

Supporting Information

Scanning electrochemical probe microscopy: towards the characterization of micro- and nanostructured photocatalytic materials

Giada Caniglia*, Sarah Horn, Christine Kranz*

Institute of Analytical and Bioanalytical Chemistry, Ulm University, Albert-Einstein-Allee, 11 89081 Ulm, Germany.

E-mail: christine.kranz@uni-ulm.de, giada.caniglia@uni-ulm.de

Table of contents

Fig. S1. Schematics of the influence of size and location of the Pt-B deposition on the cantilever – sample set-up.

Fig. S2. SEM image of the cross-section of a Pt-B AFM-SECM probe fabricated *via* pulsed deposition of Pt-B on an Au-recessed disk electrode (diameter: 250 nm).

Fig. S3. Cyclic voltammograms of Pt-B modified AFM-SECM probes in sulfuric acid.

Fig. S4. SEM and corresponding EDX images of the Pt@Si substrate.

Fig. S5. Current map recorded at the Pt@Si substrate under dark conditions using a Pt-B AFM-SECM probe immersed in 0.1 M PBS at pH 4.

Fig. S6. Cyclic voltammogram of a Pt-B modified microelectrode in sulfuric acid.

Fig. S7. Calibration curves recorded at Pt-B modified microelectrodes.

Fig. S8. Cyclic voltammograms of a Pt-B modified microelectrode and a bare Pt microelectrode.

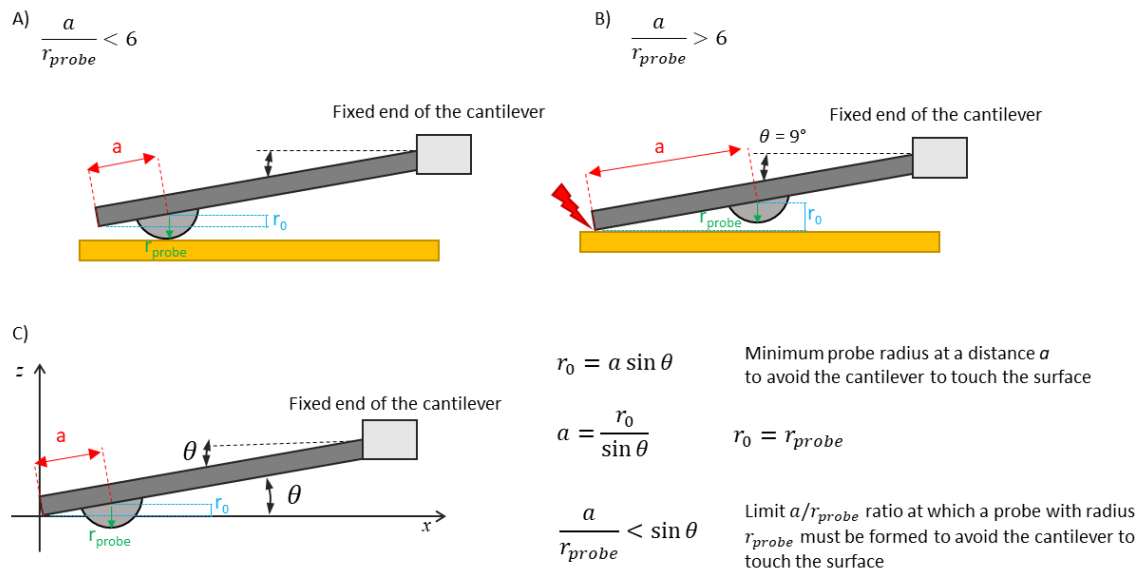


Fig. S1. (A-B) Schematics of the side view cantilever-sample set-up. (A) The probe with a radius r_{probe} is positioned at a distance close to the leading edge of the cantilever, so the probe is touching the surface and not the edge of the cantilever. (B) The probe is positioned at a distance too far from the edge of the cantilever, so that the cantilever touches the surface instead of the probe. (C) Schematic of the geometry of a typical cantilever-sample setup highlighting (i) the angle at which the cantilever is mounted within the holder of the AFM, θ ; (ii) the distance between the probe and the leading edge of the cantilever, a , and (iii) maximum radius, r_0 , of a probe positioned at a distance a to avoid that the leading edge of the cantilever touches the surface. r_{probe} denotes the actual radius of the probe.

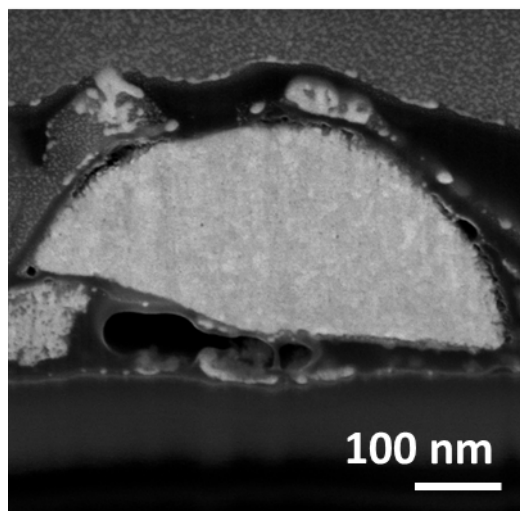


Fig. S2. SEM image of the cross-section of a hemispherical Pt-B probe obtained by pulsed electrodeposition of Pt-B onto a 250-nm-diameter recessed Au disk electrode. The probe was embedded in epoxy resin using a micromanipulator in combination with an inverted microscope prior to FIB cross sectioning to minimize beam-induced damage, as previously reported.^{1,2}

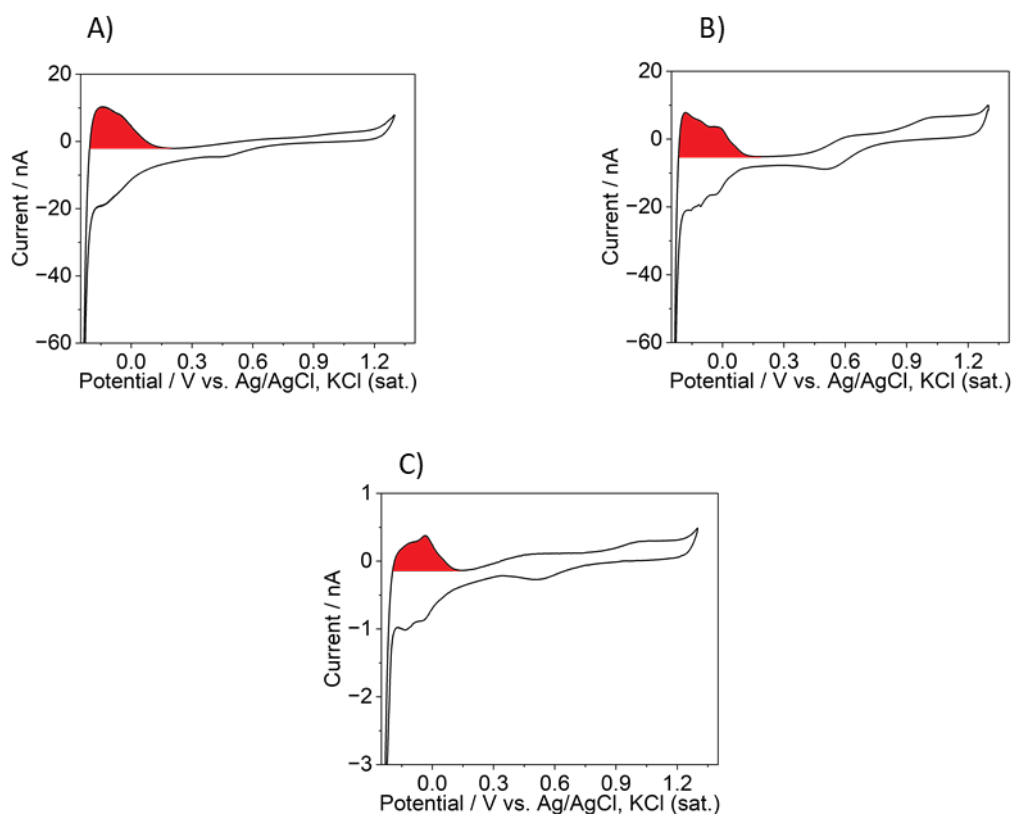


Fig. S3. Cyclic voltammograms recorded at Pt-B modified AFM-SECM probes in 0.5 M H₂SO₄. (A) Diameter of the original recessed Au disk electrode: 500 nm. Scan rate: 500 mV/s (vs. Ag/AgCl, KCl (sat.)). (B) Diameter of the original recessed Au disk electrode: 1 μm. Scan rate: 400 mV/s (vs. Ag/AgCl, KCl (sat.)). (C) Diameter of the original recessed Au disk electrode: 250 nm. Scan rate: 500 mV/s (vs. Ag/AgCl, KCl (sat.)).

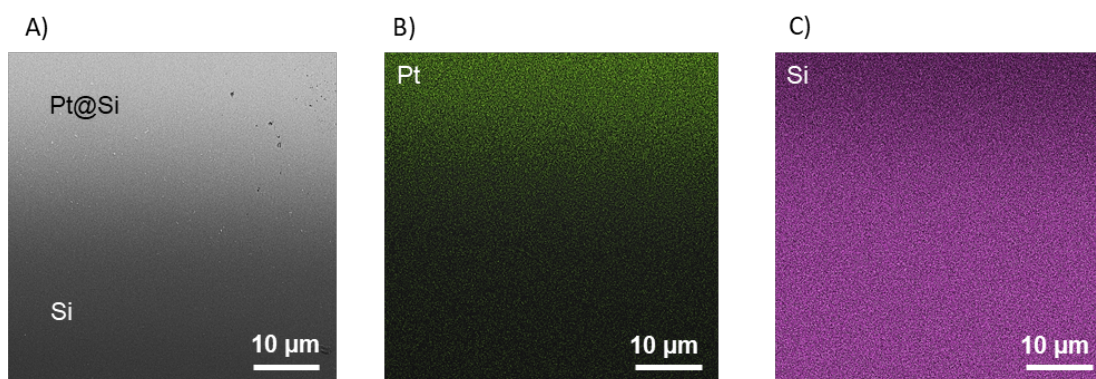


Fig. S4. (A) SEM image and (B-C) corresponding colored-coded EDX images of platinum (B) and silicon (C) of the Pt@Si substrate recorded at the border area.

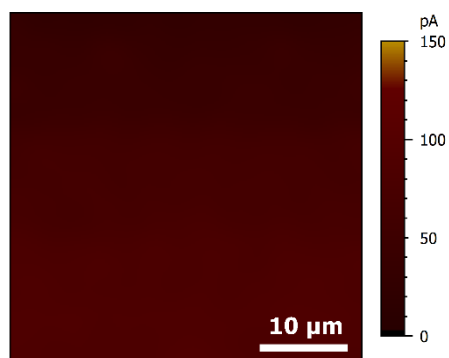


Fig. S5. Current map recorded at the Pt@Si substrate using a Pt-B AFM-SECM probe immersed in 0.1 M PBS at pH 4. ($E_{\text{probe}} = -0.15$ V vs. Ag/AgCl; $E_{\text{substrate}} =$ open circuit potential).

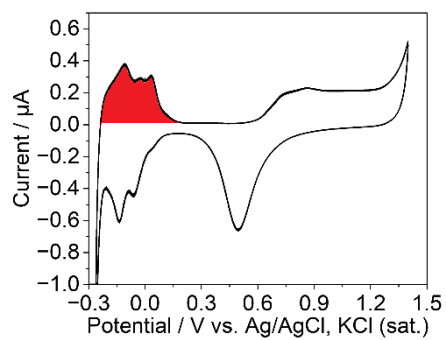


Fig. S6. CV recorded at a Pt-B modified microelectrode ($d = 25$ μm) in 0.5 M H_2SO_4 . Scan rate: 500 mV/s (vs. Ag/AgCl, KCl (sat.)).

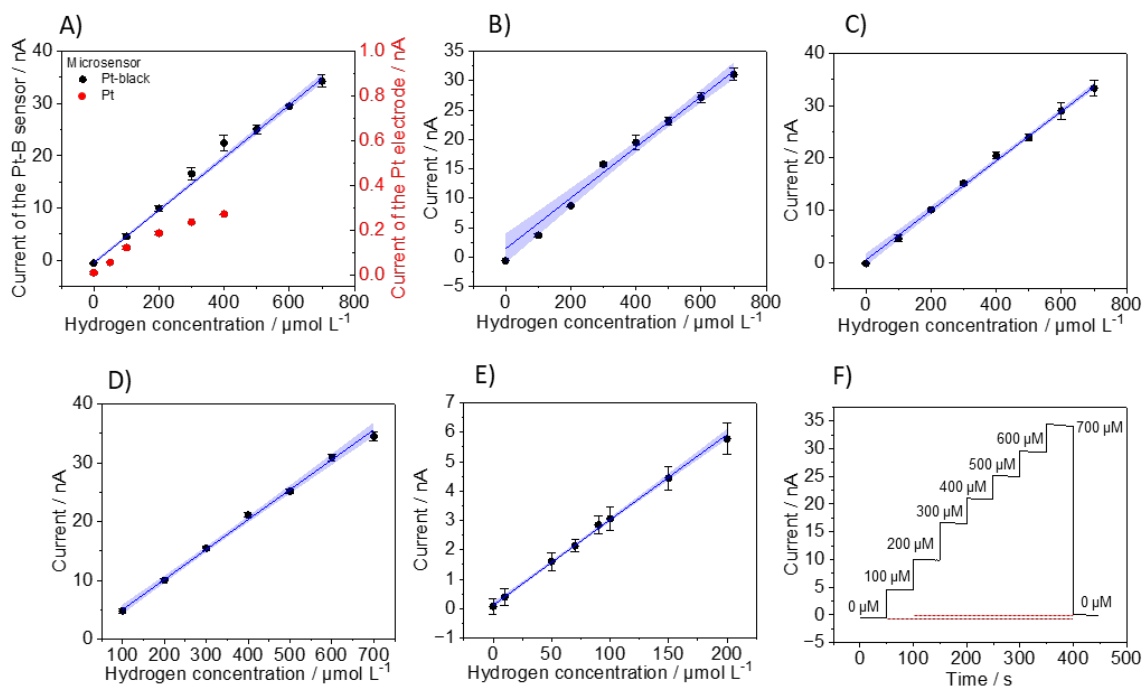


Fig. S7. (A-E) Calibration curves (blue line) of H₂ recorded at Pt-B microelectrodes (d = 25 μm) with increased H₂ concentrations immersed in (A) 0.1 M PBS at pH equal to 4 ($E_{UME} = -0.15$ V vs. Ag/AgCl); (B) 0.1 M PBS at pH equal to 7 ($E = -0.20$ V vs. Ag/AgCl); (C) 0.1 M PBS at pH equal to 10 ($E = -0.28$ V vs. Ag/AgCl); (D) 0.1 M ascorbic acid (pH 4, $E_{UME} = -0.05$ V vs. Ag/AgCl), and (E) 10 % v/v TEOA in 0.1 M HK₂PO₄ (pH 10, $E_{UME} = -0.47$ V vs. Ag/AgCl). The blue area denotes the uncertainty range, and the error bars reflect three repetitive measurements. (F) Exemplary chronoamperometry with consecutive increments of H₂ at Pt-B ME (-0.05 V vs. Ag/AgCl) in ascorbic acid 0.1 M (pH 4).

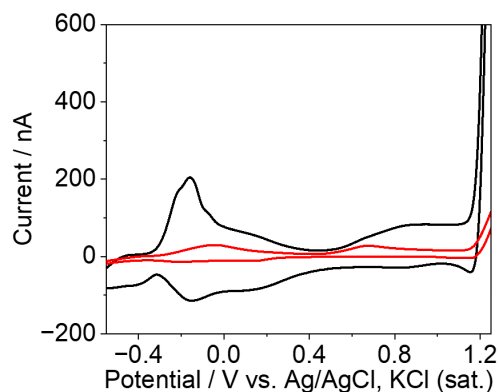


Fig. S8. Cyclic voltammograms recorded at a Pt-B modified microelectrode (d = 25 μm; black line) and a bare Pt electrode (d = 25 μm; red line) in 0.1 M PBS at pH.

References

- 1 T. Philipp, G. Neusser, E. Abouzari-Lotf, S. Shakouri, F. D. H. Wilke, M. Fichtner, M. Ruben, M. Mundsinger, J. Biskupek, U. Kaiser, P. Scheitenberger, M. Lindén and C. Kranz, *J Power Sources*, 2022, **522**, 231002.
- 2 A. Hellmann, G. Neusser, S. Daboss, M. M. Elnagar, J. Liessem, D. Mitoraj, R. Beranek, S. Arbault and C. Kranz, *Analytical Chemistry*, 2024, **96**, 3308–3317.