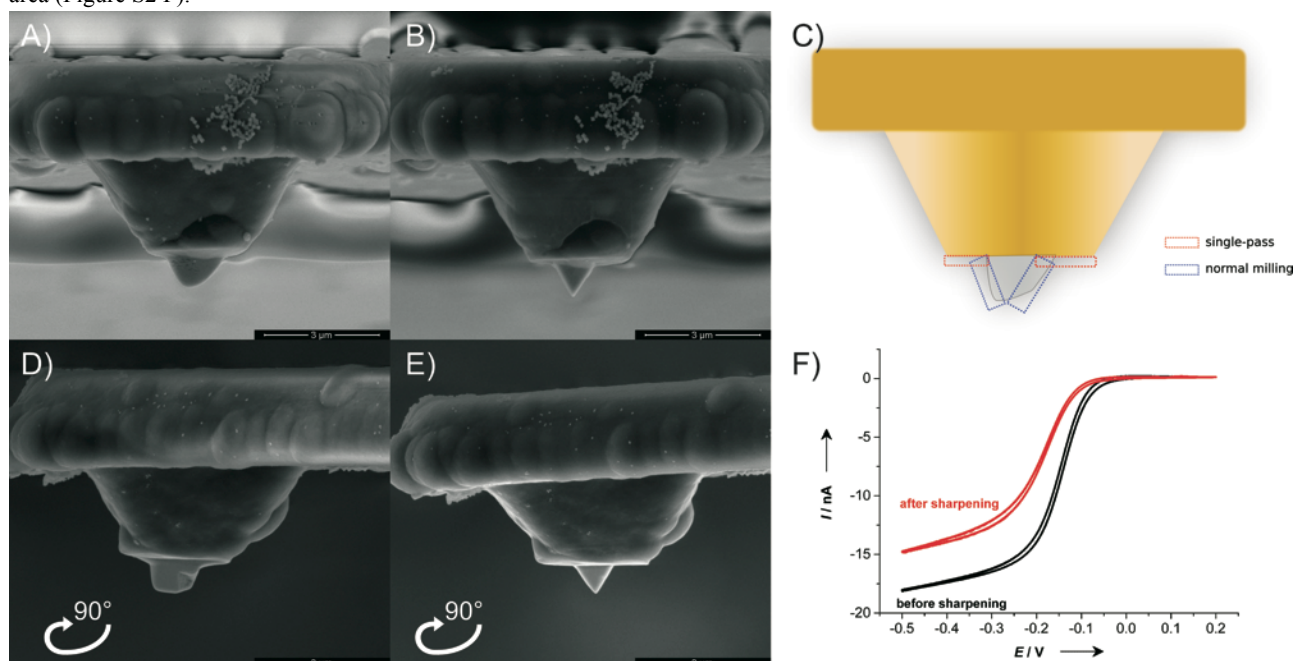


Figure S2: SEM images of the FIB milling process after Pt/C deposition. A) Before and B) after milling from side, respectively; D) and E) before and after milling of the tip turned by 90 degree. C) Scheme shows the applied milling steps and D) the CV characterization of the shown tip in $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3/0.1 \text{ M KCl}$ before and after the milling step.

3. Calculation of steady-state current from electrode area

The geometry of the exposed gold electrode was approximated as a disk, and therefore, the steady-state current of the electrodes was calculated using equation (1) [12]:

$$i_{\text{diff}} = 4nFDc^b a \quad (1)$$

For the FIB-milled electrodes, the radius of the disk (a) was approximately 150 nm, the number of transferred electrons n was 1, and the diffusion constant D was $5.3 \times 10^{-6} \text{ cm}^2/\text{s}$ for $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ [12]. F was the Faraday constant, and c^b was the bulk concentration of the redox mediator (10 mM). The calculated steady-state current was 307 pA, which is in excellent agreement with the experimentally obtained currents.

4. Band assignment of Raman measurements at the polymer-modified AFM probes before and after PPy deposition

From the recorded Raman spectra of PPy, according to literature [3] the following bands were assigned: Signals at 930 and 1050 cm^{-1} were associated with the bipolaron and the polaron structure of the polymer. At 1330 and 1420 cm^{-1} , the asymmetric C-H in plane bending and C-N stretching were observable. The band at 1600 cm^{-1} was assigned to the C=C stretching vibration (Fig. 3 red solid line). The spectrum recorded for the Parylene C coating resulted in bands at around 300 (aromatic bending vibrations) and 700 cm^{-1} (C-H out-of-plane deformation), where PPy does not scatter light, and bands at 1000, 1200 (C-H in-plane deformation), 1350 (C-H₂ wagging and twisting), 1450, and 1600 cm^{-1} (C-H scissoring in C-H₂) were in excellent agreement with band assignments reported in literature [4].

5. Force curves recorded with bare Pt/C tips

To distinguish between interactions of the Pt/C and the polypyrrole-coated Pt/C probes, force spectroscopic measurements were performed before and after deposition of PPy, respectively. As the Pt/C is electrically connected, the electrostatic field of the tip can be modulated, and hence, the interactions changed by variation of the applied potential. Force scans with a blunt Pt/C tip were recorded at a tip velocity of 0.5 $\mu\text{m}/\text{s}$ in a range of 0.5 μm , while the potential was varied between 0 to 2 V and between 0 to -1.5 V vs. Ag/AgCl, respectively. Besides minimal adhesion forces in retrace curves, a slight change in slope near the contact point was observed. When applying higher anodic potentials the slope increased until finally the trace curve showed a snap-in event at around 1.5 V vs. Ag/AgCl. In the cathodic range, at around -1 V vs. Ag/AgCl, the cantilever started to oscillate, most likely caused by onset of hydrogen reduction. Representative force curves for the applied potentials are shown in Figure S3.

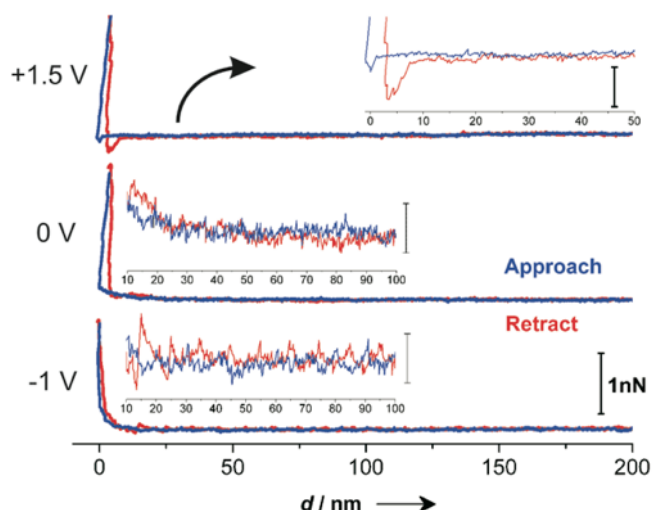


Figure S3: Force curves recorded with a bare tip on plasma-treated glass under potential control. Snap-in event in the approach curve visible at +1.5 V (inset: magnified area with scale bar of 500 pN). 0 V and -1 V no adhesion in retract part was observable, however at -1 V electrostatic repulsion near the substrate was visible by the slowly increasing slope as well as oscillations in the baseline due to the onset of hydrogen evolution (insets: scale bars are 100 pN - all potentials are reported vs. Ag/AgCl)

5. Stimulation of C2C12 cells

First force measurements of live C2C12 muscle cells (myotubes) with a PPy-modified tip were performed. The tip was approached and force curves were obtained with a maximum loading force of 5 nN. In contrast to the force curves recorded at glass, the contact part shows clearly indentation of around 1 μm and adhesion in the retract part (see Figure S4 C). To investigate the interaction of cells under potential control, the tip was approached to a cell and kept in contact for approx. 60 s. During this period of time, a potential of -1.5 V vs. Ag/AgCl was applied causing a distinct contraction of the cell. A relatively high negative potential was applied to induce the cell response by electrical stimulation. Due to the strong contraction, the tip-cell contact was lost as the feedback pulled the cantilever off the surface in order to maintain the applied force of 5 nN. The contraction of the cell was clearly visible in a recorded video. Selected frames are presented as bright field images in Figure S4 A, B).

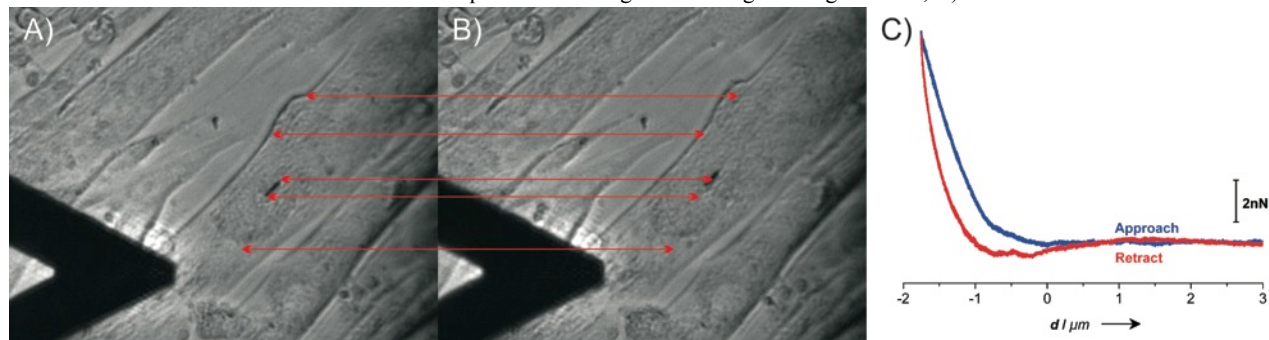


Figure S4: Bright field images of C2C12 muscle cells (myotubes) before and after stimulation with a PPy-modified tip (A,B). Red arrows show positions before and after cell stimulation, if a potential of -1.5 V vs. Ag/AgCl was applied. Force curve obtained at the cell before the stimulation is shown in (C). Note: The images are extracted from a movie file, which shows cell movement.

6. Experimental Section

Silicon nitride cantilevers NP-W (Veeco, USA) were used as substrates for fabricating AFM-SECM probes. FIB processing and HRSEM imaging was obtained with a Quanta 3D FEG or Helios Nanolab 600 instrument, respectively (FEI, Netherlands). (Methylcyclopentadienyl) trimethyl-platinum was used as precursor gas for platinum depositions. All electrochemical measurements were conducted with a CH600 series potentiostat (CHI, USA). Electrochemical characterizations of the probes were performed in aqueous solutions with 10 mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ (ABCR, GER) and 0.1 M KCl (Sigma-Aldrich, GER) as supporting electrolyte. For PPy depositions, 0.2 M distilled pyrrole (Merck, GER) and 0.1 M p-Ts (Merck, GER) in aqueous solution was used. Raman spectra were recorded with a JY HR800 Spectrometer (Horiba, JPN). The force spectroscopic measurements were conducted using a NanoWizard II instrument (JPK, GER). Plasma treatment of glass slides was performed in a PDC-32G-2 plasma-cleaner (Harrick Plasma, USA).

7. References

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